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Structural, optical, electrochemical and photovoltaic studies of spider web like Silver Indium Diselenide Quantum dots synthesized by ligand mediated colloidal sol-gel approach

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Silver indium diselenide quantum dots were successively synthesized by colloidal sol-gel method by chelating with organic ligand oleylamine (OLA). The particle size was studied by transmission electron microscopy (TEM) and the size was found about 10 nm. X-ray diffraction (XRD) was used to study crystalline structure of the nanocrystals. The grain size and morphology were further studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The elemental composition was studied by X-ray photon electron spectroscopy (XPS) and energy dispersive x-ray spectroscopy (EDAX). The capping property of OLA in nanocrystal was also demonstrated by Fourier Transform Infrared spectroscopy (FTIR). The band gap was calculated from both cyclic voltammetry and optical absorption and suggest quantum confinement. The solution processed bilayer thin film solar cells were fabricated with n-type Zinc oxide using doctor blading/spin coating method and their photovoltaic performance was studied. The best device sintered at 450 °C showed an efficiency 0.75% with current density of 4.54 mAcm^{-2}, open-circuit voltage 0.44 V and fill factor 39.4%.

1. Introduction

In the exploration of novel functional materials with improved optoelectronic properties, semiconductor nanocrystals are important materials for optical devices [1]. Colloidal sol-gel method gives a large variety of compounds with an inorganic core and a corona of organic stabilizing ligands [2]. Semiconductor nanocrystals, which are smaller in size, show unique optical and electrical properties [3]. These properties are results of quantum confinement of an electron and hole so the semiconductor nanocrystals are called quantum dots [4]. Band broadening of nanocrystals with crystal size has widely applicable in optical devices [5,6]. Chalcopyrite is one common crystal structure of I-III-VI_2 semiconductors with I and III ions ordering in the anion sub lattice sites [7]. In recent years, the colloidal nanocrystals of the type I-III-VI_2 have attracted great attention in photovoltaic and non-linear optical devices due to their unique physical and chemical properties such as low toxicity and high absorption [8] and the size and shape-tunable band gap [9-11]. Silver indium diselenide ($AgInSe_2$, AIS), a ternary semiconductor, has been widely used in a number of optoelectronic devices because of its low band gap (1.2–1.9 eV), high absorption coefficient (~10^5 cm^{-1}) and ternary analogue of Cd Se [9]. Despite the broad research on the ternary and quaternary chalcopyrite based thin film solar cells, monocrystalline silicon solar cells are still dominated in industries because of several factors such as relatively high manufacturing cost in their vacuum deposition process, the difficulty in achieving controllable and uniform composition over large area [12-14]. Cadmium based quantum dots have been used as light absorber since past decade due to their optical properties. However, their applications are becoming more and more limited because of their toxicity [5,6].

Several techniques have been reported to synthesize $AgInSe_2$ macro and nanocrystals that require either high vacuum and high temperature [15,16]. The problem of the vacuum based technique is its high manufacturing cost and low stoichiometric composition of

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Se due to the high volatility of Se-containing compounds. So, it was realized to develop solution based techniques to synthesize ternary and quaternary nanocrystals. Al-Agel & Ghamdi et al. developed a new strategy to synthesize a $AgInSe_2$ thin film by using spin coating method. They also studied the influence of annealing temperature on composition and the crystal structure [17]. Recently, the colloidal solution approaches are more effective and powerful for synthesizing nanocrystals with designed structure and shapes [3,18].

In this communication, we report a simple and relatively green colloidal sol-gel method for synthesizing ternary $AgInSe_2$ nanocrystals by using oleylamine as a chelating ligand/organic solvent. It has been reported that amine can lower the thermal decomposition temperature of the precursor and facilitate the formation of nanoparticles at lower temperature [9]. In addition, oleylamine (OAm) and dodecanethiol (DT) have been widely used as surfactants for synthesizing various nanoparticles and are reported as reagents that promote the anisotropic growth of nanoparticles [19]. Furthermore, they have unique advantages such as high boiling point, low cost, tendency to form metal-OAm complexes at intermediate temperature so that it can controllably decomposed to produce nanoparticles. OAm can form complex compounds with metal ions of the corresponding precursor leading to metastable compounds that can act as secondary precursor and thus be decomposed in a controlled way to yield nanoparticle [20].

Very few works have been reported for solution processed thin film devices using colloidal sol-gel nanocrystals. Our group already reported ternary blend polymer based bulk-heterojunction solar cells by incorporating AIS nanocrystal prepared by ball mill method [21-23]. We report solution processed bilayer device fabricated using AIS nanocrystal prepared by colloidal sol-gel method. The bilayer thin films devices ITO/AIS/ZnO/Al was fabricated on prepatterned Indium oxide tin oxide deposited sequentially by doctor blading and spin coating followed by vacuum deposition of aluminum. All the devices sintered at different temperatures showed some photovoltaic performance with highest power conversion efficiency 0.75%. This work will be promising to fabricate easily processable solution processed devices using sol-gel synthesized ternary quantum dots which are necessary for flexible devices.

2. Materials and methods

2.1. Materials

Selenium powder (Se, 99.99%) and oleylamine (OAm, 70%) were purchased from Sigma-Aldrich. Silver acetate (99.8%) and Indium acetate (99.5%) were purchased from Alfa Aesar. All the chemicals were used as received without purification. ZnO nanopowder (size~10 nm) were purchased from Alfa Aesar. The patterned Indium tin oxide (ITO) glasses (film thickness about 135 ± 15 nm, and sheet resistance is 15 Osq^{-2}) used as substrates were purchased from Luminescence Technology Corporation.

2.2. Synthesis of $AgInSe_2$ quantum dots

A solution of silver acetate (2 mmol, 0.33 g) and Indium acetate (2 mmol, 0.58 g) in 30 ml of oleylamine was heated at 180 °C under a nitrogen atmosphere with continuous magnetic stirring for 30 min resulting a transparent yellow solution as shown in Fig. S1. Next, Selenium (1.58 g, 4 mmol) was dissolved in 15 mL oleylamine by heating to 120 °C with constant stirring in vacuum. The Se solution was injected hot into the original solution resulting immediately black brown turbid precipitate as presented in Fig. S1 and the temperature was gradually increased up to 200 °C in nitrogen atmosphere under magnetic stirring. The solution was kept at that temperature for 1 h. Finally, the product was cooled rapidly to grow $AgInSe_2$ nanocrystals.

The AgInSe2 nanocrystals were separated from resulting solution by centrifugation three times with methanol and then with toluene at 4000 rpm. The nanocrystals were washed with methanol and dried in an oven at 60 °C for overnight. The dried $AgInSe_2$ nanocrystals were used for characterization and device fabrication.

2.3. Characterization

UV–visible absorption spectra were acquired using an Olid® HP8452 Diode Array Spectrometer. Luminescence was measured with a USB2000-Ocean Optics spectrometer. XRD were obtained using an Xpert Pro Philips powder X-ray diffractometer to check phase purity and crystalline nature of nanoparticles. Field emission gun scanning electron microscope (FEI Quanta 650 FEG) supplemented with EDAX (Bruker XFlash detector 1.9) was used for knowing the morphology, size and composition of nanocrystals. A transmission electron microscope (Hitachi H-7000, 75 W) was used knowing morphology of nanocrystals. FTIR spectra were obtained with a Nicolet 6700 in the ATR mode. The morphology of nanoparticles and films were characterized using an Ambios multimode Atomic Force Microscope (AFM) in tapping mode with 300 KHz resonant frequency cantilever. The XPS spectra were measured on a Microlab 310-F spectrometer equipped with an XR-4 twin anode (Al/Mg). The samples were mounted on a stub-type stainless steel holder using double-sided adhesive Cu tape and kept under high vacuum (10^{-8} mbar) overnight inside the preparation chamber before they were transferred into the analysis chamber (10^{-9} mbar) of the spectrometer. The cyclic voltammograms were recorded in the Keithly system connected with potentiostat consisting of three electrodes: working electrode (glassy carbon-carbon electrode), reference electrode (Ag/AgCl (in 3M NaCl) and counter or auxiliary electrode (Pt electrode) in 0.1M tetra butyl ammonium phosphorus Hexafluoride in acetonitrile. Current density-voltage (J-V) measurements were carried out using a Keithley 4200-SCS in the dark and under illumination. The current density-voltage (J-V) photovoltaic measurements of solar cells were carried out by employing an AM 1.5 solar simulator equipped with a xenon lamp. The power of the simulated light was calibrated to 100 W/m^2 by using a reference Si photo-diode.

3. Results and discussions

3.1. Structural and optical properties

The typical high resolution transmission electron microscopy image of the resulting $AgInSe_2$ dots is shown in Fig. 1. The nanoparticles exhibit clusters of varying shape with surfactant at high concentration as shown in Fig. 1a. However, it shows the distinct nanoparticles after dilution with methanol shown in Fig. 1b. The average size of nanoparticles is about 10 ± 2 nm.

Scanning Electron Microscope (SEM) was used for studying the surface morphology and the micro structural features of $AgInSe_2$ nanocrystals.

Scanning electron microscopy (SEM) was used to study the surface morphology and the micro structural features of the thin film. SEM image was obtained for AgInSe2 thin film on glass substrate and shown in Fig. 2. It shows a compact structure with densely packed, spherical and well defined grain with similar size nanocrystals.

Energy Dispersive X-ray Spectrometer (EDS) was carried out to determine the compositional analyses of $AgInSe_2$ nanoparticles. EDS elemental map for nanoparticle is shown in Fig. S2. The three