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Compact stable Quantum Dots via Amide-Mediated Synthesis of PMO-Based Multifunctional Ligand

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Abstract:

We present a new class of polymeric ligands for quantum dots (QDs) stabilization, to yield compact stable particles (~100-200 nm diameter), and high quantum yields (> 47 %). The uniform and tunable size of these polymer-coated QDs also allows us to demonstrate their utility in achieving bright and efficient WLEDs with superior stability.

Keywords: quantum dots, PMO, on-chip, light emitting diode

Presenter: Junjie Hao

Suggest topic area: EMISSIVE DISPLAYS (Quantum-Dot Materials)

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1. Introduction

Quantum dots (QDs), due to their wavelength tunability, have been widely used in light emitting device (LEDs)-based displays^[1-6], solar cells^[7-9] and as fluorescent biomarkers^[10-12], etc. To obtain QD based light emitting diodes (QD-LED), in most cases, high quality QDs with specific emission wavelength are uniformly dispersed in a polymer matrix to form a light converting layer. This composite sheet is then coated on LEDs to achieve desired light performance^[1-3, 13, 14]. However, up to now a major barrier toward the widespread use of QDs has been the presence of a trade-off among three desirable QD properties for LEDs: high QY, uniform size, and high stability (both over time and in a harsh environment), in particular, the abscission of QDs' outer ligands, and the deterioration of QDs by permeate oxygen and moisture^[14-18]. Such a problem is commonly found in high-temperature processes of LED packaging (e.g. silicone curing). The principle behind such a phenomenon would be given by the incompatibility between the hydrophobic surface of the QDs and that of encapsulant in WLED (e.g. silicone, or other polymers)^[19]. Consequently, it is energetically preferred for QDs to be deteriorated on surface and aggregate in host matrix, which gives the undesired quenching of photoluminescence.

In order to improve the stability of QDs, amphiphilic polymers have been widely used in cell imaging^[10, 12, 20-23], and various functionalized polymers were used to modify quantum dots. Water soluble quantum dots were even fabricated by encapsulating the QDs into (poly(maleic acid-alt-octadecene))^[24, 25]. The polymer-encapsulated QDs were electrostatically assembled to form QD-polymer-LDH (layered double hydroxide) composites, so as to multi-protect the QD surface from the environment by both the polymer and the LDH nanosheets. However, such an approach would not necessarily protect the QDs from oxygen and moisture, hence still imposing an obstacle and unravelling the full potential of stability improvement.

In this work, we report this simple method using the polymeric ligands to yield the compact **egg**-structure particles. To address

the fundamental problem of the QDs ligands instability in the traditional solid state QDs systems, the polymer employed here is a stable multifunctional poly(maleic anhydride-alt-1-octadecene) (PMO) which is expected to confine both quantum dots and ligands. The stable PMO-modified QDs effectively demonstrated a high quantum yield (> 47%), a low non-specific binding, as well as controlled and adjustable size (from 100 nm to 1 μ m). The incorporation of PMO-modified QDs into functionalized silica shell is also demonstrated^[26, 27]. For details, the QDs coupled with excess ligands were used as egg-yolk, the functional PMO as egg-white, and the functional silica as egg-shell, respectively. The uniform and tunable size of these polymer-coated QDs also allow us to demonstrate their utility in achieving bright and efficient WLEDs with superior stability. And the as-prepared high quality QDs composites have great potential to be used in high performance displays with wide color gamut.

2. Experiments

Preparation of CdSe/ZnSe/ZnS (Core/Shell/Shell) Quantum Dots (QDs):

All the chemicals were of analytical reagent grade and were used without further purification. The pure water was purchased from Wahaha. The CdSe bare nanocrystals and core/shell/shell quantum dots were synthesized via our previous "TOP-assisted SILAR" method^[28-30].

Preparation of Monoethanolamine functionalized poly(maleic anhydride-alt-1-octadecene) (PMOM):

The amphiphilic polymer PMOM was prepared through the amide reaction by using monoethanolamine and PMO. The hydrophily can be adjusted by the monoethanolamine to carbonyl functions ratio (from 0% to 100%).

Preparation of Water-Soluble Polymer-Encapsulated CdSe/ZnSe/ZnS QDs:

The quantum dots with free ligands were used for the phase-transfer process. The QDs were encapsulated by the amphiphilic polymer to transfer them into water without exchanging initial surface ligands. Typically, 100 mg PMOM was dissolved in chloroform solution at room temperature. The chloroform solution containing 1 mg QDs coupled with 5 mg ligand was added to the polymer solution (QDs: polymer= 1:100). The solution was vigorous stirred for 1 h at room temperature, and then, 10 times of water was introduced into the mixture. The chloroform was removed slowly. The particle size of PMOM-QDs composites can be adjusted by the monoethanolamine ratio in PMOM, which can be easily changed from 100 nm to 1 μ m.

Formation of the egg-structure composite particles:

APTES ((3-aminopropyl)triethoxysilane) was used as the silane coupling agent to form the egg-shell. Typically, APTES coupled with EDC/NHS was introduced into the PMOM-QDs mixture solution. After the coupling reaction completion, TEOS and $\text{NH}_4\text{OH}\cdot\text{H}_2\text{O}$ was used to form the thick silica egg-shell.

3. Results and discussion

In this work, we have successfully synthesized egg-structure composite particles. The QDs were encapsulated by the amphiphilic polymers to transfer them into water without exchanging initial surface ligands. As illustrated in Fig. 1a, the multivalent polymer ligand PMOM with alkane and carboxyl groups was synthesized by reacting poly(maleic anhydride-alt-1-octadecene) (PMO) ($M_n = 30,000\text{--}50,000$) with monoethanolamine. The high reactivity of anhydride with primary amines facilitated the quantitatively controlled reaction. The ratio of modified maleic anhydride groups can be adjusted from 0% to 100%. In an optimized structure, about 80% of the maleic anhydride groups were chemically modified.

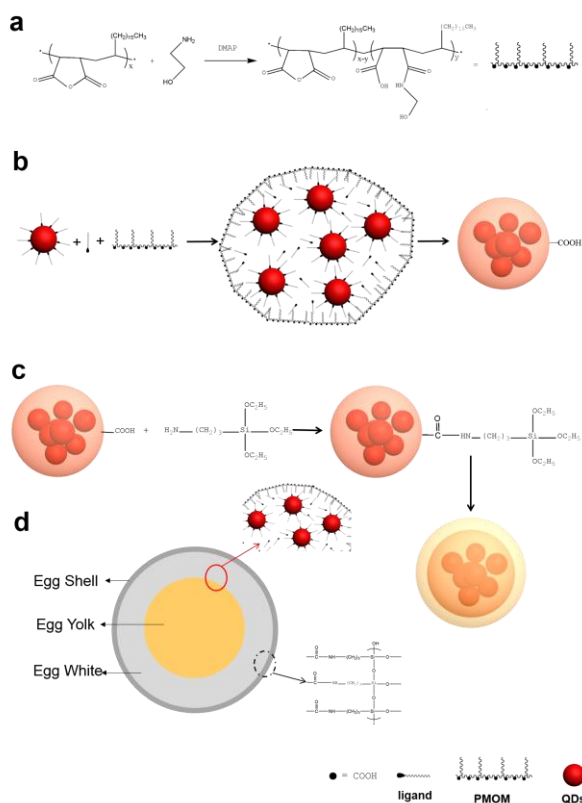


Figure 1. Schematic diagrams illustrating the process for preparing the egg-structure composite particles. (a). Schematic illustration of the synthesis of PMOM ligands, the molar ratio of $y:x$ can be changed from 0:1 to 1:0 by adjusting the amount of monoethanolamine; (b). The procedure to prepare PMOM coated QDs; (c). Approach for the fabrication of silica coated egg-structure composite particles, the hard protective layer can be obtained by the dense growth of silica; (d). Schematic diagram of different positions in egg-structure particle.

The synthesis process of PMOM coated QDs is presented graphically in Fig. 1b. After the chloroform was evaporated from

the mixed system, the uniformly sized particles were dispersed in aqueous solution. The single particle contains multiple quantum dots with free ligands, the polymers here employ the multifunctional PMOM to confine quantum dots and ligands. And then the hard shell of silica can be formed gradually, as shown in Fig. 1c, using (3-aminopropyl)triethoxysilane (APTES) as the silane coupling agent to form the egg-shell. TEOS was then used as the shell material for further growth. Finally, as can be seen in Fig. 1d, the high luminescent QDs and free ligands can be first confined inside the flexible polymer corona, and then be protected by the silica shell. The stable egg-structure particles were achieved by coupling the two kinds of protective layer.

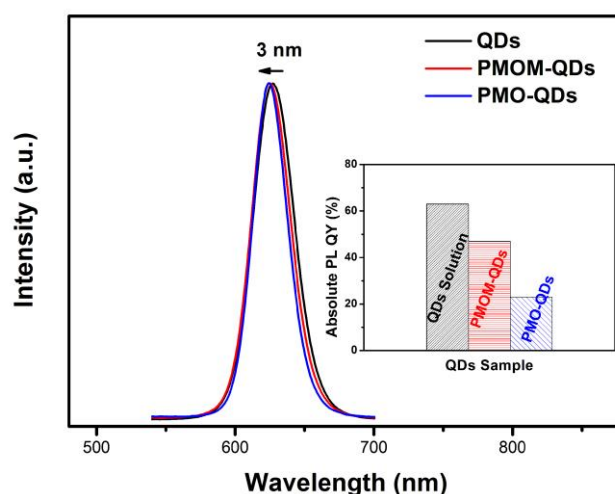


Figure 2. The PL emission of diluted QDs chloroform solution (black line), PMOM modified QDs aqueous solution (red line) and PMO modified QDs aqueous solution (blue line). Inset: comparison of PL QYs of CdSe/ZnS QDs in chloroform solution versus PMO/PMOM modified QDs in aqueous solution.

The fluorescence spectra of core-shell QDs synthesized by TOP-SILAR method is shown in Fig. 2. Comparing the emissions in Fig. 2, we can see that little PL shift (3 nm) was observed between the PL spectra of QDs in chloroform solution (black line) and PMO/PMOM modified QDs in aqueous solution (red and blue lines). The inset in Fig.2 shows the corresponding PL QYs. The QY ratio of PMOM-QDs ($y:x=1:0$) aqueous solution (47%) and QDs chloroform solution (63%) was about 75%, indicative of a relatively high utilization and low degree of self-absorption. And such characteristics are expected to cater the fabrication of high efficiency QLED. While the PMO-QDs ($y:x=0:1$) sample exhibits a very low QY (23%), which may be due to the poor dispersion of PMO in water and the large size of the composite particles.

Fig.3 shows the picture of the PMOM-modified QDs composite particles with different ratios of monoethanolamine. The left part represents 100% anhydride amide reaction (PMOM), and the right part represents 0% reaction (PMO). We can see from Fig. 3a-b, the 100% reaction samples can form a uniform and stable microemulsion solution, while in PMO-QDs system the droplet cannot disperse evenly. After the chloroform volatile completely, as shown in Fig. 3c-d, obvious Mie scattering can be seen in the right part, which corresponding to the PMO-QDs sample. This can also be confirmed by TEM, as shown in Figure 4. The particle sizes are 100 nm and 1 μm for these two samples, respectively. As shown in the inset of TEM images, the nanoparticles are dispersed very well, which provide that quantum dots and ligands can be

coated together in the vesicles in our method. We can easily achieve different sizes of QDs-polymer composite particles, and the size can be adjustable controlled from 100 nm to 1 μm . Due to the rich active carboxyl group on the surface of particles (as shown in Fig. 1c), the uniform particles can be further reacted with silane coupling agent and form the silica egg-shell.

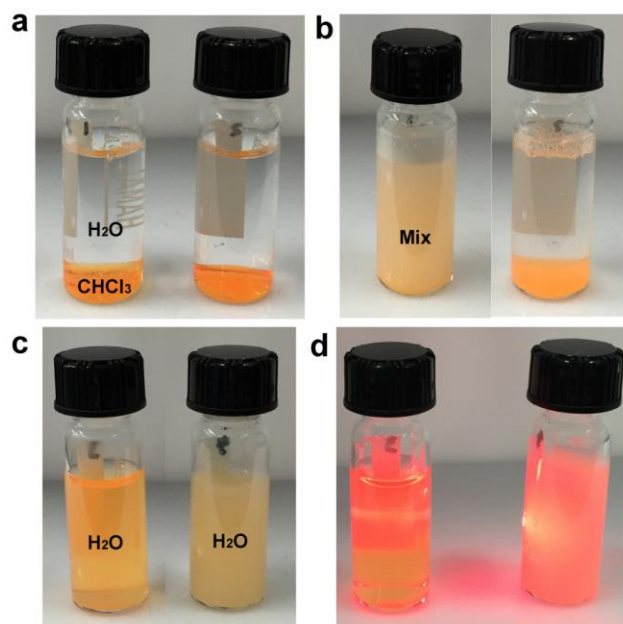


Figure 3. The images show the vials containing modified-QDs particles, the left part represents (PMOM), and the right part represents (PMO). (a) The mixture of modified, QDs, ligands, chloroform, and water; (b) Hand shaking, and then standing for 10 minutes; (c) Magnetic stirring and slow evaporation of chloroform, dispersion in aqueous solution; (d) The laser beam passes through the solution.

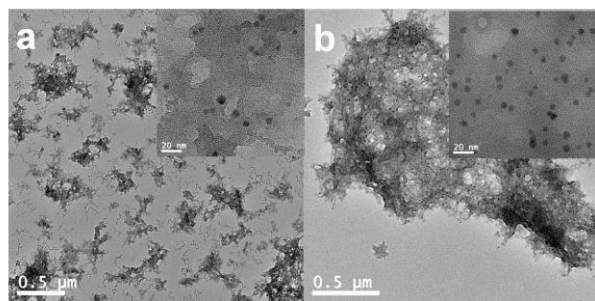


Figure 4. TEM images of PMOM-QDs particles as shown in Figure 3. (a) PMOM-QDs; (b) PMO-QDs.

4. Conclusion

In summary, we have described detailed synthetic methods for the highly luminescent, uniform size and modifiable egg-structure particles. The absolute PL QY can reach up to 47%, and the size can be controlled and adjustable from 100 nm to 1 μm . This method provides a strong advantage for delicate control of optical properties because it can apply to any type of QDs whatever their pre-existing coating. In principle, this method allows composite fabrications using QDs covering a wide range of sizes and

chemical nature. And the as prepared stable polymer-QDs particles have great potential to be used in high performance displays with wide color gamut.

5. Acknowledgements

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6. References

- [1] Dai, X., Zhang, Z., Jin, Y., Niu, Y., Cao, H., Liang, X., Chen, L., Wang, J. Peng, X. Solution-processed, high-performance light-emitting diodes based on quantum dots[J]. *Nature*. 2014, 515(7525):96-99.
- [2] Jun, S. Jang, E. Bright and Stable Alloy Core/Multishell Quantum Dots[J]. *Angewandte Chemie*. 2013, 125(2):707-710.
- [3] Sun, Q., Wang, Y.A., Li, L.S., Wang, D., Zhu, T., Xu, J., Yang, C. Li, Y. Bright, multicoloured light-emitting diodes based on quantum dots[J]. *Nat Photon*. 2007, 1(12):717-722.
- [4] Chen, W., Wang, K., Hao, J., Wu, D., Wang, S., Qin, J., Li, C. Cao, W. Highly Efficient and Stable Luminescence from Microbeans Integrated with Cd-Free Quantum Dots for White-Light-Emitting Diodes[J]. *Particle & Particle Systems Characterization*. 2015, 32(10):922-927.
- [5] Chen, W., Hao, J., Qin, J. Wang, K. P-89: Effects of Nano-TiO₂ Particles on Conversion Efficiency of Quantum Dots Light Converting Nanocomposites[J]. *SID Symposium Digest of Technical Papers*. 2015, 46(1):1491-1494.
- [6] Bin, X., Haochen, L., Run, H., Chaofan, W., Junjie, H., Kai, W. Xiaobing, L. Targeting Cooling for Quantum Dots in White QDs - LEDs by Hexagonal Boron Nitride Platelets with Electrostatic Bonding[J]. *Advanced Functional Materials*. 2018, 28(30):1801407.
- [7] Liu, H., Li, S., Chen, W., Wang, D., Li, C., Wu, D., Hao, J., Zhou, Z., Wang, X. Wang, K. Scattering enhanced quantum dots based luminescent solar concentrators by silica microparticles[J]. *Solar Energy Materials and Solar Cells*. 2018, 179:380-385.
- [8] Meinardi, F., Colombo, A., Velizhanin, K.A., Simonutti, R., Lorenzon, M., Beverina, L., Viswanatha, R., Klimov, V.I. Brovelli, S. Large-area luminescent solar concentrators based on "Stokes-shift-engineered" nanocrystals in a mass-polymerized PMMA matrix[J]. *Nat Photon*. 2014, 8(5):392-399.
- [9] Jasieniak, J., MacDonald, B.I., Watkins, S.E. Mulvaney, P. Solution-Processed Sintered Nanocrystal Solar Cells via Layer-by-Layer Assembly[J]. *Nano Letters*. 2011, 11(7):2856-2864.
- [10] Liu, W., Greytak, A.B., Lee, J., Wong, C.R., Park, J., Marshall, L.F., Jiang, W., Curtin, P.N., Ting, A.Y., Nocera, D.G.,

- Fukumura, D., Jain, R.K. Bawendi, M.G. Compact Biocompatible Quantum Dots via RAFT-Mediated Synthesis of Imidazole-Based Random Copolymer Ligand[J]. *Journal of the American Chemical Society*. 2010, 132(2):472-483.
- [11] Gao, D., Zhang, P., Sheng, Z., Hu, D., Gong, P., Chen, C., Wan, Q., Gao, G. Cai, L. Highly Bright and Compact Alloyed Quantum Rods with Near Infrared Emitting: a Potential Multifunctional Nanoplatfrom for Multimodal Imaging In Vivo[J]. *Advanced Functional Materials*. 2014, 24(25):3897-3905.
- [12] Liu, A., Peng, S., Soo, J.C., Kuang, M., Chen, P. Duan, H. Quantum Dots with Phenylboronic Acid Tags for Specific Labeling of Sialic Acids on Living Cells[J]. *Analytical Chemistry*. 2010, 83(3):1124-1130.
- [13] Yang, L., Liu, H., Lu, R., Chen, W., Hao, J., An, N., Ma, H., Wu, D., Bian, D. Wang, K. 32 - 4: In - situ Polymerization of Polystyrene for Synthesis of Quantum Dots Composite Particle for Wide Color Gamut Display[J]. *SID Symposium Digest of Technical Papers*. 2017, 48(1):459-462.
- [14] Lu, R., Chen, W., Chen, Y., Yang, L., Hao, J., An, N., Ma, H., Bian, D., Wu, D., Wang, K. Sun, X.W. 32 - 3: Stability Enhancement of Light Emitting Diode Based on Quantum Dots through Atomic Layer Deposition[J]. *SID Symposium Digest of Technical Papers*. 2017, 48(1):455-458.
- [15] Kim, J.-H., Song, W.-S. Yang, H. Color-converting bilayered composite plate of quantum-dot-polymer for high-color rendering white light-emitting diode[J]. *Optics Letters*. 2013, 38(15):2885-2888.
- [16] Jong-Hoon, K. Heesun, Y. White lighting device from composite films embedded with hydrophilic Cu(In, Ga)S₂/ZnS and hydrophobic InP/ZnS quantum dots[J]. *Nanotechnology*. 2014, 25(22):225601.
- [17] Kim, H.Y., Yoon, D.-E., Jang, J., Lee, D., Choi, G.-M., Chang, J.H., Lee, J.Y., Lee, D.C. Bae, B.-S. Quantum Dot/Siloxane Composite Film Exceptionally Stable against Oxidation under Heat and Moisture[J]. *Journal of the American Chemical Society*. 2016, 138(50):16478-16485.
- [18] Kim, H.Y., Yoon, D.-E., Jang, J., Choi, G.-M., Lee, D.C. Bae, B.-S. 32-2: Distinguished Student Paper: Quantum Dot/Siloxane Composite Film Exceptionally Stable Against Heat and Moisture[J]. 2017, 48(1):451-454.
- [19] Ziegler, J., Xu, S., Kucur, E., Meister, F., Batentschuk, M., Gindele, F. Nann, T. Silica-Coated InP/ZnS Nanocrystals as Converter Material in White LEDs[J]. *Advanced Materials*. 2008, 20(21):4068-4073.
- [20] Medintz, I.L., Uyeda, H.T., Goldman, E.R. Mattoussi, H. Quantum dot bioconjugates for imaging, labelling and sensing[J]. *Nature materials*. 2005, 4(6):435-446.
- [21] Duan, H., Kuang, M. Wang, Y.A. Quantum Dots with Multivalent and Compact Polymer Coatings for Efficient Fluorescence Resonance Energy Transfer and Self-Assembled Biotagging[J]. *Chemistry of Materials*. 2010, 22(15):4372-4378.
- [22] Zhang, P., Liu, S., Gao, D., Hu, D., Gong, P., Sheng, Z., Deng, J., Ma, Y. Cai, L. Click-Functionalized Compact Quantum Dots Protected by Multidentate-Imidazole Ligands: Conjugation-Ready Nanotags for Living-Virus Labeling and Imaging[J]. *Journal of the American Chemical Society*. 2012, 134(20):8388-8391.
- [23] Hu, D., Zhang, P., Gong, P., Lian, S., Lu, Y., Gao, D. Cai, L. A fast synthesis of near-infrared emitting CdTe/CdSe quantum dots with small hydrodynamic diameter for in vivo imaging probes[J]. *Nanoscale*. 2011, 3(11):4724-4732.
- [24] Cho, S., Kwag, J., Jeong, S., Baek, Y. Kim, S. Highly Fluorescent and Stable Quantum Dot-Polymer-Layered Double Hydroxide Composites[J]. *Chemistry of Materials*. 2013, 25(7):1071-1077.
- [25] Kumar, S., Sarita, Nehra, M., Dilbaghi, N., Tankeshwar, K. Kim, K.-H. Recent advances and remaining challenges for polymeric nanocomposites in healthcare applications[J]. *Progress in Polymer Science*. 2018, 80:1-38.
- [26] Liu, J., Song, T., Yang, Q., Tan, J., Huang, D. Chang, J. Highly stable quantum dots with silica-poly(EGDMA-co-MAA) synergistic protection and the preliminary application in immunoassay[J]. *Journal of Materials Chemistry B*. 2013, 1(8):1156-1163.
- [27] Hu, X. Gao, X. Silica-Polymer Dual Layer-Encapsulated Quantum Dots with Remarkable Stability[J]. *ACS Nano*. 2010, 4(10):6080-6086.
- [28] Hao, J., Wang, K. Sun, X. 12.3: Core-Shell Quantum Dots Synthesized by Using Tri-n-Octylphosphine-Assisted Method for High-Color-Saturation Displays[J]. *SID Symposium Digest of Technical Papers*. 2014, 45(1):138-141.
- [29] Hao, J., Liu, H., Miao, J., Lu, R., Zhou, Z., Zhao, B., Xie, B., Cheng, J., Wang, K. Delville, M.-H. A facile route to synthesize CdSe/ZnS thick-shell quantum dots with precisely controlled green emission properties: towards QDs based LED applications[J]. *Scientific Reports*. 2019, 9(1):12048.
- [30] Ren, C., Hao, J., Chen, H., Wang, K. Wu, D. Prepare core-multishell CdSe/ZnS nanocrystals with pure color and controlled emission by tri-n-octylphosphine-assisted method[J]. *Applied Surface Science*. 2015, 353:480-488.