

## Photoacoustic Spectroscopy of TiO<sub>2</sub> Nanotube Electrode Adsorbed with CdSe Quantum Dots

### セレン化カドミウムを吸着した酸化チタンナノチューブ電極の光音響分光

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## 1. Introduction

Nanostructured TiO<sub>2</sub> film have attracted much attention for the application of photocatalyst and the solar cells.<sup>1</sup> In the application of solar cells, quantum dot sensitized-solar cells (QDSSCs) have received significant interest because of their high theoretical conversion efficiency and inexpensive fabrication procedure compared with conventional silicon based solar cells.<sup>2</sup> Various morphology of TiO<sub>2</sub> electrode besides conventional nanoparticles (NP) have been studied. Recently, nanotube (NT)-TiO<sub>2</sub> electrodes have been reported as a candidate of new electrode for QDSSCs because of highly electron transfer rate and photovoltaic conversion efficiency.<sup>3</sup>

Meanwhile, the quality of quantum dots (QDs) is very important for 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 below the bandgap. These optical absorption regions provide information on the band structure, disorder, defects and electron-phonon interaction. In this study, the optical absorption properties of CdSe QDs adsorbed on NT-TiO<sub>2</sub> electrodes were investigated using the photoacoustic (PA) technique, which is useful for optical absorption characterization with highly scattering materials.<sup>4-7</sup> PA technique is based on a photothermal process (heat production) 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

### 2.1 Sample preparation

NT-TiO<sub>2</sub> films were prepared on a fluorine-doped tin oxide (FTO) substrate by liquid phase deposition (LPD) method.<sup>8</sup>

The FTO substrate with ZnO seed layer was immersed in an aqueous solution of Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (25 mM) and C<sub>6</sub>H<sub>12</sub>N<sub>4</sub> (25 mM) at 93°C for 12 h for ZnO nanorods (NR) fabrication. After the process, the substrate was transferred from the solution to outside and annealed at 400 °C for 1 h. Then, after the ZnO NR preparation, the TiO<sub>2</sub> materials were deposited on the ZnO NR by the following LPD method. Ammonium hexafluorotitanate (AHFM) was dissolved in 70 mL deionized water (the concentration was 0.07 M) and mixed with 30 mL of 0.5 M boric acid. Then, the substrate with ZnO NR was immersed in the solution. After NT-TiO<sub>2</sub> preparation, the substrate was transferred from the solution to outside and annealed at 450 °C for 2 h.

The CdSe QDs were adsorbed on the TiO<sub>2</sub> electrode using a successive ionic layer adsorption and reaction (SILAR) method.<sup>9</sup> The TiO<sub>2</sub> electrode was immersed into two different solutions for about 30 s each, one consisting of 0.03 M Cd(NO<sub>3</sub>)<sub>2</sub> dissolved in ethanol and the other containing the 0.03 M Se<sup>2-</sup> in ethanol. Following each immersion, the films were rinsed for 1 min using ethanol. This immersion cycle was repeated from 4-10 cycles.

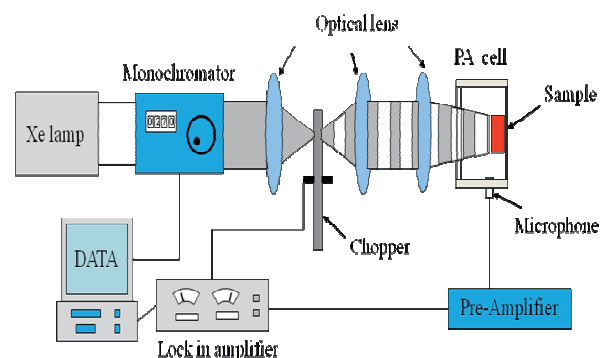


Fig. 1 Schematic diagram of PA spectrometer, in which light is incident directly on electrode surface.

### 2.2 PA measurement

Fig.1 shows the schematic diagram of PA spectrometer. PA measurements were carried out by using a gas-microphone PA technique. A

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monochromatic light is obtained through a monochromator 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. Pressure fluctuation (acoustic wave) is detected as PA signal by a microphone. PA signal intensity is proportional to optical absorption coefficient. In this study, PA measurements were carried out in the wavelength range between 273 and 850 nm with a modulation frequency of 33 Hz at room temperature.

### 3. Results and Discussions

**Figs. 2 and 3** show the PA spectra of CdSe QDs adsorbed on the NT-TiO<sub>2</sub> electrodes and on the NP-TiO<sub>2</sub> electrodes, respectively, with different SILAR cycles. The PA shoulder point can assume to be the first excitation energy ( $E_1$ ). By the effective mass approximation<sup>10</sup>, the diameters of CdSe QDs

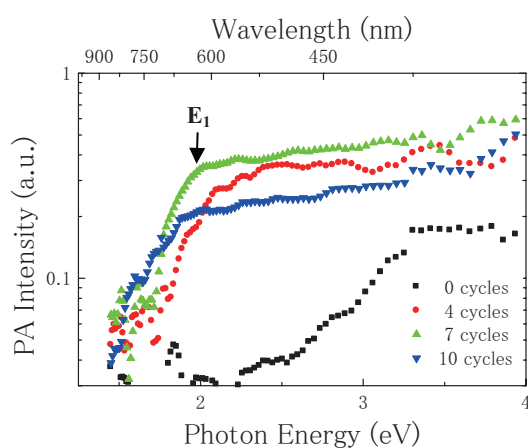


Fig. 2 PA spectra of CdSe QDs adsorbed on NT-TiO<sub>2</sub> with different SILAR cycles

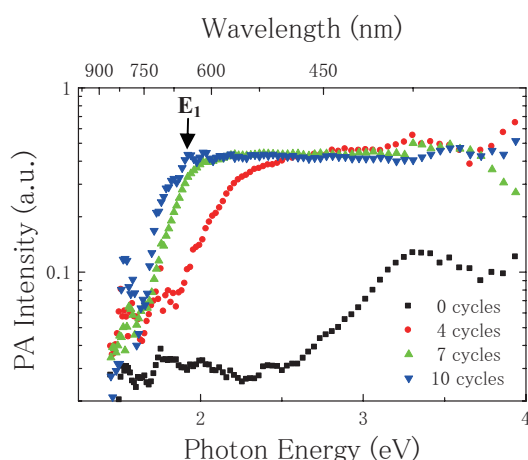


Fig. 3 PA spectra of CdSe QDs adsorbed on NP-TiO<sub>2</sub> with different SILAR cycles

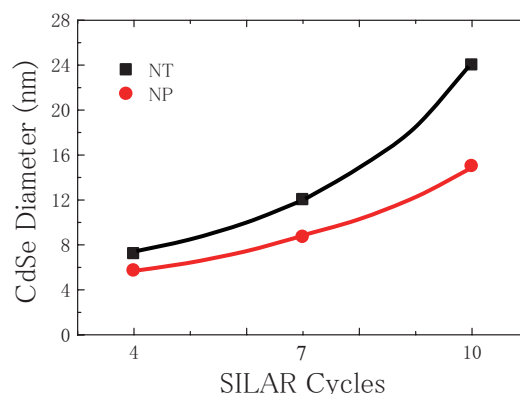


Fig. 4 Dependence of the diameter of NT- and NP-TiO<sub>2</sub> with CdSe QDs on different SILAR cycles

adsorbed on NT-TiO<sub>2</sub> and NP-TiO<sub>2</sub> can be estimated.

**Fig. 4** shows the dependence of the diameters of CdSe QDs on different SILAR cycles. The diameters of CdSe QDs adsorbed on NT-TiO<sub>2</sub> is larger than NP-TiO<sub>2</sub> one with same SILAR cycles. Therefore, the growth rate of CdSe QDs adsorbed on NT-TiO<sub>2</sub> is faster than NP-TiO<sub>2</sub> one, indicating that (1) good penetration of the precursor solution of SILAR method due to wider pore in NT-TiO<sub>2</sub>, (2) difference of crystal plane between NT- and NP-TiO<sub>2</sub>, and (3) difference of adsorbing force between NT- and NP-TiO<sub>2</sub> cause by the electrode morphology.

### References

1. B. O'Regan and M. Grätzel: *Nature* **353** (1991) 737.
2. A. J. Nozik: *Inorg. Chem.* **44** (2005) 6893.
3. D. Gong, C. A. Grimes, O.K. Varghese, W. Hu, R.S. Singh, Z. Chen, and E. C. Dickey: *J. Mater. Res.* **16** (2001) 3331.
4. A. Rosencwaig and A. Gersho: *J. Appl. Phys.* **47** (1976) 64.
5. Q. Shen, J. Kobayashi, L. J. Diguna, and T. Toyoda: *J. Appl. Phys.* **103** (2008) 084304.
6. T. Toyoda, S. Tsugawa, and Q. Shen: *J. Appl. Phys.* **105** (2009) 034314.
7. T. Toyoda, K. Oshikane, D. M. Li, Y. H. Luo, Q. B. Meng, and Q. Shen: *J. Appl. Phys.* **108** (2010) 114304..
8. J. H. Lee, I. C. Leu, M. C. Hsu, Y. W. Chung, and M. H. Hon: *J. Phys. Chem B. Lett.* **109** (2005) 13056.
9. V. Gonzalez-Pedro, X. Xu, I. Mora-Sero', and J. Bisquert: *ACS NANO.* **4** (2010) 5786.
10. A. I. Ekimov, A. L. Efros and A. A. Onushchenko: *Solid State Commun.* **56** (1985) 921.