PbS Sensitized ZnO Nanorods And Its Characterization

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Abstract. Lead sulfide nanoparticles (PbSNPs) sensitized zinc oxide nanorod arrays (ZNRs) have synthesized in the two step deposition process. The vertically aligned ZNRs have grown on the glass substrates using aqueous chemical method, followed by the deposition of PbSNPs by using chemical bath deposition (CBD) technique. The samples are characterized by optical absorption, X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). When the PbSNPs are coated on the ZNRs, the optical absorption is enhanced and band edge is shifted towards visible regime. The observed XRD patterns confirm the formation of ZnO having hexagonal wurtzite crystal structure and PbS with the cubic crystal structure. SEM study reveals the well aligned faceted hexagonal ZNRs; entirely covered with PbSNPs. Contact angle (CA) measurement shows the hydrophobic nature of ZNRs while hydrophilic of PbS/ZnO.

Keywords: Nanoparticles; Zinc Oxide Nanorods; Chemical Bath Deposition; Optical properties.

1. INTRODUCTION

The 1D structure of metal oxides such as ZnO and TiO₂ constitutes a new class of photoelectrode materials in solar cells, and number of other novel devices [1]. However, their wide band gap energy requires ultraviolet (UV) light irradiation, and therefore only a small fraction of solar spectrum is harnessed for power conversion. For this, considerable efforts like dye and narrow band gap semiconductor nanoparticle sensitization have been made and studied. But, in dye sensitized solar cells (DSSC), the carboxylic group of dye molecules reacts with Zn²⁺ ions and form aggregates, which reduces the electron injection efficiency and stability of the solar cells.

The visible band gap semiconductor sensitized solar cell (SSSC) is the best option to improve efficiency and stability in which semiconductor materials replace the organic dyes. The shape and size of semiconductor can be adjusted to cover the solar spectrum from UV to VIS range. In this paper, we have synthesized ZNRs using aqueous chemical method, and the grown arrays were sensitized with PbSNPs by CBD method. The structural and optical properties have been investigated in detail.

2.1 EXPERIMENTAL DETAILS

Initially seed solution was prepared in an absolute ethanol with 0.05M zinc acetate($Zn(CH_3COO)_2 \cdot 2H_2O$) and 0.05M diethanolamine ($HN(CH_2CH_2OH)_2$,DEA). The cleaned glass substrate was dip coated for 10 s in a seed solution and then kept at room temperature over night for drying. The dried films were annealed at 400°C for 5 min in air to yield a layer of ZnO seed on the substrate. The seeded substrates was placed vertically in 200 ml solution containing an equimolar (0.05M) zinc acetate and hexamethylenetetramine (HMTA) and refluxed at 95±3°C for 5h to grow ZNRs. The grown film was removed and then rinsed in distilled water and then used for PbSNPs coating.

The PbSNPs were deposited on ZNRs from a chemical bath containing 1M tri-sodium citrate $[Na_3C_6H_5O_7]$, 0.1 M lead acetate $[Pb(CH_3COO)_2.3H_2O]$, 1M sodium hydroxide [NaOH] and 0.5M thiourea $[H_2N.CS.NH_2]$. The substrate

containing ZNRs was vertically immersed into the chemical bath solution at room temperature 20 min. The deposited film was rinsed with distilled water and allowed to dry at room temperature overnight.

2.2 CHARACTERIZATIONS

The structure of the films was determined by X-ray diffraction (XRD) analysis [Bruker AXS Model D8 Advance X-ray Diffractometer] with Cu K α \Box target having wavelength 1.542Å. The optical absorbance was measured using a UV-vis spectrophotometer [Shimazdu UV 1800 model] in the wavelength range 400-1100 nm. The surface morphology of films was studied using scanning electron microscopy [SEM: JEOL JSM-6360A Analytical Scanning Electron Microscope]. The Fourier transform infrared (FT-IR) spectra of samples were collected using a Spectrum100 Perkin Elmer FT-IRspectrophotometer.

3. RESULTS AND DISCUSSION



FIGURE 1. XRD PatternsFIGURE 2. Optical absorptionof ZnO, PbS and ZnO/PbSspectra of ZnO, PbS andsamples.ZnO/PbS samples.

The XRD patterns of ZnO, PbS and PbS/ZnO were shown in Fig.1(a).The comparison of observed XRD patterns with the standard JCPDS data (76-0704) confirms the formation of ZnO having hexagonal wurtzite crystal structure with diffraction peaks (100), (002), (101), (102), (110), (103) and (004). The characteristic peaks along (111), (200), (220), (311), (222), (400), (331), (420), (422) and (511) planes corresponding to PbS are observed with the cubic structure (JCPDS card no. 78-1058) is shown in Fig. 2(b). XRD shows the good crystalline character for ZnO, PbS and ZnO/PbS samples.

Fig.1(c) shows the typical XRD spectrum of PbSloaded ZnO thin film deposited on glass substrate. It reveals that, besides hexagonal ZnO, there is the cubic phase PbS on the substrate. This result confirms the successful deposition of PbS on ZnO nanorods film.

From the optical absorption spectra (Fig.2), it is evident that the ZnO sample exhibits intrinsic absorption at about 425 nm. The characteristic absorption band of PbS at 762 nm. A significant shift in the spectral photoresponse (988 nm) is observed for ZnO/PbS sample. It clearly illustrates effective photon capturing in the visible region [2].



FIGURE 3. SEM of ZnO and ZnO/PbS nanorods

Fig.3 (a) shows SEM image of the ZNRs without PbSNPs with well aligned geometry. The vertical alignment of ZNRs is beneficial for the improvement in the charge transfer mechanism of the solar cells. Fig.3 (b) shows the top view SEM image of ZNRs coated with the PbSNPs. The faceted hexagonal ZnO rods are seen to be covered with PbSNPs.

Contact angle (CA) of a water drop is influenced by the roughness of the surface. Inset shows water CA measurement of ZnO and ZnO/PbS and are found to be 145^{0} and 90^{0} respectively. ZNRs film shows hydrophobic nature since the water CA is greater than 90^{0} , while ZnO/PbS film shows hydrophilic nature as compared to ZNRs film. This is beneficial to the better access of electrolyte into the film structure which enhances the PEC performance.

4. CONCLUSIONS

The PbS NPs were chemically deposited on the ZNRs at room temperature. The XRD analysis gave the formation of ZnO/PbS. The absorption spectrum shows the red shift of absorption edge, which is crucible for solar cell. The SEM images shows vertically aligned ZnO nanorods, which are helpful for the charge transfer in the PEC cell. The PbSNPs sensitized ZNRs have shown a promising candidate for an efficient solar energy conversion devices.

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