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Optical Absorption and Photocurrent Spectra of CdSe Quantum Dots Adsorbed on Nanocrystalline TiO₂ Electrode Together with Photovoltaic Properties

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1. Introduction

There is a great deal of interest in the technological applications of titanium dioxide (TiO₂) to dye-sensitized solar cells (DSCs) made from nanostructured TiO2 electrodes because of their high photovoltaic conversion efficiency, which exceeds 10% (Chiba et al., 2006). Since the initial pioneering work on DSCs (O'Regan & Grätzel, 1991), they have often been proposed as a sustainable energy source. In DSCs, the applications of organic dye molecules as a photosensitizer, nanostructured TiO₂ as an electron transport layer, and an iodine redox couple for hole transport dramatically improve the light harvesting efficiency. With Rubased organic dyes adsorbed on nanostructured TiO₂ electrodes, the large surface area enables more efficient absorption of the solar light energy. The main undertaking for those developing next-generation solar cells is to improve the photovoltaic conversion efficiency, together with the long time stability. Nowadays, there exists an intense effort aimed at developing third-generation solar cells. One of a promising approach is to replace the organic dyes by inorganic substances with strong optical absorption characteristics and longer stability over time. Recently, as an alternative to organic dyes, semiconductor quantum dots (QDs) have been studied for their light harvesting capability (Niitsoo et al., 2006; Diguna et al., 2007; Mora-Seró, 2009). The enormous potential of science and technology on nanoscale to impact on industrial output has been recognized all over the world. One emerging area of nanoscience being at the interface of chemistry, physics, biology and materials science is the field of semiconductor QDs, whose unique properties have attracted great attention by researchers during the last two decades. Different strategies for the synthesis of semiconductor QDs have been developed, so that their composition, size, shape, and surface protection can be controlled nowadays with an exceptionally high degree. The surface chemistry of semiconductor QDs is another key parameter, in many respects determining their properties related to their assembly. Semiconductor QDs exhibit attractive characteristics as sensitizers due to their tunable bandgap (or HOMO-LUMO gap) by size control (Yu et al., 2003), which can be used to match the absorption spectrum to the spectral distribution of solar light. Moreover, semiconductor QDs possess higher extinction coefficients than conventional metal-organic

dyes, and larger intrinsic dipole moments leading to rapid charge separation (Underwood et al., 2001). The demonstration of multiple exciton generation (MEG) by impact ionization has fostered an interest in colloidal semiconductor QDs (Schaller et al, 2006; Trinh et al., 2008). One of the most attractive configurations to exploit these fascinating properties of semiconductor QDs is the quantum dot-sensitized solar cell (QDSC) (Nozik, 2002; Klimov, 2006). The efficient formation of more than one photoinduced electron-hole pair (exciton) upon the absorption of a single photon is a process not only of a great current scientific interest but is potentially important for optoelectronic devices that directly convert solar radiant energy into electricity. The demonstration of MEG by impact ionization in colloidal semiconductor QDs could push the thermodynamic photovoltaic conversion efficiency limit of solar cells up to 44% (Klimov, 2006) from the current 31% of the Shockley-Queisser detailed balance limit (Shockley & Queisser, 1961). The optimization of QDSCs can benefit from the intensive effort carried out with DSC. Although the photovoltaic conversion efficiencies of QDSCs lag behind those of DSCs and the use of semiconductor QDs as light absorbers requires the development of new strategies in order to push the performance of QDSCs, QDSCs have attracted significant attention among researchers as promising thirdgeneration photovoltaic devices.

In this chapter, we describe the performance of QDSCs based on CdSe QD sensitizer on nanostructured TiO₂ electrode with a pre-adsorbed layer of CdS QDs (termed combined CdS/CdSe QDs) proposed by Niitsoo et al (Niitsoo et al, 2006) and developed by other groups (Lee & Lo, 2009; Sudhagar et al., 2009). They showed that a pre-adsorbed layer of CdS prior to CdSe adsorption improved the QDSC's performance. Hence it is interesting and useful to investigate the detailed function of combined CdS/CdSe QDs sensitizer on performance of QDSCs, together with the basic studies of optical absorption and photocurrent characteristics. Information regarding the optical absorption properties is initially necessary in order to investigate the electronic states of combined CdS/CdSe QDs for future photovoltaic cell applications. However, few accurate studies of the optical absorption properties of combined CdS/CdSe QDs adsorbed on nanostructured TiO2 electrodes have been carried out. The main reason for this is the difficulty in using the conventional transmission method because of strong light scattering by the highly porous structure of the nanostructured TiO₂ electrodes. However, scattering effects can be minimized by employing the photothermal (PT) technique. In general, an optically excited solid relaxes to thermal equilibrium by the emission of photons (radiative processes) or phonons (nonradiative processes). In the PT technique, the signal detected is directly proportional to the thermal energy (heat production) induced by the absorbed photons through nonradiative processes (emission of phonons). Heat production by nonradiative processes has been detected by several methods (Tam, 1986). The PT signal is less sensitive to light scattering effects than conventional spectroscopy signals, and the ability of the PT technique to produce optical absorption spectra from strongly scattering media has been demonstrated, in particular using photoacoustic (PA) method which is a PT technique (Inoue et al., 2006; Toyoda et al., 2009). Thus, the PT technique is a useful technique for studying the optical absorption spectra of the strongly scattering and/or opaque samples with which we are dealing in our investigations. PA method detects the acoustic energy produced by heat generation through nonradiative processes in materials (Rosencwaig & Gersho, 1977). The PA cell, which is a small gas-tight enclosure with a sensitive acoustic microphone built in one wall, monitors the temperature changes in the sample produced by absorbed photons through nonradiative processes. Periodic temperature changes in the

sample surface by modulated light by PT effect cause periodic pressure changes in the enclosed gas, which creates acoustic waves. The intensities of the acoustic waves are converted to an electrical signal by the microphone. The PA method can be applied to evaluate the optical absorption properties of combined CdS/CdSe QDs adsorbed on nanostructured TiO₂ electrodes. In order to investigate the subsequent photosensitization of combined CdS/CdSe QDs adsorbed on nanostructured TiO₂ electrodes adsorbed on nanostructured TiO₂ electrodes after optical absorption, photoelectrochemical current measurements were carried out and the incident photon-to-current conversion efficiency (IPCE, namely the quantum efficiency of photocurrent) was evaluated. Also, photovoltaic properties were characterized by solar simulator under the illumination of one sun intensity (AM 1.5: 100 mW/cm²).

2. Experimental procedure

Experimental sections are divided into three sections, 1) sample preparations on TiO_2 electrodes and CdS/CdSe quantum dots, 2) optical absorption measurements by photoacoustic technique, and 3) photoelectrochemical current (incident photon to current conversion efficiency) and photovoltaic measurements.

2.1 Sample preparation

The method for the preparation of nanostructured TiO₂ electrodes has been reported in a previous paper (Shen & Toyoda, 2003). A TiO₂ paste was prepared by mixing 15 nm TiO₂ nanocrystalline particles (Super Titanai, Showa Denko; anatase type structure) and polyethylene glycol (molecular weight: 500,000) in pure water. The resultant paste was then deposited onto transparent conducting substrates [F-doped SnO₂ (FTO), sheet resistance: 10 $\mu\Omega/sq$]. The TiO₂ electrodes were then sintered in air at 450 °C for 30 min to obtain good necking and to sublimate polyethylene glycol. The highly porous nanostructure of the films (the pore sizes were on the order of a few tens of nanometers) was confirmed from scanning electron microscopy (SEM) images. The thicknesses of the films were measured and found to be ~ 5 µm by examining the cross sectional SEM images.

At first, CdS QDs were adsorbed onto nanostructured TiO₂ electrodes (pre-adsorbed layer) from the common NH₃ bath with a solution composition of 20 mM CdCl₂, 66 mM NH₄Cl, 140 mM thiourea, and 0.23 M ammonia to obtain a final pH ~9.5 (Niitsoo et al., 2006; Jayakrishnan et al., 1996). The TiO₂ electrodes were immersed in a container filled with the final solution. The adsorption was carried out at room temperature in the dark for 40 min.

The CdSe QDs were prepared by using a chemical bath deposition (CBD) technique (Shen & Toyoda, 2004; Shen et al., 2004; Gorer & Hodes, 1994). First, for the Se source, an 80 mM sodium selenosulphate (Na₂SeSO₃) solution was prepared by dissolving elemental Se powder in a 200 mM Na₂SO₃ solution. Second, an 80 mM CdSO₄ and 120 mM of a trisodium salt of nitrilotriacetic acid [N(CH₂COONa)₃] were mixed with the 80 mM Na₂SeSO₃ solution in a volume ratio of 1: 1: 1. TiO₂ electrodes adsorbed with CdS QDs were placed in a glass container filled with the final solution at 10 °C in the dark for various times (from 2 to 24 h) to promote CdSe QDs adsorption. To investigate the role of pre-adsorbed layer of CdS QDs, the CdSe QDs only were adsorbed directly on nanostructured TiO₂ electrodes with the same sample preparation conditions as mentioned above.

After the adsorption of CdSe QDs, the samples were coated with ZnS for surface passivation of the QDs by successive ionic layer adsorption and reaction (SILAR) for three times in 0.1

M Zn(CH₂COO) and 0.1 M Na₂S aqueous solution for 1 min for each dip (Yang et al., 2002; Shen et al., 2008). In reference (Shen et al., 2008), we showed that the short-circuit-current density (J_{sc}), open-circuit voltage (Voc), and photovoltaic conversion efficiency (η) were enhanced by the ZnS coating, except for fill factor (FF). Although we applied the scanning electron microscopy (SEM) observation for visual investigation, we could not observe the difference of the morphologies with and without the ZnS coating up to 50,000 magnifications, indicating that the ZnS is coated with several atomic layers. In the future, we are going to observe the morphology of the ZnS coating layer by applying the transmission electron microscopy (TEM). To our knowledge, there are few reports in which ZnS coating has been applied to CdSe QD-sensitized solar cells, although ZnS-capped CdSe QDs dispersed in solution have been used for strong photoluminescence applications (Hines & Sionnet, 1996).

2.2 Optical absorption measurements

The optical absorption properties of nanostructured TiO₂ electrodes adsorbed with combined CdS/CdSe QDs were investigated using PA spectroscopy. The scattering effects in the optical absorption of nanostructured TiO₂ electrodes adsorbed with combined CdS/CdSe QDs can be minimized by employing the PA method. Figure 1 shows the schematic diagram of a photoacoustic spectrometer. Typical gas-microphone method was applied in the PA spectroscopic investigation (Rosencwaig & Gersho, 1977). The PA cell was composed of an aluminum cylinder with a small channel at the periphery in which a microphone (electret condenser type) was inserted (Shen &Toyoda, 2004). The inside volume of the cell was approximately 0.5 cm³. The cell was suspended by four rubber bands



Fig. 1. Schematic diagram of a photoacoustic spectrometer, composed with light source, monochrometer, mechanical chopper, cell, preamplifier, lock-in amplifier, etc.

to prevent interference from external vibration. The cell window made of quartz was highly transparent throughout the observed wavelength range, and the sample holder could be easily removed from the cell to maintain the optical configuration. A 300 W xenon lamp was used as the light source. Monochromatic light through a monochromator was modulated at 33 Hz using a mechanical chopper and was focused within the PA cell. Light was focused on the sample over an impinging area of 0.20 cm³. Modulation frequency of 33 Hz was determined to exclude the saturation effect of the spectrum. In this case (modulation frequency: 33 Hz), the optical absorption length is longer than the thermal diffusion length, indicating that the PA signal intensity is proportional to the optical absorption coefficient (no saturation effect) (Rosencwaig & Gersho, 1977). The PA signal was monitored by first passing the microphone output through a preamplifier and then into a lock-in amplifier. The data were averaged to improve the signal-to-noise ratio (S/N). The spectra were taken at room temperature in the wavelength range of 250 - 800 nm. The PA spectra were obtained by the normalization to the PA signal intensity of carbon black sheet that was proportional to the light intensity only. A UV cut filter was used for the measurements in the wavelength range of 600 - 800 nm to avoid the mixing of second harmonic light. The conditions for all the PA measurements (optical configuration, path-length, irradiation area, excitation light intensity etc.) were fixed as far as possible to compare each of the PA signals and spectra directly.

2.3 Photoelectrochemical current and photovoltaic measurements

Photocurrent measurements were performed in a sandwich structure cell (i.e., in the twoelectrode configuration) with Cu₂S film on brass as the counter electrode (termed the Cu₂S counterelectrode). The applied electrolyte was polysulfide solution (1 M Na₂S + 1 M S). It is well known that the electrocatalytic activity of Pt with a polysulfide electrolyte is not satisfactory for photovoltaic cell applications and alternative counter electrode materials with higher activity such as Cu₂S and CoS have been reported (Hodes et al., 1980). The higher electro-catalytic activities of these materials are due to a reduction in the charge transfer resistance between the redox couple and the counterelectrode (Giménez et al. 2009). The Cu₂S counterelectrodes were prepared by immersing brass in HCl solution at 70°C for 5 min and subsequently dipping it into polysulfide solution for 10 min, resulting in a porous Cu₂S electrode (Hodes et al., 1980). The cells were prepared by sealing the Cu₂S counter-electrode and the nanostructured TiO₂ electrode adsorbed with combined CdS/CdSe QDs, using a silicone spacer ($\sim 50 \ \mu m$) after the introduction of polysulfide electrolyte. The IPCE value was evaluated from the short-circuit photocurrent with a zero-shunt meter using the same apparatus and conditions as those used for the PA measurements. The incident light intensity was measured by an optical power-meter. The spectra were taken at room temperature in the wavelength of 250 – 800 nm. The conditions for all the measurements (optical configuration, path-length, irradiation area, excitation light intensity etc.) were fixed as far as possible to compare the IPCE values and spectra directly. Photovoltaic properties were characterized under a one sun illumination (AM 1.5: 100 mW/cm²) using a solar simulator by the measurements of photocurrent versus photovoltage to investigate J_{sc}, V_{oc}, FF, and n.

3. Results and discussion

Figure 2 shows the PA spectra of the nanostructured TiO_2 electrodes adsorbed with combined CdS/CdSe QDs for different adsorption times, together with that adsorbed with CdS QDs only. The pre-adsorption times for CdS QDs were fixed at 40 min (average diameter: ~ 4.2 nm).

The spectra were normalized to the photon energy of 4.0 eV. With increasing adsorption time, the red-shift of optical absorption at the shoulder point (indicated by arrows) can be clearly observed, implying the growth of CdSe QDs. Also, the comparison between the adsorption of CdSe QDs on the nanostructured TiO₂ electrodes with and without a pre-adsorbed CdS QD layer was carried out to evaluate the difference in PA spectra. For that, Figure 3 shows the PA spectra of the nanostructured TiO2 electrodes adsorbed with CdSe QDs without a preadsorbed CdS QD layer for different adsorption times. The spectra are also normalized to the photon energy of 4.0 eV. As the PA spectra below the CdSe QDs adsorption time of 8 h agree with that of pure nanostructured TiO₂ electrode within the experimental accuracy, the CdSe QDs average size is very small less than 1 nm or no adsorption. Optical absorption in the visible light region due to the adsorbed CdSe QDs can be also observed both in Figs. 2 and 3. With increasing adsorption time, the red-shift of optical absorption at the shoulder point (indicated by arrows) can be clearly observed in Fig.3, also implying the growth of CdSe QDs. The exponential slopes at the fundamental absorption edges in combined CdS/CdSe QDs adsorbed on nanostructured TiO₂ electrodes in Fig. 2 are higher than those of CdSe QDs adsorbed on nanostructured TiO₂ electrodes without a pre-adsorbed CdS QD layer in Fig. 3, indicating that the uniformity of the average sizes or crystal quality of CdSe QDs in the former is better than that of the latter. Relative to the band-gap energy of 1.73 eV for bulk CdSe, the shoulder points in PA spectra of the nanostructured TiO₂ electrodes adsorbed with CdSe QDs shown in Figs. 2 and 3 exhibit blue-shifts, which is indicative of the quantum confinement effect. This fact implies that the radii of the CdSe QDs are smaller than the Bohr radius of bulk CdSe (~5.6 nm). We assume that the photon energy at the shoulder point corresponds to the lowest excitation energy of the CdSe QDs (Shen & Toyoda, 2004). The average diameter of the CdSe QDs for each adsorption time both in combined CdS/CdSe and CdSe without a preadsorbed CdS layer adsorbed on nanostructured TiO2 electrodes can be estimated with the effective mass approximation (Shen et al., 2008; Bawendi et al., 1989). The dependence of the average diameter on the adsorption time is shown in Fig. 4, both of combined CdS/CdSe (•) and CdSe without apre-adsorbed CdS layer (°). It can be observed that the CdSe QDs on the nanostructured TiO₂ electrodes with a pre-adsorbed CdS QD layer grow rapidly during the initial adsorption process (less than 2 h adsorption). After a certain time, the crystal growth rate is slowed down, which is similar to the reference reported (Toyoda et al., 2007). When the adsorption time is sufficiently long (in this case ~ 24 h), the average diameter of CdSe QDs becomes constant at about 7.1 nm. On the other hand, it can be observed that the CdSe QDs adsorbed on the nanostructured TiO₂ electrodes without a pre-adsorbed CdS layer show very slow growth or no growth during the initial adsorption process (less than 8 hours) due to the fact that the PA spectra below the CdSe adsorption time below 8 hours agree with that of the pure nanostructured TiO_2 electrode within the experimental accuracy. Therefore, the crystal growth rate of CdSe QDs adsorbed on TiO₂ electrode with a pre-adsorbed CdS QD layer is faster than that of CdSe QDs adsorbed on the TiO₂ electrodes without a pre-adsorbed CdS QD layer. There are several possibilities for the faster crystal growth rate of CdSe QDs adsorbed on the nanostructured TiO₂ electrode with a pre-adsorbed CdS QD layer. First, it is possible that the active CdSe QDs form from the excess Cd remaining after CdS adsorption directly on the nanostructured TiO₂ electrode (Niitsoo et al., 2006). This is suggested that CdS QDs act as seed layer for subsequent CdSe growth (Sudhager et al., 2009). Second one is the passivation effect of CdS QDs on the nanostrctured TiO₂ surface to reduce defects or dislocations. Third, CdSe QDs are grown on the assembly of CdS QDs, indicating the growth on the similar crystal structure (or close lattice constant) different from the growth on TiO₂.

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Fig. 2. Photoacoustic spectra of nanostructured TiO_2 electrodes adsorbed with combined CdS/CdSe quantum dots for different adsorption times together with that adsorbed wth CdS quantum dots only (modulation frequency: 33 Hz).



Fig. 3. Photoacoustic spectra of nanostructured TiO₂ electrodes adsorbed with CdSe quantum dots without a preadsorbed CdS quantum dot layer for different adsorption times (modulation frequency: 33 Hz).



Fig. 4. Dependence of the average diameter on the adsorption time, both of combined CdS/CdSe (\bullet) and CdSe without a preadsorbed CdS layer (\circ).

Figure 5 shows the IPCE spectra of the nanostructured TiO₂ electrodes adsorbed with combined CdS/CdSe QDs for different adsorption times, together with that adsorbed with CdS QDs only. The pre-adsorption time of CdS QD layer is fixed at 40 min. Photoelectrochemical current in the visible light region due to the adsorbed CdSe QDs can be observed, indicating the photosensitization by combined CdS/CdSe QDs. With increasing adsorption time, the redshift of photoelectrochemical current can be clearly observed, implying the growth of CdSe QDs. The IPCE peak value increases with the increase of adsorption time up to 8 hours (~ 75%), then decreases until 24 h adsorption owing to the increase of recombination centers or interface states, together with the decrease of energy difference between LUMO in CdSe QDs and the bottom of conduction band of TiO₂. Also, the comparison between the adsorption of CdSe QDs on the TiO₂ electrodes with and without a pre-adsorbed CdS QD layer was carried out to evaluate the difference in IPCE spectra. For that, Figure 5 shows the IPCE spectra of the nanostructured TiO₂ electrodes adsorbed with CdSe QDs without a pre-adsorbed layer of CdS QD layer for different adsorption times. Photoelectrochemical current in the visible light region due to the adsorbed CdSe QDs can be observed in Fig. 6, also indicating the photosensitization by CdSe QDs. With increasing adsorption time, the red-shift of photoelectrochemical current can be clearly observed, implying the growth of CdSe QDs. However, the appearance of the spectrum in Fig. 6 is different from that of combined CdS/CdSe QDs, namely in the reduction of maximum IPCE value (~ 60%) and the adsorption time dependence of the spectrum shape. Also, the IPCE spectra below the CdSe QDs adsorption time of 8 h agree with that of pure nanostructured TiO₂ electrode within the experimental accuracy, indicating that the CdSe QDs adsorbed on the nanostructured TiO_2 electrode without a pre-adsorbed CdS layer show very slow growth or no growth similar to the results of PA characterization in Fig. 3. These results demonstrate that the spectral response of IPCE is enhanced upon combined CdS/CdSe sensitization rather than single CdSe QDs sensitization, indicating the possibility of the reduction in recombination centers and interface states owing to the possibilities of active CdSe QDs by the excess Cd remaining after CdS adsorption and passivation effect of CdS QDs on the nanostructured TiO₂ surface.



Fig. 5. IPCE spectra of nanostructured TiO₂ electrodes adsorbed with CdS/CdSe quantum dots for different adsorption times together with that adsorbed with CdS quantum dots only.



Fig. 6. IPCE spectra of nanostructured TiO_2 electrodes adsorbed with CdSe quantum dots without a preadsorbed CdS QD layer for different adsorption times.

The photocurrent-voltage cureves of (a) combined CdS/CdSe QD- and (b) CdSe QDsensitized solar cells are shown in Fig. 7 (a) and (b), respectively, for different adsorption times, together with that obtained with cells adsorbed with CdS only. However, the

appearance of the current-voltage curves of combined CdS/CdSe QD-sensitized solar cells is different from those of CdSe QD-sensitized solar cells. Figure 8 and 9 illustrates the photovoltaic parameters ((a) J_{sc} ; (b) V_{oc} ; (c) FF; (d) η) of combined CdS/CdSe QD-sensitized (•) and CdSe QD-sensitized (•) solar cells as a function of CdSe QDs adsorption times.



Fig. 7. Photocurrent-voltage curves of (a) combined CdS/CdSe quantm dot- and (b) CdSe quantum dot-sensitized solar cells for different adsorption times together with that adsorbed with CdS quantum dots only.

We observe that the parameter of J_{sc} in combined CdS/CdSe QD-sensitized solar cells increases with the increase of CdSe QDs adsorption times up to 8 h. On the other hand, V_{oc} and FF are independent of adsorption times. The performance of solar cells improved with

an increase in adsorption time up to 8 h due, mainly, not only to the increase of the amount of CdSe QDs but the improvement in crystal quality and decrease of interface states. However, the increase in adsorption times after more than 8 h leads to deterioration in J_{sc} and V_{oc}. High adsorption time of CdSe QDs might cause an increase in recombination centers, poor penetration of CdSe QDs, and the decrease of energy difference between LUMO in CdSe QDs and the bottom of conduction band of TiO₂. Therefore, η of the combined CdS/CdSe QD-sensitized solar cell shows a maximum of 3.5% at 8 h adsorption times. On the other hand, J_{sc} and η below the CdSe QDs adsorption time of 8 h without a pre-adsorbed CdS layer show very small values close to zero, indicating the very small amount of CdSe QDs adsorption similar to the results of PA and IPCE characterization. We can observe that J_{sc}, V_{oc}, FF, and η in



Fig. 8. Dependence of the photovoltaic parameters ((a) J_{sc} and (b) V_{oc}) on the adsorption time, both of combined CdS/CdSe (•) and CdSe without a preadsorbed CdS QD layer (\circ).



Fig. 9. Dependence of the photovoltaic parameters((c) FF and (d) η) on the adsorption time, both of combined CdS/CdSe (•) and CdSe without a preadsorbed CdS QD layer (\circ).

CdSe QD-sensitized solar cells without a pre-adsorbed CdS QD layer increase with the increase of adsorption times up to 24 h, indicating the difference of the crystal growth and the formation of recombination centers in combined CdS/CdSe and CdSe QDs.

Figure 9 shows the preliminary ultrafast photoexcited carrier dynamics characterization of combined CdS/CdSe and CdSe without a pre-adsorbed CdS layer (average diameters of both CdSe QDs are ~ 6 nm) using a improved transient grating (TG) technique (Katayama et al., 2003; Yamaguchi et al., 2003; Shen et al., 2010). TG signal is proportional to the change in the refractive index of the sample due to photoexcited carriers (electrons and holes). TG method is a powerful time-resolved optical technique for the measurements of various kinds of dynamics, such as carrier population dynamics, excited carrier diffusion, thermal

diffusion, acoustic velocity and so on. Improved TG technique features very simple and compact optical setup, and is applicable for samples with rough surfaces. Comparing with transient absorption (TA) technique, improved TG method has higher sensitivity sue to its zero background in TG signals, which avoids the nonlinear effect and sample damage. Figure 9 shows that the hole and electron relaxation times of nanostructured TiO₂ electrodes adsorbed with combined CdS/CdSe QDs are faster about twice than those with CdSe QDs without a pre-adsorve CdS layer, indicating the decreases in recombination centers.



Fig. 10. Ultrafast carrier dynamics of combined CdS/CdSe and CdS without preadsorbed CdS quantum dots layer with a transient grating (TG) technique.

4. Conclusion

We have described the performance of quantum dot-sensitized solar cells (QDSCs) based on CdSe QD sensitizer on a pre-adsorbed CdS layer (combined CdS/CdSe QDs) together with the basic studies of optical absorption and photoelectrochemical current characteristics. It can be observed from optical absorption measurements using photoacoustic (PA) spectroscopy that the CdSe QDs on the nanostructured TiO₂ electrodes with a pre-adsorbed CdS layer grow more rapidly during the initial adsorption process than those without a pre-adsorbed CdS layer grow more rapidly during the initial adsorption process than those without a pre-adsorbed CdS layer. Photoelectrochemical current in the visible light region due to the adsorbed CdSe QDs can be observed, indicating the photosensitization by combined CdS/CdSe QDs. The maximum IPCE value (~ 75%) of the CdSe QDs on the nanostructured TiO₂ electrodes with a pre-adsorbed CdS layer. It indicates the possibilities of a decrease in recombination centers, interface states, and inverse transfer rate that is suggested by the preliminary ultrafast photoexcited carrier carrier dynamics characterization owing to the possibilities of active CdSe QDs by the excess Cd remaining after CdS adsorption and passivation effect of CdS QD-sensitized solar cells shows

maxima with the increase of CdSe QDs adsorption times between 2 h and 24 h, also indicating the decrease of recombination centers, interface states, and the increase in quasi Fermi level. The open-circuit voltage (V_{oc}) and fill factor (FF) are independent of adsorption times. The photovoltaic conversion efficiency (η) of the combined CdS/CdSe QD-sensitized solar cell shows a maximum value of 3.5%.

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Solar Cells - New Aspects and Solutions

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The fourth book of the four-volume edition of 'Solar cells' consists chapters that are general in nature and not related specifically to the so-called photovoltaic generations, novel scientific ideas and technical solutions, which has not properly approved. General issues of the efficiency of solar cell and through hydrogen production in photoelectrochemical solar cell are discussed. Considerable attention is paid to the quantum-size effects in solar cells both in general and on specific examples of super-lattices, quantum dots, etc. New materials, such as cuprous oxide as an active material for solar cells, AISb for use as an absorber layer in p-i-n junction solar cells, InGaAsN as a promising material for multi-junction tandem solar cells, InP in solar cells with MIS structures are discussed. Several chapters are devoted to the analysis of both status and perspective of organic photovoltaics such as polymer/fullerene solar cells, poly(p-phenylene-vinylene) derivatives, photovoltaic textiles, photovoltaic fibers, etc.

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