Adenosine capped QDs based fluorescent sensor for detection of dopamine with high selectivity and sensitivity

Qin Mu, Hu Xu, Yan Li*, Shijian Ma, and Xinhua Zhong*

1. Synthesis of oil-soluble CdSe/CdS/ZnS core/shell/shell QDs

Synthesis of CdSe core QDs CdSe core was prepared according to a modified literature method.[1] Typically, 25.6 mg (0.2 mmol) of CdO, 1.3 g of TOPO (3.4 mmol), 0.5 mL of oleic acid and 3.5 mL of ODE were loaded into a 50 mL three-neck flask and repeated pumped down three times at room temperature to remove the air. The mixture was heated to 320 °C under a high purity nitrogen flow to form a colorless clear solution. The heating mantle was then removed. When the temperature was down to 310 °C, 1.5 mL of Se precursor solution (0.2 M) that was made by dissolving 1mmol selenium power (79.0 mg) in TOP (2.0 mL) and ODE (3.0 mL) by sonication, was injected into the reaction flask, and subsequently the nanocrystals grew in the flask. When the temperature cooled down to 70 °C, hexane/methanol (v/v, 1:1) was added to the mixture to separate the nanocrystals from byproducts and excess precursors. Then the nanocrystals were further purified by centrifugation with the addition of acetone. The obtained CdSe nanocrystals were redispersed in hexane for further use.

Stock solution preparation The Cd precursor solution (0.1 M) was prepared by dissolving 256.8 mg of CdO (2 mmol) in the mixture of oleic acid (4.0 mL)and ODE (16.0 mL) at 160 °C. The Zn precursor solution (0.1 M) was obtained by dissolving 440 mg of $Zn(OAc)_2 \cdot 2H_2O$ (2 mmol) in mixture of oleylamine (1.8 mL) and ODE (18.4 mL) at 120 °C. The sulfur precursor solution (0.1 M) was prepared by dissolving 64 mg of sulfur power (2 mmol) in 20 mL ODE at 120 °C. All of the stock solutions were stored at room temperature.

Synthesis of CdSe/CdS/ZnS core/shell/shell QDs The CdSe/CdS/ZnS core/shell/shell

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Institute of Applied Chemistry, Department of Chemistry, East China University of Science and Technology, Shanghai 200237, PR China, E-mail: yli@ecust.edu.cn; zhongxh@ecust.edu.cn; Fax: +86 21 6425 0281

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QDs were synthesized by using the SILAR method.[2,3] Typically, 0.06 mmol of CdSe which was dispersed in hexane,[4] 1.0 mL of oleylamine and 2.0 mL of ODE were mixed in a 50 mL flask. The flask was then pumped down at room temperature for 20 min to remove the hexane and at 100 °C for 20 minutes to remove any residual air in the system while flushing the reaction system twice with flow of high purity nitrogen. After that, the mixture was heated to 230 °C under high purity nitrogen flow to perform CdS shell growth. The Cd precursor stock solution was first injected into the reaction system, 10 minutes later, after the Cd precursor had been fully deposited on the CdSe surface, an equimolar amount of S precursor stock solution was injected into the mixture. After 10 minutes, when the first layer of CdS had deposited on the CdSe surface, another Cd/S precursor solution was added alternately. The amount of the precursor stock solution which was added in each cycle was calculated for the need of a whole monolayer of CdS shell and was calculated from the respective volumes of concentric spherical shells with a hypothetical signal layer (e.g. 0.65, 0.95, 1.27 mL was respectively added for the first, second, and third layer.) To realize the growth of ZnS shell, the reaction temperature was first cooled down to 200 °C, subsequently the Zn/S precursor stock solution was injected into the reaction system at intervals of 20 minutes. After the coverage of ZnS was completed, the reaction mixture was kept for 30 minutes at 260 °C and finally cooled down to room temperature. To monitor the reaction, aliquots were taken before a new cycle of injection and their corresponding UV-vis and PL spectra were recorded. For purification, hexane was added into the mixture, the unreacted compounds and byproducts were removed by successive methanol extraction for three times. Then acetone was added, and the quantum dots were separated from the mixture by centrifugation. At last, the obtained CdSe/CdS/ZnS quantum dots were redispersed in hexane for further use.

Reference

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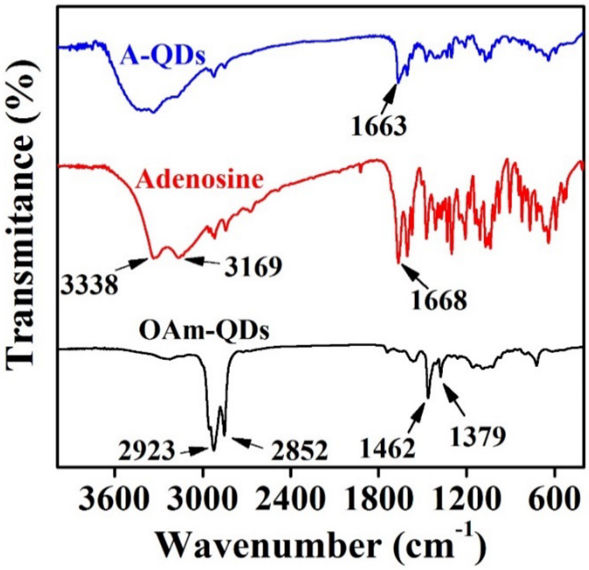

Fig. S1 FT-IR spectra of initial oil-soluble OAm-QDs (black curve), adenosine (red curve), and A-QDs (blue curve).

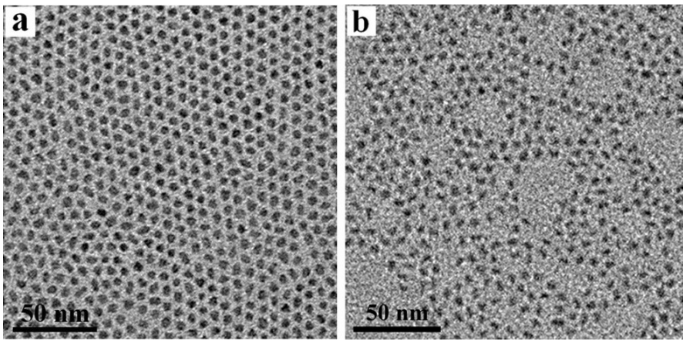

Fig. S2 TEM images of the initial oil-soluble OAm-QDs (a) and the obtained water-soluble A-QDs via ligand exchange (b)

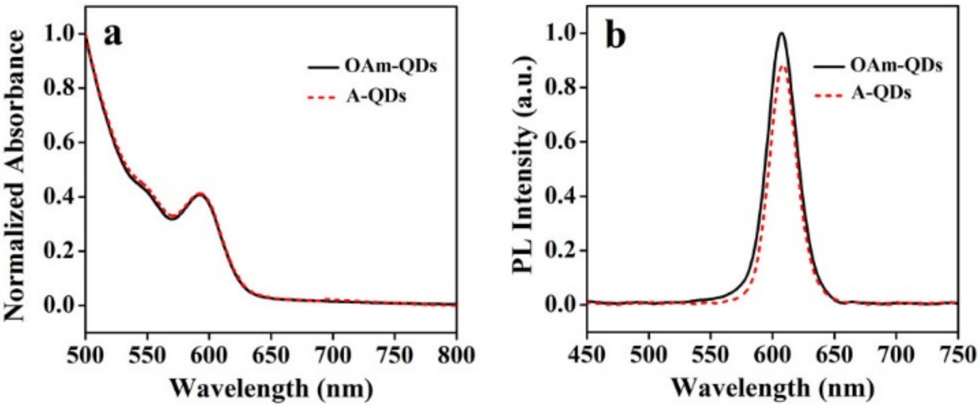

Fig. S3 UV-vis (a) and PL (b) spectra of initial oil-soluble OAm-QDs in hexane (black curves), and corresponding spectra of A-QDs in aqueous media (red dashes).

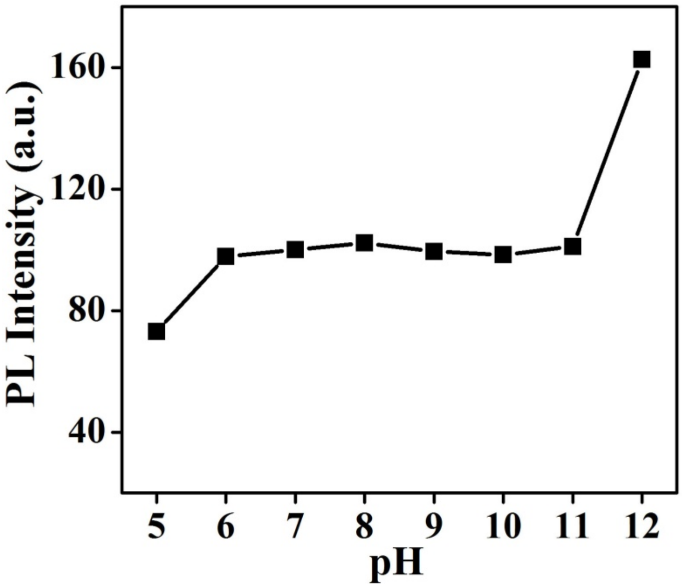

Fig. S4 Temporal evolution of the relative PL intensities of A-QDs under different pH values.

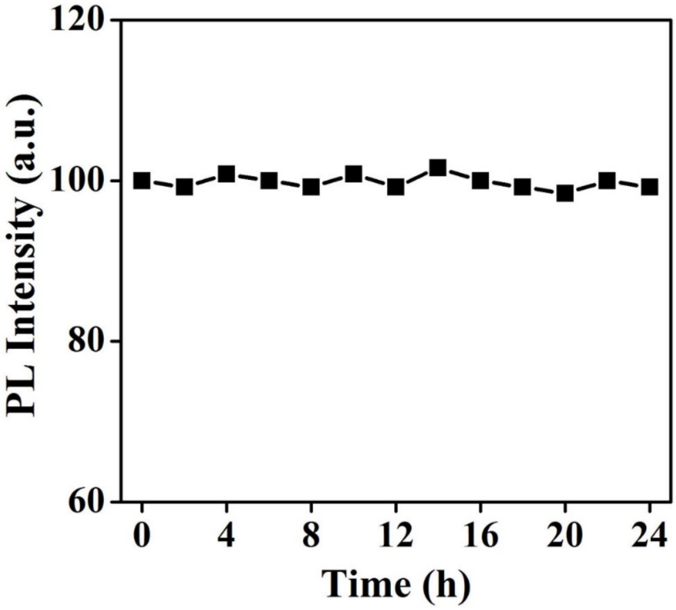

Fig. S5 Fluorescence stability of A-QDs against time in PBS solution (10 mM, pH 7.4).

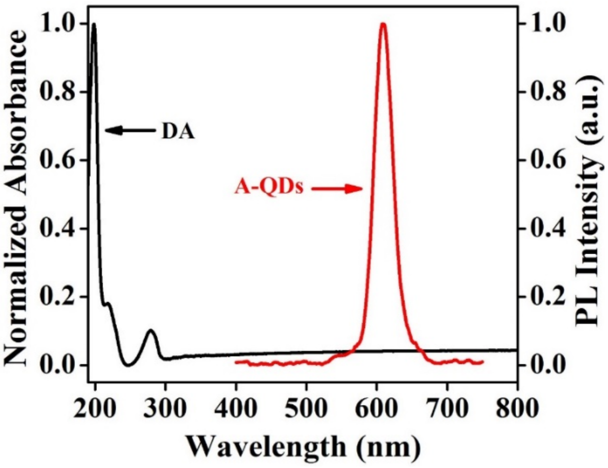

Fig. S6 Normalized UV-vis absorption spectra of DA (black curve), and normalized fluorescence emission spectra of A-QDs (red curve).

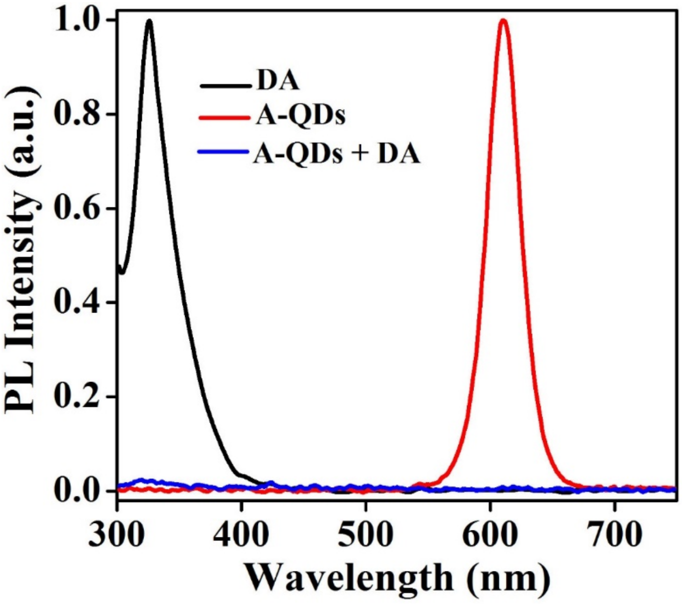

Fig. S7 Normalized fluorescence spectra of 20 μM DA (black curve), 40 nM A-QDs (red curve) and the mixture of A-QDs and DA (blue curve) in PBS buffer (10 mM, pH = 7.4).

Table S1 Fluorescence lifetime data for A-QDs in the absence and presence of DA.

Substrate	**a_1**	**τ_1 (ns)**	**a_2**	**τ_2 (ns)**	**χ^2**	**τ_{av} (ns)**
A-QDs	753.26	7.13	284.61	24.41	1.16	21.23
A-QDs + DA	2238.9	1.50	27.077	9.79	1.23	8.44

^{a}The PL decay was analyzed using the express $F(t)$ =A + $a_1$exp($-t/\tau_1$) + $a_2$exp($-t/\tau_2$). ^{b}The average lifetime values were calculated using the expression $\tau_{av} = \sum a_i\tau_i^2 / \sum a_i\tau_i$.