

Photoacoustic and Photoelectrochemical Characterization of Nanostructures TiO₂ Electrode Adsorbed with PbS Quantum Dots PbS 量子ドットを吸着したナノ構造 TiO₂ 電極の光音響・光電気化学特性

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1. Introduction

Recently, dye-sensitized solar cells (DSSCs) fabricated with organic dyes and nanostructured TiO₂ have received considerable attention due to the fact that it has a high energy conversion efficiency exceeding 10% [1]. In addition to organic dye, narrow-band-gap semiconductor quantum dots (QDs), such as CdS, CdSe and PbS, have also attracted significant interest as sensitizers in DSSCs [2, 3]. The use of semiconductor QDs as sensitizers has several advantages in solar cell applications. First, the energy gap of the QDs can be tuned by controlling their size so that the absorption spectrum can be tuned to match the spectral distribution of sunlight. Secondly, semiconductor QDs have a large extinction coefficient due to quantum confinement, and large intrinsic dipole moments leading to rapid charge separation. Thirdly, two or more excitons can be generated with a single photon due to the inverse Auger effect (impact ionization) [4]. In semiconductor QD-sensitized TiO₂ solar cells, the absorption of QDs should be in visible region. PbS QD-sensitized TiO₂ solar cells have potential to generate multiple excitons in visible light because PbS QDs has small band gap reached infra-red region. But PbS QD-sensitized solar cell were few reported so it is interesting and important to study PbS QD-sensitized solar cells [5].

In this study, the optical absorption and photoelectrochemical properties of the nanostructures TiO₂ electrodes adsorbed with PbS QDs were studied using the photoacoustic (PA) method and the measurement of incident photon-to-current conversion efficiency (IPCE). The PA method is a powerful tool for characterizing

the optical absorption of opaque and scattered sample, because it detects a signal directly proportional to thermal energy as a result of optical absorption by nonradiative process[6-8].

2. Experiment

Nanostructures TiO₂ electrodes were applied onto fluorine-doped-tin-oxide (FTO) glass substrates prepared by using TiO₂ nanoparticles (15 nm with anatase structure). The TiO₂ electrodes were heated at 450 °C for 30 min. The thickness of TiO₂ electrodes were about 5 μm. The PbS QDs were prepared using successive ionic layer adsorption and reaction (SILAR) process. The TiO₂ electrodes were immersed for 20 sec into 0.05 M Pb(CH₃COO)₂ solution; rinsed with pure water; immersed for 20 sec into 0.05 M Na₂S solution; and finally rinsed with water again. Such an immersion cycle was repeated several times (between 1 and 5 times). Next, electrodes were passivated by ZnS with the same procedure using 0.1 M Zn(CH₃COO)₂ solution and 0.1 M Na₂S solution [9]. We carried out ten times of ZnS coatings for each PbS QD-TiO₂ electrodes.

The optical absorption of the electrodes was studied using PA technique [10]. A gas micro-phone PA method was used. A monochromatic light beam was obtained by passing the light from a 300 W xenon arc lamp through a monochromator. This beam 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 270-1200 nm with a modulation frequency of 33 Hz at room temperature. PA spectra were normalized using the PA signals from a carbon black sheet.

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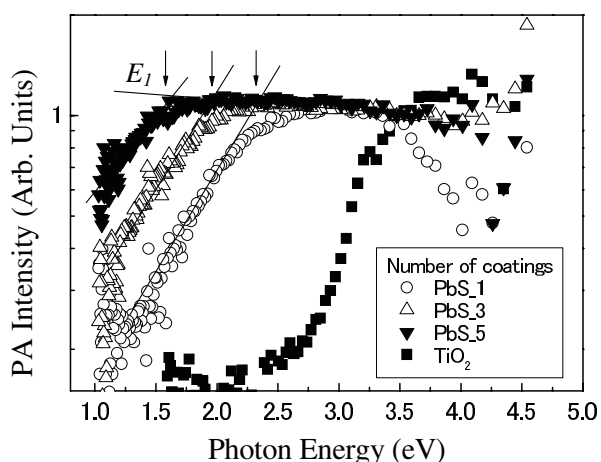


Fig. 1 PA spectra of TiO_2 electrodes after various numbers of coatings with PbS.

The photoelectrochemical properties of the electrodes were studied using IPCE spectra measurement. The IPCE spectra measurements were carried out on the sandwich structure solar cells. The counter electrode was a Cu_2S electrode on brass. Mixing of the 1 M S and 1 M Na_2S solution (polysulfide redox system) was used as the regenerate redox couple. Measurements conditions were using the same lamp, monochromator, and conditions as those used for the PA measurements. The photocurrents were detected by using a zero shuntmeter.

3. Results and discussions

Fig. 1 shows the normalized PA spectrum of TiO_2 electrodes after various numbers of coatings with PbS. The PA shoulders (\downarrow), assumed as the first excitation energy (E_1) of PbS QDs, were shifted to the low energy region with increasing numbers of coatings. For 1, 3 and 5 coatings, the value of E_1 were 2.34 eV, 1.96 eV and 1.61 eV, respectively. The larger value of E_1 relative to the energy gap of bulk PbS (~ 0.40 eV) shows the occurrence of quantum confinement effects.

Fig. 2 shows the IPCE spectrum of TiO_2 electrodes after various numbers of coatings with PbS. The photosensitization of the TiO_2 electrodes in the visible and near-infrared region resulting from PbS QDs coatings can be clearly observed. Near-infrared region of IPCE in all PbS QDs- TiO_2 electrodes were 5% or lower. This is consistent with the PA spectra of the TiO_2 electrodes, which PA intensity decreased as light wavelength increases.

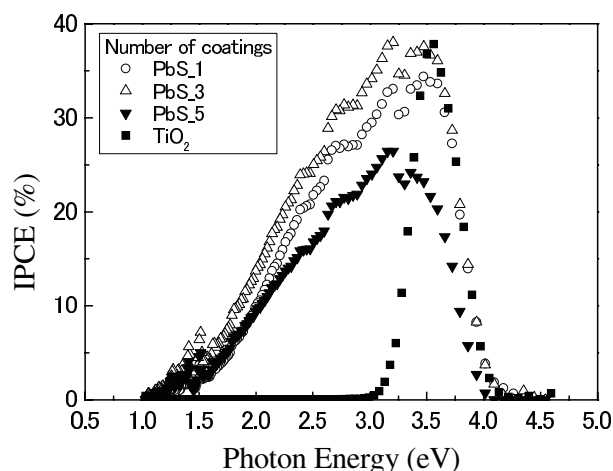


Fig. 2 IPCE spectra of TiO_2 electrodes after various numbers of coatings with PbS.

IPCE increased with increasing SILAR cycles, and for more than 3 times, IPCE decreased. The maximum peak of IPCE was about 40% at around 3.0 eV for the TiO_2 electrodes after 3 times of coatings with PbS. This is suggested that increasing SILAR cycles increased PbS QDs and TiO_2 nanoparticles interface or each PbS QDs interface. This increasing interface causes ineffective electron transfer from PbS QDs to conduction band of TiO_2 nanoparticles.

Reference

- [1]. M. Grätzel: *J. Photochem. Photobiol. C* **4** (2003) 145.
- [2]. Q. Shen, K. Katayama, T. Sawada, and T. Toyoda: *Jpn. J. Appl. Phys.* **45** (2006) 5569.
- [3]. L. J. Diguna, Q. Shen, J. Kobayashi and T. Toyoda: *Appl. Phys. Lett.* **91** (2007) 23116.
- [4]. A. J. Nozik: *Physoca E* **14** (2002) 115.
- [5]. H. Lee, et al: *Adv. Funct. Mater.* **19** (2009) 2735.
- [6]. T. Toyoda, et al: *Jpn. J. Appl. Phys.* **44** (2005) 4465.
- [7]. T. Toyoda, et al: *Jpn. J. Appl. Phys.* **45** (2006) 4604.
- [8]. T. Toyoda, et al: *Jpn. J. Appl. Phys.* **46** (2007) 4616.
- [9] Q. Shen, J. Kobayashi, L. T. Diguna, and T. Toyoda: *J. Appl.Phys.* **103** (2008) 084304.
- [10]. A. Rosencwaig and A. Gersho: *J. Appl. Phys.* **47** (1976) 64.