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Nanoarchitectured Semiconducting Photoelectrodes for Enhanced Stability and Photon Conversion Efficiency

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ABSTRACT

The characteristics of two dimensional (graphene), one dimensional (single walled carbon nanotube incorporated poly(3,4-ethylenedioxythiophene):polystyrene sulfonate, composite) and zero dimensional (ZnO quantum dots) nanostructures have been systematically analyzed to elucidate the possibility of employing such nanostructures (transparent conducting corrosion resistant (TCCR)) for the passivation of the surface of a photoelectrode. Thin layer of graphene, carbon nanotubes embedded on a conductive polymer matrix (PEDOT:PSS) and ZnO quantum dots are incorporated on the surface of photoelectrode namely 'In' rich $CuInS_2$ (ICIS) to act as corrosion resistant layers. The TCCR layers are found to be effective in inhibiting the surface recombination of charge carriers. Graphene exhibits a higher tendency towards the suppression of surface recombination across electrode-electrolyte interface, where an enhancement by a factor of 10^4 s is observed in the electron recombination life time. SWCNT/PEDOT:PSS composite films when employed as transparent conducting corrosion resistant layers enabled an enhancement of the cell stability by 95% when compared to unprotected 'In' rich $CuInS_2$ electrode. The TCCR layers are found have a positive impact on the conversion efficiency of the photoelectrode and the maximum enhancement in the conversion efficiency achieved is 71% with ZnO quantum dot sensitized electrodes.

1. Introduction

Photoelectrochemical (PEC) solar cells offer a two pronged solution for the effective capture and conversion of solar energy, one being low cost and the other, ease of fabrication. In spite of two main advantages, PEC systems could not realise widespread utilization because of the very poor stability associated with them. Therefore it becomes imperative to improve the stability of the semiconducting photoelectrodes employed in systems such as electrochemical photovoltaic cells, dye sensitized solar cells and the photoelectrochemical cells used for hydrogen production. The light harvesting ability of the photoelectrode should be improved with a substantial improvement in the cell stability for practical useful energy conversion. To achieve photoconversion efficiency and stability, photoelectrodes are now sensitized/functionalized using quantum dots, nanoparticles, polymers and hybrid/hierarchical nanostructures [1–9]. Nanostructured photoelectrodes hold advantages such as multi-exciton generation with single photon and generation of high photocurrent with good reversibility [10].

Following advancements are made in order to achieve stable and efficient photoelectrochemical systems. (i) increasing the photocurrent by engineering the semiconductor absorber layer morphology to yield better light absorption [11] (ii) improving charge-carrier transfer and collection efficiency by micro or nanostructuring of the semiconductor [12] (iii) improving charge separation by use of a surface layer to create a buried p–n junction to achieve a higher photovoltage [13] (iv) designing surface passivation layers that chemically or physically protect the semiconductor from corrosion [14] (v) reducing the rate of electron–hole recombination by surface state passivation [15,16].

Since the semiconducting photoelectrodes are in contact with the electrolyte, they are more susceptible for photocorrosion. Photocorrosion of the semiconducting electrode remains as a major challenge in case of electrochemical photovoltaic cells. The surface of the electrode can be protected by introducing a transparent conducting layer. Recently, carbon based nanomaterials have emerged as potential candidates for transparent conducting applications. Nanostructures exhibit multifaceted functionalities depending upon their size and shape. It will be rationale to tap the potential of nanostructures to address the problem of

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photocorrosion of semiconducting electrodes. Hence in the present work an attempt has been made to employ two dimensional, one dimensional and zero dimensional nanostructures as transparent conducting corrosion resistant layers. The choice of the nanostructures has been carefully made in view with the exceptional characteristics exhibited by the following materials.

Graphene is an atomic sheet of sp^2 bonded carbon atoms that are arranged into honeycomb structure. The outstanding properties of graphene include excellent electrical conductivity, high transparency due to its one atom thickness and high surface to volume ratio. Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate), PEDOT:PSS, as a conducting polymer has many advantages such as transparency and high flexibility. The conductivity has been a limiting factor for its practical applications. Many efforts have been made to enhance its conductivity by the addition of carbon nanotubes (CNTs). CNTs establish electrical interconnection between separate PEDOT islands dispersed in the insulating PSS phase thereby enhancing the electrical conductivity.

ZnO is considered as a potential candidate for quantum dot (QD) sensitized solar cells due to its high electron mobility, suitable energy-band structure, tunable bandgap depending on quantum dot size, larger extinction co-efficient, generation of multiple excitons with single photon absorption and excellent physical properties [14].

Encouraging results are obtained for stability and photon conversion efficiency when aforementioned nanostructures are used as transparent conductors in an electrochemical photovoltaic cell. This article reports the characteristics of these layers as transparent conductors and the performance of the photoelectrochemical cell with the nanoarchitectured semiconducting electrode.

2. Experimental

2.1. Deposition of ‘In’ rich $CuInS_2$ thin film

Aqueous solutions of 0.14 M copper chloride dihydrate ($CuCl_2.2H_2O$, Hi-Media), 0.25 M indium chloride ($InCl_3$, Hi-Media) and 1.02 M thiourea ($CS(NH_2)_2$, Hi-Media) are used as precursors for the deposition of Indium (In) rich $CuInS_2$ (ICIS) thin film on a glass/conducting glass substrate. ICIS thin films are deposited by nebulized spray pyrolysis technique. Substrate temperature of 350 °C is used for the deposition of ICIS thin films by nebulized spray pyrolysis. A spray rate of 0.5 ml/min., carrier gas (air) pressure of 1 bar at a substrate nozzle distance of 5 cm and a spray volume of 240 ml yielded homogeneous, well adhered films.

2.2. Synthesis of graphene film

Graphene is synthesized by the chemical reduction of graphene oxide (2 mg/ml, dispersion in H_2O, Sigma Aldrich) using dextrose and hydrazine hydrate. 0.5 ml of graphene oxide dispersion is diluted with 50 ml of deionized water. 0.1 g of dextrose is added to the dispersion under constant stirring for 30 min. The partially reduced graphene oxide-dextrose mixture thus obtained is heated at 150 °C for two minutes followed by the addition of 0.5 ml of hydrazine hydrate, during which the colour of the solution slowly changed to black indicating the reduction of graphene oxide to graphene.

Graphene film is deposited by nebulized spray pyrolysis technique. The as-prepared graphene dispersion is sprayed in air on a glass substrate heated at 200 °C with compressed air as carrier gas at a pressure of 1 bar. The spray rate and substrate - nozzle distance are optimized as 0.5 ml/min. and 5 cm respectively [17].

2.3. Synthesis of single walled CNT/PEDOT:PSS composite film

PEDOT: PSS (1.3 wt% dispersion in H_2O) and single walled carbon nanotubes (SWCNT, carbon > 90% ≥ 70%, 0.7–1.3 nm diameter) are purchased from Aldrich. 0.35 wt/vol% of SWCNT is dispersed in 3 ml of ethanol and ultrasonicated for an hour. The SWCNT dispersion is mixed with 2 ml of PEDOT:PSS dispersion followed by ultrasonication for 30 min. A homogeneous composite of PEDOT:PSS and SWCNT/PEDOT:PSS is obtained upon ultrasonication with no visible precipitation or agglomerations. The freshly prepared mixture is spin coated on the glass substrate (2000 rpm/200 s) to obtain a thin film of the composite. The as-deposited film is vacuum annealed at 100 °C for an hour.

2.4. Synthesis of ZnO quantum dots

Zinc acetate dihydrate ($Zn(ac)_2.2H_2O$, Sigma-Aldrich), potassium hydroxide (KOH, Sigma-Aldrich) are used as precursors. Cetyl trimethyl ammonium bromide (CTAB, Sigma-Aldrich) is used as surfactant. In a typical synthesis of ZnO QD, ethanolic solutions of 0.005 M $Zn(ac)_2.2H_2O$, 0.05 M KOH and 0.25 M CTAB are prepared and sonicated at 60 °C. The reaction mixture consisted of appropriate volumes of zinc acetate dihydrate, potassium hydroxide and CTAB. The reaction time has been optimized and 60 s is found to be appropriate. Further increase in the reaction time resulted in the formation larger ZnO nanoparticles.

2.5. Material characterization

Systematic analysis on the microstructural characteristics of the materials is carried out using X-ray diffractometer (PANalytical, X-Pert Pro, Cu K_α), Scanning Electron Microscope (Carl Zeiss, SIGMA HV with Bruker Quantax 200 – Z10 EDS Detector), High Resolution Transmission Electron Microscope (HRTEM,JEOL,JEM-2100) and X-Ray Photoelectron Spectrometer (Thermofisher Scientific, K_α, Al source). The optical properties of ICIS thin film, graphene layers, SWCNT/PEDOT:PSS composite and ZnO quantum dot are analyzed using UV–Vis.-NIR spectrophotometer (JASCO, V-670) and spectrofluorometer (Horiba, FluoroLog). Electrical characteristics of ICIS thin film and TCCR layers are investigated using Hall measurement system (Ecopia, HMS-3000). The characteristics of electrode-electrolyte interface is analyzed using electrochemical workstation (Biologic, SP 150) and I–V characteristics of the photoelectrochemical cell is recorded using electrometer (Keithley, 2450).

3. Results and Discussion

3.1. Characteristics of In rich $CuInS_2$ (ICIS) thin film and TCCR layers

The structural characteristics of as-deposited ICIS film (Fig. 1) is analyzed using X-ray diffraction. The films are polycrystalline in nature and are found to have crystallized in chalcopyrite phase of $CuInS_2$ (JCPDS card no. 75-0106). All the prominent peaks appearing the diffraction pattern of ICIS ($Cu/In = 0.5$) thin film are corresponding to stoichiometric $CuInS_2$. Absence of peaks corresponding to secondary phases like In_2S_3, Cu_2S and CuS_2 indicate the phase purity of the material.

Homogeneous, well adherent and continuous ICIS films are obtained by nebulized spray pyrolysis. The film is found to be nanocrystalline with uniform spherical grains (inset in Fig. 2a). Thickness of the film is determined by analyzing film cross section (Fig. 2b) and is found to be 1.2 μm. The ‘In’ rich nature of the film is confirmed by EDAX analysis (Fig. 3). As expected films are found to be indium rich and copper deficient when compared to