Highly luminescent water-soluble CdTe nanowires as fluorescent probe to detect copper(II)†

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Highly luminescent water-soluble CdTe nanowires synthesized in one step were used to detect copper(II) selectively below 0.078 μM in the presence of other physiologically relevant cations.

Nanostructured semiconductor materials with unique optical properties have generated great research interest in the past two decades. In particular, they are very attractive as fluorescent probes because of their narrower spectral bandwidth and tunable emission wavelength in comparison with dyes.[1,2] One of the major challenges is to make them water-soluble with better stability. As an important semiconductor material, CdTe has been used in numerous applications, such as light-emitting devices,[3] photoelectrochemical cells,[4,5] photonic[6] and biological labels.[7–9] Water-soluble CdTe nanomaterials have been mainly obtained by two different ways. The first way is to replace the surface-capping molecules on nanomaterials prepared in organic solvents with water-soluble thiols.[10–13] The second way is to directly synthesize CdTe nanomaterials in aqueous solution using water–thiols as stabilizing agents.[6,8,14,15] However, these two methods have been mostly used to prepare only CdTe nanoparticles. Owing to the quite different quantum confinement energies, one-dimensional(1D) nanostructures present some novel optical properties different from zero-dimensional nanostructures.[16] Recently, biological assembly of nanocircuit prototypes from protein-modified CdTe nanowires[9] (NWs) attracted much attention. Nevertheless, exploration of 1D semiconductor materials as fluorescent probes for biological samples remains at a very early stage. This is partially due to the difficulties with the dispersion of these nanomaterials in water.[17]

Currently studied CdTe NWs were prepared by spontaneous assembly of nanoparticles by controlled partial removal of the protective stabilizer, and the whole growth process lasted several days.[18] In this study, highly luminescent water-soluble CdTe NWs were synthesized in one step based, with some modifications, on previous work[17] for the preparation of CdTe nanorods. Pure Ar instead of N_2 was used to de-aerate the reaction solution and magnetic stirring continued overnight after three hours of reflux. Under these conditions, a bright-orange CdTe NWs solution resulted, which demonstrated high selectivity and sensitivity toward copper(II) without further treatment in the presence of other physiologically relevant cations.

A transmission electron microscopy (TEM) image of the resulting CdTe NWs is shown in Fig. 1. Photoluminescence (PL) measurements were obtained at 20 ± 1 °C. TEM indicated that the diameters of the NWs were about 20 nm and the length could be up to 2 μm. Futher characterizations with selected-area electron diffraction (SAED), high-resolution electron microscopy (HRTEM), energy disperse spectroscopy (EDS), and X-ray diffraction (XRD) are given in the ESI.† As shown in Fig. 2, the maximum emission peak of the CdTe NWs solution appeared at 551 nm with a maximum excitation wavelength of 460 nm. The full width half maximum of 49.6 nm indicated a relative narrow

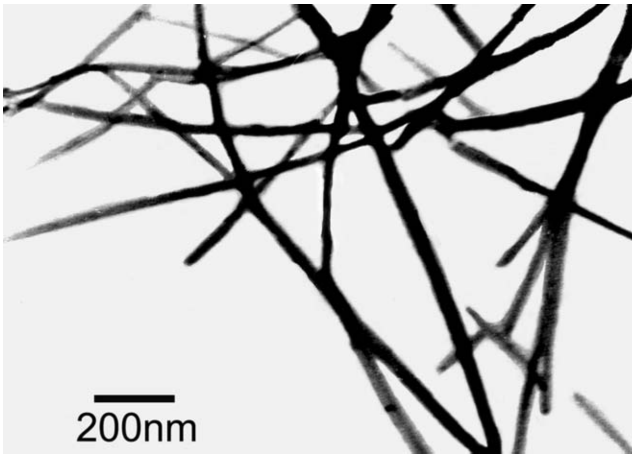

Fig. 1 TEM image of CdTe NWs.

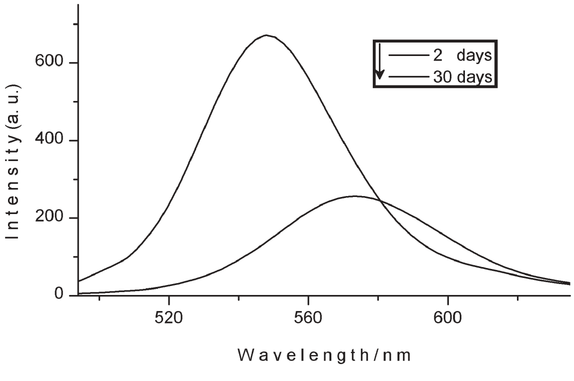

Fig. 2 PL spectra of CdTe NWs solution kept for 2 days and 30 days after synthesis. The excitation wavelength was 460 nm.

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† Electronic supplementary information (ESI) available: instrumentation, SAED, XRD, HRTEM and EDS characterizations of CdTe NWs, TEM image and PL spectrum of the CdTe QDs prepared for comparison. See http://dx.doi.org/10.1039/b502978c

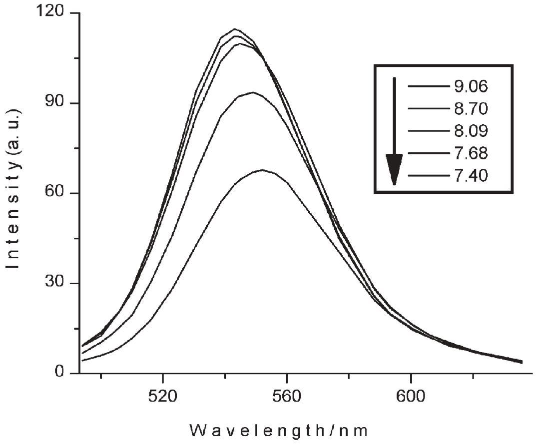

Fig. 3 Effect of pH on the luminescence of CdTe NWs.

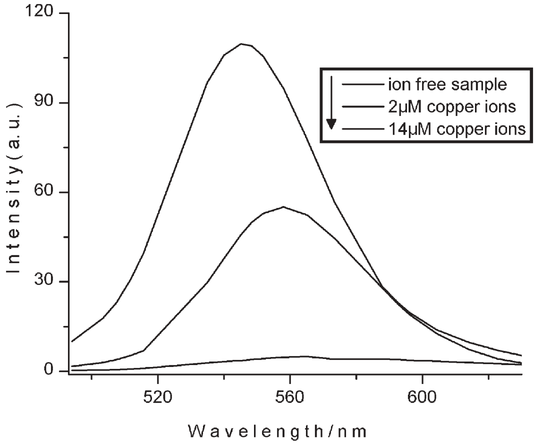

Fig. 4 Effect of copper ions on the luminescence of CdTe NWs.

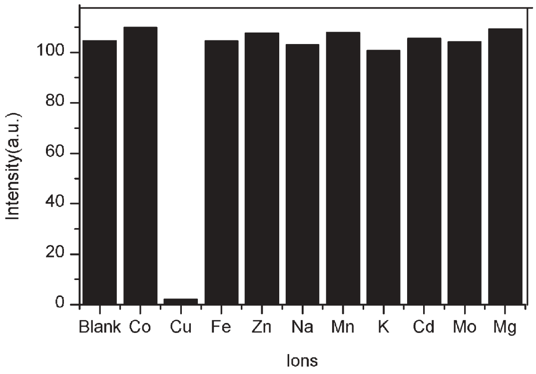

Fig. 5 Effect of 20 μM biologically relevant ions on the luminescence of CdTe NWs.

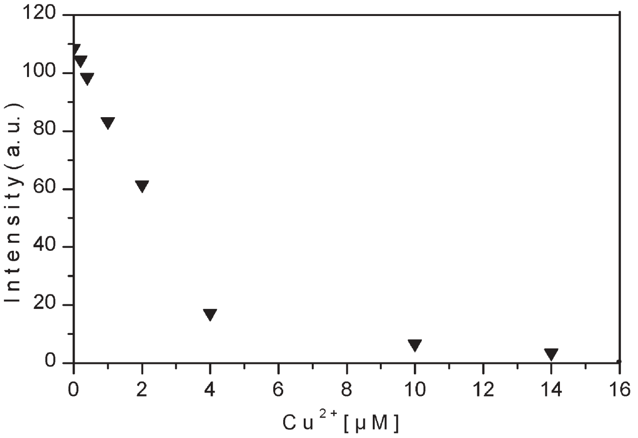

Fig. 6 Effect of copper ion concentration on the luminescence of CdTe NWs.

size distribution. The optical properties were relative stable for about 25 days for the whole detection experiments. By one month after the synthesis, the PL intensity had decreased dramatically with red-shift in wavelength.

Tris-HCl buffer solutions of 0.05 M were chosen to study the effect of pH on the luminescence of CdTe NWs (Fig. 3). A surprising phenomenon—that the intensity of the CdTe NWs decreased with decrease of pH accompanied by a slight red-shift—appeared, which is quite different from the results with CdTe nanocrystals.[19] The detailed mechanism is under discussion. Herein, a physiological buffer solution of pH 7.40 was used in the detection of copper(II).

The effect of copper ions on the luminescence of CdTe NWs is shown in Fig. 4. The luminescence intensity of CdTe NWs decreased by 50% in solutions containing 2 μM of copper ion and a red-shift of ~6 nm was observed. When the concentration of copper ions was increased to 14 μM, the luminescence of CdTe NWs was quenched almost completely. To better understand the selectivity of CdTe NWs solution toward copper ions, we compared its response to copper with its response to other physiologically relevant ionic species. As shown in Fig. 5, only copper ions effectively quenched the luminescence of these NWs.

Fig. 6 describes the copper ion concentration dependence of the luminescence intensity of CdTe NWs. It can be seen that the luminescence intensity decreased with increasing copper ion concentration. The luminescence intensity of CdTe NWs in a 10 μM copper ion solution at 559 nm is 12 times lower than their luminescence intensity in a copper ion-free solution. The standard deviation for replicate measurement of a solution containing 0.2 μM copper ions was 0.92%.

The luminescence response to copper ion concentration changes demonstrated a nearly perfect exponential behavior (R = 0.99949) in a range of 0 ~ 4 μM (Fig. 7A). The limit of detection (LOD) calculated according to IUPAC definitions is 0.078 μM. While the amount of CdTe NWs stock solution increased from 1 mL to 4 mL, its luminescence response to copper ion concentration changes demonstrated a nearly perfect exponential behavior (R = 0.99947) in a range of 0 ~ 30 μM (Fig. 7B). The LOD changed to 0.58 μM.

For comparison of the response of as-prepared CdTe NWs, thioglycolic acid-coated CdTe quantum dots (QDs) were also successfully prepared under the same conditions but without cystein introduced into the reaction system. The corresponding maximum excitation wavelength was 400 nm and the PL intensity was only one third of CdTe NWs with the same concentration. A TEM image and PL spectrum of the CdTe QDs are shown in the ESI.†

Functionalized QDs have been developed as sensors to detect different ions.[20–23] However, all of them had the excitation

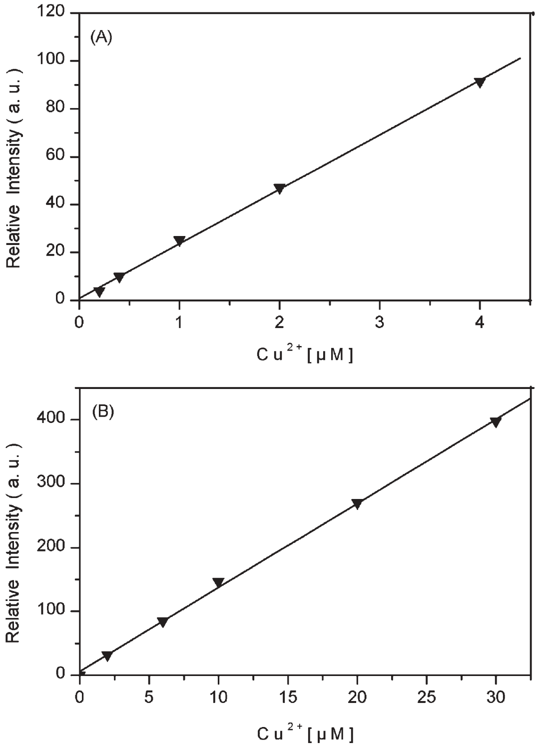

Fig. 7 Plot of decrease in luminescence intensity *vs.* copper ion concentration: (A) 1 mL CdTe NWs stock solution; and (B) 4 mL CdTe NWs stock solution.

wavelength no longer than 400 nm, and the interference of blood components that largely absorb light over this range can not be eliminated. In this study, the signal-to-noise ratio was greatly improved with the excitation wavelength of 460 nm. The broad linear range of this probe (0 ~ 30 μM) makes it possible to detect copper ions in whole blood samples (10 ~ 20 μM), serum samples (13.6 ~ 25.7 μM) and hair samples (0.09 ~ 0.157 μM). In addition, the LOD of as-prepared CdTe NWs can be further improved at higher pH values.

Compared to other investigated cations in our study, the electrode potential of Cu^{2+}/Cu^{+} made Cu^{2+} the most appropriate for the effective electron transfer from the NWs to the ions. As proposed by Rosenzweig,[20] it was the effective electron transfer from the nanomaterials to the copper ions that resulted in the effective quenching and red-shift of the luminescence of the nanomaterials.

In summary, highly luminescent water-soluble CdTe NWs synthesized in one step were used to detect copper(II) selectively below 0.078 μM in the presence of other physiologically relevant cations. Without the interference of blood components that largely absorb light at 400 nm, the as-prepared CdTe NWs with better emission signals offer an attractive alternative to fluorescent particles containing organic fluorophors and luminescent QDs for analysing biological samples. In addition, $La(OH)_3$ nanorods, La_2O_3 nanorods and $La(OH)_3$ nanospheres were successfully synthesized in our laboratory.[24,25] The interaction between as-prepared CdTe NWs and proteins is being investigated now.‡

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Notes and references

‡ Briefly, 0.0655 g of $Cd(ClO_4)_2·6H_2O$ and 0.3 ml of freshly prepared oxygen-free 0.25 M NaHTe precursors were refluxed in the mixed ligand system of cystein(Cys) and thioglycolic acid(TGA). The molar ratio of Cd^{2+}:TGA:Cys:HTe^{-} was fixed at 1:1.8:0.6:0.5. Pure Ar was used to de-aerate the reaction solution instead of N_2 and magnetic stirring continued overnight after three hours of reflux. Under the above conditions, a bright-orange CdTe nanowire solution resulted and was stored at 4 °C as stock solution for the following detection experiments. The concentration of CdTe nanowires was estimated to be 0.75 mM according to the final concentration of NaHTe. Into a series of 10 mL colorimetric tubes were added 1 mL of CdTe nanowires stock solution, 2.0 mL of 0.05 mol L^{-1} Tris-HCl physiological buffer solution (pH = 7.40) and different amounts of physiologically relevant ions sequentially. The mixture was diluted to the mark with Mill-Q water, shaken thoroughly and equilibrated at 20 ± 1 °C for 15 min. Reference solution was the same without any ions added. All of the excitation wavelengths in the following experiments were fixed at 460 nm. Relative intensity shown in Fig. 7 refers to the decreases in luminescent intensity of CdTe NWs with the addition of copper ions.

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