Functional InP Nanocrystals as Novel Near-infrared Fluorescent Sensors for Mercury Ions

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Water-soluble indium phosphide nanocrystals capped with mercaptoacetic acid were synthesized. The nanocrystals fluoresce in the near-infrared region with maximum excitation and emission wavelengths at 750 and 826 nm, respectively. The fluorescence intensity is significantly enhanced in the presence of Hg^{2+} ions. Under the optimum conditions, the fluorescence enhancement is in proportional to the concentration of Hg^{2+}.

Much attention has been focused on the development of chemical sensors for the selective and efficient detection of chemically and biologically important ionic species.[1] The toxic effect of Hg^{2+} ions in the environment has been well known. A number of selective and sensitive organic molecular sensors for the determination of Hg^{2+} ions have been continually devised.[2–4] However, these organic fluorescence molecules bear some limitation such as photobleaching and narrow excitation spectrum and often exhibit broad emission spectrum with red tailing.[5,6] Colloidal semiconductor nanocrystals, often referred to as "quantum dots", can overcome problems encountered by organic dye molecules. Surface modification of QDs may change their optical, chemical, and photocatalytic properties,[7,8] so QDs have attracted significant attention as novel luminescent sensors in recent years. Chen and Rosenzweig[9] demonstrated the first example of Cu^{2+} and Zn^{2+} ions analysis by utilizing CdS luminescent QDs capped by different ligands in aqueous media. Chen and co-workers reported Hg^{2+} ion analysis by utilizing CdTe luminescent QDs stabilized by mercaptopronionic acid in aqueous meida.[10] However, the determination was based on the fluorescence quenching with the addition of Hg^{2+} ions. The methodology based on fluorescent enhancement is interesting for analysis in terms of sensitivity.[11]

In this paper, we reported the synthesis of InP nanocrystals (NCs) as a fluorescent sensor for Hg^{2+} ion. Compared with II–VI nanocrystals (CdS, CdSe, CdTe), InP NCs fluoresce in the near-infrared (NIR) region, where relatively free of interference because only a relatively few groups of molecules are spectroscopically active. Furthermore, the fluorescence intensity was enhanced with the addition of Hg^{2+}. To our knowledge, this is the first time that InP NCs were used as chemical sensors in the near-infrared region. InP NCs were synthesized according to Yi Xie's reports.[12] This synthetic procedure was described as the supplemental information. InP powder was dispersed in distilled water with the aid of ultrasonic stirring for 30 min. Mercaptoacetic acid (MAA) was added with stirring under nitrogen. After 5 h, the color of the solution changed from brown to yellow-orange. Figure 1a shows TEM of InP NCs, the particles are spherical and dispersed in aqueous solution homogeneously. The TEM of functional NCs (MAA–InP) is shown in Figure 1b, and Figure 1c shows TEM of MAA–InP chelating Hg^{2+}. TEM of Figure 1c indicates clearly that particle diameter is increased.

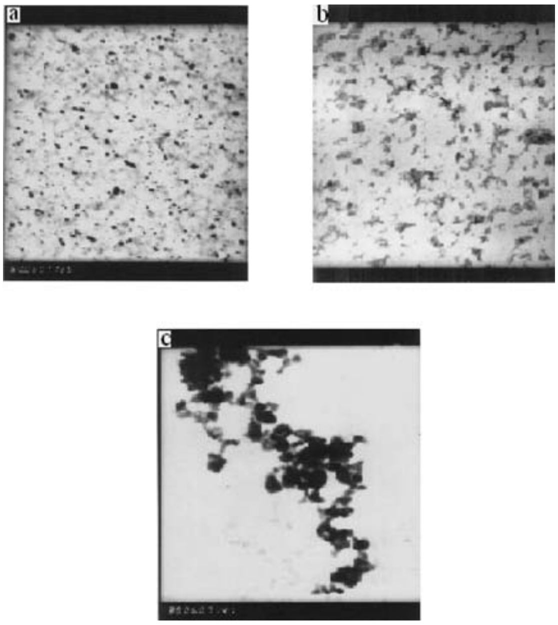

Figure 1. TEM images of InP NCs (a), MAA–InP NCs (b), and MAA–InP–Hg^{2+} NCs (c).

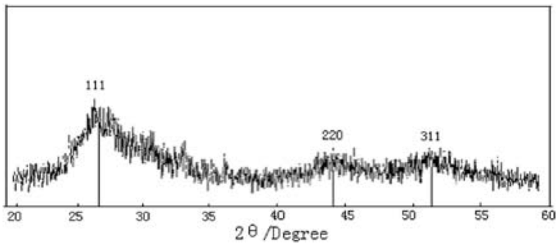

Figure 2. X-ray diffraction patterns of InP NCs.

The powder X-ray diffraction pattern of InP NCs is shown in Figure 2. According to the halfwidth of the major diffraction peaks (111, 220, and 311), the mean crystalline size of the InP NCs is 8 nm using the Debye–Scherrer formula.[13]

The UV–vis absorption spectrum of InP NCs in aqueous solution is shown in Figure 3a. A featureless rise in the absorption spectrum may be caused by the broad size distribution and two-morphology nature. The fluorescence excitation and emission spectra are shown in Figures 3b and 3c. The optical properties of InP NCs remained unaltered after modified by MAA, only the optical intensity became weaker. The FT-IR spectrum of MAA–InP NCs (not shown here) shows absorption bands that can be attributed to carboxyl and carbonyl groups, but the S–H vibration (2550–2670 cm^{-1}) for MAA–InP is not detectable as assumed for covalently bound thiols to the InP NCs surface.

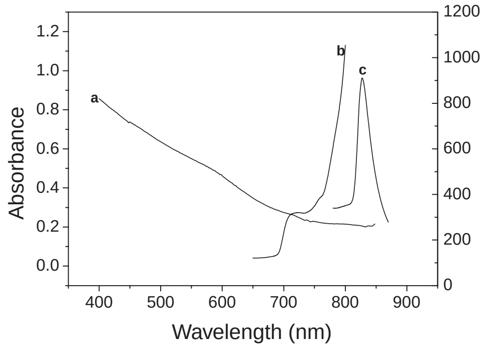

Figure 3. UV–vis and fluorescence spectra recorded from an aqueous solution of InP nanoparticles. (a) absorption spectrum (b) excitation specrum (c) emission spectrum.

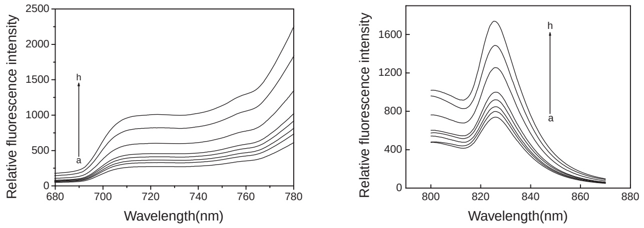

Figure 4. Fluorescence spectra of MAA–InP nanoparticles in presence of various amounts of Hg^{2+}. The excitation spectra in the left and the emission spectra in the right. Concentration of Hg^{2+} (a–h) is 0, 0.5, 1, 1.5, 2.0, 4.0, 6.0, and 8.0 (µg/mL).

The MAA–InP NCs solution (4.0 mL, 10^{-3} mol/L), phosphate buffer solution (0.5 mL, pH = 7.50) and different amount of Hg^{2+} ions were successively added into 10.0-mL calibrated test tubes, then diluted to the mark with deionized water and mixed thoroughly. The fluorescence intensity of system was measured at $\lambda_{em} = 826$ nm in 25 min. The intrinsic spectra peak of MAA–InP NCs containing Hg^{2+} is unchanged in comparison with that of MAA–InP NCs. The fluorescence intensity is significantly enhanced in the presence of Hg^{2+} ions as shown in Figure 4. Thus, a novel fluorescence method has been developed for the determination of mercury ions.

The linear range of the calibration curve is 5.0×10^{-7} g/mL–8.0×10^{-6} g/mL for Hg^{2+} ions and the linear equation is $I_{SF} = 736.75 + 125.8\,C$ (µg/mL). The detection limit is 1.0×10^{-7} g/mL and the correlation coefficient is 0.9996. As we know, the K_{sp} of HgS ($K_{sp} = 2 \times 10^{-52}$) is much lower than that of other metal sulfide. The mercapto groups on the NCs surface can coordinate with mercury ions. The luminescence enhancement is rather attributed to the formation of HgS ultrasmall particles on the surface of NCs, which act as electron–hole recombination centers. Ultrasmall particles of HgS have a larger bandgap, which can efficiently confine the excitation to the InP QDs, eliminating nonradiative relaxation pathways and preventing photochemical degradation.

Then we investigated the fluorescent behaviors of MAA–InP NCs for Hg^{2+} ion-selective sensing applications. Upon interaction with metal ions, Hg^{2+} ions exhibited the most effective enhancement efficiency. Cu^{2+} and Ag^{+} ions also induced enhancement efficiency but to a much lesser degree than Hg^{2+} ions and other metal ions induced negligible spectral changes. The selective response toward Hg^{2+} ions was hardly affected by the presence of other common mental ions in aqueous solvent system.

In conclusion, indium phosphide nanoparticles modified by mercaptoacetic acid were synthesized and characterized in terms of their optical and photochemical properties. The luminescence intensity of functional InP NCs was enhanced in the presence of Hg^{2+} ions, owing to the binding of mercury ions onto the surface of the semiconductor. The functional InP NCs have been developed a novel selective fluorescent sensor for Hg^{2+} ions. Further study of the surface effect and the fluorescent performance of InP NCs in detail are under investigation in our lab.

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