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Photoacoustic and photoelectrochemical characterization of CdSe-sensitized TiO_2 electrodes composed of nanotubes and nanowires

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Abstract

Morphology of titanium dioxide (TiO_2) electrodes and the choice of the sensitizers have been important factors for the improvement of dye-sensitized solar cell (DSSC) efficiency. TiO_2 electrodes, having a higher degree of order than random fractal-like assemblies of nanoparticles, are desirable for the improvement of the electron transport characteristics. In recent years, semiconductor quantum dots (QDs) have attracted much attention as sensitizers, replacing organic dyes in DSSCs. In this study, TiO_2 electrodes, composed of nanotubes and nanowires, were prepared from TiO_2 gels using a surfactant-assisted self-assembling method reported recently. Since use of semiconductor QDs as sensitizers has some advantages in solar cell applications, CdSe QDs were adsorbed onto the TiO_2 electrodes as a sensitizer. The photoacoustic (PA) and the incident photon-to-current conversion efficiency (IPCE) spectra were measured for the TiO_2 electrodes, both with and without CdSe QD deposition to evaluate their optical absorption property and photon-to-electron conversion efficiencies. Dependencies of the optical absorption and the IPCE on the TiO_2 electrode thickness (0.7 μm–2.8 μm) were studied. It was found that the IPCE peak value and the integrated area of the IPCE spectra for the TiO_2 electrodes with CdSe deposition increased as the electrode thickness increased. The highest IPCE value of about 45% was obtained from an electrode with a thickness of 2.8 μm. This value is as high as those obtained from CdSe QD-sensitized TiO_2 electrodes made from nanoparticles, of which the thicknesses were 10 μm.

Keywords: Titanium dioxide; Nanotube; Nanowire; CdSe quantum dot; Photoacoustic spectroscopy; IPCE; Quantum confinement effect

1. Introduction

Numerous technological applications of titanium dioxide (TiO_2), such as photoelectrochemical solar cells, photocatalysis, and gas sensors, have, in recent years, led to a wide and growing interest. In particular, a great deal of attention has been devoted to dye-sensitized solar cells (DSSC) made from nanostructured TiO_2 films, due to the high energy conversion efficiency exceeding 10%, and the good long-term stability [1,2]. Morphology of TiO_2 films is important to improve DSSC efficiency and photocatalytic activity. TiO_2 electrodes with a higher degree of order than those made from the disordered assembly of nanoparticles are desirable for the improvement of the electron transfer rate and DSSC efficiency [2]. Recently, Adachi and coworkers reported that Ru-dye sensitized thin-film electrode made of TiO_2 nanotubes showed more than double the short-circuit current densities of TiO_2 electrodes made from TiO_2 nanoparticles (P-25) in the thin-film region (with thicknesses less than 5 μm) [3]. On the other hand, semiconductor quantum dots (QDs), such as CdS, PbS, and CdSe, have also been the subject of considerable interest for light harvesters in DSSCs as an alternative to organic dyes [2,4–11]. The use of semiconductor QDs as the sensitizers has some advantages in solar cell applications

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[12]. Firstly, energy gap of the QDs can be tuned by controlling their sizes so that the absorption spectra can be tuned to match the spectral distribution of sunlight. Secondly, semiconductor QDs have large extinction coefficients due to quantum confinements, together with large intrinsic dipole moments which may lead to rapid charge separations. Thirdly, a unique potential capability of the QD-sensitized solar cell is the production of quantum yields greater than unity due to the inverse Auger effect (impact ionization) [13,14]. In this study, TiO_2 electrodes composed of nanotubes and nanowires were prepared, following a surfactant template method reported by Adachi et al. [3]. These electrodes were then sensitized with CdSe QDs [8,9]. The optical absorption and photoelectrochemical properties of the TiO_2 electrodes, with and without CdSe QDs adsorption, were studied using the photoacoustics (PA) technique and the measurement of the incident photon-to-current conversion efficiency (IPCE). Dependencies of the optical absorption and IPCE on the TiO_2 electrode thickness (0.7 μm–2.8 μm) were also studied. The PA method is a powerful tool for characterizing the optical absorption of opaque and scattered samples, because the PA method detects a signal directly proportional to the thermal energy as a result of the optical absorption by nonradiative processes.

2. Experiments

2.1. Sample preparation

TiO_2 gels of nanotubes and nanowires were synthesized using molecular assemblies composed of surfactant molecules of laurylamine hydrochloride (LAHC) and tetraisopropylorthotitanate (TIPT), modified with acetylacetone (ACA) [3]. A yellow TIPT solution was prepared by mixing TIPT with an equal molar quantity of ACA. This solution was then added to a 0.1 M LAHC aqueous solution. The mole ratio of TIPT to LAHC was 4. The solution was stirred at 40 °C for several days until it became a uniform transparent yellow. The solution was then put into an oven at 80 °C for 72 h to obtain a white TiO_2 gel with a thin yellow liquid surface layer. In order to remove the surfactant molecules from the product, the gel was washed with isopropyl alcohol and finally the alcohol solution was separated by centrifugation. To prepare the TiO_2 electrodes, the gel was applied onto fluorine doped tin oxide (FTO) coated glass substrates (sheet resistance: 12.0 Ω/□), using Scotch tape as a frame and spacer, and raking off the excess solution with a glass rod. The TiO_2 films were dried in air at room temperature for 10 min, and then heated at 450 °C for 30 min. TiO_2 electrodes of four different thicknesses were obtained by repeating this process for one or several times. The thicknesses of the TiO_2 films were measured to be 0.7, 1.5, 2.4, and 2.8 μm, using high-resolution scanning electron microscopy (SEM) (Model S-3500N, Hitachi).

The CdSe QDs were prepared using a chemical solution deposition technique [8,9,15]. Firstly, for the Se source, an 80 mM sodium selenosulphate (Na_2SeSO_3) solution was prepared by dissolving elemental Se powder in a 200 mM Na_2SO_3 solution. Secondly, 80 mM $CdSO_4$ and 120 mM trisodium salt of nitrilotriacetic acid ($N(CH_2COONa)_3$) were mixed in a volume ratio of 1:1. Finally, the above two solutions were mixed in a volume ratio of 1:2. The TiO_2 films were placed in a glass container filled with the final solution at 2 °C in the dark for various times.

2.2. TiO_2 electrode characterization

Characterization of the morphology and structure of the TiO_2 films was made by using transmission electron microscopy (TEM) (JEM2010, JEOL), together with electron diffraction (ED) and X-ray diffraction (XRD) analyses.

The optical absorption of the TiO_2 electrodes was studied using the PA technique. A gas-microphone PA method was used [16,17]. A monochromatic light beam was obtained by passing the light from a 300 W xenon arc lamp through a monochromator. This beam intensity was modulated with a mechanical chopper and focused onto the surface of a sample placed inside a sealed PA cell. Measurements of the PA spectra were carried out in the wavelength range of 270–800 nm with a modulation frequency of 33 Hz at room temperature. The PA signal was monitored by first passing the output from the microphone through a preamplifier and then into a lock-in amplifier. In order to eliminate the spectral variation of the illumination source and monochromator, the PA spectra of the samples are normalized by dividing them with a PA spectrum from a carbon black. Since the carbon black can be considered to have a constant absorption coefficient over the experimental wavelength range and its PA spectrum reflects spectral variation of the product of the Xe lamp and the monochromator.

The IPCE measurement setup consisted of a quartz cell equipped with a working electrode (TiO_2) and a Pt counter electrode in 1 M KCl+0.1 M Na_2S electrolyte [4]. The IPCE measurements were carried out under short-circuit conditions using the same apparatus and conditions as those used for the PA measurements. The nanostructured TiO_2 electrode was illuminated from both the electrolyte/TiO_2 (front-side illumination) and the electrolyte/FTO (back-side illumination) interface sides.

3. Results and discussion

3.1. TiO_2 electrodes composed of nanotubes and nanowires

Fig. 1 shows TEM images of the TiO_2 nanotubes (a) and nanowires (b) in the films. Both nanotubes (with diameters