Supplementary Information

Facile Single Step Preparation of High-performance Quantum Dot Barcodes

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Materials and instrumens

Poly(vinylpyrrolidone) (PVP K-30), styrene (99%), ethylene glycol dimethacrylate (EGDMA, 98%), polyvinyl alcohol (PVA, M_w=1,300,000), poly (acrylic acid) (PAA, M_w=2,000), 3-aminopropyltriethoxysilane (APTES), tetraethyl orthosilicate (TEOS) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich. Benzoyl peroxide (BPO) was obtained from Fluka.

Scanning electron microscopy (SEM, XL-30, Philips Corp.) was used for observing the morphology of the polymer beads and the pore size on the microspheres surface. QDs were visualized using a Tecnai G2 F20 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV.

Preparation of PSEMBs

The typical seeded polymerization was shown as follows: 1) the seed particles (2.8 μm, 0.1 g) were re-dispersed in 0.25 wt% sodium dodecylsulfate (SDS) aqueous solution (30 g) by sonication (10 min, 100W), and the swelling agent (e.g. cyclohexane, 0.3 g) was also emulsified by sonication in 0.25 wt% SDS solution (10 g). These solutions were added into the reactor, followed by stirring for 10 h at 30 ^{o}C. 2) A mixture of styrene monomer (5 g), EGDMA (5 g), MAA (1 g), toluene (7.5 g, 75 wt% relative to styrene) and BPO (0.11 g, 1 wt% relative to monomer) was emulsified in 100 g of 0.25 wt% SDS solution by sonication (10 min, 100 W), followed by pouring into the reactor. 3) After 12 h, 2.5 wt% PVA aqueous solution (80 g) and copper chloride (0.01 g, used as inhibitor) were added into the reactor before raising the temperature. The polymerization was carried out at 80 ^{o}C for 10 h. The final beads were obtained by centrifugation and washing three times. Then the beads were dried under vacuum at 30 ^{o}C.

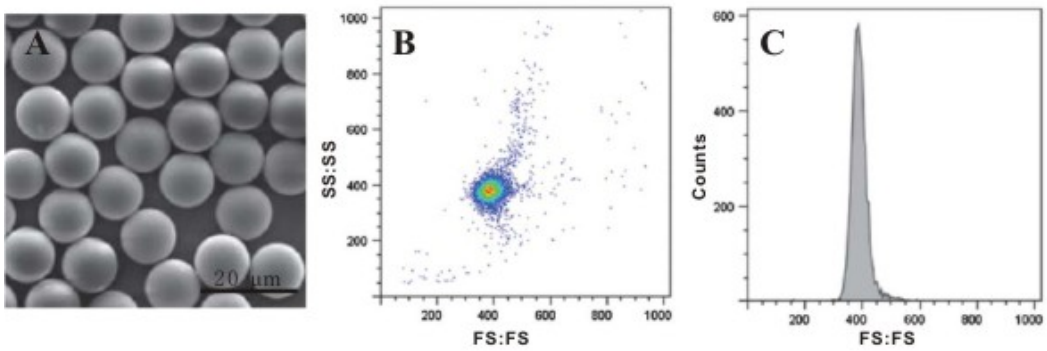

Figure S1 (A) SEM photographs of the PSEMBs using toluene (75 wt% relative to monomer) as porogen; (B, C) are the flow cytometric analysis diagrams of PSEMBs in A, the bead populations based on side light scatter (SS) vs.forward light scatter (FS); (C) the histogram of size distribution.

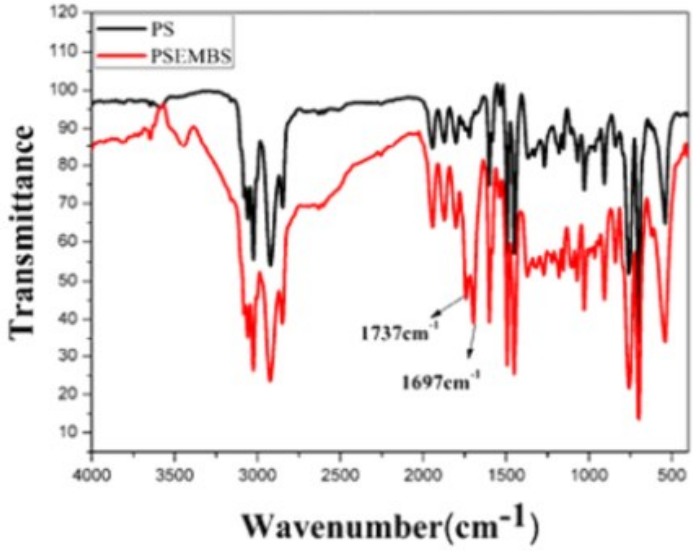

Figure S2 The FTIR spectra of PS and cross-linked PSEMBs.

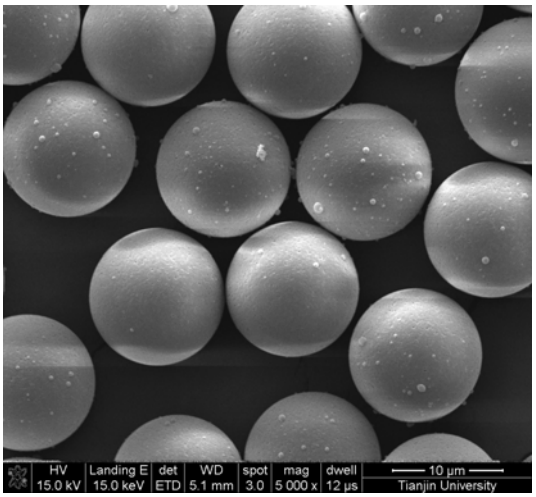

Figure S3 SEM photographs of the QD barcodes.

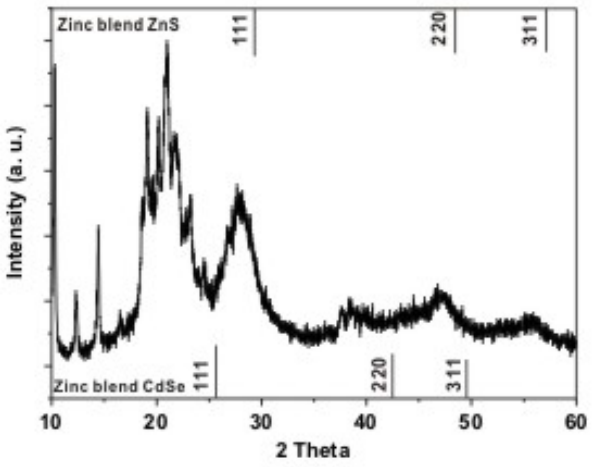

Figure S4 XRD patterns of QD barcodes. The XRD patterns of bulk zinc blend CdSe and ZnS are also shown at the bottom and top, respectively.

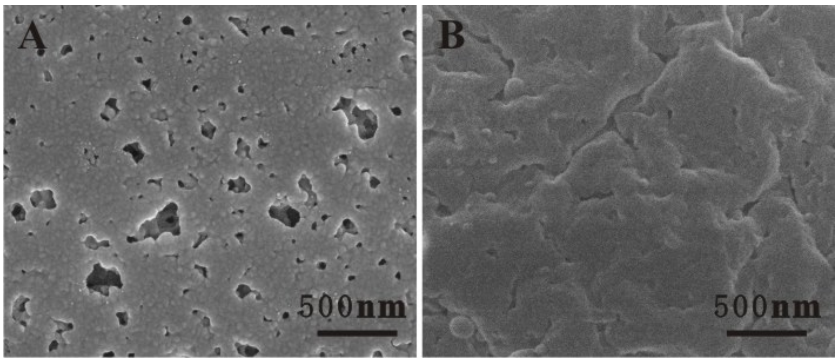

Figure S5 SEM images of (A) the surface of PSEMB and (B) the surface of QD-encoded PSEMBs.

Synthesis of PAA grafted silica-coated $Cd_{1-x}Zn_xS/ZnS$ QDs

$Cd_{1-x}Zn_xS/ZnS$ core/shell structured nanocrystals were prepared by following previously published procedures with some slight modifications.[1] 1 mmol of CdO, 10 mmol ZnO, 7 mL OA and 15 mL ODE were placed in a 100mL three-neck flask. Then the reaction system was flushed with a flow of argon for 30 min at room temperature. Subsequently, the reaction mixture was heated to 300 ^oC to form a clear solution of $Cd(OA)_2$ and $Zn(OA)_2$. At this temperature, 2 mmol S powder dissolved in 3 mL of ODE was quickly injected into the reaction flask. After the first injection of S precursors, the temperature of the reaction flask was elevated to 310 ^oC for further growth of $Cd_{1-x}Zn_xS$ cores. After 8 min of reaction, 8 mmol of S powder dissolved in TOP were injected into the reactor for another 30 minutes. After the reaction was completed, the temperature

was cooled down to room temperature. The nanocrystals were extracted and purified by acetone; then redispersed in cyclohexane for further reaction.

The silica-coated $Cd_{1-x}Zn_xS/ZnS$ QDs were synthesized according to a previously published procedure.[2] Typically, 10 mL of cyclohexane, 1.3 mL of NP-40, 200 μL of QDs (3.3×10^{-6} M) stock solution in cyclohexane, and 120 μL of TEOS were added into a flask under vigorous stirring. Thirty minutes after the microemulsion system was formed, 100 μL of ammonia aqueous solution (25 wt %) was introduced to initiate the polymerization process. After stirring at room temperature for 24 h, 20 μL APTES were introduced for another 24 h polymerization. The nanoparticles were isolated from the microemulsion using acetone and centrifuged, and the resultant precipitate was washed in sequence with ethanol and water to remove any surfactant and unreacted molecules. Then they were redispersed in double-distilled water and 0.08 g PAA and 0.23 g EDC were added.[3] The process lasted overnight. Then the resulting nanoparticles were washed with double-distilled water and centrifuged for three times

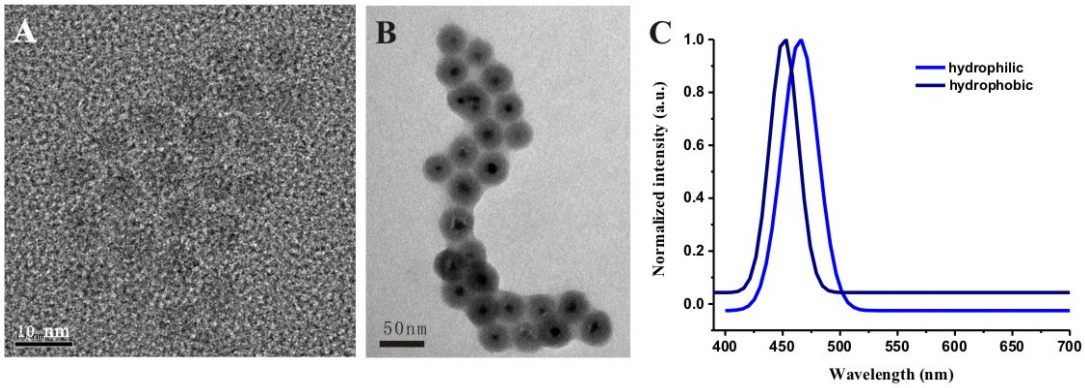

Figure S6 (A) HRTEM images of blue-emitting QDs (B) TEM images of silica-coated blue-emitting QDs (C) Fluorescence emission spectra before and after silica coated.

Preparation of QD-goat anti-human IgG conjugates

Carboxylic acid groups of PAA displayed on the QDs surface bound with the amine groups of proteins. First, water-dispersed QDs were activated with EDC/NHS in MES buffer. To 1mL MES buffer, add 200 μL QDs (2.4×10^{-7} M), 0.2 mg EDC, 0.3 mg NHS. The reaction was incubated at 25 ^{o}C for 20 min with gentle shaking. After that, the solution was centrifuged at 12000 rpm for 15

min. Then the activated QDs was dispersed in 200 μL PBS (0.1 M), and 60 μL goat anti-human IgG was added. The mixture was incubated at 25 ^{o}C for 3 h with gentle shaking. After reaction, the mixture was washed with PBS several times to remove excess goat anti-human IgG and kept at 4 ^{o}C in PBS (0.01 M, pH 7.4, 0.5% BSA).

References

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