Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C


Supporting Information:

# Transparent Luminescent Silicone Nanocomposites Filled with Bimodal PDMS-Brush-Grafted CdSe Quantum Dots

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## NMR Spectrum:

The phosphate-terminated PDMS chains were obtained via a single step modification and the conversion was monitored with a $^{31}$P NMR spectrometer. As shown in Figure S3, the large singlet at 1.57 ppm shows that the main product is mono-phosphate PDMS, while smaller peaks at −8 to −12 ppm are diphosphate esters.[1]

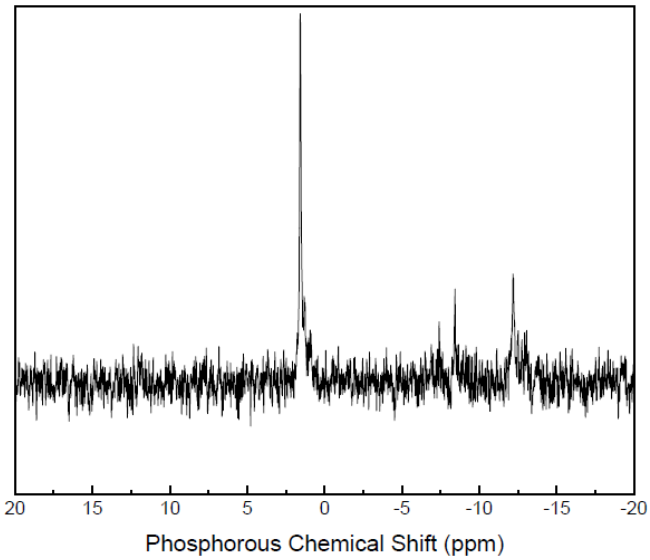


**Fig. S1 $^{31}$P NMR spectrum of phosphate-terminated PDMS (1,000 g/mol)**

**TGA Measurement:**

TGA was done on a Perkin Elmer Series 7 instrument. The NP sample was heated from 30 $^{o}$C to 800 $^{o}$C under a $N_2$ flow at a heating rate of 10 $^{o}$C/min. The weight loss can be used to calculate oleic acid layer thickness and brush graft densities. The graft density of each PDMS brush was calculated from the corresponding weight loss ratio determined by TGA, the number of grafting chains, and surface area of NPs[2],

$$\sigma = (wN_{\mathrm{A}}/M_{\mathrm{n}})/(4\pi a^2 \mathrm{n}) = \mathrm{a}\rho \mathrm{z}N_{\mathrm{A}} \times 10^{-21}/3(1-z)M_{\mathrm{n}}$$

where $w$, $N_{\mathrm{A}}$, $n$ and $z$ are the weight of organic polymers, Avogadro's number, the number of NPs and weight loss of polymer chains, respectively.

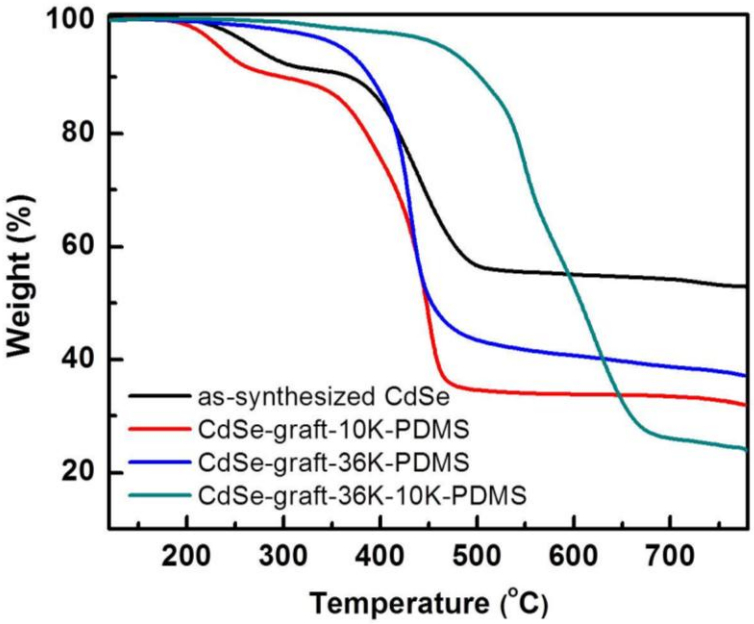


**Fig. S2. TGA curves of the as-synthesized CdSe QDs, QDs grafted with mono-modal 10 kg/mol, 36 kg/mol PDMS chains and QDs grafted with bimodal 36 and 10 kg/mol PDMS chains.**

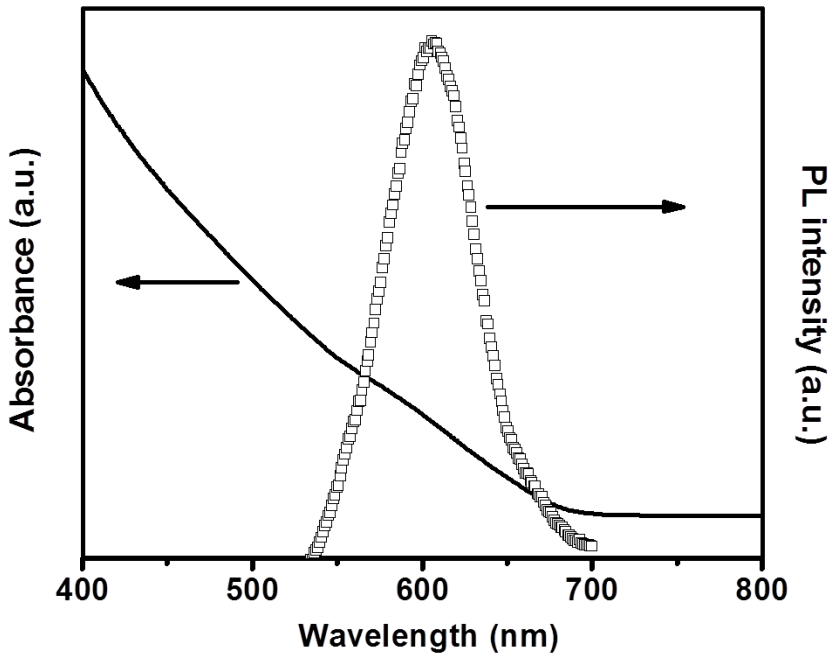


**Fig. S3. Absorbance and photoluminescence spectra of the dispersion of bimodal PDMS-grafted CdSe QDs within chloroform solvent.**

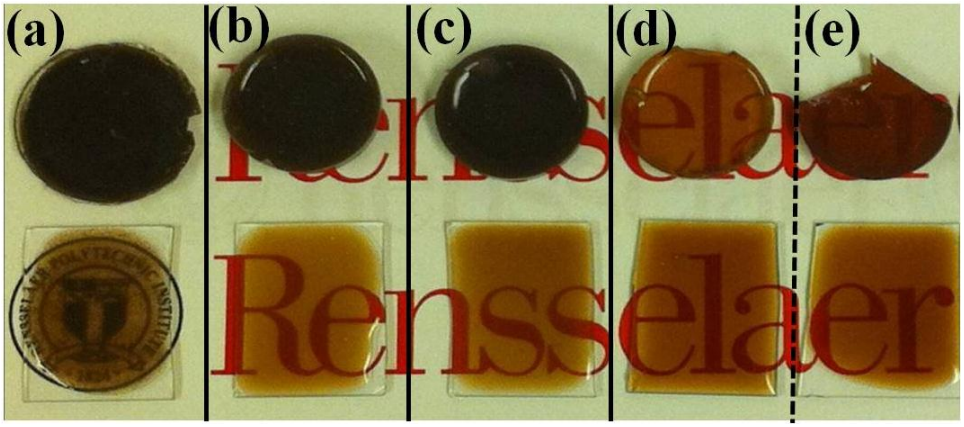


**Fig. S4 Photographs of 3 mm thick and 400 μm thick coating of CdSe/silicone nanocomposites filled with: (a) 0.2 wt% unmodified bare CdSe; (b) 0.2 wt% mono-modal 10 kg/mol CdSe; (c) 0.2 wt% mono-modal 36 kg/mol CdSe; (d) 0.2 wt% bimodal CdSe; (e) 0.4 wt% bimodal CdSe. The formation of micrometer sized aggregates within the unmodified CdSe/silicone nanocomposites can be easily identified with naked eyes. The nanocomposites filled with mon-modal CdSe lose their transparency when the samples are thick.**

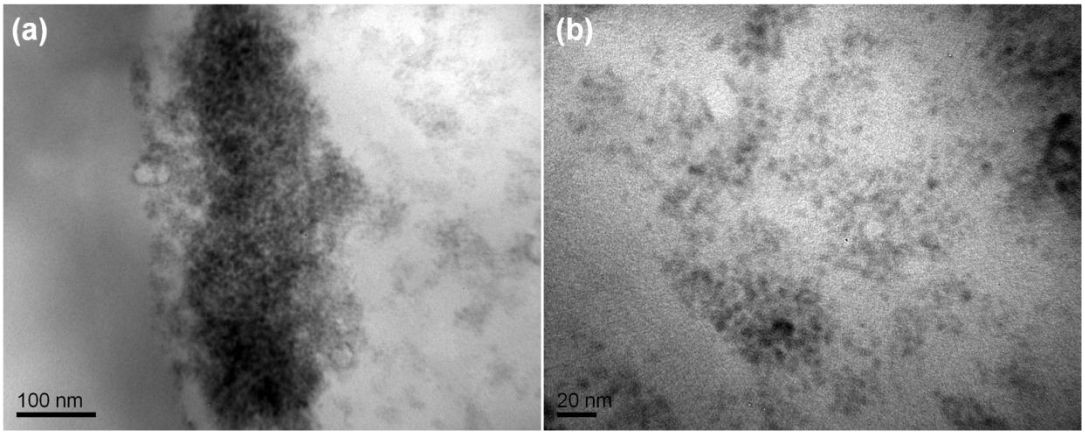


**Fig. S5 TEM image of unmodified CdSe quantum dots within silicone matrix at (a) low magnification and (b) high magnification; showing formation of sub-micrometer sized agglomerate and close packing of quantum dots within clusters.**

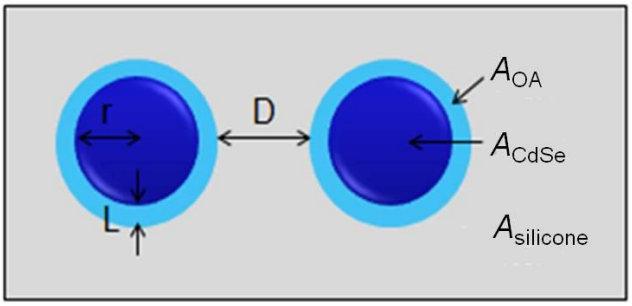


**Fig. S6 Schematic illustration of van der Waals attraction between CdSe quantum dots within silicone medium**

As shown in Fig. S6, the particles were modeled as spherical core-shell structured particles. The thickness (L) of oleic acid (OA) was determined based on TGA weight loss (z) of the as-synthesized CdSe quantum dots (the density of CdSe and oleic acid are 5.82 and 0.895 g/cm$^3$) with the following formula:

$$\frac{z/0.895}{z/0.895+(1-z)/5.82}=\frac{(r+L)^3-r^3}{(r+L)^3}$$

When calculating the van der Waals attraction between bimodal PDMS-brush grafted particles, the inner high grafting density short brush were treated as the organic coating layer similar to the oleic acid capping agent. The organic layer thickness was approximated with the radius gyration of the inner PDMS brush.

**Table S1. Parameters used for calculation of van der Waals attraction of CdSe QDs within silicone matrices**

| Component | $\varepsilon$ | $n$ | $A_H$ at 298.15 K ($10^{-20}$ J) |
|---|---|---|---|
| Silicone | 2.4 | 1.41 | 5.03 |
| CdSe | 10 | 2.54 | 38.7 |
| Oleic acid | 2.5 | 1.46 | 6.14 |

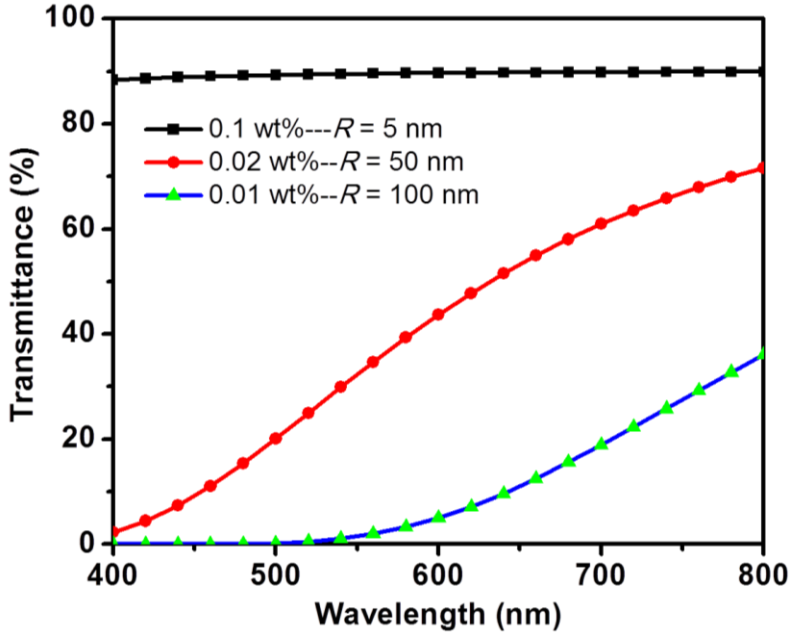


**Fig. S7 Calculated transmittance spectrum after considering the scattering loss from Rayleigh scattering with different scattering center sizes assuming the maximum transmittance being 90%.**

**References:**

1. White, M. A; Johnson, J. A; Koberstein, J. T.; Turro, N. J. Toward the Syntheses of Universal Ligands for Metal Oxide Surfaces: Controlling Surface Functionality through Click Chemistry. *J. Am. Chem. Soc.* **2006**, *128*, 11356–11357.

2. Kobayashi, M.; Matsuno, R.; Otsuka, H.; Takahara, A. Precise Surface Structure Control of Inorganic Solid and Metal Oxide Nanoparticles through Surface-initiated Radical Polymerization. *Sci. Technol. Adv. Mater*. 2006, 7, 617–628.