SUPPORTING INFORMATION

Optical Detection of Glucose by CdS Quantum Dots Immobilized in Smart Microgels

Weitai Wu, Ting Zhou, Jing Shen and Shuiqin Zhou*

S1. Experimental Section

D(+)-Glucose was purchased from ACROS, and all other chemicals were purchased from Aldrich. NIPAM was recrystallized from a hexane-toluene mixture. AA was distilled under reduced pressure. Cadmium perchlorate hydrate ($Cd(ClO_4)_2{\cdot}H_2O$) , thioacetamide (CH_3CSNH_2), AAm, *N,N'*-methylenebisacrylamide (MBAAm), ammonium persulfate (APS), sodium dodecyl sulfate (SDS), APBA, and *N*-(3-dimethylaminopropyl)-*N'*-ethyl-carbodiimide hydrochloride (EDC), were used as received.

The p(NIPAM-AAm-PBA) microgels were synthesized using the procedure described in our previous report.[16a] First, 0.231 g of APBA and 0.231 g of EDC were dissolved in 35 mL of water. The solution was cooled in an ice bath, and then adding 20 mL of purified p(NIPAM-AAm-AA) microgels obtained from the precipitation copolymerization of NIPAM, AAm (7.3 mol%), and AA (7.1mol%) using MBAAm (4.3 mol%) as a crosslinker and APS as an initiator in the presence of SDS. The reaction was kept for 4 h at 0 ºC. The resultant products were purified by dialysis against very frequently changed water for at least 1 week.

The p(NIPAM-AAm-PBA)-CdS hybrid microgels were prepared as follows: the mixture of 0.1431 g $Cd(ClO_4)_2{\cdot}H_2O$ with 20 mL p(NIPAM-AAm-PBA) microgel suspensions was stirred at room temperature for 1 day under a N_2 purge. After that, excess $Cd(ClO_4)_2$ was removed by centrifugation, decantation, and dialysis against water for 2 days. The microgels loaded with Cd^{2+} ions was then heated to 60 °C under a N_2 purge and stirring. After 30 min, a CH_3CSNH_2 solution (0.073 g/5 ml water) was dropwisely added. The temperature was then raised to 85 °C, and the color gradually turned to brilliant yellow. The mixture was further stirred for 1 h. The resulted hybrid microgels were then purified by centrifugation, decantation, and dialysis against frequently changed water for 3 days.

The UV-vis absorption spectra were obtained on a Thermo Electron Co. Helios β UV-vis Spectrometer. The PL spectra of the hybrid microgel dispersions under different conditions were obtained on a JOBIN YVON Co. FluoroMax®-3 Spectrofluorometer. The TEM images were taken on a FEI TECNAI transmission electron microscope at an accelerating voltage of 120 kV. Dynamic light scattering (DLS) was performed on a BI-200SM light scattering spectrometer with a He-Ne laser (35 mW, 633 nm) as the light source.

To confirm the reversibility of the glucose-induced optical property change, the optical spectra of the p(NIPAM-AAm-PBA)-CdS hybrid microgel dispersions were measured for three cycles with dialysis/glucose adjustment. The optical spectra were reproducible after the dialysis (pH ≈ 6) and glucose adjustment, indicating that the glucose-sensitive optical property change is reversible. We have also repeated the experiments three times from batch to batch to make sure the reproducibility of the results.

S2. Synthesis of CdS QDs without the Microgel

5.2 nm CdS QDs were synthesized using CTAB as cap agent. Typically, a mixture of 0.0475 g $Cd(ClO_4)_2 \cdot H_2O$, 0.2916 g cetyltrimethyl ammonium bromide (CTAB), and water (30 mL) was poured into a 100 mL three-neck round-bottom flask equipped with a stirrer, a nitrogen gas inlet, and a condenser. The mixture was heated to 35 °C under a N_2 purge. After a 30 min, a thioacetamide solution (0.073 g in 5 ml water) was dropwisely added. The temperature was raised to 95 °C, and the color gradually turned to brilliant yellow. The mixture was further stirred for 1 hour under N_2 atmosphere. The resulted CTAB-capped CdS QDs were then purified by centrifugation, decantation, and dialysis against very frequently changed water at room temperature for 1 day. The size of the CTAB-capped CdS QDs was characterized by TEM and DLS.

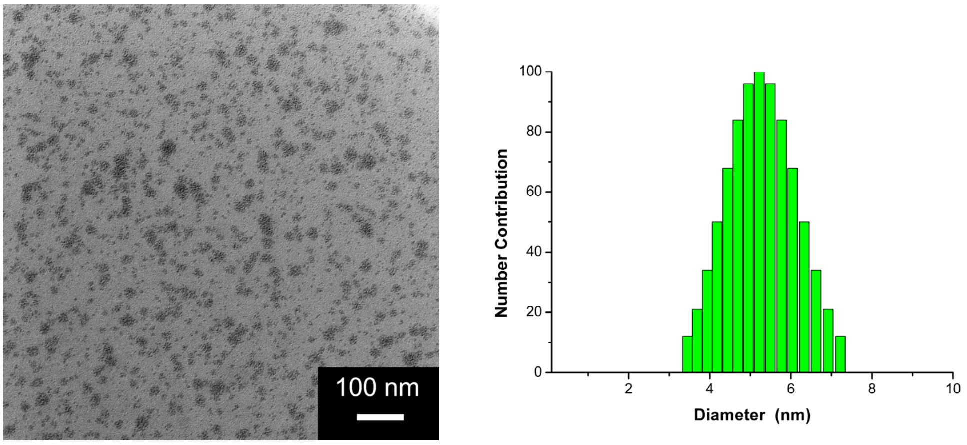

Figure S1. The TEM image (left) and the hydrodynamic diameter distribution from DLS measurement (right) of the CTAB-capped CdS QDs.

S3. PL Spectra of CTAB-Capped CdS QDs with/without Glucose

The PL spectra for CTAB-capped CdS QDs dispersions at different glucose concentrations were collected at room temperature. The excitation wavelength was 390 nm. It is clear that the curves nearly overlap for the CTAB-capped CdS samples with or without glucose. The glucose by itself does not affect the fluorescence of the QDs.

Two PL emission components can be clearly observed. The emission bands (445-540 nm) near absorption edge are likely to be related to the excitonic recombination (i.e. charge-carrier recombination) at the band edge. Those intrinsical emissions are less sensitive to the environments around the QDs. Broad emission bands near absorption edge have been observed in the luminescence spectra of bulk CdS crystals.[1-3] The low energy PL centre at 638 nm are associated with emissive surface-trap states, and predominantly due to the surface-localized defects of the crystals, such as vacancies or site-substitution.[4]

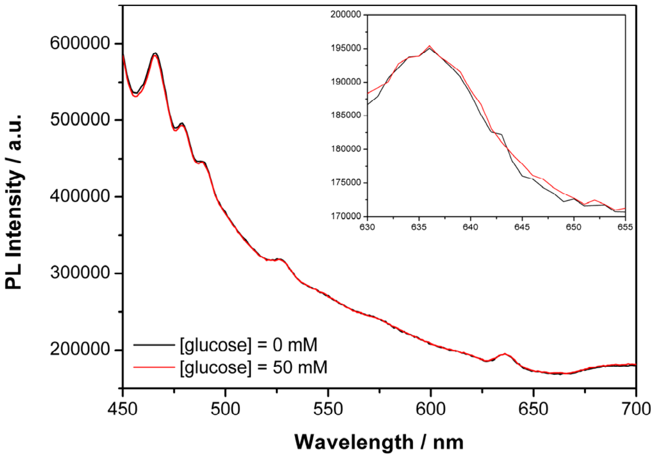

Figure S2. The PL spectra of the CTAB-capped CdS QDs in the absence of glucose and presence of 50 mM glucose.

S4. PL Spectra of as-grown p(NIPAM-AAm-PBA)-CdS hybrid microgel dispersions

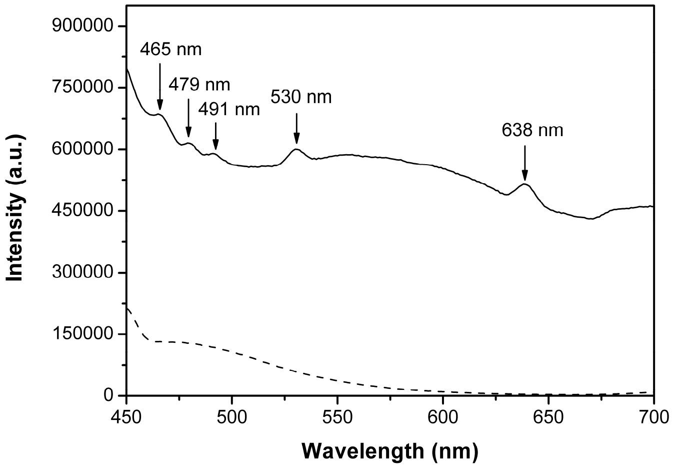

Figure S3. The full range PL spectrum of the p(NIPAM-AAm-PBA)-CdS hybrid microgels as prepared.

The PL spectrum for as-grown p(NIPAM-AAm-PBA)-CdS hybrid microgel dispersions was collected at room temperature. The PL spectra of the APBA solution were also presented, showing a weak peak at 416 nm and a broad emission band in the range of 400-500 nm. Clearly, the present p(NIPAM-AAm-PBA)-CdS hybrid microgels are superior in PL intensity to APBA.

As was discussed above, those intrinsical emissions (445-540 nm) of CdS QDs are less sensitive to the environments around the QDs. The low energy PL centre at 638 nm are associated with emissive surface-trap states, which could be highly affected by the physicochemical environment of QDs.[4] Therefore, in order to probe the glucose-sensitive PL property of p(NIPAM-AAm-PBA)-CdS hybrid microgels, we have probed the evolution of PL emissions in the low energy region (centre at 638 nm).

S5. TEM Images of p(NIPAM-AAm-PBA)-CdS hybrid microgels at High Glucose Concentration

The polyacrylamide (pAAm) segments in the copolymer microgels has been designed to complex with Cd^{2+} ions for the uptake of Cd^{2+} precursors and to stabilize the CdS quantum dots (QDs) in the microgels. Indeed, TEM observations indicate that the swelling of the p(NIPAM-AAm-PBA)-CdS hybrid microgels at high glucose concentrations does not induce the release of CdS QDs. The core-shell structure with a CdS rich core of the hybrid microgels is very stable. No sediment was observed by the revision of this paper (~3 months' placement).

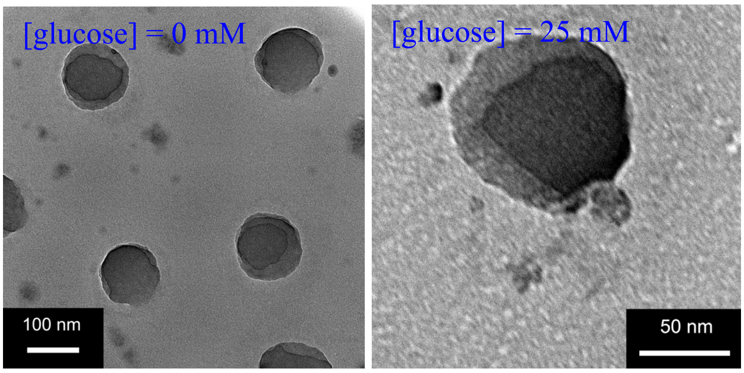

Figure S4. TEM Images of p(NIPAM-AAm-PBA)-CdS hybrid microgels at different Glucose Concentrations.

Reference

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