

## Electronic Supplementary Information Tunable Light Emission Using Quantum Dot Coated Upconverters

Tieh-Lam Nguyen<sup>a</sup>, Paul Spizzirri<sup>b</sup>, Gerry Wilson<sup>c</sup> and Paul Mulvaney<sup>a\*</sup>

*School of Chemistry & Bio21 Institute, University of Melbourne, Parkville, VIC, 3010, Australia. Fax: +613 9348 1595; Tel: +613 8344 2420; E-mail: [mulvaney@unimelb.edu.au](mailto:mulvaney@unimelb.edu.au)*

### Experimental Section:

The ZnS capped CdSe QDs were prepared by adapting recently reported methods.<sup>1-3</sup> Green fluorescing UCs (5  $\mu\text{m}$  IRUCG NIR Phosphors with an emission peaked at 552 nm) were purchased from LDP LLC (MaxMax.com) and used as received.

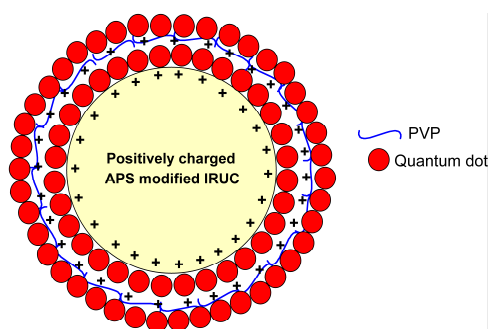
#### Surface functionalisation of UCs:

The surfaces of the UC crystals were initially functionalised using 3-aminopropyltrimethoxysilane (APS 99%) as the coupling agent. Typically, in a clean dry round bottom flask equipped with a condenser, 20mL of 2-propanol was added and heated and heated to 80 °C. To the refluxed solution, 0.1 g of UCs, 100  $\mu\text{L}$  of water and 100  $\mu\text{L}$  of APS were added, the mixture was refluxed with continuous stirring at 80 °C for 2 hours. The APS coated UCs were washed via centrifugation at 4000 rpm for 5 mins, the supernatant containing excess APS was discarded. 10 mL of isopropanol was then added to the recovered powder, the slurry was vortexed to mix, and again centrifuged at 4000rpm for 5 mins, supernatant was discarded. This process was repeated once more to remove any excess APS. The amine-functionalised UCs were then redispersed in 5 mL of chloroform.

#### Adsorption of QDs:

In a clean dry flask containing 5mL of amine-capped UCs in chloroform, 100  $\mu\text{L}$  of a 20  $\mu\text{M}$  QDs in chloroform was added. The reaction solution was stirred for 2 hours to allow the absorption of QDs onto the UCs. The QD coated UCs were washed via centrifugation at 4000 rpm for 10 mins, the supernatant containing excess QDs was discarded. 10 mL of chloroform was then added to the recovered powder, the slurry was vortexed to mix, and again centrifuged at 4000 rpm for 10 mins, supernatant containing any unbound QDs was discarded. The recovered QD coated UCs were dispersed in chloroform for further use.

Polyvinylpyrrolidone (PVP – MW 10000g/mol) were used to facilitate further attachment of QDs onto the QD coated UCs via amine bonding. Typically, in a clean dry flask, 1mL of 1mM PVP in chloroform was added to the QD coated UCs in chloroform, and the mixture was stirred at room temperature for 12 hours. Excess polymer was removed via centrifugation at 4000 rpm for 5 mins, the supernatant containing excess PVP was discarded. 5 mL of chloroform was then added to the recovered powder, the slurry was vortexed to mix and again centrifuged at 4000 rpm for 10 mins. The recovered powder was redispersed in 5 mL of chloroform, ready for further adsorption of QDs by repeating the above step. The final UCs powder coated with 2 monolayers of QDs were then air dried for analysis.



Scheme 1. Diagram illustrating the coating of QDs on the IRUC crystal

#### Zeta Potential Analysis:

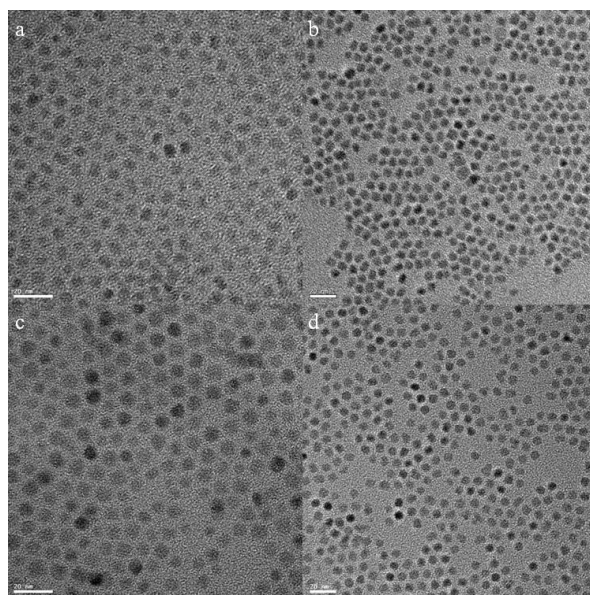
Zeta potential analysis was employed to determine the change in surface charge of the raw UCs and those coated with APS, using electrophoretic light scattering spectrophotometer, Zeta Plus zeta potential analyser (Brookhaven Instruments Corp. Holtsville, NY). The raw UC in water gives a negative zeta potential of 22.3mV at pH 6.5. The presence of APS on the UC surfaces changed the surface potential to positive and also raised the pH of the system to 9. After repetitive washing of the APS modified UCs, the pH was also adjusted to 6.5, resulting in a stable colloidal solution of zeta potential + 43.2mV.

Sample	Mobility ( $\mu\text{m/s}/(\text{V}/\text{cm})$ )	Zeta Potential (mV)	pH
UC in H <sub>2</sub> O	-1.68	-22.30	6.5
UC@APS in H <sub>2</sub> O	+1.02	+13.50	9
UC@APS in H <sub>2</sub> O pH	+3.25	+43.20	6.5

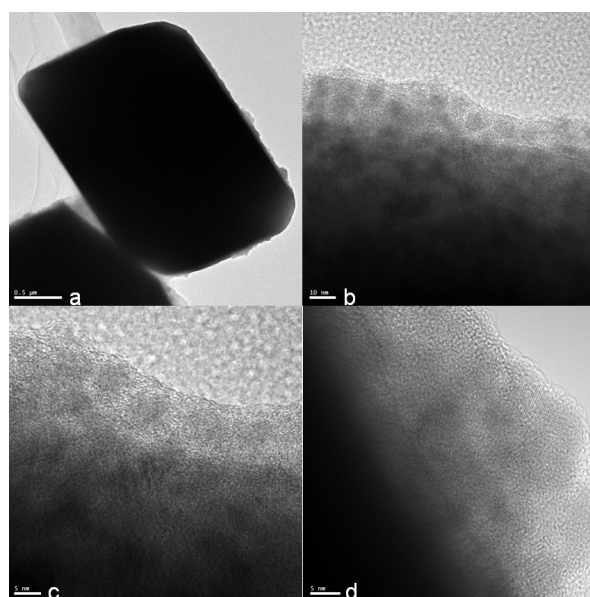
Table 1. Zeta potential measurements of the pure IRUC and the APS modified IRUC at 23 °C in water, particle diameter 5000 nm.

**TEM Analysis:**

TEM images were collected using a TE20 (FEI) TEM operated at 200 keV. Specimens for TEM analysis were prepared by the evaporation of colloidal solutions placed on a 300 mesh carbon-coated copper grid. A minimum of 120 particles were analyzed for each sample to determine the average diameter of the particles in the samples. Figure 1 shows images of the QDs used in this study, and figure 2 shows representative images of QD coated IRUC at various magnifications.



**Fig 1.** TEM images of QDs used: a – yellow emitting QD577, b – orange emitting QD593, c – dark orange emitting QD611 and d – red emitting QD631. Their average particle diameters are 5.5 nm, 6.7 nm, 7.4 nm and 7.9 nm respectively. Scale bars – 20 nm.



**Fig 2.** Representative TEM images of QDs coated IRUC at increasing magnifications: Scale bars for a – 500 nm; b – 10 nm; c and d – 5 nm.

**References:**

1. J. Jasieniak and P. Mulvaney, *Journal of American Chemical Society*, 2007, **129**, 2841-2848.
2. J. Jasieniak, C. Bullen, J. van Embden and P. Mulvaney, *Journal of Physical Chemistry B*, 2005, **109**, 20665-20668.
3. R. Xie, U. Kolb, J. Li, T. Basche and A. Mews, *Journal of American Chemical Society*, 2006, **127**, 7480-7488.