Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Cyclic Arginyl-Glycyl-Aspartic Acid (RGD) Peptide-Induced Synthesis of Uniform and Stable One-Dimensional CdTe Nanostructures in Aqueous Solution

Hua He, [a] *Xing Sun,*[a] *Xiaojuan Wang,* [a] *Yawei, Sun,*[a] *Hai Xu**[a] *and Jian R. Lu**[b]

[a] Centre for Bioengineering and Biotechnology, China University of Petroleum (East China), 66 Changjiang West Road, Qingdao Economic Development Zone, Qingdao, 266555 (China), [b] Biological Physics Laboratory, School of Physics and Astronomy, University of Manchester, Schuster Building, Manchester M13 9PL, United Kingdom.

1. Experimental Section

1.1. Materials

Tellurium powder (99.997%), $CdCl_2$ (99.99+%), and $NaBH_4$ (≥ 96%) were purchased from Aldrich. Cyclo(RGDfC), cylco(GGDfC), cylco(KGDfC), cylco(EGDfC) and acetyl-RGDfC-amide were purchased from GL Biochem Ltd. (Shanghai, China) with purities of > 95 %. All chemicals were used without additional purification. All solutions were prepared with ultra-pure water (18.2 MΩ·cm) purified on Millipore System (Millipore, USA).

1.2. Synthesis and characterization of 1D CdTe nanocrystals

NaHTe solution was freshly prepared by dissolving 0.05 g $NaBH_4$ in 3 ml water and then 0.04 g Te powder was added into the $NaBH_4$ solution. This reaction was conducted at room temperature overnight in a syringe with a needle to help release the gas generated during the reaction, and the resulting NaHTe solution was then diluted by injecting into 122 ml ultrapure water prior to use. Cd^{2+}-CRGDS precursor solution was prepared by dissolving $CdCl_2$ and a given RGD peptide in ultrapure water, and then adjusted to pH 8.5 with 1 M NaOH. The NaHTe solution was then injected into a N_2-saturated precursor solution under vigorous stirring. The typical molar ratio of Cd^{2+}, HTe^- and peptide introduced was 2 : 1 : 5 in a total volume of 12 ml with 1 mM peptide. The resulting mixture was heated to 98 °C and refluxed at different times to control the growth of the CdTe nanocrystals. Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer performed at room temperature under ambient conditions. Fourier transform infrared (FTIR) spectra were obtained using Nicolet 6700 FTIR (Nicolet Instrument Company, USA) between 500 and 4000 cm^{-1}. TEM samples were prepared by dropping the aqueous nanocrystals onto carbon-coated copper grids with excess solvent evaporated. TEM and HRTEM images and SAED were recorded on a JEM-2100 electron microscope operating at 200 kV.

2. Figures S1-S6

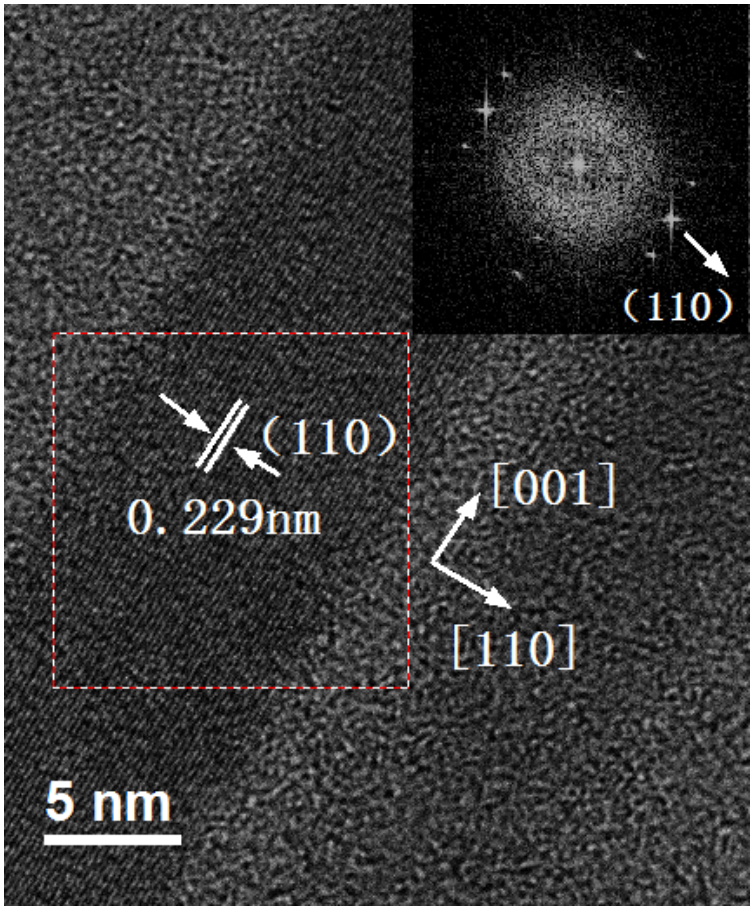

Fig. S1 HRTEM image taken from part of an individual 1D CdTe formed from a precursor solution with 0.4 mM Cd^{2+} and Cd:Te:cylco(RGDfC) = 2:1:5 after 1 h of heating. The inset shows the FFT pattern of the indicated square area. Note that the [110] orientation of the (110) plane is perpendicular with respect to the [001] direction.

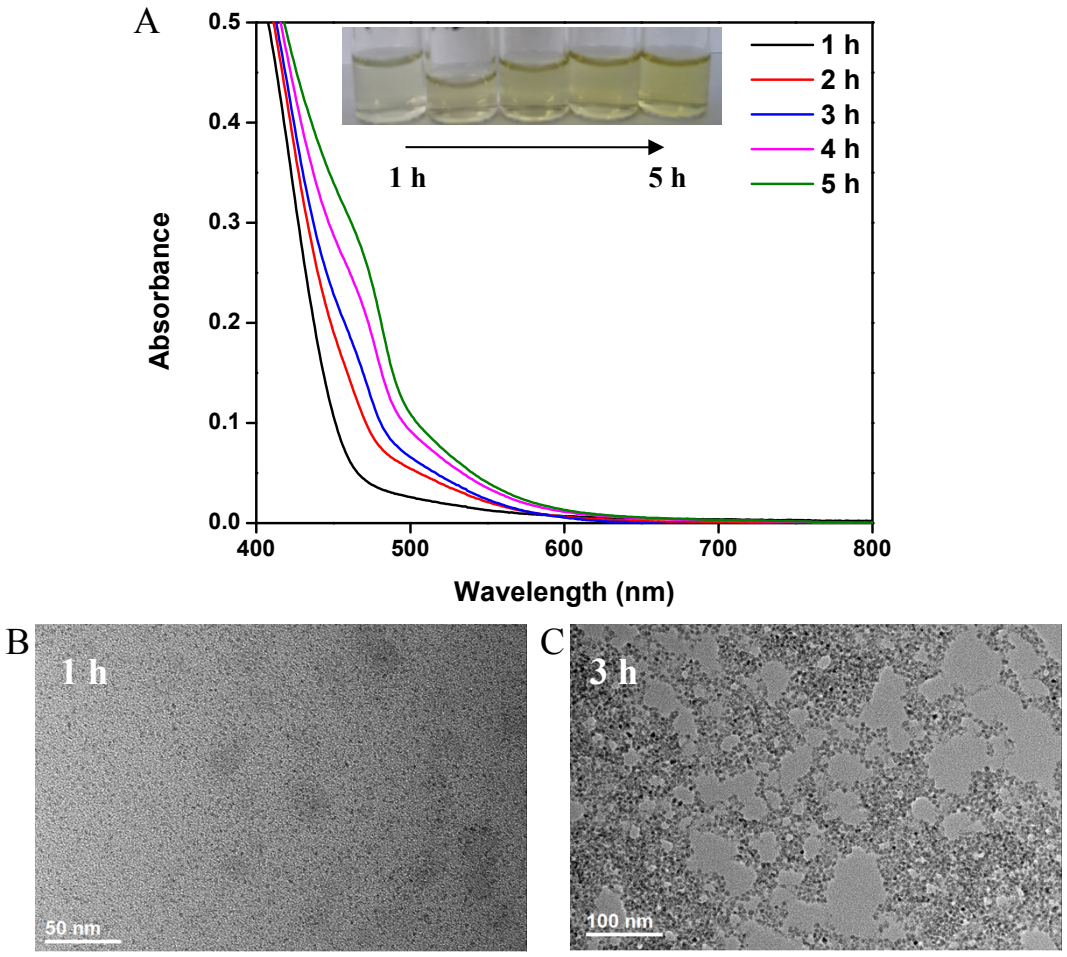

Fig. S2 (A) Absorption spectra and optical photographs (the inset) of the crude CdTe solutions prepared with the precursor Cd/Te ratio of 4/0.5 (Cd^{2+} = 0.4 mM, cyclo(RGDfC)/Cd^{2+} = 2.5/1) after different periods of heating. (B and C) TEM images of spherical CdTe nanostructures formed after 1 and 3 h of heating, respectively.

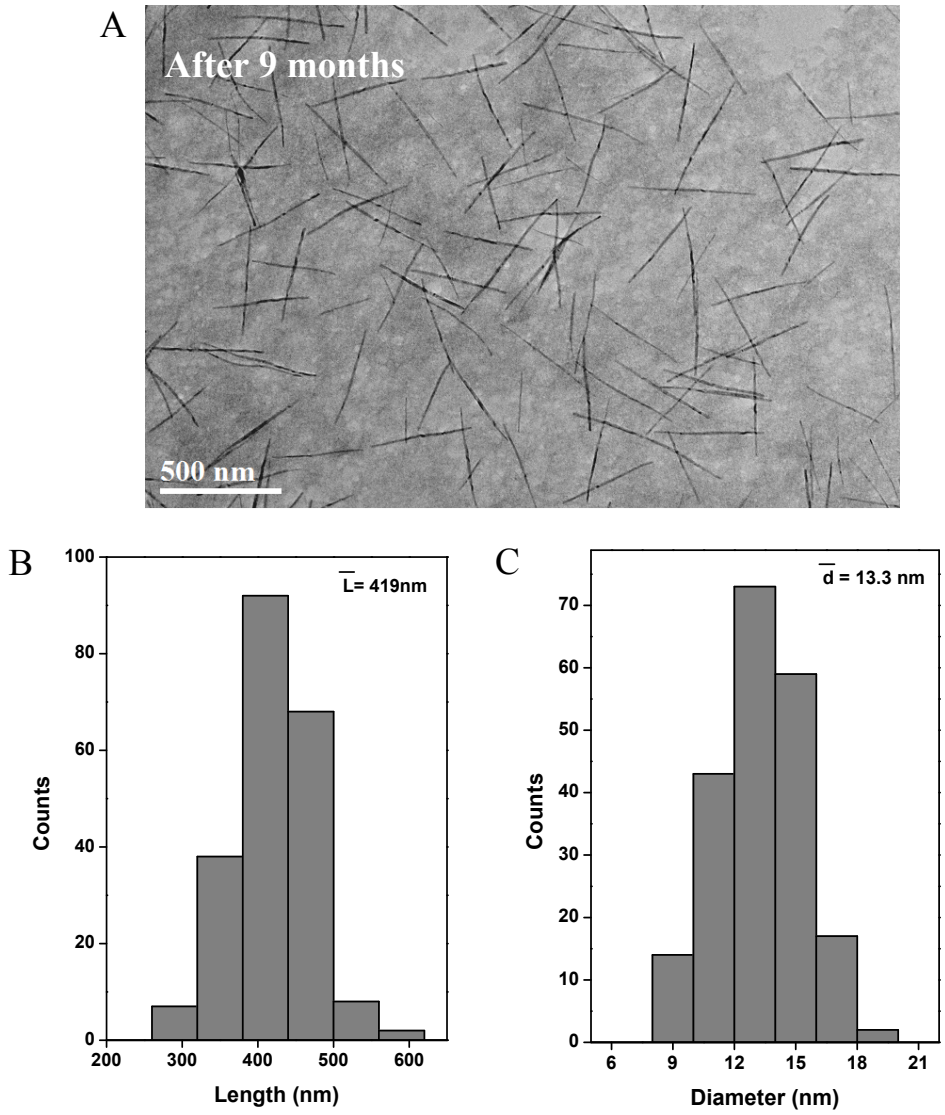

Fig. S3 (A) Representative TEM image of 1D CdTe nanocrystals after 9 months of storage at 4 °C. The nanocrystal solution was prepared with the precursor Cd/Te ratio of 2/1 (Cd^{2+} = 0.4 mM, cyclo(RGDfC)/Cd^{2+} = 2.5/1) and 1 h of heating. (B) Length and (C) diameter distribution histograms of 1D CdTe nanocrystals, which were derived from TEM imaging.

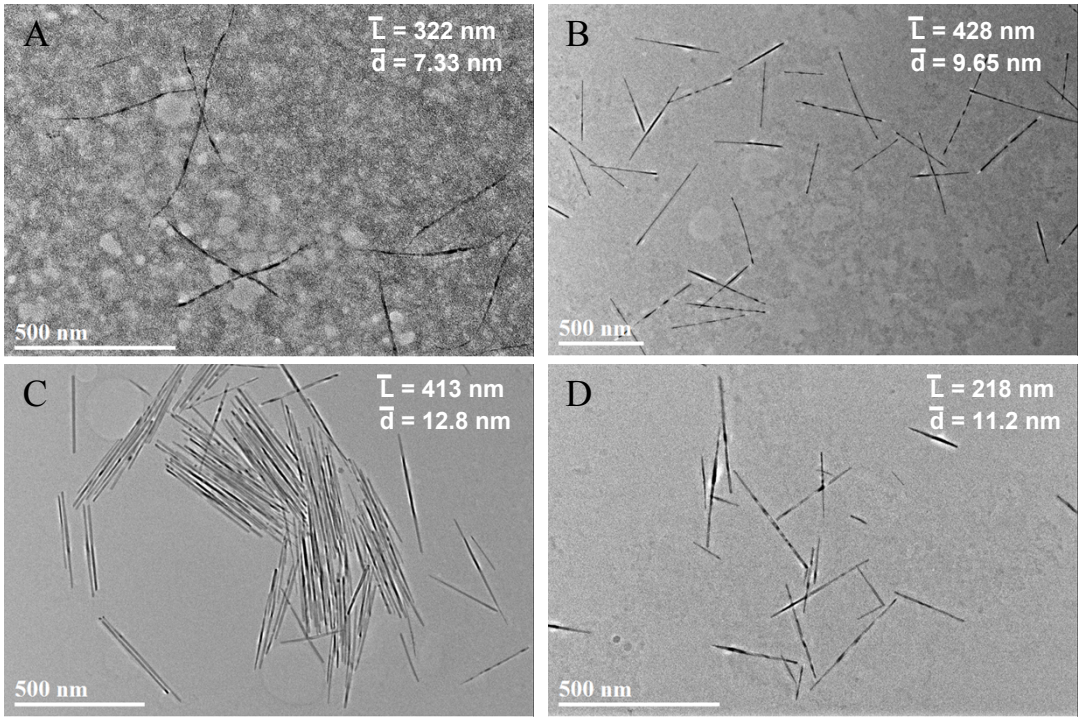

Fig. S4 TEM images of CdTe nanostructures prepared with the precursor Cd/Te ratios of (A) 4/0.75, (B) 4/1, (C) 4/2, and (D) 4/4 (Cd^{2+} = 0.4 mM, cyclo(RGDfC)/Cd^{2+} = 2.5/1) after 1 h of heating.

Fig. S5 Optical photographs of Cd-acetyl-RGDfC-amide, Cd-cyclo(KGDfC), Cd-cyclo(GGDfC) Cd-cyclo(EGDfC) and Cd-cyclo(RGDfC) precursor solutions at pH 8.5.

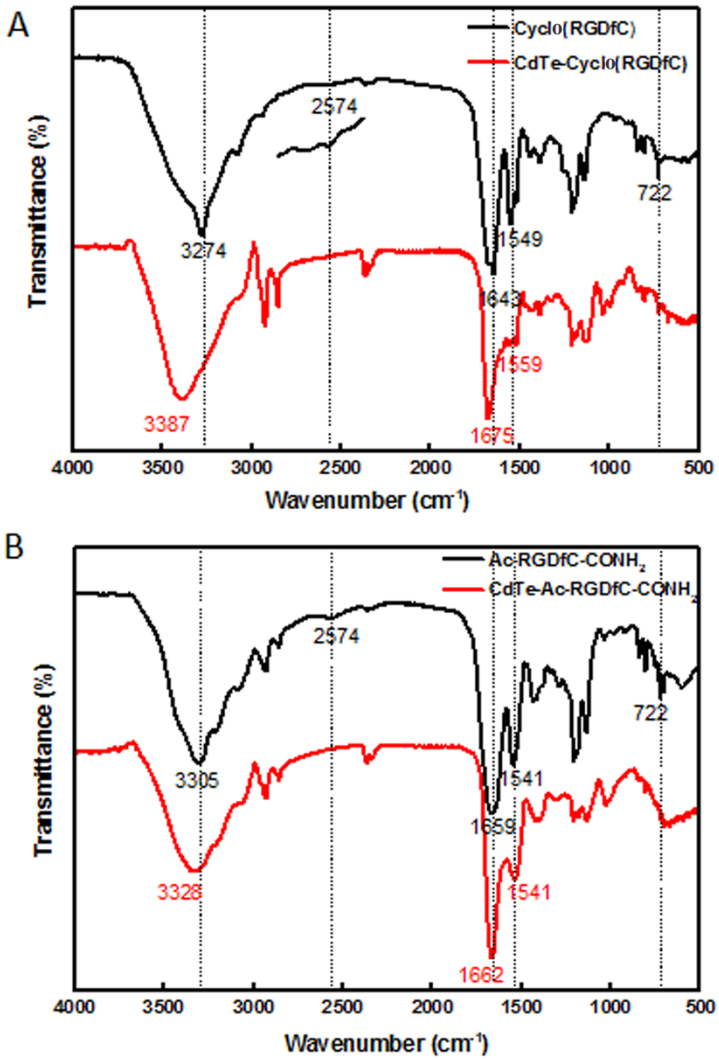

Fig. S6 FTIR spectra of (A) cyclo(RGDfC) and cyclo(RGDfC)-derived 1D CdTe nanostructures; (B) acetyl-RGDfC-amide and acetyl-RGDfC-amide-derived CdTe nanostructures. The weak bands at 2574 cm^{-1} and at 722 cm^{-1} corresponded to the thiol (-SH) in the cyclo(RGDfC) and acetyl-RGDfC-amide spectrum disappeared in peptide-derived CdTe nanostructures, suggesting the formation of thiolate (-S-CdTe).[1,2] However, , -N-H stretching (~3274 cm-1), amide I (~1643 cm-1, C=O stretching) and amide II (~1549 cm-1, N-H bending) regions in CdTe-cyclo(RGDfC) spectrum were shifted to higher energy with respect to the free cyclo(RGDfC) peptide, while these characteristic bands in CdTe- acetyl-RGDfC-amide spectrum exhibit a little or no shifts with respect to the free acetyl-RGDfC-amide. These results showed that the guanidine and amide besides the thiol in cyclo(RGDfC) were involved in the formation and stabilization of 1D CdTe nanostructures.[2-4]

Reference:

1. Krishnakumar, V.; Xavier, R. J., FT Raman and FT-IR spectral studies of 3-mercapto-1,2,4-triazole. *Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy* **2004,** *60* (3), 709-14.
2. Morales-Avila, E.; Ferro-Flores, G.; Ocampo-Garcia, B. E.; De Leon-Rodriguez, L. M.; Santos-Cuevas, C. L.; Garcia-Becerra, R.; Medina, L. A.; Gomez-Olivan, L., Multimeric system of 99mTc-labeled gold nanoparticles conjugated to c[RGDfK(C)] for molecular imaging of tumor alpha(v)beta(3) expression. *Bioconjugate chemistry* **2011,** *22* (5), 913-22.
3. Yang, H.; Zhuang, Y.; Sun, Y.; Dai, A.; Shi, X.; Wu, D.; Li, F.; Hu, H.; Yang, S., Targeted dual-contrast T1- and T2-weighted magnetic resonance imaging of tumors using multifunctional gadolinium-labeled superparamagnetic iron oxide nanoparticles. *Biomaterials* **2011,** *32* (20), 4584-93.
4. Choi, J.; Yang, J.; Park, J.; Kim, E.; Suh, J.-S.; Huh, Y.-M.; Haam, S., Specific Near-IR Absorption Imaging of Glioblastomas Using Integrin-Targeting Gold Nanorods. *Advanced Functional Materials* **2011,** *21* (6), 1082-1088.