

Supporting Information

CdSe Nanocrystal/C₆₀-Liquid Composite Material with Enhanced Photoelectrochemical Performance

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1. Experimental Details

General Procedures

Unless otherwise stated, all starting materials and reagents were purchased from commercial suppliers and used without further purification. Thin solvent-free films were prepared on a quartz substrate for the absorption, photoluminescence (PL) and flash-photolysis-time-resolved microwave conductivity (FP-TRMC) measurements. UV-vis absorption spectra of solution-phase and solvent-free film states were recorded on a Hitachi U-2900 spectrophotometer. Steady-state fluorescence measurement of solution-phase samples was carried out using a Hitachi F-7000 Fluorescence Spectrometer. The fluorescence spectra of solvent-free composite films were recorded on a custom apparatus utilizing a CW argon-ion laser (Melles Griot 400-A06) operated at 488 nm for excitation and a Princeton Instruments Spectra Pro® 2300i spectrometer equipped with a model 7509-0001 liquid nitrogen cooled CCD for PL detection. Time-resolved fluorescence lifetime measurements were carried out using a HORIBA JobinYvon FluoroCube spectroscopy system. The quality of the fit has been judged by the fitting parameters such as χ^2 (<1.4) as well as the visual inspection of the residuals. TRMC measurements were carried out using a X-band (9 GHz) microwave circuit

at low power (approximately 3 mW) and a nanosecond Nd:YAG laser (Spectra Physics Inc., INDI) irradiation at 355 nm with photon density of 9.1×10^{15} photons cm^{-2} pulse $^{-1}$. Transient absorption (TA) spectroscopy was performed by using the same laser as an excitation and a white light continuum from a Xe lamp as a probe light. The probe light was guided into a wide-dynamic-range streak camera (Hamamatsu C7700) which collects two-dimensional image of the spectrum and time profiles of light intensity. Thermo-gravimetric analysis (TGA) was conducted on a TA Instruments Q50.

2. Synthesis and characterization

2-1. Synthesis of cadmium selenide (CdSe) nanocrystals (NCs)

General synthetic procedure

Synthesis of highly monodisperse CdSe NCs was carried out using a technique adapted from Murray et. al.¹ 12 g of trioctylphosphine oxide (TOPO) (99%, Sigma) and 0.12g of tetradecylphosphonic acid (97%, Strem Chemicals) were combined in a 50 mL three-neck flask and heated to 110 °C for 2 hours under vacuum. The solution was then heated to approximately 355 °C under a nitrogen atmosphere.

Separately, in a nitrogen-filled glove box, a solution of 1.0 M selenium (99.999%, Sigma) dissolved in trioctylphosphine (97%, Strem Chemicals) was prepared by stirring at 70 °C for 8 hours. 1.555 g of this TOP-Se solution was then mixed with 4.986 g trioctylphosphine and 0.15g of dimethylcadmium (99%, Strem Chemicals). The combined solution was loaded into a syringe and transferred out of the glove box. The TOPO/tetradecylphosphonic acid solution was allowed to cool and when the solution reached 350 °C the mixture of TOP/TOP-Se/(Me)₂Cd was rapidly injected, causing the contents of the flask to change from clear to dark orange over the course of approximately 5 minutes, indicating the presence of CdSe nanocrystals. The temperature was allowed to stabilize at 280 °C and the solution held at this temperature for 20 minutes before cooling.

Approximately 10 mL of toluene was added to the flask at ~60 °C. The contents of the flask were then withdrawn and placed in two 50 mL centrifuge tubes. To each tube, 20 mL of ethanol and 10 mL of acetone were added, causing flocculation of the CdSe NC phase. The CdSe NCs were precipitated under centrifugation and redispersed in hexane. Resulting CdSe NCs were 2.4 nm in diameter as measured by UV-vis absorption spectroscopy and TEM analysis.

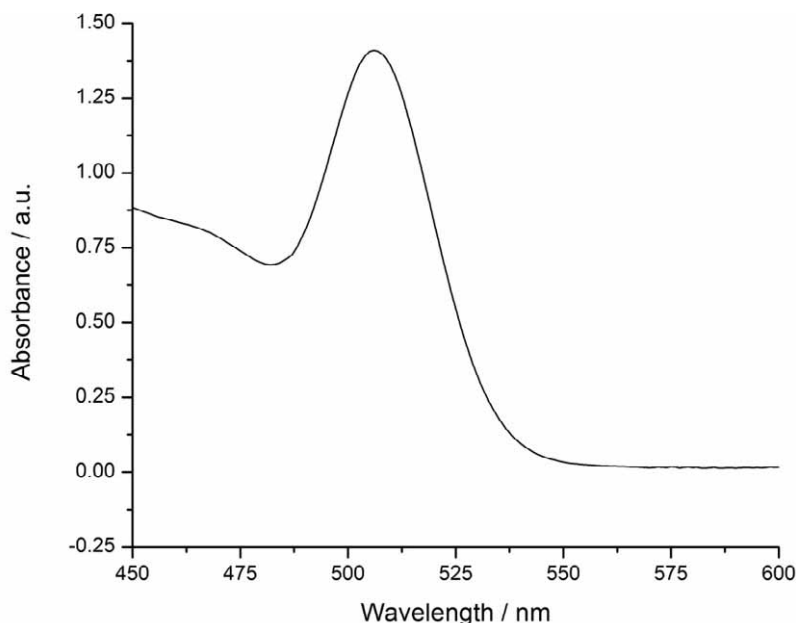


Figure S1. UV-visible absorption spectrum of as-synthesized CdSe NCs ($1.4 \times 10^{16} \text{ cm}^{-3}$) exhibiting first exciton transition at 506 nm.

Ligand Exchange

CdSe NCs dispersed in hexane were precipitated with methanol under centrifugation. The solid precipitate was dispersed in pyridine under sonication at 60 °C over the course of 4 hours. *n*-Hexane was added to the clear CdSe NC-pyridine solution leading to a cloudy suspension of flocculated NCs. This solution was centrifuged and the precipitate was again dispersed in fresh pyridine under sonication. Successful exchange of the original TOPO ligands with pyridine was confirmed using fluorescence spectroscopy (485 nm excitation), which showed virtually complete quenching of NC fluorescence.²

Pyridine-capped CdSe NCs dissolved in pyridine were precipitated with *n*-hexane under centrifugation. The solid precipitate was then dispersed in a 50 mM solution of hexadecylamine (HDA) in *n*-hexane. The initially cloudy suspension was sonicated for two hours resulting in a clear solution. CdSe NCs were then precipitated with methanol under centrifugation and again dispersed in a 50 mM HDA solution under sonication. In a final step the CdSe NC/HDA solution was precipitated with methanol under centrifugation and the CdSe NC precipitate was dispersed in pure monochlorobenzene, resulting in a clear solution. Successful exchange of the pyridine with HDA was verified using fluorescence spectroscopy (485 nm excitation), which showed strong fluorescence from the HDA-capped CdSe NCs.

3. Sample Preparation

3-1. Preparation of solution-phase samples

Solution-phase mixtures of HDA-capped CdSe NCs and liquid- C_{60} derivative (**1**) were prepared by combining appropriate quantities of CdSe NC in monochlorobenzene with **1** in monochlorobenzene under ambient conditions. The quantity of CdSe NC in each sample was held constant while the quantity of **1** was varied (total volume of each solution was fixed at 3 mL). All mixtures were allowed to age over-night in order to ensure a steady-state equilibrium was reached between ligands bound to the NC cores and free ligands in solution.

3-2. Preparation of solvent-free film samples

Mixtures of HDA-capped CdSe NCs and **1** were prepared by combining appropriate quantities of CdSe NC in monochlorobenzene with **1** dissolved in anisole under ambient conditions. The quantity of CdSe NC in each sample was held constant while the quantity of **1** was varied (total volume of each solution was fixed at 80 μ L). These solutions were aged over-night before being drop-cast on quartz substrates (0.75 x 2 cm²). After drop-casting each solution was allowed to dry at room temperature under argon for approximately 30 minutes until the majority of solvent had evaporated and the sample formed a smooth film. Samples were then held under vacuum (> 30 mm Hg) at 70 °C over-night.

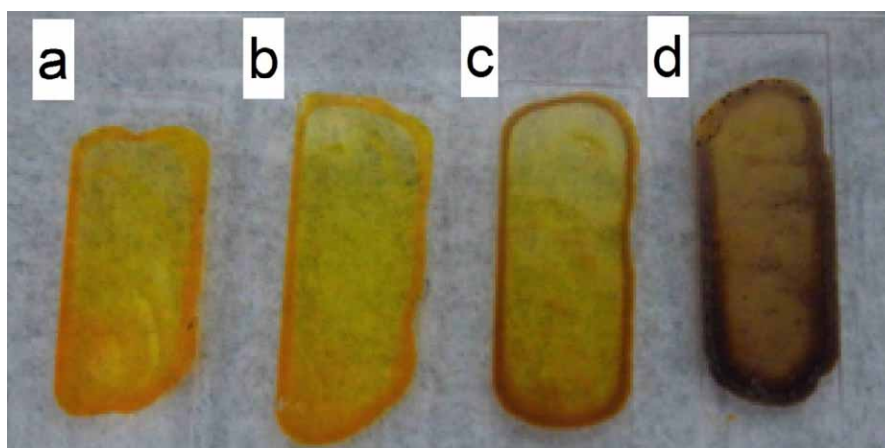


Figure S2. Photo images of solvent-free films containing (a) pure CdSe NC, (b) 2:1 CdSe NC/**1** (by weight), (c) 1:2 CdSe NC/**1** (by weight), and (d) pure **1** drop-cast on quartz substrates.

3-3. Preparation of electrolyte for photoelectrochemical measurements.

An aqueous solution of 1.0 M sodium sulfide (Na_2S)/saturated ($< 0.1 \text{ M}$)! sulphur was prepared by addition of the solid precursors to 18 M Ω dionized water in a 50 mL centrifuge tube. The contents of the tube were sonicated for two hours yielding a slightly cloudy solution. The contents of the tube were then centrifuged for 5 minutes at 8000 rpm causing a small amount of sulphur to precipitate and yielding a transparent solution. It indicates now the electrolyte solution contains 1.0 M Na_2S and saturated sulphur. This solution was used for photoelectrochemical measurements without further purification.

4. Characterization

4-1. Thermo-gravimetric Analysis (TGA)

A 350 μL sample of the solution-phase composite material (1:1 by weight CdSe NC:1) dissolved in a 50/50 blend of monochlorobenzene/anisole was drop cast in a Pt TGA sample pan and vacuum dried at 70 °C over night, yielding an initial solvent-free sample mass 6.6 mg. The pan and film contained within were then analyzed using TGA. Samples were heated to 200 °C at 2 °C/min under nitrogen and then held at 200 °C for 90 minutes to ensure complete evaporation of solvent. During this stage of heating the sample was observed to loose approximately 4.4 wt.% of its initial mass. This loss of mass is attributed to evaporation of the monochlorobenzene/anisole mixture and indicates that the films analyzed in this study contain only trace amounts of solvent and can be reasonably be assumed to be “solvent-free”. After holding at 200 °C under nitrogen the sample was heated to 800 °C at 10 °C/min under oxygen. A precipitous loss of sample mass occurs at approximately 400 °C indicating combustion of alkane groups, followed by a more gradual loss of mass attributed to the gradual combustion of the fullerene phase. At approximately 600 °C the inorganic phase is observed to undergo oxidation.

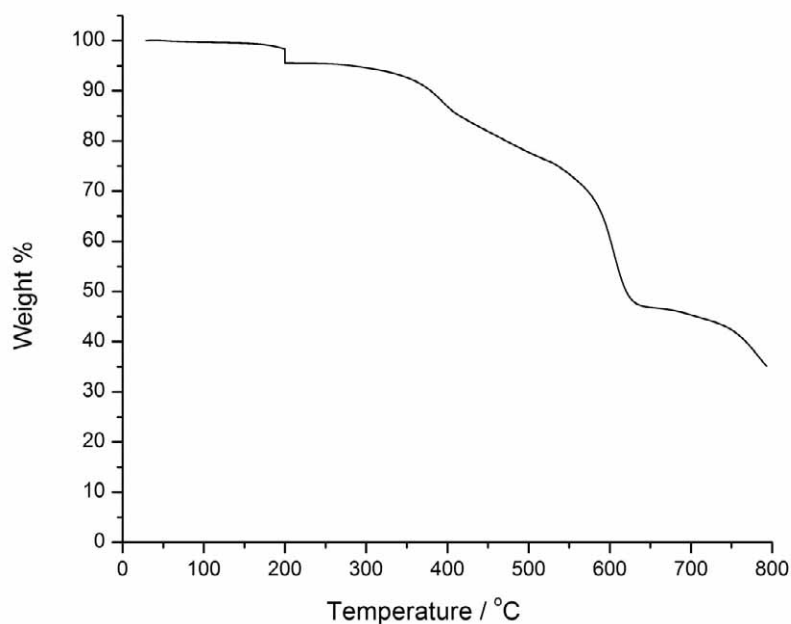


Figure S3. Thermogravimetric analysis of solvent-free CdSe NC/1 (1:1 by weight) composite.

4-2. Flash-photolysis-time-resolved microwave conductivity (FP-TRMC)

The obtained transient conductivity ($\Delta\sigma$ in S m^{-1}) was converted to the product of the quantum yield: ϕ and the sum of charge carrier mobilities: $\Sigma\mu (= \mu_+ + \mu_-)$, by $\phi\Sigma\mu = \Delta\sigma (eI_0F_{\text{light}})^{-1}$, where e , I_0 , and F_{Light} are the unit charge of a single electron (in C), incident photon density of excitation laser (in m^{-2}), a correction (or filling) factor (in m^{-1}), respectively. F_{Light} was calculated by taking into consideration the geometry and optical properties of the sample such as the size, laser cross-section, and absorption of the excitation laser.

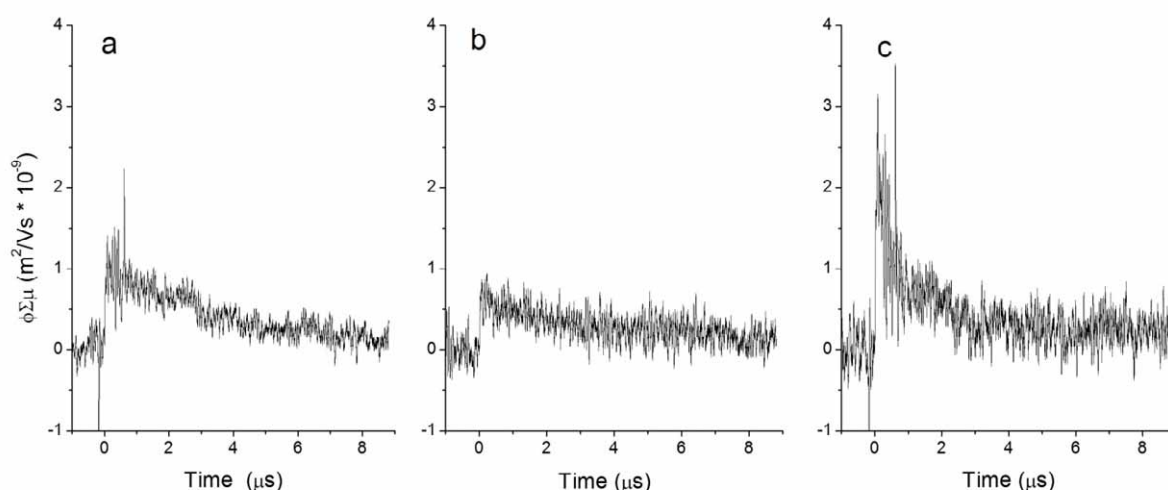


Figure S4. TRMC transient decay profiles from solvent-free films consisting of (a) pure **1**, (b) 1:1 blend (by weight) of CdSe NC and **1**, and (c) pure CdSe NC under an excitation at $\lambda = 355 \text{ nm}$ by $9.1 \times 10^{15} \text{ photons cm}^{-2} \text{ pulse}^{-1}$.

4-3. Transient absorption of solvent-free composite films at 600-800 nm

The transient absorption (TA) of solvent-free composite films was recorded at wavelengths ranging from approximately 400 nm to 800 nm. Figure S5 presents TA data over the range of 600-800 nm that is not presented in the main text. The TA signal detected at approximately 700 nm is attributed to the optically excited triplet state of **1**.³ Absorption by the charged **1** cation resulting from CdSe NC/**1** charge transfer is also expected to begin in this range and extend into the infrared (~800-1200 nm). Unfortunately absorption in the NIR is beyond the sensitivity of the detector used in this study, making it impossible to resolve absorption by the charged **1**.^{4,5}

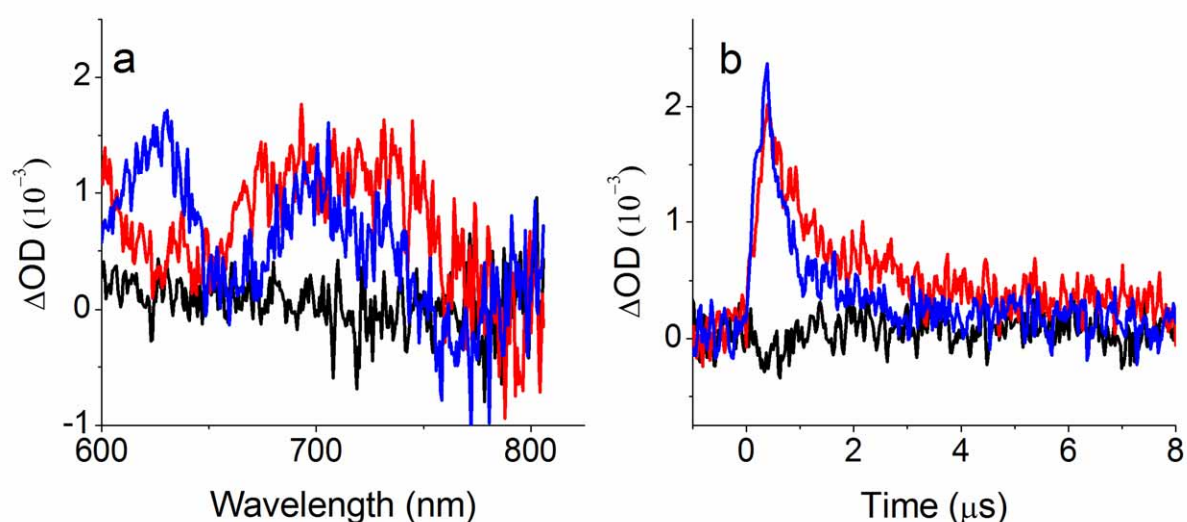


Figure S5. (a) Transient absorption spectrum of solvent-free CdSe/**1** composite films containing 100% CdSe NC (black), 50 wt.% CdSe NC (red), and 17 wt.% CdSe NC (blue) recorded 500 ns after excitation (b) Decay profile at 700 nm by solvent-free CdSe/**1** composite films containing 100% CdSe NC (black), 50 wt.% CdSe NC (red), and 17 wt.% CdSe NC (blue). Balance in all cases is **1**. A 355 nm pulse from a Nd:YAG laser was used as an excitation.

References

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