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Reversible Surface Electronic Traps in PbS Quantum Dot Solids Induced by an Order−Disorder Phase Transition in Capping Molecules

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Supporting Information

ABSTRACT: The electronic properties of semiconductor quantum dots (QDs) are critically dependent on the nature of the ligand molecules on their surfaces. Here we show the reversible formation of surface electronic trap states in the model system of solid thin films of PbS QDs capped with thiol molecules. As the temperature was increased from cryogenic to room temperature, we discovered a phase transition in the fluorescence spectra from excitonic emission to trap emission. The critical temperature (T_c) of the phase transition scales with molecular length and in each case is close to the bulk melting temperature of the capping molecules. We conclude that an order−disorder transition in the molecular monolayer above T_c introduces surface mobility and the formation of a disordered atomic lead layer at the QD/capping molecule interface, leading to electronic trap formation.

The large surface-to-volume ratio of semiconductor quantum dots (QDs) dictates that their electronic and optical properties are dominated by the surface electronic structure,[1] particularly band-gap electronic states.[2−5] Understanding and controlling electronic states on QD surfaces is an area of intense interest.[6−10] Colloidal QDs are synthesized with a variety of capping ligands that provide solubility and surface electronic passivation.[11] Applications in electronic/optoelectronic devices require QDs in solid thin film formats as well as replacement of the insulating ligands from colloidal synthesis with shorter, more conductive ones. Indeed, such ligand exchanges have been shown to dramatically increase the electric and photoelectric conductivity of QD thin films.[12−18] Past studies of the role of ligands have focused on their chemical nature (e.g., anchoring groups, conjugation, and molecular length). However, there is little information on how the physical structure of the capping molecule layer influences the electronic properties of QDs.

Studies of self-assembled monolayers (SAMs) on flat surfaces have led us to believe that the capping molecule layer surrounding each QD is not static. SAMs of alkanethiolates on Au(111) have demonstrated various monolayer structures and molecular mobility depending on the surface density, temperature, and alkyl chain length.[19−22] While little is known experimentally about the monolayer structures and phase behavior of alkanethiolate SAMs on Au nanoparticles,[23−25] molecular dynamics simulations have shown that an order-to-disorder phase transition (melting) occurs at transition temperatures near the bulk melting temperature of the alkanethiol.[26] These results concerning thiolates on gold are particularly important for QDs, as thiols are commonly used as capping molecules, particularly for the narrow-band-gap Pb-based IV−VI semiconductors.[27] We hypothesize that thiolates on QDs also undergo a similar order−disorder phase transition, as predicted for Au nanoparticles.[26] Such a hitherto unidentified transition should lead to changes in interfacial chemical bonding and thus in the surface electronic structure. To prove this hypothesis, we used a model system of PbS QDs with alkanethiol and -dithiol capping molecules. We chose PbS QDs[27,28] because of current interest in this nanomaterial system for applications in charge transport, solar energy conversion, and photon detection.[29−32] Small thiol molecules are commonly used to replace the insulating oleic acid (OA) capping molecules to increase the conductivity and photovoltaic performance of PbS QD-based devices. We used fluorescence spectroscopy as the main experimental tool, as it is known to be sensitive to band-gap trap states.[33−35]

We synthesized OA-capped PbS QDs (diameter = 3.2 ± 0.3 nm) using a standard procedure.[36] The long, insulating OA capping molecules were replaced with short alkanethiols and -dithiols in solution or in thin films. For solid thin films, this exchange from OA to alkanethiols and -dithiols induced a red shift of ~50 meV in the optical absorption spectra (Figure S1 in the Supporting Information), in agreement with our recent study on the same exchange reactions on PbSe QD thin films.[37] Within the experimental uncertainty, small differences in the extent of the red shifts for different thiol molecular lengths could not be unambiguously resolved in PbS thin films. Similar magnitudes of red shifts were also observed in fluorescence spectra after the ligand exchange reaction (Figure S2).

The ligand replacement process introduces band-gap surface states only in the thin-film format and not in solution-phase QDs. Figure 1 compares the fluorescence spectra of PbS QDs capped with OA or an alkanethiolate (octane, hexane, butane) in solution (left) and in solid films (right) at room temperature (298 K). In the solution phase, there was little change in the fluorescence spectra when the OA capping molecules were replaced by alkanethiolates with different alkyl lengths. When the OA-capped PbS QDs were deposited as a solid thin film, we observed a red shift of 0.227 eV in the first exciton emission

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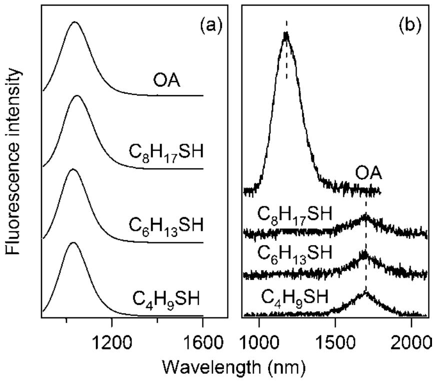

Figure 1. Room-temperature fluorescence spectra of PbS QDs capped with oleic acid (OA), octanethiol ($C_8H_{17}SH$), hexanethiol ($C_6H_{13}SH$), or butanethiol (C_4H_9SH) in (a) tetrachloroethylene solution and (b) thin films. The emission peak of OA-capped QDs in solution is located at 1040 nm (1.19 eV), and there is little change when the OA ligands are replaced with monothiols. For QD thin films, the emission peak is located at 1280 nm (0.97 eV) for OA-capped QDs and 1694 nm (0.73 eV) for monothiol-capped ones.

relative to the corresponding spectrum in solution. This red shift is due to efficient resonant energy transfer in the close-packed solid film, as previously reported by Clark et al.[38] The most important result in Figure 1b is the dramatic change when we replaced OA by the alkanethiolates. The first exciton emission at 0.97 eV was almost completely quenched upon thiolate capping. A new and much weaker (by ~1 order of magnitude) fluorescence peak appeared at 0.73 eV, which is 0.24 eV lower in energy than that of the first exciton transition. We assign this new fluorescence peak to radiative recombination of a surface-trapped electron with a hole in the valence band, as the 0.24 eV red shift is in good agreement with the depth of the electron-trap states observed in a time-resolved IR spectroscopy experiment by Tang et al.[5] Nagpal and Klimov[39] suggested that these mid-gap electron-trap states in ethanedithiol-capped PbS QD thin films are also responsible for electrical conductance in the dark. The trap states cannot result simply from the formation of the Pb−S bond on the QD surface, as they are absent for the same capping chemistry in solution. To explore further the origin of the surface trap states, we turned to the temperature dependence of the fluorescence spectra of the solid thin film.

Figure 2 shows pseudocolor plots of fluorescence spectra as a function of sample temperature (77−337 K) for both (left) monothiol- and (right) dithiol-capped PbS QDs. The fluorescence intensity (color) is presented on a logarithmic scale to show both peaks clearly. The white circles are peak positions obtained from Gaussian fits to the fluorescence spectra. As each sample was cooled to 77 K, we saw the disappearance of the weak trap emission at ~0.73 eV and recovery of the intense first exciton peak at 0.97 eV. The transition between the two electronic states was akin to a first-order phase change characterized by a critical temperature (T_c). The process was completely reversible upon heating or cooling of the sample. In each case, we obtained T_c values by taking the second derivative of the peak intensity versus temperature curve and finding the zero-crossing point. The T_c values for all of the capping molecules investigated here are listed in Table 1, along with the melting points (T_m) of the bulk capping molecules. We make two important observations: (1) the T_c values for both the monothiols and the dithiols scale positively with molecular size, and (2) the T_c values are close to the T_m values.

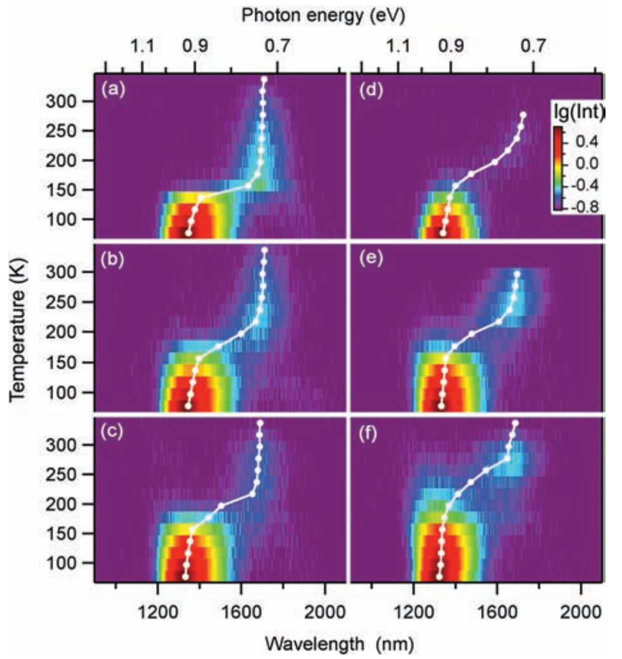

Figure 2. Temperature-dependent fluorescence spectra of PbS QDs treated with monothiols [(a) butanethiol; (b) hexanethiol; (c) octanethiol] and dithiols [(d) ethanedithiol; (e) butanedithiol; (f) hexanedithiol]. The white dots show fluorescence peak positions. The fluorescence intensity (Int) is shown using a logarithmic color scale.

Table 1. Phase Transition Temperatures (T_c) Obtained from the Fluorescence Spectra in Figure 2 and Melting Temperatures (T_m) of Bulk Thiol Molecules

ligand	T_c (K)	T_m (K)[a]
butanethiol	152 ± 5	157.5
hexanethiol	185 ± 5	192.6
octanethiol	195 ± 5	224
ethanedithiol	186 ± 5	232
butanedithiol	196 ± 5	219
hexanedithiol	245 ± 5	252

[a] Data from ref 40.

The observed first-order phase transition and the correlation of T_c with the molecular length and T_m of the capping molecules points to a monolayer structural origin for surface electronic trap state formation. Studies on flat metal surfaces have shown that a thiolate SAM undergoes an order-to-disorder transition upon heating.[19−22] Molecular dynamics simulations of monothiols on gold nanoparticles predicted a loss of order between the alkyl chains near the bulk melting temperature of the alkanethiol.[26] The transition to a disordered phase means more freedom for the molecules within the adsorbed layer. This freedom of movement is not confined to the molecules but also includes the surface metal atoms. Scanning tunneling microscopy studies have revealed extensive diffusion of surface gold atoms along with adsorbed thiolates[20] or atomic chorine.[41]

With the above information, we now discuss the origin of surface electronic traps on PbS QDs capped with thiolates. Lead salt QDs are nonstochiometric and have an excess of Pb^{2+} on the surface.[42,43] As is the case on metal surfaces,[44] the strong covalent interaction between the S atom on the thiolate and a

Pb atom on the QD weakens the bonding between the surface Pb atom and the underlying PbS lattice. Upon heating to T_c, alkanethiolates in the capping layer undergo an order-to-disorder transition and acquire more freedom and mobility. The movement of the capping molecules can in turn carry along the surface Pb atoms, similar to the observed movement of surface Au atoms in the presence of adsorbates such as thiolates.[20] This movement produces liquidlike surface Pb atoms with reduced chemical bonding to the rest of the PbS lattice, thus creating surface electronic traps. A related study of a Pb monolayer showed that the formation of a liquidlike layer with reduced periodicity localizes charge carriers.[45] The interpretation outlined above is essentially a capping-molecule-assisted surface premelting mechanism for trap state formation on PbS QDs. It should be noted that formation of surface trap states is observed only for dry thiolate-capped QD thin films and not for alkanethiol-capped QDs in solution (Figure 1a). We believe that solvation of the capping molecules and intercalation of solvent molecules into the capping layer can lead to a tightly packed molecular shell, reducing the molecular mobility.

The above mechanism for surface electronic trap state formation must depend strongly on the chemical nature of the capping molecule bonding to the QD surface. When the molecule−Pb bond is weaker, the bonding between surface Pb atoms and the underlying PbS lattice should be stronger. This would lead to a lower propensity for the surface Pb atoms to move with the capping molecules and a lower probability for the kind of surface trap state formation observed for thiolate capping. To test this idea, we carried out control experiments using OA- and butylamine (BA)-capped PbS QDs. In both cases, the ionic and adaptive bonds to the QD surface are weaker than the more covalent S−Pb bonds for thiolates. Figure 3 shows fluorescence spectra as a function of temperature (77−297 K) for (left) OA- and (right) BA-capped PbS QD thin films. For OA-capped QDs, we observed only a slight red shift in the fluorescence spectrum with decreasing temperature, consistent with temperature-dependent energy transfer,[46] but no evidence of trap state formation. For the BA-capped PbS QDs, the fluorescence intensity decreased with increasing temperature, but fluorescence due to the first exciton emission persisted from 77 to 297 K. There was no evidence for the kind of phase transition to trap-state emission as in Figure 2.

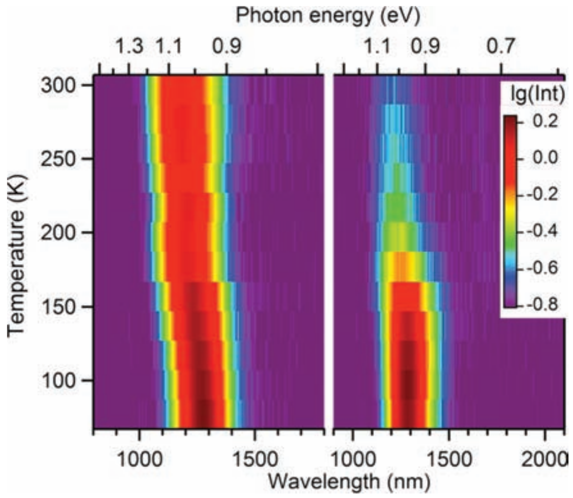

Figure 3. Temperature-dependent fluorescence spectra of (left) OA- and (right) BA-capped PbS QDs in solid thin films.

In summary, we have shown that the reversible formation of surface electronic trap states on thiolate-capped PbS QDs can be attributed to the mobility of surface capping molecules. We have discovered a phase transition in surface electronic trap state formation due to an order−disorder transition in the molecular monolayer. We have proposed a mechanism of capping-molecule-assisted premelting of surface Pb atoms above the phase transition temperature, leading to a disordered and liquidlike Pb atom layer on the QD surface and the formation of band-gap surface trap states.

■ ASSOCIATED CONTENT

Supporting Information

QD synthesis, sample preparation, fluorescence measurements, and absorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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