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Luminescence Studies of Individual Quantum Dot Photocatalysts

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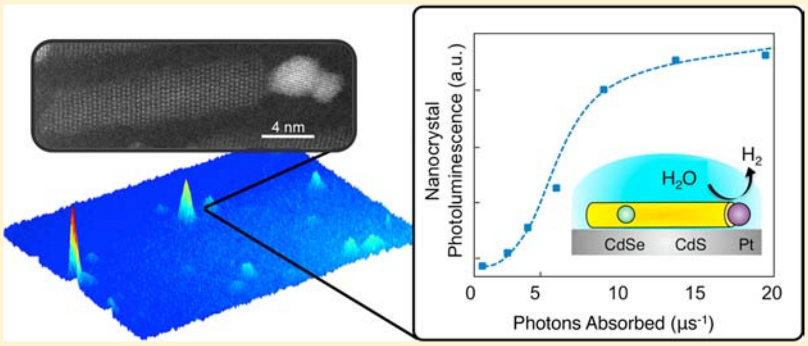
S Supporting Information



ABSTRACT: Using far-field optical microscopy we report the first measurements of photoluminescence from single nanoparticle photocatalysts. Fluence-dependent luminescence is investigated from metal-semiconductor heterojunction quantum dot catalysts exposed to a variety of environments, ranging from gaseous argon to liquid water containing a selection of hole scavengers. The catalysts each exhibit characteristic nonlinear fluence dependence. From these structurally and environmentally sensitive trends, we disentangle the separate rate-determining steps in each particle across the very wide range of time scales, which follow the initial light absorption process. This information will significantly benefit the design of effective artificial photocatalytic systems for renewable direct solar-to-fuel energy conversion.

INTRODUCTION

By comparison to natural photosynthetic systems, we know that the design of effective artificial photocatalytic systems will depend on our ability to observe and control an extended sequence of events for the electrons and holes that are generated following the absorption of a photon in a designed nanoscale system. In the natural photosystem II, a remarkable series of events unfold, which range from quantum coherence across many chromophores in the initial light absorption process, to sequential electron transfer processes in a cascade, followed by near barrierless multielectron redox processes on catalytic sites that are separated across a membrane.[1] An important tool for learning how to create analogous artificial photosynthetic systems is the ability to observe photocatalytic events at *individual* catalytic sites, because unlike the natural system, our fabrication methods are as yet imperfect. Such studies yield insight into the structure-dependent function of catalytic components, free from the blurring present in ensemble measurements. Indeed, even in relatively well-controlled synthetic systems, catalysts are characterized by a distribution of distances and interfaces between the multiple necessary components, and thus a wide distribution of catalytic activity occurs. Here we describe a quantum dot system in which it is possible to observe photocatalytic events at the single nanocrystal level as well as an approach for disentangling the separate rate-determining steps in each particle across the very wide range of time scales following the initial light absorption process.

RESULTS AND DISCUSSION

We consider a well-controlled model (nanoparticle-based) artificial system catalyzing a reduction half reaction. The system relies upon state-of-the-art nanocrystal synthesis and consists of a cadmium selenide (CdSe) quantum dot embedded asymmetrically within a cadmium sulfide (CdS) quantum rod,[2−5] with a Pt reduction catalyst placed on the opposite end of the rod.[6,7] These structures are illustrated in Figure 1. The light absorption and charge separation events in this system can be tuned by variations of the dot diameter and the rod length.[6,8] This system has several distinguishing characteristics which allow us to perform the first controlled observations from single photocatalytic sites. Foremost is the system's strong absorption of light and very high photoluminescence quantum yield in the absence of a reduction catalyst (>60%). Photoluminescence is one of the most powerful tools for studying single quantum systems, but an efficient photocatalytic system will only rarely emit light, as the photogenerated charges are ordinarily consumed to drive the redox chemistry, rather than by light emission. However, the catalyst-decorated quantum dot/rod system employed here is still bright enough to observe at the

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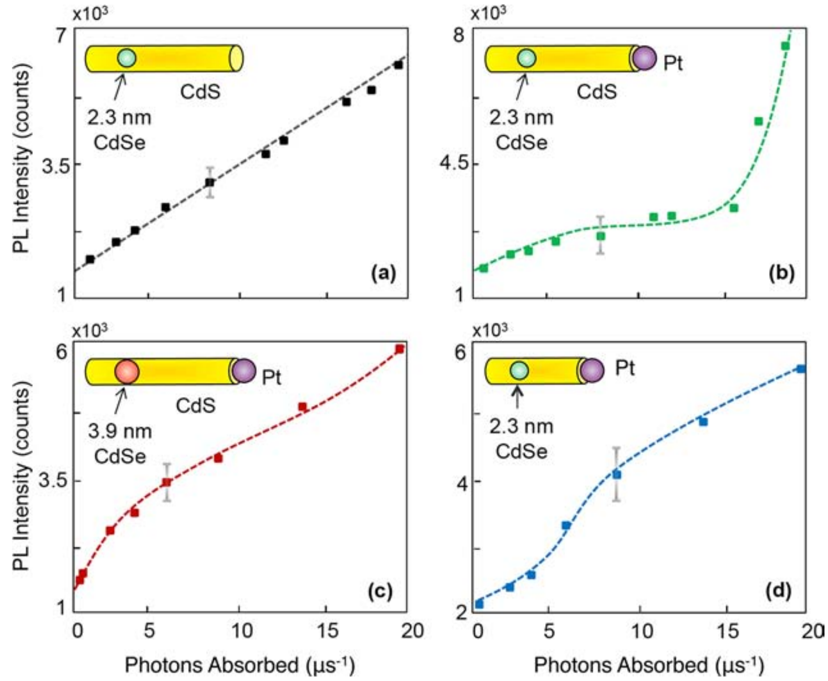

Figure 1. Characteristic fluence-dependent photoluminescence obtained in gaseous argon from a few dozen of individual photocatalysts consisting of (a) colloidal CdSe quantum dot embedded asymmetrically within a CdS quantum rod; (b) with reduction Pt catalyst placed on the opposite end of the rod. (c) The rod length is held constant, and the dot diameter is increased from 2.3 to 3.9 nm. (d) The quantum dot size is held fixed, and the rod length decreases from 60 to 40 nm. Dashed lines serve as guides to the eye.

single particle level, while capable of yielding hydrogen at a quantum efficiency as high as 20%. This residual photoluminescence probe provides an inverse measure of the efficiency of the photocatalysis for each particle. Furthermore, since the radiative rates of the system absent the reduction catalyst are well-known, the intensity of the luminescence as a function of the incident light intensity can be used as a clock to probe processes on multiple time scales.

Our results indicate a complex, highly nonlinear power dependence of the light emission when catalysis is active. From these trends, we are able to separately deduce the rates at which holes and electrons are photochemically consumed on each particle (the holes are consumed from the embedded quantum dot by a scavenger). We emphasize that even in this system, where the distances and the interfaces have been controlled with our most advanced fabrication techniques, these rates vary widely from one particle to the next. This study would be very difficult in a system that relied upon stochastic arrangements of the semiconductor and metal components and impossible in semiconductors with low intrinsic photoluminescence quantum yields.

Quantum size effects enable engineering of the catalyst's optical and electronic properties. Visible light is absorbed by the system, creating electron wave functions that are delocalized throughout the CdS rod and hole wave functions that are three-dimensionally confined to the CdSe quantum dot (with fast hole localization, in ~650 fs).[9] When a Pt tip is added, the route of electrons transfer from the seeded rod to Pt competes effectively enough with the route of radiative emission. Consequently, with this design, the electrons are separated from the holes via three distinct components and by a tunable physical length and are subsequently available for reductive processes.

To explore these effects, we probe the fluence-dependent photoluminescence from individual photocatalysts using far-field optical spectroscopy. While the actual particle cannot be imaged by this technique, as it is smaller than the diffraction limit of visible light, the light emitted from individual nanocrystals is sufficiently localized such that the position of the nanocrystal can be determined and the emitted light can be analyzed (the sample concentration was adjusted for single particle measurements). The catalysts are deposited on a quartz substrate and exposed to a variety of environments including gaseous argon, liquid water, and water containing a selection of hole scavengers. They are illuminated with an Ar laser (457.9 nm) using a set of ND's to modify the excitation light intensity. The photon flux was calculated using the laser beam measured intensity, divided by the illuminated area, and multiplied by the average particles absorption cross section. The photoluminescence signal from the sample was directed through Acton spectrometer onto a Princeton Instruments liquid nitrogen cooled CCD. No spectral changes were observed with fluence (top of Figure 3). Individual catalysts each exhibit a characteristic nonlinear fluence dependence that depends systematically upon the environment.

We start by considering the power-dependent emission from CdSe/CdS dot/rod systems in argon with no Pt tip (Figure 1a). The rod length is set to 60 nm, and the seed diameter is 2.3 nm. These untipped nanocrystals show very bright luminescence, and the power dependence is either completely linear or just slightly sublinear at the highest fluxes (20 photons/μs). However, when a small (<3 nm diameter) Pt tip is added, the power dependence is dramatically altered, as illustrated in Figure 1b. About 97% of the rods examined demonstrated the same trends (Figure S4). The photoluminescence, which is linear for low photon fluxes (typically below 6 photons/μs), shows a pronounced saturation at intermediate fluxes (typically between 8 and 15 photons/μs) and exhibits a surprising increase in light emission at the highest fluences employed here. We have examined this fluence dependence in a hundred individual dots in four different chemical environments (Figures 1b and 2a,b) and with three different dot and rod size combinations (Figure 1b–d). From these studies a systematic picture of electron–hole transfer events in these metal-semiconductor photocatalysts has emerged.

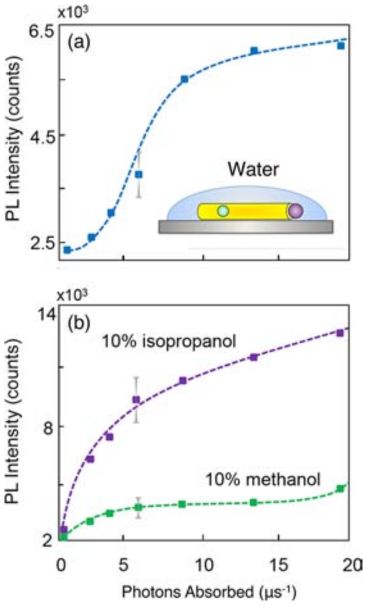

Figure 2. Characteristic fluence dependence in individual dots exposed to (a) pure liquid water and (b) water with 10% methanol (green) or 10% isopropanol (purple) as hole scavengers. The saturation in the fluence dependence, and overall intensity, can be used to monitor processes that consume the photogenerated hole. Dashed lines serve as guides to the eye.

The saturation in the light emission at intermediate photon fluxes is due to the presence of an excess hole in the quantum dot. When the metal catalyst is present, the electron transfers rapidly to the Pt, temporarily leaving an extra hole behind in the quantum dot. In argon and at low photon fluxes, this hole will eventually recombine with the Pt-based electron. However, at higher fluxes, a second photon can be absorbed before such a recombination can occur. In this case, a new exciton is created in the presence of a residual hole remaining from the prior photon absorption event. This excess hole can efficiently relax the new electron–hole pair through Auger processes, providing an additional nonradiative relaxation channel.[10,11] This quenches the intermediate flux luminescence and produces the saturation we observe. Thus, the onset of the saturation in the light emission serves as a clock for probing the charge-separated state lifetime. We estimate it to be on the order of 10^{-7} s, 3 orders of magnitude slower than the separation measured for nonseeded Pt-tipped CdS rods.[12] This serves as a strong demonstration of how photoinduced charge carriers can be manipulated via structural engineering of the photocatalyst. Facilitating a longer-lived charge-separated state is expected to be critical for the promotion of chemical reactions on the photocatalyst surface.

Of significance for the design of this photocatalytic system is the fact that the saturation onset obtained in the presence of gaseous argon (Figure 1b) does not appear to significantly shift when pure liquid water is introduced (Figure 2a). In both environments, saturation is observed at ∼8 photons/μs. This indicates that nonradiative back recombination of the hole with the electron formerly residing on the Pt is still favorable over photochemical consumption (water oxidation).

This assignment can be further confirmed by experiments in the presence of hole scavengers with varying efficiency. Figure 2 shows that the onset of this saturation shifts to lower photon fluxes when scavengers, such methanol or isopropanol, are added to pure water. The estimated charge-separated state lifetime in water (120 ns ±40 ns) becomes about twice as long with the introduction of methanol as a hole scavenger (250 ns ±35 ns) ns and close to three times longer with the use of isopropanol (330 ns ±35 ns). The polar scavenger molecules act to stabilize the holes, making them less reactive for nonradiative back recombination with the electron and thus prolonging the charge-separated state lifetime. In other words, the excess hole will remain on (or at the vicinity of) the quantum dot for a longer duration, thus enabling the slower chemical consumption as a valid alternative to recombination with the electron. It is particularly interesting to note that an increase of the effective charge-separated state lifetime by ∼80 ns, or one-third as a percentage, obtained when substituting methanol by isopropanol, results in a 3-fold increase in activity toward hydrogen production.

When the excess hole, which is a radiative quencher, is finally removed from the quantum rod, light emission from the system is expected to recover. As seen in Figure 2b, the emission in the presence of isopropanol is consistently brighter than in the presence of methanol, confirming that propanol is a faster hole scavenger that acts to quickly remove the excess hole. These results are in good agreement with our previously reported relative activity for hydrogen production.[6]

Our results imply that manipulating photoinduced charge-transfer rates and prolonging the charge-separated state lifetime, on the 10^{-7} s time regime, might suffice for significant improvement of the catalytic efficiency. Such management of charge carriers can be obtained via simple geometrical modifications of the photocatalyst on the nanoscale.

While the saturation in the fluence dependence can be used to monitor processes which consume the photogenerated hole, the increase in photoluminescence at still higher fluxes (seen in Figure 1b) can be used to monitor processes that consume the photogenerated electrons. At low to intermediate fluxes, photogenerated electrons are typically transferred to the Pt tip, where they either recombine nonradiatively on a much longer time scale with the hole (in Ar) or are consumed photochemically (in water). However, at the highest fluxes, the possibility exists that a second electron–hole pair will be photogenerated before the electron on the Pt has been consumed. In this case, the second electron must overcome the Coulomb repulsion of the first.[13] Likewise, if the rate of photon arrival increases still further, a third electron would have to overcome the Coulomb repulsion from two electrons on the Pt. This Coulomb repulsion will favor a situation in which the electron stays behind in the quantum rod and recombines radiatively with a hole. The increase in luminescence at high flux is thus due to the electrons backing up on the Pt. This effect can be seen most clearly by comparing the behaviors in Ar (Figure 1b) and water (Figure 2a). In Ar, the increase at high flux in the photoluminescence is pronounced; in water, where the electron transfers from the Pt to a hydrogen ion in solution, it is barely observable if not entirely absent. This

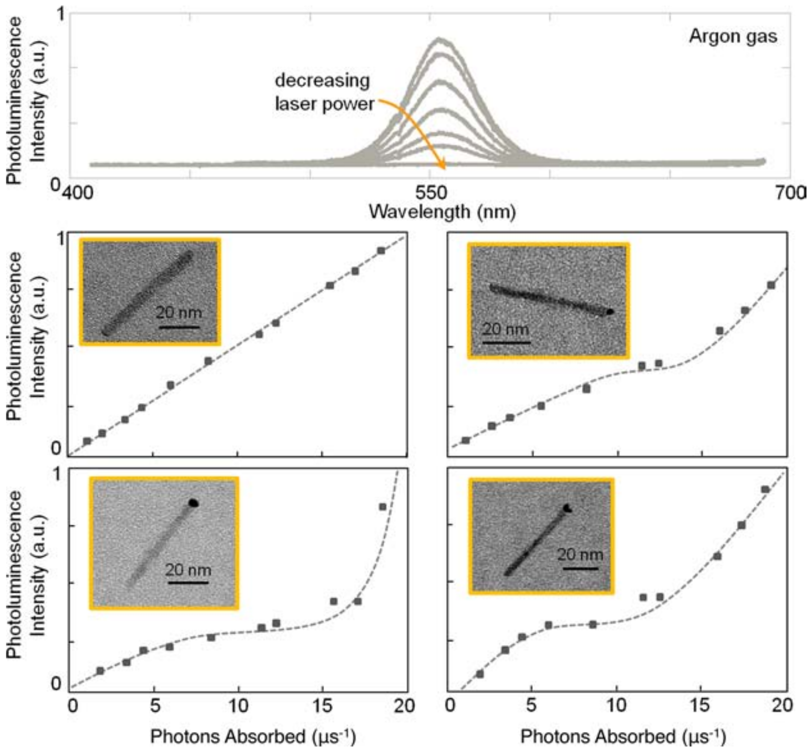

Figure 3. Top: Spectra from a single particle. Bottom: Examples of single particle fluence-dependent photoluminescence originating from four individual particles, along with their corresponding TEM micrographs. Performing correlated single particle photoluminescence and electron microscopy studies will enable more detailed examination of individual characteristics. Dashed lines serve as guides to the eye.

indicates that the rate for electron transfer from the Pt to the solution is comparable to the rate by which a new electron transfers onto the Pt, with an upper estimate of 50 ns. Interestingly, since we found that nonradiative back recombination of the hole with the electron formerly residing on the Pt is favorable over photochemical consumption, we speculate that it is the second electron on the Pt which is the catalytically active one.

This increase in the photoluminescence is partially recovered when hole scavengers are added to the water, since in the presence of stabilized and less reactive holes, faster accumulation of electrons on the Pt tip can be attained.

The two different nonlinear trends observed here, photoluminescence suppression due to hole saturation and enhancement due to electron saturation, can be clearly distinguished for a sample composed of a 2.3 nm seed embedded in a 60 nm long rod. This sample was also found to be the most active for hydrogen generation.[6] The nonlinear power dependence is highly sensitive to the quantum dot and rod dimensions. Experiments in which the dot diameter and rod length are separately varied provide additional support for the necessity of single particle characterization. When the rod length is held constant and the dot diameter is increased from 2.3 to 3.9 nm (Figure 1c), we see that the onset of the photoluminescence suppression shifts to lower photon flux, while the photoluminescence enhancement at high flux becomes more gradual. Similar variations are obtained when the quantum dot size is held fixed and the rod length is decreased from 60 to 40 nm (Figure 1d). In these situations, the consumption of electrons and holes occurs at very similar time scales, producing a wide variety of very complex fluence dependencies. Of greatest interest here is the fact that in the shorter rod, the suppression and enhancement occur at nearly the same photon flux. This strongly implies that the presence of just one electron suffices to prevent a second from entering the Pt catalyst tip.

Single particle measurements have played an essential role in disentangling the important time scales governing the photocatalysts studied here. First, ensemble studies are always overwhelmed by the very small percentage of extremely bright dots that are catalytically inactive, either because the Pt–metal interface is poor or because they have no metal tip on them. Second, the saturation and enhancement onsets might vary significantly from dot to dot within any sample (Figures S4 and S5). We have been able to perform experiments on a very thin substrate compatible with electron microscopy, so that we could examine each dot afterward by transmission electron microscopy (TEM). Examples of single particle fluence-dependent photoluminescence originating from four individual particles, along with their corresponding TEM micrographs, are presented in Figure 3. Given sufficient statistics and careful analysis, such data will enable future studies in which we can try to correlate each photocatalysts' unique and reproducible fluence dependence with detailed individual structural characteristics (precise dot diameter and rod length, metal tip size and faceting, nature of the metal–semiconductor interface, etc.).

■ CONCLUSION

We demonstrate the first controlled observations from single photocatalytic sites, under realistic conditions for hydrogen formation. Our studies yield insight into the structure-dependent function of catalytic components, free from the blurring present in ensemble measurements. Our results imply that manipulating photoinduced charge-transfer rates and prolonging the charge-separated state lifetime, on the 10^{-7} s time regime, might suffice for significant improvement of the catalytic efficiency. Such management of charge carriers can be obtained via geometrical modifications of the photocatalyst on the nanoscale. This greatly extends the domain of fundamental photocatalysis research and significantly benefits our ability to design effective artificial photocatalystic systems for renewable direct solar-to-fuel energy conversion.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed description of the synthesis of our photocatalytic system (Pt tipped CdSe/CdS rods), the experimental apparatus, and methods used for data analysis. This information 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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