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Synthesis of colloidal InAs/ZnSe quantum dots and their quantum dot sensitized solar cell (QDSSC) application

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ABSTRACT

We report the synthesis of colloidal InAs/ZnSe core/shell quantum dots (QDs) by the hot injection method. InAs nanocrystals have a narrow band gap of 0.38 eV, a high absorption coefficient, and multiple exciton generation; hence, they are promising candidates for application in solar cells. However, poor coverage of the titania layer causes a low solar efficiency of ~1.74%. We synthesized type-I InAs/ZnSe core/shell QDs as an effective solution; they are expected to have enhanced solar cell efficiency because of the different wettability of the ZnSe shell and their superior stability as compared to that of the unstable InAs core. We characterized the QDs by powder X-ray diffraction, transmission electron microscopy, and absorption and emission spectroscopy. The particle size increased from 2.6 nm to 5 nm, whereas the absorption and emission spectra exhibited a slight red shift, which is typical of type-I structured core/shell QDs. We then fabricated QD-based solar cells and investigated the cell properties, obtaining an open-circuit voltage (V_{OC}) of 0.51 V, a short-circuit current density (J_{SC}) of 12.4 mA/cm^2, and a fill factor (FF) of 44%; the efficiency of 2.7% shows an improvement of more than 50% as compared to the values in previous reports.

1. Introduction

Colloidal semiconductor nanocrystals (i.e., quantum dots, QDs) have received much attention because their absorption and emission properties are controlled by their sizes. Therefore, intensive research has been performed on the fabrication of QDs, and their properties and applications have been investigated. Notably, fabrication is usually based on modification of the structure, including alloying, core/shell fabrication, and doping [1]. Meanwhile, cadmium toxicity has recently emerged as an issue, and thus alternatives to CdSe QDs, the most frequently used QDs, are urgently needed. Among the possible substitutes, III–V QDs are widely valued because of their large Bohr radius and good quantum confinement effects. Although they present synthetic difficulties due to their covalent bonding character, the potential for opto-device applications is immense because of their high photoelectron efficiency [2–4]. Their peculiar optical characteristics have resulted in various applications such as light-emitting diodes (LED) [5–7], solar cells [8–10], and bio imaging [11–13]. Especially, QD-sensitized solar cells (QDSSCs), which are analogs of the dye-sensitized solar cells (DSSCs), have been extensively investigated because QDs have various benefits as sensitizers, including having absorption coefficients higher than those of dyes and a wide absorption range. QDSSC operation is based on charge separation by a sensitizer and subsequent charge transport through the mesoporous TiO_2 and poly(3-hexylthiophene) (P3HT) layers (see Scheme 1). QDs frequently used as sensitizers are CdSe, CdS, $CuInS_2$, InP, and PbS [14–19]. However, their solar efficiency is either below expectations or unobtainable because of loading problems within the mesoporous TiO_2 layer. As a solution, mercaptopropionic acid (MPA) was reported to enhance the surface interaction between TiO_2 and QDs, as well as the short-circuit current density (J_{SC}) and open-circuit voltage (V_{OC}) [20,21]. Other reports presented the use of core/shell-structured QDs to improve the solar efficiency [22–25]. The inorganic shell, which removes the surface traps, enhances the mean electron lifetime and electron diffusion length, significantly improving the efficiency of the cell [15]. InAs, which is representative of III–V QDs, has a very narrow band gap of 0.38 eV; as a result, it absorbs light in the near-infrared (NIR) region and shows multiexciton generation effects [26,27]. Therefore, InAs QDs are expected to be successful materials for solar cells, similar to PbS QDs, showing superior quantum efficiency [28]. However, until now, research on InAs

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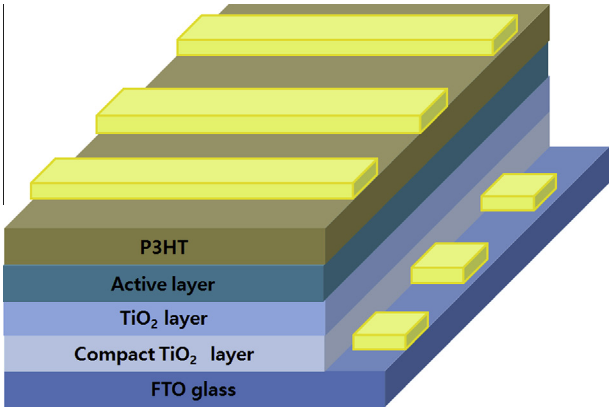

Scheme 1. Solar cell structure of InAs/ZnSe QDs.

QDs for solar cells has rarely been reported, although their bioimaging applications are widely known. The difficulty in achieving an optimum band alignment between the TiO_2 (electron transport layer) and the QD layers and the poor coating of the TiO_2 layer are among the main reasons InAs QDs are rarely used [21]. Thus, to our knowledge, there are very few reports on solar cells based on InAs QDs, and the best results show an efficiency of 1.74% [29]. Here, we present photovoltaic devices based on InAs/ZnSe core/shell QDs. ZnSe shells are coated on the InAs core to improve the adsorption properties and stability of the core by removing the surface traps, thus increasing the short-circuit current [30–32]. The shell thickness in particular was finely controlled to prevent exciton entrapment inside the core by the type-I core/shell band alignments [33–35].

2. Experimental

2.1. Materials

Indium (III) acetate (Sigma Aldrich, >99%), myristic acid (Sigma Aldrich, >99%), 1-octadecene (ODE, Sigma Aldrich, 90%), diethylzinc solution (Sigma Aldrich, 1 M in hexane) were purchased. The other chemicals, tris(trimethylsilyl) arsenide ($(TMS)_3As$) [36] and trioctylphosphine selenide (TOP-Se, 1 M) were prepared accordingly. The TOP-Se stock solution was prepared in a glove box; TOP (10 ml) and selenium shot (Se, 10 mmol, 0.79 g) were mixed in a 100 ml Erlenmeyer flask to prepare a 1 M solution. The flask was heated at 280 °C for approximately 30 min, until the dark grey metals were dissolved.

2.2. Synthesis of InAs/ZnSe QDs

Indium (III) acetate (0.25 mmol, 73 mg), myristic acid (0.75 mmol, 171 mg), and ODE (5 ml) were added to a 50 ml three-neck flask. The solution was degassed at 110 °C for 2 h. After degassing, the solution in the flask was heated to 300 °C and $(TMS)_3As$ (0.04 mmol, 11.8 mg) mixed with 1 ml of ODE was swiftly injected under nitrogen flow. After the injection, the solution was left to age at 290 °C for 20 min to stabilize the nanocrystals. Sequentially, $(TMS)_3As$ (0.08 mmol, 23.5 mg) mixed with ODE (1 ml) was dropped into the reaction solution during a period of 1 h at 280 °C to stimulate the growth. To cover the nanocrystals with the inorganic ZnSe shells, the precursors, which are a diethylzinc solution ($(Et)_2Zn$, 0.1 ml) and a TOP-Se solution (0.1 ml), were added to 2 ml of ODE. The solution was added dropwise to the reaction flask at 230 °C for 1 h. Then, the flask was removed from the heating mantle and cooled down to room temperature; the QDs were subsequently purified by high-performance liquid chromatography (HPLC) in ethanol and centrifuged.

2.3. Device fabrication

In fabricating the bottom electrode, 20 nm TiO_2 nanoparticles (ENB Korea) were dispersed in ethanol (1:3 by weight, Aldrich, anhydrous) and spin coated onto a fluorine-doped tin oxide (FTO) substrate (AMG Tech) at 3500 rpm (58 s^{-1}) for 30 s. The covered TiO_2 electrode was sintered at 500 °C for 2 h in a muffle furnace and then subjected to $TiCl_4$ treatment in a 40 mM solution in deionized (DI) water at 70 °C for 30 min. The substrates were removed, rinsed with DI water, and heated at 450 °C for 60 min. The thickness of the main active layer was 400 nm.

For colloidal QD (CQD) deposition, InAs/ZnSe at a concentration of 35 mg/ml in hexane was deposited by a spin coater in a layer-by-layer fashion onto the substrate through a 0.45 μm filter and spin casted at 4000 rpm for 20 s. Finally, the sample was rinsed with methanol by spinning the substrate at 2500 rpm for 10 s. The same process was repeated 10 times until the desired thickness of the InAs/ZnSe CQD film was reached. The P3HT hole transfer material was spin coated using a 10 mg/ml P3HT solution in chlorobenzene; the solution was filtered through a 0.45 μm filter for 20 s and then spin casted at 3500 rpm. Finally, the top electrode was deposited by evaporation of a 70-nm-thick Au film. Each device had an area of 0.145 cm^2.

2.4. Characterization

Optical absorbance spectra of the solutions were recorded using a ultraviolet–visible–NIR (UV–vis–NIR) spectrophotometer (V-670, JASCO) and a spectrofluorometer (USB-4000, Ocean Optics). Transmission electron microscopy (TEM) images were taken on a FEI Tecnai G2 F30 Super-Twin microscope operating at 300 kV. X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima III diffractometer equipped with a rotating anode and a Cu Ka radiation source ($\lambda = 0.15418$ nm).

3. Results and discussion

3.1. Characteristics of InAs and InAs/ZnSe core/shell QDs

The QD synthetic procedure adopted in the present study is similar to the method developed by Xiaongang Peng [37]. The size of the InAs core could be controlled by the precursors and surfactants. In this study, $In(OAc)_3$ and $(TMS)_3As$ were used as the precursors for the InAs core, while myristic acid was used as the surfactant. For the ZnSe shell growth, $(Et)_2Zn$ and TOP-Se solutions were slowly added to the core solution. The detailed procedure is presented in Section 2. Grown InAs cores had a diameter of 2.63 nm and their size distribution was equal to 0.11 nm, indicating that they were highly monodispersed nanoparticles (Fig. 1a and c). An absorption peak is observed at 730 nm. After the ZnSe shell growth, the particle size increased (4.98 ± 0.28 nm, Fig. 1b and d) and the absorption peak shifted to 740 nm (Fig. 1e), indicating that ZnSe shells of two monolayers were deposited (the lattice constant of ZnSe is 0.567 nm). The red shift in the absorption spectra is a general phenomenon in type-I core/shell QDs. After the ZnSe shell was grown epitaxially, the QDs showed improved photoluminescence because the core surface was converted into an interface between the core and shell; as a result, the surface traps disappeared. In such systems, the electron and hole carriers are confined to the core because of the type-I band offsets. In addition, core/shell-structured QDs as sensitizers stabilize the surface; therefore, in solar cell devices, the excitons