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Photocatalytic properties for different metal-oxide nanomaterials

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ABSTRACT

We here demonstrate the synthesis of different nanostructures, including nanoparticles, nanorods, core-shell structures, and compound metal oxide nanostructures all synthesized by a low temperature chemical process. We further investigated their photocatalytic properties for degradation of toxic waste and their photochemical efficiency for water splitting. All the photocatalytic properties as well as the photochemical properties were utilized using sun radiation. The results presented indicate huge potential for the investigated processes with positive impact to energy consumption and benefits for the environment.

Keywords: Single nanostructures, compound nanostructures, core-shell structures, photocatalytic degradation, Solar driven photocatalysis

1. INTRODUCTION

Photocatalysis activities of semiconductors such as dyes photodegradation, hydrogen production via photoelectrochemical water oxidation have been studied, due to their positive impact to the environment and energy availability issues [1–4]. These semiconductors include WO_3 , TiO_2 , Fe_2O_3 , BiVO_4 , and ZnO [5–10]. From above mentioned semiconductors, ZnO has a wide band gap ($E_g \sim 3.3$ eV), and relatively high carriers' mobility [8,11,12]. However, the high recombination rate of photo-generated charge carriers is the most influential factor that limits the efficiency of the photocatalytic processes of the ZnO [1, 13–16]. To tackle this obstacle, and to increase the photocatalytic activities of the ZnO under visible solar light, variety of studies are conducted to increase the photocatalytic response of the ZnO through doping with metals (e.g. Ag, and Pb. etc) and transition metals (e.g. Mn, and Co) [17] or through coupling with other semiconductors or photosensitizer to form an efficient heterostructure material [13, 14, 16]. Magnesium (Mg) is a promising metal for doping ZnO and then can improve the photocatalytic activities of ZnO NPs under solar radiation and can be used for decomposition of organic dyes into less toxic compounds [18,19]. Herein, we report an efficient photocatalytic activity of ZnO NP doped with Mg under illumination of solar light. The NPs were grown through the low temperature (~ 60 °C) co-precipitation method. We studied the photocatalytic activities of the ZnO nanoparticles (NPs) and Mg-doped ZnO NPs for degradation of methylene blue (MB). We show the photodegradation efficiency of MB using the pure and Mg-doped ZnO NPs. In addition, Ag-based compounds are regarded as an excellent candidate as a co-catalyst that can largely enhance solar energy conversion efficiency and

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charge separation, which lead to further boost the PEC performance. Recent studies have proven that the deposition of Ag-containing species on the surface of composites, can lead to effectively improve harvesting visible light and increase the photo-generated charge carriers separation owing to the surface plasmon resonance (SPR) effect [13,14,16]. The net result will be an enhanced PEC activity of the Ag containing composites. In this regard, silver tungsten (Ag_2WO_4) with a band gap between 2.9–3.1 eV, have been used for preparation of different outstanding plasmonic photo-catalysts [14,20–22]. Accordingly, we report the synthesis, characterization, and PEC activities of Ag/ Ag_2WO_4 grown on top of ZnO nanorods (NRs). Firstly, ZnO NRs is synthesized using the hydrothermal low temperature chemical method. This was followed by the Ag/ Ag_2WO_4 deposition on top of the ZnO NRs using the SILAR method. The results showed an enhancement on the photocurrent and the current-voltage measurements, which are promising results for water splitting application

On the other hand, water contamination due to non-biodegradable organic dyes from industrial waste is a very serious environmental hazard. Pollutants that are emitted from various sources pose severe ecological problem. Therefore, removal of these dyes from industrial wastewater is highly desirable. All existing protocols for the treatment of wastewater are categorized as physical, chemical or biological processes. However, most of these treatments have intricacy in realistic uses. Biological processes, as an example, have been extensively used and show potential towards dairy and agricultural wastewater treatment. These processes have limitations, which can potentially affect degradation efficiency through control pH range, rapid organic-load variations, and the effluents physicochemical behavior. Among the chemical process, the advanced oxidation processes (AOP), is a heterogeneous photocatalysis that deals with photocatalysts like TiO_2 , ZnO are the most studied photocatalysts mediated degradation of the industrial wastewater, appears as an emerging technology leading to the total mineralization of most of the organic pollutants. However, it has a drawback that it can operate only under ultraviolet light due to the band gap limitations. Furthermore, this method could be a more expensive when it is scaled-up because particle-recovery of the photocatalyst particles is a difficult task and leads to an amplification in process costs. In this connection, and to develop a system for heterogeneous photocatalytic treatment of organic dyes in aqueous media under solar light irradiation, it is a key task to exploit photocatalysts with high stability (recycled), high efficiency, low recombination rate of negatively charged electrons and positive holes, and with low cost. One of the most advanced artificial photocatalysis material candidate is BiM_2AO_6 (with M: Mg, Ca, Cd, Cu, Pb, Mn or Zn, and A: V, P or As) so called mixed metal oxide (MMO) semiconductors have great potential to be used as photocatalysts. However, so far only a few candidates of this family have been investigated, namely BiCu_2VO_6 [23] and BiZn_2VO_6 [24]. That is due to, to date all the grown BiM_2AO_6 compounds were to our knowledge prepared for growth durations more than 10 h and by high-temperature ($\geq 700^\circ\text{C}$) solid-state reactions [23–25]. This render them expensive and does not allow neither a doping using an organic compound as a means to control the nanostructure morphology nor the utilization of soft substrates. Instead, aqueous chemical growth (ACG), “green chemistry”, is a low-temperature method for production of metal oxide nanostructures [26, 27]. In addition to the low cost of this synthesis route, the ACG can be operated at sufficiently low-temperatures ($< 100^\circ\text{C}$).

In core-shell morphology, the inner nanostructure is encapsulated by outer shell of a different material. In addition, the hetero coupling of noble metallic nanomaterials (Ag, Au, Pd, etc.) to ZnO nanostructures is a widely accepted method to

enhance the photocatalytic properties [28-30]. Besides these methods, semiconductor oxides and hydroxides have also been employed to the fabrication of heterostructures with ZnO nanostructures [31-33]. Moreover, layered double hydroxides (LDHs) have shown promising properties for photocatalysis and are considered the best replacement to TiO_2 based photo-catalysts due to their layered structure, flexibility in composition, controlled dimension, low cost, and simple methodologies for preparation [34]. Among LDHs, the features of Ni-Fe are highly appealing such, facile fabrication availability, inexpensive, exhibit high specific surface area, high density of the active centers that can facilitate the interaction with different catalytic materials. Therefore, Ni-Fe (LDHs) might play an active role during coupling with ZnO and creates a synergistic effect, which could remain responsible for superior performance for photochemical water splitting in alkaline media. By harvesting these unique avenues of Ni-Fe layered double hydroxides, and further the deposition of Ni-Fe layered double hydroxide may prevent the dissolution of ZnO in aqueous solution under light irradiation and results in an efficient photocatalysis. Based on our knowledge, and reported literature there is no report about Ni-Fe layered double hydroxide deposited on ZnO nanowires/nanorods for photochemical water splitting.

In this paper we present our recent results on the utilization of the photocatalytic properties of single, composite (mixed metal oxide), and core-shell nanostructures. We adopt the low temperature chemical approach for synthesizing all samples. Structural characterization and the utilization of all the synthesized samples for efficient optical processes is demonstrated.

2. EXPERIMENTAL

Below we discuss briefly the different metal oxide samples preparation. For all the samples, we followed low temperature chemical approach. Further, for all samples we have used analytical grade chemicals purchased from Sigma Aldrich and used without further purification.

2.1 Magnesium doped ZnO NPs

The ZnO NPs have been grown using the co-precipitation method according to our recent work [35]. However, as a brief explanation, two solutions of zinc acetate dehydrate (0.1 M) and sodium hydroxide (0.2 M) were prepared by dissolving them in deionized water and magnetically stirred overnight at room temperature. Then the two solution were mixed into one beaker and magnetically stirred at 750 rpm for 2 hours under temperature of 60 °C in a hot plate at room conditions. After 2 hours of stirring, the precipitated white milky solution was separated by centrifugation (4500 rpm for 2 minutes). Afterward, the precipitation product was washed with distilled water and acetone. Finally, ZnO NPs in the form of powder was obtained by drying the precipitation product into a laboratory oven at 75 °C for 6 hours. For Mg-doped ZnO NPs samples preparation, a diluted solution of magnesium nitrate hexahydrate with atomic concentration 7 % was mixed with sodium hydroxide and stirred overnight at room temperature. Then mixed with zinc acetate dehydrate (0.1 M) solution that stirred also overnight into one beaker and stirred at 750 rpm for 2 hours under temperature of 60 °C in a hot plate at room conditions. After 2 hours of stirring, the precipitated was separated by centrifugation and then washed with distilled water and acetone.

2.2 ZnO/Ag/Ag₂WO₄ heterostructures

The ZnO NRs were grown on an Au-coated glass that containing a seed layer of ZnO NPs, by low temperature aqueous chemical growth method [38]. The precursor solution was prepared by dissolving equal molecular (0.05 M) of zinc nitrate hexahydrate and hexamethylenetetramine in deionized (DI) water. The prepared substrates that contain seed layer of ZnO NPs were immersed horizontally after they were fixed in Teflon sample holder into the precursor solution and loaded into a preheated oven at 90 °C for 5 hours. Then samples were cleaned with DI water to remove any undesired particles, and then dried with blowing nitrogen for few seconds.

Ag/Ag₂WO₄ particles were deposit on the prepared ZnO NRs using SILAR method. An anionic and cationic aqueous precursor solution was prepared separately using 0.05 M of silver nitrate and 0.05 M of sodium tungstate, respectively. The deposition done by immersion of the above prepared ZnO NRs samples into silver nitrate solution for 2 minutes to absorb the silver ions (Ag⁺) and then they were washed with DI water to remove excess ions or any other particles. Then the sample immersed into the sodium tungstate solution for 2 minutes and again washed with DI water. This cycle was repeated for 15 times to obtain enough Ag/Ag₂WO₄ nanoparticles on the ZnO NRs.

2.3 Synthesis of BiZn₂VO₆

A two-step low-temperature aqueous chemical growth (ACG) process was used to prepare the BiZn₂VO₆ compound nanostructures. Doped and undoped ZnO nanorods were prepared as previously reported [36]. Briefly, the growth solution used in this experiment was prepared from an equimolar concentration of 0.05 M solutions of zinc nitrate hexahydrate Zn(NO₃)₆·6H₂O and hexamethylenetetramine (C₆H₁₂N₄) in deionized water. For doped samples, the growth was also in the presence of 0.1% weight to volume (w/v) polyethylene glycol (PEG, molecular weight 2000). the homogenous solution was placed in an oven for 5 hours at 90 °C. Afterwards, the separated precipitates were washed in deionized water and acetone, and then dried overnight at 60 °C. In the next step, the BiZn₂VO₆ compound was formed by adding a 0.10g as-prepared PEG modified ZnO NRs to BiVO₄ growth solution. They were covered with aluminum foil and placed in the pre-heated oven for 4 at 80 °C. BiVO₄ growth solution was prepared according to Zhou's and co-workers report albeit at modified growth time [37]. In a typical synthetic route, equimolar concentration of 0.02 M of bismuth (III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O) and ammonium metavanadate (NH₄VO₃) were dissolved in 10 mL of nitric acid, 70% (HNO₃) solution. 20 mL deionized water was added into this solution under vigorous stirring until the salts were completely dissolved. Then, ~12.8 g of sodium hydrogen carbonate (NaHCO₃) was added to adjust the pH value to 6.5 until the formation of a yellow homogeneous solution. The final products were washed with deionized water and acetone, dried with nitrogen gas and then dried at 80 °C for 10 h in the oven. Field emission scanning electron microscopy (SEM) for morphological analysis was performed by using a LEO 1550 Gemini field emission gun at 5kV.

2.4 Synthesis of the Ni–Fe layered double hydroxides (LDHs) /ZnO nano-hetero-structures

The Ni–Fe (LDHs)/ZnO nanostructures were prepared through three steps: the fabrication of ZnO NRs, the synthesis of Ni (OH)₂/ZnO heterostructure precursors and Ni–Fe (LDHs)/ZnO nanostructures

The FTO substrates (surface resistivity $\sim 8 \Omega \text{ cm}^{-2}$ and transmittance 80-81.5% (visible)) used were first ultrasonically cleaned by acetone, isopropanol, and deionized (DI) water respectively each for 5 min and were then dried up using blowing nitrogen. Then, the FTO substrates were seeded with zinc acetate dehydrate layer via spin coating technique at 2000 rpm for 30s. The seed solution of 0.01 M zinc acetate dehydrate in 99% methanol was prepared at constant stirring and heating at 60 °C. A solution of potassium hydroxide (KOH) in methanol (0.03 M) was added dropwise to this solution for a duration of 2 hours. This coating step was repeated three times to ensure uniform coverage of the ZnO seeds. This step was then followed by annealing in a normal laboratory oven for 10 minutes at 120 °C. Afterwards, the seed coated substrate were fixed horizontally upside-down in Teflon sample holder and kept in equimolar 0.05 M solution of hexamethylenetetramine and zinc nitrate hexahydrate. The beaker containing the samples and the growth solution were covered with aluminium foil and placed in preheated laboratory oven at 90 °C for 5h. Finally, these samples were rinsed and cleaned deionized (DI) water and dried using blowing nitrogen.

For the photochemical deposition process, first an electrolyte was prepared by dissolving 0.15 M of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 50 mL DI water under continuous stirring. Secondly the ZnO NRs were immersed into this electrolyte and potentiostatic deposition was carried out at a potential of -1.0 V (vs Ag/AgCl reference electrode) for 60 s.

The $\text{Ni}(\text{OH})_2/\text{ZnO}$ were immersed into an aqueous solution of 0.15 M of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in 50 mL DI water under stirring in a N_2 atmosphere to prevent the oxidation of Fe^{2+} and the potentiostatic deposition was carried out at a potential of -1.0 V (vs Ag/AgCl) for different durations.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the synthesized pure and Mg-doped ZnO NPs samples. As can be seen the all obtained XRD diffraction peaks belong to the hexagonal wurtzite pure phase of ZnO with lattice parameters (JCPDS no. 36-1451) which suggest that there are no other phases of ZnO or impurities have been observed. Also, a similar XRD diffraction peaks were obtained from the Mg-doped ZnO NPs sample which confirm that there was no second phase such as MgO formed in the prepared samples. In addition, lower intensities from Mg-doped ZnO NPs XRD diffraction peaks were observed.

Figure 1. XRD spectra of the bare and magnesium doped ZnO NPs.

Figure 2 shows the FM-SEM images of the synthesized pure and Mg-doped ZnO NPs. As it can be seen, the pure ZnO NPs sample showed a better uniform size distribution as compared with Mg-doped ZnO NPs samples. From the FM-SEM images, the NPs average size were estimated to be ~ 58 , and ~ 100 nm for pure ZnO NPs and Mg-doped ZnO NPs with 7 % atomic weight doping concentration, respectively. The variation in the NPs average size might be due to the agglomeration of the small particles.

Figure 2. FM-SEM images of synthesized pure and Mg-doped ZnO NPs.

Figure 3. XPS core level spectra of (a) Zn 2p and, (b) Mg 2p, and (c) O1s of ZnO NPs and Mg-Doped ZnO NPs.

Figure 3 (a) shows the XPS core level spectra of Zn 2p of the synthesized pure ZnO NPs sample which is composed of two peaks centered 1022.3 and 1045.3 eV. These peaks are attributed to binding energy lines of Zn 2p_{3/2} and Zn 2p_{1/2}

Figure 4. Absorbance spectra of MB during photocatalytic activities for pure and Mg-doped ZnO NPs under dark and solar light.

Figure 5. The concentration of MB during photocatalytic process for pure and Mg-doped ZnO NPs under dark and solar light.

and they explain the formation of Zn-O bonds within the ZnO crystal lattice [39]. Fig.3 (b) shows the Mg 2p XPS peak of Mg-doped ZnO with 7% atomic weight of doping concentration. The peak is centered at ~ 50 eV which could be attributed to the presence of Mg^{2+} that replaces the Zn^{2+} . The O1s core level XPS spectra of pure and Mg-doped ZnO NPs are shown in Fig. 3 (c), which decomposed into two Gaussian peaks. For pure ZnO NPs, the peak at low binding energy centered at 531.10 eV could be related to O^{2-} ions [39, 41]. Whereas the peak at higher binding energy centered at 532.05 eV can be ascribed to the oxygen O_2 on the ZnO surface and water molecules H_2O [41]. The Mg-doped ZnO sample shows a slight shift towards higher binding energy with two Gaussian peaks centered at 531.26 and 532.07 eV and could be related to the formation of Zn-O-Mg bond and confirm that Mg^{2+} has substituted Zn^{2+} . Figure 4 shows the absorbance spectra of MB during the photodegradation reaction time of the synthesized pure and Mg-doped ZnO NPs samples. The absorption peak of the MB exhibits the main band at 663 nm and decreases with the irradiation time, which indicates the degradation of MB has taken place. The concentration of the dye (C/C_0) versus illumination time of MB was calculated and presented in Fig. 5. 45% of the dye remained for the pure ZnO, whereas only 4% remained using Mg-doped ZnO. This result is probably due to the modifications of the physical and chemical properties of the ZnO by Mg doping [42, 43]. When Mg^{2+} was introduced into the ZnO crystal lattice, more oxygen defects could be produced, which improve the separation and migration efficiency of the photo-generated electron-hole pairs. The result of that higher degradation efficiency was found from Mg-doped ZnO NPs.

Figure 6 (Left). XRD patterns of the ZnO NRs and the ZnO/Ag/Ag₂WO₄ heterostructure. Figure 7 (Right). FM-SEM image of the ZnO/Ag/Ag₂WO₄ heterostructure.

Figure 6 shows the structural characteristics obtained by XRD for the ZnO/Ag/Ag₂WO₄ heterostructures. It could be observed that the XRD diffraction peaks of the planes (002), (101), (102), and (103) are belonging to the hexagonal wurtzite pure phase of ZnO (JCPDS no. 36-1451) which suggest that there are no other phases of ZnO or impurities have been observed. The planes of (042), (025), and (135) were assigned for Ag₂WO₄ (JCPDS no 33-1195). The peak at 2θ equal to 78° is assigned to the reflections of cubic Ag (JCPDS no 65-2871). Figure 7 shows the morphology of ZnO/Ag/Ag₂WO₄ heterostructure that was measured by the FE-SEM imaging. It could be observed that the ZnO NRs were vertically aligned and with hexagonal shape and estimated diameter size of ~100 nm. Also, the Ag/Ag₂WO₄ could be observed clearly distributed on the surface of ZnO NRs indicating the formation of ZnO/Ag/Ag₂WO₄ heterostructure. Figure 8 shows The plot of (αhν)² versus the (hν) to estimate the band gap of the ZnO NRs and the ZnO/Ag/Ag₂WO₄ heterostructure. The optical band gaps were found to be 3.2 and 3.1 eV for ZnO and ZnO/Ag/Ag₂WO₄ heterostructures, respectively. This result could be explained due to formation of Ag₂WO₄ on the top of the ZnO NRs forming the heterostructure (i. e. bandgap engineering) which led to increase the band gap of the ZnO slightly. It is worth to note that metallic silver could be produced during the sample preparation and can trigger surface plasmonic effect [14,16].

Figure 8 (Left). The plot of $(\alpha h\nu)^2$ versus the $(h\nu)$ to estimate the band gap of the ZnO NRs and the ZnO/Ag/Ag₂WO₄ heterostructure. Figure 9 (Right). Linear sweep voltammetry curves of the ZnO NRs, and the ZnO/Ag/Ag₂WO₄ photo-electrodes under light and dark conditions.

The photoelectrochemical activities were studied by using three electrode photoelectrochemical measurements using SP-200 potentiostat (Bio-Logic, Claix, France). A platinum (Pt) sheet was used as the counter electrode and a standard Ag/AgCl in 3 M KCl (as a reference electrode) was used with (0.1 M) of sodium sulfate (Na₂SO₄) electrolyte. The total area of the electrode that immersed in the electrolyte was 1 cm². The sun light was obtained by a solar simulator that uses a 100 W ozone free xenon lamp with an output power of 1 sun (AM 1.5). Figure 9 shows the linear sweep voltammetry measurements for both pristine ZnO NRs and ZnO/Ag/Ag₂WO₄ photoelectrodes. A reasonable response upon illumination by solar light was observed, whereas the response at dark is relatively very low with flat curves. However, the I-V curve of the ZnO/Ag/Ag₂WO₄ photo-electrode under simulated sun light confirms a higher photoelectric conversion than that of the ZnO NRs photo-electrode. The observed photocurrent density at the potential of 1.23 V (vs. Ag/AgCl) is 0.9 mA/cm² for ZnO NRs and increased to 1.4 mA/cm² for the ZnO/Ag/Ag₂WO₄ photo-electrode. This result might be attributed to the higher separation and transportation of photo-induced charge carriers [44] due to the presence of the Ag/Ag₂WO₄ particles that might change the band gap of the heterostructure. moreover, the presence of metallic Ag⁰ particles would enhance the absorption of visible light and then improve the separation rate of the photo-generated electrons-holes pairs because of the SPR [14].

The photocatalytic performance of the prepared BiZn₂VO₆ compound nanostructures was measured by through the photodegradation of 20 mg L⁻¹ Congo red (CR), solutions as the pollutant. The light source was a 300 W xenon lamp used without any filter to simulate sunlight irradiation. At first, 50 mg photocatalyst was dispersed in a 100 mL dye aqueous solution, and the suspension was stirred in the dark for 30 minutes to ensure the adsorption-desorption equilibrium between the photocatalyst and the dye molecules prior to the exposure to the simulated solar irradiation. While the lamp was turned on, the samples were taken in specific desired time intervals within 90 minutes of the reaction time. The change in the concentration of the dye solution was measured using UV-vis absorption spectroscopy at the characteristic absorption wavelength of 497, 664, and 553 nm for CR.

Figure 10. UV-vis spectra for degradation of Congo red under solar irradiation over the (a) PEG doped ZnO NRs, (b) BiVO_4 , (c) BiZn_2VO_6 , and (d) PEG doped BiZn_2VO_6 .

SEM imaging (not shown here) was carried out to determine the morphology of the different $\text{ZnO}/\text{BiZn}_2\text{VO}_6$ nanocompounds. In order to identify possible changes of the ZnO nanorods during BiZn_2VO_6 growth, we examined ZnO nanorods films that were exposed to a modified BiZn_2VO_6 growth solution not containing the actual growth material. Comparing the initial ZnO nanorods and the post-treated films shows that there is a clear etching effect of the nanorods, and they are reformed into nanobelts. The lengths of these ZnO NBs were about 3-5 μm , their average side thickness is around 100 nm, and their widths range between around 300 and 700 nm. The morphology of ZnO nanostructures is known to be sensitive to external conditions like pH, and we attributed the observed morphological change to the lower pH of the BiZn_2VO_6 growth solution ($\text{pH} \approx 6.0\text{--}6.5$) compared with the growth solution of the initial ZnO nanorods ($\text{pH} \approx 6.5$ and 7). The samples were investigated after growth of the PEG-doped BiZn_2VO_6 nano-compound by ACG. The nanocompounds have a rice-like shape, with average height of 1.3-1.8 μm and widths between 1.9 μm and 2.6 μm . As clearly seen on the SEM pictures the agglomeration and the size of BiZn_2VO_6 capped ZnO NBs.

Figure 11. (a) Pure ZnO NRs grown on FTO glass substrated, (b) Ni-Fe LDHs/ZnO at 10 seconds deposition, (c) Ni-Fe(LDHs)/ZnO 20 seconds deposition, and (d) Ni-Fe(LDHs)/ZnO 30 seconds deposition.

The CR was chosen as the typical refractory dye to assess the photocatalytic performance of the obtained samples. Figure 11 shows UV-vis spectra of the visible-light induced PEG-doped BiZn_2VO_6 NCs photocatalytic degradation of Congo red dye. Changes in the UV-vis absorbance spectra of CR as a function of irradiation time in the presence of PEG modified ZnO NRs, BiVO_4 , BiZn_2VO_6 , and PEG doped BiZn_2VO_6 (0.10%w/v) samples are shown in Fig. 11 (a-d). Obviously, the characteristic absorption peak of Congo red just diminishes a little over the PEG modified ZnO NRs, BiVO_4 , BiZn_2VO_6 samples with the prolongation of light time. However, as shown in Fig. (11 d), the intensity of the major peak has rapidly weakened until being very smooth, indicating that the CR structure was successfully restructured by the PEG doped BiZn_2VO_6 (0.10%w/v) photocatalyst. Although BiVO_4 can strongly adsorb visible light due to the narrow band-gap energy. However, The 0.1 % (w/v) PEG-doped ZnO NRs doped BiVO_4 nanocompounds was found to be the optimal for Cong red degradation under simulated solar light. We noted that, after 40 minutes the Cong red is 97% degraded. Clearly, the introduction of PEG enhanced the photocatalytic degradation ability of BiZn_2VO_6 . This can be explained as follows: The synergistic effect of PEG and BiZn_2VO_6 has greatly promoted the separation of the photo-induced electrons and holes, which has a positive effect on the photocatalytic reactions.

Figure 12. (Above). The I-V curve of pure ZnO NRs, Ni-Fe (LDHs)/ZnO 10 seconds, Ni-Fe(LDHs)/ZnO 20 seconds, and Ni-Fe(LDHs)/ZnO 30 seconds under the illumination of light and dark. (Below) Photo response of pure ZnO NRs, Ni-Fe (LDHs)/ZnO 10 seconds, Ni-Fe (LDHs)/ZnO 20 seconds, and Ni-Fe (LDHs)/ZnO 30 seconds.

The morphological features of the Ni-Fe(LDHs)/ZnO were investigated by scanning electron microscopy as depicted in Figure 10. Figure 10 a show a hexagonal facets structure of ZnO NRs as expected. However, the deposition of the Ni-Fe

layered double hydroxide on the ZnO NRs indicates a core-shell morphology as depicted in Figure 10 c. The layer thickness is not increased significantly for longer deposition durations.

The photoelectrochemical response of various, Ni-Fe(LDHs)/ZnO photo-anodes was measured in 1M KOH solution of pH 14. Figure 12 (Above) shows the LSV response for pure ZnO NRs, Ni-Fe (LDHs)/ZnO at 10 seconds deposition, Ni-Fe(LDHs)/ZnO at 20 seconds deposition, and Ni-Fe(LDHs)/ZnO at 30 seconds deposition. Importantly, in dark the response of photo-anodes is very weak and requires more potential for water oxidation. However, with illumination of 1 Sun (AM 1.5G) of light there is a drastic decrease in the redox potential of water, still higher potential is required which is due to the fact part of energy is required for the oxidation provided by the light. The Ni-Fe layered double hydroxide/ZnO showed the maximum response and the lowest redox potential for water oxidation that could be assigned to the tuned properties of ZnO after the deposition of the Ni-Fe layered double hydroxide that created the chemical coupling and the synergistic effects during the chemical growth. Figure 12 (Below) shows the photocurrent response under the illumination and dark conditions, photo response is fast and stable and the photo-anode of Ni-Fe layered double hydroxide with deposition of 20 s is giving high photocurrent and stable response due to tedious photocatalytic activity of the hybrid material.

4. CONCLUSION

In summary we have shown the potential of the low chemical approach as a useful strategy to synthesize high quality metal oxide nanostructures from different materials as well as for obtaining different morphologies. Among the investigated nanostructures, bare ZnO NPs as well as magnesium doped, were utilized for photodegradation of methylene blue using sun light. The results showed that doping can improve the degradation efficiency. Starting by synthesizing ZnO NRs, we further processed with more steps to obtain ZnO/Ag/Ag₂WO₄ heterostructures. Such heterostructure with ionic silver has indicated further efficiency due to the plasmonic effect which further enhance the photocatalytic and photochemical properties. BiZn₂VO₆ compound nanostructures were also synthesized and utilized for the degradation of Congo red dye. Here both bare as well as BiZn₂VO₆ compound nanostructures were utilized. Again, doping indicated that it can be utilized for tuning and improving the photocatalytic efficiency. Finally, the photoelectrochemical response of various, Ni-Fe (LDHs)/ZnO photo-anodes was investigated and promising results were observed. In general the demonstrated results in this paper indicated that metal oxide nanostructures could be a popular alternative for many photocatalytic, photoelectrochemical processes. This is due to the rather high efficiency, easy for synthesis with possibility of scale-up for industrial production, and the possibility of utilizing sun radiation.

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