Linköping Studies in Science and Technology
Dissertations No. 2130

Synthesis and Characterization of ZnO/Graphene Nanostructures for Electronics and Photocatalysis

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Department of Science and Technology
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Linköping University, Sweden
Norrköping 2021

Cover image:

The cover image shows a cross-sectional SEM image of ZnO nanorods on a CL-patterned rGO/ZnO:Al seed layer on a Si substrate. The different layers are artificially colored for a better perspective.

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Printed in Sweden by LiU-Tryck, 2021

ISSN: 0345-7524

ISBN: 978-91-7929-682-7

این بحر وجود آمده بیرون ز نهفت کس نیست که این گوهر تحقیق بسفت
هر کس سخنی از سر سودا گفتند زآن روی که هست، کس نمی داند گفت

The universe has emerged from hidden depths
How? that's a pearl of wisdom no one has pierced
Everyone has conjectured idly,
But none can describe what it really is

Omar Khayyam – 1131 CE

Abstract

Recent rapid development of electronics and electro-optical devices demands affordable and reliable materials with enhanced performance. Forming nanocomposites of already well-known materials is one possible route towards novel functional materials with desirable synergistic enhanced properties. Incompatible chemical properties, mismatched crystal structures and weak bonding interactions between the substances, however, often limit the number of possible nanocomposites. Moreover, using an inexpensive, facile, large-area and flexible fabrication technique is crucial to employ the new composites in industrially viable applications.

This thesis focuses on the synthesis and characterization of different zinc oxide/graphene (ZnO/GR) nanocomposites, well suited for optoelectronics and photocatalysis applications. Two different approaches of i) substrate-free random synthesis, and ii) template-assisted selective area synthesis were studied in detail. In the first approach, ZnO nanoparticles/rods were grown on GR. The obtained nanocomposites were investigated for better GR dispersity, electrical conductivity and optical properties. Besides, by adding silver iodide to the nanocomposite, an enhanced plasmonic solar-driven photocatalyst was synthesized and analyzed. In the second approach, arrays of single, vertically aligned ZnO nanorods were synthesized using a colloidal lithography-patterned sol-gel ZnO seed layer. Our demonstrated nanofabrication technique with simple, substrate independent, and large wafer-scale area compatibility improved the alignment and surface density of ZnO nanorods over large selective growth areas. Eventually, we found a novel method to further enhance the vertical alignment of the ZnO nanorods by introducing a GR buffer layer between the Si substrate and the ZnO seed layer, together with the mentioned patterning technique.

The synthesized nanocomposites were analyzed using a large variety of experimental techniques including electron microscopy, photoelectron spectroscopy, x-ray diffraction, photoluminescence and cathodoluminescence spectroscopy for in-depth studies of their morphology, chemical and optical properties.

Our findings show that the designed ZnO/GR nanocomposites with vertically aligned ZnO nanorods of high crystalline quality, synthesized with the developed low-cost nanofabrication technique, can lead to novel devices offering higher performance at a significantly lower fabrication cost.

Keywords: zinc oxide, graphene, nanostructure, nanocomposite, conjugated electronics, photocatalysis, nanofabrication, colloidal lithography, chemical bath deposition, sol-gel

Populärvetenskaplig sammanfattning

I dag introduceras ny teknik i våra liv i en allt snabbare takt. Nya elektroniska produkter förväntas underlätta vår vardag genom att göra saker snabbare, mer exakt, säkrare och billigare. Utvecklingen av nya inbäddade teknologier som Internet-of-things (IoT), 5G-kommunikation, artificiell intelligens och maskininlärning vilar tungt på utvecklingen av ny hårdvara, som i sin tur förutsätter tillgång till nya avancerade material med förbättrade elektroniska egenskaper och ett konkurrensmässigt pris.

Att utveckla nya funktionella material med önskvärda egenskaper är en komplicerad process som involverar olika grenar inom naturvetenskapen, inklusive fysik, kemi och materialvetenskap. Att koppla samman etablerad halvledarindustri med nanoteknik är ett utmärkt exempel på detta partnerskap mellan olika vetenskapsområden för bättre materialinnovation. I denna process skapas ofta nya funktionella material med önskvärda förbättrade egenskaper genom att integrera konventionella halvledarmaterial med varandra på nya innovativa sätt. Även om detta kan tyckas enkelt i teorin, begränsas utvecklingen i praktiken ofta av utmaningar som till exempel oförenliga kemiska egenskaper, olika kristallstrukturer eller inkompatibla elektriska bindningar mellan ämnena antalet möjliga kombinationer. Dessutom är det viktigt att utveckla nya enkla, billiga och flexibla tillverkningsmetoder för storskalig produktion av dessa nya kompositmaterial.

Den här avhandlingen fokuserar på utveckling av nya funktionella nanokompositer, bestående av halvledarmaterialet zinkoxid (ZnO) och det två-dimensionella materialet grafen, för tillämpningar inom optoelektronik och fotokatalys. Zinkoxid kan odlas som tunna nålliknande strukturer som kallas nanostavar med en billig lösningsbaserad teknik. Tack vare sina utmärkta elektriska och optiska egenskaper har ZnO använts flitigt i många applikationer som till exempel lysdioder, elektrokemiska sensorer och gassensorer. Grafen har utmärkt sig som ett fantastiskt material med helt unika elektriska, optiska och mekaniska egenskaper som väsentligt förbättrar den optoelektroniska och fotokatalytiska effektiviteten hos ZnO/grafen nanokompositer.

Jag har i mitt arbete studerat elektrisk ledningsförmåga, optiska egenskaper och fotokatalyseffektivitet hos våra designade ZnO/grafen nanokompositer under simulerad solstrålning. Dessutom har jag odlat vertikalt ordnade ZnO nanostavar i små nanohål på möntrade substrat belagda med ett tunt lager av antingen ZnO, eller med ett sandwichlager bestående av ZnO och grafen med hjälp av en ny billig metod som kallas kolloidal litografi. Denna tillverkningsmetod erbjuder enkel odling av högkvalitativa (kristallina) ZnO nanostavar med god kontroll över ytdensiteten på stora godtyckliga materialytor. Våra resultat visar att dessa nya högkvalitativa ZnO/grafen nanokompositer potentiellt erbjuder en ny materialplattform för tillverkning av exempelvis billig högpresterande optoelektronik.

Acknowledgment

The past five years were the most challenging but exciting part of my life. Many people helped me during this journey, although only one name appears on the cover of this thesis. I would like to express my sincere gratitude to all of you.

My main supervisor **Håkan Pettersson** for giving me the opportunity and freedom to work on this project. Not only did I learn scientific matters from you, but also your precision, tolerance and respectful behavior will be my intentions. I always felt comfortable working with you during these years, oh wait...! maybe I should exclude the deadline times.

My co-supervisors, **Magnus Willander** and **Omer Nour**, for all your supports, encouragement, fruitful discussions, and always accessible communication. Also, thanks go to the lab crew, **Lars Gustavsson**, **Thomas Karlsson** and **Meysam Karami**, for keeping the lab running.

I also would like to thank my colleagues at Halmstad University. **Emil Nilsson**, who taught me the very basics of RF components and measurements, and also for assisting me on the first days after I arrived in Sweden. **Pererik Andreasson** for all his support and always pleasant discussions. **Jessika Rosenberg** and **Stefan Gunnarsson** for all their help with administrative issues. I especially thank **Struan Gray** for revising this thesis.

Also, I appreciate all my former and current friends at Halmstad University and Linköping University.

Being a PhD student not only shaped my life but also affected my beloveds' lives. With my deepest gratitude, I wish the best for my **mother** and my **father**, who endured the distance to us and their grandchildren during these years, and for my **wife** for her endless love and kind support.

Ebrahim Chalangar,
Linköping, March 2021

List of publications

Papers included in this thesis:

Paper I.

Influence of Morphology on Electrical and Optical Properties of Graphene/Al-Doped ZnO-Nanorod Composites

Ebrahim Chalanger, Houssaine Machhadani, Seung-Hyuk Lim, K. Fredrik Karlsson, Omer Nur, Magnus Willander, and Håkan Pettersson.
Nanotechnology, 2018. <https://doi.org/10.1088/1361-6528/aad3ec>.

Contribution: I prepared and characterized the samples and wrote the first draft. I was actively involved in conceiving the research idea and analyzing the results.

Paper II.

Graphene-Based Plasmonic Nanocomposites for Highly Enhanced Solar-Driven Photocatalytic Activities

Rania E. Adam*, Ebrahim Chalanger*, Mahsa Pirhashemi, Galia Pozina, Xianjie Liu, Justinas Palisaitis, Håkan Pettersson, Magnus Willander, and Omer Nur.
RSC Advances, 2019. <https://doi.org/10.1039/C9RA06273D>. (* Both co-first author)

Contribution: I took part in material synthesizing and performed the electron microscopy analysis. I contributed to analyzing the data, writing the first draft and revising the final manuscript.

Paper III.

Synthesis of Vertically Aligned ZnO Nanorods Using Sol-Gel Seeding and Colloidal Lithography Patterning

Ebrahim Chalanger, Omer Nur, Magnus Willander, Anders Gustafsson, and Håkan Pettersson.
Nanoscale Research Letters, 2021. <https://doi.org/10.1186/s11671-021-03500-7>.

Contribution: I prepared and characterized the samples and wrote the first draft. I was actively involved in conceiving the research idea, analyzing the results, and revising the final manuscript.

Paper IV.

Nanopatterned reduced graphene oxide/Al-doped ZnO seed layer for vertical growth of single ZnO nanorods on various substrates

Ebrahim Chalanger, Elfatih Mustafa, Omer Nur, Magnus Willander, Anders Gustafsson and Håkan Pettersson. In manuscript

Contribution: I prepared and characterized the samples and wrote the first draft. I was actively involved in conceiving the research idea, analyzing the results, and revising the final manuscript.

Papers not included in this thesis:

Efficient Photo Catalysts Based on Silver Doped ZnO Nanorods for the Photo Degradation of Methyl Orange

Muhammad Ali Bhatti, Aqeel Ahmed Shah, Khalida Faryal Almani, Aneela Tahira, Sayed Ebrahim Chalanger, Ali dad Chandio, Omer Nur, Magnus Willander, and Zafar Hussain Ibupoto.

Ceramics International, 2019. <https://doi.org/10.1016/j.ceramint.2019.08.027>.

Contribution: I was involved in sample preparation for electron microscopy, performed the SEM and EDS measurements and read the final manuscript.

Facile Synthesis of Copper Doped ZnO Nanorods for the Efficient Photo Degradation of Methylene Blue and Methyl Orange

Aqeel Ahmed Shah, Muhammad Ali Bhatti, Aneela Tahira, Ali Dad Chandio, Iftikhar A. Channa, Ali Ghulam Sahito, Ebrahim Chalanger, Magnus Willander, Omer Nur, and Zafar Hussain Ibupoto.

Ceramics International, 2020. <https://doi.org/10.1016/j.ceramint.2019.12.024>.

Contribution: I was involved in sample preparation for electron microscopy, performed the SEM and EDS measurements and read the final manuscript.

Table of Contents

Abstract.....	v
Populärvetenskaplig sammanfattning	vii
Acknowledgment	ix
List of publications	x
Table of Contents.....	xiii
1 Introduction.....	17
1.1 Zinc oxide/graphene nanocomposites	18
1.2 Zinc oxide/graphene heterostructures.....	20
1.3 Thesis Aim and Outline	21
2 Materials background.....	23
2.1 Semiconductors and electronic band structure	23
2.2 Zinc oxide.....	24
2.2.1 Defect levels in ZnO	25
2.2.2 Doping of ZnO.....	26
2.2.3 Polarity in ZnO nanorods	27
2.2.4 Surface defects and band bending in ZnO nanorods	28
2.3 Graphene and graphene oxide.....	29
2.4 ZnO-graphene heterojunctions	31
3 Zinc oxide-graphene nanocomposites	33
3.1 Synthesis method.....	33
3.1.1 Chemical bath deposition of ZnO nanorods.....	34
3.1.2 ZnO nanoparticles growth on GR nanoplates	36
3.1.3 Aluminum doping in ZnO.....	37
3.1.4 Adding silver iodide into ZnO/GR nanocomposites	38
3.2 Characterization methods	39

3.2.1	Electron microscopy	39
3.2.2	UV-Vis absorption spectroscopy	40
3.2.3	Photoluminescence spectroscopy (PL)	41
3.2.4	Cathodoluminescence spectroscopy	42
3.2.5	X-ray diffraction analysis (XRD).....	42
3.2.6	X-ray photoelectron spectroscopy (XPS).....	42
3.2.7	Surface resistivity measurements	43
3.2.8	Photoconductivity measurements.....	44
3.2.9	Photodegradation efficiency measurements.....	45
3.3	ZnO-NRs/GR for electronics applications.....	46
3.3.1	Effects of pH on the morphology of ZnO-NRs/GR.....	46
3.3.2	Improving the conductivity of ZnO-NRs/GR by Al-doping ...	47
3.3.3	Bonding quality between GR and ZnO-NRs	48
3.3.4	Optical properties of ZnO/GR nanocomposites	49
3.4	ZnO-NPs/GR for photocatalytic applications.....	52
3.4.1	Silver iodide	52
3.4.2	Characterization of ZnO/GR/Ag/AgI nanocomposites	53
3.4.3	Photocatalytic performance of the nanocomposites.....	55
4	Template-assisted nanofabrication of ZnO-NRs/GR.....	57
4.1	Synthesis methods.....	57
4.1.1	Synthesis of GO using the improved Hummer's method	58
4.1.2	ZnO sol-gel solutions.....	60
4.1.3	CBD of ZnO-NRs on patterned substrates.....	60
4.2	Nanofabrication of patterned substrates	61
4.2.1	Spray coating of GO buffer layers.....	62
4.2.2	Dip-coating of the ZnO sol-gel solution	64
4.2.3	Colloidal lithography (CL) patterning.....	64
4.2.4	Thermal evaporation	65
4.2.5	Dry etching.....	67
4.2.6	Wet etching.....	67
4.3	Characterization methods – Atomic force microscopy	68
4.4	Characterization of the CL-patterned substrates.....	70

4.4.1	Why using Si/GO substrates?	70
4.4.2	Improved ZnO seed layers by dip-coating.....	71
4.4.3	Reduced GO/Al-doped ZnO seed layers.....	73
4.4.4	Distribution of polystyrene nanobeads on surfaces.....	73
5	Conclusions and Outlook.....	77
	References.....	79
	Part II: Papers.....	89

1 Introduction

Today, electronic devices are evolving very rapidly, with greater functionality and faster and more reliable operations. This progress has affected our daily lives and led to further integration of the latest technologies into various aspects of our lives. The Internet-of-things (IoT), comprised of novel embedded systems with a massive number of collective sensors, is now being marketed to assist with health, education, transportation, and many more. 5G-communication, with its remarkable predicted advantages, provides the faster, ultra-reliable, and massive wireless connection between devices that is demanded by other applications. In step with the expansion of these technologies, the need for more energy, and the consequent increase in environmental pollution, become more pronounced. So, the future of sustainable growth relies on developing more efficient hardware to balance requirements with resources. To improve devices' efficiency, additional new functional materials are required. The new devices should also be affordable and inexpensive to facilitate widespread adoption of new massively embedded applications.

Despite all efforts, the range of materials with the desired electrical and optical properties is still limited by their functionality or cost. One way to overcome these challenges is to develop new composites of already existing, well-known materials with desirable synergistic enhanced properties. In fact, recent advances in nanotechnology have provided more insights towards a better understanding and implementation of novel composite materials in various applications. This thesis particularly deals with semiconductor materials with nanometer-scale dimensions and their composition with other nano-electronic materials.

Research into innovative nanocomposite materials and their new applications has attracted much recent interest and effort. A vast number of metal-semiconductor [1], multiple metal oxides [2], and organic-inorganic [3] nanocomposites with improved properties have been generated and used in broad fields of applications such as energy, hydrogen evolution, the environment, disinfection and purification. A combination of semiconductors and 2D materials such as graphene (GR) is another exciting class of composite materials with promising characteristics for photocatalysis, sensors, energy, and electronic applications [4]. To date, various such nanocomposites, including group IV (Si), group II-VI (ZnO, ZnS), group III-V (GaAs, GaN), and metal oxide semiconductors (TiO₂, ITO), have been realized [4].

The research presented in this thesis is mainly focused on the possible composites of zinc oxide (ZnO) and GR, exploring their fundamental properties and realizing their potential applications in electronics and photocatalysis. The materials were selected based on their suitable intrinsic optical and electrical properties for the mentioned applications. Individually, these two well-known materials have been thoroughly investigated in many previous studies. But the combination of the two has recently gained popularity due to the resulting synergistic enhanced properties, which are not available in each of the single materials.

1.1 Zinc oxide/graphene nanocomposites

Composites of ZnO and GR have been realized in several research reports [5–8] with strong evidence of a good crystal growth compatibility due to excellent matching of their crystal lattices [9–11]. Growth of various ZnO structures on a GR surface in the forms of nanoparticles (0D) and nanorods (1D) can be found in the literature, prepared by various higher-temperature, vacuum-required, or solution-based growth techniques. Also, a wide range of applications of these composite materials in electronics, optoelectronics, photovoltaics, and sensors have been demonstrated [4]. Despite these efforts, a research gap between the optimal functionality and the fabrication simplicity of ZnO/GR is still observable. In other words, in the majority of the reports, production of high-

performance ZnO/GR nanostructures usually required sophisticated methods, leading to more expensive products. Further developments in the nanocomposite's growth procedure with significant control over the final structure are crucially needed to meet the criteria of optimal desired properties and low-cost production. This is what motivated us to conduct this research work.

This PhD study, therefore, probes ways to fill this gap by combining a simple growth technique and precisely designing the ZnO/GR structures suited for electronics or as a photocatalyst. Growth of different morphologies of ZnO on the GR nanoplates was achieved, and the nanocomposites were investigated for higher electrical conductivity, optical properties, and enhanced photocatalytic efficiency. Moreover, we pursued a method to fully control the final structures of the nanocomposites with respect to their density, alignment, ordering, and feature size, using colloidal lithography and optimized seed layers.

Our results show successful growth of Al-doped ZnO nanorods (NRs) on GR nanoplatelets with optimized porosity and electrical conductivity, suitable for electronic applications in which inexpensive large-volume of conductive materials are required, e.g., 3D printing. Also, highly efficient solar-driven photocatalysts of ZnO, GR and silver iodide (AgI) for removing organic pollutants from water were achieved and exhibited. Additionally, a novel nanofabrication method of vertically aligned ZnO nanorods on different substrates, using a combination of colloidal lithography and sol-gel seeded layers, was demonstrated.

Our findings are important for further understanding the basic charge carrier transport mechanism in the semiconductor-graphene interfaces, photocarrier generation and recombination, and energy defect levels in the ZnO/GR nanocomposites. The results can be used to tailor the conductivity of future 3D-printable material with large volumes and inexpensive porous structures. Also, the solar-driven photocatalysts developed here are beneficial for environmental purification since they can remove organic pollutants from water using the energy in sunlight. Moreover, our nanofabrication method offers a simple and inexpensive solution for controlling the NRs' growth and enhancing their alignment with substrate-independent flexibility. Finally, our work can help to produce cheaper, porous, conjugated graphene-semiconductor composites to

fabricate high-performance devices where vertically ordered ZnO-NRs of high crystalline quality are essential.

1.2 Zinc oxide/graphene heterostructures

Similar to conventional metal-semiconductor junctions, GR-semiconductor junctions generally show rectifying characteristics [12]. When two materials are atomically close to each other, a junction is formed at their interface. The type of junction depends on the similarity of the crystal structure, e.g., bandgap difference, valence band matching, lattice mismatch, and the type and level of doping in the two materials. If the materials are the same, a homojunction is formed at the interface, for example, a p-n junction of a semiconductor with different donor and acceptor dopants.

A heterojunction forms at the interface of two dissimilar semiconductor materials, usually by heteroepitaxial growth of fairly lattice-matched semiconductors on top of each other. The crystal lattice mismatch is the limiting parameter for the epitaxial growth, inducing atomic displacements (strain) and dislocations at the interface unless the epitaxial layer is extremely thin. As a result of the difference in bandgap energy and the band alignments at the interface, such heterojunctions are the building-blocks for many interesting applications, including laser diodes, light-emitting diodes (LEDs), resonant tunneling diodes, photodetectors, and solar cells.

The lattice mismatch between the joint materials can be tolerated if lower-dimensional materials, e.g., nanoparticles (0D) or nanorods (1D), with a lower interfacial area, are used. In this case, the strain energy at the heterojunction is relieved via elastic relaxations, leading to more stable structures [13, 14]. The stability of the structure depends on the lattice mismatch factor and the size of the interfacial area, or equivalently, the diameter of the grown particles. Fig. 1-1 shows a typical stability diagram for a heterostructure nanorod system with two stable and unstable regions, depending on the NRs' diameter and the lattice mismatch factor. The nanoparticle and nanorod morphologies of ZnO in our developed nanocomposites were chosen based on this consideration.

Fig. 1-1. Stability diagram for a heterostructure nanorod system with respect to the formation of misfit dislocations. Reprinted by permission from Springer Nature: MRS Online Proceedings Library [13].

1.3 Thesis Aim and Outline

This thesis mainly focuses on a two-material system of ZnO and GR nanocomposites. Two different approaches for synthesizing the ZnO/GR nanocomposites were employed. In the first approach, substrate-free random ZnO/GR structures were synthesized and optimized for electronics and photocatalysis applications. Paper I covers the most important results for ZnO-NRs/GR nanocomposites suited to electronics application, including the effect of the growth parameters on the NRs' morphologies; Al-doping impact on the final conductivity; optical properties; and photocarrier generation and recombination in the nanocomposites.

In Paper II, various composites of ZnO nanoparticles, GR and AgI, with a broader absorption peak in the visible range, were fabricated and tested for higher photocatalytic efficiency. The prepared nanocomposites were characterized using various experimental techniques and were employed to remove organic pollutants from water.

In the second approach, we attempted to improve the order and alignment of the ZnO-NRs, by first appropriately seeding a Si substrate and then patterning the selective area using colloidal lithography (CL). Paper III demonstrates

the patterning technique and the seed layer preparation method used later in Paper IV to fabricate the GR/ZnO-NRs vertically aligned nanostructures.

The thesis places all the experimental achievements in a united context by providing background information in Chapter 2, along with more details about the experiments and the analytical techniques employed. Chapter III deals with Papers I and II, describing the use of ZnO/GR nanocomposites as a conductive, printable material and a photocatalyst. Chapter IV introduces the CL-patterning technique and summarizes the work reported in Papers III and IV. Finally, my PhD research is concluded in Chapter V, followed by a discussion of future challenges and outlooks.

2 Materials background

Before going into our nanocomposite synthesis process in detail, an introduction to the basic concepts of semiconductors, including heterostructures, energy levels, defects, and doping, is given here. This chapter aims to familiarize the reader with the concepts that will be used later, and summarizes what I learned during my experimental research.

2.1 Semiconductors and electronic band structure

Although conductors conduct electrical currents very well, semiconductors are the most exciting materials in electronics. The difference between conductors and semiconductors comes from their atomic structure and the electronic configuration in their crystal lattices. Atoms of an element can form chemical bonds with each other and arrange themselves in a periodic crystal lattice by reforming their electron orbitals to a hybrid orbital configuration. The periodic atom positions introduce a periodic electric potential in the crystal lattice. By applying Bloch's theorem and solving Schrödinger's equation in the tight-binding model, including spin-orbit coupling, the material's electronic band structure can be derived. Detailed equations are to be found in most solid-state textbooks, and only the most important results are given here.

The electronic band structure of a crystalline solid is determined by the density of states in its different energy levels, including the valence band (E_v), conduction band (E_c), and the bandgap (E_g), which has zero density of states. The electrons fill the available energy levels from lower to higher energies according to the Pauli principle, which results in the well-known Fermi–Dirac distribution function (Eq. (2.1)) at a given temperature (T), where k_B is the Boltzmann's constant and E_F is the Fermi energy level.

$$F(E) = \frac{1}{1 + e^{(E-E_F)/k_B T}} \quad (2.1)$$

E_F is defined as the energy level with a 50% probability of occupation under conditions of thermodynamic equilibrium. Equivalently, E_F is the total chemical potential of the electrons, which is equal to the energy required to add or remove an electron into the system. E_F can be measured directly by a voltmeter relative to a reference point. E_F changes result from any variation in the kinetic or potential energy of the electrons, such as from an external potential, adding acceptor or donor impurities to semiconductors, or many kinds of mechanical, photonic, or thermal excitation in materials. Fig. 2-1 shows the typical E_F position in various types of materials relative to their valence and conduction bands.

Fig. 2-1. Energy band gap diagram for various materials. The horizontal and vertical axes indicate the density of states and the energy levels, respectively. The black-white contrast shows the Fermi–Dirac distribution of electrons. From Wikipedia under CC0 1.0 License.

2.2 Zinc oxide

Zinc oxide has been studied for decades as a well-characterized, unintentionally n-type semiconductor. It has a hexagonal wurtzite crystal structure and a wide direct bandgap of 3.2–3.4 eV at room temperature. Because of its high mechanical and thermal stability, large exciton binding energy of 60 meV, and promising electrical and optical properties [15], it has attracted a great deal of interest in a broad range of applications, including LEDs, sensors, piezoelectrics, and electrochemistry [16]. The other beneficial aspect of using ZnO is the excellent

flexibility in growth techniques and the various possible morphologies of nanoparticles (NPs), NRs and thin films. In the following section, the defects and dopants in a ZnO crystal, which are the main origin of its electrical and optical characteristics, are briefly reviewed.

2.2.1 Defect levels in ZnO

During the ZnO growth process, various defects may be introduced in the crystal lattice, with corresponding defect energy levels in the ZnO band structure. Donor-like defects of oxygen vacancy (V_O) and interstitial zinc (Zn_i), and acceptor-like defects of zinc vacancy (V_{Zn}) and interstitial oxygen (O_i) are the most likely native point defects in ZnO.

In many publications, the unintentionally n-type conductivity of ZnO has been attributed to the V_O and Zn_i , but more accurate studies have shown that these point defects cannot be the cause of the n-type behavior, as neither engaged in the conductivity [17]. The reason is that the donor-like native defects in ZnO are either deep level donors or have a high formation energy and so a very low formation probability [17–19]. In general, only the shallow defect levels, close to the band edges, can be thermally ionized at room temperature and participate in the conductivity, and not the deep levels [19]. Fig. 2-2 shows the energy levels of the native defects in the ZnO bandgap in comparison to H and Al donor levels. Although V_O^{2+} and Zn_i shallow defects are relatively close to the CB, they are unlikely to form due to their high formation energy, showing very low concentrations in the ZnO band structure under conditions of thermodynamic equilibrium [19]. These defect levels are the origin of the visible emissions in the luminescence spectra caused by electron-hole recombination.

Instead, the interstitial hydrogen (H_i^+) impurity has been proposed as a shallow donor and the source of the n-type conductivity of ZnO at room temperature. Hydrogen impurity atoms can bond to an O atom, forming an -OH group, or replace O in ZnO and form four equal bounds to four neighboring Zn atoms with relatively low formation energies. The unintentional presence of H in ZnO comes from the available H in the growth precursors. It can be enhanced by

annealing the grown ZnO in an H_2 atmosphere, resulting in higher electrical conductivity.

Fig. 2-2. Energy band diagram of native defects and H and Al donor impurities in ZnO. Filled and empty bars represent donor and acceptor levels, respectively. Gathered from Refs. [17–21].

2.2.2 Doping of ZnO

In addition to the unintentional native defects and H impurity, ZnO can be intentionally doped by group-13 impurities of B, Al, Ga and In, or by F [22]. Among these n-type dopants, Al, with its low formation energy and relatively low ionization energy of 120 meV (Fig. 2-2), is a promising candidate, particularly in solution-based ZnO growth techniques. High levels of Al-doping, up to the degenerate level with a carrier concentration of 10^{20} cm^{-3} , have been achieved, changing the electrical properties of ZnO from an insulator to a metal. In contrast to the success achieved with n-type material, p-type doping of ZnO is notably difficult and still challenging.

As a potential application, Al-doped ZnO (AZO) has been widely studied as a transparent conductive oxide (TCO) and is presently considered for substituting conventional TCOs on the market with 85% optical transmittance in the visible range and electrical resistivity down to $10^{-3} \Omega \cdot \text{cm}$ [23–25]. A comparison of different TCOs, including AZO, can be found in Ref. [26]. Usually, post-treatments of thermal or UV annealing are required to improve the conductivity of the final Al-doped ZnO structures.

The bandgap of ZnO can be changed corresponding to the doping level and the carrier concentration. The shift of the bandgap is governed by the contribution of two opposite phenomena, which usually compensate each other: increasing the bandgap proportional to the carrier density (Burstein-Moss effect) and bandgap narrowing [27].

2.2.3 Polarity in ZnO nanorods

Hexagonal ZnO-NRs exhibit an electric dipolar moment along the c-axis and six non-polar m-plane sidewalls in [1100] directions with relatively low free surface energy. The polarity direction is defined as the direction of a vector from the positively-charged Zn-polar to the negatively-charged O-polar face terminations at each unit cell (Fig. 2-3). The Zn- and O-polar faces, with various chemical reactivities, adsorb ambient OH⁻ hydroxyl groups and H⁺ ions, respectively, minimizing their free energies and forming a double electrical layer on the surface [28].

Fig. 2-3. O-polar and Zn-polar faces along the c-axis with flipped-over polarities. Reprinted from [29], Copyright 2020 with permission from Elsevier.

Growing of ZnO-NRs on non-epitaxial substrates is usually required a precoat-optimum nuclei (so-called seed layer) on the surface. The polarity of the seed layer is transferred up into the NRs by a layer-by-layer homo-epitaxial growth

of the O- and Zn-polar unit cells on the bottom polar faces. In fact, the polar c-plane top front is the driving force for the anisotropic one-dimensional growth of the ZnO-NRs [28]. Thus, any induced surface charge or applied normal-to-substrate electric field will facilitate the polar alignment and can lead to higher NRs alignment [30]. Fig. 2-4 shows the polarity transfer from the seed layer into the grown ZnO nanorods.

The polarity in ZnO-NRs also has a vast influence on the native defects' spatial distribution within the NRs. It has been shown that the V_O defects have a much smaller formation energy on the non-polar m-plane surfaces, which will lead to higher V_O concentration on the surface of ZnO-NRs [29]. The high surface defect concentration has an important effect on persistent photoconductivity in ZnO, which is explained below.

Fig. 2-4. Effect of a (a) poorly and a (b) highly polar oriented polycrystalline seed layer on the growth of ZnO-NRs. Reproduced with permission from [31]. © IOP Publishing. All rights reserved.

2.2.4 Surface defects and band bending in ZnO nanorods

Due to the high concentration of V_O defects on the ZnO surface, oxygen molecules in the atmosphere are attracted and chemisorbed on the ZnO surface with a thermal energy barrier of about 0.25 eV [32]. The surface chemisorbed O_2 molecules attract and capture free electrons from the ZnO core. Due to the low concentration of free electrons in undoped samples, the electric field inside the semiconductor, induced by the surface chemisorbed ionized O_2^- , cannot be effectively screened. In this scenario, a built-in electric field is formed near the surface, and the energy bands are bent. Consequently, the area is depleted of free

carriers, similar to a p-n junction [33–36]. Fig. 2-5 shows schematically band bending on the surface of a ZnO-NR and the free carrier depletion shell.

Fig. 2-5. Energy band bending on a ZnO-NR surface due to the surface chemisorbed O_2 . The yellow area indicates the depletion region.

Usually, UV exposure increases the conductivity of ZnO by oxidizing the chemisorbed species, e.g., oxygen or water, on the ZnO surface. Under UV irradiation, the photogenerated holes migrate toward the surface and are consumed by the surface ionized O_2 species, leaving behind excess photoelectrons in the conduction band. These excess free electrons enhance the ZnO conductivity [37]. After switching off the UV, ambient species are chemisorbed again on the surface, and the persistent conductivity decays.

2.3 Graphene and graphene oxide

Graphene (GR), one of the most famous 2D materials, has attracted great interest over the last 15 years due to its remarkable electrical properties. In GR, a single layer of carbon atoms forms a 2D honeycomb-lattice structure with unique properties, such as high carrier mobility (up to $10^6 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), low electrical surface resistivity ($0.1\text{--}6 \text{ k}\Omega/\square$ for a single layer with 97.7% optical transparency), and excellent chemical stability and mechanical strength [38]. Each carbon atom in graphene is bonded to neighboring C atoms by three strong σ -

bonds formed of hybridized sp^2 orbitals, and an out-of-plane conjugated π -bond, which is responsible for GR's electrical conductivity.

The attainable characteristics of GR significantly depend on the layers' singularity. As the number of graphene layers is increased, its properties change dramatically into those of graphite. As a standard arbitrary threshold, backed up by the International Organization for Standards (ISO), more than ten graphene layers are considered graphite instead of graphene [39]. According to this standard, graphene as a single layer is abbreviated as 1LG, bilayer graphene as 2LG, and few-layered graphene as FLG.

Graphene can be synthesized using the three main techniques of i) CVD growth on an appropriate substrate, ii) epitaxial growth on SiC surface, and iii) exfoliation of graphite flakes [38–40]. The bottom-up CVD and epitaxial growth techniques typically result in high quality and large wafer-scale areas of single and multiple-layer graphene films, suitable for high-performance carbon-based electronic applications. Although these methods are effective in terms of quality, their potential applications are limited by production costs.

In the other, inexpensive approach, a high volume of GR can be produced using a top-down, low-cost and facile technique based on exfoliation of bulk graphite into graphene nanoplates (GNPs). In the chemical exfoliation technique, chemicals are intercalated between the graphite layers, which weakens the cohesive van der Waals forces, causing graphite expansion and finally exfoliation [41, 42]. The final product of the exfoliation technique consists of a dispersion of synthesized graphene oxide (GO) flakes in a liquid, with a range of different thicknesses and lateral sizes that can further be dried in a powder form. Despite the simplicity and cost-effectiveness of this method, a significant portion of the final flakes have excess layers due to agglomeration between the particles. In this research, chemically exfoliated GNP has been used to develop the other nanocomposites.

Despite all the electrical advantages of GR, it also has disadvantageous characteristics that make it undesirable for direct use in some applications. Generally, graphene is highly hydrophobic with a strong tendency not to interact

with other materials, making it almost non-dispersible in water or any organic solvent [43]. In addition, the GNPs undesirably agglomerate into large particles due to their high aspect-ratio and the existence of van der Waals forces between the flakes.

On the other hand, GO shows completely different characteristics compared to GR. Due to the presence of high-density oxygen functional groups (in the range of 40-70% oxygenated carbon atoms [44, 45]) on its surface, GO is highly water dispersible, easy to interact with, and convenient to process. However, GO is an insulator and should be reduced to GR after the deposition process, usually by strong reductant chemicals like hydrazine, thermally [46], or by UV irradiation [47].

2.4 ZnO-graphene heterojunctions

As explained in the previous chapter, epitaxial heterostructures are formed by strong covalent bonding between two dissimilar semiconductors, in which lattice matching is a critical parameter. Alternatively, van der Waals forces between a 2D material and other materials can also form stable heterostructures with interesting electronic properties. These van der Waals heterojunctions are formed by weaker van der Waals interactions between a 2D material and any passivated, dangling-bond-free material, independent of the lattice matching [48]. It is worth noting that the charge-transfer mechanism at the interface of these heterojunctions is by tunneling and hopping of electrons since the band structure is discontinuous at the interface [48].

In addition to van der Waals interactions, it has been shown that ZnO can also efficiently be grown on the GR surface [5, 8, 9, 49] with a relatively small lattice mismatch of about 2% [10, 50]. From an electrical point-of-view, this fairly well-matched interface between ZnO and graphene can lead to a Schottky or low-ohmic contact, depending on the doping level and heterojunction band alignment [7].

3 Zinc oxide-graphene nanocomposites

The low cost and simplicity of any novel material fabrication process greatly influence potential applications of the developed materials. Among different fabrication techniques, solution-based methods are simple, inexpensive and energy-efficient, with important practical industrializing capabilities. The main advantages of these techniques come from the low-temperature and atmospheric pressure growth conditions. This chapter describes how the chemical bath deposition technique was used to synthesize various substrate-free ZnO/GR nanocomposites, mainly developed for electronics and photocatalysis applications. The synthesized nanocomposites, with random grown structures, have been investigated for improved dispersity, morphology, electrical and optical properties, and photocatalytic efficiency. Papers I and II address the material discussed in this chapter.

3.1 Synthesis method

Several synthesis methods of ZnO-NRs have been realized during the last two decades. Most of these techniques require high temperature or sophisticated vacuum equipment for NRs growth that causes the final grown structures to more expensive, usually harder to industrialize, and applicable to limited areas. Chemical vapor deposition (CVD) is one of the most reported ZnO-NRs growth techniques that can provide high-quality NRs at a high-temperature range of 500-950 °C, but at atmospheric pressure [51, 52]. The high-temperature growth limits the usage of some potentially interesting substrates, especially flexible substrates, in such a growth process. Some other techniques, e.g., pulsed laser deposition (PLD) [53], vapor-liquid-solid (VLS) [52] and sputtering [54], operating at high vacuum conditions, result in high crystal quality but with a low

deposition rate. Generally, using vacuum deposition techniques raises the production cost, and it is not favored in industry.

3.1.1 Chemical bath deposition of ZnO nanorods

Among the available growth techniques, solution-based growth methods, with advantages including simplicity, low-temperature and atmospheric pressure growth, are promising for synthesizing materials at a lower cost. Chemical bath deposition (CBD) and hydrothermal growth (HTG) are the two types of solution-based growth techniques that sometimes are used conversely by mistake. While CBD refers to the growth process at low temperature and atmospheric pressure, HTG indicates the process at a higher temperature and higher pressures, using a metal or Teflon autoclave.

In CBD of ZnO-NRs, a saturated aqueous solution of the precursors is prepared. Then, an appropriately prepared substrate is suspended in the solution, and the temperature is elevated to a specific range. The CBD process includes two steps of nucleation and crystal growth. At the early stages, nuclei sites are formed by making a solid phase of ZnO from the growth solution. Subsequently, the ZnO crystal continues to grow epitaxially, forming the final crystal structure. However, a drawback of the CBD technique is that homogenous nucleation takes place in the bulk solution, causing many undesired grown structures and higher wastage of chemicals.

Several Zn precursors, including zinc nitrate, zinc acetate¹ and zinc chloride², have been investigated for CBD of ZnO, with a strong influence on the final grown morphologies [55–58]. In this thesis, we have always used an optimized bath solution of equimolar zinc nitrate³ and hexamethylenetetramine⁴ (HMT) for the ZnO-NRs growth. The involved chemical reactions can be summarized as below:

¹ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$

² ZnCl_2

³ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

⁴ $\text{C}_6\text{H}_{12}\text{N}_4$

Dissolving of zinc nitrate and HMT provides Zn^{2+} and OH^- ions in the aqueous solution (equations (3.1) to (3.3)), respectively. The intermediate species produced are sensitively dependent on the pH of the solution. Fig. 3-1 shows that the Zn^{2+} cations are dominant in the pH range of 6-7, while in a higher pH range of 10-11, the $\text{Zn}(\text{II})$ hydroxide complex ions are more pronounced. During anisotropic c-axis growth of ZnO-NRs, the reactive cations diffuse in the bath solution and crystallize on the polar c-plane top face of ZnO-NRs.

In our experiment, two different concentrations of 25 mM and 50 mM zinc nitrate, with the equimolar HMT in DI water, were prepared as the CBD solution. In addition, the pH of the growth solutions was adjusted to the values of 6.6 and 11 by adding ammonia (NH_3). The growth temperature was set to 75 °C and maintained for 2 h. In this approach, the seeded GRs (explained in the next part) were added to the growth solution under mild stirring.

Fig. 3-1. Ionic species concentrations in different pH values for an aqueous solution of 20 mM of zinc nitrate and HMT at 95 °C, Reprinted from [59] under CC BY 4.0 License.

3.1.2 ZnO nanoparticles growth on GR nanoplates

The ZnO-NPs were prepared by hydroxylating the Zn^{2+} in an aqueous solution, using zinc acetate and KOH. The reaction was performed in the presence of GR, to grow the NPs directly on the GR surface. First, an ultrasonicated dispersion of GR in DI water was mixed with a solution of zinc acetate while stirring. Subsequently, a dissolved KOH aqueous solution was added dropwise to the first solution at 60 °C, while under ultrasonication. The seeding process continued in these conditions for 10 min to complete the growth. Then the decorated GR with ZnO-NPs was washed with water and centrifuged at 3000 rpm for 10 min several times and annealed at 300 °C for 30 min.

The grown ZnO-NPs on the GR have two distinguished applications in our research. In the first application, the NPs played a seed layer role to assist the ZnO-NRs growth on the GR nanoplates in subsequent steps. Seeding the GR by NPs improves the GR hydrophobicity and will enhance the attachment between the GR and the ZnO-NRs. For this aim, a low NPs surface density was synthesized using a 500 mg/L dispersion of GR, a 5 mM solution of zinc acetate and 25 mM KOH. An SEM image in Fig. 3-2 shows typical seeded GRs with low-density NPs.

Fig. 3-2. SEM image of the GRs seeded with ZnO-NPs. Reprinted from Paper I [60].

In the other application, an optimized photocatalyst, with a high ZnO-to-GR weight ratio of 99:1, was fabricated. A 10 mg/L dispersion of GR powder, a 10 mM and 50 mM aqueous solution of zinc acetate and KOH, respectively, were used to synthesize the nanocomposite. The NPs here act as photogenerator of charge carriers by absorbing UV light and producing electron-hole pairs.

3.1.3 Aluminum doping in ZnO

The Al-doped samples were synthesized by introducing a specific amount of aluminum nitrate⁵ into the growth solution. Dissolving the Al nitrate provides different Al(III) hydroxide complex species in the solution with a strong dependency on the solution's pH value. As shown in Fig. 3-3, the Al(OH)₃ and anion Al(OH)₄⁻ species are dominant at pH ranges of 6-7 and 10-11, respectively.

The amount of added Al nitrate was selected in a way that the final concentration of 2 mM in the growth solution was met. It is essential to stir the solution for enough time before adding it to the growth solution. The aluminum nitrate solution is a weak acid, reducing the pH of the growth solution to a range of 5-5.5. This pH range is too low for the ZnO growth, and it can also dissolve the seed layer. Before adding the seeded GRs into the growth solution, the pH of the growth solution should be adjusted to desired values by adding enough ammonia.

The Al-doping of the ZnO-NPs was performed differently by immersing a pure piece of Al in the seed solution. The seed solution, explained in the previous part, has a high pH value of 13 that guarantees partial dissolution of the Al and the desired doping level of the ZnO-NPs [61].

⁵ Al(NO₃)₃·9H₂O

Fig. 3-3. Ionic species distribution in different pH values for an aqueous solution of 1.5 mM of aluminum nitrate at 90 °C. Reprinted with permission from [62]. Copyright 2017, American Chemical Society.

3.1.4 Adding silver iodide into ZnO/GR nanocomposites

Silver iodide⁶ was introduced to the optimized photocatalytic ZnO-NPs/GR nanocomposite, with a high ZnO-to-GR ratio, to enhance the light absorption of the final product. First, the prepared ZnO-NPs/GR nanocomposite was dispersed in DI water using an ultrasonic bath for 10 min. Then, silver nitrate⁷ was added to the suspension, stirred for 30 min. Subsequently, an aqueous sodium iodide⁸ solution was introduced dropwise into the solution and ultrasonicated for 1 h. The weight ratio of ZnO-NPs/GR to AgI was chosen as three different values of X=10%, 20% and 30%. The synthesized ZnO/GR/Ag/AgI(X) nanocomposites were washed with DI water and acetone and collected by centrifugation, followed by drying in an oven at 75 °C for 6 h.

⁶ AgI

⁷ AgNO₃

⁸ NaI

3.2 Characterization methods

The synthesized nanocomposites were analyzed using a large variety of experimental techniques. In this part, a brief description of the characterization techniques used in this thesis work is given. It can help the readers to understand better and interpret the results.

3.2.1 Electron microscopy

Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) were used to study the structure and the morphology of the synthesized nanocomposites. In contrast to optical microscopes, electron microscopes use a focused electrons beam, with a relatively much shorter electron *de Broglie* wavelength than photons, to produce higher magnifications.

The Zeiss Sigma 500 Gemini microscope, equipped with a field emission gun operating at 10 kV and Gemini Inlens secondary electron detector, was used to capture the SEM images. In SEM analysis, since the scattered electrons are detected on the same side as the incident beam, having enough conductivity in the samples for discharging is the only criterion to measure the specimens.

In TEM, electrons pass through the sample and the scattered beam is detected on the other side of the sample. Thus, the samples should be thin enough (<100 nm) to be electron transparent. This usually means more sample preparation steps are required for TEM measurement. The FEI Titan³ 60-300 microscope, equipped with image and probe Cs correctors and a monochromated high brightness XFEG gun, operated at 300 kV, was used for TEM imaging, scanning TEM (STEM) and high-angle annular dark-field imaging (HAADF).

Interaction between the incident electron beam in SEM and TEM and the subshell electrons in the sample atoms leads to X-ray emission, with a characteristic fingerprint of the specific elements in the sample. This method, called dispersive x-ray spectroscopy (EDS), was used to identify the elements' spatial distribution and perform chemical analysis of the sample. Using STEM-EDS, elemental map images with a resolution of a few nanometers can be obtained.

3.2.2 UV-Vis absorption spectroscopy

In UV-Vis spectroscopy, the absorption of the medium at each wavelength is measured by transmitting monochromated light through a medium. The absorption spectra were measured using the spectrometer PerkinElmer Lambda 900, equipped with two radiation sources of deuterium and tungsten lamps, and two PbS and PMT photodetectors. The spectrometer can measure in a wavelength range of 175 to 3300 nm. The tungsten lamp provides radiation in the near-infrared (NIR) and visible (Vis) ranges, down to 320 nm wavelength, while the deuterium lamp covers the UV range. Dispersing the radiation beam at a grating produces a nearly monochromatic beam with which to irradiate the sample.

The beam alternatively passes in two different paths, one from the sample and one from a reference (usually an empty cuvette or the substrate), as shown schematically in Fig. 3-4. The transmitted intensities are detected as I and I_0 , respectively. The PMT and PbS photodetectors are used in the UV-Vis range up to 860 nm and in the NIR range, respectively. The transmittance (T) and the absorption (A) are calculated based on equations (2.1) and (3.7), only if the reflection from the samples is negligible; otherwise, the adsorption in (3.7) will be an approximation.

$$T = \frac{I}{I_0} \quad (3.6)$$

$$A = -\log T \quad (3.7)$$

Fig. 3-4. Schematic of the monochromated beam paths, passing through the reference and the sample with corresponding transmittance intensities of I_0 and I .

3.2.3 Photoluminescence spectroscopy (PL)

According to *Planck's* law of black-body radiation, hot materials can emit electromagnetic radiation, a phenomenon called incandescence. However, heating is not the only way to excite the materials. Alternatively, atoms and molecules can be excited by receiving energy in other forms, such as electrical current, impinging electrons, or absorbing photons. When these other forms of excitation result in spontaneous emission of light from a substance (cold-body emission), the names electroluminescence, cathodoluminescence, and photoluminescence are used, respectively.

In this work, a micro-PL (μ -PL) setup, schematically shown in Fig. 3-5, was used to study the optical characteristics of the samples. The PL measurement was conducted at room temperature with an 80 μ W, 266 nm excitation laser. A microscope lens focuses the laser beam on the sample with about 1 μ m spatial resolution. The photon energy of the excitation laser (here 3.4 eV) determines the excitation type in the experiment, band-to-band excitation (for the ZnO samples with the bandgap energy of 3.3 eV), or sub-bandgap excitation due to the defect levels. Alternatively, the intensity of the incident laser controls the density of photoexcited carriers. Radiative recombination between the photoexcited electron-hole pairs can occur through band-to-band recombination and sub-bandgap defect levels. This means the obtained PL spectrum gives direct information about the energy level structure and the system's impurity states [63].

Fig. 3-5. Schematic of the μ -PL setup.

3.2.4 Cathodoluminescence spectroscopy

Very similar to PL, cathodoluminescence uses a focused electron beam to excite the sample locally. Then the luminescence is recorded as a spectrum. With a spatial resolution of tens of nanometers, this technique is relatively more local probing compared to μ -PL. One difference between PL and cathodoluminescence is the lower penetration depth of electrons into the substance compared to photons. This leads to more surface-related data in cathodoluminescence compared to bulk-related PL measurement. The cathodoluminescence study was performed in a dedicated SEM at room temperature, operated at 5 kV. In this thesis, the acronym CL, often used for cathodoluminescence, is reserved for colloidal lithography, as described in the next chapter.

3.2.5 X-ray diffraction analysis (XRD)

X-ray diffraction is a form of scattering from a periodic array with long-range order that ensures constructive interference at specific angles and so forms diffraction patterns. The diffraction pattern contains information about the atomic arrangement, the crystal plane orientation, and the element's fingerprint. The constructive interference angles from the parallel planes of a crystalline structure are calculated according to *Bragg's law*.

In this work, we used the PANalytical X'Pert Pro diffractometer, equipped with the Empyrean Cu X-ray tube, operating at 45 kV and an electron current of 40 mA, with the X-ray emission at the Cu K α line with 1.5418740 Å wavelength. An X'Celerator detector, in scanning line operation mode, and a nickel β -filter were used on the diffracted beam side.

3.2.6 X-ray photoelectron spectroscopy (XPS)

XPS is a photoelectric experiment in which a sample is irradiated with monochromatic X-ray, with a photon energy higher than the work function (ϕ_0) of the sample, causing emission of electrons (so-called photoelectrons) from the sample. The kinetic energy (E_K) of the emitted electrons is measured by a spectrometer in ultra-high vacuum (UHV) conditions. Knowing E_K , the binding energy

(E_B) of the electrons in the material can be calculated according to *Einstein's* equation (3.8).

$$E_K = h\nu - E_B \quad (3.8)$$

E_B is defined as the energy difference between the total ground state energy of an atom and the total energy of a cation with a core hole. In contrast to the valence electrons, the core-level electrons are tightly bound to the nucleus in an atom and do not participate in chemical reactions. In XPS, only the core-level electrons, with an E_B smaller than the energy of the X-ray source, are probed. This detectable E_B range is 0-1200 eV for a typical Al K α X-ray source. In the XPS spectra, each element in the sample shows a unique set of binding energies as a fingerprint, denoted by its relevant quantum energy level (n), the angular momentum quantum number (l), and the total angular momentum number ($j=l\pm s$) (s is the spin quantum number).

Because of the short inelastic mean free path of electrons in materials, XPS analysis is extremely surface sensitive, with the highest conveyed information from a depth of a few atomic layers and a small fraction from deeper layers. The technique has a relatively low lateral resolution, about 150 nm to 15 μ m, but an excellent detection limit of about 0.1 at% for essentially all elements except hydrogen.

One important application of XPS is to analyze chemical bonding in complex samples, e.g., nanocomposites, by precisely determining the chemical shifts in the E_B of the core electrons. Although the core-level electrons are not involved in chemical reactions, the electronegativity of the neighboring atoms can shift their binding energy. In general, a lower charge density around an atom shifts the E_B of the core electrons toward higher energies.

3.2.7 Surface resistivity measurements

The surface resistivity was measured by the four-point probe method using a Keithley 4200-SCS semiconductor characterization system. The method is based on an in-line four-point array of probes, touching the sample surface with an equal distance (s) from each other. A current (I) passes from the outer probes

while the potential difference between the inner probes (V) is measured. For an infinite sample with infinitesimal thickness, the sheet resistivity (ρ_s) is calculated based on (3.9). For finite samples with finite thickness, depending on the ratio of the sample dimensions to the probe spacing (d/s) and the ratio of the sample thickness to the probe spacing (w/s), different correction factors (C) are required. A table of the corresponding correction factors can be found in [64].

$$\rho_s = \frac{V}{I} \frac{\pi}{\ln 2} = \frac{V}{I} C, \quad C \cong 4.5324 \quad (3.9)$$

3.2.8 Photoconductivity measurements

The conductivity (σ) of a substance is the product of the carrier density (n) and the carrier mobility (μ_q) in the substance, according to (3.10), where q is the elementary charge. In semiconductors, increasing the carrier density by any form of excitation in the material, e.g., photoexcitation, leads to enhancing its conductivity (so-called photoconductivity).

$$\sigma = n \cdot q \cdot \mu_q \quad (3.10)$$

To measure the photoconductivity (PC) of the synthesized nanocomposites, the materials were sandwiched between two ITO electrodes with specified area and spacing to form an ITO/nanocomposite/ITO structure. A pulsed monochromatic excitation light, at room temperature and bias of 1 V, irradiated the samples. A Keithley 2400 SourceMeter recorded the current during optical excitation with different wavelengths from 320 to 400 nm.

Using the decay curve in the PC, after switching off the excitation light, the time-dependence of the PC of the samples can be calculated. The PC is proportional to the density of photoelectrons in the conduction band (CB), and it decays exponentially with time due to recombination of the photogenerated carriers [65]. The equations below relate the PC variation rate to the photoelectron lifetime, where σ_{ph} is the photoconductivity after subtracting the dark conductivity, τ_d is the decay time constant (photoelectron lifetime) and σ_0 is the observed PC directly after switching off the light.

$$\frac{d\sigma_{ph}}{dt} = -\frac{\sigma_{ph}}{\tau_d} \quad (3.11)$$

$$\ln \sigma_{ph} = -\frac{t}{\tau_d} + \ln \sigma_0 \quad (3.12)$$

3.2.9 Photodegradation efficiency measurements

The photodegradation efficiency of the nanocomposites, which were developed for photocatalysis applications, was investigated by the degradation of Congo red (CR) dye under simulated solar light. A small amount of the nanocomposite (50 mg) was mixed with 100 ml of CR-dye solution with an initial concentration of 20 mg/l. After reaching the adsorption-desorption equilibrium conditions between the nanocomposite and the dye molecules in the dark, the mixture was exposed to the simulated solar light for 60 min in 15 min interval steps. Time-resolved UV-Vis absorption spectra of the remaining CR-dye were recorded at each step. The CR-dye has a specific adsorption peak at 497 nm, which decays with irradiation time, verifying the degradation of the CR-dye.

The photodegradation efficiency was calculated based on the Beer-Lambert law, stating that the absorption is proportional to the dye concentration [66], using equation (3.13), where A_0 is the initial absorption, and A is the absorption after irradiation.

$$\text{Degradation (\%)} = \frac{A_0 - A}{A_0} \times 100 \quad (3.13)$$

In addition, the degradation rate constant was also calculated based on the Langmuir-Hinshelwood's pseudo-first-order kinetic model [67]. It was achieved by linear fitting to the logarithm scale plot of the relative concentration of CR-dye vs. time, according to the equation below: C_0 is the initial concentration of dye and $C(t)$ is the concentration of the dye after irradiation time t .

$$\text{Degradation rate constant} = \frac{\ln \left(\frac{C_0}{C(t)} \right)}{t} \quad (3.14)$$

3.3 ZnO-NRs/GR for electronics applications

The ZnO-NRs/GR nanocomposite was developed and assessed for higher electrical conductivity. At the beginning of this research project, the ambition was to fabricate conductive nanocomposites based on ZnO and GR for 3D-printed electronics. The advantages of such a composite stem from its high macroporosity, thermal and mechanical stability and cost-effectiveness, suitable for bulk printing applications. Many electronic components can be produced by additive manufacturing in the case of existing highly conductive and inexpensive printable materials. Here, we report the electrical and optical properties of our developed ZnO-NRs/GR nanocomposite and the effect of morphology and Al-doping on the properties of the final nanocomposites. This section is addressed in Paper I.

3.3.1 Effects of pH on the morphology of ZnO-NRs/GR

The ZnO-NRs/GR nanocomposites were grown at two different pH values of 6.6 and 11, with and without Al-doping. The pH values were chosen to avoid unstable and opaque precipitation during the growth (Section 3.1.1). The results in Fig. 3-6 show that the growth of ZnO-NRs at pH 6.6 leads to a hexagonal, thicker (mean diameter 313 nm), longer (1–2 μm), and sparser structure compared to growth at pH 11. Alternatively, growing at pH 11 results in more needle-like NRs with a mean diameter and length of 196 nm and 0.5–1.5 μm , respectively. In addition, the average density of NRs on the GR surface was increased from 1.4 μm^{-2} to 2.4 μm^{-2} in the corresponding growths at pH 6.6 and 11.

Fig. 3-6. SEM images of ZnO-NRs/GR nanocomposites grown at (a) pH 6.6 and (b) pH 11. The insets show the size distribution of the NR diameter. Reprinted from Paper I [60].

3.3.2 Improving the conductivity of ZnO-NRs/GR by Al-doping

It is expected that the growth of wide bandgap ZnO-NRs on GR will reduce the conductivity of the composite. To solve this issue, we degenerately doped the ZnO-NRs by 0.5-1.5 at% Al, as explained above in Section 3.1.3. Subsequently, the electrical resistivity of the samples was measured by the four-point probe technique on the deposited materials. A comparison of the measured resistivities is demonstrated in Fig. 3-7. It shows that spacing between the GRs, either

by NPs or more pronounced by NRs, leads to higher resistivity. Also, it is readily observed that Al-doping strongly improved the nanocomposite conductivity. Since the GRs are the most conductive agent in the nanocomposite, it is reasonable that any introduced spacing between them will result in lower conductivity in the nanocomposite.

The very high resistivity in the undoped samples indicates a good dispersion of the GRs by ZnO-NRs, and also shows that the main portion of the current flows through the NRs. It is worth noting that even though the synthesized ZnO-NRs/GR nanocomposites show relatively lower electrical conductivity, they occupy more space with relatively greater free space in their macroporous structure. This is very useful when mixing with other polymer materials, e.g., thermoplastics, for 3D-printing applications. In this perspective, we believe that the product of the conductivity and the macropores vol% ($\sigma \times \frac{V_{\text{macropores}}}{V_{\text{nanocomposite}}} \times 100$) is a better quantity to be compared between the nanocomposites.

Fig. 3-7. Comparison of measured electrical resistivity of GRs, ZnO-NPs/GR and ZnO-NRs/GR nanocomposites grown at pH values of 6.6 and 11, with (green bars) and without (red bars) Al-doping. Reprinted from Paper I [60].

3.3.3 Bonding quality between GR and ZnO-NRs

The quality and the strength of bonding between the GR and the grown ZnO-NRs are essential aspects of our developed synthesis method, with a direct effect

on the composite conductivity and its optical properties. The time-dependent UV-Vis spectroscopy reveals the existence of different material phases in the dispersion of the nanocomposite. The separate phases in the dispersion precipitate with different speeds, and consequently, can be identified using their different absorption spectra. Our results in Paper I show a uniform decrease in absorption for the ZnO-NRs/GR nanocomposites grown at higher pH values 11 and a non-uniform change for the samples grown at pH 6.6. This suggests that the growth at a higher pH solution leads to a better attachment of ZnO-NRs to the GRs.

3.3.4 Optical properties of ZnO/GR nanocomposites

The effect of the pH growth solution and Al-doping on the optical properties of the ZnO/GR nanocomposites was studied by PL analysis. In Paper I, the PL data show variation in the near-bandedge emission (NBE) in the UV range, and deep-level emission (DLE) in the visible spectrum for the various nanocomposites. Table 3-1 shows the ratio of NBE-to-DLE integrated intensities ($I_{\text{NBE}}/I_{\text{DLE}}$) for different ZnO-NRs nanocomposites.

To summarize, growing at higher pH 11 caused a significantly lower UV-to-visible emission ratio in all the samples. This lower emission ratio indicates higher defect levels concentration in the samples grown at pH 11, due to the increased surface-to-volume ratio in the structure compared to growing at pH 6.6. It was also observed that Al-doping reduced the $I_{\text{NBE}}/I_{\text{DLE}}$ ratio for all samples. This reduction can be explained by the introduced Al donor levels in the bandgap and by the lower crystalline quality of the doped ZnO [68, 69].

The results also show an increase in UV-to-visible emission ratio for ZnO/GR composite samples compared to the pure ZnO structures. Reviewing the literature, this increase in the emission ratio can be attributed to the reduction of the surface defects concentration of the ZnO by the oxygen groups on the GR surface, or to resonant excitation of GR plasmons. More information can be found in Paper I.

Table 3-1. The NBE-to-DLE integrated intensity ratio ($I_{\text{NBE}}/I_{\text{DLE}}$) for different ZnO-NRs/GR nanocomposites.

	Grown at pH 6.6	Grown at pH 11
ZnO-NRs	2.46	0.15
ZnO:Al-NRs	1.78	0.11
ZnO-NRs/GR	4.25	0.46
ZnO:Al-NRs/GR	1.85	0.21

In addition to PL analysis, the samples were also characterized with respect to the photogenerated carrier's lifetime and the spatial charge separation efficiency. Irradiating the samples with a photon energy close to the ZnO bandgap energy will generate free charge carriers in the ZnO conduction band (CB), causing increased electrical conductivity. By switching off the light, the number of free electrons in the CB will reduce due to recombination between the electron-hole pairs, and it shows up in the sample conductivity decay. The more recombination in the sample, the faster the decay in the photoconductivity will be. Spatial separation of the photocarriers at the ZnO-GR interface reduces the recombination rate. This reduced recombination rate leads to a longer photocarrier lifetime and, consequently, more persistent photoconductivity (PPC) in the samples.

Fig. 3-8. A typical rise and fall curve of the current due to the PPC change in ZnO/GR nanocomposites grown at pH 6.6 under/after 350 nm illumination at 300 K and 1 V applied bias. Reprinted from my Lic. Thesis [70].

A typical rise and decay curve of the current due to the PPC change in ZnO/GR nanocomposites is shown in Fig. 3-8. We did not detect any photoresponse in the samples, using excitation wavelengths longer than 400 nm. Also, no PPC was observed in the highly Al-doped samples.

The time-dependence of the PPC of the undoped ZnO-NRs/GR samples with different morphologies, after 350 nm illumination at room temperature and under 1 V applied bias is shown in Fig. 3-9. Using Fig. 3-9 and the equation (3.12), the excess electron lifetime for the samples of ZnO-NRs/GR grown at pH 6.6 and pH 11, and the pristine ZnO-NRs were extracted as 877, 107 and 56 s, respectively. The results show a more efficient charge transfer of photogenerated electrons from ZnO to the graphene in the sample grown at pH 6.6 compared to the sample grown at pH 11. This electron injection into the GR causes efficient spatial charge separation, a strongly reduced recombination rate, and consequently, an enhanced PPC.

Fig. 3-9. Time-dependence of the PPC (σ_{ph}) after switching off the light for three different ZnO-NRs/GR nanocomposites, after 350 nm illumination at 300 K and 1 V applied bias. Reprinted from Paper I [60] under CC BY 3.0 License.

3.4 ZnO-NPs/GR for photocatalytic applications

Our last PPC results inspired us to use the developed ZnO/GR nanocomposite for photocatalytic applications, an area where the charge separation phenomena and the photocarrier's lifetime are of great importance. In this application, the charge separation interfaces are more important than the bulk of the materials. For this reason, the nanoparticle form of ZnO, instead of NRs, was chosen to increase the ZnO-GR interfaces. In addition, the weight ratio of ZnO to Gr was increased to 99:1, as the primary light absorption material in the nanocomposite.

Although the tested ZnO/GR samples showed a promising charge separation capability, they are not active in the visible light range. The large bandgap of ZnO can only absorb incident wavelength in the UV range. This will limit the photocatalytic efficiency of these materials under solar irradiation, with its broad intensity peak in the visible range. To overcome this drawback, we introduced different weight ratios of lower bandgap (2.8 eV) AgI-NPs into the ZnO/GR nanocomposites. The new ZnO/GR/AgI nanocomposites were analyzed with respect to their crystallinity, morphology, chemical structure, and photodegradation efficiency of an organic pollutant. This work is described in Paper II.

3.4.1 Silver iodide

Narrow bandgap silver-based semiconductors, including silver oxide, silver sulfide and silver halides, particularly AgI, with its excellent visible light absorption, have been widely studied for photocatalysis applications [71]. Historically, these Ag-based materials have been extensively used in photography for many years due to their highly sensitive light decomposing behavior. They will quickly decompose to metallic silver atoms (Ag^0) when exposed to light. However, this Ag^+ to Ag^0 reduction will quickly be stopped at the initial stage of the reaction by a self-stabilizing mechanism. Clusters of reduced Ag^0 atoms are formed on the AgI-NPs, preventing further decomposition of the semiconductor [71]. Therefore, we use the Ag/AgI in our notation instead of only AgI.

The metallic Ag⁰ atoms play two roles in the AgI nanocomposites, i) trapping the other photogenerated electrons and stabilizing the AgI-NPs (as explained) and ii) acting as local surface plasmon resonators (LSPR) that lead to enhanced visible light absorption and higher photocatalysis performance. Our results show a shift in the absorption peak toward the visible range when adding AgI to the ZnO/GR composite.

3.4.2 Characterization of ZnO/GR/Ag/AgI nanocomposites

The XRD data and SEM images in Paper II, confirm the high crystalline quality and a uniform synthesis of the ZnO/GR/Ag/AgI nanocomposites. The TEM image in Fig. 3-10 shows a conjunction of GR and ZnO-NPs and/or AgI-NPs in the nanocomposite. The GR nanoplates act as a substrate to assemble the NPs and also serve as an electrical bridge between them. The GRs can be considered as an electron sink for the photogenerated electrons in ZnO and AgI, boosting the charge separation efficiency at the GR-NPs interface. This will positively affect the final photodegradation performance subsequently.

Fig. 3-10. TEM image of a ZnO/GR/Ag/AgI (20%) nanocomposite.

The STEM-EDS analysis in Fig. 3-11 shows the elemental distribution of Zn, O, Ag and I atoms in the ZnO/GR/Ag/AgI (20%) nanocomposite. As we discussed earlier, the formation of the Ag^0 clusters on the AgI-NPs is essential for highly efficient photocatalysts. Fig. 3-11(c) shows two displaced phases of Ag and I, indicating the formation of the Ag^0 atoms on the AgI-NPs. This well elemental distribution in the nanocomposites can lead to higher photodegradation efficiency.

The existence of the metallic Ag^0 atoms in the composition was further confirmed using XPS analysis. The binding energy of the Ag^+ shows a chemical shift toward lower energies compared to the Ag^0 . This negative BE shift in the Ag/Ag⁺ systems is opposite to the typical BE shift of metal cations [72] that we explained in the previous section 3.2.6. The relevant XPS spectra can be found in Paper II.

Fig. 3-11. (a) STEM-HAADF image of a ZnO/GR/Ag/AgI (20%) nanocomposite. (b-d) Corresponding STEM-EDS elemental maps, displaying Zn, Ag/I and O distributions, respectively. Reprinted from my Lic. Thesis [70].

3.4.3 Photocatalytic performance of the nanocomposites

First, the optical absorption and the optical emission of the ZnO/GR/Ag/AgI nanocomposites, with different weight percentages of Ag/AgI, were inspected by UV-Vis spectroscopy and cathodoluminescence spectroscopy. An absorption peak at 430 nm wavelength, corresponding to 2.8 eV bandgap energy of AgI, was only detected in the samples with AgI-NPs. The cathodoluminescence spectra also confirmed the 430 nm wavelength emission in the AgI involved nanocomposites, as well as a broad emission with a peak centered at 600 nm, related to ZnO defect levels. We found that the samples with a 20% weight ratio of AgI in the nanocomposite exhibit the highest absorption and emission at 430 nm, which in turn is expected to show the highest photocatalytic performance.

The results of photodegradation of CR-dye under simulated solar light (explained in section 3.2.9) also confirm the highest photocatalytic efficiency for the ZnO/GR/Ag/AgI (20%) nanocomposite. Fig. 3-12 compares the photodegradation efficiency at different irradiation times for different nanocomposites. As observed in this graph, the degradation of CR-dye is negligible without using an appropriate photocatalyst.

Fig. 3-12. Photodegradation efficiency of CR-dye at different irradiation times, using ZnO, ZnO/GR, ZnO/Ag/AgI, and ZnO/GR/Ag/AgI photocatalysts with varying percentages of the weight of Ag/AgI. Reprinted from Paper II [73], published by The Royal Society of Chemistry.

A proposed photodegradation mechanism, including the energy band structure, can be found in Paper II. Briefly described, both ZnO and AgI absorb light at different wavelengths and generate electrons and holes in their conduction band (CB) and valence band (VB). Because of the band offsets, the electrons in the CB of AgI are transferred to CB of ZnO. The holes migrate in opposite direction, from the VB of ZnO to the VB of AgI. This charge separation enhances the carrier lifetime by reducing the recombination probability between the e/h pairs. Subsequently, the photogenerated electrons can migrate even further to the GR, causing strongly enhanced photocatalytic performance.

The separated electrons react with oxygen molecules to produce superoxide and hydroxyl radicals. The organic pollutant molecules (CR-dye) are decomposed by reacting to these active species in the solution. In the other reaction, the photogenerated holes can directly oxidize the adsorbed dye molecules and decompose the organic pollutants.

4 Template-assisted nanofabrication of ZnO-NRs/GR

In the previous chapter, we used CBD for the synthesis of the ZnO/GR nanocomposites. Although various composites and nanostructures can be produced by this simple and inexpensive method, the final product usually consists of random structures, and it is hard to control their architecture and alignment. In many applications, especially for device fabrication, it is important to be able to control the nanostructure's alignment, ordering, density, and growth area.

This chapter describes a completely different approach, in which vertically aligned arrays of ZnO-NRs were grown on appropriately seeded Si wafer substrates. To accurately control the NRs surface density and selectively grow the NRs only in specific areas, colloidal lithography (CL) was employed to pattern the substrates in a relatively simple process.

To further improve the ZnO-NRs alignment and fabricate electronic devices, a graphene oxide (GO) buffer layer was introduced between the Si substrate and the ZnO seed layer. This GO layer, after reduction to reduced graphene oxide (rGO), served as a compensator for the crystalline lattice mismatch between the Si and the ZnO and also as a back contact for device fabrication on insulating substrates.

4.1 Synthesis methods

The synthesis process of the aligned ZnO-NRs is essentially the same as described in the previous chapter. It includes seed layer preparation and ZnO-NRs growth on the seeded layers. However, a few changes in the chemicals used and the growth recipe were necessary to adapt the CBD technique for selective NR growth on different substrates. First, we needed to prepare a better GR dispersion. The GR nanoplates in the last part were purchased commercially in powder

form and dispersed in DI water using ultrasonication. The prepared GR dispersion was not stable enough to make uniform spray-coated layers on the substrates required for this part of our research. So, we synthesized the GO using the improved Hummer's method, which will be explained below.

The ZnO-NP seed layer was also prepared differently by sol-gel and dip-coating techniques. The former solution of zinc acetate and KOH used to decorate the GR with ZnO-NPs, results in NP clusters and a non-uniform coating on the substrates. Therefore, we used the sol-gel solution to deposit perfectly uniform ZnO thin film layers on various substrates independently. Also, the CBD process was modified a little to achieve the highest alignment and quality of the ZnO-NRs.

4.1.1 Synthesis of GO using the improved Hummer's method

Graphene oxide (GO) was prepared using the improved Hummer's method according to the recipe described in [45]. The process is based on the chemical exfoliation of natural graphite flakes. Two types of natural and synthetic graphite are available commercially [74], and only the natural type can be used for GO synthesis.

First, 1 g of graphite flakes (mesh -20+100, with a particle size range of 150-850 μm) were oxidized using a mixture of concentrated sulfuric acid⁹ and phosphoric acid¹⁰ with a volume ratio of 9:1 (60:7 ml), stirring at 80 °C for 30 min. The mixture cooled to room temperature, followed by 30 min ultrasonication (Fig. 4-1(a)). Subsequently, the mixture container was moved into an ice bath at 0 °C, and 6 g of potassium permanganate¹¹ was added to the mixture very slowly while stirring vigorously. The reaction is extremely exothermic; thus, caution is needed not to allow the mixture temperature to rise above 20 °C while adding the KMnO_4 . After this, the ice bath was removed, and the mixture was stirred at 35 °C for 2 h. Subsequently, the mixture was diluted by adding 120 ml of DI

⁹ H_2SO_4 (98%)

¹⁰ H_3PO_4 (85%)

¹¹ KMnO_4

water into the acidic mixture. This diluting also produces much heat, increasing the mixture temperature to 95 °C. The temperature was held at 95 °C for an extra 30 min, using a heated bath while stirring. After cooling to room temperature, the mixture was diluted again with a solution of DI water and hydrogen peroxide¹² (240:3 ml).

The final brownish solution contains the synthesized GO, non-exfoliated graphite flakes, residual sulfates, and oxidants at a very low pH (Fig. 4-1(b)). The solution was left overnight to precipitate the bigger particles, and the upper part of the solution was collected for further washing and purification. The collected mixture was centrifuged at 4500 rpm for 30 min and washed with HCl solution in DI water (10%) to remove any metals and other residuals. This washing process was repeated four times, followed by dispersing the collected precipitated solids in isopropanol alcohol. We noticed that the GO nanoplates were only collectible by centrifuging in an acidic solution (HCl solution). As soon as the pH of the solution was neutralized by DI water washing, it was impossible to precipitate all the GOs, even at a higher centrifugal rotation speed of 12000 rpm.

Fig. 4-1. (a) The mixture of graphite flakes in the acidic solution after stirring at 80 °C for 30 min. (b) The mixture of synthesized GO nanoplates in the acidic solution after terminating the reaction by adding H₂O₂.

¹² H₂O₂ (30%)

4.1.2 ZnO sol-gel solutions

The ZnO-NPs synthesis procedure discussed in the previous chapter leads to NPs with size distribution in a range of 50-120 nm. The seed layers, produced by the spin coating of these NPs on a substrate, showed a non-uniform island-like coating of NPs. Although changing the growth solvent to methanol and repeating the spin-coating step improved the seed layer surface coverage, it was not uniform enough for our nanofabrication process (Fig. 4-2(a)).

To improve the uniformity and the smoothness of the seed layers, a sol-gel solution of 8.25 g of zinc acetate and 2.26 ml of monoethanolamine¹³ (ethanolamine), with an equimolar final concentration of 375 mM, in 100 ml of pure ethanol was prepared [75, 76]. The solution was stirred at 60 °C for 10 h and then at room temperature overnight. Fig. 4-2(b) shows an SEM image of a seed layer of ZnO-NPs, deposited on a Si substrate using the sol-gel method and dip-coating technique. Compared to the other method, the sol-gel process yields a highly uniform and dense seed layer with almost full surface coverage.

4.1.3 CBD of ZnO-NRs on patterned substrates

The same CBD method, explained in the previous chapter, was used for growing the ZnO-NRs, with and without Al-doping. The only change was to increase the growth temperature from 75 °C to 95 °C. Increasing the growth temperature causes a merging of the multiple closely packed narrow NRs into a single thicker NR. The growth of a single NR is crucial in our novel nanofabrication method, as will be explained below [77].

It is also worth noting that the ZnO-NRs growth is performed on substrates in this approach, in contrast to the previous chapter. The prepared substrates were mounted upside down in the CBD solution to prevent any precipitant falling on the growth surface. We noticed that bubbles are formed in the solution during the experiment and may be trapped under the substrate, causing damaged or un-grown areas on the substrate surface. A little tilted mounting of the

¹³ NH₂CH₂CH₂OH

substrate in the solution lets the bubbles gradually escape from under the substrate, improving growth uniformity.

Fig. 4-2. SEM images of ZnO-NPs seed layers on Si substrate produced by (a) three times spin coating of the solution of zinc acetate and KOH according to the previous chapter, and (b) sol-gel and a dip-coating method.

4.2 Nanofabrication of patterned substrates

Our developed nanofabrication process consists of three steps: i) substrate preparation, ii) patterning the substrate using colloidal lithography, and iii) CBD of

ZnO-NRs on the patterned substrates. Two types of Si/ZnO-NPs and Si/GO/ZnO-NPs seeded substrates were prepared using the sol-gel solution and a dip-coating technique. In the first structure, described in Paper III, the ZnO seed layer was directly formed on the Si substrate. In the second structure, discussed in Paper IV, a GO layer was deposited on the Si substrate prior to the ZnO seed layer. This GO layer serves as a buffer layer to compensate for the crystal lattice mismatch between the Si and the ZnO, and also as a back contact for device fabrication on insulator substrates. The CL patterning process is basically the same for both substrate preparation methods.

4.2.1 Spray coating of GO buffer layers

A dispersion of the synthesized GO in N,N-Dimethylformamide¹⁴ (DMF) with a final concentration of 2 mg/ml was prepared by ultrasonication for 30 min. Alternatively, isopropanol alcohol can also be used, although DMF results in more uniform layers. Both solutions remained stable for more than two weeks.

We used spray coating to deposit the GO dispersion on two-inch Si wafers. However, prior to that, the adhesion of GO to the Si substrate was enhanced by spin coating a thin layer of Adhesion Promoter AP3000 from the Advanced Electronics Materials, containing vinyltriacetoxysilane¹⁵ in 1-Methoxy-2-propanol solvent, at 4000 rpm for 30 s. It is critical to preheat the substrates at 120 °C for 5 min immediately before spin-coating to desorb surface moisture, and to perform soft baking at 120 °C for 10 min after the coating.

Subsequently, the coated Si substrate was placed on a hotplate at 120 °C under a fume hood, and 20 ml of the GO solution was pulse-wise sprayed on the sample with 1 s spraying and 3 s waiting times. An airbrush at a 10 cm distance from the sample, operating with nitrogen carrier gas at 2 bar pressure, was used. Fig. 4-3 shows the spray-coated GO on a Si wafer with and without substrate silanization. The silane-coated sample survived after five cycles of tape

¹⁴ HCON(CH₃)₂

¹⁵ (CH₃CO₂)₃SiCH=CH₂

stripping, while the piece without adhesion promoter was delaminated during the liftoff process.

The thickness of the spray-coated GO layer was measured using a stylus Dektak-3ST profilometer to be in the range of 100-150 nm. Fig. 4-4 shows a corresponding cross-sectional SEM image of a sample.

Fig. 4-3. Spray-coated GO on Si substrate (a) with, and (b) without silanization, after five-cycles of a tape stripping test. The samples also have a PMMA coating on top that will be explained below.

Fig. 4-4. Cross-sectional SEM image of spray-coated GO on Si substrate.

4.2.2 Dip-coating of the ZnO sol-gel solution

A computer-controlled dip-coater was used to dip in and pull out the substrates into the ZnO-NPs sol-gel solution with a speed range of 10-30 mm/s at room temperature. In this work, the dip-coating of the seed layers was carried out on two different substrates, a bare Si wafer and the GO coated Si (Si/GO). For the bare Si samples, the coating process was repeated twice, including an annealing step at 300 °C for 10 min after each dip-coating step.

However, the Si/GO samples cannot tolerate high temperatures for a long time because of combustion of the GO layer in air. We measured a burning rate of 50-65 nm/min for the GO layer at 300 °C in air. The annealing duration was limited only to 1 min to avoid oxidizing all the C atoms of the GO layer. In the end, a thickness of about 85-100 nm of the GO layer remained after the annealing process.

4.2.3 Colloidal lithography (CL) patterning

A polymer resist layer was spin coated on the seeded substrate to identify the selected growth areas on the samples. An array of nanoholes was then fabricated in the resist layer using the CL technique. CL allows for flexibility in the fabrication process and results in low-cost nanopatterning. Among other advantages, it is inexpensive, substrate independent, offers excellent control of the nanohole size, and is suitable for large wafer-scale area patterning [78–80].

In this work, we used a double-layer resist of a sacrificial PMMA¹⁶ electron-beam resist and then a positive MICROPOSIT S1805 photoresist on the seeded substrates. Various PMMA solutions in different solvents, including toluene, anisole, diethyl carbonate and DMF, were tested for spin coating of the first resist layer. Regarding the thickness and the uniformity of the layers, toluene results in a thick uniform layer, while anisole and diethyl carbonate solvents give thinner and uniform coating layers. In contrast, samples produced using DMF solvent showed a non-uniform coating.

¹⁶ poly(methyl methacrylate), MW = 950k

After coating the resist layers, 5 min UV-Ozone treatment was necessary to improve the hydrophilicity of the resist for the following steps. A positively charged monolayer of PDDA¹⁷ was then pipetted on the sample surface and thoroughly rinsed with DI water after 1 min of settling. The positively charged monolayer of PDDA will electrostatically adhere the negatively charged polystyrene nanobeads (PS-NBs) to the substrate in the next step. The PS-NBs adhesion to the surface depends strongly on the number of the PDDA layers and will be reduced by multilayer-thick PDDA layers. Rinsing the PDDA layer under DI water flow for about 10 s improves the coated PS-NBs surface coverage.

A range of PS-NBs diameter sizes from 100 nm to 100 μm , suspended in water, is commercially available from microParticles GmbH, Germany. In this thesis, we used the PS-NBs with mean diameters of 107, 140 and 320 nm for CL-patterning. Various concentrations of 0.1, 0.02, 0.01 and 0.003 wt% of the PS-NBs suspension in DI water were prepared by ultrasonication. Subsequently, a monolayer of PS-NBs was dispersed on the sample surface and gently rinsed with DI water after 1 min of settling. Fig. 4-5(a) shows a schematic of the sample at this stage.

4.2.4 Thermal evaporation

Thermal evaporation is a member of a bigger category of physical vapor deposition (PVD) techniques in which the materials are transported from a source to the growth substrate in the vapor phase. First, a material source is evaporated by receiving energy in various ways, including resistive heating in thermal evaporation, ion bombardment in sputtering, from an electron-beam in EBPVD, or a laser beam in pulsed laser deposition (PLD). In all these cases, a high or ultra-high vacuum is needed to i) prevent the vaporized materials and the heated parts in the evaporator from oxidation, ii) reduce the materials' evaporation temperature, and iii) increase the mean free path of the vaporized particles, allowing transport without intermolecular collisions.

¹⁷ poly(diallyldimethylammonium), MW = (200-350)k

The vaporized particles are adsorbed on exposed surfaces inside the chamber, including the substrate, and condensation of material takes place. The thickness of the deposited materials is simultaneously monitored using a quartz crystal microbalance (QCM) and can be controlled by the deposition time.

In this thesis, a Balzers BA 510 evaporator was used to thermally evaporate a 30 nm thick Al layer on the samples at a high vacuum (HV) pressure of 6×10^{-7} Torr (Fig. 4-5(b)). The evaporator was equipped with a diffusion pump with 2000 l/s pumping speed and a combination of Pirani and cold cathode vacuum gauges to cover all the operating pressure ranges. The molten Al at high temperature is highly corrosive to the tungsten boat, penetrating it and alloying with the tungsten. To avoid this, the deposition rate was increased as high as possible to about 5-10 nm/s. After Al-coating, the Al-coated PS-NBs were removed by tape stripping using acrylic silicon-free Ultron 1009R tape, leaving behind open nanoholes in the Al film (Fig. 4-5(c)).

Fig. 4-5. Schematic of the CL nanofabrication process steps. (a) A substrate coated with a ZnO-NP seed layer, a double-layer polymer resist, and dispersed PS-NBs. (b) Thermal evaporation of an Al mask. (c) Removing the Al-coated PS-NBs by tape stripping. (d) Dry etching of the resist. (e) Wet etching of the Al mask. (f) Selective ZnO-NR growth in the holes of the patterned resist template. Reprinted from Paper III [81] under CC BY 4.0 License.

4.2.5 Dry etching

Etching is a micro or nanofabrication technique that selectively removes materials from unprotected areas using chemical etchant species. In dry etching, ionized gases such as SF_6 , Ar, O_2 or CF_4 are used as the etchant agents. The etchant gases are converted to plasma and bombard the surface in an applied electric field, causing the material to be removed from unprotected patterned areas. The reaction between the ions and the material can be purely physical (in sputter etching) or physical and chemical (in reactive ion etching) with a significantly higher etching rate.

In reactive ion etching (RIE), the plasma is formed by an applied radiofrequency (RF) electromagnetic field between two parallel plane electrodes, a grounded electrode on top and a negatively charged electrode at the bottom, under the sample. The positively charged ions are accelerated toward the sample under vacuum conditions, and because of the perpendicular electric field to the surface, etch away the materials directionally. Thus, the technique gives a highly anisotropic etching profile with a low lateral etching rate.

An RIE-Plasma Enhanced CVD from Advanced Vacuum, with operational parameters of pressure 150 mTorr, O_2 flow 40 sccm, RF power 60 W and etching time 90 s, was used to duplicate the Al-mask pattern into the bottom resist layer. The patterned Al film works as an etching protection mask, defining the selected areas. Using these optimized operational parameters, etching rates of 3.3 nm/s in the resist layer and 3.7 nm/s in the GO layer were measured. Fig. 4-5(d) shows the etched nanoholes in the resist layer down to the ZnO seed layer.

4.2.6 Wet etching

In wet etching, a particular chemical solution etches a target material (usually a metal) without dissolving the others. Opposite to RIE, wet etching is usually isotropic with simultaneous lateral etching. In our research, the Al metal mask was removed at room temperature, using a particular etchant solution of KOH and

potassium hexacyanoferrate III¹⁸ in DI water with respective concentrations of 30 mM and 50 mM for 1 min. This chemical solution etches the Al layer without damaging the exposed ZnO seed layer [82]. After thoroughly rinsing with DI water and blow-drying with nitrogen, the nanopatterned samples are ready for the CBD of ZnO-NRs, as previously explained in section 4.1.3.

4.3 Characterization methods – Atomic force microscopy

In addition to the analytical techniques demonstrated in the previous chapter, atomic force microscopy (AFM) was extensively used to study the roughness and morphology of the seed layers. AFM is a part of a large family of scanning probe microscopy (SPM) techniques used for topography and local surface interactions studies and manipulating the surface structure [83]. The technique is based on probing the interactions (mechanical, electrical or chemical) between a sharp tip and a surface at an atomically-close distance. The system consists of a Si or Si₃N₄ vibrational cantilever with a sharp tip that oscillates close to its resonance frequency (f_0) in tapping-mode operation. The f_0 sensitively shifts due to the tip-surface interactions while approaching a surface. A photodetector measures a laser beam deflection from the cantilever, determining the frequency shift and measuring the tip Z-displacement. A feedback control loop mechanism and a piezoelectric Z-actuator maintain the tip-surface distance in a defined safe margin and record the displacements. Fig. 4-6 shows a schematic of an AFM system.

We used the Veeco Dimension 3100 AFM, equipped with a quad photoreactor, an acoustical-vibrational isolation table with hood, and a piezo scan head with 90 μm x-y and 6 μm movement range which can operate in contact and tapping modes. Fig. 4-7 demonstrates an AFM image of the synthesized GO deposited on a Si wafer surface and the corresponding liner profile scan.

¹⁸ K₃Fe(CN)₆

Fig. 4-6. AFM system schema.

Fig. 4-7. AFM image of a GO nanoplate on Si wafer. The bottom graph shows a liner profile scan of the GO nanoplate with a thickness of about 1 nm.

4.4 Characterization of the CL-patterned substrates

A full detailed characterization of the CL-patterned substrates has been reported in Paper III and IV. Here, more detailed information is provided to fill the gap between these two works and connect them logically.

4.4.1 Why using Si/GO substrates?

The CL method was tested on different substrates, including fluorine-doped tin oxide (FTO) and Ti and Au-coated glass substrates. An electrically conductive substrate is required to make a device. The other requirement is the stability of the substrate during the fabrication process. On the other hand, growing on Si has the significant advantage of being integrated with the well-developed Si industry.

Testing the CL on FTO substrates was not very successful due to the relatively high surface roughness of the FTO. High points on the surface apexes are usually exposed through the resist layer before etching, and depths are rarely accessible through the patterned nanoholes. A cross-section SEM image of a typical CL-patterned resist layer on an FTO substrate is shown in Fig. 4-8.

Fig. 4-8. Cross-sectional SEM image of the CL-patterned resist layer on FTO surface before wet-etching of the Al mask.

The metal-coated substrates were not stable during the wet-etching process, and it caused delamination of the resist layer due to under-etching of the metal. Due to these practical limitations, the GO-coated Si was chosen as the basis for the CL patterning. However, bare GO is not a suitable nucleation surface for CBD of ZnO, and it should be activated by the ZnO-seed layer.

4.4.2 Improved ZnO seed layers by dip-coating

The ZnO seed layers with single and double dip-coating steps were produced and studied with respect to their smoothness, crystalline quality, and their influence on the grown ZnO-NRs. For the Si/ZnO samples, repeating the dip-coating process improved the smoothness and the crystal grain size of the seed layer. The AFM images in Fig. 4-6 show single-dip-coated seed layers with RMS roughness of 1.2 nm and small particle grain boundaries. In comparison, the double-dip-coated samples have a smoother surface with an RMS roughness of 0.9 nm and larger grain boundaries.

Fig. 4-6. AFM images of ZnO seed layers prepared on a Si wafer by a sol-gel method by (a) single and (b) double dip-coating. The samples were annealed at 300 °C after each coating step. A background has been subtracted from the AFM images.

From the literature, it is well understood that the crystal grain boundaries are increased by the thickness of the deposited layers [26, 84]. In our case, repeating the deposition process linearly increased the layers' thickness. In contrast, the presence of impurities during layer deposition and the annealing process reduces the grain sizes [85]. The size of the grain boundaries is important for our vertically aligned single NR growth through the patterned nanoholes.

Although the smoothness and the grain size of the seed layers were improved by multiple dip-coating, the XRD analysis did not confirm any enhancement in the desired (002) crystalline orientation. This result suggests that the self-forming process of polycrystalline ZnO-NPs is strongly dependent on the substrate crystallinity and cannot be improved only by increasing the layer thickness.

To compensate the crystal lattice mismatch between the Si substrate and the ZnO seed layer, a GO buffer layer was introduced on the Si surface by spray coating, as explained in section 4.2.1. The AFM data show higher waviness in the GO layer due to the imperfectness of the spray-coating process with an RMS roughness of about 11 nm. Fig. 4-9 shows the AFM image of a ZnO-NPs seed layer on a Si/GO sample after annealing at 300 °C for 1 min with an RMS roughness of 4 nm.

Fig. 4-9. AFM image of ZnO-NPs seed layer on the spray-coated GO layer on a Si wafer, produced by dip-coating in the sol-gel solution and annealed at 300 °C for 1 min.

As mentioned before, due to the rate of combustion of the GO layer at 300 °C, annealing in air was limited to only 1 min. This leads to non-merged small ZnO particles with smaller crystalline grain boundaries compared to the samples that were annealed for 10 min. The SEM images in Fig. 4-10 show the ZnO-NP size and the crystal grain boundaries for different annealing durations of 1 and 10 min. The samples were prepared by dip-coating the substrates with the sol-gel

solution on Si/GO and Si-wafer substrates, followed by annealing in air at 300 °C for 1 and 10 min, respectively.

Fig. 4-10. SEM images of ZnO-NPs deposited by the dip-coating method and the sol-gel solution on (a) Si/GO and (b) Si-wafer substrates, followed by annealing in air at 300 °C for 1 and 10 min, respectively.

4.4.3 Reduced GO/Al-doped ZnO seed layers

The thermal annealing [46] of the Si/GO/ZnO seed layers and exposure to UV irradiation [47] reduce GO to rGO. This GO-to-rGO transformation is along with a conductivity increasing and a transparency reduction. Higher conductivity of seed layers is important for electronic device fabrication, particularly on the insulating substrates. To obtain the maximum electrical conductivity, the ZnO NP seed layer was also highly doped with Al by adding 7.5 mM aluminum nitrate into the sol-gel solution, explained in section 4.1.2, prior to the deposition on GO layers.

A minimum sheet resistivity of 8 K Ω /□ was measured for an rGO/ZnO:Al seed layer after annealing at 300 °C for 1 min and 10 min UV irradiation. This conductive seed layer serves not only as a nucleation surface for the ZnO-NRs growth but also as a back contact to NRs, for later device fabrication.

4.4.4 Distribution of polystyrene nanobeads on surfaces

As explained in section 4.2.3, a suspension of PS-NBs was dispersed on the resist layer to define the opening areas in the CL technique. The PS-NBs are distributed on the surface due to the electrostatic net repulsive forces between the

negatively charged particles. The radial distribution function (RDF) of the nanoholes was calculated based on SEM image analysis to analyze the particle distribution order.

For a 2D particle distribution, the RDF is defined as the ratio of particle surface density in an infinitesimal ring at a distance r from a reference particle to the average particle surface density when all particles are uniformly distributed. Based on Fig. 4-11, the RDF is calculated according to equation (4.1) or equivalently (4.2), where $dn(r)$ is the number of particles at a distance between r and $r+dr$, ρ is the average particle surface density ($=N/A$, N is the total number of the particles in the entire area of interest), and $g(r)$ is the RDF [86, 87].

The calculated $g(r)$ values are independent of the original reference point and can have any value equal to or greater than zero. A $g(r)$ value greater than one indicates higher particle surface density than the average density (ρ), meaning a dominant spacing between the neighboring particles.

Fig. 4-11. A 2D particle distribution scheme.

$$g(r) = \frac{(dn(r)/N)}{(dA(r)/A)} \quad (4.1)$$

$$dn(r) = 2\pi r \rho g(r) dr \quad (4.2)$$

The open-source ImageJ software and the additional incorporative Radial Distribution Function macro were used to calculate the $g(r)$ functions. The

calculation is based on the autocorrelation of the particle-center positions with respect to the various original preference points [88]. Using this algorithm and the fast Fourier transform (FFT), repeated patterns in the interparticle spacing can be identified from an apparently random distribution.

An example of using the RDF method for pattern-ordering analysis of an array of particles is shown in Fig. 4-12, compared with other alternative methods of 2D-FFT and the spatial distribution function (SDF) [88]. A specific amount of noise in terms of the interparticle spacing and particle dimension has been added to a computer-generated hexagonal array of particles with an interparticle spacing of 100 a.u., converting it to an apparently disordered and random particle distribution. Then, the obscured ordering in the structure has been retrieved using the described image analysis methods, as shown in Fig. 4-12(b-d).

Each peak in the RDF, or the intense bright points in the DSF images, represents the degree of periodicity in the structure. Samples with several RDF peaks have long-range ordering, while fewer peak numbers in the RDF indicate a short-range ordering structure. Our PS-NBs distributions show only one primary peak in their RDF graphs, meaning one period ordering between only the first neighboring particles.

Fig. 4-12. (a) A computer-generated hexagonal array of particles with specific added noises of 20% interparticle spacing and 15% particle dimension. (b) 2D-FFT, (c) the RDF, and (d) the spatial distribution function (SDF) of the particles array in (a). Adapted with permission from [88]. Copyright 2019, American Chemical Society.

5 Conclusions and Outlook

This research work started by exploring potentially 3D-printable conductive materials with maximum porosity for electronics. Among the possible candidates, ZnO/GR nanocomposites were selected based on their promising electrical and optical properties, and also because of the accumulated knowledge and experiences for working with ZnO in our research group.

Using a simple and inexpensive solution-based growth technique, several ZnO-GR nanocomposites with and without doping in various morphologies were successfully grown and characterized with respect to electrical conductivity, dispersity, bonding quality between the species, and optical properties. Our results demonstrate the dependence of the electrical and optical characteristics of the nanocomposites on the growth parameters, like the pH value.

Optical characterization of the developed composites showed an effective charge separation at the ZnO-GR interface, which results in a longer lifetime of the photogenerated charge carriers and enhanced persistent photoconductivity. In addition, the growth of ZnO-NRs on the GR surface introduced effective spacers, leading to a high porosity in the final structure and significantly promoted GR wettability, essential for integrating the nanocomposite with other materials such as polymers for 3D printing.

The observed charge separation mechanism encouraged us to investigate the photocatalytic performance of our materials. The ZnO-GR nanocomposites were sensitized to visible light by adding a low bandgap AgI semiconductor to the composite. A significantly enhanced solar-driven photocatalytic performance was observed in the final optimized ZnO/GR/Ag/AgI nanocomposites due to the increased visible light absorption by AgI, and efficient charge separation of photogenerated carriers at the ZnO-GR interface.

To precisely control the growth area, density, and alignment of NRs for advanced electronics and photonics, a template-assisted selective area growth method was developed to synthesize arrays of single vertically aligned ZnO-NRs on Si or glass substrates. This technique is based on colloidal lithography patterning and preparing a compact and uniform ZnO seed layer by a sol-gel and dip-coating process. Compared to the ZnO-NRs grown on non-patterned substrates, it was shown that much better aligned NRs, with a tunable diameter and density, can be achieved by our method. However, a (100)-oriented Si substrate is not the preferred choice of crystalline substrate for vertical ZnO-NR growth. We developed a novel route to mitigate this problem in Paper IV, where a GO buffer layer was introduced between the substrate and the ZnO seed layer. A significant improvement in the ZnO-NR growth was verified using a non-crystalline ZnO seed layer on the partially reduced GO (rGO) buffer layer, together with the previous patterning technique.

A considerable effort was put into realizing a method to produce ordered arrays of vertical ZnO-NRs. Due to time constraints, the final optimized aligned structures were not yet tested for exciting applications, e.g., biosensors, LEDs, or field-emission devices. Due to thermal and oxidation stability, high-aspect ratio, and controllable length and diameter of the aligned ZnO-NRs on conductive rGO/ZnO:Al layers, a great potential of these structures is foreseen in all of the abovementioned applications.

Despite the improvement in vertical alignment of the ZnO-NRs using the CL-patterning technique, the nanoholes' exact position is not controllable. To achieve such a control, precise nanoimprint lithography (NIL) can be employed to create the desired patterns on the rGO/ZnO seed layers. A more systematic study is required to optimize the parameters and realize the nanohole patterns with specific diameter and pitch. Further research, based on this thesis work deals with developing novel spray-coated conductive and transparent rGO top contacts for realizing disruptive ZnO NR-based optoelectronics.

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Part II: Papers

PAPER

I

Influence of morphology on electrical and optical properties of graphene/Al-doped ZnO-nanorod composites

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Received 15 May 2018, revised 26 June 2018

Accepted for publication 17 July 2018

Published 1 August 2018

Abstract

The development of future 3D-printed electronics relies on the access to highly conductive inexpensive materials that are printable at low temperatures ($<100^\circ\text{C}$). The implementation of available materials for these applications are, however, still limited by issues related to cost and printing quality. Here, we report on the simple hydrothermal growth of novel nanocomposites that are well suited for conductive printing applications. The nanocomposites comprise highly Al-doped ZnO nanorods grown on graphene nanoplatelets (GNPs). The ZnO nanorods play the two major roles of (i) preventing GNPs from agglomerating and (ii) promoting electrical conduction paths between the graphene platelets. The effect of two different ZnO-nanorod morphologies with varying Al-doping concentration on the nanocomposite conductivity and the graphene dispersity are investigated. Time-dependent absorption, photoluminescence and photoconductivity measurements show that growth in high pH solutions promotes a better graphene dispersity, higher doping levels and enhanced bonding between the graphene and the ZnO nanorods. Growth in low pH solutions yields samples characterized by a higher conductivity and a reduced number of surface defects. These samples also exhibit a large persistent photoconductivity attributed to an effective charge separation and transfer from the nanorods to the graphene platelets. Our findings can be used to tailor the conductivity of novel printable composites, or for fabrication of large volumes of inexpensive porous conjugated graphene-semiconductor composites.

Keywords: graphene, zinc oxide, nanorods, nanocomposites, persistent photoconductivity, printing

(Some figures may appear in colour only in the online journal)

1. Introduction

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The development of 3D-printing technologies for realizing electronic components and materials is evolving very quickly. Presently, there is a strong interest in developing novel 3D-printable

functional nanocomposites for device fabrication. For instance, conductive nanocomposites can be optimized for low-temperature printing of conductors using the well-developed fused deposition modeling printers available on the market today [1–3]. Carbon-based nanocomposite materials, containing graphene in particular, are inexpensive attractive candidates with remarkable physical properties that make them well suited for 3D-printing of electronics [4–6].

Demonstrated properties that make graphene promising for electronics include excellent (i) carrier mobility (up to $10^6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [7], (ii) electrical resistivity ($0.1\text{--}6 \text{ k}\Omega/\square$ for a single layer with 97.7% optical transparency) [7], (iii) chemical stability and (iv) mechanical strength (double to that of CNTs) [7]. However, graphene is highly hydrophobic and hardly interacts with other materials. Moreover, the high-aspect-ratio of graphene nanoplatelets (GNPs), combined with large van der Waals forces typically lead to issues with undesired agglomeration into large particles. In order to use graphene in printing applications, it must therefore be properly dispersed in a suitable medium. High-quality dispersions are typically facilitated by introducing chemical surfactants, [8] which unfortunately influence the electrical properties of graphene in an undesired way. A different approach to synthesize a conductive screen printing graphene ink with a resistance of $30 \Omega/\square$ at $25 \mu\text{m}$ thickness by gelation of a graphene dispersion was recently reported [9]. Despite all of these efforts it still remains a challenge to make a highly conductive graphene dispersion in a viscous medium, suitable for printing applications.

Here we propose a new approach to realize a graphene dispersion, effectively forming a conductive network, by growing zinc oxide nanorods (ZnO-NRs), degenerately doped with aluminum (Al), as highly conductive spacers on the surface of the GNPs. The potential advantages of these composites stem from the remarkable charge transport characteristics of graphene, combined with the excellent optical characteristics of ZnO. The expected enhancement of the optoelectronic properties of this composite might lead to important applications in optoelectronics, photovoltaics and photocatalysis [10].

Zinc oxide is a well-known unintentionally n-type semiconductor with a wide direct bandgap of $3.2\text{--}3.4 \text{ eV}$ at room-temperature. It can be grown in different nanostructured shapes e.g. nanorods by inexpensive low-temperature ($<100^\circ\text{C}$) hydrothermal solution-based procedures [11, 12]. The morphology, length and diameter of the ZnO-NRs can be controlled by tuning the pH value, temperature of the growth solution, precursor concentration and growth duration [13].

ZnO-NRs can be grown on GNPs with excellent result despite of their hydrophobicity. It has been shown that the reduced lattice mismatch of less than 2% [14, 15] between ZnO-NRs and GNPs causes strong atomic level interactions which lead to strong bonding and high mechanical stability [16]. Moreover, the electrical interface between GNPs and ZnO-NRs shows excellent low-ohmic metallic behavior [17, 18] of great importance for conductive applications.

2. Experimental details

All the chemicals required for the hydrothermal growth presented in this work, including the multilayer GNP powder, were purchased from Sigma-Aldrich. The first step was to seed the GNPs with a layer of ZnO nanoparticles (ZnO-NPs) [19]. GNPs with a concentration of 0.5 g l^{-1} were initially dispersed in DI-water using an ultrasonic bath for 10 min. Subsequently this solution was mixed with a 100 ml solution of 0.005 M of zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and 0.025 M of KOH in water at 60°C in an ultrasonic bath for 10 min. The seeded GNPs were subsequently washed in water and centrifuged (3000 rpm, 10 min) three times, followed by annealing in nitrogen at 300°C for 30 min to enhance the attachment of the ZnO-NPs to the GNPs. For the growth of ZnO-NRs, we prepared two solutions of 0.025 M of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.025 M of $\text{C}_6\text{H}_{12}\text{N}_4$ (HMT) in DI-water with pH 6.6 and pH 11 (by adding ammonia), respectively. These two different pH growth solutions resulted in significantly different ZnO-NRs morphologies. A 0.002 M aqueous solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was stirred overnight and added to the growth solution to supply the Al for doping of the NRs. Finally the seeded GNPs were added to the growth solution under stirring for 2 h at 75°C .

3. Results and discussion

Figure 1(a) shows a schematic of the grown nanostructures. The ZnO:Al-NRs play two major roles for the final composites. First, they make a physical spacer between the GNPs proportional to their length. These physical spacers prevent GNPs from agglomerating and make the structure more porous. The porosities can, depending on the application, be filled by a proper matrix material. Second, degenerately doped ZnO-NRs grown on one GNP will form low-ohmic electrical connections to a neighboring GNP. Previous studies have shown that the formation of low-resistance direct contacts between the particles is the most crucial factor for realization of highly conductive polymer composites [20]. The sharp NRs can also more easily penetrate through any polymer matrix filling up the porosities between the GNPs and increase the probability of direct contact formation between GNPs. The overall electrical transport properties depend on the resulting complex conductive network between the GNPs in the matrix.

To make sure that the ZnO-NPs in the seed layer are also doped with Al, a piece of pure Al was inserted into the solution during the seeding of the GNPs. The high pH value of 13 of the seed solution will lead to a partially dissolving of Al in the solution and to doping of the ZnO-NPs [21]. Figure 1(b) shows GNPs decorated with ZnO:Al-NPs. The photoluminescence (PL) measurements discussed below clearly show the effects of the high Al-doping on the optical properties of the ZnO-NPs.

The two different morphologies of ZnO-NRs grown at different pH (6.6 and 11) were investigated for better performance

Figure 1. (a) Schematics of ZnO-NRs grown on both sides of GNPs by the hydrothermal solution-based procedure. (b) Scanning electron microscopy (SEM) image of GNPs decorated with Al-doped ZnO nanoparticles. (c) Thick hexagonal low-density ZnO-NRs grown at pH 6.6. (d) Thin needle-like, high-density ZnO-NRs grown at pH 11. The insets show the size distribution of the nanorods diameter.

Figure 2. (a) Energy dispersive x-ray spectroscopy (EDS) spectra for GNP/ZnO:Al-NRs grown at pH 11. (b) Resistivity of GNPs, GNP/ZnO:Al-NPs, GNP/ZnO-NRs (pH 6.6 and 11) and GNP/ZnO:Al-NRs (pH 6.6 and 11) measured by a four-point probe method.

regarding both conductivity and dispersity. ZnO-NRs grown at pH 6.6 (figure 1(c)) are hexagonal, thicker (mean diameter 313 nm), longer (1–2 μm) and more sparse compared to ZnO-NRs grown at pH 11. The NRs grown at high pH are more needle-like with a mean diameter and length of 196 nm and 0.5–1.5 μm respectively (figure 1(d)). The density of ZnO-NRs on the GNP surface was estimated, 1.4 μm^{-2} for the samples grown at pH 6.6 and 2.4 μm^{-2} for the samples grown at pH 11 by counting in the SEM image.

Figure 2(a) shows the abundance of different elements in the samples extracted from energy dispersive x-ray spectroscopy (EDS). Carbon (C) is the most abundant element observed in all composites with an atomic ratio of 6.5 compared to Zn. The presence of 0.5–1.5 at% Al is also detected in the doped composites, which basically represents the lower boundary for a typical EDS system. The doping concentration in the samples is estimated in the range of 0.7–1.2 at% based on the dopant concentration in the growth solution [22, 23]. The presence of

oxygen (O) is almost 60 at% higher than Zn in the samples. This excess of O could be related to the hydroxyl groups OH^- and/or carboxyl groups $-\text{COOH}$, or to adsorbed water on the GNPs or ZnO surfaces during the synthesis [24].

The resistivity of the composite layer samples, comprising the investigated microparticles, is measured by a standard four-point method. To do that, the layered materials must first be smoothly deposited. To deposit the randomized GNP/ZnO:Al-NRs microparticles, we used a vacuum filtration method [8]. A water dispersion containing the microparticles was filtered by an Anodisc membrane filter from Whatman (25 mm diameter, $0.2\ \mu\text{m}$ poresize) and dried at 70°C in an oven. The layer thickness, varying from 20 to $50\ \mu\text{m}$, was measured by a contact profilometer. As shown in figure 2(b), the resistivity of pure GNPs is the lowest and it increases after decoration with ZnO:Al-NPs. This increase can be explained by the synthesis procedure and/or the spacing induced by the doped ZnO nanoparticles. Growth of undoped ZnO-NRs on the decorated GNPs results in a further increase of the resistivity for both investigated morphologies, effectively converting the layers to insulators. This high resistivity shows that the GNPs are physically separated from each other by the non-intentionally doped ZnO-NRs. For the doped samples, the resistivity strongly decreased and the nanocomposites again became conductive due to the enhanced conductivity of the degenerately doped ZnO:Al-NRs. This shows that the electrical current is passing through the ZnO-NRs. The ZnO-NRs (nanoneedles) grown at pH 11 show a comparably higher resistivity compared to those grown at pH 6.6. This suggests that nanoneedle-shaped GNPs are better dispersed. This hypothesis is supported by the optical UV-vis data discussed below.

To compare the dispersity of the two morphologies, and the attachment of ZnO-NRs to the GNPs, time-dependent UV-vis spectroscopy was employed. Figures 3(a)–(c) show the absorption spectra of the GNPs with different morphologies of grown ZnO:Al-NRs, dispersed in isopropanol, after every 5 min and after 24 h. The absorption spectra of pure GNPs exhibit a rather flat absorption characteristics dominated by spectral features beyond $1500\ \text{nm}$ related to hydroxyl and/or carboxyl groups on the GNP surfaces (figure 3(a)). Figures 3(b) and (c) display a strong absorption peak at about $380\ \text{nm}$ for dispersions of GNP/ZnO:Al-NRs due to the ZnO bandgap. The broad absorption shoulder, and spectrally unresolved absorption edge, reflect various scattering mechanisms [25] in the samples, which lead to strong spectral convolution effects. The dispersions of GNPs and GNP/ZnO:Al-NRs grown at pH 11 show a uniform decrease in absorption with excitation time due to particles settling. Figure 3(b) shows that the absorption in GNP/ZnO:Al-NRs grown at a pH 6.6 changes non-uniformly with wavelength. The long wavelength absorption response in our dispersions is dominated by the GNPs, while it relates to ZnO at short wavelength. The non-uniform decrease in absorption observed in 3(b) indicates the presence of two phases (separated GNPs and ZnO:Al-NRs) in the dispersion. The ZnO:Al-NRs settle faster than the GNPs. In contrast, GNP/ZnO:Al-NRs grown at a pH 11 forms a single phase in the dispersion, as evident from the uniform settling rate in figure 3(c). This

Figure 3. Time-dependent UV-vis spectroscopy. Temporal evolution of the absorption spectra after 0, 5, 10, 15, 20 min and 24 h, respectively, for the dispersion of (a) GNPs, (b) GNP/ZnO:Al-NRs grown at pH 6.6 and (c) GNP/ZnO:Al-NRs grown at pH 11 in isopropanol. (Figure (a) has a different vertical scale.)

implies that ZnO:Al-NRs are better attached to GNPs in high pH growth solutions.

To study the quality of bonding between the GNPs and the ZnO-NRs, and also to see the effects of Al-doping level in

Figure 4. μ -PL room-temperature measurement for different ZnO-NRs composites grown at (a) pH 6.6, (b) pH 11, and (c) different GNP/ZnO-NPs composites. (d) Comparing PL spectra for GNP/ZnO:Al composites for three different ZnO morphologies.

the ZnO-NRs, room-temperature micro-PL (μ -PL) measurements were pursued on nanostructure deposits on gold coated silicon wafers using a 80 μ W, 266 nm laser excitation. The main peak in figure 4 shows the ZnO near-bandedge emission (NBE) at 3.25–3.38 eV in agreement with the absorption measurements. The broad peak at 2.4 eV indicates the visible light emission via deep levels in ZnO caused by zinc and oxygen vacancies [19]. The origin of the oscillations at 1.7–2 eV are not well understood but they are a common feature for all the samples. For easier comparison, all the PL data were normalized to the peak at 1.9 eV. Three sets of ZnO-nanorod morphologies (ZnO-NPs and ZnO-NRs grown at pH 6.6 and 11) in four different composites (undoped ZnO, ZnO:Al, GNP/ZnO, GNP/ZnO:Al) were investigated under the same conditions (figures 4(a)–(c)).

Two distinct changes are readily observed in the μ -PL spectra after doping the ZnO-NRs with Al; first, the deep level

emission (DLE) is suppressed due to filling of the defects levels by electrons (Al is a donor in ZnO). This observation has previously been reported for Ga-doped ZnO-NRs [26]. Furthermore, the NBE is also suppressed by Al-doping more significantly. The ratio of NBE-to-DLE integrated intensities ($I_{\text{NBE}}/I_{\text{DLE}}$) for different samples are summarized in table 1. In all the samples the $I_{\text{NBE}}/I_{\text{DLE}}$ ratio is decreased by adding Al to the composite. This decrease in the UV-to-visible emission ratio can be explained by introducing impurity levels in the bandgap with the doped metal ions and reducing the crystalline quality of ZnO [27–29]. Although it has been reported that post thermal treatment can improve the ZnO:Al crystallinity [28], our samples were measured without thermal treatment. Second, a blue-shift in the band-edge emission is observed which we attribute to the Burstein–Moss effect [23, 27, 30].

Another interesting general observation in the μ -PL spectra is that ZnO-NRs grown on GNPs exhibit a significantly stronger

Table 1. The NBE-to-DLE integrated intensity ratio ($I_{\text{NBE}}/I_{\text{DLE}}$) for different ZnO-NRs composites.

	Grown at pH 6.6	Grown at pH 11
ZnO-NRs	2.46	0.15
ZnO:Al-NRs	1.78	0.11
GNP/ZnO-NRs	4.25	0.46
GNP/ZnO:Al-NRs	1.85	0.21

band-edge PL emission intensity compared to isolated ZnO-NRs. Previous reports in the literature attribute this to a reduction in the concentration of oxygen vacancy surface defects in the ZnO by oxygen groups adsorbed on the GNPs [31, 32] or more probably to resonant excitation of graphene plasmons [33–35].

Comparing the μ -PL for the two ZnO-NRs morphologies in figure 4(d) shows that thicker ZnO-NRs grown at pH 6.6 display a stronger band-edge PL emission than the thinner needle-like ZnO-NRs grown at pH 11 due to a lower surface-to-volume ratio. A high surface defect concentration on the thinner Zn-NRs not only causes a lower band-edge emission in the optical characteristics, but also leads to a higher electrical contact resistance (figure 2(b)).

To further support our conclusions, we measured the spectrally resolved photoconductivity of our samples. A significant persistent photoconductivity (PPC) in ZnO has been demonstrated in many articles [36–39]. The PPC observed in ZnO is attributed to a spatial charge separation mechanism induced by the built-in electric field caused by a surface space-charge layer [40]. Oxygen vacancies in the ZnO structure can chemically absorb oxygen from the air and become a hole trap. During illumination with photons with larger energy than the bandgap of ZnO, photogenerated holes will migrate to these surface traps and photodesorb the oxygen. At this point the separated mobile photoelectrons remain in the ZnO conduction band and result in a PPC.

Figure 5 below shows the results of pulsed optical excitation of an undoped GNP/ZnO-NR sample at 300 K. The measured current is recorded at a bias of 1 V under optical excitation with different wavelengths from 320 to 400 nm. There was no detected photoresponse for wavelengths longer than the corresponding bandgap energy. A large PPC effect was observed that increased at shorter wavelengths. In contrast, no PPC was observed in any of the highly Al-doped samples, not even under 254 nm illumination. This absence of PPC in highly doped samples can be explained by electrostatic screening of the surface oxygen ions that prevents holes from migrating towards the surface [40].

Time-resolved PPC was measured in detail to compare the effect of nanocomposite morphology on the lifetime of the photogenerated electrons. Figure 6 shows the time-dependence PPC of undoped GNP/ZnO-NR samples with different morphology after 350 nm excitation. After switching on the light, the surface chemisorbed oxygen traps the migrating photogenerated holes leaving behind an increasing density of mobile electrons in the conduction band, which results in an increasing PPC. Eventually, the complex processes involving

Figure 5. The cycled PPC response for a GNP/ZnO-NRs sample at 300 K and 1 V applied bias. **Figure 6.** Time-dependence of the PPC (σ_{ph}) after switching off the light for three different GNP/ZnO-NRs morphologies under 350 nm illumination at 300 K and 1 V applied bias.

charge carrier dynamics and surface oxygen chemisorption/desorption are in balance and the PPC saturates. By switching off the incident light, the PPC slowly decays due to recombination of photogenerated electrons and surface oxygen chemisorption. A detailed analysis of the continuity equation for the investigated complex composite materials is beyond the scope of this paper. Instead we focus on a more qualitative analysis of the decay process.

During the decay, the PPC is proportional to the density of electrons in the conduction band which in general decays stretched exponentially with time [41]. Evidently (figure 6), the photoconductivity (after subtracting the dark conductivity) σ_{ph} decays exponentially according to:

$$\frac{d\sigma_{ph}}{dt} = -\frac{\sigma_{ph}}{\tau_d}, \quad (1)$$

$$\ln \sigma_{ph} = -\frac{t}{\tau_d} + \ln \sigma_0. \quad (2)$$

Table 2. Dark conductivity (σ_d), PPC directly after switching off the light (σ_0) and excess electron lifetime (τ_d) of three different undoped samples at 300 K.

Sample	σ_d (S cm ⁻¹)	σ_0 (S cm ⁻¹)	τ_d (s)
ZnO-NRs	1.7×10^{-9}	1.1×10^{-10}	56
GNP/ZnO-NRs, pH 11	7.3×10^{-10}	3.9×10^{-10}	107
GNP/ZnO-NRs, pH 6.6	2.1×10^{-6}	3×10^{-7}	877

Here, τ_d is the decay time constant (excess electron lifetime) and σ_0 is the observed PPC directly after switching off the light. The extracted electron lifetime for samples with different morphology are calculated by a linear fitting to equation (2) and reported in table 2.

While the ZnO-NRs sample exhibits a long electron lifetime of about 56 s, the composite samples of graphene and ZnO-NRs have much longer electron lifetimes (107 and 877 s). The prolonged electron lifetime in these composites can be explained by an efficient transfer of photogenerated electrons to the graphene. This electron injection into the graphene causes a strongly reduced recombination rate and thus an enhanced PPC. The sample grown at pH 6.6 shows a significantly longer electron lifetime compared to the sample grown at pH 11. We conclude that the charge transfer between the ZnO-NRs and the graphene is more effective in the samples with thicker NRs grown at lower pH compared to the thinner needle-like NRs grown at higher pH.

The two morphologies of GNP/ZnO-NRs have different advantages and drawbacks. Thinner ZnO-NRs grown in a high pH solution exhibit a better dispersity and an improved attachment between the GNPs and ZnO-NRs, but also show a higher resistivity due to more surface defects and lower charge transfer between ZnO-NRs and GNPs. In contrast, the thicker ZnO-NRs grown at a lower pH display a lower resistivity and better charger transfer between ZnO-NRs and GNPs, but also a weaker GNP/ZnO-NRs bonding and a poorer dispersity. For conductive printing applications, lower resistance samples with thick ZnO-NRs are preferred. However, if the surface of the nanorod defects could be passivated by a proper post-growth treatment, the thinner GNP/ZnO-NRs morphology could be advantageous.

Growth and *in situ* doping of conjugated GNP/ZnO-NRs nanocomposites by a simple solution-based method as demonstrated in this work is economically desirable for mass production. For conductive purposes, the nanocomposite materials can be mixed by different polymers and tested for printing performance. Although we have primarily focused on conductive applications, our reported nanocomposites can be used in any optoelectronic, photochemical or photovoltaic application that requires high-porosity conjugated organic/semiconductor hybrids with a tunable conductance level.

4. Conclusion

In conclusion, we report on hydrothermal solution growth and characterization of different GNP/ZnO-NRs nanocomposites.

The ZnO-NRs were degenerately doped by Al for enhanced conductivity suitable for 3D-printing applications. Two different morphologies of ZnO-NRs, grown at different pH, were compared with respect to dispersity, GNP/ZnO-NRs bonding quality and conductivity. Our results show that a better graphene dispersion and improved bonding quality between the GNPs and NRs can be achieved in growth solutions with higher pH, however with a lower electrical conductivity in deposited GNP/ZnO-NRs layers. From μ -PL measurements we also infer that surface defects play an increasingly important role for thin ZnO-NRs with large surface-to-volume ratio. Although ZnO-NRs spacers on the GNPs surface decreases the conductivity between individual GNPs, they provide open free space porosities which promotes its capability to form a composite with other materials like thermoplastics and can be used in conductive bulk printing application, specifically 3D-printing. Finally, we demonstrate a strong enhancement in the PPC in undoped ZnO-NRs grown on graphene, compared to bare ZnO-NRs, which we attribute to an effective transfer of photogenerated electrons from the rods to the graphene.

Acknowledgments

The authors acknowledge financial support from the Knowledge Foundation, Linköping University and Halmstad University. The authors also thank Emil Nilsson and Urban Bilstrup for fruitful discussions.

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Cite this: *RSC Adv.*, 2019, 9, 30585

Graphene-based plasmonic nanocomposites for highly enhanced solar-driven photocatalytic activities

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High-efficiency photocatalysts are crucial for the removal of organic pollutants and environmental sustainability. In the present work, we report on a new low-temperature hydrothermal chemical method, assisted by ultrasonication, to synthesize disruptive plasmonic ZnO/graphene/Ag/AgI nanocomposites for solar-driven photocatalysis. The plasmonic nanocomposites were investigated by a wide range of characterization techniques, confirming successful formation of photocatalysts with excellent degradation efficiency. Using Congo red as a model dye molecule, our experimental results demonstrated a photocatalytic reactivity exceeding 90% efficiency after one hour simulated solar irradiation. The significantly enhanced degradation efficiency is attributed to improved electronic properties of the nanocomposites by hybridization of the graphene and to the addition of Ag/AgI which generates a strong surface plasmon resonance effect in the metallic silver further improving the photocatalytic activity and stability under solar irradiation. Scavenger experiments suggest that superoxide and hydroxyl radicals are responsible for the photodegradation of Congo red. Our findings are important for the fundamental understanding of the photocatalytic mechanism of ZnO/graphene/Ag/AgI nanocomposites and can lead to further development of novel efficient photocatalyst materials.

Received 12th August 2019
Accepted 19th September 2019

DOI: 10.1039/c9ra06273d

rsc.li/rsc-advances

1 Introduction

Research on solar energy-driven photocatalysts is growing fast due to environmental concerns and to the need for utilization of sustainable energy resources.^{1–4} So far, semiconductor-based nanostructures are among the most studied materials for photocatalytic purposes due to their remarkably high efficiency.^{5–9} However, many of these semiconductors suffer from issues with poor absorption of light and high recombination rates of photogenerated electron–hole (e^-/h^+) pairs.^{1,10} Heterostructure materials offer the possibility of advanced bandgap engineering to drastically improve the scavenging of energy from the sunlight for degradation of harmful organic compounds and contaminants. Various heterostructure materials have been

explored with the aim to find materials with enhanced photocatalytic properties under solar light irradiation. Zinc oxide (ZnO) is a remarkable photocatalyst that can be composited with other materials to improve visible light harvesting and, thus, the photocatalytic efficiency. ZnO–graphene nanocomposites are particularly interesting heterostructures with a capability of inhibiting the recombination of photogenerated charge carriers during the photocatalytic process. Graphene (GR) is a well-known 2D material consisting of carbon atoms arranged in a honeycomb lattice structure.^{11,12} It possesses many fundamentally interesting electronic properties such as zero bandgap, zero effective mass, high charge carrier mobility, large surface area, and high optical transparency over a very large spectral range from IR to UV, which makes it an excellent candidate for enhancing the performance of photocatalysts.^{10,11,13–15} It was found that GR and GR oxide can significantly improve the separation efficiency of photogenerated e^-/h^+ pairs in photocatalytic processes.^{10,11,16–20} For instance, Tian *et al.*²¹ fabricated ZnO nanorods/reduced GR oxide nanocomposites for enhancing the photodegradation of methylene blue dye. Also, Sawant *et al.*²² showed an enhancement of the photodegradation capability of methylene orange and rhodamine B using ZnO/GR nanosheets.

Many different metal–semiconductor nanostructures have been studied as plasmonic photocatalysts.^{6,23,24} Recently, Ag–

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based semiconductors exhibiting a strong surface plasmon resonance effect (SPR)^{23,25–29} were extensively investigated as visible light photocatalysts for degradation of organic pollutants and toxic dyes. In order to further increase the photocatalytic activity of the ZnO/GR photocatalyst under visible light irradiation, a narrow bandgap silver halide *e.g.* silver iodide (AgI) can be added to the nanocomposite.²⁵ The blending of AgI with ZnO shifts the absorption of the nanocomposite significantly towards the visible light region.^{11,27,30} In addition, the excellent conductivity of AgI nanostructures can promote electron transfer that suppresses e^-/h^+ recombination and, thus, enhances the interfacial charge transfer.²⁵ Therefore, it is expected that the addition of Ag/AgI to ZnO/GR would result in a new nanocomposite with excellent photocatalytic performance. So far, to the best of our knowledge, there are no reports on photocatalytic properties of nanocomposites comprising Ag/AgI and ZnO/GR with respect to degradation of CR dye under solar light irradiation.

In the present work, we report on new plasmonic ZnO/GR/Ag/AgI nanocomposites with highly enhanced photocatalytic capability under simulated solar light irradiation. The nanocomposites were prepared *via* an ultrasonic-assisted hydrothermal solution-based procedure and used for photodegradation of CR dyes. First, ZnO/GR nanocomposites were prepared through hydrothermal growth of ZnO nanoparticles (NPs) on GR nanosheets.²⁰ Subsequently, Ag/AgI NPs were grown on the ZnO/GR nanocomposites *via* an ultrasonic irradiation method.²⁰ Also, pristine ZnO NPs and ZnO/Ag/AgI

nanocomposites were prepared as reference samples. The ZnO/GR/Ag/AgI nanocomposite exhibits superior photocatalytic performance compared to ZnO NPs, ZnO/GR, and ZnO/Ag/AgI nanocomposites. The enhanced photodegradation of CR dyes is primarily attributed to increased light absorption and separation of photogenerated charge carriers by the unique heterojunctions formed between the ZnO, GR, and Ag/AgI counterparts. We present a detailed model of the enhanced photocatalytic mechanism based on the calculated band structure profile of the ZnO/GR/Ag/AgI heterojunctions.

2 Experimental part

2.1 Materials

All the chemicals used in this work were purchased from Sigma Aldrich and used without any further purification, including the multilayer GR powder, zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), potassium hydroxide (KOH), silver nitrate (AgNO_3), and sodium iodide (NaI). Deionized (DI) water was used in all steps.

2.2 Samples preparation

2.2.1 ZnO/GR. The ZnO/GR nanocomposite with a GR-to-ZnO weight ratio of 1:99 was synthesized by adding a 10 mg L^{-1} dispersion of GR powder in a zinc acetate dehydrate solution (0.01 M) in DI water. Subsequently, KOH (0.05 M) was added dropwise to the above solution at 60°C in an ultrasonic bath and kept for 10 minutes. The obtained ZnO/GR nanocomposite was then washed in water and acetone and

Fig. 1 Schematic diagram for preparation of ZnO/GR/Ag/AgI nanocomposites.

centrifuged at 3000 rpm for 10 minutes three times, followed by drying in an oven at 120 °C overnight.

2.2.2 ZnO/GR/Ag/AgI. To prepare the ZnO/GR/Ag/AgI nanocomposites, Ag/AgI was added to the as-prepared ZnO/GR with three different weight ratios $X = 10\%$, 20% , and 30% forming the corresponding nanocomposite denoted ZnO/GR/Ag/AgI ($X\%$). First, ZnO/GR was dispersed into 200 mL of DI water with ultrasonic irradiation for 10 minutes and then AgNO_3 was added to the suspension and stirred for 30 minutes. Next, an aqueous solution of NaI was added dropwise and the final suspension was ultrasonicated for one hour. The nanocomposites were separated by centrifugation and washed two times with DI water and acetone to remove any residuals, and finally dried in an oven at 75 °C for 6 hours. Fig. 1 shows the preparation steps for fabricating the ZnO/GR/Ag/AgI nanocomposites.

2.3 Sample characterization

Powder X-ray diffraction (XRD) was used to study the structural properties of the prepared samples using a Philips powder diffractometer (1729 PW) equipped with a Cu K(α) radiation source at 40 kV/40 mA. The sample morphology was investigated with a field-emission scanning electron microscope (FE-SEM), equipped with a Sigma 500 Gemini field emission gun operating at 10 kV. Samples for transmission electron microscopy (TEM) analysis were prepared by dispersing the obtained nanocomposites onto a lacey carbon

film suspended by copper TEM grids. Scanning TEM (STEM) high-angle annular dark-field imaging (HAADF), energy-dispersive X-ray spectroscopy (EDS) as well as TEM imaging were performed in the double-corrected Linköping FEI Titan³ 60–300, operated at 300 kV. The microscope is equipped with image and probe Cs correctors and a monochromated high brightness XFEG gun and an efficient high solid angle Super-X EDX detector. The chemical composition of the samples was investigated by X-ray photoelectron spectroscopy (XPS) using a Scienta ESCA-200 spectrometer equipped with a monochromatic Al K(α) X-ray source with a photon energy of 1486.6 eV. The optical properties were analyzed by UV-Visible spectrophotometry (PerkinElmer Lambda 900 system) and cathodoluminescence (CL) spectroscopy (Gatan Mono CL4 system combined with FE-SEM). We have also carried out Mott-Schottky tests using a set-up comprising a PGSTAT302N workstation and a standard three-electrode system.

2.4 Photocatalytic experiments

The photocatalytic experiments were performed using a solar simulator (100 W ozone-free xenon lamp with a power of 1 sun). In brief, each sample (0.05 g) was mixed with 100 mL of CR dye solution with an initial concentration of 0.02 g L^{-1} and pH ~ 7 to investigate the photocatalytic activities prior to exposure. These mixtures were then stirred for 30 minutes in dark to reach the adsorption-desorption equilibrium between the photocatalyst and

Fig. 2 (a) XRD spectra of pristine ZnO NPs, ZnO/GR, ZnO/Ag/AgI, and ZnO/GR/Ag/AgI nanocomposites with a different weight percentage of Ag/AgI. (b) High-resolution XRD patterns revealing composition-dependent diffraction peak shifts.

the dye molecules. After a given interval of irradiation time, a small amount of the mixtures was withdrawn and centrifuged. Finally, the UV-Vis absorbance spectra of the CR dye solution were recorded by the UV-Visible spectrophotometer.

3 Results and discussion

3.1 Analysis of sample characteristics

Fig. 2 shows the XRD spectra of pristine ZnO NPs, ZnO/GR, ZnO/Ag/AgI, and ZnO/GR/Ag/AgI nanocomposites. It can be observed in Fig. 2(a) that the pristine ZnO NPs exhibit characteristic peaks at 2θ values of 31.8° , 34.6° , 36.5° , 47.8° , 56.8° , 63.0° , 66.8° , 67.9° , and 69° , which correspond to the crystal planes (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively, which all belong to the pure hexagonal wurtzite phase of ZnO (JCPDS no. 36-1451). These results strongly imply that the samples are of good crystalline quality and free from defects. Similar XRD diffraction peaks were in fact observed from the ZnO/GR nanocomposites. The fact that no diffraction peaks from carbon species were observed can be attributed to the low amount of GR (1 wt%) in the samples^{18,19} and to the relatively low diffraction intensity of GR.³¹ The presence of GR in the nanocomposites was identified by TEM and XPS analysis (see below). The addition of AgI nanoparticles to the ZnO and ZnO/GR nanocomposites show diffraction patterns at 2θ values of

23.9° , 39.2° , and 46.0° , which could be related to the crystal planes (111), (220), and (311), respectively, of the cubic AgI structure (JCPDS no 01-0503).²⁷ This conclusion is supported by the observed increase in the intensity of the AgI-related peaks with increasing AgI content. In addition, a small peak at $\sim 77^\circ$ was observed in ZnO/Ag/AgI and various ZnO/GR/Ag/AgI nanocomposites, which can be assigned to the reflections of Ag^0 (JCPDS no 65-2871)^{27,32} produced during the sample preparation. The effect of GR and Ag/AgI on the crystal structure of the pristine ZnO NPs was examined by more accurate XRD measurements in the region of $30\text{--}40^\circ$ as shown in Fig. 2(b). A small shift of the XRD peaks towards smaller angles was not only observed for the ZnO/GR nanocomposites compared to the pristine ZnO NPs, but in fact detected for all GR incorporated nanocomposites. This shift indicates that the lattice constants of ZnO and Ag/AgI NPs have changed due to the presence of the carbonaceous material, in agreement with previous reports.^{33,34} The crystallite size of the NPs can be calculated by the Scherrer equation:³⁵

$$D = \frac{k\lambda}{\beta_{hkl} \cos \theta}$$

Here D is the crystallite size of the ZnO NPs, λ is the X-ray wavelength, θ is the Bragg diffraction angle, β is the full width at half maximum of the diffraction peak corresponding to the

Fig. 3 FE-SEM images of (a) pristine ZnO NPs, (b) ZnO/GR, (c) ZnO/Ag/AgI, and (d) ZnO/GR/Ag/AgI (20%) nanocomposites. The insets show the size distribution of the NPs.

Fig. 4 TEM image of ZnO/GR/Ag/AgI (20%) nanocomposites. The inset shows the conjunction of GR and particles (ZnO or Ag/AgI) at higher magnification (region marked by the yellow circle in the main image).

(101) plane, and k is the Scherrer constant equal to 0.9. It was found that the crystallite size of ZnO NPs is increased slightly after the addition of the Ag/AgI from 17 to 20 nm.

Fig. 3 shows FE-SEM images of the synthesized (a) pure ZnO, (b) ZnO/GR, (c) ZnO/Ag/AgI, and (d) ZnO/GR/Ag/AgI (20%) samples. The pure ZnO NPs sample shows a uniform size

Fig. 5 (a) STEM-HAADF image of a ZnO/GR/Ag/AgI (20%) nanocomposite, (b–e) STEM-EDS elemental maps displaying Zn, O, Ag, and I distributions, respectively, and (f) integrated EDS spectra.

distribution as compared to the ZnO/Ag/AgI and ZnO/GR/Ag/AgI (20%) nanocomposites. The average size of the ZnO NPs was found to be ~ 80 nm, as estimated from the size distribution inset in (a). The average NPs size increased significantly to ~ 100 nm (inset in (c)) when Ag/AgI was added to the ZnO NPs, which reflects the formation of ZnO/Ag/AgI agglomerates. The particle size observed in the FE-SEM images is much larger than that extracted from the XRD measurements, indicating a polycrystalline structure of the NPs.

TEM investigations confirm the conjunction of NPs and GR nanoplatelets in ZnO/GR/Ag/AgI (20%) nanocomposites as shown in Fig. 4. The GR nanoplatelets act as a substructure to assemble the nanoparticles enabling an electrical bridge between them. Additionally, it was observed that the GR nanoplatelets have different size and shape caused by the ultrasonic irradiation during the synthesis procedures.

The elemental distribution of the ZnO/GR/Ag/AgI (20%) nanocomposites were examined using STEM-HAADF imaging (Fig. 5(a)) and STEM-EDS elemental mapping (Fig. 5(b–e)). The integrated EDS spectra, extracted from EDS maps, confirmed the presence of Zn, O, Ag, and I elements in the

nanocomposites. The corresponding elemental EDS maps revealed that the cluster of NPs forming the nanocomposite is mainly composed of ZnO, while Ag/AgI NPs are present in localized areas of the cluster. Carbon mapping did not display any spectral signatures from GR due to overlap with the underlying carbon support grid (not shown). It is worth noting that a better distribution of the elements in the nanocomposites provides a stronger bond between different counterparts. This leads to a more efficient generation and separation of charge carriers under solar irradiation, which in turn leads to excellent photocatalytic activities and higher photodegradation efficiency.

Furthermore, the chemical oxidation state of the elements in the ZnO/GR/Ag/AgI (20%) nanocomposite was identified by XPS analysis. From the XPS survey scan spectrum in Fig. 6(a) we could clearly identify the existence of Zn, O, C, Ag, and I in the nanocomposite. The high resolution of the C 1s spectrum shown in Fig. 6(b) was deconvoluted into three Gaussian peaks. Besides the C–C bond peak at 284.79 eV, which demonstrates the introduced impurities from the surface contamination,³⁶ there are two dominant peaks at 285.57 and 288.71 eV assigned to C–O–C and C=O bonds,^{11,36,37}

Fig. 6 XPS spectra for a ZnO/GR/Ag/AgI (20%) nanocomposite. (a) Survey scan, and high resolution core level spectra of (b) C 1s, (c) Zn 2p, (d) O 1s, (e) Ag 3d, and (f) I 3d.

respectively. As shown in Fig. 6(c), the XPS core level spectrum of Zn 2p is composed of two peaks centered at 1022.16 and 1045.23 eV, which are ascribed to the binding energy of Zn 2p_{3/2} and Zn 2p_{1/2} respectively.³⁸ The core-level spectrum of O 1s is presented in Fig. 6(d) and it is divided into two Gaussian fitted peaks. The peak centered at 530.50 eV corresponds to oxygen in the ZnO NPs lattice in the nanocomposite structure.^{37,39,40} The peak at 532.37 eV can be ascribed to oxygen bonded to carbon atoms (the functional group present on GR) and also to the hydroxyl group adhering to the surface of nanocomposite.^{41,42} The XPS spectrum of Ag 3d is shown in Fig. 6(e). The main peaks at 368.13 and 374.06 eV are assigned to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively. The Ag 3d_{5/2} is further divided into two peaks at 367.82 and 368.28 eV and the Ag 3d_{3/2} peak is also divided into two peaks at 373.79 and 374.32 eV. The low energy peaks at 367.82 and 373.79 eV are attributed to Ag⁺, whereas the peaks at 368.28 and 374.32 eV are related to metallic Ag⁰.^{27,43} Accordingly, metallic Ag⁰ is produced at the surface of the ZnO/GR/Ag/AgI (20%) photocatalyst during the sample preparation, an observation consistent with the XRD results shown in Fig. 2(a). The chemical state of the I element, which is present in the form of I⁻ ions in the nanocomposite, is revealed in Fig. 6(f). Two clearly resolved peaks related to I 3d_{5/2} and I 3d_{3/2} are located at 619.02 and 630.58 eV, respectively.³⁰

The optical characteristics of the nanocomposites were examined by UV-Vis spectroscopy and CL measurements. The UV-Vis absorbance spectra of ZnO NPs, ZnO/GR, ZnO/Ag/AgI, and ZnO/GR/Ag/AgI nanocomposites with different weight percent of Ag/AgI are shown in Fig. 7(a). It is clear that pure ZnO NPs exhibit a strong interband absorption edge around 400 nm. The weak absorbance in the visible region is attributed to the presence of native point defects.²⁹ The addition of GR to ZnO slightly redshifts the absorbance edge. This redshift can be explained by the influence of GR on the surface electric charge in the ZnO/GR photocatalyst.^{10,44} In the case of ZnO/GR/Ag/AgI nanocomposites, a broader absorbance is observed in the visible region ($\lambda > 400$ nm) which increases with the weight percent of Ag/AgI. Therefore, the blending of Ag/AgI into the nanocomposite can increase its photocatalytic performance under solar irradiation. The observed absorbance peak at $\lambda = 430$ nm is assigned to the surface plasmon absorption of the Ag/AgI NPs, indicating the presence of Ag⁰ at the surface of the nanocomposites.⁴⁵ As a result, due to contributions from different counterparts, the fabricated plasmonic nanocomposite displays the highest optical absorbance, which is beneficial for the photocatalytic performance under solar irradiation. Fig. 7(b) shows CL spectra of ZnO, ZnO/GR, ZnO/Ag/AgI, and ZnO/GR/Ag/AgI (20%) samples, measured at room temperature. Interestingly, all samples exhibit a broad emission band covering the whole visible region with a luminescence peak centered at ~ 600 nm. This band can be attributed to radiative transitions associated with intrinsic deep levels such as oxygen vacancies and interstitials (V_O, O_i), as well as to the presence of hydroxyl groups at the surface of the ZnO NPs.^{46–48} In addition, the observed peak at $\lambda = 430$ nm is attributed to surface plasmon-enhanced luminescence, induced by the Ag/AgI NPs, in

agreement with the UV-Vis spectrum in Fig. 7(a). The ZnO/GR/Ag/AgI (20%) nanocomposite exhibits broader band luminescence than that of the pure ZnO NPs and ZnO/GR, again consistent with the results presented in Fig. 7(a). Evidently, the presence of Ag/AgI has a significant positive effect on the emission properties in the visible region, which in turn is expected to improve the photocatalytic capability of the nanocomposite.

3.2 Photocatalytic performance

3.2.1 Photodegradation of toxic wastewater.

We studied the photocatalytic activities of ZnO, ZnO/GR, ZnO/Ag/AgI and ZnO/GR/Ag/AgI samples through the degradation of CR dye under simulated solar irradiation. Fig. 8(a–f) shows the recorded UV-Vis absorbance of the CR dye mixed with the nanocomposite in 15 min steps of up to 60 min irradiation. First, the nanocomposite/CR dye was kept in dark for 30 min to reach the adsorption-desorption equilibrium state between the photocatalysts and CR molecules. Then the light was turned on, and the absorbance spectra were recorded after each 15 min step for all samples. It is well-known that carbon-based materials have

Fig. 7 (a) UV-Vis absorbance spectra of pristine ZnO NPs, ZnO/GR, ZnO/Ag/AgI, and ZnO/GR/Ag/AgI nanocomposites with a different weight percentage of Ag/AgI, and (b) corresponding CL spectra.

Fig. 8 UV-Vis absorbance spectra of CR dyes recorded after different photodegradation time intervals using (a) ZnO, (b) ZnO/GR, (c) ZnO/Ag/AgI, (d) ZnO/GR/Ag/AgI (10%), (e) ZnO/GR/Ag/AgI (20%), and (f) ZnO/GR/Ag/AgI (30%) photocatalysts. The spectra marked by “–30 min” were recorded for the CR only. The spectra marked by “0 min” were recorded for the samples kept in darkness for 30 min (no irradiation).

an excellent adsorption capacity. This plays a key role in the present nanocomposites where the enhanced dye adsorption on the surface of the photocatalysts strongly increases their photocatalytic performance.⁴⁹ With increasing irradiation time, the main absorbance peak at 497 nm related to CR reduces progressively, verifying the degradation of the CR dye. After 60 min irradiation, the absorbance peak for the ZnO/GR/Ag/AgI (20%) nanocomposite has almost disappeared (Fig. 8(e)). In contrast, the variation of the absorbance peaks for the ZnO, ZnO/GR, and ZnO/Ag/AgI samples were small as shown in Fig. 8(a, b, and c), respectively. The enhanced photocatalytic performance of ZnO/GR/Ag/AgI nanocomposites can be assigned to the synergistic effect of ZnO/GR and Ag/AgI, and the improved charge transfer ability of the photo-generated carriers at their interfaces as discussed in detail below.

The photodegradation efficiency (%) was calculated according to eqn (1) and the results are shown in Fig. 9.

$$\text{Degradation (\%)} = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

where A_0 is the initial absorbance of the dye, and A is the absorbance after a specific irradiation time.

Fig. 9(a) displays the calculated degradation efficiency of the ZnO, ZnO/GR, ZnO/Ag/AgI, and ZnO/GR/Ag/AgI samples under solar irradiation. In the absence of any photocatalyst, the

photolysis of the CR is negligible, which shows that this pollutant has high stability during extended periods of irradiation. In contrast, the usage of ZnO NPs and ZnO/GR nanocomposites enhance the photocatalytic performance. In particular, the incorporation of GR leads to a significantly higher photodegradation efficiency of 75% compared to 58% for pure ZnO NPs, an effect primarily attributed to inhibition of the recombination of photogenerated e^-/h^+ pairs during the photocatalytic reaction. However, in comparison to pure ZnO NPs, and ZnO/GR, the plasmonic ZnO/Ag/AgI and ZnO/GR/Ag/AgI nanocomposites show superior photocatalytic activities for CR photodegradation. This important result originates first of all from the addition of Ag/AgI which increases the absorption of photons, and thus, the number of photogenerated e^-/h^+ pairs in the visible region of the solar spectrum. Interestingly, the photocatalytic performance of the plasmonic nanocomposites depends strongly on the Ag/AgI weight ratio. The ZnO/GR/Ag/AgI (20%) nanocomposite exhibits the highest photodegradation efficiency reaching 90% after 60 min of irradiation. However, with increasing Ag/AgI weight ratio up to 30%, the photodegradation efficiency decreased to only 60% after 60 minutes of irradiation. This drop in efficiency can be explained by the excess of Ag/AgI acting as efficient recombination centers. Moreover, the Ag/AgI species might cover the active sites on the nanocomposite surface and thereby passivate

the effective junctions between the counterparts which lead to a reduced charge separation efficiency in ZnO/GR/Ag/AgI (30%) sample. A specific content of Ag/AgI is thus crucial for optimizing the photocatalytic performance of plasmonic ZnO/GR/Ag/AgI nanocomposites.

The photodegradation of the CR dye may follow two different processes of direct mineralization or stepwise *N*-deethylation. The direct mineralization involves gaseous end-products such as CO₂, NO₃⁻, and NO_x, whereas the stepwise *N*-deethylation leads to a destruction of the conjugated structure of the CR dye which results in a complete degradation. In our photodegradation experiments, the absorption of the CR is decreasing with time without any shift in the absorbance spectrum after 60 min of irradiation (Fig. 8(e)). This suggests that the CR dye was directly mineralized, producing end-products of CO₂, NO₃⁻, and NO_x.^{15,50,51}

To further reveal the photoreactivity mechanisms involved in photodegradation of the CR dye with the ZnO/GR/Ag/AgI (20%) nanocomposite, trapping experiments were performed to identify the reactive species that are involved in the photocatalytic mechanisms. For this purpose, ethylenediaminetetraacetic acid (EDTA), benzoquinone (BQ) and 2-propanol were used as scavengers for h⁺, superoxide radicals, and hydroxyl

radicals, respectively.^{52–55} As shown in Fig. 9(b), the photodegradation process was suppressed with the addition of BQ due to the quenching of the superoxide radicals, indicating that the superoxide radicals are the main reactive species involved in the photodegradation of the CR dye. Also, it was observed that the addition of 2-propanol showed partial inhibition of the degradation of the CR, suggesting that the hydroxyl radicals also play an important role for the photocatalytic performance. Surprisingly, the addition of EDTA did not have any noticeable effect at the beginning of the degradation process. However, the quenching of holes due to the addition of the EDTA gradually increased after 30 min of irradiation.

To further investigate the photocatalytic stability and reusability of the ZnO/GR/Ag/AgI (20%) nanocomposite, recycling tests of the efficiency for photodegradation of CR were performed. After four successive degradation experiments (Fig. 9(c)), only a small reduction in the efficiency was observed, indicating an excellent stability of the nanocomposite.

To rule out any effects of photosensitization of the CR dye under visible light, the photocatalytic performance of the various nanocomposites in this work was investigated for colourless phenol (0.02 g L⁻¹), well known to be insensitive to visible light. A mixture of 100 mL of a phenol solution with

Fig. 9 (a) Photodegradation efficiency of CR dyes using ZnO, ZnO/GR, ZnO/Ag/AgI and ZnO/GR/Ag/AgI photocatalysts with different weight percentage of Ag/AgI, (b) photocatalytic activities of CR with ZnO/GR/Ag/AgI (20%) nanocomposite in the presence of different scavengers, (c) recycling of ZnO/GR/Ag/AgI (20%) nanocomposite during degradation of CR, and (d) photodegradation of phenol with ZnO and ZnO/GR/Ag/AgI (20%) nanocomposite.

0.05 g of the respective nanocomposite was stirred for 30 min in dark to reach the adsorption–desorption equilibrium. Then UV-Vis absorbance spectra of the different mixtures were recorded in 60 min time intervals. The absorption peak of phenol at 270 nm was used to calculate the concentration of phenol at each time (Fig. 9(d)). It is obvious that the concentration of phenol is decreasing gradually with irradiation time, indicating the decomposition of phenol. In comparison to pure ZnO NPs, the ZnO/GR/Ag/AgI (20%) nanocomposite shows a superior efficiency for photodegradation of phenol. This result also implies that the effect of dye sensitization on the degradation efficiency is small for both phenol and CR.

To develop a deeper understanding of the photocatalytic mechanisms, the apparent reaction constant for each photocatalyst was investigated according to the Langmuir–Hinshelwood's pseudo-first order kinetics model⁵⁶ shown in eqn (2) below.

$$K_{\text{app}} = \frac{\ln \left[\frac{C_0}{C(t)} \right]}{t}, \quad (2)$$

where K_{app} is the apparent reaction constant (min^{-1}), t is the irradiation time (min), C_0 is the initial concentration mol L^{-1} of the dye, and $C(t)$ is the concentration mol L^{-1} of the dye after irradiation time t . The plot of $\ln \left[\frac{C_0}{C(t)} \right]$ versus irradiation time is shown in Fig. 10(a) and found to be in excellent agreement with the Langmuir–Hinshelwood model. The degradation rate constant of CR is found to be 105×10^{-4} , 160×10^{-4} , 208×10^{-4} , 208×10^{-4} , 266×10^{-4} , and $110 \times 10^{-4} \text{ min}^{-1}$ for ZnO, ZnO/GR, ZnO/Ag/AgI, ZnO/GR/Ag/AgI (10%), ZnO/GR/Ag/AgI (20%), and ZnO/GR/Ag/AgI (30%), respectively. It is clear that the degradation rate constant for ZnO/GR/Ag/AgI (20%) is superior to those of the other GR-based nanocomposites.

In Table 1 we show a comparison of the degradation efficiency of different reported GR-based photocatalysts. Summarized, this survey demonstrates that the present plasmonic ZnO/GR/Ag/AgI (20%) nanocomposite has very high photodegradation efficiency with respect to the irradiation time of the photocatalytic reaction and with reasonable degradation rate constant.

3.2.2 Proposed photocatalytic mechanism. To experimentally probe the electronic band structure of ZnO/GR/Ag/AgI nanocomposites, Mott–Schottky analysis of both ZnO and AgI semiconductors were performed to determine the conduction and valence band edge energies (E_{CB} and E_{VB}).^{57,58} As readily observed in Fig. 11(a and b), both the ZnO and AgI samples exhibit capacitance vs. potential characteristics consistent with n-type semiconductors. The flat band potentials can be determined from the extrapolation of $1/C^2$ to zero, which found to be -0.44 V and -0.52 V vs. Ag/AgCl (*i.e.*, -0.24 V and -0.32 V vs. NHE) for ZnO and AgI semiconductors, respectively. It is worth noted that the flat band potential for n-type semiconductor is placed at 0.1 eV more positive potential than the E_{CB} . Accordingly, E_{CB} for the ZnO and AgI was obtained to be -0.34 and

-0.42 eV , respectively. In addition, considering the band gap values and based on Mullikan theory calculations,⁵⁹ the E_{VB} of ZnO and AgI was computed to be $+2.86 \text{ eV}$ and $+2.37 \text{ eV}$, respectively.

In Fig. 12 we show a schematic of the proposed photocatalytic mechanism deduced from the combined results of the different measurements and analysis methods discussed in this work. In the presence of solar light, ZnO and AgI simultaneously play a key role in absorbing the solar light. Especially AgI, with its smaller bandgap than ZnO, can efficiently increase the absorption in the visible light region.²⁷ When solar light impinges on the ZnO/GR/Ag/AgI photocatalyst surface, electrons, and holes are generated in the conduction band (CB) and valence band (VB) in ZnO and AgI, respectively. Owing to the band offsets, the electrons residing in the CB of AgI migrate to the CB of ZnO and, in a likewise manner, holes in the VB of ZnO move to the VB of AgI. This leads to an efficient charge carrier separation and transportation which mitigates the undesired recombination of charge carriers. In addition, the plasmonic Ag NPs act as efficient generators of electrons and holes when

Fig. 10 (a) $\ln(C_0/C)$ versus irradiation time, and (b) degradation rate constant of CR dyes using ZnO, ZnO/GR, ZnO/Ag/AgI and ZnO/GR/Ag/AgI photocatalysts with a different weight percentage of Ag/AgI.

Table 1 Comparison of state-of-the-art GR-based nanocomposites for photodegradation of organic dyes

Photocatalyst	Synthesis method	Light source	Dye	Degradation min/ efficiency	K_{app} (10^{-2} min^{-1})	Year
AgI-mesoTiO ₂ /4 wt% RGO	Hummers and ultrasound	150 W tungsten lamp	Methylene orange	90/92%	—	2016 (ref. 11)
P25/1 wt% GR	Modified Hummers method	500 W xenon lamp	Methylene blue	65/65%	—	2010 (ref. 60)
ZnSe/1 wt% GR	Modified Hummers method	Solar simulator with a power of 1 sun	Methylene blue	240/99.5%	1.27	2015 (ref. 61)
Ag/Ag ₂ CO ₃ -1 wt% RGO	Physical mixing and chemical bath deposition	350 W xenon lamp	Methylene orange	15/7%	1.80	2016 (ref. 62)
BiVO ₄ /5.5 wt% RGO/Bi ₂ O ₃	Chemical bath deposition	150 W metal halide lamp	Bisphenol A	240/60%	0.031	2017 (ref. 63)
Ag/ZnO/1 wt% GR	Low-temperature microwave-assisted solution	300 W high-pressure Hg lamp	Methylene orange	80/99.6%	0.5	2015 (ref. 64)
1.78 wt% RGO-ZnO	Chemical bath deposition	400 W Hg lamp	Rhodamine B	60/61.5%	—	2015 (ref. 65)
3 wt% GR/ZnO	Hydrolysis deposition	3 W LED lamp	X3B	45/80%	0.34	2015 (ref. 66)
ZnO/10 wt% RGO	Hummers and arc discharge	90 W halogen light	Methylene orange	90/100%	0.47	2015 (ref. 67)
1 wt% GR/ZnO	Hydrothermal	250 W mercury lamp	Methylene blue	450/90%	—	2016 (ref. 68)
Ag ₂ CrO ₄ -1 wt% GR	Precipitation	300 W xenon lamp	Methylene blue	15/50%	2.80	2015 (ref. 69)
ZnO/1 wt% GR/Ag/AgI	Ultrasonic-assisted hydrothermal	Solar simulator (100 W xenon lamp with a power of 1 sun)	Congo red	60/90%	2.66	Current work

Fig. 11 Mott-Schottky plots for (a) ZnO and (b) AgI samples.

excited by visible light *via* the SPR effect. These generated electrons are subsequently injected into the CB of AgI and ZnO, respectively.^{15,37} Subsequently, the photogenerated electrons are transferred from the CB of ZnO to the GR. The GR plays a dual role of electron acceptor and transporter, which improve the photocatalytic behavior of the nanocomposite under solar irradiation. The efficient transfer of electrons and the reduction of the recombination rate at the surface of the photocatalyst strongly enhance the photocatalytic efficiency. The trapped electrons react with oxygen

molecules to produce superoxide radicals that subsequently get converted into hydroxyl radicals through multi-electron reduction reactions. Finally, these active species can react with pollutant (dye) molecules and decompose them into H₂O, CO₂, and mineral compounds. The photoinduced holes can directly oxidize the adsorbed dye molecules to produce degraded products. As a result, the high photodegradation efficiency of ZnO/GR/Ag/AgI nanocomposites is related to the uniform distribution of the nanoparticles at the surface of the GR nanosheets, and strong synergy effects

Fig. 12 Schematic diagram showing the energy band structure and possible e^-/h^+ pair separation and charge carrier transport mechanisms in ZnO/GR/AgI nanocomposites.

between GR, ZnO NPs, and Ag/AgI that favours interfacial charge transfer and prevents e^-/h^+ recombination.

4 Conclusion

In summary, we have reported on a novel low-temperature chemical route, assisted by ultrasonication, to prepare ZnO/GR/Ag/AgI nanocomposites for state-of-the-art photocatalytic performance for degradation of CR and phenol. The prepared plasmonic nanocomposites have been characterized by various techniques to unravel their structural, morphological, electrical, optical and photocatalytic properties. The synthesized ZnO/GR/Ag/AgI (20%) nanocomposite exhibits the highest photodegradation efficiency (90%) and the highest degradation constant rate ($308 \times 10^{-4} \text{ min}^{-1}$) for degradation of CR dye. The key advantages of the optimized nanocomposites include increased light absorption in the visible range due to a strong plasmonic resonance effect involving metallic Ag^0 , and to the improved electronic transfer due to hybridization with graphene. In addition, the nanoparticles in the plasmonic nanocomposite facilitate an effective charge separation of the photoexcited charge carriers, mitigating e^-/h^+ pair recombination. The scavenger experiments suggest that superoxide and hydroxyl radicals are responsible for the photodegradation of CR. The recycling test confirms a sufficient durability of the nanocomposite. We believe that the proposed plasmonic

nanocomposites are promising for high photocatalytic performance applications such as removal of organic and inorganic pollutants, photoelectrochemistry and water oxidation.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The authors acknowledge the Department of Science and Technology (ITN) at Campus Norrköping, Linköping University, Sweden for partial financial support. The Knut and Alice Wallenberg Foundation is acknowledged for support of the Electron Microscopy Laboratory at Linköping University.

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PAPER

III

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Synthesis of Vertically Aligned ZnO Nanorods Using Sol-gel Seeding and Colloidal Lithography Patterning

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Abstract

Different ZnO nanostructures can be grown using low-cost chemical bath deposition. Although this technique is cost-efficient and flexible, the final structures are usually randomly oriented and hardly controllable in terms of homogeneity and surface density. In this work, we use colloidal lithography to pattern (100) silicon substrates to fully control the nanorods' morphology and density. Moreover, a sol-gel prepared ZnO seed layer was employed to compensate for the lattice mismatch between the silicon substrate and ZnO nanorods. The results show a successful growth of vertically aligned ZnO nanorods with controllable diameter and density in the designated openings in the patterned resist mask deposited on the seed layer. Our method can be used to fabricate optimized devices where vertically ordered ZnO nanorods of high crystalline quality are crucial for the device performance.

Keywords: Zinc oxide, Nanorod arrays, Vertical growth, Colloidal lithography, Nanofabrication, Sol-gel, Seed layer, Chemical bath deposition

Introduction

The ability to realize a desirable precise nanomaterial architecture with respect to dimensions, arrangement, and density of the nanostructures is crucial for most advanced nanodevices. One viable route to accomplish this is to combine a top–bottom patterning technique with a self-assembling bottom-up growth method.

Zinc oxide (ZnO), one of the most widely studied semiconductors, shows an excellent potential for self-assembled optoelectronic nanodevices. Among the key properties of ZnO in this context can be mentioned, a simple growth procedure, a wide direct bandgap of 3.2–3.4 eV, a large exciton binding energy of 60 meV and a high mechanical and thermal stability [1]. Different high-temperature growth techniques such as chemical vapor deposition (CVD) [2], pulsed laser deposition (PLD) [3]

and vapor–liquid–solid (VLS) growth [4], as well as low-temperature growth techniques including electrodeposition [5] and chemical bath deposition (CBD) [6] have been used to grow a plenitude of ZnO nanostructures. Among all these growth techniques, CBD is more favorable due to its simplicity, cost-effectiveness and large-area applicability.

One-dimensional (1D) wurtzite ZnO nanorods (ZnO NRs) have attracted huge interest in the last two decades due to their interesting fundamental electronic and mechanical properties, as well as to their great promise for novel electronics [6], photonics [7], electrochemical [8] and clean-tech applications. The growth of ZnO NRs using CBD is highly dependent on the crystallographic surface quality of the substrate. The two most frequently used substrates to this date are i) single crystal lattice-matched substrates (single-crystalline ZnO [9], Al₂O₃ [10] and GaN [11]) with a thin heteroepitaxial ZnO film, and ii) non-epitaxial substrates precoated with a textured seed layer to provide suitable nucleation sites [12]. While single-crystalline substrates

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generally result in significantly higher NR growth quality, the high substrate cost limits their application. Conversely, the growth of NRs on low-cost non-epitaxial substrates, supplied with a textured polycrystalline seed layer, leads to a randomly oriented NR growth.

In many high-performance device applications, a precise engineering of the NR surface density, lateral ordering, and vertical alignment is of great importance. Growth of NRs by CBD offers several straightforward ways to engineer the NR architecture on the substrate by controlling growth parameters such as solution concentration [13], temperature [14], pH [15], and deposition duration. Unfortunately, changing any of these growth parameters typically also causes undesired changes in the NR growth result. For this reason, up to now, substrate patterning is the most effective way to control the position, density and alignment of ZnO NRs. In the vast majority of reported studies, patterning of the substrate includes the following steps: substrate preparation and cleaning, deposition of a mask resist layer, opening holes in the resist layer by lithography for selective area growth, and CBD growth of NRs in the holes.

During the past decade, various efforts have been made to grow ordered vertical ZnO NR arrays. In the majority of these studies, using the same CBD technique, the authors have focused on two key processing steps: preparation of appropriate substrates, and usage of different patterning techniques, e.g., electron-beam lithography (EBL), laser interference lithography (LIL), and nanoimprint lithography (NIL). Wang et al. demonstrated non-epitaxial growth of vertically aligned ZnO NRs on EBL-patterned polycrystalline ZnO-coated Si and GaN substrates [11]. Later, they reported on perfectly aligned heteroepitaxial ZnO NR growth on GaN substrates patterned by LIL [16]. In an effort to replace the expensive ZnO and GaN substrates with low-cost Si or glass substrates, they successfully used a 30- μm -thick textured ZnO layer as a flat (0001) ZnO seed layer. In a series of articles, Volk et al. successfully performed homoepitaxial growth of ZnO NRs on single-crystalline ZnO substrates patterned by EBL [10, 17–19]. The impact of different patterned substrates [10], a Zn-terminated versus O-terminated surface of the ZnO substrate [17], a sputtered polycrystalline ZnO thin film [18], and a ZnO seed layer deposited by atomic layer deposition (ALD) [19] on the quality of CBD-grown ZnO NRs have been deeply investigated. In a different approach, PLD was used for heteroepitaxial growth of a ZnO seed layer on a single-crystalline Al_2O_3 (0001) substrate, followed by NIL patterning [20]. More details about the Zn concentration window in CBD and its effect on the ZnO NR morphology were discussed in the same article. Selective area growth of ZnO NRs on different substrates, including Si

(111), GaAs (111) and InP (111), using EBL patterning and electrochemical deposition has also been reported [21].

In all the reviewed references, the growth of ZnO NRs on a single-crystalline ZnO substrate results in the highest crystal quality, while a coating with a thin polycrystalline ZnO layer on other expensive single-crystalline substrates leads to excellent vertically aligned ZnO NR growth. Employing sophisticated patterning techniques, e.g., EBL, for selective growth of ZnO NRs also has an essential impact on the final product cost and, consequently, on the potential application. To overcome demanding complexity issues related to pattern definition and expensive substrates in the fabrication of vertically aligned ZnO NR arrays, we propose to combine a simply prepared, highly uniform thin ZnO NP film on Si substrates with colloidal lithography (CL) patterning.

A sol-gel technique, described in [22], can be used to prepare a highly uniform, dense and thin seed layer of polycrystalline ZnO NPs on virtually any substrate, including Si or glass. In contrast to the spin-coating of a ZnO NP dispersion on a substrate, which usually leads to non-continuous dispersed islands of NP clusters [23], the sol-gel method results in a thin (tens of nm) continuous and highly uniform layer of ZnO NPs. For selective area CBD growth, a polymer resist layer is subsequently spin-coated on the ZnO seed layer and patterned by CL. Besides being a low-cost lithography method, CL is also suitable for large wafer-scale area patterning, high throughput, and compatibility with any substrate, offering excellent control over feature size and pitch [24–26].

Figure 1 shows a schematic of the processing and growth steps used in the present work. After dip-coating the Si substrate with a ZnO NP seed layer and spin-coating with a resist, respectively, a monolayer of polystyrene nanobeads (PS-NBs) with a diameter of 140 nm was deposited on the resist mask and covered by a thermally evaporated 30 nm thick Al film. After evaporation, the Al-coated PS-NBs were removed by tape stripping, leaving behind open nanoholes in the Al film. Dry etching of the resist in the holes down to the ZnO NP seed layer finalized the preparation of the growth mask. After CL, CBD was used to grow vertically aligned ZnO NRs with well-controlled diameter, length and surface density. While CL and CBD have previously been deployed to grow ZnO NRs on micrometer-sized areas on ITO glass substrates, resulting in large uncontrolled batches of grown NRs [27], the present study is, to the best of our knowledge, the first demonstrated selective growth of single vertically aligned ZnO NRs in CL-patterned masks on sol-gel prepared Si substrates. The results show a uniform distribution of nanoholes on a large wafer-scale area

and a homogeneous growth of vertical ZnO NRs using a facile and controllable CBD technique.

Methods

Materials

All the chemicals used in this work were purchased from Sigma-Aldrich and used without any further purification. The suspension of PS-NBs with a mean diameter of 140 ± 5 nm in water was purchased from microParticles GmbH, Germany.

Preparation of the ZnO NP Seed Layer

The ZnO NP sol-gel solution was prepared according to [22] by dissolving 8.25 g of zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and 2.26 ml of monoethanolamine (ethanolamine) in 100 ml of pure ethanol with final concentrations of 375 mM. The solution was stirred on a hotplate at 60°C for 10 h and then at room temperature overnight. A two-inch, highly doped n-type Si (100) wafer was cleaned by sequential ultrasonication in acetone, isopropanol, and DI water, followed by drying on a hotplate at 120°C for 5 min. The cleaned Si substrate was dipped into the ZnO NP sol-gel solution and pulled out at a constant speed of 30 mm/s using a computer-controlled dip-coater. Finally, it was annealed on a hotplate at 300°C for 10 min to remove the residual organics and improve the

ZnO NP crystallinity. The dip-coating and the annealing steps were repeated two times to increase the layer homogeneity and surface coverage.

Patterning the Seeded Sample by CL

The CL was carried out on a double-layer resist, consisting of a sacrificial PMMA (poly(methyl methacrylate), $M_w = 950$ k) electron-beam resist and a positive MICRO-POSIT S1805 photoresist. First, 0.3 ml of a 4 wt% solution of PMMA in toluene was spin coated on the seeded sample at 4000 rpm for 30 s, followed by soft baking at 170°C for 10 min. Subsequently, 0.3 ml of S1805 was spin coated on the sample at 4000 rpm for 30 s, followed by soft baking at 110°C for 90 s and hard baking at 145°C for 5 min. Next, the sample was treated by UV-ozone for 5 min, improving the surface hydrophilicity, and then 1 ml of a 0.2 wt% solution of PDPA (poly(diallyldimethylammonium), $M_w = (200-350)$ k) in DI water was pipetted on the sample surface. After 1 min. of settling, the sample was thoroughly rinsed with DI water and blow-dried with N_2 . The positively charged monolayer of PDPA guarantees electrostatic adhesion of negatively charged PS-NBs to the surface in the next step. Afterward, 1 ml of a 0.1 wt% suspension of PS-NBs in DI water was dropped on the sample surface. After 1 min. of settling, the sample was gently rinsed with DI water, and blow-dried with N_2 . A 30 nm thick Al layer was thermally evaporated on the beaded sample as a metal etch mask.

After evaporation, the Al-coated PS-NBs were removed by tape stripping using acrylic silicon-free Ultron 1009R tape (Fig. 1c). Reactive-ion etching (RIE, pressure 150 mTorr, O₂ flow 40 sccm, RF power 60 W and etching time 90 s) was employed to etch the resist layer down to the ZnO NP seed layer (Fig. 1d). Finally, to wet-etch the Al metal mask (Fig. 1e) without etching the exposed ZnO NP seed layer, a particular solution of potassium hydroxide (KOH) and potassium hexacyanoferrate III (K₃Fe(CN)₆) in DI water with a concentration of 30 mM and 50 mM respectively was used [28]. The wet etching was conducted at room temperature for 1 min. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of the fabrication steps are provided in Additional file 1: Figures S1 and S2.

CBD of ZnO NRs on the CL-Patterned Sample

A solution of 50 mM zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and 50 mM hexamethylenetetramine (HMT) in 100 ml DI water was prepared to grow the ZnO NRs. The patterned seeded substrates were kept upside down in the growth solution for 2 h at 95 °C in an oven. After the growth was completed, the samples were cooled to room temperature, removed from the solution, and rinsed with DI water (Fig. 1f).

Results and Discussion

ZnO Seed Layer

The growth of well-aligned vertical ZnO NRs with high crystallinity relies on the quality of the seed layer. For this, we developed smooth seed layers with large grain sizes and optimal crystal orientation. The prepared ZnO NP seed layer was investigated with respect to surface roughness and crystal structure using AFM and X-ray diffraction (XRD) analysis. The AFM images in Fig. 2

show significant improvement in the homogeneity and the smoothness of the seed layer after repeating the dip-coating, as explained above. After a single-step dip-coating of a Si substrate in the sol-gel solution, a 21 ± 5 nm thick ZnO NP layer with an RMS roughness of 1.2 nm (Fig. 2a) was formed on the Si surface. Repeating the dip-coating resulted in a smoother 40 ± 5 nm thick ZnO NP layer with an RMS roughness of 0.9 nm at a grain boundary (Fig. 2b). Each dip-coating step was followed by an annealing treatment at 300 °C for 10 min that sintered the NPs together into bigger crystal grain sizes.

Three factors mainly influence the crystal grain boundaries observed in AFM images: (1) the thickness of the ZnO seed layer that is proportional to the number of dip-coating steps, (2) the temperature and the duration of subsequent annealing steps, and (3) impurities or dopants present in the crystal structure. It has been shown that larger grain sizes are achieved by increasing the thickness of the ZnO layers [29, 30]. Also, annealing at a higher temperature and for a longer time leads to better sintering of the small particles and increased grain sizes. In addition, unintentional impurities present during the synthesis process, or added dopants to the ZnO seed layer results in smaller grain sizes [31]. Although our samples are not intentionally doped, the presence of monoethanolamine in the sol-gel solution most likely introduces impurities during the annealing, causing smaller grain sizes. The crystal grain zones are comparably larger than the 140 nm diameter PS-NBs used for the CL. Consequently, the probability of ending up with grown ZnO NRs in holes on top of a single crystal grain without a grain boundary is increased.

To grow vertically aligned ZnO NRs, a (002)-oriented ZnO seed layer is desirable. The XRD results in Fig. 3 show the crystal structure and orientation of one- and

two-step dip-coated seed layers. In both samples, the polycrystalline ZnO seed layer exhibits crystal plane orientations of (100), (002) and (101). The self-forming

process of polycrystalline ZnO NPs has previously been studied in more detail [5, 32]. Applying the second dip-coating and annealing treatment increased the ratio between the integrated XRD peak areas produced by the (100) and (002) planes in agreement with a previous report [29]. Although repeating the dip-coating process improves the seed layer smoothness and grain size, the crystal structure thus becomes less favorable for ZnO NR growth by the increased presence of (100) planes.

CL patterning and ZnO NRs Growth

The deposition of the ZnO seed layers was directly followed by CL-patterning of selected areas. Figure 4a shows an SEM image of a CL-patterned resist layer after RIE etching and Al removal. A uniform, large-area CL patterning is clearly demonstrated on the ZnO-seeded Si substrate, with a nanohole surface density of 4.2 nanohole/ μm^2 and a diameter distribution centered around 190 nm (Fig. 4b). The final nanohole diameter was found to be 36% larger than the diameter of the PS-NBs, which is attributed to the 90 s RIE of the resist layer. The diameter of the nanoholes can simply be tuned by choosing a different PS-NB size. Here, we chose an optimized 140 nm bead size to ensure a single ZnO NR growth in each nanohole by CBD. Using a smaller PS-NB size makes the CBD growth more difficult due to the insufficient flow of the growth solution into the hydrophobic patterned resist. Using larger diameter PS-NBs instead

results in undesired growth of clusters of ZnO NRs in each nanohole [21, 27, 33].

In addition to the nanohole feature size, the pitch of the pattern can also be tuned by controlling the average distance between the dispersed PS-NBs. Negatively charged PS-NBs are distributed on the surface by electrostatic net repulsive forces, which can be controlled by screening the electrostatic repulsion forces between the PS-NBs. This has been done by adding a controlled amount of salt into the PS-NB suspension, as previously reported at length in literature [25, 26]. Here we instead considered the effect of PS-NB concentration on the nanohole surface distribution. In addition to the 0.1 wt% PS-NB suspension mentioned above, three lower concentrations of 0.02 wt%, 0.01 wt% and 0.003 wt% were used to fabricate CL-patterned samples. Additional file 1: Figure S4 shows that a reduction of the NB concentration to the mentioned values results in nanohole surface densities of 3.2, 1.5, and 0.4 nanohole/ μm^2 , respectively. Interestingly, the radial distribution function (RDF) of the nanoholes for the different samples (Fig. 4c and Additional file 1: S4d) shows a short-range order in the distribution of the nanoholes due to the net force between the PS-NBs in the CL process. From the extracted primary peak positions for different PS-NBs concentrations, it was extracted that the average nanohole separation to

its neighbor counterintuitively reduces with decreasing PS-NB concentration to 392 nm, 374 nm, 336 nm, and 298 nm, respectively. From this can be concluded that lower PS-NB concentrations result in a less uniform nanohole distribution, as visible in the SEM images in Additional file 1: Figure S4.

To investigate the growth mechanism of ZnO NRs on the CL-patterned substrates more in detail, a study of the growth rate versus growth time was carried out. Figure 5a, and 5b show the early stages of the ZnO NR growth after 5 min and 25 min, respectively. In the beginning, the exposed opened seeded holes form a wetting layer template for the growth solution with random crystal orientation, providing nucleation sites for CBD of ZnO NRs. Multiple ZnO NRs epitaxially grow from the nuclei sites along random directions (Fig. 5a). The nanohole walls restrict the growth of NRs with large deviation angles, and only those few NRs with a near-vertical direction will continue to grow, as seen in Fig. 5b.

By continuing the CBD process, the nanoholes are filled up by short off-direction NR stubs and only a few NRs grow out from the patterned resist layer. At a high enough growth temperature (95 °C in our experiment), a few near-vertical ZnO NRs in each nanohole merge together, forming a single NR growing out from each opening in agreement with a previous report [11]. The

Fig. 5 Cross-sectional SEM images of CBD-grown ZnO NRs on CL-patterned ZnO NP seed layers on (100) Si substrates after a growth time of **a** 5 min, **b** 25 min, **c** 2 h and **d** 2 h at 45° tilt

optimal ZnO NR array obtained on a large wafer-scale sample is shown in Fig. 5c and 5d.

To quantify the vertical NR alignment, we performed an XRD analysis of ZnO NR growth on similar non-patterned and CL-patterned seed layers. Figure 6 shows that the ZnO (002) reflection is dominant for the CL-patterned sample, indicating a better ZnO NR c-axis alignment. In contrast, the non-patterned sample shows more pronounced ZnO (100) and (101) reflections resulting from a poor vertical alignment. In addition, a statistical analysis of the SEM images of CL-patterned (Fig. 5c) and non-patterned samples (Additional file 1: Figure S3a) was carried out. The distributions of the deviation angle from the surface normal in Additional file 1: Figures S3b

and S3c show a mean deviation angle of 18° for the non-patterned sample and 13° for the CL-patterned sample, respectively. This result provides further support for the conclusion that ZnO NR growth on CL-patterned samples yields better vertical alignment compared to non-patterned samples.

Two additional CL-patterned samples, using 107-nm- and 320-nm-diameter PS-NBs, were prepared and examined by SEM (images added in Additional file 1: Figure S5). The small 107-nm-diameter PS-NBs resulted in a poor and inhomogeneous CBD of ZnO NRs while the bigger 320-nm-diameter PS-NBs led to rather uniform, but multiple star-shaped and randomly aligned ZnO NRs. This result strongly indicates that choosing an optimal nanohole size, depending on the diameter of the NRs, is crucial to grow a single, vertically aligned ZnO NR in each nanohole.

A chemical analysis of the final optimal CBD-grown ZnO NR array was done using dispersive X-ray spectroscopy (EDS). The spatial EDS maps (Additional file 1: Figure S6) show clear presence of the expected elements O, Zn, Si and C. The thin ZnO seed layer was not identified due to the spatial resolution limit.

Finally, in Fig. 7, we show spatially resolved cathodoluminescence mapping of a single ZnO NR. The cathodoluminescence study was performed in a dedicated SEM at room temperature, operating at 5 keV with a probe current of 25 pA. The luminescence was recorded by a CCD detector in hyperspectral mode, where a full spectrum is recorded in each pixel of the images. An average cathodoluminescence intensity spectra (Fig. 7a), and

hyperspectral maps along a line (Fig. 7b), is presented as a false-color image in Fig. 7c. Interestingly, the strong near-band-edge emission, with a peak at 380 nm, was observed in the bottom segment of the NR. It becomes weaker further up, where instead strong deep-level recombination results in a broad emission band with a 620-nm peak position. The overall top view cathodoluminescence in Additional file 1: Figure S7, also shows the two spectral features luminescence in a larger area.

It is well known that the deep-level emission is due to the native point-defect levels of Zn and O vacancies in the crystal structure. The non-uniform spatial distribution of the deep-level emission thus indicates an inhomogeneous defect distribution along the NRs, with higher defect density in stronger emission regions. This local defect variation can be attributed to the change of the growth parameters, e.g., precursor concentrations, during the CBD process, as previously reported in the literature [34, 35].

As frequently reported in the literature, the vertical growth of ZnO NRs is claimed only by demonstrating top-view SEM images or integrated XRD diffraction patterns. But more accurate cross-sectional imaging typically shows that growth on non-patterned substrates, in the early phase, results in a compact, textured ZnO layer with vertical alignment at the top of the short NRs [36]. The individual NRs are more or less indistinguishable from one another, leaving no open paths to the substrate (Additional file 1: Figure S3a). In contrast, growth on patterned substrates results in NR arrays with open space in between. Evidently, the nanofabrication technique demonstrated here is capable of synthesizing a bottom-up, density-controlled, substrate-independent, and selective growth of single ZnO NRs with high quality. Because of the intrinsic behavior of epitaxial growth on a polycrystalline seed layer, the final NR arrays do not exhibit a perfect vertical alignment. However, a significant improvement in vertical alignment is readily observed compared to non-patterned samples (Additional file 1: Figure S3a). Further in-depth investigations are needed to further improve and control the critical crystal orientation of the seed layer.

Conclusions

In summary, we realized an almost vertical growth of ZnO NRs on CL-patterned (100) Si substrates, precoated with a ZnO NP seed layer. The seed layer was uniformly deposited using a sol-gel technique by dip-coating the Si substrates in the sol-gel solution. Our findings show that two-step dip-coating enhances the smoothness and the crystal grain size of the seed layer, leading to a better NR alignment. Moreover, a selective area nanohole patterned resist template with tunable diameter and pitch

was fabricated on the seeded substrates using CL. Subsequently, we grew a density-controlled array of single ZnO NRs in the patterned nanoholes by CBD and investigated them by XRD and cathodoluminescence with respect to crystal quality. Also, the ZnO NR growth stages were studied by SEM after different growth time intervals. Our demonstrated nanofabrication technique, offering simplicity, uniformity over large wafer-scale areas, and controllable growth of vertical ZnO NRs can be used to fabricate high-performance devices.

Abbreviations

ZnO NRs: Zinc oxide nanorods; NPs: Nanoparticles; CBD: Chemical bath deposition; CL: Colloidal lithography; PS-NBs: Polystyrene nanobeads; DI: Deionized water; RIE: Reactive-ion etching; SEM: Scanning electron microscopy; EDS: Energy-dispersive X-ray spectroscopy; AFM: Atomic force microscopy; XRD: X-ray diffraction; RMS: Root mean square; RDF: Radial distribution function.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s11671-021-03500-7>.

Additional file 1: Figure S1: SEM images after different colloidal lithography steps. **Figure S2:** AFM image and surface line profile of dry-etched resist layer. **Figure S3:** SEM image of CBD-grown ZnO-NRs and vertical alignment distribution plots. **Figure S4:** Nanohole surface distributions on CL-patterned resist layers. **Figure S5:** SEM images of CBD-grown ZnO-NRs on CL-patterned ZnO-NP seed layers. **Figure S6:** EDS mapping of CBD-grown ZnO-NRs. **Figure S7:** Top-view cathodoluminescence mapping of ZnO-NR sample in Fig. S6.

Acknowledgements

Not applicable.

Authors' Contributions

EC and HP conceived the research idea and analyzed the data. EC prepared and characterized all samples and wrote the original draft. AG conducted the cathodoluminescence measurements. HP supervised the research and acquired funding. HP, AG, ON and MW read and revised the manuscript and discussed the research results. All authors read and approved the final manuscript.

Funding

Open access funding provided by Lund University. This research was funded by the ÅForsk Foundation (project number 19-725), with additional financial support from Halmstad University, Linköping University and Lund University. The detector used for the cathodoluminescence was financed by the Crafoord Foundation.

Availability of Data and Materials

All data relevant for the reproduction of the results presented in this work are included in this published article or in its supplementary information (SI) file.

Declarations

Competing interests

The authors declare that they have no competing interests.

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Received: 20 November 2020 Accepted: 21 February 2021

Published online: 12 March 2021

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Paper IV

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