Electrochemical Impedance Spectroscopic Analysis of ZnS Nanorod Fabricated Using Butterfly Wings as Biotemplate

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Abstract This article describes the growth of zinc sulfide (ZnS) nanorod on glass/aluminum foil by employing butterfly wings as biotemplate. Upon calcinating (at 400 °C), the butterfly wings soaked in ZnS nanoparticle suspension, with uniform cage-like nanostructures in nanodimensions, were found on glass/aluminum surface. The transverse and longitudinal dimensions of the nanorods were evaluated from scanning electron microscopy micrographs as 132 and 159 nm, respectively. Purity of the ZnS nanorod found on the specimen was checked by recording XRD (28.877°, 48.038°, and 57.174°) and Fourier transform infrared spectrometer spectra (663.7 and 551.68 cm⁻¹). Luminescence natures of the nanorods were examined using photoluminescence spectral studies. The characteristic emission peak is shown in the visible region with strong intensity, while the excitation peak is shown at 267 nm. Electrochemical impedance spectroscopic analysis of ZnS nanorod exhibits double-layer capacitance value ($C_{dl} = 6.7$ nF), and the Bode plot explains the stability of ZnS nanorod under the influence of electrical field.

KEY WORDS: Semiconducting material; Biotemplate; Photo luminescence (PL); Nanorod; Bode plot; Capacitance

1 Introduction

Nanostructured materials are a new class of materials, having dimensions in nanoranges, which possess improved performance with extended capabilities of products in a wide range of applications [1]. Nanostructures with mono disperse size and shape have unique optical and physical properties compared with bulk materials. Based on the nanostructure shapes, they can be classified into three types, namely, zero-dimensional, one-dimensional (1D), and two-dimensional (2D) materials. 1D nanostructures represent the smallest

dimension structure that can efficiently transport electrical carriers. The different types of the nanostructures can be synthesized in the purest form with the different controlled environments, such as chemical composition, temperature, concentration of precursors, etc. The ability to produce 1D nanostructures with controlled dimensions allows making functional nanoscale devices [2].

Among various nanomaterials, semiconductor nanomaterials, especially metal chalcogenide materials, have been studied for the optical and electronic properties since they are associated with quantum confinement effect. As an important wide band gap II-VI group semiconducting material, zinc sulfide (ZnS) is a promising candidate with 3.65 eV [3]. It attracted many researchers, since it is having varieties of applications in photoconductors, flat panel displays, electroluminescent devices, light emitting diodes (LEDs), solar cell, infrared windows, sensors, lasers, bio-devices, etc. [4–6]. ZnS nanobelts have been utilized as UV—light sensors, UV—light photo detectors by many

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researchers [7–9]. They are also anticipated to play an important role in the interconnects and functional units in fabricating electronic and optoelectronic devices. Some methods, such as sonochemical method, sol–gel technique, solvothermal method, template method, etc., have been reported recently for the preparation of ZnS nanocrystallites [10]. Among the different types of fabrication techniques, controlling the size and shape is a critical issue. However, the shape and size of ZnS nanorods in required dimensions have been achieved by modifying various parameters [11–13]. Biotemplate-assisted technique is a common technique which allows for fabrication of nanorod, nanobelt, hollow spheres, etc.

The wings of the butterflies are composed primarily of cuticle, a multilayered material consisting of chitin microfibers embedded in a protein matrix [14]. The cuticle is arranged in the form of tubular, supporting veins and thin deformable membranes. Veins found on the wings are naturally micro-capillary tubular structures, through which fluid medium containing nanoparticles can enter by capillary movement [15]. This study makes a novel attempt in the loading of ZnS nanoparticles in the hollow veins present on the wings of the butterflies, to develop the nano-ZnS cages with cross sections in nanometer size range on aluminum foil. The nano-ZnS presenting in the suspension easily penetrated into the hollow veins through capillary action. Precursor-loaded butterfly wings on calcination at moderate temperature yields pure ZnS nanorods mimicking the cage-like arrangements found in butterfly wings.

The structural properties of the ZnS nanorods developed over glass and Al foil were investigated by X-ray diffraction technique, scanning electron microscopy, FTIR analysis, etc. The electrical property of ZnS is measured by electrochemical impedance spectroscopy (EIS). The capacitance value (C_{dl}) and electron life time (τ_n) of ZnS nanostructures were evaluated through EIS.

2 Experimental

2.1 Materials

Zinc acetate and sodium sulfide as a source material used in this work were purchased from E-Merck Ltd., India, and used without purification.

2.2 Preparation of ZnS Nanorod

0.1 mol of zinc acetate and 0.1 mol of sodium sulfide were dissolved in 50 mL of distilled water separately and mixed slowly by constant stirring. The ZnS nanoparticles are formed during the addition of sodium sulfide into the zinc acetate solution as white precipitate. The ZnS nanoparticles separated

were removed by centrifugation, and each particle is repeatedly washed with distilled water for removing the unreacted impurities. Then, the ZnS in wet condition was poured into 70 mL of distilled water, sonicated for 30 min to get a ZnS-dispersed suspension. The cleaned and dried butterfly wing was soaked in the suspension for 30 min, removed, and dried in air. After drying, the wings were placed in between two glass slides. It looks like a sandwich model. The glass slide was kept at 400 °C for about 1 h in muffle furnace. Biological materials like chitin, cuticle, etc., upon calcination were burnt out leaving the nanorod pattern of ZnS. Similarly, ZnS nanorods were also grown over aluminum foil by employing the same technique. Before placing the precursor-loaded butterfly wings, the glass slide was covered using a cleaned aluminum foil. Remaining ZnS nanoparticles found in the aqueous suspension were separated as nanopowder by centrifuging with the supernatant medium. The obtained nanorods made of ZnS were used for further analysis.

2.3 Electrochemical Impedance Spectroscopy

The EIS has been widely used for studying the electrochemical mechanisms occurring at electrode/electrolyte interface, and it establishes an equivalent electrical circuit model for the electrochemical processes [16]. The Nyquist plot gives the information about impedance value and the capacitance values of semiconducting material, whereas from Bode plot, the charge carrier life time was evaluated.

From Nyquist plot, the capacitance (C_{dl}) of ZnS is calculated using the following equation:

$$C_{dl} = \frac{1}{2\pi f Z''}, \quad (1)$$

where f is the frequency of the applied electric potential signal; Z'' is the phase component of the measured impedance.

Z'' value was calculated from the maximum of real part of impedance multiplied by the angle (between the line and the X-axis) of the impedance graph.

The life time (τ_n), known as an average time of excited electron residing on the conduction band before recombining to the hole, was calculated from Bode plot obtained from impedance analysis [17]:

$$\tau_n = \frac{1}{2\pi f_{\max}}, \quad (2)$$

The maximum frequency ($f_{\max}$) was calculated from the phase plot.

2.4 Characterization Techniques

Crystal parameter of the nanoparticle and nanorods were analyzed using an X-ray diffractometer (Philips X'pert pro

X ray diffractometer) by $\text{CuK}_{\alpha 1}$ ($\lambda = 1.54056 \text{ \AA}$) radiation by measuring the 2θ values varied from 15° to 60° at scanning rate of $0.05^\circ/\text{s}$. The confirmation of compounds was studied by Fourier transform infrared spectrometer (FTIR Alpha—Bruker optics, Germany). The morphology of the sample was characterized using a scanning electron microscope (SEM) Model: SU1510, Hitachi, Japan. The surface characteristic was studied by atomic force microscopy (AFM) (Park System South Korea-XE70). The photo luminescence spectra were measured by exciting the specimen with the wavelength of 267 nm using a 150-W xenon lamp as an excitation source (Shimadzu spectrometer—RF 530 IPC, Japan). The impedance spectroscopy of the samples was recorded using Electrochemical workstation CHI 660C, USA.

3 Results and Discussion

3.1 FTIR Study

FTIR spectrum of ZnS powder is presented in Fig. 1. The infrared spectrum is formed due to the absorption of electromagnetic radiation at the frequencies, which correlates to the vibration of chemical bonds that exist within a molecule. The spectrum exhibits characteristic vibrations for Zn and S at 663.7 and 552.68 cm^{-1} , respectively [18]. A peak at $1,416.62 \text{ cm}^{-1}$ is attributable to the C–H band's presence in the wings of butterfly in trace amounts as organic contents like chitin, cuticle, etc. Another peak appearing at $1,555.67 \text{ cm}^{-1}$ is due to the C–O–H stretching vibrations of organic contents [18].

3.2 XRD Analysis

Figure 2a represents the XRD pattern of ZnS nanopowder synthesized by co-precipitation method. The XRD of ZnS nanorod obtained by biotemplate method is shown in Fig. 2b. Both XRD patterns have three major peaks at 2θ values of 28.877° , 48.038° , and 57.174° corresponding to a diffraction planes of (101), (111), and (022) planes, respectively (JCPDS no: 892425), which correspond to the

Fig. 1 FTIR spectrum of ZnS nanorod

hexagonal structure [19]. The XRD patterns of ZnS nanorod and nanopowder do not show any other peaks, confirming that the samples are free from impurities. The crystallite sizes of the ZnS nanopowders and nanorods were calculated using Scherer equation [20], and the measured crystallite sizes are 65.93 and 39.948 nm, respectively.

3.3 SEM Analysis

Figure 3 shows the typical SEM images of ZnS nanorods grown on glass slide using biotemplate method. Figure 3a shows well-organized porous hierarchical architecture of the ZnS nanorod at low magnification. Maximum length of the nanorod found vertically is about $3 \mu\text{m}$, while that of the horizontal nanorod is more than $10 \mu\text{m}$. Such a long-sized nanostructure fabrication is possible only with the help of biotemplate method, and not by other methods [21]. A higher magnification image in Fig. 3b clearly exhibits the parallel ridges that are aligned by stack of the multi-layer, and it is possible to determine the dimensions of longitudinal and transverse directions. SEM observation demonstrates that the diameters of the nanorods found in longitudinal and transverse directions are 159 and 132 nm, respectively.

3.4 AFM Studies

Atomic Force Microscopy (AFM) image of the ZnS nanorod is shown in Fig. 4. The nanotextured structure is well explored by this image, and it shows 3D image of ZnS nanorod [22]. The ZnS nanorods were observed on the glass substrate, where it is possible to identify the groups of the nanorods with similar dimensions and nearly the same orientation. The structural features of the nanorod have been explored by the XEI-image processing software supplied by PARK system, South Korea. As-grown ZnS nanorod appears as a thick cover over the aluminum foil with a thickness of about 400–500 nm.

3.5 Photoluminescence (PL) Properties

Luminescence is a characteristic property of semiconducting materials, the absorption and emission characteristics of which are size dependent [23–25]. The information obtained from the PL spectra is useful to detect and analyze the electronic states of the ZnS nanopowder and nanorod. The PL spectra of the as-synthesized ZnS nanopowder and the as-grown ZnS nanorod are shown in Fig. 5. Strong emission peaks found at about 365 and 476 nm (For ZnS nanopowder) are revealed on exciting the specimen using 267-nm source radiation. The exciton peak around 365 nm indicates that, it is a near-band edge emission that originated due to the recombination of excitons of ZnS nanopowder [26]. The broad band

Fig. 2 XRD patterns of ZnS nanopowder **a**, ZnS nanorod **b**

Fig. 3 SEM images of ZnS nanorod with low **a**, high magnifications **b**

Fig. 4 AFM image of ZnS nanorod

emission at 476 nm is attributed to the stoichiometric vacancies or interstitial impurities. Compared to that of ZnS nanopowder, ZnS nanorod exhibits the band edge emission at 360 nm (blue shift). The precise weak peak found at 452 nm is

attributable to interstitial impurities existing in the nanorod [27]. Another broad band originating from the nanorod located at 470 nm is assigned to stoichiometric vacancy or interstitial impurities. The ZnS nanorods have shorter emission wavelength than that of the ZnS nanopowder. The concentration of the defects increases with the increasing degree of crystallinity. The emission intensity characteristic to nanopowder is high since it is associated with higher percentage of stoichiometric vacancy or interstitial impurities. At the same time, ZnS nanorod displays a low-intense spectrum attributed to the defect-free structures [28].

3.6 EIS Analysis

Thin film of semiconducting materials possesses electrical properties such as A.C impedance, charge transport, etc. [29, 30]. All such behaviors have been measured through

Fig. 5 PL spectra of ZnS nanopowder and nanorod

EIS using electrochemical workstation. The ZnS nanorod grown on the aluminum foil is used as working electrode; platinum wire and Ag/AgCl are used as counter and reference electrodes, respectively [31]. The electrolyte solution used for obtaining EIS spectra is 3.5% NaCl solution. Impedance values are measured in the frequency range from 1 MHz to 1 Hz at room temperature.

It is evident from the Fig. 6a that the ZnS nanorod exhibits the charge transfer resistance value of about 651 Ω and double-layer capacitance of 6.7 nF with a characteristic semicircular-like impedance curve [30].

Figure 6b represents Bode plot obtained for the ZnS nanorod developed on aluminum foil, in which the phase angle versus frequency is plotted. The electron life time transport from conduction band to valence band for a semiconducting material is thickness dependent [17]. From AFM analysis, the thickness of the as-grown ZnS nanorod is found to be about 500 nm. The semicircle form of Nyquist plot is a characteristic of the electron injection phenomenon taking place at the counter electrode–electrolyte interface. The recombination of electron residing on the conduction band to its valence band has been calculated using the Eq. (2). The electron life time transport value found for the ZnS nanorod is about $7.402 \times 10^{-5} \text{ s}^2$. This value is less in comparison with the semi-conducting materials of quantum dot type [32].

Employing similar methodology which was reported in Ref. [33], the stability of ZnS nanorod also evaluated from the details of EIS data. The magnitude and phase angle plots of the open-loop frequency transfer function are evaluated from Bode diagrams illustrated in Fig. 6c and d. In particular, Fig. 6c is drawn by taking the magnitude in y-axis and the logarithmic frequency in x-axis. The high-frequency and low-frequency asymptotes are drawn from

Fig. 6 Nyquist plot a, bode plot b, magnitude plot c, phase angle plot d, equivalent circuit model e of the ZnS nanorod

both sides of the Bode plot—the point at which the two asymptotes intersect with each other is called as corner frequency or break frequency or break point. From the Fig. 6c, it is clear that the magnitude at the corner frequency is 60 dB (on y-axis). Based on the asymptotic plot approximation, the deviation from the corner frequency has been evaluated and found to be about 3 dB. These results are in accordance with the fact that if a plot differs by a factor of $20 \times \log(1/\sqrt{2})$ or 3 dB [34], then it can serve as an efficient electrode material for storing data.

Further, the Bode plot is reconstructed using phase angle and log frequencies, as represented in Fig. 6d. The corresponding phase angle at corner frequency is -45° which frequency is known as Φ_{gc} . From the equation $\gamma = 180^\circ + \Phi_{gc}$, the phase margin value is determined as 135° . The gain margin is calculated by the transfer function ($f(\omega)$) of the phase plot from the equivalent circuit model:

$$f(\omega) = \frac{1017.95(1 + 1.5649 \times 10^{-6}j\omega)}{1 + 1.593 \times 10^{-3}j\omega}, \quad (3)$$

where j and ω are $\sqrt{-1}$ and frequency, respectively. The capacitance and the resistance values of the equivalent circuit model have been taken from the EIS data.

Obtained transfer function is converted into corresponding polar coordinates, and thus it is found to be equal to -180° as evaluated using the following equation:

$$\tan^{-1}(1.5649 \times 10^{-6})\omega - \tan^{-1}(1.593 \times 10^{-3})\omega = -180^\circ, \quad (4)$$

Using the above expression, the value of ω is evaluated, and on substituting the value into the transfer function Eq. (3), it gives the gain margin value, which is found to be equal to infinity. From these results, it is apparent that the system, possessing both phase margin and gain margin as positive values, becomes electrically and electronically stable.

Figure 6e represents the equivalent circuit model drawn by considering solution resistance as R_s , a double-layer capacitance as C_{dl} , and a charge transfer or polarization resistance as R_{ct} . The resistance was ascribed to the impedance of the charge transfer behavior of the ZnS-coated aluminum foil due to the 3.5% NaCl-electrolyte interface. Higher capacitance ($C_{dl} = 6.7$ nF) value found in this system is attributable to the electron-storing capability of the ZnS nanorod. These results substantiate that the ZnS semiconducting material developed on aluminum foil have capacitance characteristics.

4 Conclusions

A novel method for the synthesis of ZnS nanorod using biotemplate method was established. XRD confirms the

formation of ZnS of the corresponding materials. The morphology of ZnS nanorod was checked through SEM. The PL study of ZnS nanoparticle and nanorod indicated that the band-to-band transition and exciton recombination were size dependent. The EIS study shows that the capacitance and life time of electron were greater in ZnS nanorod coated over the aluminum substrate. AC impedance analysis proves that the developed nanorods possess electrical and electronic stabilities.

References

- [1] X.S. Fang, T.Y. Zhai, U.K. Gautam, L. Li, L.M. Wu, Y. Bando, D. Golberg, *Prog. Mater. Sci.* **56**, 175 (2011)
- [2] G.Z. Shen, D. Chen, *Optoelectron. China* **3**, 125 (2010)
- [3] D.H. Lee, J.Y. Jung, E.J. Bae, T.J. Lee, S.O. Ryu, *J. Korean Phys. Soc.* **53**, 102 (2008)
- [4] B.P. Singh, S.P. Singh, S. Vishnoi, R. Kumar, *J. Optoelectron Biomed. Mater.* **4**, 29 (2012)
- [5] R. John, S.S. Florence, *Chalcogenide Lett.* **7**, 269 (2010)
- [6] R.I. Sharma, *Int. Multidiscip. Res. J.* **1**, 8 (2011)
- [7] X.S. Fang, Y. Bando, M.Y. Liao, U.K. Gautam, C.Y. Zhi, B. Dierre, B.D. Liu, T.Y. Zhai, T. Sekiguchi, Y. Koide, D. Golberg, *Adv. Mater.* **21**, 2034 (2009)
- [8] X.S. Fang, Y. Bando, M.Y. Liao, T.Y. Zhai, U.K. Gautam, L. Li, Y. Koide, D. Golberg, *Adv. Funct. Mater.* **20**, 500 (2010)
- [9] L.F. Hu, J. Yan, M.Y. Liao, H.J. Xiang, X.G. Gong, L.D. Zhang, X.S. Fang, *Adv. Mater.* **24**, 2305 (2012)
- [10] N.T. Tuan, N.D. Trung-Kien, P.T. Huy, N.H. Tung, *J. Surf. Sci. Nanotechnol.* **9**, 521 (2011)
- [11] X.S. Fang, C.H. Ye, L.D. Zhang, Y.H. Wang, Y.C. Wu, *Adv. Funct. Mater.* **15**, 63 (2005)
- [12] X.S. Fang, Y.S. Bando, C.H. Ye, G.Z. Shen, D. Golberg, *J. Phys. Chem. C* **111**, 8469 (2007)
- [13] C. Jin, Y. Cheng, X. Zhang, W. Zhong, Y. Deng, C. Au, X. Wu, Y. Du, *Cryst. Eng. Commun.* **11**, 2260 (2009)
- [14] K. Kertesz, G. Molnar, Z. Vertesy, A.A. Koos, Z.E. Horvath, G.I. Mark, L. Tapasztó, Z. Balint, I. Tamaska, O. Deparis, J.P. Vigneron, L.P. Biro, *Mater. Sci. Eng. B* **149**, 259 (2008)
- [15] J.Y. Huang, X.D. Wang, Z.L. Wang, *Nano Lett.* **6**, 2325 (2006)
- [16] T. Kuwabara, M. Nakamoto, Y. Kawahara, T. Yamaguchi, K. Takahashi, *J. Appl. Phys.* **105**, 1 (2009)
- [17] J.J. Tian, R. Gao, Q.F. Zhang, S.G. Zhang, Y.W. Li, J.L. Lan, X.H. Qu, G.Z. Cao, *J. Phys. Chem.* **116**, 18655 (2012)
- [18] T.Y. Yesu, R. Anitha, B. Kavitha, *Int. J. Appl. Sci. Eng. Res.* **1**, 282 (2012)
- [19] S.C. Kim, J.W. Kim, H.S. Chung, D.H. Kim, K.H. Oh, *J. Korean Phys. Soc.* **55**, 978 (2009)
- [20] P. Sana, L. Hasmi, M.M. Malik, *Int. Scholar. Res. Netw.* **1**, (2012)
- [21] Y. Ding, S. Xu, Z.L. Wang, *J. Appl. Phys.* **106**, 1 (2009)
- [22] S. Velumani, J.A. Ascencio, *Appl. Phys. A* **79**, 153 (2004)
- [23] C.S. Tiwarya, P. Kumbhakara, A.K. Mitraa, K. Chattopadhyay, *J. Lumin.* **129**, 1366 (2009)
- [24] C.H. Ye, X.S. Fang, M. Wang, L.D. Zhang, *J. Appl. Phys.* **99**, 063504 (2006)
- [25] B. Bhattacharjee, C.H. Lu, *Thin Solid Films* **514**, 132 (2006)
- [26] Y. Zhao, J.M. Hong, J.J. Zhu, **270**, 438 (2004)
- [27] H.S. Moon, C.H. Nam, C.W. Kim, B.S. Kim, *Mater. Res. Bull.* **41**, 2913 (2006)

- [28] N. Soltani, A. Dehzangi, E. Saion, B.Y. Majlis, M.R. Zare, A. Kharazmi, M. Navasery, Chalcogenide Lett. **10**, 27 (2013)
- [29] M. Ahmad, K. Rasool, M.A. Rafiq, M.M. Hasan, Paper presented at *Communications and Photonics Conference (SIEPCP)*, Saudi International, 24–26 April, (2011)
- [30] J.R. Macdonold, Annu. Biomed. Eng. **20**, 289 (1992)
- [31] R. Hrdy, H. Kynclova, J. Drbohlavova, V. Svatos, J. Chomoucka, J. Prasek, P. Businova, J. Pekarek, L. Trnkova, R. Kizek, J. Hubalek, Int. J. Electrochem. Sci. **8**, 4384 (2013)
- [32] A. Nakhmani, M. Lichtsinder, E. Zeheb, paper presented at *IEEE 24th Convention of Electrical and Electronics Engineers in Israel*, 26 November (2006)
- [33] R. Mancini, Feedback and Stability Theory, Excerpted from Op Amps for Everyone, (2006) <http://www.ti.com/lit/ml/sloa077/sloa077.pdf>. Accessed 12.12.2013
- [34] Zohar Z. Karu, Signals and Systems Made Ridiculously Simple, ZiZi Press, Huntville, AL35802, USA, 1995, Chapter 6, Page No. 26