Research Article

Synthesis and Characterization of ZnO/ZnS Core/Shell Nanowires

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ZnO nanowires of approximately 3 μm length and 200 nm diameter are prepared and implanted vertically on substrate glass which is coated with thin layer of ITO which is too covered with bulk ZnO thin layer via electrodeposition process by cyclic voltammetry-chronoamperometry and with a chemical process that is described later; we have synthesized a ZnS nanolayer. ZnO/ZnS core/shell nanowires are formed by ZnO nanowires core surrounded by a very thin layer of porous ZnS shell principally constituted with a crystal which is about 15–20 nm in diameter. In the method, ZnS nanoparticles were prepared by reaction of ZnO nanowires with Na_2S in aqueous solution at low temperature and also we have discussed the growth mechanism of ZnO/ZnS nanowires. The morphology, structure, and composition of the obtained nanostructures were obtained by using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). For the structure, SEM and XRD measurements indicated that the as-grown ZnO nanowires microscale was of hexagonal wurtzite phase with a high crystalline quality, and TEM shows that the ZnS is uniformly distributed on the surface of the ZnO nanowires.

1. Introduction

The physical and chemical characteristics of the material remain the functioning soul of devices dedicated to industrial and societal needs in the information and health field. In these last years investigations are oriented heavily in creations of new materials. The diversity of their properties is mainly due to recent advances in technology development, structuring, emergence of new properties related to the size effect, interfaces stability, and electrical and optical properties.

Otherwise, the surface treatment has experienced major advances combining scientific and technical research needs for their industrial importance in everyday life and especially the deposition of thin nanostructured alloys which has known good success and high efficiency [1].

Many techniques have been tried to create thin nanostructured layers [2, 3], including those that are expensive, those that are difficult, and those that are very sensitive and require a lot of very accurate monitoring equipment

which are mostly not unavailable in the majority of laboratories. From these new composites which have gained much importance, we can cite ZnO nanowires that have been recognized as one of the most promising nanomaterials due to their various properties and applications [4–7]. As the most important semiconductor material, ZnO possesses a wide direct band gap, strong piezoelectric properties, and a large binding energy.

Modification of ZnO properties by impurity incorporation and surface coating is currently another important issue for possible applications in ultraviolet optoelectronics and spintronics [8–10]. For semiconductor materials doping with different elements can adjust its electrical, optical [11, 12], and magnetic properties [13–19]. Surface modification has been recognized as one of the most advanced methods to build tailored materials which are nanostructured, effective, and reliable [16–22].

Also, ZnS material is a well-known material which has an important wide band gap semiconductor that allows it to be

FIGURE 1: Experimental setup: 1—working electrode, 2—against electrode, 3—reference electrode, 4—Potentiostat, and 5—chemical solution.

applied in several areas such as optical [10–12], photocatalyst [20], and photovoltaic devices [23].

Furthermore, core/shell structured ZnO/ZnS nanowires have been demonstrated to possess improved physical and chemical properties for electronics, magnetism, optics, catalysis, and other applications. Therefore, considerable effort has been devoted to the design and controlled fabrication of core/shell structured ZnO/ZnS nanowires. Up to now, different preparation methods have been explored for the synthesis of ZnO and ZnS nanowires and different morphologies were obtained.

In this study, we report the growth of vertically well-aligned ZnO nanowires by cathodic electrodeposition in aqueous zinc chloride electrolyte moreover and after we produce nanocomposites of ZnO/ZnS by partial conversion via a sulfidation operation in surfaces ZnO nanowires which reacts with Na_2S that is used as sulphur source. By this simple chemical method, ZnO nanowires can be partially converted to ZnO/ZnS nanocomposites. The structural, electrical, morphological, and optical properties of ZnO nanowires and ZnO/ZnS nanocomposites are studied in detail, which showed the production of a material that is more efficient than that produced in other works.

2. Experimental Study

2.1. Materials. The experimental setup used to synthesize ZnO nanowires consists of the following elements (Figure 1). Auto Lab PGSTAT-30 (potentiostat/galvanostat) which involves three electrodes such as: a platinum rod served as against electrode; a saturated silver/silver chloride (Ag/AgCl in saturated KCl) was used as a reference electrode; and a polycrystalline glass, coated with Sn-doped In_2O_3 (ITO), was used as a substrate named working electrode. The electrolyte was an aqueous solution of ZnCl_2 (5×10^{-4} M) and KCl (0.1 M), saturated with oxygen, bubbled for 45 min before, and remains there during the experience. Ultrapure

water ($18 \text{ M}\Omega\cdot\text{cm}$) was provided by a Millipore setup. Anhydrous ZnCl_2 salt (Aldrich, purity > 98.0%) was used as the Zn^{2+} precursor. KCl (Aldrich, purity > 99.5%) served as a supporting electrolyte. Sodium sulfide ($\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$) used for sulfidation conversion of ZnO Nanowires to ZnO/ZnS core/shell nanocomposites. The chemicals were purchased from Aldrich Chemical Corporation and used without further purification.

2.2. Used Devices for Characterizations. The morphology of the produced ZnO nanowires and ZnO/ZnS core/shell nanocomposites was studied by transmission electron microscopy (TEM) performed on a JEOL 2100F microscope operating at 200 kV.

The structures of the produced ZnO nanowires was characterized by X-ray diffraction (XRD) using a PANalytical Empyrean equipped with a multichannel detector (Pixel 3D) using ($\text{Cu K}\alpha$ 45 kV-40 mA) radiation in the $20\text{--}90^\circ$ 2θ range, with a scan step of 0.026° for 297 s. A five-axe cradle with motorized movements is used to obtain a perfectly planned position of the sample and a mirror with a $1/16^\circ$ slit is installed in the incident path to form a parallel beam necessary to analyze the samples in grazing incident beam (GIXRD).

The microstructure was analyzed using a Supra40 ZEISS field emission gun scanning electron microscope (FEG-SEM) operating at 5 kV. We observed samples with an in-lens detector. The composition of the coating was analyzed using a Jeol 6510 scanning electron microscope (SEM) equipped with an SDD (Silicon Drift Diode) detector and operating at 10 kV. The software to obtain the EDX spectrum is Iridium Ultra TM Spectra with constant time of 16 and a preset time of 50.

The UV-visible diffuse reflectance spectra of ZnO nanowires and ZnO/ZnS core/shell nanocomposites were recorded on a Perkin Elmer-Lambda 1050 spectrophotometer equipped with a PTFE coated integration sphere.

Surface composition was further investigated by X-ray photoelectron spectroscopy (XPS) measurements using

FIGURE 2: ZnO forming process.

FIGURE 3: Current variation versus the electrodeposition duration.

a Thermo VG ESCALAB 250 instrument equipped with a microfocused, monochromatic Al K α X-ray source (1486.6 eV) and a magnetic lens. The X-ray spot size was 500 μm (15 kV, 150 W). The spectra were acquired in the constant analyzer energy mode with pass energy of 150 and 40 eV for the general survey and the narrow scans, respectively. The sample was fixed on holder using adhesive tapes with double sides and rapidly returned in the airlock for at least 5 hours at 2×10^{-7} mbar or better. The “Avantage” software, version 4.67, was used for data acquisition and processing.

2.3. Synthesis of ZnO Nanowires. Before electrodeposition, ITO substrates were cleaned by a chemical product such as the trichlorethylene, acetone, isopropanol alcohol, and pure water under the ultrasonic treatment, and ITO is set as working electrode.

In our technique the first necessary step (Figure 2) is to reduce oxygen that is fully filled in the solution. The electrochemical reduction of oxygen depends on the pH of the solution [24]. At pH > 6 there is formation of OH $^-$ according to the following reaction (1):

These OH $^-$ ions are absorbed by the working electrode surface; ZnCl $_2$ dissociates in several species such as Zn $^{2+}$ and Zn(OH) $_x$ Cl $_y$ [25] which react with the OH $^-$ adsorbed on the cathode. When conditions are optimized, ZnO is deposited at the cathode according to the following reaction (2):

In a first step, a solution of distilled water containing 0.1 M KCl and 5×10^{-3} M ZnCl $_2$ which was purchased from Aldrich Inc. A constant cathodic current ($J = -0.13 \text{ mA/cm}^2$) is applied for 2500 s at room temperature and the result is simply a ZnO thin film on a 2 cm 2 geometric surface. The grown thin layers are annealed at 100°C for 10 min which gives a buffer layer on which are deposited nanowires ZnO. ZnO nanowire arrays were electrodeposited under a constant potential (−1 V) and the galvanostat potentiostat is settled in chronoamperometric mode. The potentiostat was monitored by the Auto Lab software. The compact thin layer was deposited at 25°C, while the nanowires were obtained at 80°C. Note that the deposition conditions used to obtain ZnO nanowires, namely, $V = -1 \text{ V}$ versus SCE, $T = 80^\circ\text{C}$, $[\text{ZnCl}_2] = 5 \times 10^{-4} \text{ M}$ and $[\text{KCl}] = 0.1 \text{ M}$ are named “standard conditions” in this paper.

The variation of the current measured between working and against electrodes evolves as shown in Figure 3. We note that this curve is essentially composed of two parts, the first part gives a rapid decrease of the current intensity, stage giving the formation of the first ZnO grains, and the second part is a horizontal portion giving the step of ZnO forming.

The four-point probe measurements demonstrated good conductivity of the ZnO nanowires with surface resistivity of $\approx 5 \cdot 10^{-3} \Omega\text{-cm}$ which permits us to conclude that the formed nanowires can be classified as a good conductor.

2.4. Synthesis of ZnO/ZnS Core/Shell Nanoparticles. To prepare ZnO/ZnS core/shell nanowires arrays we use ZnO nanowires that will be put into a glass bottle containing 0.32 mol·L $^{-1}$ Na $_2$ S aqueous solution, this is, the sulfidation that will remain for 4 h at 60°C. The final product was washed

FIGURE 4: SEM images of ZnO nanowires: (a) top view, (b) cross section view, and (c) one ZnO nanowire.

with deionized water repeatedly to remove the possible impurities and then dried at 80°C for 2 h before being studied. The exchange of a thin layer from ZnO nanowires to ZnS is done in three steps.

Na_2S salt decomposes in aqueous solution with Na^+ and S^{2-} ions as follows:

A thin layer of ZnO nanowires reacts with hydroxide ions (HO^-) present in the aqueous solution according to the following reaction equation:

which allows the exchange of the stable ZnO molecules with the unstable ZnO_2^{2-} ions.

This ZnO_2^{2-} ions react with S^{2-} ions giving the expected ZnS as follows:

Thereby, there are forming ZnS nanoparticles that will cover ZnO nanowires in which the final structure is called ZnO/ZnS core/shell.

3. Results and Discussion

The morphology of ZnO and ZnO/ZnS core/shell nanostructures observed by SEM is shown in Figure 4. From this figures, we observe that the highly ordered ZnO nanowires are grown at the ITO/ZnO substrate and tend to be perpendicular thereto. We also note that the section of each nanowire formed is of hexagonal shape (Figure 4(b)) which proves that the finest method was used to produce ZnO nanowires.

Figure 5 shows the composition of ZnO/Zn core/shell nanowires determined by the XPS. The peaks located at 162 eV, 532 eV, 1022 eV, and 1045 eV are, respectively, due to the S(2p), O(1s), Zn(2p_{3/2}), and Zn(2p_{1/2}) binding energies for XPS spectrum concerning the as-produced ZnO/ZnS core/shell nanostructures on substrate constituted

by (ITO/ZnO thin film). By measuring peaks areas we can deduce the atomic percentages of each element present in the formed structure. This atomic percentage is summarized in Table 1, when we find elements corresponding to the peaks and comprised in established nanowires and we provide the successful sulfidation of S elements into ZnO nanowires. Also we notice the existence of carbon which may be a contaminant in the sample and indium traces arising from the substrate.

In order to confirm the chemical composition of the obtained products, we have employed the EDX and XRD spectroscopy to analyze the synthesized products. XRD characterization can establish the crystal structure of the obtained products. Its spectrum, shown in Figure 6, gives peaks corresponding to the ITO glass substrate and peaks of these ZnO nanowires which can be readily related to hexagonal structure with cell constant. $a = 3.24 \text{ \AA}$ and $c = 5.19 \text{ \AA}$ characterizing the wurtzite structure (Joint Committee for Powder Diffraction Standards (JCPDS) number 36-1451).

And for the ZnO nanowires spectrum, the existence of the (002) peak at the smaller angle (34.5°) shows that this orientation is the most dominant; that is, these prepared nanowires are quasialigned along c -axis.

The morphology of ZnO/ZnS core/shell nanostructures observed by SEM is shown in Figure 7(a). We note the existence of a layer having a form apparently less dense or arising from a product different than that of ZnO and also others. Figures 7(b) and 7(c) present, respectively, the TEM (b), HRTEM (c), and the corresponding selected area electron diffraction (SAED) pattern (d) images of thin ZnS coating deposited onto ZnO nanowire obtained after 1 h duration of insertion, within which the ZnO nanowires appear with a diameter of about 193 nm, surrounded by a thin ZnS layer of 18 nm thick. In SAED pattern we observe three diffraction rings corresponding to the (111), (220), and (311) planes of zinc blende ZnS, and also it should be noted that the diffraction rings in the SAED pattern are discontinuous and consist of rather sharp spots, which indicates that the nanowires are well crystallized.

Figure 8 shows the UV-Vis absorption spectra of ZnO and ZnO/ZnS core/shell nanowires. we can see that for both

FIGURE 5: XPS spectra for the ZnO/ZnS core/shell nanostructures.

TABLE 1: Experimental data for peaks of ZnO/ZnS nanowires.

Name	Peak BE	FWHM eV	Area (P) CPS·eV	At. %
Cl _{1s}	285.04	1.55	14594.49	41.97
In _{3d}	444.61	1.74	7100.11	0.94
Na _{1s}	1072.49	0.02	987.24	0.47
O _{1s}	531.87	2.13	13823.91	14.39
S _{2p}	161.67	2.08	14154.20	23.84
Zn _{2p}	1022.17	1.64	136789.95	18.40

FIGURE 6: XRD spectra of the ITO substrate and the ZnO nanowires.

FIGURE 7: (a) SEM image, (b) TEM image, (c) HRTEM image, and (d) selected area electron diffraction (SAED) pattern image from (c) of ZnO/ZnS core/shell nanowires.

FIGURE 8: UV-visible spectra of ZnO and ZnO/ZnS core/shell nanowires.

materials the absorption is higher in the UV range mainly in the vicinity of 280 nm when it passes through a maximum, and we remark in the visible range an intensity improvement after the sulfidation operation. This feeble shift is maybe related to the quantum size effects imposed by the ZnS thin layer having a thickness in the order of 18 nm.

From the results of electrical conductivity, XRD, SEM, and UV-Vis analyses for ZnO/ZnS core/shell nanowires, we note that they have a very high quality which can be applied on the electrode of solar cell to improve its efficiency.

4. Conclusion

In summary, ZnO nanowires of approximately 3 μm length and 200 nm diameter are prepared and implanted vertically on (ITO/ZnO thin layer) substrates via electrodeposition process, and these nanowires have been covered by a ZnS thin film of about 20 nm thick using a sulfidation process. XRD, SEM, TEM, and HRTEM results confirm the existence of the ZnO/ZnS core/shell nanocomposite. The electrical conductivity, structural properties, and UV-visible study reveal that the prepared nanowires have high quality which can be applied on the electrode of solar cell.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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