

Photoelectrochemical Studies of CdS Nanoparticle Modified Electrodes: Absorption and Photocurrent Investigations

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This paper is concerned with studies of the absorbance spectrum of an electrode modified with a submonolayer of cadmium sulfide nanoparticles. It is shown that the absorbance is potential dependent; a near band-edge bleaching is reported at negative potentials. The bleaching closely resembles that reported in radiolysis and nonlinear optical studies of CdS nanoparticles. Photocurrent investigations performed in conjunction with these absorbance studies indicate that the bleaching occurs only when electrons are injected into the conduction band of the nanoparticles and that charge transfer to surface states does not affect the absorption. The significance of the results is discussed with reference to the various models of absorbance bleaching in semiconductor nanoparticles.

Introduction

The influence of excess charge carriers on the absorption spectra of nanosized CdS particles has been extensively studied. In a series of radiolysis experiments, performed by Henglein and co-workers, on colloidal sols containing nanosized CdS particles a change in the adsorption spectrum was observed as a result of carrier injection.^{1,2} Excess charge carriers are also formed when a nanoparticle absorbs radiation. The influence of photogenerated carriers on subsequent absorption has been investigated using pump–probe spectroscopy techniques.^{3–9} It has been found that the absorption of supra-band gap radiation leads to a bleaching in the UV–visible absorption spectrum near the band-edge. This nonlinear optical effect has been observed for particles that possess an optical band gap identical to that of bulk material and for particles that exhibit an increased optical band gap as a result of the quantum confinement of charge carriers. Transient bleaching, using femtosecond pulses, in conjunction with photoluminescence studies have been performed in order to determine whether bleaching results from free or trapped carriers. In addition, electron donors and acceptors have been introduced to colloidal sols of semiconductor nanoparticles to allow the effects of excess holes and electrons to be decoupled. Despite such exhaustive studies the mechanism of bleaching remains contentious and several different models to explain the effect have been advanced.^{6,10–13}

To gain further information into the nonlinear optical effects observed for CdS nanoparticles we have undertaken potential modulated absorption spectroscopy (EMAS) studies of CdS nanoparticle modified electrodes. In a recent publication¹⁴ we reported a method of depositing a submonolayer of sterically stabilized CdS nanoparticles onto an optically transparent conducting substrate. It was demonstrated that when quantum-confined nanoparticles were employed the photocurrent spectra of the as-prepared electrodes were found to be identical to the UV–visible spectra of the colloidal sols used in the preparation. This indicates that the nanoparticles in the surface layer act individually and not as coupled arrays. In previous studies^{15–17} of CdS nanoparticle modified electrodes Intensity Modulated

Photocurrent Spectroscopy (IMPS) has been employed to investigate the kinetics of charge-transfer processes. It has been demonstrated that electrons are able to tunnel between the nanoparticles and the conducting substrate, through the CdS stabilizing surface layer. This ability to control electron occupation of the CdS nanoparticles via the applied potential suggests that such modified electrodes may be employed in studies of the nonlinear bleaching phenomenon. This paper is concerned with spectroelectrochemical investigations of CdS nanoparticle modified electrodes, both the photocurrent spectrum and the absorption spectrum are studied at a range of potentials. The results obtained are discussed with reference to existing models of absorption bleaching in semiconductor nanoparticles.

To the authors knowledge this is the first time that the influence of excess charge on the absorption spectrum of CdS has been studied using electrodes modified with nanoparticles that display an increased band gap as a result of quantum confinement. It is noted that spectroelectrochemical techniques have been employed to study changes in the absorption spectra of electrodes modified with multilayers of metal oxide semiconductor particles, including ZnO,^{18,19} TiO₂,²⁰ and WO₃.²¹ In addition, a charge-induced absorption-edge shift has been observed for thin CdS layers prepared by evaporation of highly purified CdS powder.²²

Experimental Section

A detailed description of the CdS nanoparticle modified electrode preparation may be found in ref 14. In brief; a tin oxide electrode was functionalized using (3-mercaptopropyl) trimethoxysilane (MPTMS) to yield a surface with pendent thiol groups. The electrode was then immersed in a THF solution containing 1×10^{-3} mol dm⁻³ of Cd(ClO₄)₂ and a measured amount of hexanethiol stabilizer. CdS nanoparticles were formed, both in the solution and at the electrode interface, when hydrogen sulfide was bubbled into the solution. Varying the stabilizer-to-reactant ratio controlled the size of the nanoparticles so formed.²³

All the electrochemical measurements reported in this paper were performed in a 1 mol dm⁻³ aqueous Na₂SO₃ solution

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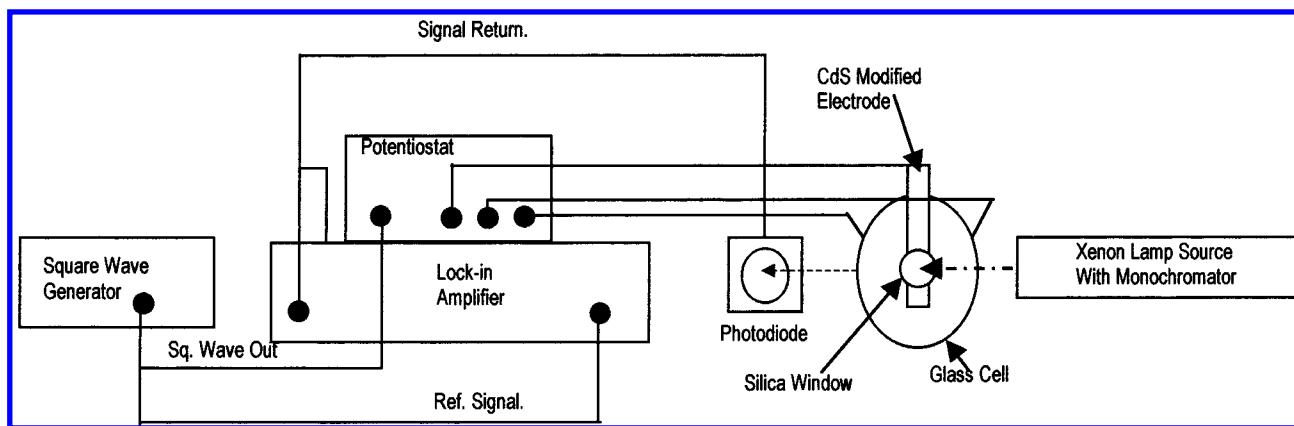


Figure 1. Schematic of the apparatus use to record EMAS spectra.

buffered at pH 12. This electrolyte was selected in order to suppress the photodissolution of CdS.²⁴ Potential control of the modified electrode/electrolyte interface was achieved using a potentiostat in three electrode mode; a platinum gauze counter electrode and a silver/silver chloride reference electrode. All potentials are reported relative to the silver/silver chloride reference electrode.

A Xenon light source was used in all the spectroelectrochemical measurements; the illuminated electrode area was approximately 0.15 cm². Photocurrent spectra at an applied potential of 0.2 V were recorded using a monochromator with a spectral resolution of approximately 1 nm. The illumination was chopped at a frequency of 10 Hz and the modulated current measured using a lock-in amplifier. The influence of applied potential on the transient photocurrent was also investigated. EMAS spectra were recorded as the applied potential was modulated using a square wave generator; to ensure a steady-state response a frequency of 5 Hz was employed. The monochromatic light, resolution 1 nm, was focused onto the modified electrode and the transmittance (*T*) monitored using a photodiode. As the illumination wavelength was scanned the function $\Delta T/T$ was recorded using a lock-in amplifier. The potential modulated change in absorbance (ΔA) was then calculated using the fact that for small changes in the transmittance $\Delta T/T$ is approximately $-2.303\Delta A$. A schematic of the apparatus employed in the EMAS experiments is shown in Figure 1.

Results

The photocurrent spectrum of the CdS nanoparticle modified electrode was recorded, Figure 2. Analysis of the spectrum yielded a band-edge wavelength for the particles of 495 nm. The fact that the band-edge of the nanoparticles was shifted to shorter wavelengths than that of bulk CdS indicated the charge carriers were quantum confined.²⁵ A band gap of 2.50 eV indicates an average particle radius of 5 nm.

Photocurrent transients were recorded at 100 mV intervals in the potential range -1.0 to $+0.5$ V. An incident wavelength of 400 nm and a spectral resolution of 26 nm were employed for these transient measurements. Two distinct shapes of transient were obtained, Figure 3b is representative of the response observed in the potential range -0.8 to -0.5 V, while Figure 3a is characteristic of the photocurrent–time relationship at more positive potentials. The steady-state photocurrent as a function of applied potential is displayed in Figure 3c. The potential dependence of the photocurrent is discussed in detail below.

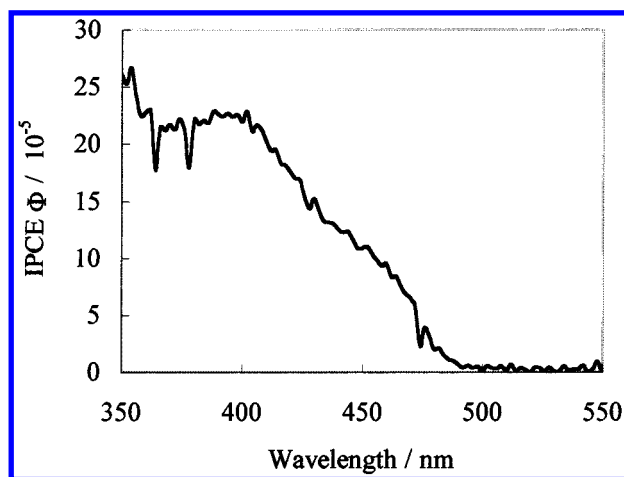


Figure 2. Photocurrent efficiency, recorded at an applied potential of 0.2 V, as a function of the wavelength of illumination.

EMAS spectra, between 350 and 550 nm, were recorded for CdS nanoparticle modified electrodes, MPTMS coated tin oxide electrodes and bare tin oxide electrodes. Initial experiments were performed using a potential modulation amplitude of 200 mV peak to peak. EMAS spectra were obtained for applied potentials (E_{app}) in the range of $+0.2$ to -1.0 V, where E_{app} represents the highest potential in the modulation cycle. For the control electrodes, bare tin oxide and MPTMS coated tin oxide, the EMAS spectra displayed no signal over the entire potential range. Similarly no peaks were detected in the EMAS spectra of CdS nanoparticle modified electrodes in the potential range $+0.2$ to -0.7 V. However, for values of E_{app} of -0.8 V or less an EMAS signal was detected that corresponded to a bleaching of the modified electrode absorption near the band-edge. With E_{app} set at -0.8 V the effect of modulation amplitude on the EMAS spectrum of the CdS nanoparticle modified electrode was studied. A set of spectra that shows the change in signal with modulation amplitude is displayed in Figure 4. As the modulation amplitude was increased the magnitude of the potential induced bleaching increased and a peak corresponding to increased absorbance at short wavelengths developed.

Discussion

The modified electrode interface may be viewed as a metal–insulator–semiconductor junction.^{26,27} Current flows across such a junction as a result of electrons tunneling between the semiconductor and the metal. A photocurrent flows when photogenerated charge carriers are transferred between the surface of the electrode and the underlying substrate. Previous

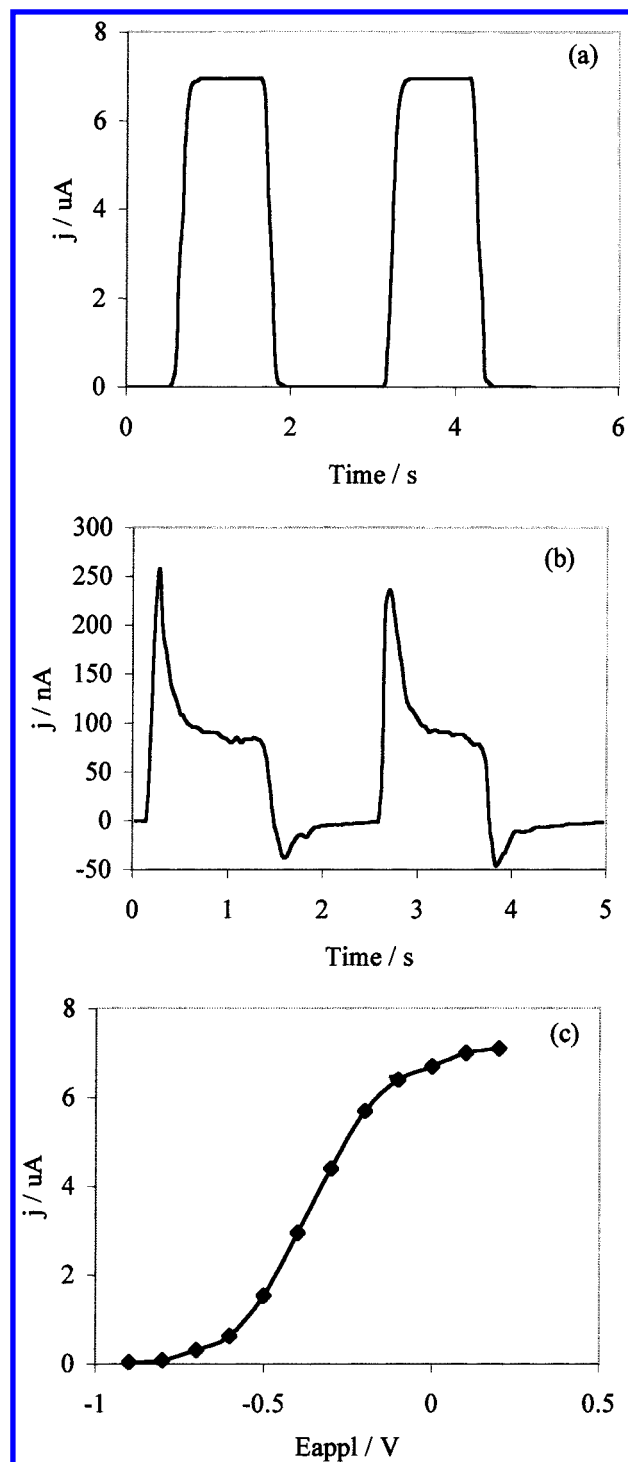


Figure 3. (a) Photocurrent transient recorded at an applied potential of +0.1 V. (b) Photocurrent transient recorded at an applied potential of -0.8 V. (c) Steady-state photocurrent as a function of the applied potential.

studies of CdS nanoparticle modified electrodes indicate that the electrons are able to tunnel between the CdS and the substrate.^{15–17} The simplest model of the process involves the transfer of photogenerated electrons from the conduction band of the semiconductor to the free energy levels in the tin oxide and the capture of the photogenerated holes by the sulfite ions. In this basic model the photogenerated electrons are transferred to the substrate when the Fermi level of the tin oxide lies below the conduction band edge of the nanoparticle. However, the photocurrent falls to zero when the Fermi level of the metal is higher than the conduction band-edge of the semiconductor. The

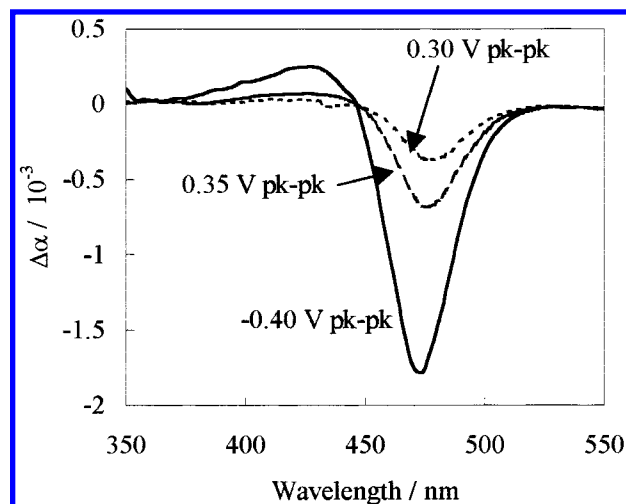


Figure 4. EMAS spectra recorded for a range of modulation amplitudes. An E_{app} of -0.8 V was employed.

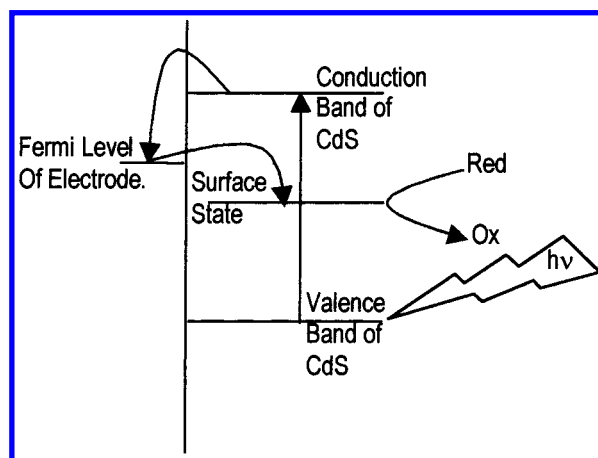


Figure 5. Schematic of the charge-transfer processes that occur at the CdS nanoparticle modified electrode interface.

data shown in Figure 3c indicates that for the CdS nanoparticle modified electrodes employed in these studies the conduction band-edge of the CdS was -1.0 V. This value is in excellent agreement with that reported previously.²⁸

The simple model described above predicts that the photocurrent should rise to a maximum value when the light is switched-on and decay to zero when the illumination is removed. Such behavior was observed at potentials of -0.4 V or greater. However, at more negative potentials a cathodic current flowed when illumination was terminated. This result cannot be explained in terms of electron transfer from the nanoparticles to the substrate only. The cathodic photocurrent observed in these transient investigations indicates a back electron transfer process competes with hole scavenging by the solution species. The back electron transfer step will only occur when the Fermi level of the substrate lies at higher energy than that of the photogenerated holes. Therefore, the absence of a cathodic photocurrent in the transients recorded at potentials greater than -0.4 V indicates that the energy level of the holes is approximately -0.5 V with respect to the silver/silver chloride electrode. Given that the conduction band lies at a potential of -1.0 V on the same potential scale this observation indicates that the back electron-transfer step involves trapped holes. A schematic of the model is shown in Figure 5. A similar scheme was employed to explain the photocurrent transients observed at CdS nanoparticle electrodes in which the organic moieties contained an electron relay.²⁹ This model of the charge-transfer

processes has been verified by ourselves^{15,17} and, independently, by Bakkers and co-workers,¹⁶ using intensity modulated photocurrent spectroscopy (IMPS). The IMPS data, in agreement with the transients displayed above, indicates that the steady-state photocurrent increases continuously with potential. Such a relationship between applied potential and steady-state photocurrent is in accordance with recent results reported by other groups.²⁹

The EMAS spectra displayed in Figure 4 show a potential dependent bleaching near the band-edge. It was noted above that modulations in the absorbance of the nanoparticles occur only when applied potentials of -1.0 V, or less, are achieved in the potential cycle. That is when the Fermi level of the substrate lies above the conduction band-edge of the nanoparticles. This indicates that the bleaching phenomenon is related to the injection of electrons into the nanoparticles and not to modulations in the electric field at the substrate electrolyte interface. In bulk semiconductors injection of electrons into the conduction band may result in a Moss-Burstein shift in the absorbance band edge, the energy of the band edge shifting with applied potential.^{13,22} Such a shift in band-edge with applied potential has been reported for thin films of CdS. Analysis of the full width at half-height⁵ of the EMAS spectra recorded for the quantum confined CdS nanoparticle electrodes employed in these studies indicates that there is no change in the absorbance band edge with applied potential. Indeed the spectra simply show a bleaching of the lowest energy exciton at all potentials, the intensity of the bleaching increasing as the potential is stepped to more negative values. The bleaching spectra obtained are similar to those reported for radiolysis and nonlinear optical studies of CdS nanoparticles. In the literature two models have been proposed to explain why excess charge carriers lead to such a bleaching in the absorbance of nanoparticles. In the first model^{11,12} band filling results in excess carriers being located on the lowest exciton state and the resultant bleaching of transitions to that state. The second model involves the electrostatic effect of surface trapped electrons on the oscillator strength of an exciton.^{6,10} The dynamic photocurrent studies discussed above indicate that electron transfer from the substrate to surface states can occur directly. Therefore, if surface trapped electrons are responsible for the observed bleaching one would expect to observe the phenomenon at potentials below the conduction band-edge, at potentials for which the Fermi level of the substrate is higher than the energy of the traps. The fact that in these studies bleaching was not observed until potentials at which the Fermi level was above the conduction band of the semiconductor indicates that the band filling mechanism is the most probable reason for the observed potential dependent bleaching. It has been reported that the enhanced absorption observed at shorter wavelengths results from lifetime broadening of the higher excitonic states.

Conclusions

It has been demonstrated that the influence of excess charge on the absorbance spectrum of CdS nanoparticles may be

investigated using modified electrodes. Photocurrent studies show that at positive potential photogenerated electrons are able to tunnel from the CdS nanoparticles, anchored to the electrode surface, to the underlying substrate. Transient photocurrent investigations indicate that at more negative potentials the holes that are trapped at the CdS electrode surface may recombine with substrate electrons. The EMAS spectra recorded display a bleaching of the lowest energy exciton. The fact that the changes in the absorbance spectrum are not observed until the Fermi level of the substrate is coincident with the conduction band-edge of the CdS nanoparticles supports a band-filling model of the bleaching process and indicates surface states are not involved in the process.

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