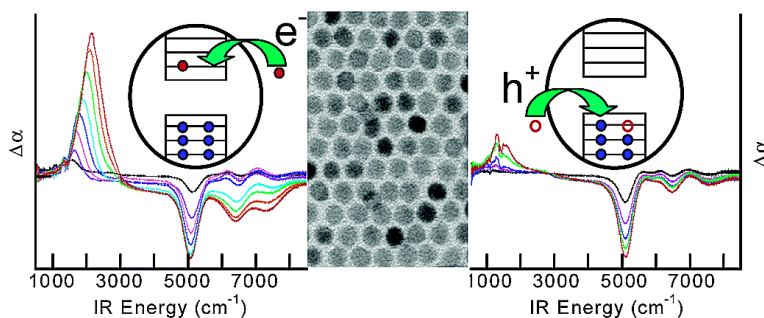


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## Electron and Hole Injection in PbSe Quantum Dot Films

Brian L. Wehrenberg and Philippe Guyot-Sionnest\*

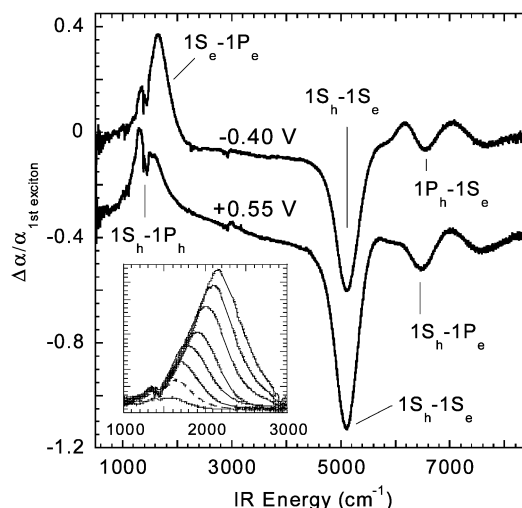
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The ability to dope quantum dots both n- and p-type promises to facilitate the fabrication of several novel optoelectronic devices, just as it did for bulk semiconductors. However, inclusion of a dopant into the interior of a nanocrystal can be difficult, calling for the more direct approach of charge injection. Electrochemical studies have been performed on several nanocrystal systems, including silicon,<sup>1</sup> PbS,<sup>2</sup> CdS,<sup>3</sup> and CdSe.<sup>4</sup> Electrochemistry may allow the determination of the number of charges injected into the nanocrystals; however, it does not distinguish if the charges are injected into delocalized quantum confined states or are placed into localized trap states. In contrast, injection of electrons into quantum confined states of colloidal semiconductor nanocrystals, can be unambiguously confirmed by monitoring changes in both the visible and the IR absorption spectra.<sup>5–7</sup> To date, we know of no studies that have achieved hole injection into quantum confined states and recorded the corresponding spectroscopic changes needed to confirm this fact.

The search for a quantum dot system in which both holes and electrons can be injected into quantum confined states, essentially doping the dots n- and p-type, has lead us to study PbSe quantum dots. It was reasoned that the small band gap of PbSe (0.278 eV at 298 K) should bring both hole and electronic states into the range of stable electrochemical charge injection. In addition, the small effective mass of the charge carriers in PbSe means that well-separated quantum confined states can be obtained for relatively large quantum dots. The larger size might lessen the role of surface trap states, thus favoring the injection of charge into quantum confined states. Here, for the first time, the injection of electrons and holes into quantum confined states of colloidal quantum dots is reported.

The synthesis of PbSe quantum dots capped with oleic acid has been described previously.<sup>8</sup> All measurements are performed in an airtight Teflon electrochemical cell with a ZnSe optical window for spectroscopic measurements. The working electrode is a platinum disk, 1 cm in diameter, with a polished surface treated with a 30 mM solution of 1,6-hexanedithiol in hexane to anchor the dots to the electrode.<sup>9</sup> The thin films of PbSe nanocrystals are drop-cast on the electrode using a 9:1 hexane:octane solution. Shortly after drying, the film is dipped into a 40 mM solution of 1,7-diaminoheptane in methanol for approximately 1 min, heated at 70 °C for 1 h, and then placed under vacuum for several hours to thoroughly dry the film. This treatment is thought to cross-link the quantum dots,<sup>10</sup> and it is repeated two more times. The electrode is then loaded into the electrochemical cell. An Ag wire is used as a pseudoreference electrode. All voltages reported below are relative to this Ag pseudoreference. The electrolyte is an anhydrous 0.1 M solution of LiClO<sub>4</sub> in acetonitrile. Preparation of the films and assembly of the electrochemical cell are performed in a glovebox to minimize exposure to oxygen and water. The cell is transferred under nitrogen to an FT-IR spectrometer (Nicolet Nexus 670). The absorption measurements are taken in reflection geometry with the



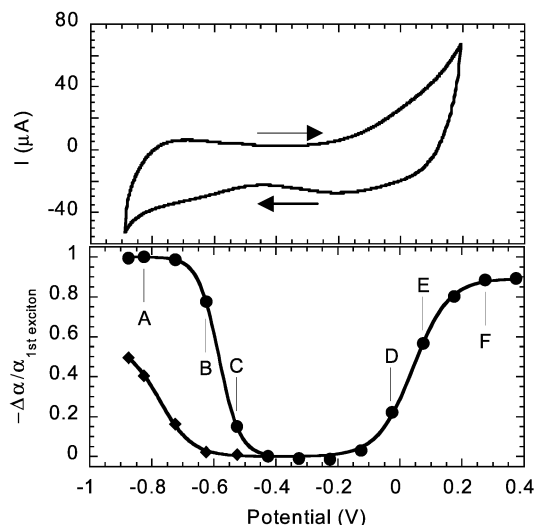
**Figure 1.** Difference spectra for a film of 7.2 nm diameter PbSe dots at  $-0.40$  and  $+0.55$  V, offset for clarity. The inset shows the induced absorption for a series of voltages between  $-0.35$  and  $-0.70$  V; the dotted line is the feature at  $-0.40$  V. Solvent absorption peaks in the  $1000$ – $2000$   $\text{cm}^{-1}$  range disrupt the induced absorption feature.

incident beam at 20° from the surface normal of the ZnSe window, against which the working electrode is pressed. All spectroscopic measurements are made 1 min after application of the desired potential to allow for equilibration. All reported optical changes are reversible.

Upon injection of a charge carrier into the lowest quantum confined state of a neutral semiconductor nanocrystal, the optical properties of the quantum dot change remarkably. Shown in Figure 1 are the difference spectra between a thin film of PbSe dots under no applied potential and after the application of a positive or a negative potential. The film of 7.2 nm diameter PbSe quantum dots (first exciton at  $5100$   $\text{cm}^{-1}$  at 298 K) has an optical density of 0.015 at the first exciton peak and was determined, by ellipsometry, to have a thickness of approximately 25 nm. Optical studies of the interband and intraband transitions of PbSe have been reported previously<sup>8</sup> and are used here to aid in assignments.

At negative potentials, electrons occupy the  $1S_e$  state, and there is a bleach of the interband transitions to that state, accompanied by induced intraband absorptions to higher energy states in the conduction band. At  $-0.40$  V versus the Ag pseudoreference, Figure 1 shows that the first exciton ( $1S_h-1S_e$ ) at  $5100$   $\text{cm}^{-1}$  and the second exciton ( $1P_h-1S_e$ ) at approximately  $6600$   $\text{cm}^{-1}$  are bleached and the intraband ( $1S_e-1P_e$ ) transition at around  $1500$   $\text{cm}^{-1}$  turns on. The robust strength of the  $1S-1P$  interband transitions in PbSe, despite being forbidden by parity, has been observed previously<sup>8</sup> and remains unexplained.

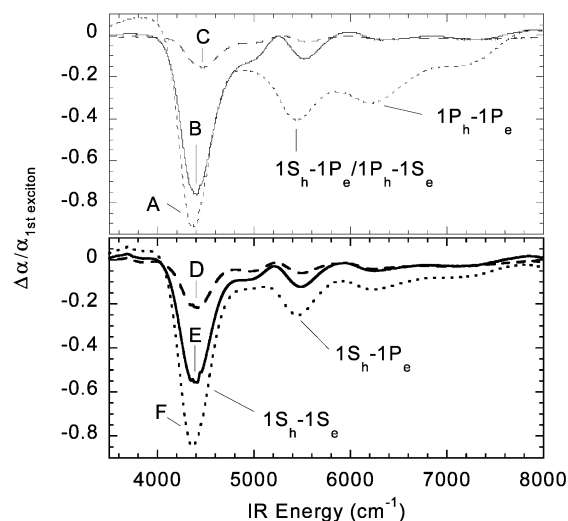
At positive potentials, holes occupy the  $1S_h$  state, causing a bleach of the interband transitions involving that state and inducing intraband absorptions to higher energy hole states in the valence



**Figure 2.** The top panel shows the cyclic voltammetry for a film of 8.8 nm diameter PbSe quantum dots with a scan rate of 17 mV/s. The bottom panel shows the normalized optical bleach of the first (●) and third (◆) excitons, as a function of the applied potential.

band. At +0.55 V, Figure 1 shows the bleach of the first exciton ( $1S_h-1S_e$ ) and the second exciton ( $1S_h-1P_e$ ) around  $6500\text{ cm}^{-1}$ . These bleach features are accompanied by an induced absorption feature at around  $1400\text{ cm}^{-1}$ , assigned to the  $1S_h-1P_h$  intraband transition. Because of the similarity in the effective mass of the electrons and the holes, the electrochromic effects of hole and electron injection appear strikingly similar, with only small shifts in the energies of the transitions.

Figure 2 plots the magnitude of the bleach of the first exciton versus the potential applied to a film of 8.8 nm diameter dots with the first exciton at  $4400\text{ cm}^{-1}$  at 298 K. Also shown in Figure 2 is the cyclic voltammetry of the same sample, which demonstrates the correspondence between the reduction and oxidation current waves and the optical bleach. The cyclic voltammetry was stable, showing no variance over several cycles. At potentials more negative than  $-0.725\text{ V}$ , a 100% bleach of the first exciton is observed. This corresponds to the filling of the  $1S_e$  state in all of the quantum dots in the film. The exact number of electrons per dot needed to fill the  $1S_e$  state in PbSe nanocrystals is of interest and will be reported in a more detailed investigation. For this sample, the bleach of the first exciton due to hole injection plateaus at  $\sim 90\%$ . The application of more positive potentials causes irreversible changes to the film. The voltammetry shows a much more reversible feature for the reduction than for the oxidation, consistent with the lesser stability of the injected hole. Similar behavior is observed for the films of 7.2 nm diameter PbSe nanocrystals; however, for those dots, hole injection bleached the first exciton by  $\sim 75\%$ . For dots smaller than those two sizes mentioned here, no significant hole injection was observed, although electron injection was still possible. Injection of charge carriers into higher energy states was only observed for electrons. The magnitude of the bleach of the third exciton ( $1P_h-1P_e$ ) is plotted as a function of the applied potential in Figure 2.



**Figure 3.** Difference spectra for a film of 8.8 nm diameter PbSe quantum dots taken at the potentials labeled in Figure 2.

The bleach of the third exciton occurs after the first exciton is completely bleached, demonstrating the sequential filling of first the  $1S_e$  and then the  $1P_e$  state, separated by  $\sim 0.2\text{ V}$ . Figure 3 shows the bleach spectra of the film of 8.8 nm diameter dots, taken at several potentials. The rather dramatic effect that filling the  $1P_e$  state has upon the induced absorption can be seen in the inset to Figure 1. The filling of the  $1P_e$  state makes the  $1P_e-1D_e$  transition available, causing both a blue shift and a large increase of the induced absorption. Neither the change in the bleach spectrum nor the shift of the induced absorption is observed in the hole spectra, indicating that hole injection into states lying higher in energy than the  $1S_h$  state does not occur.

We have reported here, for the first time, that both electrons and holes can be injected from an electrode into the quantum confined states of a semiconductor nanocrystal film. While hole injection is less robust than electron injection, this ability should nevertheless allow the development of novel applications, several of which are currently under investigation.

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