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Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Mushtaque Hussain, Zafar Hussain Ibupoto, Mazhar Ali Abbasi, Omer Nur and Magnus Willander, Effect of anions on the morphology of Co_3O_4 nanostructures grown by hydrothermal method and their pH sensing application, 2014, *Journal of Electroanalytical Chemistry*, (717), 78-82.

<http://dx.doi.org/10.1016/j.jelechem.2014.01.011>

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<http://www.journals.elsevier.com/journal-of-electroanalytical-chemistry/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-106984>

Effect of anions on the morphology of Co₃O₄ nanostructures grown by hydrothermal method and their pH sensing application

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Abstract:

A fast, reliable, accurate, precise and sensitive pH sensor device is highly demanding for the monitoring of pH in biological, clinical and food industry samples. In this research work, the effect of anions on the morphology of cobalt oxide (Co₃O₄) nanostructures is investigated using low temperature chemical approach for the growth. Different anions have shown visible effect on the morphology of Co₃O₄ nanostructures. Scanning electron microscopy, X-ray diffraction and transmission electron microscopy techniques were used for the material characterization. This study has shown highly dense, uniform and good crystal quality of fabricated Co₃O₄ nanostructures. The nanostructures obtained from the cobalt chloride were used for the development of potentiometric pH sensor electrode. The pH sensor electrode showed excellent linearity and close to Nernstian response for the pH range of 3–13 with a sensitivity of –58.45 mV/pH. Moreover, the proposed sensor showed a fast response time of 53 s, and acceptable reducibility and repeatability. The highly sensitive and a fast time response of the proposed sensor device indicate its potential application for the monitoring of pH from real samples including biological fluids.

Keywords: Anion effect, Cobalt oxide nanostructures, Morphology pH sensor, Potentiometric response

1. Introduction

Recently, a lot of research on the synthesis of nanostructures of different materials has increased largely because of their unique electrical, optical, magnetic, and catalytic properties in comparison to their bulk phase. It is now believed that the behaviors of nanophase materials strongly depend on the shapes and sizes of the particles, which is thus a key factor to their ultimate performance and applications [1, 2]. It is important to study the fundamental aspect of nanocrystalline Co_3O_4 by various routes. Therefore more attention has been paid on growth mediums to control the morphologies and the size of nanomaterials. The compounds with the same compositions but different morphologies and sizes exhibit substantial differences in properties [3–7]. As one of the most intriguing magnetic p-type semiconductors, cobalt (II, III) oxide is an inorganic compound with the formula Co_3O_4 . It is one of the two well characterized cobalt oxides. Co_3O_4 adopts the normal spinel structure, with Co^{2+} ions in tetrahedral interstices and Co^{3+} ions in the octahedral interstices of the cubic close-packed lattice of oxide anions [8]. Co_3O_4 is also known as a promising material that has applications in many fields, such as heterogeneous catalysts, solid-state sensors and electrochemical devices [9–15]. Co_3O_4 nanostructures are expected to show even more excellent and tunable properties due to their versatile morphologies and structures. So far, many interesting nanostructures of Co_3O_4 , including nanowires/nanorods [16, 17], nanotubes [18,19], nanocubes [20–22], nanospheres [23–25], nanoplates [26] and nanowalls [27], have been prepared by using different growth methods. He et al. synthesized Co_3O_4 nanocrystals by a solubility controlled method using surfactant [28]. Co_3O_4 nanocrystals have also been synthesized via a facile combustion method by Feng et al. [29]. Beside these several other methods have also been used for the synthesis of spinel Co_3O_4 nanocrystals such as sol-gel method, polyol process, solvothermal synthesis, polymer assisted synthesis, thermal decompositions, reflux/microwave assisted methods and hydrothermal synthesis for Co_3O_4 nanorods [30, 23, 31–36]. All these methods produce high

quality nanostructure with different morphologies, but the requirement of high temperature limits the compatibility of growth e.g. on organic substrates for applications in the field of flexible electronics [37]. The low temperature hydrothermal synthesis has been widely used for variety of nanostructures on different substrates, mainly because of its simplicity, non-toxicity, cost effectiveness and the ability to produce various nanostructures on large scale. Liu et al. reported the large-scale synthesis of Co_3O_4 nanowires by hydrothermal method [38].

The monitoring of the pH has essential demand in laboratories, clinics and food industries because several chemical processes are depending on the pH. Hence the development of fast, precise and accurate, reliable and sensitive pH sensor device is important in several applications [39, 40]. The pH measurement is performed by different methods including potentiometric [41], ion sensitive field effect transistor [42], and conductometric/capacitive [43]. However, potentiometric technique is widely used due to its simplicity, does not require skilled person and can be used for longer periods of time.

To the best of our knowledge, there is no report published about the effect of anions on the morphology of Co_3O_4 nanostructures grown by hydrothermal method, therefore in the present work substantially we observed the effect of anions on the morphology of cobalt oxide nanostructures by hydrothermal method which is the novelty of presented work. Then grown nanostructures were potentially used for the development of an excellent pH sensor device.

In this work, various nanostructures are obtained by the effect of different anions using low temperature aqueous chemical growth method. The nanostructures are characterized by the scanning electron microscopy and X-ray diffraction techniques. In addition to this, the cobalt oxide nanostructures were used in the development of highly sensitive pH sensor device.

2. Experimental

For synthesis of the studied nanostructures the following chemicals were purchased from Sigma–Aldrich, Sweden and have been used without any further purification. Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt acetate tetra hydrate ($(\text{CH}_3\text{COO})_2 \text{Co} \cdot 4\text{H}_2\text{O}$), cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), and urea ($\text{CH}_4\text{N}_2\text{O}$).

A low temperature aqueous chemical growth method has been employed for the growth of Co_3O_4 nanostructures with different mediums on p-type silicon substrates. First of all the substrates were sonicated in ultrasonic bath for 20 min in isopropanol, then washed with acetone and dried by nitrogen gas. A cobalt acetate anhydrous seed crystal solution was deposited on these substrates by the help of Spin-coater. This procedure was repeated two times at 3000 r.p.m for 20 s and after that the samples were left for annealing at 120°C for 20 min. Meanwhile the growth solutions for different mediums of cobalt salts have been prepared by equimolar ratio of 1:1 for all precursors. The first solution was prepared by taking 0.1 M of cobalt nitrate +0.1 M of urea, the second solution was prepared by taking 0.1 M of cobalt acetate +0.1 M of urea, the third solution was prepared by taking 0.1 M of cobalt chloride +0.1 M of urea, and finally for the fourth solution we used 0.1 M of cobalt sulfate +0.1 M of urea, each in 50 ml of deionized water and then all solutions were left on stirring for 30 min. After annealing, the Si substrates decorated with Co_3O_4 particles were placed in these growth solutions by the help of a Teflon sample holder facing downward. Then samples were kept in preheated oven at 95°C for 5–6 h. After the growth duration samples with the Co_3O_4 nanostructures were taken out from the growth solution and washed in the deionized water in order to remove residual solid particles from the surface. Then, the samples were dried in air at room temperature. Finally the samples having $\text{Co}(\text{OH})_2$ phase were annealed at 450°C for 4 h for the complete conversion of cobalt hydroxide into Co_3O_4 nanostructures.

The morphology and structural properties of different nanostructures of Co₃O₄ were studied by LEO 1550 Gemini field emission scanning electron microscope running at 15 kV. The crystal quality of these nanostructures was studied by X-ray powder diffraction (XRD) using a Phillips PW 1729 powder diffractometer equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) using a generator voltage of 40 kV and a current of 40 mA. A high-resolution transmission electron microscopy (HRTEM) analysis was carried out using an FEI Tecnai G2 TF20 UT with a field emission gun working at 200 kV and a point resolution of 1.9 $\text{\AA}$ and linked with an energy-dispersive X-ray (EDX).

The electrochemical response of the developed pH sensor device based on Co₃O₄ nanostructures fabricated on gold coated glass substrate was measured against silver–silver chloride as reference electrode using Metrohm pH meter model 744. The response time was measured by an electrical instrument Keithley 2400 model. The pH range of 3–11 of phosphate buffer solution was adjusted using 0.1 M hydrochloric acid and 0.1 M sodium hydroxide. All the measurements were performed at room temperature.

3. Results and discussion

3.1. The morphological study of Co₃O₄ nanostructures

It is always interesting to know the effect of different anions of similar source of precursor on the morphology of metal oxides nanostructures. A typical SEM image of Co₃O₄ nanostructures with nanoporous morphology is obtained from the precursor of cobalt nitrate and urea on the p-type silicon substrate as shown in Fig. 1(a). The nitrate anion has effectively changed the morphology of Co₃O₄ into honey comb like porous nanostructures. The typical reactions involved in the formation of nanoporous like honey comb nanostructures of Co₃O₄ are summarized as:

The cobalt hydroxide is thermodynamically unstable and it under goes dehydration and finally results in Co_3O_4 nanostructures. For the study of chloride anion effect on the morphology of Co_3O_4 nanostructures, an equimolar solution was prepared by dissolving the 0.1 M cobalt chloride and 0.1 M urea. In this case the nanostructures of interconnected network of nanowires were obtained as shown in Fig. 1(b). For the study of acetate anion effect on the morphology of Co_3O_4 nanostructures a grass like morphology based on thin wires is observed as shown in Fig. 1(c). In fourth condition of precursors solution of a cobalt sulfate and urea were used and we observed that sulfate anion is suppressing the growth pattern along the 101 plane, thus Co_3O_4 nanosheets like morphology is obtained as shown in Fig. 1(d). Similar reactions were participated in the synthesis of various morphologies of Co_3O_4 nanostructures irrespective source of Co^{2+} ion was different.

The crystal arrays of cobalt oxide nanostructures were examined by powder X-ray diffraction technique as shown in Fig. 2. The most intense peak appearing at around 32.9° belongs to Si (002). The XRD pattern in Fig. 2 identifies that the product is pure-phase of Co_3O_4 and all the diffraction peaks can be indexed to (JCPDS No. 43–1003) of the cubic symmetry. The well-resolved diffraction peak at $2\theta = 36^\circ$ (311) in all four parts of Fig. 2 reveal the good crystallinity of the Co_3O_4 specimens.

Fig. 3(a–c) shows the high magnification TEM image of single Co_3O_4 nanowire obtained from the cobalt chloride which clearly demonstrate that Co_3O_4 nanowire consist of independent nanoparticles which are aggregated together and finally giving nanowire morphology. The SAED pattern of multi nanowires (as an inset in Fig. 3d) reveals that Co_3O_4

nanowires exhibit polycrystalline phase. The TEM results are in good agreement with the XRD information.

3.2. The pH sensing application of Co_3O_4 nanostructures

The pH sensing mechanism of a particular pH sensor is explained in terms of the electromotive force (EMF) of the electrodes and more precisely for the ion-sensitive layers, the charge density of surface which helps in the generation of surface potential based on different pH values around the electrodes. The pH based output potential of the Co_3O_4 nanostructures is defined by the activity of electrolyte- Co_3O_4 nanostructures at the interface thereby H_3O^+ ions are present on the surface of Co_3O_4 nanostructures that may be protonated at the time of electrolytic interaction with cobalt oxide surface. During the protonation or deprotonating at the interface of Co_3O_4 , a surface potential is appeared and its value depends on the pH of electrolytic medium. At the time of interaction of ions or molecules to the surface provided by the Co_3O_4 nanostructures, a Helmholtz layer is developed through the dipole orientation or surface bonds by the active ions which are the part of the electrolytic medium. Particularly it is the cobalt atom which gives sufficient charge density on the oxygen which further firmly binds with the H_3O^+ ions and also metal ion must have enough electronegativity for capturing the electrons from the surrounding OH^- ions [44,45].

The output potential of Co_3O_4 nanostructure for different pH values was measured against the silver–silver chloride as a reference electrode that has a constant potential, thus the observed potential is only attributed to the nanostructures of Co_3O_4 . The working principle of the device is represented as following [45].

The output potential (EMF) of the nanostructures of Co_3O_4 is the potential difference between the working electrode (Co_3O_4) and the known potential of silver-silver chloride as a reference electrode [45].

$$E = E_{\text{Co}_3\text{O}_4 / \text{Co}_3\text{O}_4\text{H}^+} - \text{Ag} / \text{AgCl} / \text{Cl}^- \quad (3)$$

Using the Nernst equation at the equilibrium, the electrode potential can be described as [45]:

$$E_{\text{Co}_3\text{O}_4 / \text{Co}_3\text{O}_4\text{H}^+} = E_0_{\text{Co}_3\text{O}_4 / \text{Co}_3\text{O}_4\text{H}^+} - (RT/nF) \times \ln (a_{\text{Co}_3\text{O}_4} \text{H}^+ / a_{\text{Co}_3\text{O}_4} \cdot a_{\text{H}^+})$$

$$\begin{aligned} E_{\text{Co}_3\text{O}_4 / \text{Co}_3\text{O}_4\text{H}^+} &= E_0_{\text{Co}_3\text{O}_4 / \text{Co}_3\text{O}_4\text{H}^+} - (RT/nF) \times \ln (a_{\text{Co}_3\text{O}_4} \text{H}^+ / a_{\text{Co}_3\text{O}_4}) - (RT/nF) \ln(1/a_{\text{H}^+}) \\ &= E_0_{\text{Co}_3\text{O}_4 / \text{Co}_3\text{O}_4\text{H}^+} - (2.303.R.T/F)\text{pH} \end{aligned} \quad (4)$$

$$= E_0_{\text{Co}_3\text{O}_4 / \text{Co}_3\text{O}_4\text{H}^+} + m. \text{pH} \quad (5)$$

where $E_0_{\text{Co}_3\text{O}_4 / \text{Co}_3\text{O}_4\text{H}^+}$ is the redox potential of Co_3O_4 nanostructures, R is the ideal gas constant (8.314 J/mol K), T is the absolute temperature (298 K), F is the faraday constant ($96487.3415 \text{ C mol}^{-1}$), n describes the number of electrons per mole, and a_{H^+} is the activity of hydrogen ion. By using the linear equation:

$$E = -0.0591 \text{ pH} + E_0 \quad (6)$$

where E is the voltage measured for a specific pH of a buffer and E_0 depends on the internal reference. The theoretical slope at room temperature (298 K) was found to be

$$m = -59.1 \text{ mVpH}^{-1} \quad (7)$$

The calibration curve for the selected range of pH from 3 to 13 of phosphate buffer solution for the proposed pH sensor is shown in Fig. 4. It can be seen that the Co_3O_4 nanostructures has shown Nernstian response by demonstrating a slope of -58.45 mV/pH and correlation coefficient of 0.9963. The close response to the theoretical slope could be attributed to the high surface to volume ratio of Co_3O_4 nanostructures. Moreover, high sensitivity of the presented pH sensor is related to the sensitive surface provided by the nanostructures of Co_3O_4 .

The characteristics of a particular pH sensor include response time, reproducibility, repeatability and stability which show the working performance of proposed device. The repeatability of presented pH sensor was checked by conducting a series of experiments for three consecutive days using similar pH sensor electrode and the observed response of the developed pH sensor is shown in Fig. 5. The sensor device maintained its performance configuration without any abrupt change in the sensitivity and a similar response for the selected range of pH. The observed repeatability indicates the application of proposed pH in monitoring of pH for real samples. Moreover, the sensor to sensor response was also examined for the determination of reproducibility and the fabricated device showed a reproducible with a relative standard deviation of less than 5% as shown in Fig. 6. A response time of 53 s was also observed which could be correlated to the highly sensitive surface of Co_3O_4 nanostructures as shown in Fig. 7. The pH sensor device based on Co_3O_4 nanowires showed excellent stability without any abrupt change during the usage for three consecutive days.

4. Conclusion

In conclusion, anion effect on the morphology of Co_3O_4 nanostructures was examined by hydrothermal method. Different anions have shown significant effect on the morphology of Co_3O_4 nanostructures. The SEM, XRD and TEM were used for the characterization of cobalt oxide nanostructures and the obtained information showed that material is highly dense and uniform on the substrate with good crystal quality. Furthermore, the prepared cobalt oxide nanostructures were employed for the development of pH sensor in a pH range of 3–13. The presented pH sensor showed Nernstian response and excellent linearity for the pH range of 3–13. Moreover, pH sensor exhibits a fast response time of 53 s, acceptable repeatability and reproducibility. All the obtained results indicate the possible usability of presented pH sensor in biological and food industry samples.

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Figure captions:

Figure 1. The SEM images of different Co_3O_4 nanostructures grown in precursors of (a) cobalt nitrate, (b) cobalt chloride, (c) cobalt acetate and (d) cobalt sulfate.

Figure 2. XRD spectra of cobalt oxide nanostructures grown in different growth mediums. (a) Cobalt nitrate, (b) cobalt chloride, (c) cobalt acetate and (d) cobalt sulfate.

Figure 3. (a–c) HRTEM image of single nanowire (d) TEM image of Co_3O_4 nanowires, inset is the SAED pattern of Co_3O_4 for multi nanowires.

Figure 4. The calibration curve of pH sensor based on Co_3O_4 nanostructures grown in precursor's solution of cobalt chloride for the pH range of 3–13.

Figure 5. The repeatability of proposed pH sensor.

Figure 6. The reproducibility of pH sensor measured in pH 6.

Figure. 7. The response time of pH sensor measured in pH 7.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.