Photocatalytic Events of CdSe Quantum Dots in Confined Media. Electrodic Behavior of Coupled Platinum Nanoparticles

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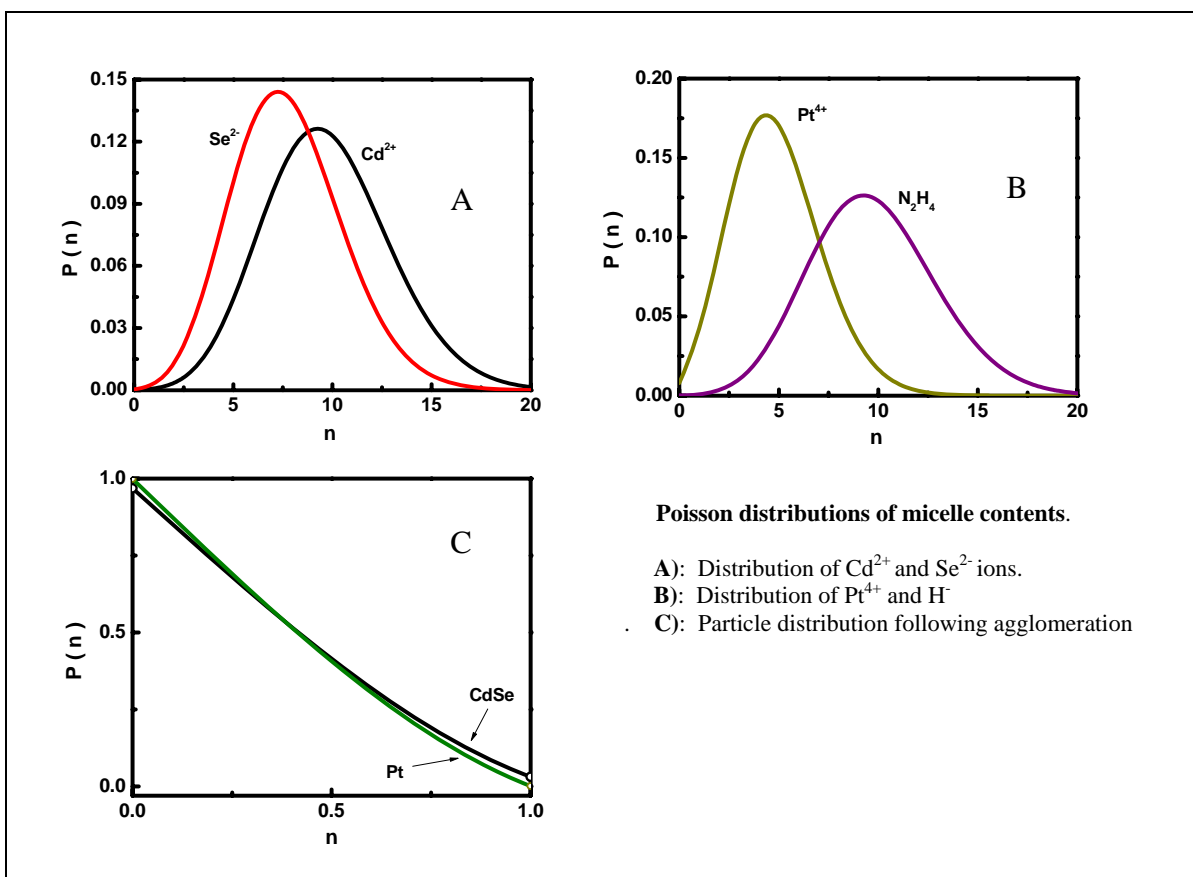University of Notre Dame, Notre Dame, IN 46556

SI-1

Poisson analysis of the ionic and particulate contents of the micelles before and after intermicellar exchange.

The expected probabilities of a micelle containing a given species are shown below in figures SI-1 (A-C). P($\bar{n}$) defines the probability of a micelle containing $\bar{n}$ species. Figures A and B show the distribution of the precursor ions of CdSe and Pt, respectively. Figure C shows the distribution of particles following the formation of CdSe and Pt nanoparticles after micellar mixing. The probability of a micelle containing one CdSe particle, $P_{CdSe}(1)$, and one Pt particle, $P_{Pt}(1)$, are approximated to .03 and .01, respectively. Based on the Poisson analysis, if the micelle concentration is held constant, the expected probability of a micelle containing <u>both</u> a CdSe and Pt particle, $P_{CdSe/Pt}$ **(1)**, is defined as the product shown below:

$$P_{CdSe/Pt} (1) = P_{CdSe}(1) \times P_{Pt}(1) = .0003$$

However, because electron transfer is clearly observed between CdSe and Pt, we conclude that the coupling of the particles is spontaneous, and thus, particle distributions, unlike ion distributions, can not be predicted using mathematical modeling due to such external factors as electrostatic interaction, thermodynamic stability, etc..

Poisson distributions of micelle contents.

A): Distribution of Cd^{2+} and Se^{2-} ions.
B): Distribution of Pt^{4+} and H^-
. **C**): Particle distribution following agglomeration

SI-2

**Distribution of MV^{2+} ions across the micellar medium.**

The following shows the Poisson distribution of MV^{2+} molecules across the micellar medium. The concentration of MV^{2+} is 1mM and the water to surfactant ratio, w_o, is 16.5. As shown, $[MV^{2+}] >> [CdSe]$, $[Pt]$ and every micelle contains a MV^{2+} molecule.
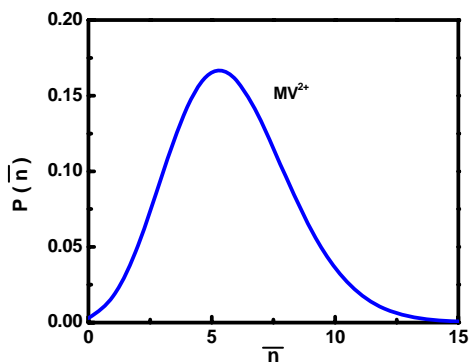
SI-3

Transient absorption-time profiles of a micellar solution containing CdSe and various concentrations of MV^{2+}.

The maximum concentration of the reduced radical species, $MV^{+\bullet}$, obtained following laser excitation of $CdSe/MV^{2+}$, is independent of the starting concentration of MV^{2+} at values beyond the μM range. This indicates surface saturation of CdSe by MV^{2+}. At the time scale displayed in the figure, only MV^{2+} ions at the CdSe surface can be reduced, since diffusion of unbound MV^{2+} to the surface occurs on a much slower timescale. Increasing the laser power also showed no real change in the $MV^{+\bullet}$ yield.
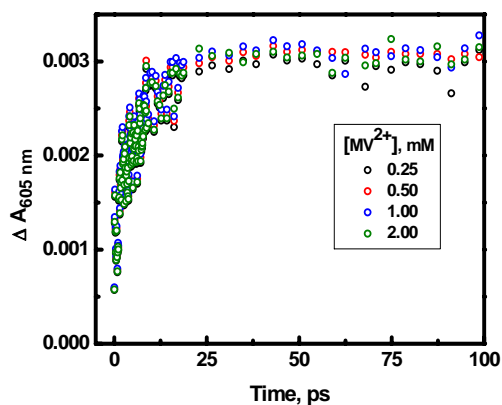
SI-4

Absorbance spectra of the MV$^{+\bullet}$ radical.

The spectra features of a solution containing the MV$^{+\bullet}$ radical are shown below. The strong, broad absorbance in the 600 nm region makes MV$^{+\bullet}$ an ideal probe molecule.
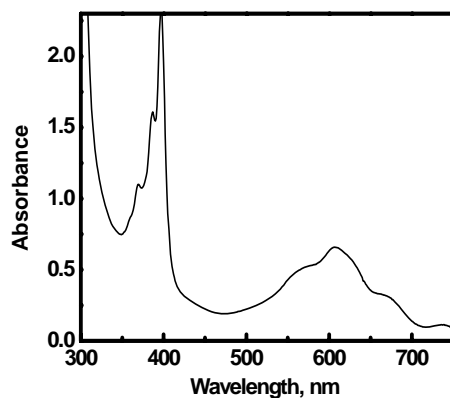
SI-5

Transient absorption spectra of CdSe/MV^{2+} at various probe delay times.

Using femtosecond transient absorption, the transient absorption spectra of CdSe in the presence of MV^{2+} was obtained. The concentration of MV^{2+} was 1mM. As shown in SI-3, the CdSe surface is saturated by MV^{2+}. At a delay time of t=0 ps, no characteristic absorbance of the MV$^{+\bullet}$ radical is observed. At longer times, the broad absorption in the 600 nm range following excitation of the CdSe confirms the formation of the MV$^{+\bullet}$ radical.