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Communication

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Sensitization of p-GaP with CdSe Quantum Dots: Light-Stimulated Hole Injection

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Supporting Information

ABSTRACT: The sensitization of p-GaP by adsorbed CdSe quantum dots has been observed. Nondegenerately doped, planar p-GaP(100) photoelectrodes consistently showed sub-band-gap (>550 nm) photoresponsivity in an aqueous electrolyte containing $Eu^{3+/2+}$ when CdSe quantum dots (diameters ranging from 3.1 to 4.5 nm) were purposely adsorbed on the surface. Both time-resolved photoluminescence decays and steady-state photoelectrochemical responses supported sensitized hole injection from the CdSe quantum dots into p-GaP. The observation of hole injection in this system stands in contrast to sensitized electron injection seen in other metal oxide/quantum dot material combinations and therefore widens the possible designs for photoelectrochemical energy conversion systems that utilize quantum dots as light-harvesting components.

Inorganic semiconductor nanocrystals are attractive as light-harvesting components in solar energy conversion/storage systems.[1−3] As chromophores, inorganic semiconductor nanocrystals often possess larger extinction coefficients and show greater panchromaticity of visible light than molecular dyes.[4,5] Through quantum-confinement effects, light absorption by inorganic semiconductor nanocrystals can be tuned deterministically through changes in size and shape.[6,7] For such quantum dots, extraction of multiple charge carriers per absorbed photon has been reported.[8,9] To date, photoelectrochemical studies involving sensitization of a semiconductor photoelectrodes by quantum dots have focused almost exclusively on light-stimulated *electron* transfer, since many quantum dots can inject photoexcited electrons into the conduction bands of most metal oxides.[6,10−13] In contrast, the paucity of information on sensitized *hole* transfer from photoexcited quantum dots to a semiconductor photoelectrode directly speaks to the difficulty in finding quantum dots capable of injecting holes into the valence bands of most oxide semiconductors. The discovery of a sensitized photoelectrode/quantum dot pairing that shows facile sensitized hole injection from the quantum dots would aid both the fundamental understanding and practical development of improved photoelectrochemical energy conversion/storage systems.

Recently, planar p-type GaP electrodes have been identified as excellent platforms for the study of sensitized hole injection processes.[14,15] Unlike the majority of metal oxides, GaP can easily be rendered p-type with precisely controlled doping levels, can support sufficiently high charge-carrier mobilities, and in water natively has a comparatively negative valence-band edge potential (ca. +1.0 V vs Ag/AgCl).[14,16,17] The first two features can be leveraged to minimize deleterious charge back-transfer after sensitized charge injection.[14] Since CdSe quantum dots have reported valence-band edge potentials (i.e., standard potentials for initial oxidation of CdSe) that are more positive than +1.0 V vs Ag/AgCl in water,[18−20] the latter feature suggests that hole injection from a CdSe quantum dot into p-GaP should be thermodynamically permissible. Accordingly, this communication describes photoelectrochemical and spectroscopic data that support the contention that CdSe quantum dots can sensitize p-type semiconductor photoelectrodes through light-stimulated hole injection.

Figure 1 shows two separate observations that indicate sensitized hole injection into single-crystalline p-GaP from adsorbed quantum dots. Preparation details and a description of the methods employed for data collection are provided in the Supporting Information. First, Figure 1a shows two representative time-resolved photoluminescence decays after pulsed excitation at $\lambda = 561$ nm. When deposited from solution onto insulating glass, isolated CdSe quantum dots capped with ethylenediamine (EDA) exhibited an excited state that persisted for more than 30 ns. When deposited from solution onto planar p-GaP(100) substrates, the same CdSe quantum dots exhibited a photoluminescence decay that decreased below the detection limit within 20 ns, indicating that a new quenching pathway had become operative. As commonly observed in time-resolved luminescence studies of dry films of sensitizer−semiconductor composites,[21] the photoluminescence decays measured here could not be fit satisfactorily with a single-exponential function. Instead, a multiexponential approach was used.[11] Triexponential fits of the data recorded for CdSe quantum dots yielded average lifetimes of 8.8 ns on glass and 1.4 ns on GaP. An approximate hole injection rate from CdSe into GaP of 6.0×10^8 s^{-1} was inferred[11−13,22] from the luminescence decay data (see the Supporting Information). For comparison, the electron injection rates from 3.7 nm diameter CdSe quantum dots into n-TiO_2[11] and n-ZnO[23] were recently estimated as 6.3×10^8 and 1.0×10^{10} s^{-1}, respectively.

Second, Figure 1b shows representative steady-state photoelectrochemical data for a p-GaP photoelectrode sensitized by adsorbed 4.5 nm diameter CdSe quantum dots and immersed in an aqueous electrolyte (0.1 M KCl + 0.002 M $EuCl_3$) that

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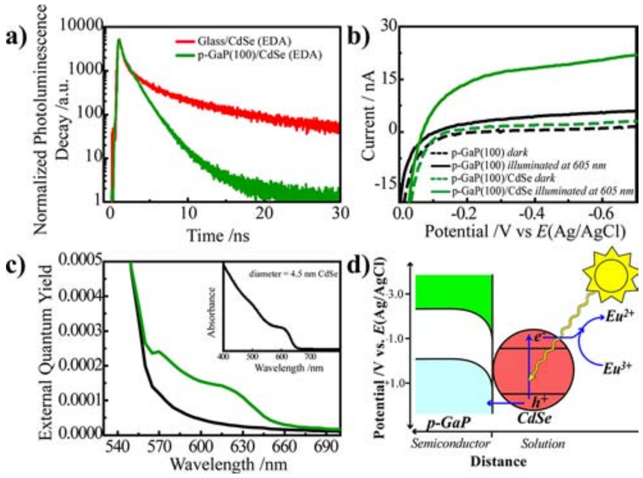

Figure 1. a) Time-resolved photoluminescence decays measured from 4.5 nm diameter CdSe quantum dots adsorbed on (red) glass and (green) p-GaP(100). The pulsed excitation wavelength was 561 nm. b) Steady-state current−potential responses for (black) a mirror-polished, bare p-GaP(100) photoelectrode and (green) a mirror-polished p-GaP(100) photoelectrode with adsorbed 4.5 nm diameter CdSe quantum dots in the absence of any illumination (dashed lines) and under monochromatic illumination at 605 nm at 0.33 mW cm^{-2} (solid lines). (c) External quantum yield spectra for (black) a bare p-GaP(100) photoelectrode and (green) a p-GaP(100) photoelectrode coated with a monolayer of CdSe quantum dots. Inset: absorption spectrum for the same CdSe quantum dots dispersed in hexanes. (d) Schematic depiction of sensitized hole injection from a CdSe quantum dot into p-GaP.

had been sparged with N_2. This electrolyte has previously been shown to induce strong-depletion conditions in p-GaP.[14] To adsorb CdSe quantum dots, the p-GaP(100) electrodes were first treated with $(NH_4)_2S(aq)$[24] to populate the surface with ammonium groups that facilitated subsequent quantum dot adsorption.[25] These electrodes were then immersed in a suspension of CdSe quantum dots in hexanes for 20 min, rinsed with hexanes, soaked in a solution with excess EDA for ligand exchange, and finally immersed in the aqueous test electrolyte for analysis. As shown in Figure 1b, p-type GaP(100) photoelectrodes with or without adsorbed CdSe quantum dots exhibited a strongly rectifying current−potential response in this electrolyte in the absence of illumination. Under illumination with sub-band-gap monochromatic light (λ = 605 nm), a markedly enhanced photoresponse was observed after the electrode was coated with a film of CdSe quantum dots. Specifically, the photocurrent at −0.6 V vs Ag/AgCl increased by a factor of 3.5 after incorporation of the layer of CdSe quantum dots. In addition, the open-circuit potential shifted by +35 mV upon the addition of adsorbed CdSe quantum dots. Figure 1c illustrates the wavelength-dependent external quantum yield values for these photoelectrodes under sub-band-gap illumination out to 700 nm at E = −0.6 V vs Ag/AgCl. For the bare p-GaP photoelectrode, the measured external quantum yield values dropped off sharply at wavelengths longer than the band-gap wavelength (λ = 549 nm). After the photoelectrode was coated with CdSe quantum dots, the spectral profile changed: increased external quantum yield values were measured out to $\lambda \approx$ 660 nm with a profile that qualitatively matched the absorption spectrum measured for a suspension of the same CdSe quantum dots in hexanes (Figure 1c inset). These data strongly suggest that the CdSe quantum dots were able to inject photoexcited holes into the valence band of p-GaP according to the scheme shown in Figure 1d.

To determine whether the sensitized hole injection process was sensitive to the physicochemical properties of the CdSe quantum dots, three separate photoelectrochemical studies were performed. To augment the low photoresponse seen for CdSe sensitization on flat p-GaP(100) in Figure 1, subsequent measurements used textured p-GaP photoelectrodes for sensitizer loading. The sub-band-gap photoresponse of roughened p-GaP(100) was larger than that for mirror-polished p-GaP(100), but the general spectral response profile was nominally the same (see the Supporting Information). Figure 2a,b illustrate the observed dependence of the external quantum yield versus wavelength profile on the size of the CdSe quantum dots. Figure 2a highlights the CdSe exciton signature in absorbance measurements for a series of CdSe quantum dot suspensions in hexanes. On the basis of the relationship between the position of the first exciton peak and the size of the quantum dots,[26] the average diameter of these CdSe quantum dots ranged from 3.1 to 4.5 nm, with the peak exciton wavelength extending from 547 nm to ca. 610 nm. When adsorbed onto p-GaP photoelectrodes biased at −0.6 V vs Ag/AgCl in the same electrolyte as in Figure 1, these CdSe quantum dots showed sub-band-gap sensitization but with different spectral profiles (Figure 2b). The longest wavelength that showed external quantum yields above the native sub-band-gap response of p-GaP tracked strongly with quantum dot size. The largest CdSe quantum dots in this study extended the photoresponsivity of p-GaP in this electrolyte out to 660 nm.

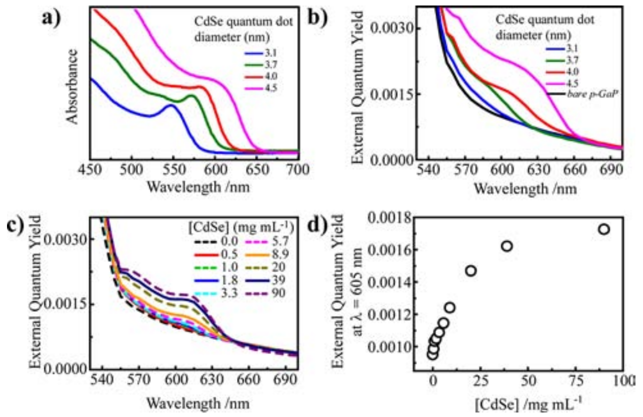

Figure 2. (a) Absorption spectra of CdSe quantum dot suspensions in hexanes. (b) External quantum yield spectra for roughened p-GaP(100) photoelectrodes sensitized with CdSe quantum dots spanning a range of sizes. (c) External quantum yield spectra for p-GaP(100) photoelectrodes with various loadings of CdSe quantum dots. The photoelectrodes were soaked for 20 min in hexanes solutions containing various concentrations of dissolved CdSe quantum dots. (d) Dependence of the external quantum yield measured at 605 nm on the concentration of the CdSe quantum dots in solution.

Separate measurements were performed to assess how the quantity of adsorbed CdSe quantum dots impacted the detectable sub-band-gap photoelectrochemical response of the p-GaP photoelectrodes. Figure 2c shows a representative series of sensitization studies in which the concentration of the 4.0 nm diameter CdSe quantum dot suspension used in the adsorption soaking step was varied. For a constant soaking time, the external quantum yield values increased when the

CdSe loading step was performed at a higher quantum dot suspension concentration. The longest wavelength at which the external quantum yield was measured to be above that in the blank p-GaP control experiments was 645 nm at all loadings, suggesting that the spectral profile was affected by the size and not the surface concentration of the CdSe quantum dots. Figure 2d shows how the measured external quantum yield at 605 nm tracked with the concentration of the CdSe suspension used to coat the p-GaP photoelectrode. A nonlinear correlation was observed, with an apparent saturation of the external quantum yield at high CdSe suspension concentration. To determine whether these data indicated that a high surface concentration of CdSe always precluded increased levels of sensitized hole injection, separate measurements were performed with intentionally thick films of CdSe prepared by drop-casting (see the Supporting Information). In these measurements, comparatively higher external quantum yields were routinely measured, consistent with the notion of either charge or exciton migration in thick quantum dot films.[27−29] Furthermore, this observation indicated that the saturated photoresponse in Figure 2d represented a maximum surface loading obtainable by the immersion method rather than an intrinsic issue with observing sensitized hole injection at high loadings of quantum dots.

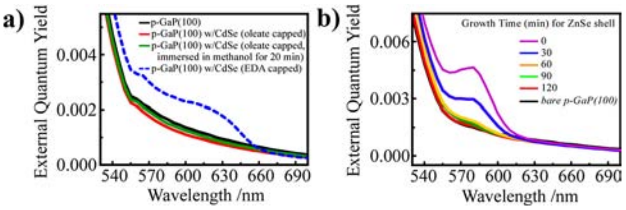

Figure 3. (a) External quantum yield spectra for a textured p-GaP(100) photoelectrode sensitized with 4.5 nm diameter CdSe quantum dots after various quantum dot surface treatments. (b) External quantum yield spectra for textured p-GaP(100) photoelectrodes sensitized with 3.7 nm diameter CdSe quantum dot cores coated with ZnSe shells. The shell thickness was controlled by varying the ZnSe shell growth time.

The surface conditions of the CdSe quantum dots strongly influenced the observed photoresponse. Figure 3a shows wavelength-dependent external quantum yield values at various stages of CdSe quantum dot surface treatment. To obtain these data, a roughened p-GaP photoelectrode was used to augment the total available surface area for adsorption. With the original oleate ligands from the CdSe quantum dot synthesis, there was no significant sensitization above the background (i.e., no measurable sub-band-gap photoresponse for bare p-GaP). When the same p-GaP/CdSe quantum dot photoelectrode system was then immersed in a methanol solution containing EDA and then tested for photoactivity, the sub-band-gap wavelength photoresponse increased significantly. Immersion in neat methanol did not change the measured photoresponse above the baseline activity for bare p-GaP, implicating the specific exchange of the insulating oleate ligands for the more compact EDA as the key enabling factor for hole injection. Similarly, Figure 3b shows photoresponses collected for p-GaP photoelectrodes sensitized with an adsorbed quantum dot film composed of CdSe particles with ZnSe shells having various thicknesses. CdSe/ZnSe represents a type-I core/shell system (i.e., the band-edge energies for ZnSe extend both above and below the band-edge energies for CdSe). Increasing the thickness of the wide-band-gap ZnSe shell progressively attenuated the detectable photoresponse. Separate photoluminescence measurements showed increased photoluminescence levels after the CdSe quantum dots were coated with ZnSe, indicating that the presence of the shell layers did not decrease the intrinsic quality of the core CdSe nanoparticles (see the Supporting Information). Hence, ZnSe acted primarily as an additional barrier for charge transfer between the photoexcited CdSe core quantum dot and the p-GaP photoelectrode.

The data here collectively argue that CdSe quantum dots adsorbed onto p-GaP photoelectrodes are a viable material combination for studying sensitized hole injection from quantum dots. The inclusion of comparatively large (≥4.5 nm diameter) CdSe quantum dots successfully extended the photoresponsivity of p-GaP photoelectrodes out to 660 nm. The energetics of these large CdSe quantum dots, coupled with the advantage of using p-GaP photoelectrodes operating under strong-depletion conditions, facilitated several basic tests of charge injection.

The preliminary evidence indicates that the sensitized hole injection in this system mirrors sensitized electron transfer in other photoelectrode/quantum dot systems in terms of sensitivity toward quantum dot size and surface condition. The precise rate of hole injection was not separately determined from the steady-state photoelectrochemical responses. The slow injection implied by the time-resolved photoluminescence data and the small values of the light flux-to-current flux quantum yields are generally consistent with our previous modeling studies.[14] Specifically, nondegenerately doped p-GaP photoelectrodes operating under strong-depletion conditions can support detectable net quantum yields for charge injection even without excessively high hole injection rates. Additional work that incorporates more controlled elements (covalent tethering of the quantum dots to the surface, precisely defined surface coverage) in order to estimate the internal quantum yield for sensitized hole injection in this system is needed. Still, the data already imply that increasing the surface area is an effective means to boost the measurable external quantum yield. We anticipate that further development of the p-GaP photoelectrode form factor will facilitate higher loadings of CdSe quantum dot sensitizers and accordingly better overall energy conversion properties.

Although it was not a primary focus of this study, these data also show that $Eu^{3+/2+}$(aq) is a possible redox mediator for this system. The $Eu^{3+/2+}$ redox couple does not have a large standard rate constant[30] but apparently does have a sufficiently positive standard potential to capture the photoexcited electron from CdSe quantum dots successfully (Figure 1d). Additional redox couples need to be identified in order to determine whether $Eu^{3+/2+}$ is an optimal choice as a mediator in a cell with p-GaP sensitized by CdSe quantum dots.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods; materials syntheses; and additional luminescence, electrochemical, and X-ray diffraction characterization 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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