Supplementary Information

Controlled self-assembly of CdTe Quantum Dots into different microscale dendrite structures by using proteins as templates

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Experimental section

The ITC experiments were carried out by using a MicroCal VP-ITC calorimeter (Northampton, MA).

Results and Discussion

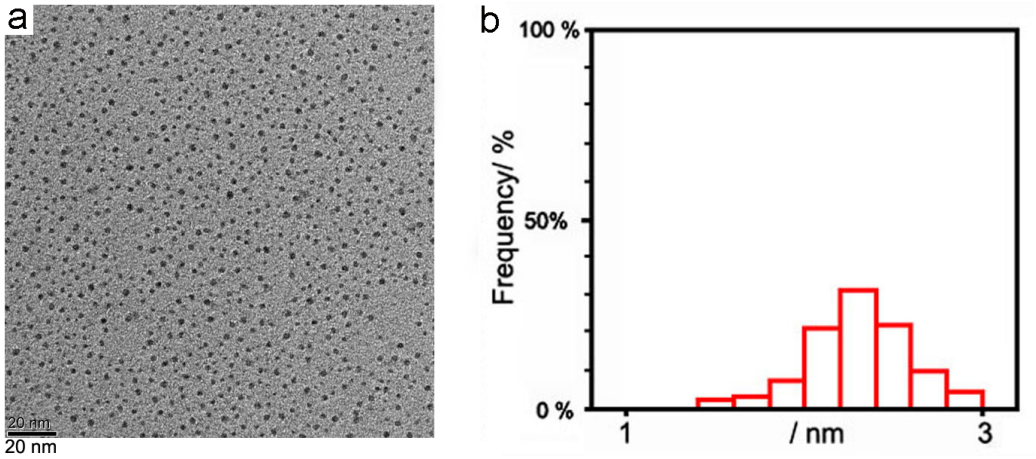

Fig. S1. a: TEM image of thioglycolic acid (TGA) capped CdTe QDs (scale bar: 20 nm); b: CdTe QDs particles size distribution histogram. It shows that the diameter of the CdTe QDs is approximately 2.3 nm and the dispersion of the CdTe QDs particles is excellent.

The interaction between CdTe QDs and proteins

In order to understand the interaction between CdTe QDs and proteins, isothermal titration calorimetry (ITC) is used to quantify the thermodynamics of CdTe QDs binding to proteins, where pepsin (pI: 1–2.5) and trypsin (pI: 10.5) are chosen as examples. Pepsin with the pI value lower than the pH of buffer (pH 7.4) is negatively charged, while trypsin with the pI higher than the pH of buffer has positive charges. The ITC profiles for the binding of CdTe QDs with proteins (pepsin and trypsin) and the thermodynamic parameters (K, ΔH and ΔS), which describe the binding affinity in the interaction between QDs and proteins [1], are shown in Fig. S2. It reveals that the ITC curve for CdTe QDs with pepsin (Fig. S2a) and that for CdTe QDs with trypsin (Fig. S2b) is similar to each other, indicating that the interactions of CdTe QDs with the two proteins are the same. As can be seen the thermodynamic parameters inserted

in Fig. S2a and b, it is observed that there are two binding sites for CdTe QDs with proteins; and the results demonstrate that $\Delta H_1<0$, $\Delta S_1<0$ and $\Delta H_2>0$, $\Delta S_2>0$. It was reported that the interactions of QDs and protein could be indicated through the thermodynamic parameters ΔH and ΔS [2]: when $\Delta H<0$ and $\Delta S<0$, the interaction is controlled by hydrogen bonding and van der Waals interactions; when $\Delta H>0$ and $\Delta S>0$, the interaction is manipulated by hydrophobic force; when the absolute value of $\Delta H\approx0$ and $\Delta S>0$, the interaction depends on electrostatic interactions. The results reveal that the interactions of CdTe QDs with proteins are mainly controlled by hydrophobic force, hydrogen bonding and van der Waals interactions.

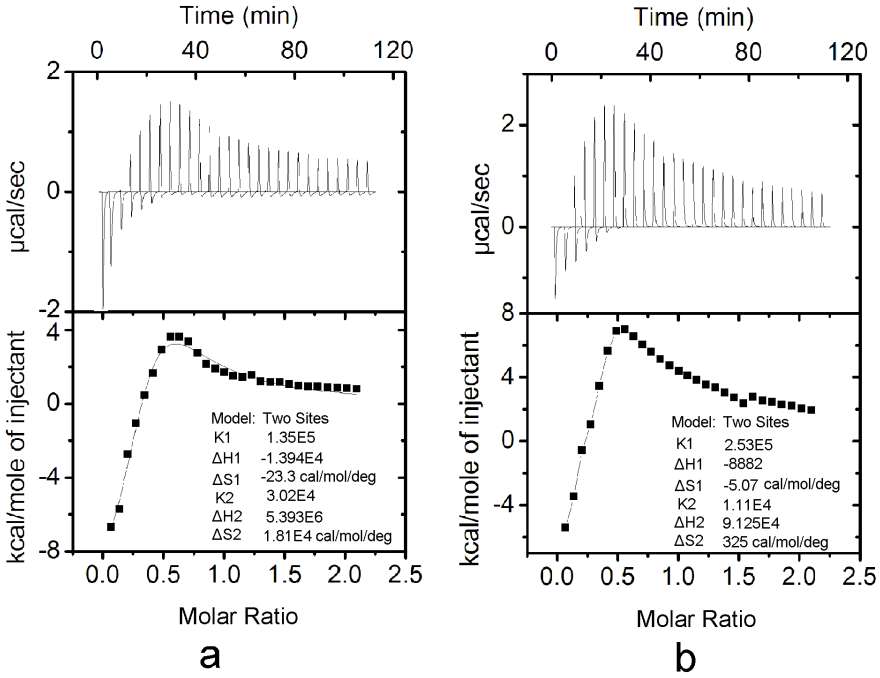

Fig. S2. Isothermal titration calorimetry (ITC) profiles for the binding of CdTe QDs with (a) pepsin and (b) trypsin.

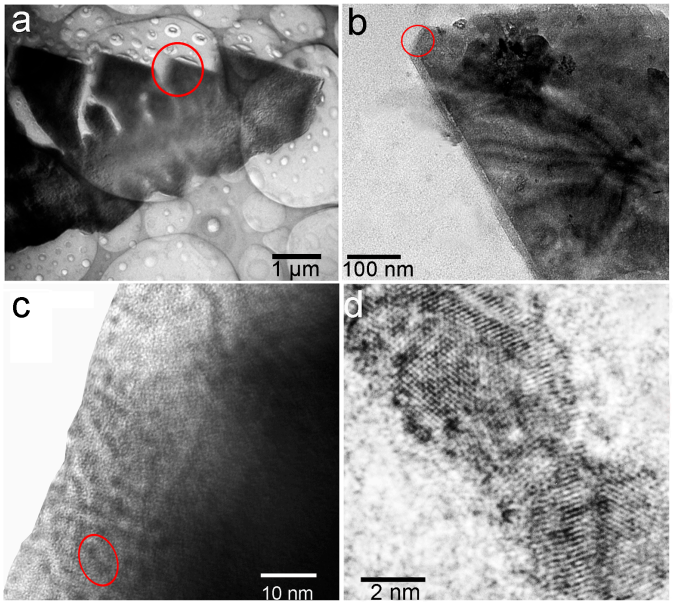

Fig. S3. (a-c) TEM images of CdTe dendrites with different magnifications; (d) HRTEM image of two fused CdTe QDs recorded from a tip of the CdTe dendrites circled in c. The CdTe dendrites are formed by using collagen type I as templates.

TEM images of typical CdTe dendrites formed by protein templating (using collagen type I as an example) are shown in Fig. S3a-c. As can be seen in Fig. S3a, it is observed that nanosheets paralleling to each other are aligned on the stem orderly, and the angles between the nanosheets and stem are mostly about 90°. Fig. S3c shows the TEM image taken from a tip of a CdTe dendrite (marked by a circle in Fig. S3b), demonstrating that the dendrites are composed by lots of aggregates of CdTe QDs. The HRTEM image of the aggregates is shown in Fig. S3d, which shows the lattice fringes and a robust connection of two fused CdTe QDs along the same crystal orientation, indicating that the dendrites are formed from the self-assembly of CdTe QDs.

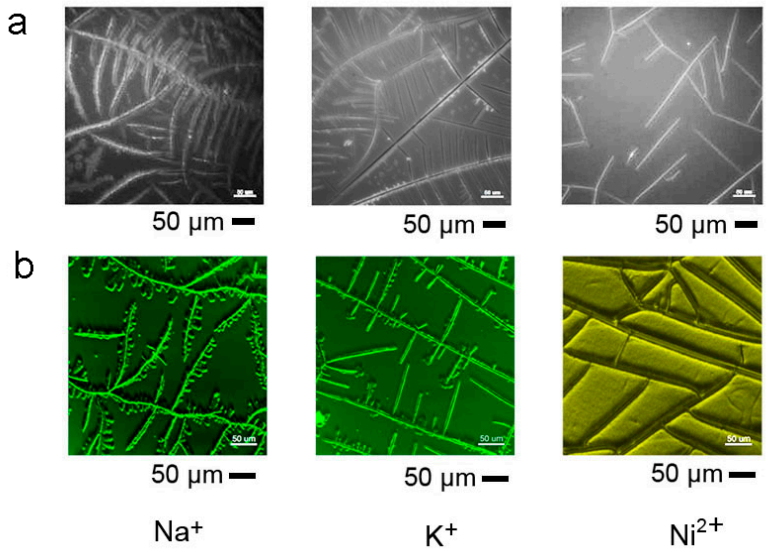

Fig. S4. a: Microscopy images of the patterns formed by HSA, which is dissolved in different metal salts solutions. b: Fluorescent microscopy images of CdTe dendrites by HSA templating, the HSA is dissolved in different metal salts solutions. The concentration of CdTe QDs is 1.2 mM and that of HSA is 22.5 mg/mL.

The influence of different parameters on the structure of CdTe dendrites

a. Effect of protein concentration

The effect of protein concentration on the structure of CdTe dendrites is investigated. Here mucins from pig stomach, collagen type I and HSA are selected as examples. In the experiment, the concentration of the proteins varies from 24 mg/mL to 3 mg/mL while keeping the evaporation condition, CdTe QDs concentration, buffer concentration and pH values constant. As can be seen in Fig. S5, it is observed that the morphologies of CdTe dendrites templated by the three proteins are apparently different. However, when using the same protein as scaffolds, no significant change of the structure of CdTe dendrites is observed with the variation of protein concentration. For CdTe dendrites templated by mucins from pig stomach (Fig. S5Aa-Ad), although the structures formed under lower concentrations are less dense and more intricate than those formed under higher concentrations, the structures are similar to each other. The results demonstrate that in a certain protein concentration range, the CdTe QDs

can self-assemble into a specific structure under specific conditions. Therefore, it is reasonable to achieve CdTe dendrites with desired structures upon the control of the protein concentration.

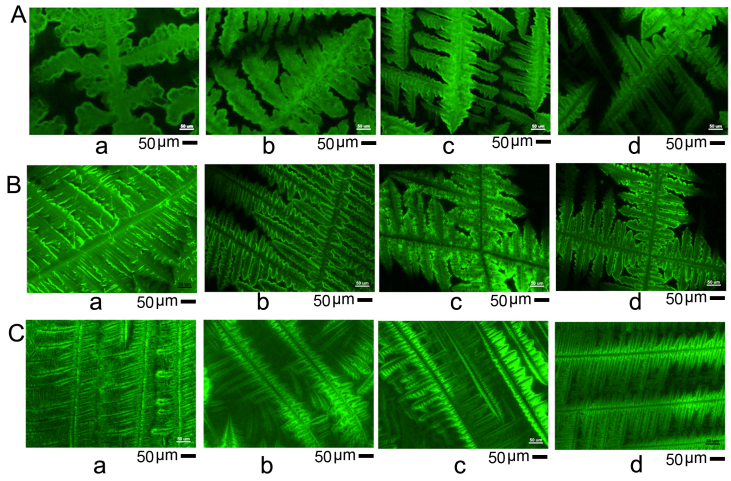

Fig. S5. Fluorescent microscopy images of CdTe dendrites templated by three kinds of proteins (A: mucins from pig stomach; B: collagen type I and C: HSA) at different protein concentrations: a: 24 mg/mL; b: 12 mg/mL; c: 6 mg/mL and d: 3 mg/mL. The concentration of CdTe QDs is fixed at 1.2 mM and the buffer is PBS (0.01 M, pH= 7.4).

b. Effect of CdTe QDs concentration

The influence of the concentration of CdTe QDs on the structure of CdTe dendrites is researched here, where HSA is used as an example. The concentration of CdTe QDs is decreased from 1.2 mM to 0.06 mM, while keeping the other conditions constant such as evaporation condition, pH values, concentration of PBS buffer and that of HSA (9 mg/mL). The results are shown in Fig. S6, which exhibit that as the increase of the CdTe QDs concentration, the architectures of the CdTe dendrites are similar to each other even though with subtle differences. Besides, it can also be noted that with the increase of the concentration of CdTe QDs, the photoluminescence (PL) of the CdTe dendrites gets stronger. This phenomenon ascribes to the increase of the

amounts of CdTe QDs connected with HSA. Thus it is hypothesized that the amount of HSA is excessive in comparison with that of CdTe QDs, which results in the similarity of the formed CdTe dendrites.

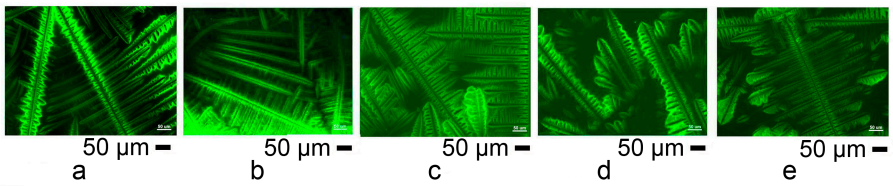

Fig. S6. Fluorescent microscopy images of CdTe dendrites formed by HSA as a template at different CdTe QDs concentrations (a: 1.2 mM; b: 0.6 mM; c: 0.24 mM; d: 0.12 mM; e: 0.06 mM), while the concentration of HSA is fixed at 9 mg/mL, all the samples are prepared in PBS buffer (0.01 M, pH=7.4).

c: Influence of volume ratio of CdTe QDs to HSA on the formation of CdTe dendrites

To investigate the influence of the volume ratio of CdTe QDs to HSA on the formation of CdTe dendrites, a series of solutions of CdTe QDs (initial concentration is 1.2 mM) mixed with HSA (initial concentration is 24 mg/mL) at different volume ratios (1:4, 1:2, 1:1, 2:1, 3:1) is prepared. The solution is dropped on clean glass slides and the droplets are evaporated at room temperature under ambient conditions. The morphologies of the formed CdTe dendrites are characterized by a fluorescence microscopy.

Fig. S7 shows the fluorescence microscopy images of CdTe dendrites formed with (Fig. S7A1, B1) and without (Fig. S7A2, B2) HSA as a template. It can be seen that when the volume ratio of CdTe QDs to HSA is under 1:1, the CdTe dendrites take on the shape more like the one of HSA (as can be seen in Fig. 1), *i.e.* leaf-like or plumose shape. When the volume ratio of CdTe QDs to HSA is 1:1, the structure of CdTe dendrites is still leaf-like or plumose, similar to the ones formed below the ratio 1:1 but more rough. When the volume ratio of CdTe QDs to HSA is beyond 1:1, the CdTe

dendrites are snow shaped and more straight. Through comparing the dendrites formed with and without HSA as templates, it reveals that as the increase of the volume ratio of CdTe QDs to HSA, the structure of CdTe dendrites templated by HSA is more and more like the ones formed by pure CdTe QDs. It has been reported that if more than one dendrite morphology is possible, only the fastest one is nonlinearly stable and can be observable [3]. Hence, it is hypothesized that only when the amount of CdTe QDs is insufficient to that of HSA, CdTe QDs can grow into the dendrites with the same shape to that of HSA.

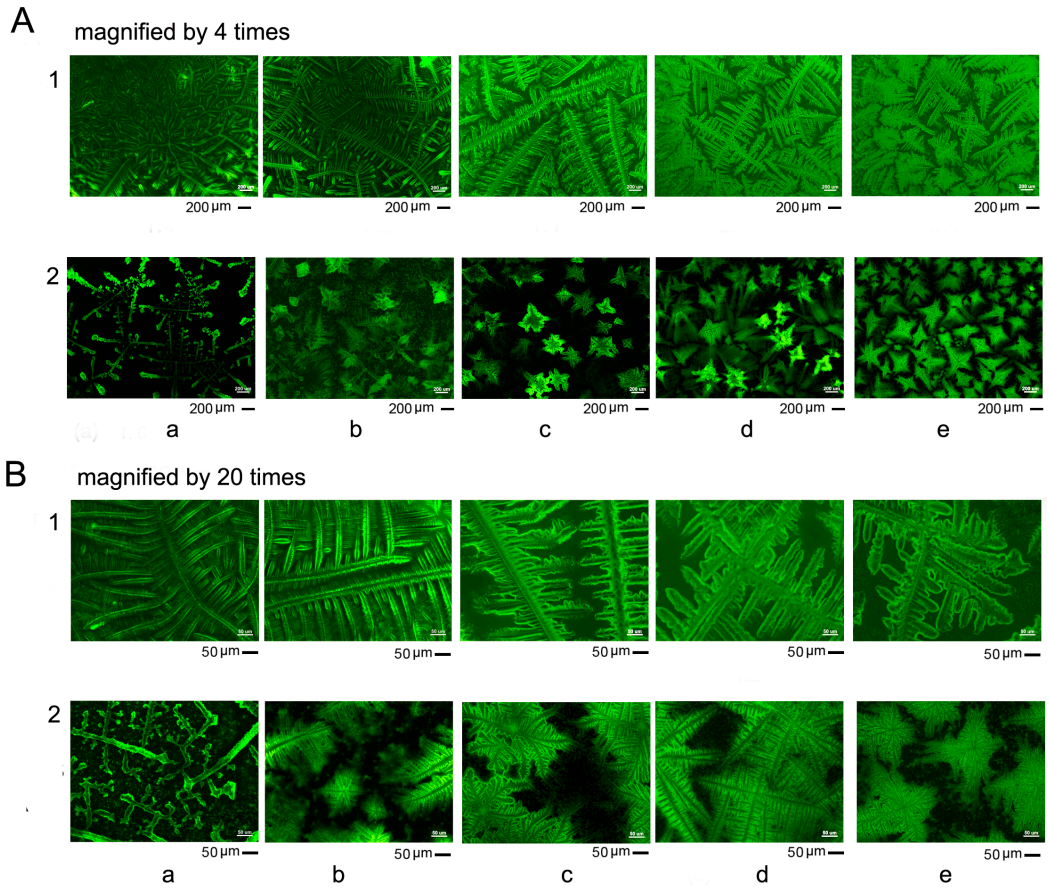

Fig. S7. Fluorescent microscopy images of CdTe dendrites magnified by different times (A: 4 times; B: 20 times). Fig. S7A1 and S7B1 show the images of CdTe dendrites formed by HSA as a template at different volume ratios of CdTe QDs to HSA, from a to e: 1:4, 1:2, 1:1, 2:1 and 3:1. Fig. S7A2 and S7B2 are the images of CdTe dendrites without the addition of HSA; the CdTe QDs are prepared at the same concentrations with those using HSA as a template. The initial concentration of CdTe QDs is 1.2 mM and that of HSA is 24 mg/mL. All the samples are dissolved in PBS

buffer (0.01 M, pH=7.4).

Reference

[1] B. J. Yang, R. T. Liu, X. P. Hao, Y. Z. Wu and J. Du, Effect of CdTe Quantum Dots Size on the Conformational Changes of Human Serum Albumin: Results of Spectroscopy and Isothermal Titration Calorimetry. *Biol. Trace Elem. Res.,* 2013, **155**, 150.

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