Metal-Enhanced Fluorescence from CdTe Nanocrystals: A Single-Molecule Fluorescence Study

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Supporting Information:

Experimental Section

All the reagents and spectroscopic grade solvents were used as received from Fisher or Aldrich. Nanopure water (>18.0 M) purified using Millipore Milli-Q gradient system, was used in all experiments.

Preparation of CdTe nanocrystals. The synthesis of CdTe nanocrystals was performed using a modified Weller procedure, described below.[1,2] Briefly, a solution of 1.970 g $Cd(ClO_4)_2 \cdot 6H_2O$ (4.70 mmol) and 1.380 g stabilizing ligand thioglycolic acid (11.54 mmol) was placed in 250 mL MilliQ-water. The solution pH was adjusted to 11.0 by adding a few drops of diluted NaOH, and then the solution was continuously stirred for 30 min at room temperature with nitrogen purging to eliminate dissolved oxygen. The source of tellurium (NaHTe) was prepared separately, which involved the reduction of metallic tellurium powder (0.383 g, 3 mmol) suspended in 10 mL MilliQ-water with sodium borohydride (0.227 g, 6 mmol in 5 mL water) at 0-5 ^oC. In an about 30 min the

suspended tellurium powder completely dissolves in water and the color of solution was changed to pinkish. Under vigorous stirring, the obtained NaHTe solution was injected slowly into the solution of $Cd(ClO_4)_2 \cdot 6H_2O$ containing thioglycolic acid at room temperature. The reaction mixture was refluxed for 24 hours and then cooled down to room temperature.

Silver island film (SIF) preparation: The glass slides (Corning, NY) used for silver island film (SIF) preparation were first cleaned by soaking them for overnight in 10:1 (v/v) mixture of H_2SO_4 (95–98%) and H_2O_2 (30%), commonly known as piranha (*Warning: piranha solution reacts strongly with organic compounds and should be handled with extreme caution; do not store the solution in closed containers*). After washing rigorously with MilliQ deionized water, the glass slides were air-dried. SIFs were deposited on clean glass slides using the method reported previously by us.[3] Briefly, about 1.5 mL of freshly prepared 5% NaOH solution was added to a stirring aqueous silver nitrate solution (0.375 g in 45 ml water) in a glass beaker. Subsequently, the resulted dark-brown precipitate was redissolved by slowly adding 1 mL of NH_4OH. The solution was cooled to 5^oC in an ice bath and a fresh solution of D-glucose (0.540 g in 11 mL water) was added, followed by four pairs of dried glass slides placed into this solution. The mixture was stirred for 2 min in ice bath and then allowed to warm up to 30^oC for the next 5 minutes. As the color of the mixture turned from yellow-greenish to yellow-brown, the color of the slides became greenish. The slides were removed from the beaker, rinsed with Milli-Q water. Excess and non-adhesive silver particles on the glass surface were removed by mild sonication of the SIF coated glass slides for 1 minute. The

SIF slides were stored in Milli-Q water until they were used. SIFs displayed the characteristic surface plasmon resonance with an absorption maximum near 460 nm.

Spin coated films on glass and SIF surfaces: Polyvinylalcohol (PVA, MW ~ 13000 – 23000) purchased from Aldrich and used as received. For the ensemble experiments, CdTe nanocrystals were dispersed into 1 wt% solution of PVA in water and spin coated onto regular glass slides (3" x 1" Corning Inc.) with 3000 rpm. For the single molecule studies PVA films were prepared on standard glass coverslips or SIFs deposited coverslips. Films on both cover glass and SIFs were deposited by spin-casting solutions of the CdTe nanocrystals dispersed in PVA (0.1 wt% in water). Before spin casting CdTe nanocrystals dispersed PVA, a layer of PVA with CdTe free were obtained by spin coating 0.1wt% solution PVA to render ~10 nm distance between the silver islands and CdTe nanocrystals to avoid quenching of CdTe fluorescence by silver nanoparticles.

Absorption and Fluorescence Spectroscopy: Absorption spectra were collected using a Hewlett-Packard 8453 spectrophotometer. Fluorescence spectra were recorded using a Varian Cary Eclipse Fluorescence Spectrophotometer using front face illumination geometry with 470 nm excitation from a Xenon arc lamp. Time-resolved intensity decays were recorded using a PicoQuant Fluotime 100 time-correlated single-photon counting (TCSPC) fluorescence lifetime spectrometer. The excitation at ~ 470 nm was obtained using a pulsed laser diode (PicoQuant PDL800-B) with 20 MHz repetition rate. The Instrument Response Function (IRF) is about 300 ps. The excitation was vertically polarized and the emission was recorded through a polarizer oriented at 54.7^{o} from the vertical position. A bandpass filter at 685±35 nm (Chroma Inc.) was used in the collection path to record the fluorescence from the CdTe nanocrystals.

Data Analysis: The fluorescence intensity decays were analyzed in terms of the multi-exponential model as the sum of individual single exponential decays:[4]

$$I(t) = \sum_{i=1}^{n} \alpha_i \exp(-t/\tau_i) \qquad (1)$$

In this expression τ_i are the decay times and α_i are the amplitudes and $\sum_i \alpha_i = 1.0$. The fractional contribution of each component to the steady-state intensity is described by:

$$f_i = \frac{\alpha_i \tau_i}{\sum_j \alpha_j \tau_j} \qquad (2)$$

The average lifetime is represented by:

$$\bar{\tau} = \sum_i f_i \tau_i \qquad (3)$$

The values of α_i and τ_i were determined using the PicoQuant Fluofit 3.3 software with the deconvolution of instrument response function and nonlinear least squares fitting. The goodness-of-fit was determined by the χ^2 value.

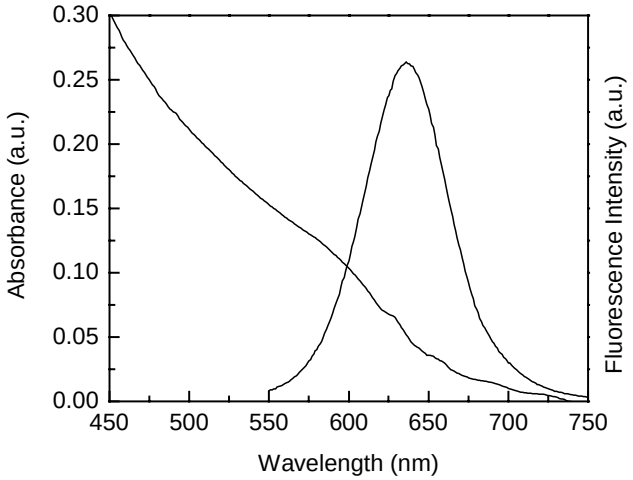

Figure S1. Absorption and emission spectra of CdTe nanocrystals in water. λ_{ex} = 470 nm.

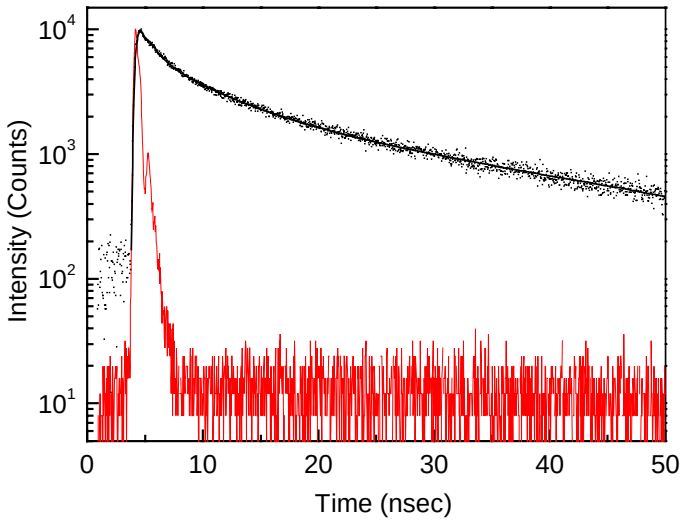

Figure S2. Intensity time decay of CdTe nanocrystals in water. Instrument response function is also included.

References

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