Ultrafast Carrier dynamics of CdSe Quantum Dots Adsorbed on Nanostructured TiO_2 Films

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A dye-sensitized solar cell (DSSC) based on nanostructured TiO_2 electrodes has received much attention in recent years, since it shows high energy conversion efficiency exceeding 10% and good long term-stability.[1)] Besides organic dyes, narrow-band-gap semiconductors, such as CdS, CdSe and CdTe, can also be used as sensitizers. To optimize the DSSC for higher efficiency, it is very important to study its properties such as optical absorption, charge injection, carrier transport and recombination. In this paper, we report the ultrafast carrier dynamics of nanostructured TiO_2 photoelectrodes sensitized with CdSe quantum dots using lens-free heterodyne detection transient grating (LF-HD-TG) technique.[2)] The TG method is a powerful time-resolved optical technique to measure various kinds of dynamics. Comparing to conventional TG technique, the LF-HD-TG method has high sensitivity and its optical alignment is so simple that is can be applied for samples with roughness surfaces.

The TiO_2 electrodes were prepared by using a squige printing method with a TiO_2/water paste, in which TiO_2 nanoparticles with anatase structures (27 nm in diameter) and the binder addition polyethylene glycol (PEG) (molecular weight: 500,000) was added. CdSe quantum dots to adsorb on the nanostructured TiO_2 electrodes were produced using a chemical solution deposition technique with different adsorbing time.[3)] The LF-HD-TG measurement was carried out using titanium/sapphire laser with the wavelength of 800 nm, the repetition rate of 1 kHz and the pulse width of 200 fs. The pump pulses were frequency doubled to a wavelength of 400 nm, and the probe pulses were 800 nm in wavelength. The intensity of the pump light was about 5 μJ/pulse. Sensitization of the TiO_2 electrodes in the visible region by the CdSe nanoparticles was demonstrated from both photoacoustic and photoelectrochemical current spectra. Fig. 1 shows the LF-HD-TG responses of a TiO_2 nanostructured film and the signal intensity is very small, because there is a little absorption at the pump wavelength of 400 nm. The signal was normalized at the peak positions. Fig. 2 shows the LF-HD-TG responses of TiO_2 nanostructured films adsorbed with CdSe QDs of different adsorbing times (5 and 44 h, respectively). The responses were normalized at the peak positions. The signal intensity for TiO_2 sample with CdSe QDs became larger as the deposition time became longer and the shapes of the responses are quite different from that of the sample without CdSe deposition. Thus the signals for TiO_2 samples with CdSe QDs were due to the optical absorption of the CdSe QDs at the pump light wavelength of 400 nm. As shown in Fig. 2, the LF-HD-TG signal intensity became larger and the decay rates of the response became slower as the deposition time increased. The LF-HD-TG signal in the fast time scale corresponds to photoexcited carrier dynamics. It resulted from a change in the refractive index of the sample surfaces induced by the generation of photoexcited carriers, i.e., a population grating. We fitted the experimental LF-HD-TG signals shown in Fig. 2 to a double exponential decay plus an offset using a least-square fitting method, convoluting with a 1ps Gaussian representing the laser pulse. Two decay processes with time scales of 2 ps (τ_1) and 16 - 30 ps (τ_2) were observed in the LF-HD-TG signals. The fast decay process was considered to attribut to photoexcited hole relaxation due to trapping by the surface states of CdSe QDs. While the slow decay process reflected photoexcited electron relaxation processes, i.e. the recombination and/or electron transfer from the CdSe QDs to TiO_2. It was found that the fast decay time constant τ_1 was almost constant for all samples. However, the slow decay time constant τ_2 increased with the increase of CdSe deposition time, i.e. the increase of the CdSe QDs sizes. This result implied that the electron transfer efficiency from CdSe QDs to TiO_2 was larger when the QD size was smaller.

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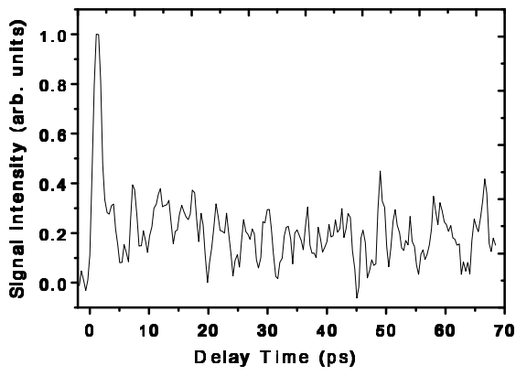

Fig. 1. Transient response of TiO_2 nanostructured electrode.

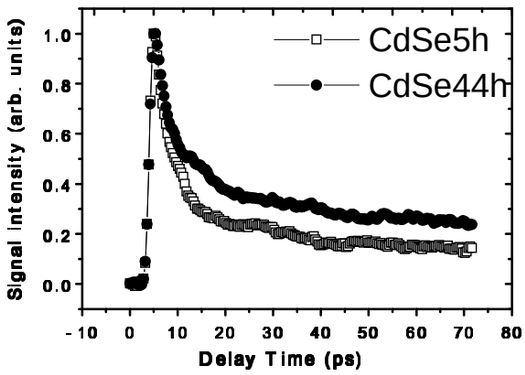

Fig. 2 Transient responses of TiO_2 nanostructured electrodes adsorbed with CdSe quantum dots for different adsorbing time.

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