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Spectral broadening in quantum dots-sensitized photoelectrochemical solar cells based on CdSe and Mg-doped CdSe nanocrystals

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ABSTRACT

In order to absorb a broad spectrum in visible region, a co-sensitized TiO_2 electrode was prepared by CdSe and Mg-doped CdSe quantum dots (Q dots). The power conversion efficiency of the co-sensitized Q dots photoelectrochemical solar cells (PECs) showed 1.03% under air mass 1.5 condition (I = 100 mW/cm^2), which is higher than that of individual Q dots-sensitized PECs. The incident-photon-to-current conversion efficiency of the co-sensitized PECs showed absorption peaks at 541 and 578 nm corresponding to the two Q dots and displayed a broad spectral response over the entire visible spectrum in the 500–600 nm wavelength domains.

1. Introduction

Due to rapid growth in the world economy, energy problems have considerable attention in the past several decades [1]. To provide energy alternatives, researchers have been developing renewable energies including solar, nuclear, wind, hydraulic, and bio power [2]. Among these alternatives, solar-to-electric energy conversion systems have always been a fascinating and challenging frontier for science and applications [1–3].

One classic example of such solar-to-electric energy conversion systems are dye-sensitized photoelectrochemical solar cells (PECs), which consist of three main components: a dye-sensitized nanocrystalline TiO_2 layer on a transparent conductive oxide (TCO) electrode, an iodide/triiodide redox couple in an organic solvent as an electrolyte, and platinum on a TCO as a counter electrode [1,4]. Another example is bulk heterojunction solar cells, which consist of a hole transporting materials on a TCO electrode, organic semiconductor layers with three-dimensional bicontinuous network, and a metal layer as counter electrode [3,5]. However, even though dye-sensitized PECs and bulk heterojunction solar cells have showed high efficiency, combinations of materials and device architectures are still being sought to further improve the performance and cost of solar cells.

As an alternative, semiconductor quantum dots (Q dots) that adsorb light in the visible region, such as CdS [6], CdSe [7], and PbS [8] have been used as sensitizers in PECs. In general, Q dots have significant advantages over dyes [6–8]. Q dots provide the ability to match the solar spectrum better because their absorption spectrum can be controlled by changing the size of the Q dots. In addition, it is also possible to use hot electrons to generate multiple electron–hole pairs (exciton) per photon through the impact ionization effect. However, despite of these advantages Q dots-sensitized PECs still show low photoconversion efficiency (<1%) [7,8].

In order to improve the photoconversion of dye-sensitized PECs, one special method called co-sensitization has been used. It consists of two sensitizers with different absorption regions used to extend the photoresponse of the TiO_2 electrode into the visible region [9,10]. Grätzel and colleagues reported the co-sensitization of the TiO_2 electrode with two organic dyes that are complementary in their spectral responses [9]. The power conversion efficiency of the co-sensitized organic dye solar cell showed 6.4% under air mass (AM) 1.5 condition (100 mW/cm^2), which is higher than that of individual dye-sensitized PECs. However, the improvement of photoconversion in PECs by co-sensitization has not yet been fully understood. Despite their expected potential to enhance solar energy conversion efficiency due to complementary in their spectral

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responses, no reports have been found in the literature where co-sensitization has been used in Q dots-sensitized PECs.

With the aid of previous research on PECs [6,11,12], we describe a methodology for improved photoconversion efficiency of Q dots-sensitized PECs using co-sensitization. The power conversion efficiency of the co-sensitized PECs showed 1.02% under AM 1.5 condition (I = 100 mW/cm^2), which is higher than that of individual Q dots-sensitized solar cells. The incident-photon-to-current conversion efficiency (IPCE) of the co-sensitized solar cell showed absorption peaks at 541 and 578 nm corresponding to the two Q dots and displayed a broad spectral response over the entire visible spectrum in the 500–600 nm wavelength domains.

2. Experimental details

2.1. Materials

Chemicals were purchased from Aldrich and used as received. Indium tin oxide (ITO, 10 Ω cm) glass substrates were purchased from Samsung Corning Co. (Korea). The synthesis of CdSe (~6 nm) and Mg-doped CdSe (~9.8 at.%, ~8 nm) Q dots were carried out similar to the reported procedure [13,14].

2.2. Preparation of co-sensitized TiO_2 electrode with CdSe and Mg-doped CdSe Q dots

The TiO_2 on ITO were prepared using a doctor blade method and then annealed at 450 °C for 30 min. The TiO_2 films had a thickness of 4 μm [6]. The annealed film obtained was impregnated with a mixture of CdSe and Mg-doped CdSe (1:1) in water for 72 h at room temperature. The resulting co-sensitized TiO_2 film was washed with ethanol. Ligand exchange procedure was carried out similar to as reported [7]. All samples were characterized by UV–vis absorption spectroscopy (Varian, CARY100).

2.3. Measurements

To measure power conversion efficiency, the co-sensitized TiO_2 electrode was incorporated into thin-layer sandwich-type cells with Pt sputtered ITO as the counter electrode, a spacer film, and an electrolyte solution. The electrolyte was 0.1 M polysulfide solution. The co-sensitized photo-electrode (0.28 cm^2) was illuminated by 100 mW/cm^2 white light intensity. The IPCE measurements were carried out without bias illumination with respect to a calibrated Melles–Friot silicon diode. IPCE was measured by changing the excitation wavelength (Photon counting spectrometer, ISS Inc. and Kiethley 2400 source meter).

3. Results and discussion

3.1. Preparation of CdSe, Mg-doped CdSe Q dots and co-sensitized TiO_2 electrode

Fig. 1 shows high-resolution transmission electron microscope (HR-TEM) images of CdSe and Mg-doped CdSe Q dots, which present particle diameter of ~6 nm and ~8 nm, respectively. Furthermore, the inset of magnified HR-TEM images show the high crystalline morphology with the preferential growth along (1 1 1) and (2 2 0). We also took X-ray diffraction (not shown), which present (1 1 1), (2 2 0) and (3 1 1) planes.

Fig. 2a shows UV–vis absorption spectra of individual CdSe, Mg-doped CdSe solution and (CdSe + Mg-doped CdSe) (1:1) in solution. By comparing the excitonic transition to the absorption curve reported by our recent paper, once again, we identified the particle diameter of these samples as ~6 nm (λ_{max} = 578 nm) and ~8 nm (λ_{max} = 541 nm), respectively [13,14]. In general, the shift of the onset absorption to lower wavelengths with decreasing particle size represents size quantization effects in these particles [7]. However, compared to typical cases, even though size of Mg-doped CdSe Q dots is higher than that of those without doped CdSe Q-dots, the Mg-doped CdSe Q dots show the obvious blue shift in the UV–vis absorption spectra due to the increase in the bulk energy band gap, which is decisive evidence for the real Mg doping in the CdSe lattices [13,14]. In mixture solution of CdSe and Mg-doped CdSe Q dots, the UV–vis absorption spectrum appeared as both maximum absorption park of CdSe (578 nm) and Mg-doped CdSe Q dots (541 nm). This phenomenon also appeared after formation of Q dots on TiO_2 electrode (Fig. 2b), which thus confirms both the binding of CdSe and Mg-doped CdSe Q dots to the TiO_2 surface. It is important to note that complementary in their spectral responses can enhance photoconversion efficiency of PECs [9,10].

3.2. Performance of co-sensitized Q dots PECs

The J–V characteristics of co-sensitization of TiO_2 electrode with two different CdSe Q dots under the illumination condition (I = 100 mW/cm^2) are shown in Fig. 3a. The corresponding photovoltaic parameters [short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (ff), and power conversion efficiency (E_{ff})] of these

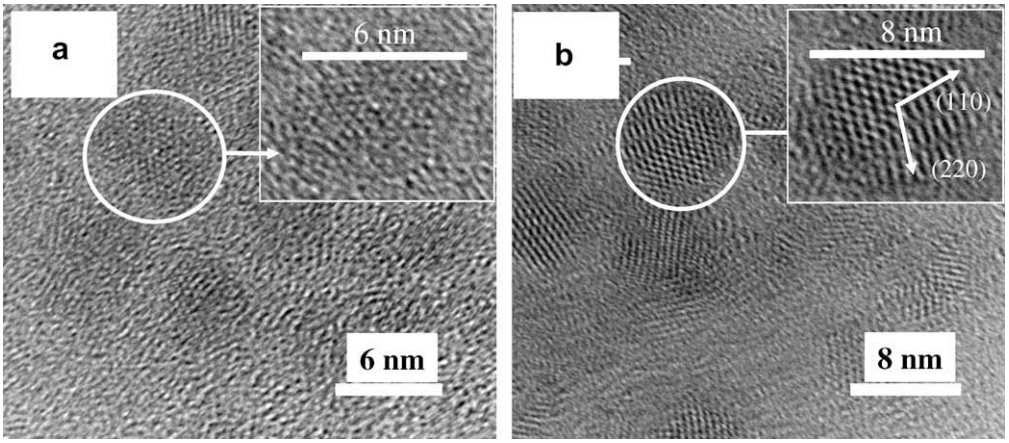

Fig. 1. HR–TEM images of (a) CdSe and (b) Mg-doped CdSe (inset: magnified TEM image).