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COMMUNICATION

Semiconductor Nanocrystals in Fluorous Liquids for the Construction of Light-Emitting Diodes

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This communication reports a materials handling strategy based on *fluorous materials chemistry* using CdSe/CdS/CdZnS core-shell type semiconductor nanocrystals. When the crystals were treated with the semi-perfluoroalkanethiol ligands in the presence of $^iPr_2EtN$, the surface-modified nanocrystals (R_F1-NC and R_F2-NC) became soluble in the fluorous liquids. Solutions of R_F1-NC and R_F2-NC in HFE-7500 enabled the solution-casting of nanocrystalline films on top of a small-molecular hole-transporting layer and provided layered structures suitable for light-emitting diode fabrication.

Colloidal semiconductor nanocrystals have prompted widespread research interest with the expectation of revolutionizing the current technology in display,[1-4] light harvesting,[5] bio-imaging,[6, 7] and sensing applications.[8] When they are harnessed, particularly as luminescent materials in light-emitting diodes (LEDs), the resulting displays are believed to outperform their competitors by taking advantage of the superior colour purity, quantum efficiency and stability of semiconductor nanocrystals.[9, 10] In addition to the performance, the inherent solubility imparted by surface-stabilizing ligands is another benefit for the affordable production of large-area, flexible displays using solution-based printing methods.[2, 3, 11]

The solution processing of electronic materials has been anticipated to be the heart of the next generation fabrication protocol with numerous advantages, but there are still practical limitations. For the successful production of multiply stacked devices, e.g., LEDs, by solution printing, conflicting requirements for materials and solvents must be met: a material being deposited should be soluble in a solvent but the resulting solution must not harm the integrity of the underlying layer.[12] In the case of LEDs containing a solution-processed nanocrystals layer, the pre-defined film of the hole-transporting material must maintain its performance throughout exposure to the nanocrystal solution. Generally, the films of small-molecular hole-transporting materials are not sufficiently resistant to organic solvents. This hurdle has been overcome to some extent by employing more robust polymeric hole-transporters,[13-15] and the construction of inverted LEDs adopting a solvent-resistant metal oxide electron-transporting layer underneath the nanocrystal emitting film.[9]

Despite these creative approaches for the solution casting of semiconductor nanocrystals, a question still remains unanswered, "*How can organic small-molecular charge-transporting materials together with a nanocrystal solution be adopted?*". Success in this challenge would bring in greater freedom in incorporating functional organic materials into diverse applications. Therefore, this study focused on finding answers, particularly in the context of *Fluorous Materials Chemistry*.

In general, fluorous liquids, including hydrofluoroethers and perfluorocarbons, do not interact extensively with non-fluorinated materials.[16-18] The large number of F atoms with their highest electronegativity is responsible for the unique character of fluorous materials, which enables the micro-patterning of delicate organic semiconductors[19-26] and biologically active materials without imposing serious damage.[27] This communication reports another interesting possibility of fluorous liquids in the solution-processing of colloidal semiconductor nanocrystals, which is expected to provide genuine freedom of choosing charge-transporting materials for solution-processed LEDs.

To demonstrate the processing concept in practice, the first step was to achieve a semiconductor nanocrystal solution in a suitable fluorous liquid. Preliminary tests indicated that HFE-7500 (**Fig. 1a**) is a strong candidate because of its relatively high boiling point (130 °C) and chemical inertness.[18, 28] When a

vacuum-deposited film of tris(4-carbazoyl-9-ylphenyl)amine (TCTA) was immersed in HFE-7500 and examined by UV-Vis spectroscopy, there were no changes in its absorption spectrum compared to the pristine sample. On the other hand, the same test in hexanes damaged the film seriously, as reported in the Supporting Information (**Fig. S1**). In addition to the spectroscopic measurements, the solvent-treated TCTA samples were examined by atomic force microscopy (AFM) to observe any changes to the film morphology or surface roughness. As shown in the Supporting Information (**Fig. S2**), no significant changes were observed on the TCTA film dipped in HFE-7500. On the other hand, the sample treated with hexanes was damaged because the surface was barely uniform with bigger roughness. The root-mean-square (RMS) roughnesses of the pristine, HFE-7500 and hexanes-dipped samples were 1.6, 1.7 and 4.4 nm, respectively.
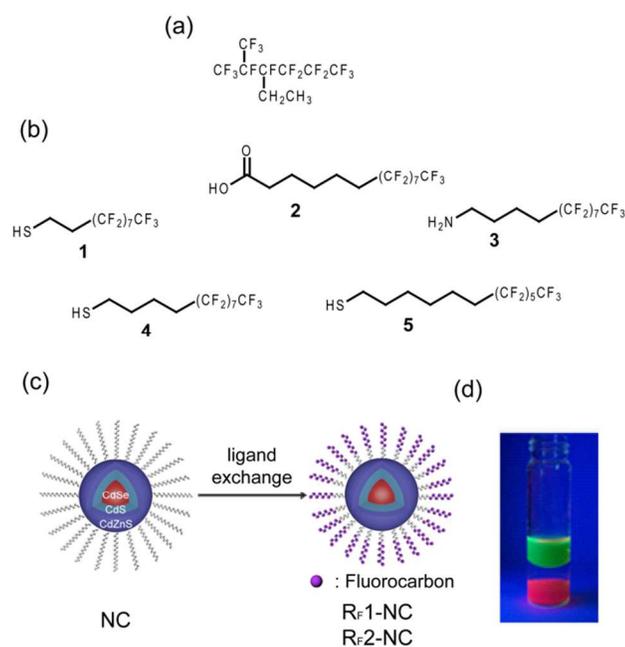

Fig. 1 (a) Chemical structure of HFE-7500, (b) functionalized semi-perfluoroalkanes, (c) ligand substitution reactions with functionalized semi-perfluoroalkanes, (d) ligand-exchanged nanocrystal solution in HFE-7500 (bottom layer), the top one is a nanocrystal solution with oleic acid ligands in hexanes and the middle is water).

The next task was to endow the nanocrystals with sufficient solubility in HFE-7500. Two possible routes were considered. Semiconductor crystals are either synthesized with highly fluorinated stabilizing ligands, or ready-made nanocrystals are modified with those fluorinated ligands. Although the former appears intriguing, it will require a tedious optimisation study with a new materials system. Recently, Lim *et al*. reported that the latter is effective in the case of CdSe nanocrystals.[29] Stirring the crystals with semi-perfluoroalkyl thiol **1** (**Fig. 1b**) in toluene for 36 h provided perfluorocarbon-soluble nanocrystals, which were used for bio imaging. This ligand exchange method appears satisfactory for the current target but it needs to be

tuned to accommodate a shorter reaction time and semi-perfluoroalkyl ligands with longer alkyl spacer units. As inductively electron-withdrawing perfluoroalkyl moieties, such as $(CF_2)_7CF_3$, are likely to affect the electronic properties of semiconductors,[30-32] it is thought desirable to insulate this effect in the current study.

The preparation of a fluorous nanocrystal solution was carried out by replacing oleic acid ligands on the periphery of CdSe/CdS/CdZnS core-shell type nanocrystals (**NC** in **Fig. 1c**) with functionalised semi-perfluoroalkanes **2**, **3** and **4** (**Fig. 1b**).[33] The nanocrystal **NC** was ultrasonicated for 30 min with the carboxylic acid **2**, amine **3** and thiol **4** in $CHCl_3$ at room temperature. After adding MeOH, the precipitate was recovered by centrifugation and rinsed twice with $CHCl_3$. None of the products appeared to be soluble in HFE-7500. It was considered that the binding affinities of the carboxylic acid and amine functional groups are not strong enough to replace the existing oleic acid molecules or a much larger amount of those functionalized semi-perfluoroalkanes are required to push the equilibrium to the product side. For thiol **4**, its reduced acidity by the insertion of a longer alkyl unit, $(CH_2)_4$, was regarded one of the reasons for the failure, recalling the successful exchange reaction with thiol **1** by Lim *et al*. Based on this hypothesis, non-nucleophilic $^{i}Pr_2EtN$ was added to the reaction mixture to compensate for the weaker acidity of thiol **4**,[34] resulting in nanocrystals (**R_F1-NC** in **Fig. 1c**) that were soluble in HFE-7500 but not in $CHCl_3$ or acetone. Particle size analysis of the fluorous solution of **R_F1-NC** confirmed the nanometre scale distribution of crystal sizes, and FT-IR spectroscopy also showed that thiol **4** had been introduced onto the nanocrystal surface (**Fig. S3** and **Fig. S4** in Supporting Information).

In addition to chemical analyses, measurements of the HOMO energy levels were conducted on the nanocrystal **NC** and **R_F1-NC**. Ultraviolet photoelectron spectroscopy (UPS) showed that the introduction of thiol **4** onto the surface slightly depressed the HOMO energy level compared to the oleic acid ligand (**Fig. S5** in Supporting Information). Despite the insulating effect of the butylene unit, the perfluoroalkyl moiety appears to extend its electron-withdrawing power to the electronic properties of the semiconductor.
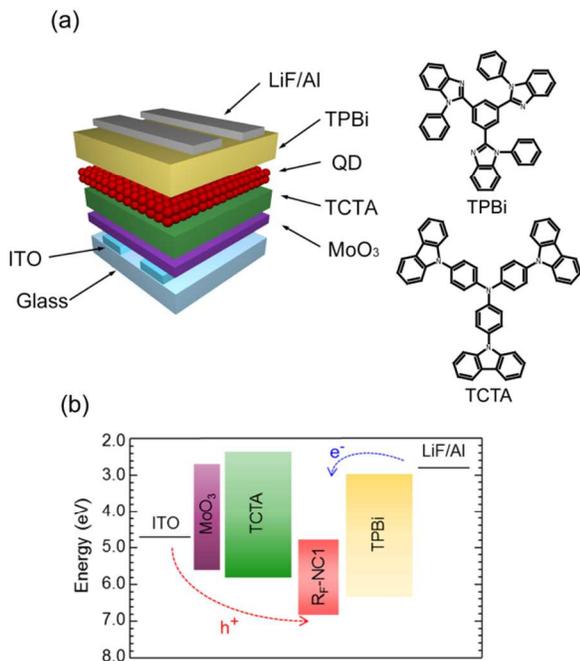
Fig. 2 (a) Device structure of a nanocrystal LED; MoO_3 (10 nm), TCTA (40 nm), TPBi (40 nm) and (b) energy level diagram of the constituents in the LED.

A fluorous solution of R_F1-NC was then evaluated for the construction and operation of LEDs. For comparison, the nanocrystals **NC** with oleic acid ligands were solubilized in hexanes and examined under the same conditions. As shown in **Fig. 2a**, the test devices were composed of patterned indium tin oxide (ITO) / MoO_3 / TCTA / CdSe nanocrystal layer / 1,3,5-tris(N-phenyl-benzimidazol-2-yl)benzene (TPBi) / LiF / Al. **Fig. 2b** presents the energy band diagram of the device. A MoO_3 film was used as the hole-injecting layer, on top of which TCTA molecules were sublimed forming a model hole-transporting layer. The next step was the deposition of nanocrystals from their solution, which is a key process for the proof-of-concept in this study. When the R_F1-NC solution in HFE-7500 was spin-coated on top of the TCTA layer, no physical damage was observed visually in the stacked films, as in the preliminary test (**device A**). On the other hand, the solution in hexanes caused partial wash off of the TCTA layer (**device B**).
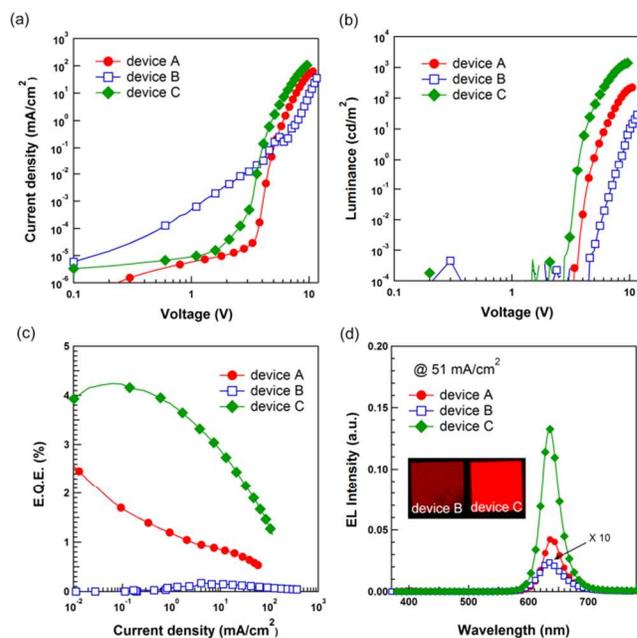

Fig. 3 Electrical characteristics of the LEDs fabricated with a R_F1-NC solution in HFE-7500 (**device A**), **NC** solution in hexanes (**device B**) and R_F2-NC in HFE-7500 (**device C**) in terms of (a) current density-voltage, (b) luminance-voltage characteristics, (c) external quantum efficiency-current density, and (d) normalized EL spectra of the LEDs at a current density of 51 mA cm^{-2} (inset: pictures of operating devices; pixel size = 1.4 mm x 1.4 mm).

The visual detections were confirmed by the electrical measurements after depositing the electron-transporting layer and cathode (**Fig. 3**). Although ordinary operating characteristics were recorded in the case of **device A** (**Fig. 3a** and **3b**) fabricated using the R_F1-NC solution, abnormal behaviours, including a much higher current density but lower luminance, were observed with **device B**. In particular, the turn-on voltage of **device B** was much higher than that of **device A**. The maximum brightness of **device A** was 10 times higher than that of **device B**. This difference could be attributed to the critical damage in the TCTA layer that occurred during its contact with hexanes. The AFM topography images in the Supporting Information (**Fig. S2**) indicate that the rougher surface of the TCTA film in **device B** caused non-uniform nanocrystal layer deposition between the TCTA and electron-transporting TPBi film, providing shortcuts for charge carriers and resulting in inefficient charge injection into the emitting nanocrystal domain. On the other hand, the same situation is not probable in the case of **device A**, which has a TCTA surface as smooth as the pristine sample. As shown in **Fig. 3c**, the maximum external quantum efficiency (E.Q.E.) and luminous efficiency reached 3.2% and 2.3 cd A^{-1}, respectively, in the case of **device A**, but those indices were too low for **device B**. A narrow electroluminescence (EL) spectrum of **device A** (**Fig. 3d**) centred at around 630 nm is another indication that the fluorous solution enabled the uniform coverage of a R_F1-NC film on top of the small-molecular TCTA layer. No parasitic emission was observed in the blue

region, which typically originates from defects in the emitting layer.

Overall, the successful solubilisation of **R$_F$1-NC** in fluorous liquids was accomplished, and quality film formation on top of a small molecular organic semiconductor and good operation of the resulting devices were demonstrated. These results suggest that the proposed strategy has the potential to achieve higher performance. Attention was thus directed to the semi-perfluoroalkyl ligand. Although the UPS data showed that thiol **4** with a $(CF_2)_7CF_3$ moiety does not affect the electronic properties of the nanocrystal **NC** significantly, it was expected that something favourable would be observed by shortening the $(CF_2)_7CF_3$ chain and lengthening the $(CH_2)_4$ spacer unit. Another thiol, $HS(CH_2)_6(CF_2)_5CF_3$ (**5** in **Fig. 1b**) was synthesised (Supporting Information), and employed in the ligand exchange reaction, resulting in a transparent solution of nanocrystal **R$_F$2-NC** in HFE-7500. LED fabrication with the solution was completed to give **device C**, the performance of which outperformed that of **device A**, as shown in **Fig. 3**. The maximum external quantum efficiency (E.Q.E.) and luminous efficiency were as high as 4.2% and 4.4 cd A^{-1}, respectively. These numbers were comparable to or higher than the literature values reported with an inverted device structure using small molecular hole-transporting layers and LEDs constructed using a polymeric hole-transporting layer,[9,13] but lower than the values (E.Q.E. 18% and luminous efficiency 19 cd A^{-1}) published by QD Vision Inc.[10] In addition, uniform brightness over the entire pixel of operating **device C** demonstrated the processing capabilities of the fluorous solutions for large-area display fabrication (inset in **Fig. 3d**).

As a related topic to illustrate the utility of the proposed concept, other well-established, small-molecular hole-transporting materials were also employed for LED fabrication using the **R$_F$2-NC** solution. **Fig. S6** in the Supporting Information shows that the LEDs constructed with 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl (CBP) and *N*,*N*′-di-(1-naphthyl)-*N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB) worked equally well, which provides another possibility to achieve enhanced performances of nanocrystal LEDs. Following the series of these experiments, more study, including the incorporation of charge-transporting functions into the semi-perfluoroalkyl thiols and examination of suitable perfluoroalkyl moieties in the device operation,[35] will be needed to realize the true capabilities of this materials-processing concept.

Conclusions

This paper proposed a materials handling strategy based on *fluorous materials chemistry* and demonstrated its effectiveness with semiconductor nanocrystals. Fluorous solutions of **R$_F$1-NC** and **R$_F$2-NC** in HFE-7500 enabled the solution-casting of nanocrystal films on top of the organic hole-transporting layers, and provided layered structures suitable for LED fabrication. Currently the maximum external quantum efficiency and luminous efficiency reached 4.2% and 4.4 cd A^{-1}, respectively, and it is believed that this method will provide a way of selecting the most appropriate organic functional materials for the construction of devices with semiconductor nanocrystals, which is expected to lead to improved device performance in the near future.

Notes and references

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Fluorous liquid-soluble semiconductor nanocrystals enable the solution-casting of inorganic films on top of an organic small-molecular hole-transporting layer, providing stacked structures suitable for light-emitting diode fabrication.