

Turn-on Fluorescent InP Nanoprobe for Detection of Cadmium Ions with High Selectivity and Sensitivity

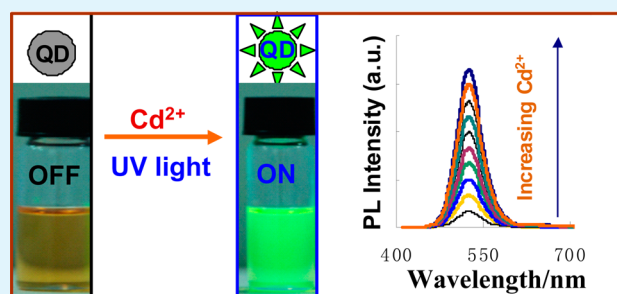
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Supporting Information

ABSTRACT: We reported a “turn-on” fluorescent InP nanoprobe for detection of cadmium ions in hydrophobic and hydrophilic media. The method based on the turn-on fluorescence detection of cadmium ions has shown its high selectivity and sensitivity, which are independent of the pH of the tested samples. Also, this approach exhibits an immediate response to cadmium ions, and visualized detection of cadmium ions has further been demonstrated under a UV lamp.



KEYWORDS: cadmium ions, detection, fluorescence, indium phosphide, nanocrystals

1. INTRODUCTION

Cadmium is extremely toxic and widely found in plastics, fossil fuel combustion, phosphate fertilizers, and so on.¹ These sources of cadmium often lead to contaminations in water, soil, and food,^{2,3} causing serious environmental and health problems such as lung, prostate, and renal cancers.^{4,5} Accordingly, the development of facile techniques enabling one to monitor cadmium temporally are of considerable significance. In comparison to the traditional methods such as atomic absorption spectrometry^{6,7} and inductively coupled plasma mass spectrometry,⁸ fluorescent sensing is considered as an alternative approach for fast and visualized detection of metal ions.^{9–11} There are a number of recent reports on the detection of cadmium ions using organic dyes^{12–28} and quantum dots.^{29–38} Their sensing mechanism is mostly based on the quenching of fluorescence (“turn-off”) or the change in fluorescence intensity and/or emission wavelength.

In this report, we developed a fluorescence “turn-on” probe for detecting cadmium ions. This approach can directly detect cadmium ions in hydrophobic media as well as those in hydrophilic media such as water via a phase transfer process. Also, this approach exhibits an immediate response to cadmium ions with high selectivity, and visualized detection of cadmium ions has further been demonstrated under a UV lamp.

2. EXPERIMENTAL SECTION

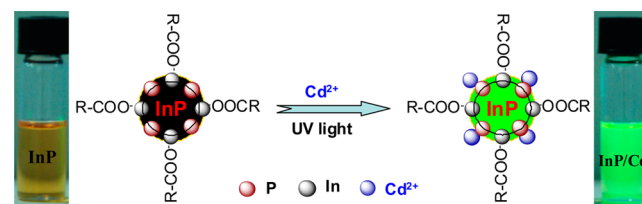
2.1. Synthesis of InP Nanocrystals. An injection solution was first prepared by dissolving tris(trimethylsilyl) phosphine (0.1 mmol, P(TMS)₃, Alf. 95%) and 1-octylamine (2.4 mmol, Alf. 99%) in 1-octadecene (1.0 mL, ODE, Alf. 90%) in a glovebox. For a typical synthesis, indium acetate (0.3 mmol, Alf. 99.99%), myristic acid (1.0 mmol, MA, Alf. 98%), and ODE (4.0 g) were loaded into a three-neck flask. When the mixture was heated to 188 °C under an argon flow, the

freshly prepared P(TMS)₃/amine solution was injected into the hot reaction mixture. The cold injection brought the temperature down to 178 °C for the growth of InP nanocrystals for 10 min. The solution was then cooled to room temperature. After washing with chloroform/methanol solvents, the purified InP nanocrystals were dispersed in 20 mL of hexane (2.0 μM) for further characterization and the detection of metal ions.

2.2. Detection of Cadmium Ions in Organic Phase. The as-prepared InP nanocrystals (2.0 μM) dispersed in 2.0 mL of hexane and different amounts of cadmium ions (cadmium oleate) dissolved in 2.0 mL of hexane were first mixed into a quartz cuvette followed by shaking for 10 s prior to the photoluminescence measurement. Excitation and emission measurements were performed with a slit width of 5 nm and an excitation wavelength of 440 nm. The emission spectra were recorded from 450 to 700 nm, and the emission intensity at 528 nm was used for quantitative analysis of cadmium ions as depicted in Scheme 1. Other metal ions were also detected using an identical approach.

2.3. Detection of Cadmium Ions in Water. The as-prepared InP nanocrystals (2.0 μM) dispersed in 1.0 mL of hexane and different

Scheme 1. Schematic Illustration of the Detection of Cadmium Ions in the Organic Phase with InP Nanocrystals



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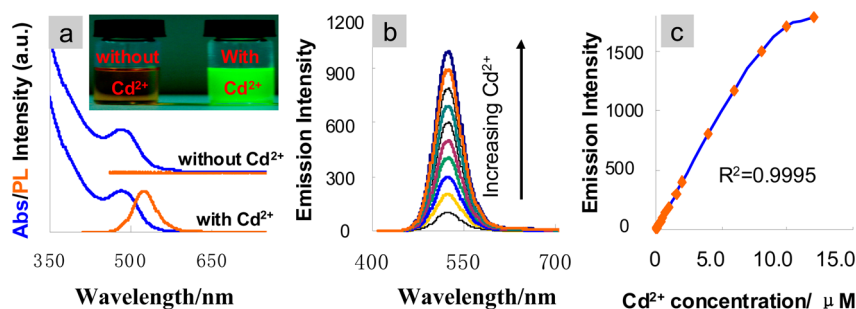


Figure 1. Sensitive detection of cadmium ions in organic solution. (a) Absorption (blue line) and emission (orange line) spectra of the InP nanocrystals before and after the addition of cadmium ion. Inset: Digital pictures of the sample without and with cadmium ions taken under a 365 nm UV lamp. (b) Emission spectra of InP nanocrystals (2 μM) after the addition of cadmium ion with different concentrations. (c) Variation in the emission intensity of InP nanocrystals at 528 nm with the concentrations of cadmium ions.

amounts of cadmium ions in 1.0 mL of water were first mixed into a quartz cuvette followed by shaking for 15 min prior to the photoluminescence measurement. The cadmium concentration in the water layer was determined by inductively coupled plasma mass spectrometry (ICP-MS). The cadmium concentration in the organic layer was also determined by ICP-MS. The InP nanocrystals in the organic layer were first precipitated by the addition of 2 mL of methanol and dried by gentle heating under argon. The dried sample was digested by 0.5 mL of aqua regia followed by diluting with 3.5 mL of water for ICP-MS measurement. Other metal ions were also detected using an identical approach.

2.4. Characterizations. TEM images were taken on a JEOL 100CX transmission electron microscope with an acceleration voltage of 100 kV. A drop of as-prepared hexane solution of InP nanocrystals was dropped onto carbon-coated copper grids and dried in air. Elemental compositions were determined by energy-dispersive spectroscopy (EDS) on a Shimadzu SSX-550 instrument. UV–visible absorption and emission spectra were recorded on a HP8453 UV–visible spectrophotometer and a FS900 steady-state fluorescence spectrometer, respectively. Inductively coupled plasma mass spectrometry (ICP-MS) was collected on a Perkin-Elmer Optima3300dv.

3. RESULTS AND DISCUSSION

InP nanocrystals were prepared by the method reported in the literature.³⁹ There was no observable emission for the as-prepared InP nanocrystals in hexane (2 μm) at room temperature. After adding cadmium oleate in hexane (20 μM) and then shaking for 10 s, a green emission from the InP nanocrystals was clearly observed under UV irradiation as shown in Figure 1a, showing that the InP nanocrystals are very sensitive to cadmium ions. Importantly, the fluorescence of the mixture reached its maximum rapidly within 10 s as shown in the video (see the Supporting Information video, am402768w_si_002.avi), indicating that a simple “add and mix” process can perform fast detection of cadmium ions by using the InP nanocrystals as nanoprobes in organic solutions.

Figure 1b shows the emission spectra of the InP nanocrystals in the presence of cadmium ions (cadmium oleate dispersed in hexane/toluene). As the cadmium concentration increased, the emission wavelength (peak position: 528 nm) of the InP nanocrystals was kept unchanged, and the fluorescence intensity increased until a saturation point was reached. The obtained fluorescence signal was also fairly stable, with no noticeable decrease in the intensity during continuous monitoring for several hours. More importantly, the emission intensity of the nanoprobe at 528 nm was proportional to the concentration of cadmium ion added in the range of 0.2 to 10 μM as shown in Figure 1c (linearly dependent coefficient: $R^2 = 0.9995$). This indicated that the InP nanocrystals can be

potentially used for quantitative detection of cadmium ion with a detection limit of about 0.1 μM . Different from the “turn-off” probe, such a “turn-on” fluorescence nanoprobe allowed one to have facile judgment of whether the cadmium concentration has exceeded a definite value (about 2.0 μM) by naked eyes.

The “turn-on” fluorescence may be attributed to the elimination of the surface defect of InP nanocrystals in the presence of the cadmium ions. Generally, InP nanocrystals have been classified as having a zinc blende structure, whose microstructure and optical properties are similar to II–VI nanocrystals such as CdS, CdSe, and CdTe. For example, the emission intensity of CdTe nanoprobe could be enhanced by cadmium ion as reported by Gao’s group.⁴⁰ Similarly, cadmium ion is easy to conjugate with the phosphor atoms on the surface of InP nanocrystals, which has been verified by X-ray photoelectron spectroscopy (XPS) measurements (see Supporting Information Figure S1). Scheme 1 illustrates the detection process for cadmium ion by InP nanocrystals. The cadmium ions were adsorbed on the surface of the InP nanocrystals, which resulted in the “turn-on” fluorescence of the InP nanocrystals via the generation of a “shell of InP/Cd-R” complex microheterojunction.⁴¹ Aggregation of the InP nanocrystals, which may also induce the change in fluorescence intensity, was excluded by TEM observations (see Supporting Information Figure S2).

The selectivity of the nanoprobe was further investigated by determining the specificity of the InP nanocrystals toward cadmium ions. Similar to InP nanocrystals without cadmium ion, no fluorescence was observed in the presence of 20 μM Cs⁺, Na⁺, K⁺, Zn²⁺, Pb²⁺, Cu²⁺, Hg²⁺, Ba²⁺, Mg²⁺, Ca²⁺, Ni²⁺, Cr³⁺, or Fe³⁺ (Figure 2a). In contrast, the fluorescence of InP nanocrystals was only observed in the presence of 20 μM cadmium ion, which could be readily observed via naked-eye under a 365 nm UV lamp. Meanwhile, competition experiments were also conducted for InP nanocrystals in which the equivalent amount of cadmium ion (20 μM) was added into the samples shown in Figure 1a, respectively (except for the sample with the addition of cadmium ion). Figure 2b gives the photos of the samples after the addition of 20 μM cadmium ion. Emission intensity of the samples was almost similar to that of InP nanocrystals in the presence of only cadmium ion (20 μM). The samples that contained Fe³⁺, Hg²⁺, Cr³⁺, Ni²⁺, or Cu²⁺ exhibited weaker brightness than other samples, possibly due to the quenching effect of these metal ions as verified in our previous work.⁴²

Apart from detecting the cadmium ion in hydrophobic media, the proposed nanoprobe is also suitable for the

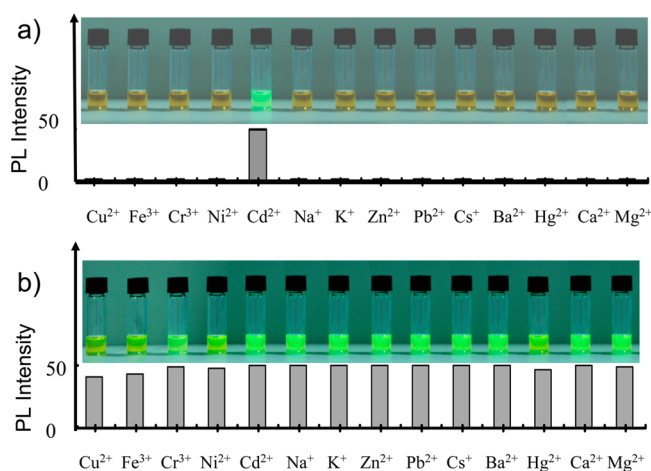


Figure 2. Comparison of the responses of InP nanocrystals to common metal ions with cadmium ions. (a) The fluorescence intensity of InP nanocrystals ($2.0 \mu\text{M}$) in the presence of different metal ions ($20 \mu\text{M}$) and their corresponding digital pictures taken under a 365 nm UV lamp (inset). (b) The fluorescence intensity of InP nanocrystals at 528 nm after the addition of an equiv cadmium ion and their corresponding digital pictures taken under a 365 nm UV lamp (inset) (except for the sample with the addition of the cadmium ions).

detection of cadmium ion in aqueous solution via the two-phase approach. InP nanocrystals dispersed in hexane (or chloroform) were mixed with an aqueous solution containing metal ions under stirring for several minutes (Figure 3a,b). Green emission of nanocrystals was only observed under the UV irradiation for the sample with the addition of $20 \mu\text{M}$ cadmium ion (Figure 3c), attributed to the transfer of cadmium ion from the aqueous to organic phase. The successes on cadmium phase transfer from water to hexane were confirmed by energy dispersive X-ray spectroscopy analysis as shown in

Figure 4 where cadmium ion was only found from the InP nanocrystals with fluorescence (InP was mixed with cadmium acetate in water), indicating the adsorption of cadmium ions onto the InP nanocrystals. It is found that the emission of the InP nanocrystals was kept almost unchanged when the mixture of cadmium ions with other metal ions was used in the detection experiments as shown in Figure 3d, although the brightness of the nanocrystals decreased slightly in presence of Cu^{2+} , Fe^{3+} , Cr^{3+} , or Hg^{2+} . This clearly demonstrated the high selectivity of the InP nanocrystals toward cadmium ion in aqueous solution.

It is identified that the fluorescence intensity of the InP nanocrystals remained nearly constant whether the same amount of cadmium ions is dispersed in aqueous or nonaqueous media (Figure 5a), indicating the cadmium ions in water had been collected almost completely by hydrophobic InP nanocrystals via a phase transfer process. Common fluorescence probes are sensitive to pH when being used for detection of metal ions in aqueous solution.⁴³ Furthermore, the solution containing metal ions to be detected should be avoided of contaminants prior to subsequent analyses. The approach reported here showed a number of advantages over traditional methods as follows: the detection of cadmium ion was almost independent of the sample pH in the range of 3.0–8.0 (Figure 5b). When pH of the solution was lower than 3.0, the InP nanocrystals become unstable and lack the emission. On the contrary, no emission from the InP nanocrystals was detectable when cadmium ions were dispersed in a solution with high pH (>10) due to the formation of cadmium hydroxyl ($K_{\text{sp}}(\text{Cd}(\text{OH})_2) = 7.2 \times 10^{-15}$).

To demonstrate the potential practical application of the method to detect cadmium ion in groundwater, we collected water samples that were contaminated with cadmium ion from Changchun, Jilin Province, and compared the data with samples collected from bottled water from Wahaha Co., Ltd. A two phase technique as described in Figure 6 was used for detection

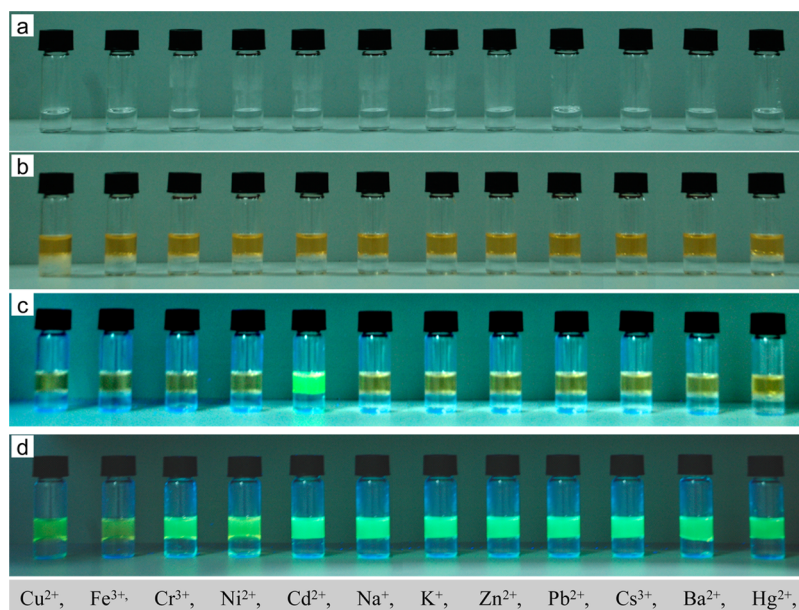


Figure 3. Sensitive detection of cadmium ions in aqueous solution via a phase transfer process. (a) Room light photos of various metal ions in water (concentration: $20 \mu\text{M}$). (b) Room light photos of the aqueous solutions in (a) after adding the as-prepared InP nanocrystals in hexane ($2.0 \mu\text{M}$) (top layer) followed by shaking for 15 min. (c) Photos of the samples in (b) under a 365 nm UV lamp and room light. (d) Photos of the samples in (c) after being further mixed with $20 \mu\text{M}$ cadmium ions under a 365 nm UV lamp.

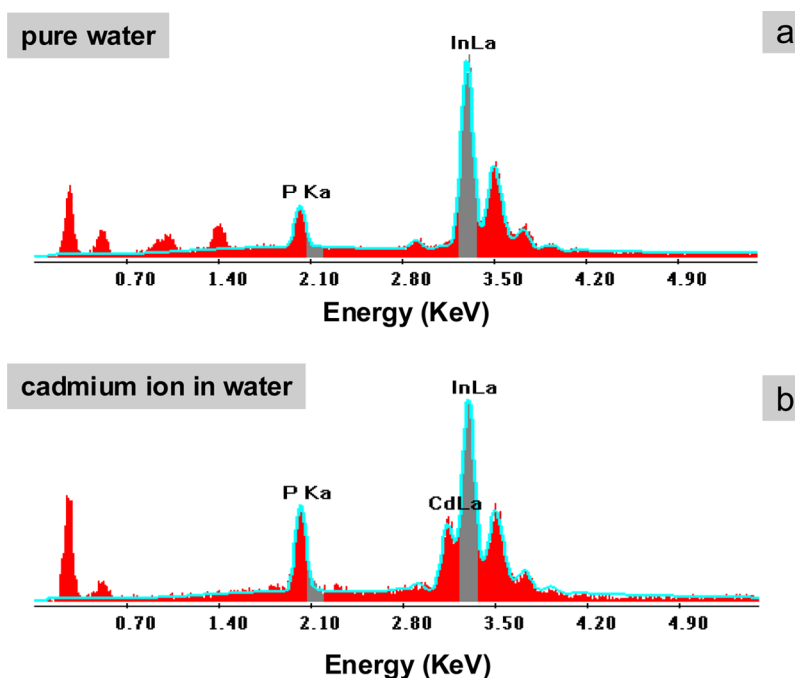


Figure 4. EDS spectra of InP nanocrystals dispersed in hexane in the absence (a) and presence (b) of cadmium ions in water.

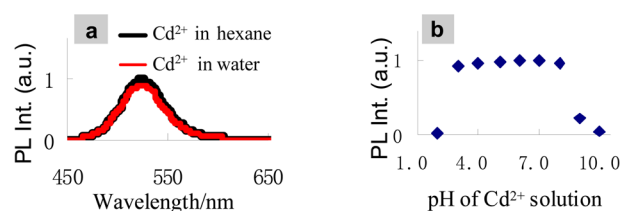


Figure 5. (a) The normalized emission spectra of the InP nanocrystals ($2.0 \mu\text{M}$) in the presence of the same amount of cadmium ion dispersed in hexane (black line) and water (red line) (cadmium ion concentration: $50 \mu\text{M}$). (b) The normalized fluorescence intensity of the InP nanocrystals ($2.0 \mu\text{M}$) at 528 nm in the presence of the same amount of the cadmium ion under various pH. The concentration of cadmium ions was $50 \mu\text{M}$.

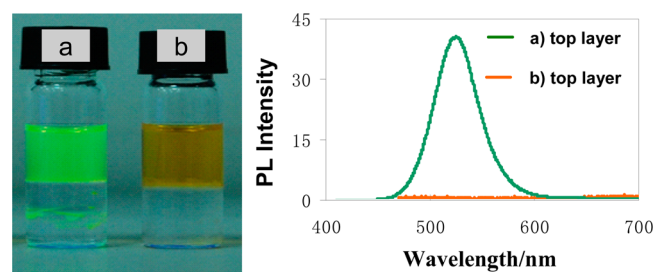


Figure 6. (Left) Digital pictures of InP nanocrystals taken under a 365 nm UV lamp and (Right) corresponding emission spectra of InP nanocrystals ($2.0 \mu\text{M}$) taken with (a) the spiked contaminated water sample extracted from soils and (b) the sample from the bottled water. The excitation wavelength was at 400 nm .

of cadmium ion. The digital pictures taken under a 365 nm UV lamp and emission spectra showed the sample contaminated by cadmium ions presented “turn-on” green fluorescence (Figure 6). In contrast, the probe showed no fluorescence signal for the sample from the bottled water. By using this current approach, the concentration of cadmium ion in the contaminated water was determined to be about $12 \mu\text{M}$, which was comparable to

that ($15 \mu\text{M}$) obtained by using inductively coupled plasma mass spectrometry.

4. CONCLUSIONS

Here, we report sensitive, selective, and fast detection of cadmium ions in aqueous solutions as well as in organic solvents using InP nanocrystals as a fluorescence “turn-on” probe. This approach can directly detect cadmium ions into hydrophobic media as well as those into hydrophilic media such as water via a phase transfer process. It is expected that such a “turn-on” fluorescence probe would be very useful in quantitative and on-the-spot visual detection of cadmium ions in various systems.

■ ASSOCIATED CONTENT

Supporting Information

A movie illustrating the visualization on the detection of cadmium ions with InP nanocrystals and supplementary figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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