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Photoacoustic characterization of CdSe quantum dots adsorbed on different morphologies of nanostructured TiO_2 for photovoltaic applications

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1. Introduction

Dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO_2 semiconductor electrodes have received significant attention because of their high efficiency and relatively inexpensive fabrication procedure compared with conventional silicon based solar cells.[1] Instead of using molecular dyes, inorganic quantum dots (QDs), such as CdS, CdSe, and PbS, are considered as highly promising next-generation sensitizer, which have the following advantages over dyes.[2] Firstly, easy tuning of the optical band gap is tuned by controlling the QD size and composition. Secondly, larger extinction coefficient enables the device thickness to be thinner. Thirdly, possibilities of generating multiple excitons from single photon absorption create through the impact ionization effect, which can push the theoretical maximum conversion efficiency of the devices to 44%.[3]

The quality of QDs is very important for quantum dot sensitized solar cells (QDSSCs) performance because of recombination sites, such as surface states and internal defects. Optical absorption measurements for QDs are useful, and the quality can be studied by optical absorption spectra, which are proportional to exponential changes in the absorbed light energy below the absorption edges. These edges provide information on the band structure, disorder, defects and electron-phonon interaction. In this study, the optical absorption properties of CdSe QDs adsorbed on TiO_2 electrodes were investigated using the photoacoustic (PA) technique, which is useful for highly scattering materials.[4] PA technique is based on a photothermal process and has several advantages as follows: (1) enables light absorption measurements of opaque and scattering media, (2) nondestructive and noncontact measurement, (3) characterizations of thermal and optical properties, (4) spectral depth profiling.

2. Experiments

Inverse opal (IO) TiO_2 films were prepared on a fluorine-doped tin oxide (FTO) substrate by method described by Diguna et al.[5] The polystyrene (PS) colloidal crystals were assembled by immersing FTO substrate vertically in 0.1 wt.% monodisperse PS suspension and evaporating the solvent in an oven at 40 °C for 2 days. The voids in PS templates were infiltrated with 10 µl drop of 2% $TiCl_4$ in methanol solution. Thereafter, the infiltrated templates were submitted to a hydrolysis process for 30 min and subsequently heated to 80 °C in the air. This process was repeated three times. Finally, the template was removed by heating at 450 °C for 1 h in the air. For comparison, nanostructured TiO_2 was fabricated by method as previously report.[6] The TiO_2 pastes were applied onto FTO substrates using the doctor blade method, followed by sintering at 450 °C for 30 min.

The CdSe QDs were adsorbed on the TiO_2 electrode using a successive ionic layer adsorption and reaction (SILAR) method. The TiO_2 electrode was immersed into two different solutions for about 30 s each, one consisting of 0.03 M $Cd(NO_3)_2$ dissolved in ethanol and the other containing the 0.03 M Se^{2-} in ethanol. Following each immersion, the films were rinsed for 1 min using ethanol. This immersion cycle was repeated from 3-27 cycles.

PA measurements were carried out by using a gas-microphone PA technique. A monochromatic light is obtained through a monochromater and its intensity is modulated using a mechanical chopper. The modulated light is irradiated on the sample placed inside the PA cell. The light absorbed by the sample is converted into heat by nonradiative relaxation process, which results in a pressure fluctuation of the air inside the cell. The pressure fluctuation is detected as the PA signal by a microphone. In this study, PA measurements were carried out in the wavelength range between 273-800 nm with a modulation frequency of 33 Hz at room temperature.

The photovoltaic properties were studied using J-V measurement. Sandwich structure solar cells were assembled using a CdSe QD sensitized electrode as the working electrode and a counter electrode prepared of Cu_2S film on brass. A polysulfide electrolyte was used as the redox couple. The photovoltaic characteristics were measured using a solar simulator with the standard

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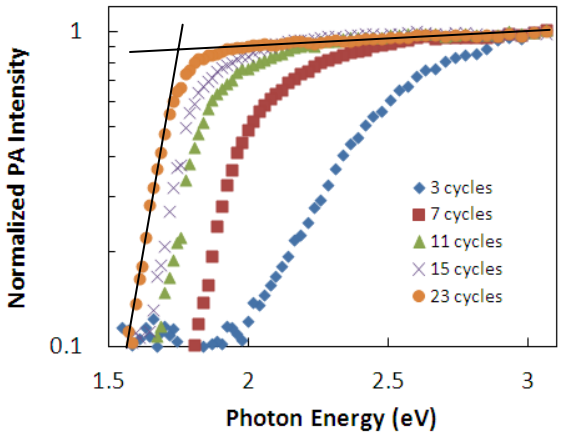

Fig. 1 PA spectra of CdSe adsorbed on inverse opal TiO_2 with different SILAR cycles

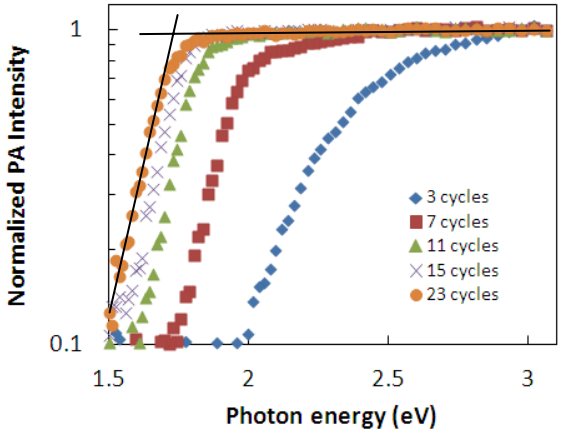

Fig. 2 PA spectra of CdSe adsorbed on nanostructured TiO_2 with different SILAR cycles

test condition (AM1.5, 100 mW/cm^2).

3. Results and Discussions

Fig. 1 shows the PA spectra of CdSe QD adsorbed on the inverse opal TiO_2 electrodes and **Fig. 2** shows the PA spectra of CdSe adsorbed on the nanostructured TiO_2 electrodes with different SILAR cycles. The spectra are normalized to the photon energy of 3 eV. The PA shoulder point can assume to be the first excitation energy (E_1). The plot of logarithmic PA intensity versus photon energy is linearity below the PA shoulder point, which is the Urbach tail and follows the functional dependence.[7]

$$P = P_0 \exp[\sigma(h\nu_0 - h\nu)/kT] \quad (1)$$

Where $h\nu$ is the energy of the incident radiation, P_0 and ν_0 are material parameters. The steepness factor, σ, is the slope of the exponential optical absorption edge below the first excitation energy, and reflects the crystal quality of the material, such as defects, impurities, etc.

Figs. 3 and **4** show the dependence of the steepness factors and the efficiency of CdSe adsorbed on TiO_2 with different SILAR cycles. The steepness factor increases significantly from 3 to 7

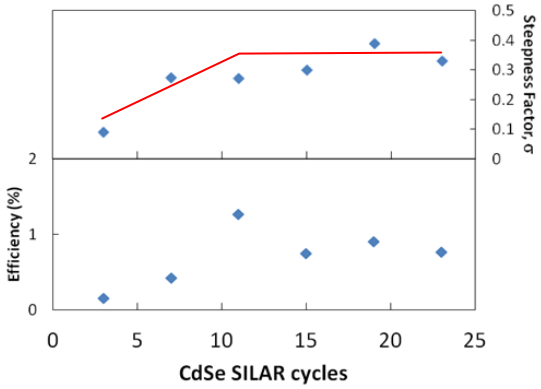

Fig. 3 Dependence of the steepness factors and the efficiency of CdSe adsorbed on inverse opal TiO_2 with different SILAR cycles

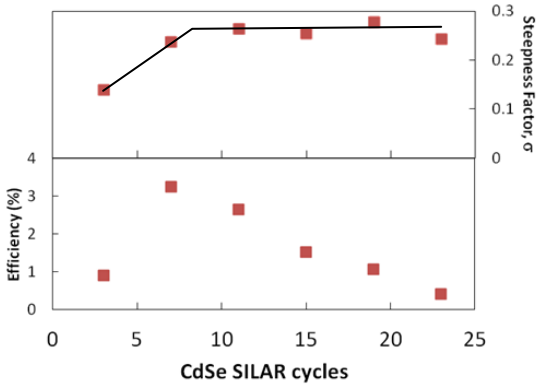

Fig. 4 Dependence of the steepness factors and the efficiency of CdSe adsorbed on nanostructured TiO_2 with different SILAR cycles

cycles, in which this trend is similar for both of inverse opal and nanostructured TiO_2 electrode. For the energy conversion efficiency, the maximum efficiency conditions are 11 cycles for inverse opal TiO_2 electrodes and 7 cycles for nanostructured TiO_2 electrodes. The tendencies of the steepness factor and the efficiency have a possibility that they correlate with each other.

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