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Invasion of CdSe Nanoparticles for Photosensitization of Porous TiO_2

Ju-Hyun Ahn, R.S. Mane, V. V. Todkar and Sung-Hwan Han[*]

Inorganic Nanomaterials Laboratory, Department of Chemistry, Hanyang University, Sungdong-Ku,
Haengdang –dong 17, Seoul, Korea 133-791
[*]E-mail: shhan@hanyang.ac.kr

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Invasion of CdSe nanoparticles in porous TiO_2 film is carried out using low temperature chemical process. The presence of self-grown CdSe nanoparticles in porous TiO_2 was confirmed from optical absorption study. The structural and surface morphological properties were studied by using and X-ray diffraction and scanning electron microscopy techniques, respectively. Increase in electrochemical performance due to CdSe nanoparticles invasion is observed and reported.

Keywords: CdSe nanoparticles; Porous TiO_2; Surface morphology; Optical absorption;
Photoelectrochemical cells

1. INTRODUCTION

The major goals of modern science and engineering that will have a great impact on technological applications are the efficient utilization of solar energy [1]. TiO_2 has been one of the most extensively studied oxides because of its remarkable optical and electronic properties. Due to the strong confinement effects, the electrical and optical properties of nanocrystalline thin films are varying significantly with grain size. This tuned physical properties of nanocrystalline thin films makes them an important category materials that can find potential applications in photoelectronic devices [2]. The use of semiconductor nanocrystalline thin films as a sensitizer has some advantages in solar cells as, (a) the band gap of the nanocrystals can be tuned by controlling their size to that the absorption spectrum can be tuned to match the spectral distribution of sunlight and a full-spectrum solar cell can be fabricated more easily, (b) nanocrystals have a large extinction coefficient due to their quantum confinements and intrinsic dipole moments, leading to rapid charge separation, and (c) semiconductor nanocrystals have a robust inorganic nature [3].

In this communication, we report the effect of CBD self-grown CdSe nanoparticles into porous TiO_2 films prepared by spin coating method on the structural, optical, morphological and photoelectrochemical properties. The self-grown CdSe nanoparticles into porous TiO_2 improved overall photoconversion efficiency.

2. EXPERIMENTAL PART

The transparent indium-doped-tin oxide (ITO) glass substrate was supplied by SAMSNG (In-SnO_2 coated glass, 80 Ω/sq, 90% transmittance in the visible light). The substrates were sonicated consecutively with distilled water, acetone, and ethanol. Commercial TiO_2 nanoparticles of P25 (Degussa) in the form of powder was used as a raw material. A viscous slurry of TiO_2 prepared by mixing with surfactants such as Triton X-100, 2,4-Pentanedione (99%), was applied on the ITO-coated glass with 2000 rpm for 30 s. For pre-thermal treatment, spin coated TiO_2 film electrode was calcined in static air at 450 ^{0}C temperature for 30 min, which was used for next step as a porous TiO_2 for CdSe nanoparticles invasion. The nanoparticles of CdSe were prepared by CBD using the procedure described previously [4, 5]. Namely, we used the deposition solution containing 0.1 M cadmium chloride and 0.1 M sodium selenosulphate (obtained by constant stirring the mixture of selenium powder and sodium sulphite for 6 h at 50 ^{0}C). It is to be noted that invasion of CdSe nanoparticles was carried out at room temperature since at higher temperature; a quick reaction was observed resulting into an increase in grain growth inefficient to penetrate into TiO_2 pores. Before the deposition, the TiO_2 electrode was degreased thoroughly with distilled water. The substrates were then placed at an angle of ca. 20^0 off normal in glass containers with the deposition solution. The deposition proceeded at room temperature for 10 h, as after this deposition time, solution became deep red indicating growth of large CdSe nanoparticles. After the deposition, porous TiO_2 electrode with self-grown CdSe nanoparticles was taken out from the bath, and dried. Here for improving crystallinity of CdSe, air annealing of self-grown CdSe nanoparticles into porous TiO_2 was carried out at 100 ^{0}C for 1 h [6, 7].

An electrode of porous TiO_2 with self-grown CdSe nanoparticles was characterized with X-ray diffraction (XRD, Rigaku, Cu-Karadiation) operated at 40 kV and 100 mA for the structural elucidation, scanning electron microscopy (SEM, Jeol) for the film thickness and surface morphology study. The self-growth of CdSe nanoparticles in porous TiO_2 was confirmed by comparing the optical absorbance spectrum of porous TiO_2 with and without CdSe nanoparticles using UV-vis photospectrometer in the wavelength range of 370 to 800 nm. The band-gap energies of TiO_2 film electrodes with and without CdSe were determined using the band edge relation of semiconductor. The photocurrent–voltage (*I-V*) curves of TiO_2 electrode with and without CdSe nanoparticles were measured by fixing it with platinum electrode of 1 mm thick spacer using cello tape and filling with 0.1M polysulphide electrolyte at 80 mW/cm^2 light intensity illumination (The light intensity was measured with a power analyzer and a calibrated thermal smart sensor) by exposing an effective surface area of 0.28 cm^2 .

3. RESULTS AND DISCUSSION

The porous TiO_2 electrode formed with spin coating method provides 30-40 nm pore size and 5-6 μm thickness, can permit CdSe nanoparticles growth by itself which is one of the sensitizers. It is

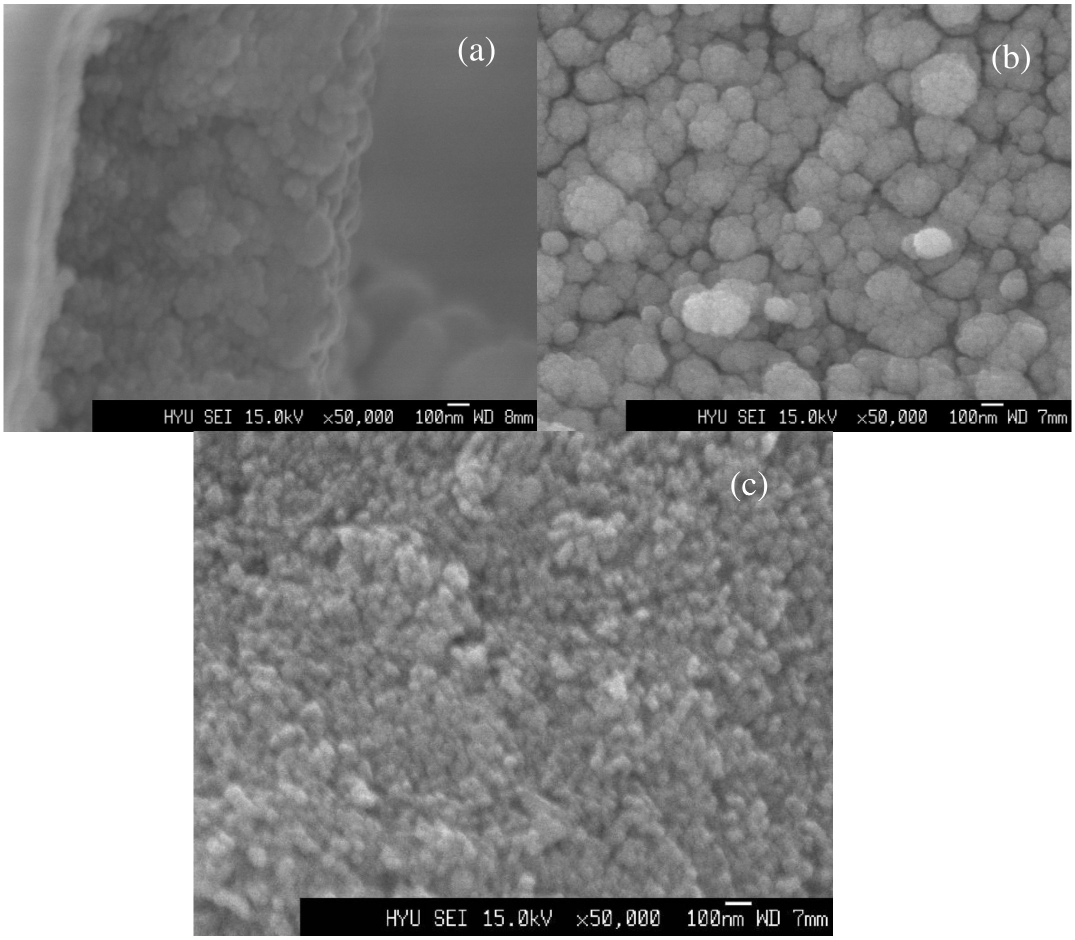

Figure 1. (a) Cross-section SEM image of self-grown CdSe into TiO_2 porous electrode in addition to its surface morphology with (b) and without (c) CdSe nanoparticles.

well known that the $SeSO_3^{2-}$ undergoes rapid hydrolysis to give Se^{2-}, which reacts with $Cd(NH_3)_4^{2+}$ (formed from the reaction of $CdCl_2$ and ammonium hydroxide solution) to precipitate CdSe. In the present case, due to high pH (~10), deposition was carried out for 10 h at room temperature. Due to the self growth of CdSe, white TiO_2 film electrode became red in color and after annealing turned blackish which was homogeneous and strongly adherent to the substrate. Fig.1 (a) shows the cross-sectional view (5-6 micrometer thick) porous TiO_2 film electrode with self-grown CdSe nanoparticles. It is expected that the CdSe nanoparticle nucleation started into the pores of TiO_2 covering TiO_2 grains as inside the film there is no much grain size difference between the TiO_2 and CdSe. Once, the critical grain size is reached (i.e. the size of CdSe grain is equal to the pore size provided by TiO_2), further the grain growth might have prohibited making difficult to distinguish them. Fig.1 (b, c) shows the surface morphologies of TiO_2 electrode with (b) and without (c) CdSe. The film surface of porous TiO_2 is smooth and uniform with equally distributed nanometer sized grains. However, after CdSe deposition the film surface changed as it is of islands aggregated of 30 to 40 nanoparticles. This surface morphology is not surprising here; as is well known for the chemically deposited CdSe film surfaces

[6] with indication that the only limited (self-grown CdSe nanoparticles) are enclosed into porous TiO_2 leaving larger grains onto the surface in relatively big size islands [8].

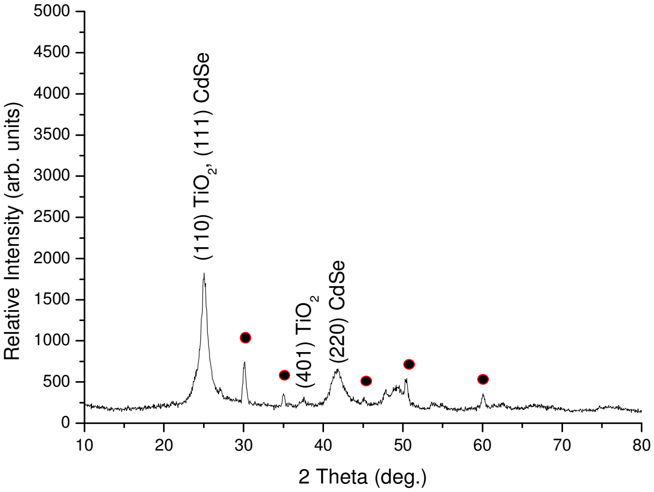

Figure 2. The XRD pattern of TiO_2 film electrode with CdSe nanoparticles.

Fig. 2 shows the XRD pattern of self-grown CdSe nanoparticles in porous TiO_2 electrode. The XRD pattern shows sharp, distinct TiO_2 and CdSe reflection peaks in addition to ITO substrate at 30, 35, 45, 51, 61 degrees, as marked by filled circles. The presence of CdSe peak at 42.44^0 [1901-91 JCPDF File] is the indication that CdSe is self-grown into porous TiO_2. In Fig. 3 we show the optical absorbance as a function of incident photon radiation wavelength of TiO_2 film with and without CdSe nanoparticles. The position of band edge for porous TiO_2 is very close to 500 nm which is in fact due to the formation of relatively thick film in spite of knowing TiO_2 is a direct band gap semiconductor of 3.2 eV. For self-grown CdSe porous TiO_2 film, there is a considerable red-shift with respect to the porous TiO_2, confirming the invasion of CdSe self-grown nanoparticles. Here, as reported earlier [5],

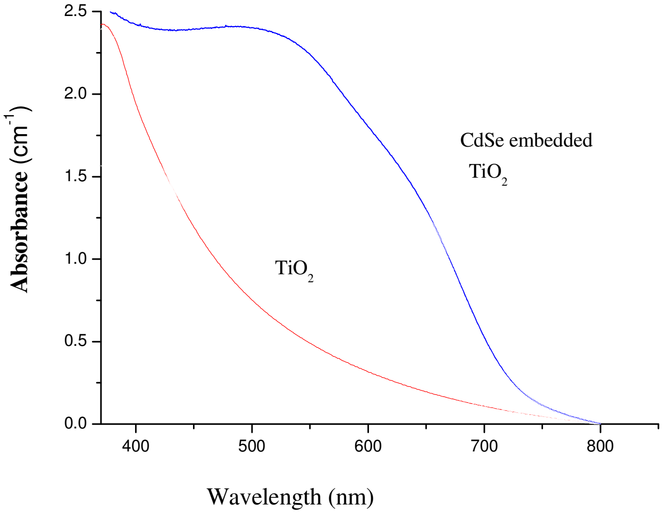

Figure 3. Optical absorbance change with and without CdSe nanoparticles TiO_2 electrode.

no separate transitions for CdSe and TiO_2 are noticed, revealing the formation of composite film instead of bilayers. Due to self-grown CdSe nanoparticles, almost all range of visible region is covered by porous TiO_2 film electrode which has advantaging features for photoelectrochemical cell. Fig.4 shows the *I-V* performance of self-grown CdSe nanoparticles intoTiO_2 electrode in dark and under illumination of light in polysulphide electrolyte. The non-photoactivity of TiO_2 electrode in polysulphide electrolyte is well-familiar due to its high band gap energy. After light illumination, the enhancement of the photocurrent and photo-voltage for the CdSe self-grown TiO_2 electrode was observed which can be ascribed to the effective charge carrier separation and transportation throughout the particles [9]. Under visible light irradiation, only CdSe can be activated. The conduction band level of CdSe is deemed to be higher than that of TiO_2[10]. This may facilitate the interfacial electron transfer from CdSe to TiO_2. The photo-generated electrons are injected from the conduction band of CdSe into TiO_2 and accumulate at the lower-lying conduction band of TiO_2 resulting the generation of photocurrent and photo-voltage. For present case, with CdSe nanoparticles, porous TiO_2 electrode showed photoconverion efficiency of 0.08%, fill factor of 31%, open circuit voltage of 0.15 V and short circuit current of 1.77 mA/cm^2. The poor performance of the cell may be due to the poor fill factor and short circuit current and open circuit voltage. Direct contact of CdSe nanoparticles to the ITO surface may be responsible for poor cell performance.

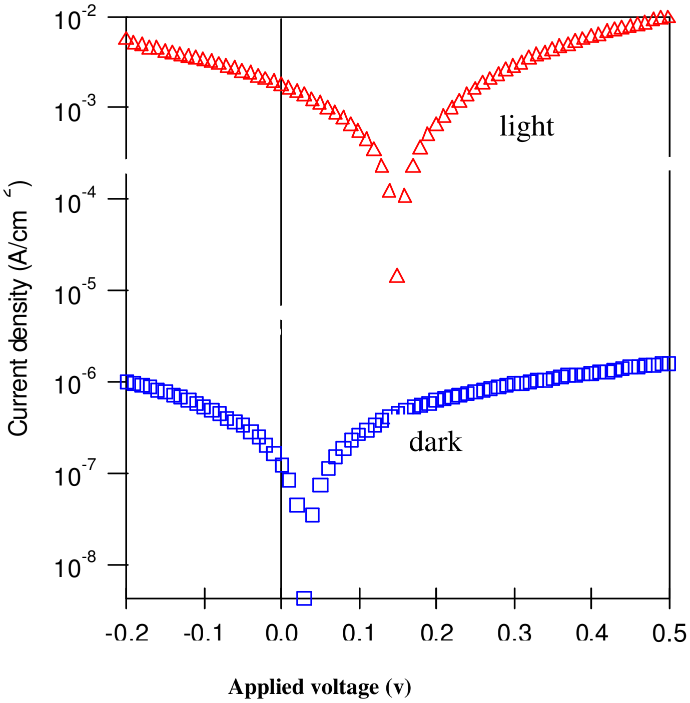

Figure 4. The *I-V* performance of self-grown CdSe nanoparticles into porous TiO_2 film electrode (□-dark and Δ-light).

4. CONCLUSIONS

In conclusion, this study demonstrates the invasion of CdSe nanoparticles into porous TiO_2 for developing efficient photoelectrochemical solar cells. Invasion of CdSe nanoparticles into porous TiO_2 was confirmed from optical absorption study. Invasion of CdSe nanoparticles into porous TiO_2 electrode increases the photoconversion efficiency of 0.08%, fill factor of 31%, open circuit voltage of 0.15 V and short circuit current of 1.77 mA/cm^2, respectively.

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