Supporting information

Rapidly Detecting of Antibiotics via Magnetic Nanoparticle Coated CdTe Quantum Dots

Chaoxi Chen,[a] Yuhan Li, [a] Yunlu Zhou,[a] Junhao Zhang,[a] Qizhuang Wei,[a] Tao Dai*[b] and Lu Wang*[a]

a College of Life Science&Technology, Southwest Minzu University. Chengdu 610041

E-mail: luwangbest@163.com. chaoxi8832@163.com

b College of Chemistry&Environmental Protection Engineering, Southwest Minzu University. Chengdu 610041 E-mail: tdaicat@163.com

Materials

Cadmium chloride ($CdCl_2$, anhydrous), tellurium (Te), sodium borohydride($NaBH_4$) and tetraethoxysilane(TEOS) and 3-aminopropyltriethoxysilane (APTES) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Enrofloxacin, Sarafloxacin, Chloramphenicol and Ciprofloxacin were purchased from J&K Chemical Technology. Ferric chloride hexahydrate($FeCl_3 \cdot 6H_2O$) and Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were purchased from Kelong chemical co., LTD. Other reagents and solvents were of analytical grade and were used directly without further purification.

1. Instruments and Measurements

The transmission electron microscopy (TEM) was measured by Jeol JEM-100CX at an accelerating voltage of 80 KV.Fluorescence spectra experiment was detected with Varioskan LUX (Thermo, USA).The thermogravimetric analysis (TGA) was characterized by Thermal Analyzer EXSTAR 6000 (Seiko Instruments Inc, Japan).The bonding properties of sample pellets were recorded on a fourier transform infrared spectroscopy(FTIR).

3. Experimental section

3.1 Preparation of CdTe quantum dot (CdTe QD).

CdTe QD was synthesized according to Li's work[1]. Tellurium(40 mg, 0.3 mmol) and $NaBH_4$ (115 mg, 3.0 mmol) were stirred in water under argonatmosphere for 6 h in ice bath. Thus, colorless NaHTe solution was obtained. Then, mercaptopropionic acid (MPA, 52 μL,0.6 mmol) was added in $CdCl_2$ solution (110 mg, 0.6 mmol in 200 mL UP water)quickly. The pH was adjusted to 8 by adding NaOH solution (1 mol L^{-1}). Finally, NaHTe (2.0 mL) was added to the

second solution and refluxed for another one hour to obtain CdTe QD.

3.2 Preparation of magnetic nanoparticles(MNPs).

Fe_3O_4 MNPs were prepared based on a traditional coprecipitation methods.[2-5] $FeCl_3 \cdot 6H_2O$ (5.835 g, 0.0216 mol) and $FeSO_4 \cdot 7H_2O$ (3.001 g, 0.0108 mol) were dissolved in deoxygenated water (100 mL) at 85 ^oC under a flow of nitrogen gas. Then, ammonium hydroxide (7.5 mL) was quickly injected into the reaction mixture in one portion. The color of solution turned into black immediately. The formed black precipitates were Fe_3O_4 MNPs. After the mixture cooled to room temperature, the magnetic precipitates were washed with pure water and the MNPs were dried in a vacuum desiccator for 24 h at 30^oC

3.3 Preparation of porous silicon dioxide coated magnetic nanoparticles (MNP-SiO_2)

The method was according to the reported literature.[6] The MNPs powder (300 mg) was dispersed in ethanol (90 mL) and water (1 mL) by sonication. 3-aminopropyltriethoxysilane (APTES, 120 uL) was added into the mixture solution. After mechanical agitation for 7 h at 60^oC, the suspended substance was separated under magnetic field and the solution was poured out. The precipitated product (MNP-SiO_2) was dried at RT under vacuum.

3.4 Preparation of quantum dot magnetic nanoparticles complex(MNP-SiO_2-QD)[7]

The MNP-SiO_2 was mixed with QD solution (10mg/mL) under room temperature. And cetyltrimethyl ammonium bromide (CTAB, 0.3 g, 0.823 mmol) and tetraethoxysilane (TEOS, 120 uL) were added to the mixture. After mechanical agitation for 24 h, the suspended substance was washed with acetone by sonication to remove CTAB. Then, the final product was washed by water for three times and removed from solution under magnetic field (1T).

3.5 Detection of Analytes

MNP-SiO_2-QD fluorescence spectroscopy (λ_{ex}= 380 nm) were obtained before detecting analytes. According to the fluorescence spectroscopy, the median fluorescence intensity around the maximum emission wavelength (MFI, $\lambda_{em} \pm$ 5 nm) was used as the quantitative standard. In the case of detecting antibiotic, 5 μL of antibiotic solution (Enrofloxacin, Sarafloxacin, Chloramphenicol and Ciprofloxacin) was added to the MNP-SiO_2-QDsolution. After 5 min, the median fluorescence intensity(MFI) was evaluated to calculate the concentration of the sample. For recycling test, the MNP-SiO_2-QD was washed by water for 3 times. Finally, the products dried at room temperature to obtain MNP-SiO_2-QD for the next cycle of detection.

4. Results

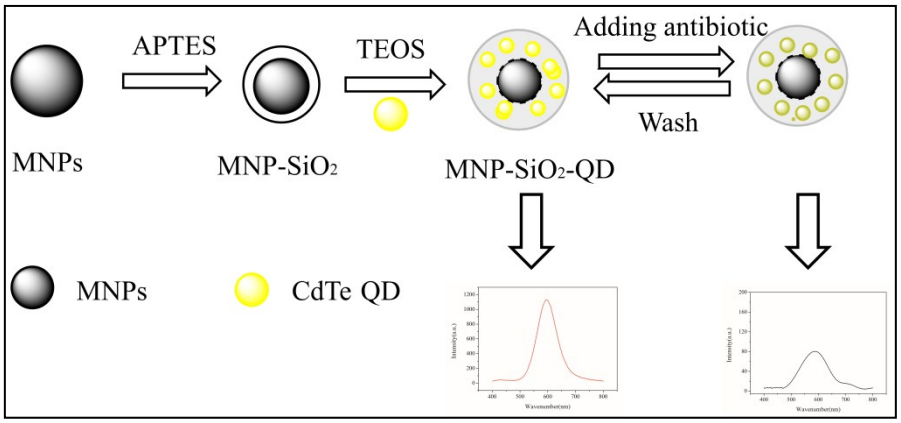

Figure S1. The schematic diagram for preparation of MNP-SiO_2-QD nanoparticles

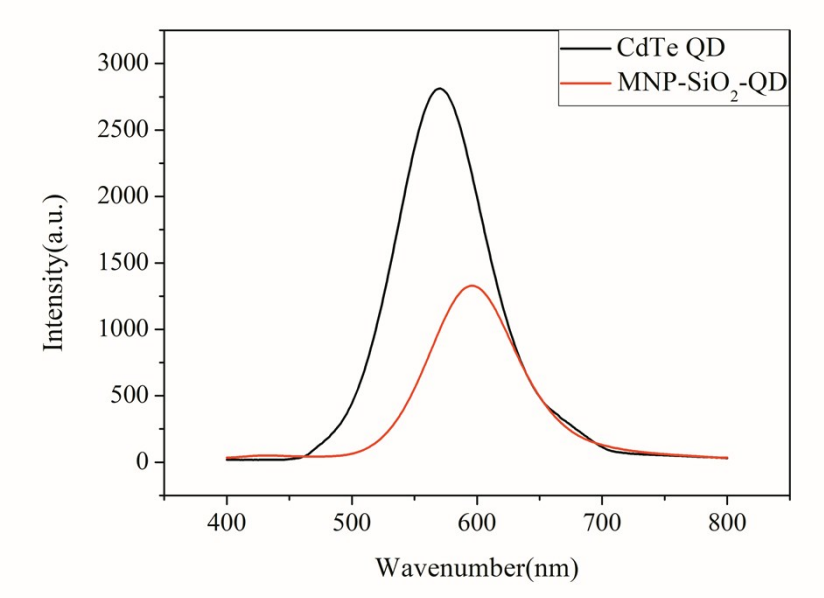

Figure S2 The fluorescent spectra of MNP-SiO_2-QD and CdTe QD. (The fluorescence intensity of CdTe QD was set as 100%. The fluorescence retention rate of MNP-SiO_2-QD was calculated according to the following formula.

Fluorescence retention rate=The fluorescence intensity of MNP-SiO_2-QD/ The fluorescence intensity of CdTe QD)

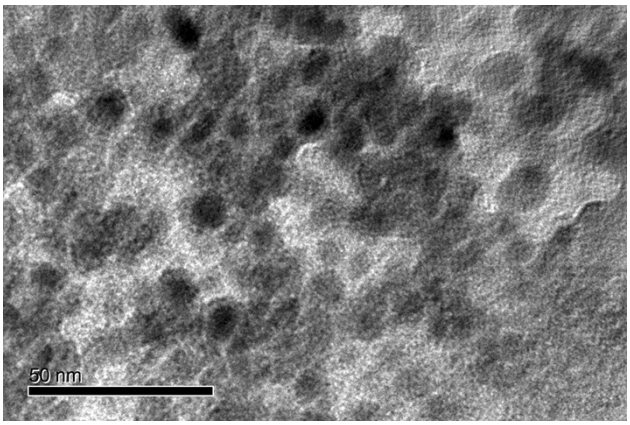

Figure S3 The TEM image of CdTe QD.

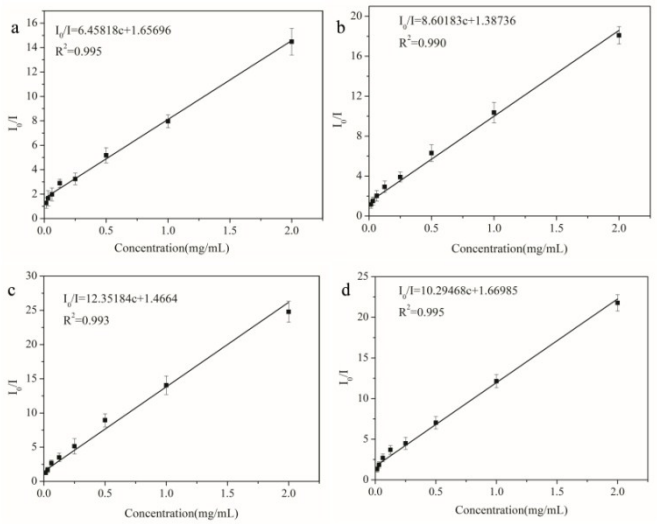

Figure S4. The standard curves between I_0/I and antibiotics. (a)enrofloxacin, (b) ceftiofur, (c) doxycycline and (d) chloramphenicol.

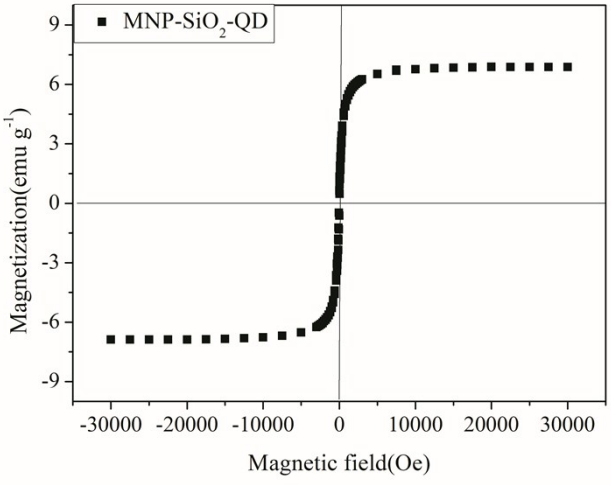

Figure S5. Magnetization curves of MNP-SiO_2-QD after first cycle used.

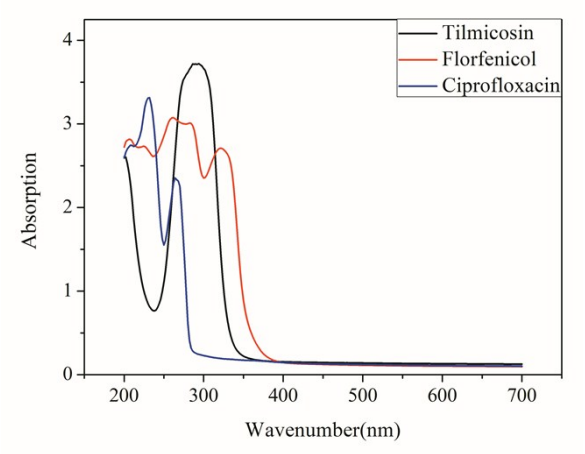

Figure S6. The UV-Vis absorption spectrum of antibiotics.

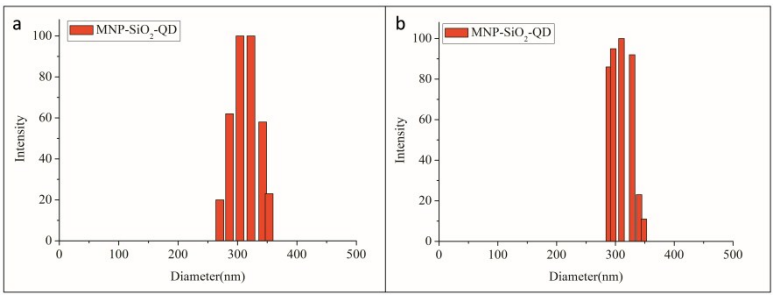

Figure S7. The DLS results of MNP-SiO_2-QD before(a) and after(b) adding antibiotics.

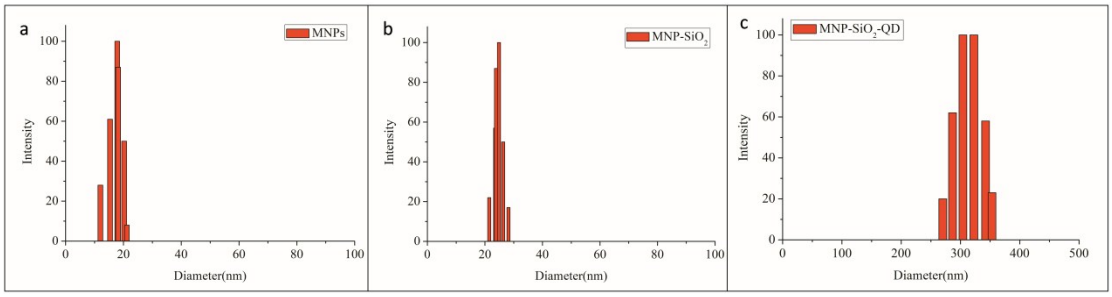

Figure S8. The DLS results of MNPs(a), MNP-SiO_2(b), MNP-SiO_2-QD(c)

Reference

1.X.-Y. Liang, L. Wang, Z.-Y. Chang, L.-S. Ding, B.-J. Li and S. Zhang, *Polymers*, 2018, **10**, 310.

2.A. Badruddoza, K. Hidajat and M. Uddin, *J. Colloid Interface Sci.*, 2010, **346**, 337-346.

3.H. Cao, J. He, L. Deng and X. Gao, *Applied Surface Science*, 2009, **255**, 7974-7980.

4.Y. Ding, S. Z. Shen, H. Sun, K. Sun, F. Liu, Y. Qi and J. Yan, *Materials Science and Engineering: C*, 2015, **48**, 487-498.

5.J. Huang, P. Su, J. Wu and Y. Yang, *RSC Advances*, 2014, **4**, 58514-58521.

6.A. Z. M. Badruddoza, L. Junwen, K. Hidajat and M. S. Uddin, *Colloids and Surfaces B: Biointerfaces*, 2012, **92**, 223-231.

7.Q. Ma, Y. Nakane, Y. Mori, M. Hasegawa, Y. Yoshioka, T. M. Watanabe, K. Gonda, N. Ohuchi and T. Jin, *Biomaterials*, 2012, **33**, 8486-8494.