Electronic Supplementary Information

Synthesis of Highly Stable Quantum-Dot Silicone Nanocomposites via In-situ Zinc-terminated Polysiloxane Passivation

Yangyang Xie, Chong Geng, Xinyue Liu, Shu Xu,* Weishuo Xing, Xinsu Zhang, Zi-hui Zhang, Yonghui Zhang, Wengang Bi*

Tianjin Key Laboratory of Electronic Materials and Devices, School of Electronics and Information Engineering, Hebei University of Technology, 5340 Xiping Road, Beichen District, Tianjin 300401, P.R. China.

** Corresponding authors. E-mail: shu.xu@hebut.edu.cn; wbi@hebut.edu.cn*

Experiment

1. Materials

Sodium diethyldithiocarbamate trihydrate ($NaDDTC{\cdot}3H_2O$, 98%), selenium powder (Se, 325 mesh, 99.5%), and cadmium acetate dehydrate ($Cd(Ac)_2{\cdot}2H_2O$, 98%) were purchased from Alfa Aesar (China) Chemicals Co., Ltd. Tributylphosphine (TBP, 95%), n-octane (98.5%) and stearic acid (98%) were purchased from TCI (Shanghai) Development Co., Ltd. Other materials are shown in the manuscript. All chemicals were used directly without any further purification unless otherwise stated.

2. Synthesis of Cadmium Stearate ($Cd(St)_2$)

The synthetic procedure was based on the report in the literature.[S1] Typically, Stearic acid (20 mmol) was neutralized with equal-mole of tetramethylammonium hydroxide in 200 ml of methanol. Into this solution, $Cd(Ac)_2{\cdot}2H_2O$ (10 mmol) dissolved in 50 ml methanol was added dropwisely under vigorous stirring. White $Cd(St)_2$ immediately precipitated, and the mixture was stirred for another 20 min to ensure the reaction was completed. Subsequently, the white precipitate was collected through filtration and then washed three times with methanol. The final product was obtained by drying overnight under vacuum.

3. Synthesis of Cadmium Diethyldithiocarbamate ($Cd(DDTC)_2$)

The synthetic procedure was based on the report in the literature.[S1] Typically, $Cd(Ac)_2 \cdot 2H_2O$ (10 mmol) was dissolved with 100 ml of distilled water in a 400 ml beaker. Into this solution, $NaDDTC \cdot 3H_2O$ (20 mmol) dissolved in 60 ml distilled water was added dropwisely under vigorous stirring. White precipitates of $Cd(DDTC)_2$ quickly formed. The mixture was stirred for another 20 min after mixing to ensure the reaction was completed. The white precipitate was separated from the solution by filtration and washed three times with distilled water. The final product in white powder form was obtained by drying overnight under vacuum.

4. Synthesis of CdSe QDs

The CdSe QDs were synthesized according to ref. 1 with some modifications. $Cd(St)_2$ (135.6 mg, 0.2 mmol) was loaded into a 25 ml three-neck flask with 3 ml ODE. After stirring well and thoroughly with nitrogen bubbling, the flask was heated to 240 ℃. The suspension of Se (0.2 mmol Se powder dissolved in 1 ml ODE, stirred well) was rapidly injected into the flask and maintained at 240 ℃ for 10 min, and then the flask was cooled to 50 ℃. After an in situ purification procedure,[S1] 4 ml QDs solution was extracted. For work-up, 4 ml ethanol was added to 1 ml QDs solution and centrifuged (10000 rpm) for 10 min. The colorless solution was discarded while the colored precipitate was re-dispersed into 2 ml toluene and then washed two more times, and the resulting solid was re-dispersed into 10 ml DMS-B12 to form the CdSe solution for further reaction.

5. Synthesis of zinc oleate (Zn-OAc)

Under a nitrogen atmosphere, 1.1M OAc were slowly injected into 1M diethyl zinc – toluene solution with slow stirring until no obvious bubble appears. The prepared Zn-OAc solution was stored under nitrogen.

6. Synthesis of OA & Zn-OAc co-passivated CdSe/CdS/ZnS QDs

The synthesis of OA & Zn-OAc co-passivated CdSe/CdS/ZnS QDs adopts the same procedure and the reaction parameters as the synthesis of NH_2-PDMS & Zn-PDMS co-

passivated QDs descripted in the manuscript. The same method was used to prepare other different surface encapsulation QDs, and to ensure the uniform amount of reactant and the final solution concentration

7. Synthesis of NH_2-PDMS encapsulated CdSe/CdS/ZnS QDs

Except for the process involving Zn-PDMS, the method is the same as synthesis of NH_2-PDMS & Zn-PDMS co-passivated CdSe/CdS/ZnS QDs shown in the manuscript.

Characterization

1. The photoluminescence properties of QDs with different shell isolation

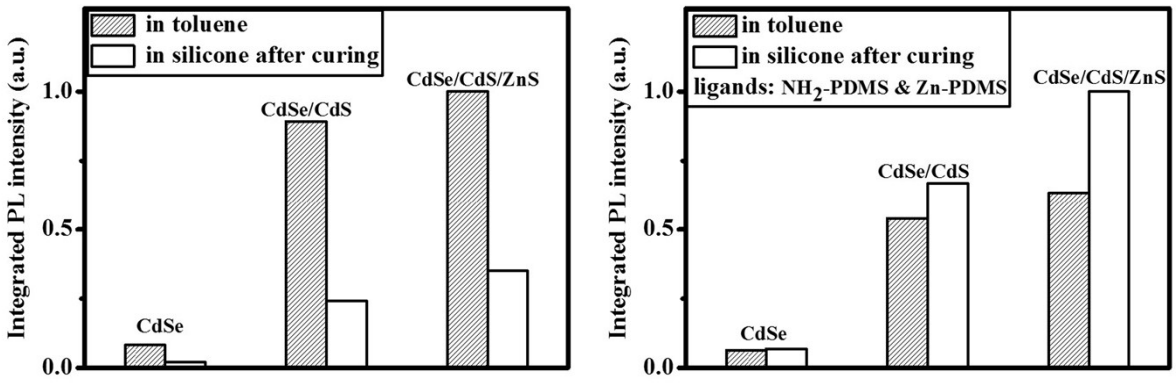

Fig. S1 Integrated PL intensity of the different shell isolation QDs developed without (left) and with (right) the NH_2-PDMS and Zn-PDMS co-passivation. All the samples comprise 1 wt% QDs and are prepared by physical stirring of QD-silicone mixture for 30 min and then cured via standard procedure.

The results clearly exhibit that the NH_2-PDMS and Zn-PDMS co-passivation works for all kind of QDs regardless of their heterostructure. Though the CdS and ZnS shelling can effectively improve the quantum efficiency of the CdSe QDs, they are not able to prevent QDs from fluorescent quenching. On the other hand, all QDs synthesized with NH_2-PDMS and Zn-PDMS co-passivation have certain PL enhancement in silicone after curing. It proves

that the Zn-PDMS passivation is a general approach for the development of high performance QD-silicone nanocomposite.

2. Different Zn-PDMS concentration for QDs preparation

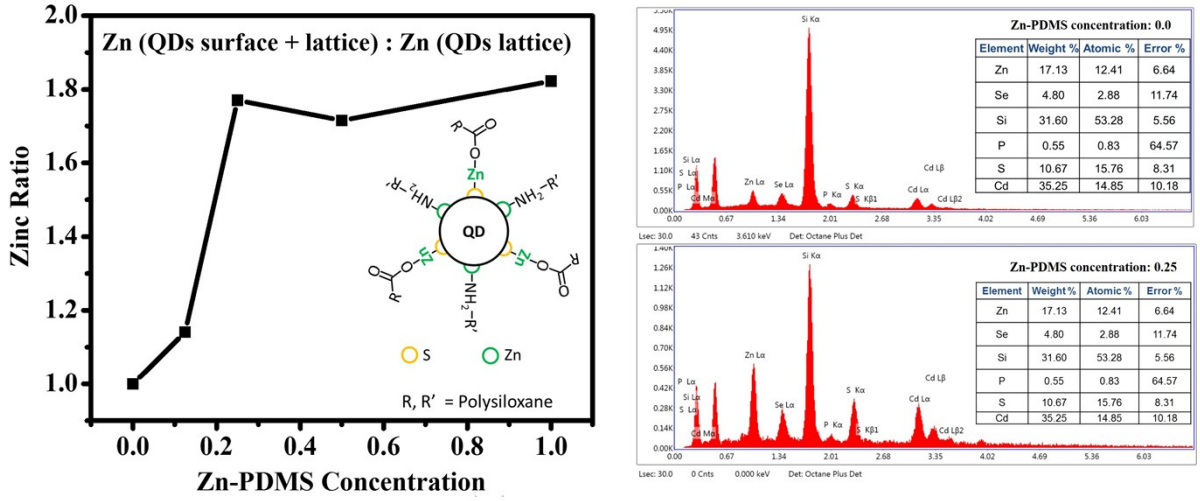

Fig. S2 Left: Ratio of total zinc element amount in QDs and that inside ZnS layer (data acquired from EDS characterization of as-prepared QDs synthesized with different Zn-PDMS concentration and the inserted image shows the Zn cation-rich surface in as-prepared QDs). Right: EDS characterization of as-prepared QDs synthesized without Zn-PDMS passivation (top) and with Zn-PDMS passivation via 0.25 M Zn-PDMS precursor solvent (bottom).

3. Optical property characterization for LED package

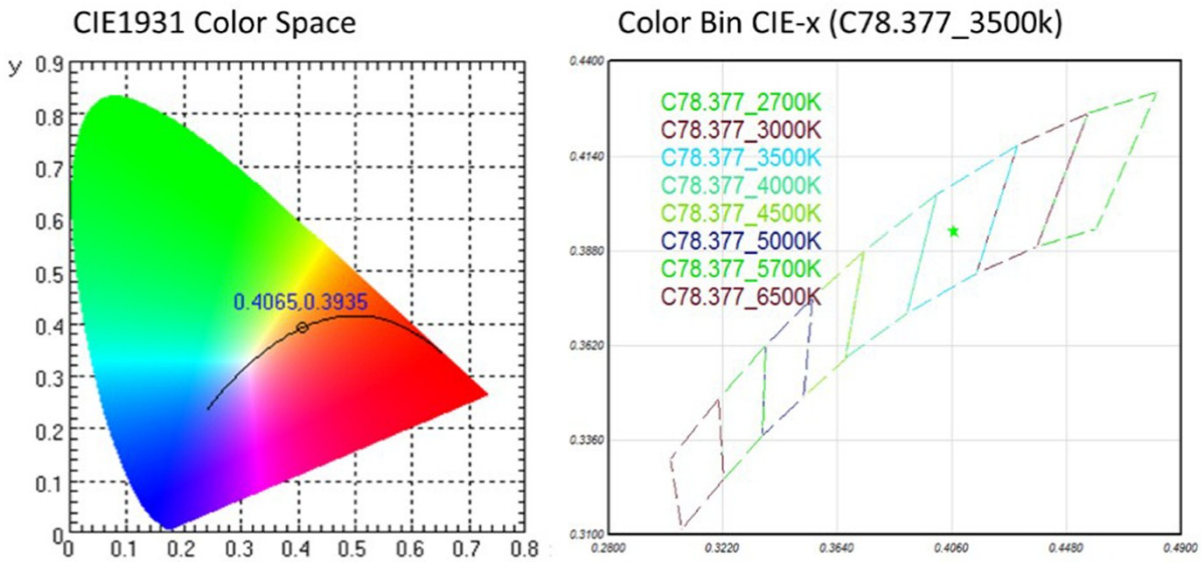

Fig. S3 Color point and correlated color temperature (CCT) of the LED prototype shown in Fig. 5. Here we choose 3500k because it is the most suitable color temperature for reading. High CRI at 3500k is more significant for application.

References

S1. W. N. Nan, Y. A. Niu, H. Y. Qin, F. Cui, Y. Yang, R. C. Lai, W. Z. Lin, X. G. Peng, *J. Am. Chem. Soc.* **2012**, *134*, 19685.