Synthesis of Novel Nanocrystals as Fluorescent Sensors for Hg*²^þ* Ions

Bo Chen,** Ying Yu,^{\dagger ,††} Zhentao Zhou,^{††} and Ping Zhong[†]

[†]Department of Chemistry, South China Normal University, Guangzhou, 510631, P. R. China

 $\ddot{\rm u}^{\dagger}$ College of Material Science and Engineering, South China University of Technology, Guangzhou, 510631, P. R. China

(Received September 3, 2004; CL-041042)

CdTe nanocrystals as fluorescent sensors for Hg^{2+} ions were synthesized. These nanocrystals were highly sensitive for Hg^{2+} ions and the selectivity was found to be $Hg^{2+} > Cu^{2+} >$ other representative heavy metal ions. Moreover, they bear the following merits. First, they are easily synthesized; second, they have a narrow, tunable, symmetric emission spectrum.

In recent years considerable efforts have been given to the design and synthesis of functional molecules that could serve as sensors for the analytical detection of chemically and biologically important ionic species.¹ Especially, the detection of Hg^{2+} ions has been one of the most important topics because they pose significant public health hazards when present in drinking water at parts per million concentrations or higher.² So the analysis and measurement of trace mercury in environmental and biological samples are extremely important. The advantages of fluorescence signaling in its intrinsic sensitivity have encouraged the development of a variety of fluorescent sensors for Hg^{2+} ions.^{3,4} However, these fluorescent dye molecules suffer notorious limitations such as low signal intensities and photobleaching; furthermore, most of them tend to have narrow excitation spectra and often exhibit broad emission bands with red tailing.5 The challenge is to find proper fluorescent sensors for tracing Hg^{2+} ions.

Colloidal semiconductor nanocrystals, often referred to as "quantum dots" or "QDs," have the potential to overcome problems encountered by organic dye molecules in certain fluorescent probing applications by combining the advantages of high photobleaching threshold, good chemical stability, and readily tunable spectral properties.⁵ In recent years QDs have attracted considerable attention as novel luminescent sensors. Chen and Rosenzweig⁶ demonstrated the first example of Cu^{2+} and Zn^{2+} ions analysis by utilizing CdS luminescent QDs capped by different ligands in aqueous media. However, these QDs showed wider emission peaks, indicating that these particles contain a larger number of surface defects. Peng and co-workers⁷ reported that the photostimulated responses of the CdSe QDs to different gases vary dramatically. They believe that it is possible to develop sensitive and simple sensors using QDs.

In this paper, we report synthesis of novel fluorescent sensors (CdTe nanocrystals, NCs) for Hg^{2+} ions. Compared with CdS QDs mentioned above, these NCs are more stable against photobleaching; furthermore, the full width at half maximum is about one-third as wide as that of CdS QDs. Their emission spectra are narrow and tunable according to their size and material composition, allowing closer spacing of different sensors without spectral overlap, which provide a possibility to develop multiplexed detection schemes. Here we will report preliminary results of Hg^{2+} ions recognition by these NCs.

The synthetic procedure of NCs stabilized by mercaptopronionic acid (MPA) was modified from previous literature re-

ports^{8,9} and described as follows. The nitrogen-saturated aqueous solution (125 cm³) containing 0.1142 g of CdCl₂ \cdot 2.5H₂O and 0.1274 g of MPA was reacted with NaHTe solution at pH 11.2. NaHTe was generated by the reaction of Te powder with NaBH₄. The molar ratio of Cd^{2+} :HTe⁻:MPA was 1:0.5:2.4. It was found that the emission peak of these NCs shifted red with prolonging the duration of reflux time. Because of quantum size effect, the red shift of the emission peak indicated the increase of the particle size. 8 So different sizes of the NCs were easily obtained by controlling duration of reflux time. A reflux time of ca. 2 h was adopted in this assay to promote growth of NCs. The crude solution of the NCs was dialyzed against water to remove excess MPA and ions. The final concentration of NCs was ca. 4.0×10^{-3} mol dm⁻³ according to the Cd²⁺ concentration. The particle size and degree of the dispersion were determined by HRTEM (Hitachi HR 2000, 200 kV accelerating voltage), and the TEM images were shown in Figure 1a, the particles are monodisperse in shape and the lattice fringes can be clearly observed. In order to estimate the particle size distribution, the NCs were dispersed on the TEM sample holder grid and recorded. The histogram of cluster size obtained was shown in Figure 1b, indicating an average particle diameter of 3.0 nm with a standard deviation of 0.20 nm. Fluorescence spectra were measured by using $\lambda_{\rm ex} = 365 \,\rm nm$ at wavelengths between 450 and 650 nm with a Hitachi F-2500 fluorometer. Fourier transform infrared spectroscopy was conducted on a FT-IR 1730 infrared spectrometer (Perkin-Elmer, USA).

Figure 1. TEM images of NCs (a) and particle size distribution diagram based on TEM images (b).

Curves A, B in Figure 2 showed the FT-IR spectra of free MPA and MPA–NCs, respectively. The most pronounced IR absorption bands occurred at 3034 cm^{-1} (ν OH, COOH), 2946 cm⁻¹ (vCH_2), 2550-2670 cm⁻¹ ($vS-H$), 1707 cm⁻¹ ($vC=O$), $1426 \text{ cm}^{-1}(\nu_s \text{ COOH})$, $1250 \text{ cm}^{-1}(\nu \text{C}-\text{O})$, $940 \text{ cm}^{-1}(\delta \text{OH})$ for MPA and at $3568 \text{ cm}^{-1}(\nu \text{OH}, \text{H}_2\text{O})$, $3185 \text{ cm}^{-1}(\nu \text{OH}, \text{COOH})$, $2900 \text{ cm}^{-1}(\nu \text{CH}_2)$, 1420–1580 cm⁻¹ (ν_s COOH), 1250 cm⁻¹ $(\nu$ C–O), 930 cm⁻¹(δ OH) for MPA–NCs. Both IR spectra of MPA and MPA–NCs showed absorption bands that can be attributed to carboxyl and carbonyl groups, but the S–H vibration $(2550-2670 \text{ cm}^{-1})$ for MPA–NCs was not detectable as assumed

Figure 2. Infrared transmission spectra of MPA(A) and MPA– $NCs(B)$.

for covalently bound thiols to the NCs surface.

We found that when this crude NCs solution was condensed by solvent evaporation and precipitated by ethanol, then redispersed in proper volume of water, the resulting fluorescence intensity decreased greatly in comparison with crude NCs solution. So dialysis was used in this assay rather than the method mentioned above. As shown in Figure 3a, the fluorescence intensity of dialyzed NCs is much stronger than that of crude NCs.

The NCs solution (1.0 cm^3) , phosphate buffer solution $(0.50 \text{ cm}^3, \text{PH } 7.40)$ and different amount of Hg^{2+} ions were successively placed into a 10 cm³ calibrated test tube, then diluted to the mark with water and mixed thoroughly. The resulting fluorescence spectra were shown in Figure 3b. The intrinsic spectral peak of NCs–Hg²⁺ was unchanged in comparison with that of free NCs. But the fluorescence intensity was significantly decreased with increasing the concentration of Hg^{2+} ions. On this basis a novel quantitative assay of Hg^{2+} ions was developed. The linear range of the calibration curve was $0-25.6$ ng cm⁻³ for Hg^{2+} ions and the detection limit was 0.10 ng cm⁻³. The quenching phenomenon is possibly attributed to the effective electron transfer from MPA to Hg^{2+} ions. The carboxyl groups on the NCs surface can coordinate with Hg^{2+} ion sites.¹⁰ Moreover, Hg^{2+} ions can also effectively quench the luminescence of NCs by facilitating nonradiative recombination of excited electrons (e^-) in the conduction band and holes (h^+) in the valence band.

Then we investigated the fluorescent behaviors of NCs for Hg^{2+} ion-selective sensing applications. Upon interaction with metal ions, the emission of NCs was affected and Hg^{2+} ions exhibited the most effective quenching efficiency. The quenching efficiency of Hg²⁺ and Cu²⁺ ions were found to be larger than 68 and 30% with 9.6 ng cm⁻³ equiv. of added metal ions, respectively. Other metal ions did not show so significant, at best less than 8%, quenching efficiency. This result indicates that these

Figure 3. Fluorescence spectra of NCs before and after dialyze (a) and fluorescence spectra of NCs– Hg^{2+} solution system (b).

NCs can be used as sensors for effective recognition of Hg^{2+} ions.

To investigate the possibility of practical application, the influence of diverse substances (Na⁺, Ba²⁺, Ca²⁺, Fe³⁺, Zn²⁺, Al^{3+} , Cd^{2+} , K^+ in the form of chloride, Pb(NO₃)₂, Mn(NO₃)₂, and so on) on determination of Hg^{2+} ions was examined under the standard condition. Although somewhat residual quenching due to the presence of a large amount of background metal ions was observed, these NCs showed a clear Hg^{2+} -dependent quenching behavior, which implies that these NCs can be used for the analysis of Hg^{2+} ions in the presence of other commonly interfering metal ions in aqueous media.

In conclusion, we have developed new selective and sensitive fluorescent sensors (NCs) for Hg^{2+} ions; these NCs exhibited a highly selective signal for Hg^{2+} ions in the presence of commonly interfering metal ions. It is expected that interaction between nanochemistry and organic molecules may open a new route for preparation of fluorescent sensors. Future work will be directed toward studying the surface effect of the NCs on the fluorescent performance of the NCs in detail and attempting to design ideal fluorescent sensors for other biological assays.

The present work was supported by the Natural Science Foundation of Guangdong Province (No. 04010369).

References

- 1 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. Mccoy, J. T. Rademacher, and T. E. Rice, Chem. Rev., 97, 1515 (1997).
- 2 According to the EPA guidelines(http://oaspub.epa.gov), tolerance limit for mercury in drinking water is no greater than $0.002 \,\mathrm{mg}\, \mathrm{L}^{-1}$.
- 3 E. M. Nolan and S. J. Lippard, J. Am. Chem. Soc., 125, 14270 (2003).
- 4 S. Y. Moon, N. R. Cha, Y. H. Kim, and S. K. Chang, J. Org. Chem., 69, 181 (2004).
- 5 a) M. B. Jr., M. Moronne, P. Gin, S. Weiss, and A. P. Alivisatos, Science, 281, 2013 (1998). b) W. C. W. Chan and S. Nie, Science, 281, 2016 (1998).
- Y. F. Chen and Z. Rosenzweig, Anal. Chem., **74**, 5132 (2002).
- 7 A. Y. Nazzal, L. Qu, X. Peng, and M. Xiao, Nano Lett., 3, 819 (2003).
- 8 M. Gao, S. Kirstein, H. Möhwald, A. L. Rogach, A. Kornowski, A. Eychmüller, and H. Weller, J. Phys. Chem. B, 102, 8360 (1998).
- 9 E. Hao, H. Zhang, B. Yang, and H. Ren, J. Colloid Interface Sci., 238, 285 (2001).
- 10 Y. Kim, R. C. Johnson, and J. T. Hupp, Nano Lett., 1, 165 (2001).