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COMMUNICATION

CdSe Nanocrystal/C_{60}-liquid composite material with enhanced photoelectrochemical performance†

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The unique optoelectronic properties of a nanocomposite material comprised of cadmium selenide (CdSe) nanocrystals (NCs) embedded in a photoconductive liquid C_{60} have been investigated. CdSe NCs are shown to sensitize the composite material to visible light, resulting in charge transfer from optically excited CdSe NCs to the solvent-free liquid C_{60} phase.

Functional composites of inorganic nanocrystals (NCs) and organic molecules are an attractive platform for the economical utilization of NCs in optoelectronic applications. It has already been shown that composite materials of this kind can exhibit a variety of novel optical and electronic properties.[1] Of the many nanocomposites studied to date, some of the most technologically promising examples consist of semiconducting inorganic NCs embedded in an organic photoconducting matrix.[2] At the heart of the rich behavior observed in this type of nanocomposite is the phenomenon of inter-phase energy transfer. In photovoltaic applications energy transfer from excited NCs to a surrounding semiconducting matrix can lead to efficient broad-band device performance.[3] Similarly, charge injection from an organic conductive material to embedded semiconducting NCs has led to flexible displays with bright emission over a wide portion of the visible spectrum.[4]

Here we report on the optical and photo-electrochemical properties of a nanocomposite comprised of CdSe NCs embedded in an alkylated room temperature liquid C_{60} derivative (**1**, Fig. 1a).[5] Solvent-free, photoconducting or emissive organic liquids are an important new class of organic soft materials that exhibit the unique property of sustaining infinite mechanical deformation at ambient temperatures, opening the door to a variety of industrially attractive processing techniques, especially towards printable optoelectronics.[6] The low viscosity, low melting point (below room temperature), and relatively high charge carrier mobility of **1** make it a particularly promising material for a variety of advanced organic optoelectronic applications.[5]

In its pure form **1** absorbs UV light efficiently ($E_g \sim 2.6$ eV) but does not absorb or emit effectively in the visible light spectrum. By incorporating CdSe NCs that absorb and emit visible light, we sought to develop a novel composite material that combines the tunable optical properties of the constituent NC phase[1,7] with the physical and electrical properties of **1**.

The synthesis of **1** has been reported in detail elsewhere.[5] CdSe NCs were synthesized following a previously reported method,[8] resulting in 2.4 nm NCs capped with trioctylphosphine oxide (TOPO) ligands. Multiple ligand exchange steps were carried out to yield hexadecylamine (HDA) capped particles with high photoluminescent (PL) efficiency. HDA-capped CdSe NCs were dispersed in monochlorobenzene and combined with **1** dissolved in monochlorobenzene or anisole for solution-phase and solvent-free studies respectively. Solvent-free samples were drop-cast from solution onto appropriate substrates and vacuum dried overnight at 70 °C to remove residual solvent. See ESI† for further details regarding NC synthesis and sample preparation.

Transmission electron microscopy (TEM) studies of solvent-free composite samples indicate good dispersion of CdSe NCs in the liquid phase of **1**. Fig. 1b depicts a 1 : 1 blend (by weight ratio) of **1** and CdSe NCs. It is apparent that NCs tend to organize in relatively short (~10 nm) serpentine structures, but that macroscopic aggregation is not present. High-resolution TEM (HRTEM) analysis reveals the crystalline features of the constituent CdSe NC phase (Fig. 1b inset). Thick solvent-free composite films are stable for days, and upon dissolution of the aged composite film in monochlorobenzene virtually all NCs can be recovered *via* centrifugation

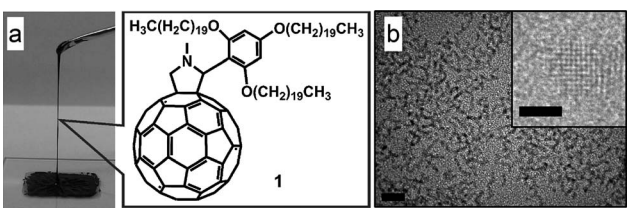

Fig. 1 (a) Photograph of room temperature liquid C_{60} (**1**) with depiction of the molecule and (b) TEM image of the CdSe NC/**1** composite (scale bar 20 nm) with a HRTEM inset of the CdSe NC (scale bar 2 nm).

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techniques. These results suggest that CdSe NCs are well dispersed and highly stable in the solvent-free composite material.

As seen in Fig. 2, steady-state PL measurements show that PL from optically excited CdSe NCs is dramatically quenched in the presence of **1**. In solution-phase samples it is seen that the quenching is highly efficient and approximately linear for **1** : CdSe NC molar ratios of up to approximately 6, after which point the quenching efficiency is decreased (Fig. 2c).

This type of behavior is consistent with clustering of **1** around CdSe NCs, possibly driven by favorable van der Waals interaction between the NC HDA ligands and the alkyl pendant groups of **1**. Fig. 2b shows that CdSe NC PL quenching in the solvent-free film state is highly efficient resulting in a seven-fold decrease in PL upon addition of 10 wt% (62 mol%) of **1**. The observed PL quenching in both types of sample is attributed to the existence of a non-radiative relaxation mechanism for NC excitons in the presence of **1**. The observed blue-shift of NC PL upon addition of **1** indicates that PL from lower energy (and longer lived)[9] excitons is preferentially quenched.

Time-resolved PL lifetime measurements elucidate the origin of CdSe NC PL quenching in the CdSe NC/**1** composites. A Horiba Fluorocube spectrometer utilizing a 485 nm excitation wavelength was used to excite solution-phase and solvent-free composite samples (Fig. 2d). Using a bi-exponential decay model and applying eqn (1),

$$\langle \tau \rangle = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} \quad (1)$$

we calculated the average emission lifetime for pure CdSe NC samples to be 12.3 and 14.4 ns for solution-phase and solvent-free samples, respectively. The closeness in the observed PL lifetime between solution-phase and solvent-free samples indicates that radiative relaxation in both types of sample is mechanistically similar. When an equal molar amount of **1** is added to the solution-phase sample, the PL lifetime is decreased to 11.1 ns.

It was not possible (using our present detector) to collect PL lifetime data for solvent-free composite films as a result of the dramatic quenching of CdSe NC PL upon addition of even small quantities of **1** (~10 wt%).

Transient absorption (TA) measurement of solvent-free CdSe NC/**1** composite samples shows a pronounced 480 nm bleach signal paired with a 515 nm absorption band, indicative of absorption by charged CdSe NCs (Fig. 3a).[10] The decay rate of the 515 nm absorption signal (Fig. 3b) is found to be 2.5×10^5 s^{-1} and 5.6×10^4 s^{-1} in composite films consisting of 50 wt% and 17 wt% of CdSe NC (balance **1**), respectively. By comparison, a film consisting of 100% CdSe NC shows a relatively rapid recovery of 1.0×10^6 s^{-1}, indicating that the excited CdSe NCs return to the ground state more quickly after excitation when **1** is absent.

The existence of charged CdSe NCs in optically excited **1**/CdSe NC composite samples is evidence of direct electron transfer from CdSe NCs to **1**.[1,10] Although the actual charge transfer event is expected to occur on a nanosecond or picosecond timescale[10,11] (more quickly than the response time of the instruments used in this study), TA measurements allow us to monitor the long-lived ionic species that result from the relatively rapid charge transfer event. As **1** content is increased we see that the lifetime of the resulting ionized CdSe NCs species also increases. We attribute this observation to delocalization of electrons in the organic liquid phase **1** following charge transfer. Furthermore it is evident that hole scavenging from charged CdSe NCs in this composite material is a comparatively slow process. The subtle shift in the bleach and absorption peaks (Fig. 3a) is attributed to a change in the intrinsic photoabsorption by CdSe NCs originating from small differences in the dielectric constant of the surrounding matrix.[12]

Flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements[13] were carried out in order to determine if the energy transfer process observed in PL studies leads to mobile charge carriers (see ESI†). We investigated solvent-free composite films containing various amounts of CdSe NC ranging from 0–100 wt% CdSe NCs dispersed in the liquid **1** (CdSe NCs content constant) mounted on quartz substrates. Using a 355 nm light from a Nd:YAG

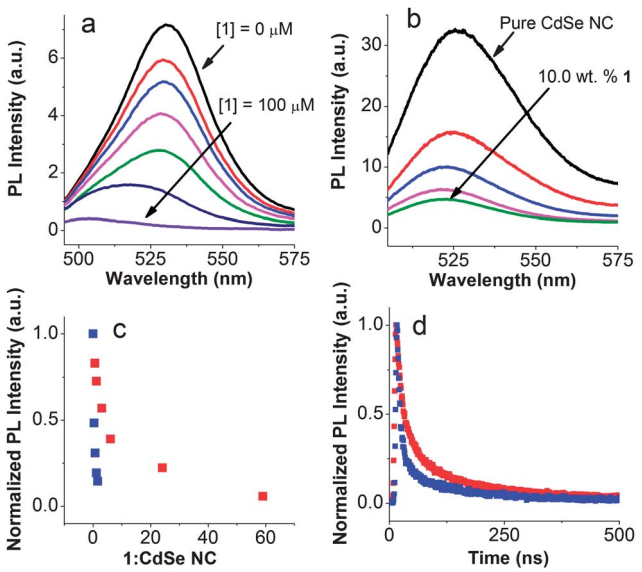

Fig. 2 (a) Steady-state PL of monochlorobenzene solutions containing CdSe NC (1.7 μM) and various amounts of **1** ranging in concentration from 0 μM (top, black) to 100 μM (bottom, purple). (b) Steady-state PL of solvent-free CdSe NC/**1** films containing CdSe NC alone (black), 2.5 wt% (red), 5.0 wt% (blue), 7.5 wt% (magenta) and 10 wt% (green) of **1**. (c) Normalized PL intensity *vs.* **1** : CdSe NC molar ratio for solution-phase samples (red squares) and solvent-free films (blue squares). (d) Time-resolved PL from a solution-phase sample of CdSe NCs (red squares) and a solvent-free film of CdSe NCs (blue squares) in the absence of **1**. In all cases, the excitation wavelength is 485 nm.

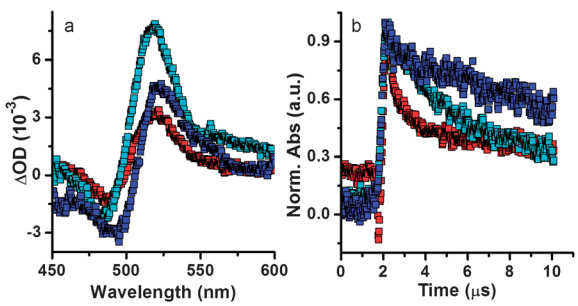

Fig. 3 (a) Transient absorption spectrum and (b) decay profile at 515 nm of solvent-free CdSe/**1** composite films containing 100% CdSe NC (red squares), 50 wt% CdSe NC (cyan squares), and 17 wt% CdSe NC (blue squares) recorded 500 ns after excitation. A 355 nm pulse from a Nd:YAG laser was used as an excitation.

laser each sample was optically excited within a resonant microwave cavity and the reflected microwave power was monitored as a function of time. Immediately following optical excitation all samples showed a rise of photoconductivity signal within the time resolution, after which the transient conductivity of the samples decreased to the baseline. These results indicate a combination of low carrier population and/or the existence of a tightly bound charge-separated state that cannot freely move through the composite material.

Solvent-free CdSe NC/**1** composite films were cast on FTO-coated glass and used as the anode in photoelectrochemical measurements (0.2 cm^2 active area). A platinum wire was used as the counter electrode, and a 1.0 M Na_2S/saturated (<0.1 M) sulphur (S) aqueous solution was used for electrolyte.[14] Samples were subjected to 10 second periods of illumination followed by 10 second dark periods using a 150 W Xe lamp (Asahi Spectra, USA) equipped with a LAX-Cute Airmass 1.5 G filter. Light intensity was measured using a calibrated silicon power meter. The steady-state short-circuit current was monitored as a function of time. A dramatic increase in cathodic photocurrent is observed for composite CdSe NCs/**1** samples compared to pure **1** or pure CdSe NCs (Fig. 4). Under white light illumination (1000 W m^{-2}) (Fig. 4a), we have measured a 200% increase in photocurrent for a composite film containing 25 wt% CdSe NCs compared to a pure CdSe NCs film with an equal amount of NCs material. The same film exhibits a 300% increase in cathodic photocurrent under blue-light illumination (480 nm light, 25 W m^{-2}) compared to a film of pure CdSe NCs (Fig. 4b). The increase in photocurrent obtained from composite films is even more dramatic when compared to pure **1** films. Under white-light illumination we observe a 32-fold increase in photocurrent for a composite sample containing 25 wt% CdSe NCs compared to the film of **1** itself (Fig. 4a). Under blue-light illumination (Fig. 4b), pure **1** samples show virtually zero response ($\sim 10^{-10}$ A cm^{-2}) while composite samples produce a photocurrent of 1.5×10^{-6} A cm^{-2}, an increase by four orders of magnitude. The transient photocurrent observed at the beginning of each illumination segment is attributed to the formation of a diffusion-limited electrolyte depletion region at the surface of the electrodes under steady-state operating conditions.

We attribute the observed increase in photocurrent and the corresponding decrease in NC PL intensity within these nanocomposites to charge transfer (CT) between CdSe NCs and the liquid **1** according to mechanism 1. The position of the CdSe NC LUMO level has been reported to lie at approximately −3.84 eV (relative to vacuum).[11] This lies at a slightly higher energy than the LUMO level of C_{60} which lies at −4.30 eV,[11] facilitating exciton separation of photo-generated excitons in the CdSe NC phase and electron transfer to **1**.[10] TA measurements indicate that this process leads to a long-lived CT state in which **1** attains a net negative charge and the CdSe NCs is left with a net positive charge.[11] The cationic and anionic species are expected to favor reduction and oxidation reactions respectively in order to achieve charge neutrality.

$$\mathrm{Cdse} + h\upsilon \rightarrow \mathrm{Cdse}^{*}$$

$$\mathrm{Cdse}^{*} + \mathrm{C}_{60} \rightarrow \mathrm{Cdse}^{(h^{+})} + \mathrm{C}_{60}^{(e^{-})}$$

Mechanism 1

Photoelectrochemical measurements show that the photo-induced charge transfer state in CdSe NCs/**1** composites can effectively be harnessed to carry out electrochemical work (Fig. 4). The cathodic

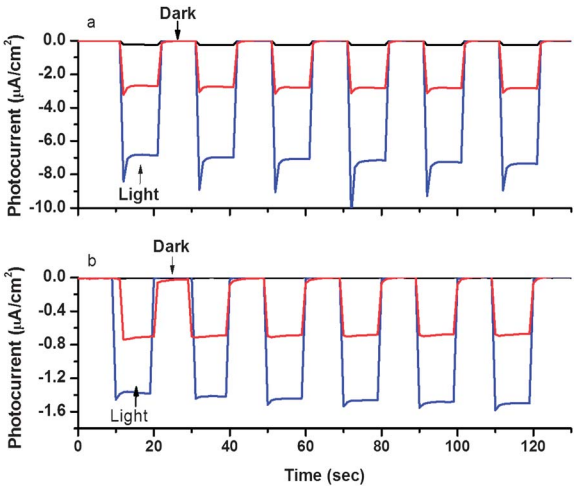

Fig. 4 Photoelectrochemical activity of solvent-free CdSe NC/**1** composite films on FTO-coated glass containing **1** alone (black), 25 wt% CdSe NC (blue), and CdSe NC alone (red) under (a) white light illumination and (b) blue light (at 480 nm) illumination.

photocurrent in these measurements indicates that when electrons are transferred to **1**, they are subsequently conducted to the FTO substrate, while the electrolyte (S^{2-}) acts as a hole scavenger for the charged CdSe NCs. The comparatively poor electrochemical efficiency of films composed of a single phase (*i.e.* CdSe NCs or **1** alone) suggests that inter-phase charge transfer within the composite films provides a convenient route for conversion of optical energy to electrical energy. This emergent photoelectrochemical characteristic is expected to make this composite nanomaterial a good candidate for use in photo-sensitized photovoltaic devices,[15] however the fabrication of such devices was beyond the scope of this study.

In summary we have shown that a novel class of composite nanomaterial can be fabricated by combining inorganic CdSe NCs with a photoconductive liquid-C_{60}. The resulting composite material exhibits phase behavior similar to the liquid C_{60} matrix phase (Fig. S3†), while the optical properties can be independently tuned by selection of an appropriate NC phase. Furthermore, favorable electronic band alignment between the NCs and the organic matrix phase enables inter-phase charge transfer, resulting in a long-lived charge transfer state that is amenable to use in sensing applications and photoelectrochemical processes.

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