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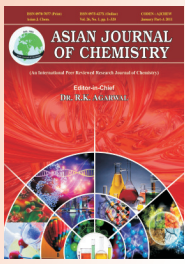

Synthesis of Glutathione Modified CdSe Quantum Dots and Its Application in Determination of Trace Hg^{2+} Ions

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The water-soluble glutathione (GSH) modified CdSe quantum dots (QDs) were prepared. Results show that the optimum $NaBH_4$:Se:(Cd^{2+}): glutathione molar ratio is obtained to be 3:1:3:9. Meanwhile, the glutathione modified CdSe quantum dots synthesized by the optimum process have a single face centered cubic phase. It is found that the fluorescence quenching occurred as Hg^{2+} ions interact with glutathione modified CdSe quantum dots. Hg^{2+} ions can be determined in the concentration range of 0.3-15 μg/L, which is proposed to determine the trace quantities of Hg^{2+} ions as fluorescence probe.

Keywords: CdSe, Quantum dots, Glutathione, Fluorescence probe.

INTRODUCTION

Nowadays, because of some human activities such as combustion and fusion of solid wastes, mercury directly enters to soil or water. Mercury in water contamination can enter the body of marines and then nutritious chain of human beings. Mercury(II) ion, as a hypertoxic heavy metal ion, poses a direct threat to the central nerve and endocrine systems[1]. Because of high poisonousness of Hg^{2+} ion, identification of ultra trace amounts of Hg^{2+} ions in environmental water and in the body of aquatics like fishes is of great importance and worthy of high attention to chemists. At present, there are many methods for detecting Hg^{2+} ions in water, such as cold-vapor atomic absorption spectrometry[2], atomic fluorescence spectrometry[3], inductively coupled plasma-mass spectrometry[4], spectrophotometry[5] and voltammetry[6], *etc*. However, these methods are time-consuming for sample's preparation, expensive and require sophisticated equipment[7]. Therefore, simple, rapid and selective methods for detecting Hg^{2+} ions are still in demand.

Recently, semiconductor nanocrystals, often referred to as quantum dots, have attracted increasing attention due to their quantum confinement effect and remarkable optical, electrical properties[8,9], which has been widely used in biology, medicine, analytical chemistry, especially in sensors[10-12]. The fluorescent properties of quantum dots are sensitive to their surface states, which can be used to detect heavy metal ions in aqueous solutions. When quantum dots are synthesized in aqueous solution, sulfhydryl compounds are often used as a modifier and stabilizer[13,14]. However, the sulfhydryl compounds are toxic substance and very sensitive to light, which is easy to fall off from the surface of quantum dots and then causes the agglomeration of quantum dots.

Glutathione (GSH) is a small molecule peptide found in most organisms and can be used to detoxify heavy metal ions in medicine due to its chelating capability[15]. Recently, glutathione has been also used in the synthesis of CdTe and ZnS nanocrystals as a modifier and stabilizer[15,16]. In the present study, the water-soluble glutathione modified CdSe quantum dots have been synthesized and the influence of synthesis condition on fluorescence intensity of quantum dots and their interaction with Hg^{2+} ions have been investigated.

EXPERIMENTAL

Selenium powder (99.99 %), $Cd(OAc)_2{\cdot}2H_2O$ (99.99 %) and glutathione (98 %), were purchased from Aladdin Reagent Co. Ltd. $NaBH_4$ (96 %), NaOH (85 %) and $HgCl_2$ (99.5 %) were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents used were of analytical grade without further purification. The water used in the experiments was deionized to a resistively of 18.2 MΩ/cm.

Room temperature fluorescence (FL) spectra were recorded by a FL3-211-Pluminescence spectrometer (Jobin-Yvon, French). X-ray diffraction analysis was performed using powder X-ray diffraction (Bruker D2, Germany).

Preparation of glutathione modified CdSe quantum dots were synthesized in an aqueous solution according to the literature procedure with some modification[17]. 0.1 mmol Se and

0.1 mmol $NaBH_4$ were transferred into three-necked flask under N_2-flow followed by the addition of 10 mL deionized water. The mixture was reacted under magnetic stirring in a water bath at 60 °C for 1 h to form the colourless NaHSe solution. Then 0.3 mmol $Cd(OAc)_2{\cdot}2H_2O$ was diluted to 100 mL in a three-necked flask in the presence of 0.9 mmol glutathione as a stabilizing agent under N_2-flow and the pH value was adjusted to 8 by dropwise addition of 1 M NaOH aqueous solution. The freshly prepared NaHSe solution was injected slowly into the Cd precursor solution under vigorous stirring. The molar ratio of $NaBH_4$:Se:Cd^{2+}:glutathione was fixed at 1:1:3:9. The resulting mixture was refluxed at 90 °C for 1 h under N_2 atmosphere protection to promote the growth of quantum dots. Other $NaBH_4$:Se:Cd^{2+}:glutathione molar ratios (2:1:3:9, 3:1:3:9, 4:1:3:9, 5:1:3:9, 6:1:3:9 and 3:1:3:12, 3:1:3:15, 3:1:3:18) were investigated to optimize the reaction conditions.

The general procedure for Hg^{2+} detection was as follows: in a dry 10 mL volumetric flask, 0.5 mL PBS buffer solution was added. Then a series of 100 µL different concentration $HgCl_2$ standard solution was transferred into a 10 mL volumetric flask and finally diluted to 10 mL with water and mixed thoroughly. The relative fluorescence intensity was measured at λ_{ex} = 430 nm.

RESULTS AND DISCUSSION

In order to study the influence of $NaBH_4$ concentration on the fluorescence intensity of glutathione modified CdSe quantum dots, the molar ratio of Se:Cd^{2+}:glutathione keeps unchanged. Fig. 1 shows fluorescence spectra of synthesized CdSe quantum dots with the different molar ratio of $NaBH_4$:Se:Cd^{2+}:glutathione. As the concentration of $NaBH_4$ is increased, the fluorescence intensity is firstly enhanced and then weakened. For the CdSe quantum dots synthesized by high $NaBH_4$ concentration, the low fluorescence intensity is due to the quenching effect of the fluorescence. Excessive $NaBH_4$ can hydrolyze to form $NaBO_2$, which hinders the combination of Cd^{2+} and NaHSe.

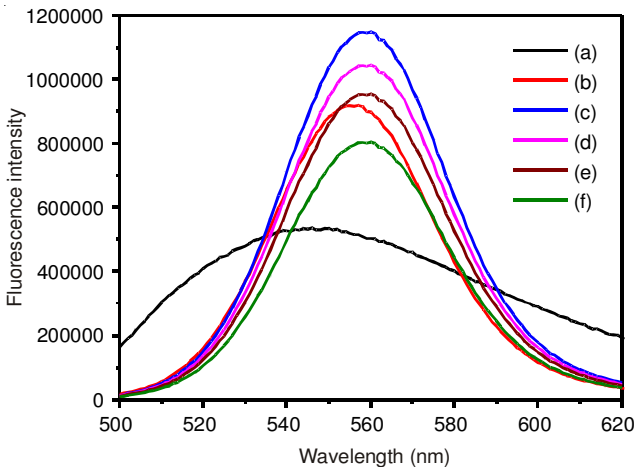

Fig. 1. Fluorescence spectra of synthesized CdSe quantum dots with the different molar ratio of $NaBH_4$:SeCd^{2+}:GSH: (a) 1:1:3:9, (b) 2:1:3:9, (c) 3:1:3:9, (d) 4:1:3:9, (e) 5:1:3:9 and (f) 6:1:3:9

Glutathione has two -COOH group, which can provide further reactions and functional graft. So it is necessary to study the influence of glutathione concentration on the fluorescence intensity of glutathione modified CdSe quantum dots. Fig. 2 shows fluorescence spectra of synthesized CdSe quantum dots with the different molar ratio of $NaBH_4$:Se:Cd^{2+}:GSH. As the concentration of glutathione is increased, the fluorescence is quenched.

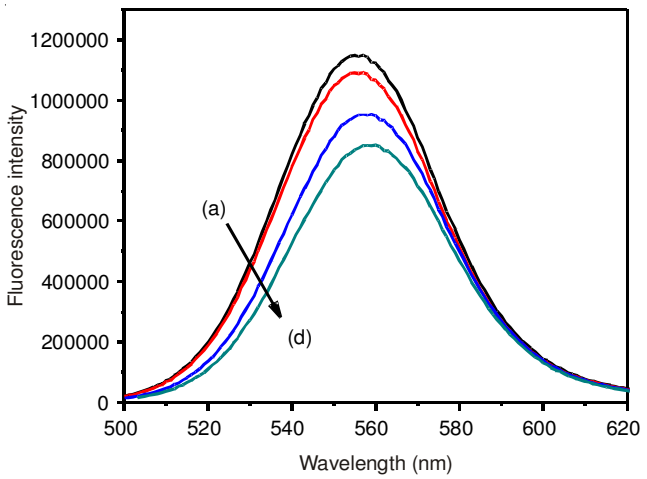

Fig. 2. Fluorescence spectra of synthesized CdSe quantum dots with the different molar ratio of $NaBH_4$:SeCd^{2+}:GSH: (a) 3:1:3:9, (b) 3:1:3:12, (c) 3:1:3:15 and (d) 3:1:3:18

Based on the above analysis, the optimum $NaBH_4$:Se:Cd^{2+}:GSH molar ratio is obtained to be 3:1:3:9. The maximum λ_{em} of glutathione modified CdSe quantum dots synthesized by the optimum process is 552 nm. Fig. 3 gives XRD pattern of glutathione modified CdSe quantum dots synthesized by the optimum process. It is obvious that there is a single face centered cubic phase without impurity phase for glutathione modified CdSe quantum dots, according to JCPDS card No. 19-0191.

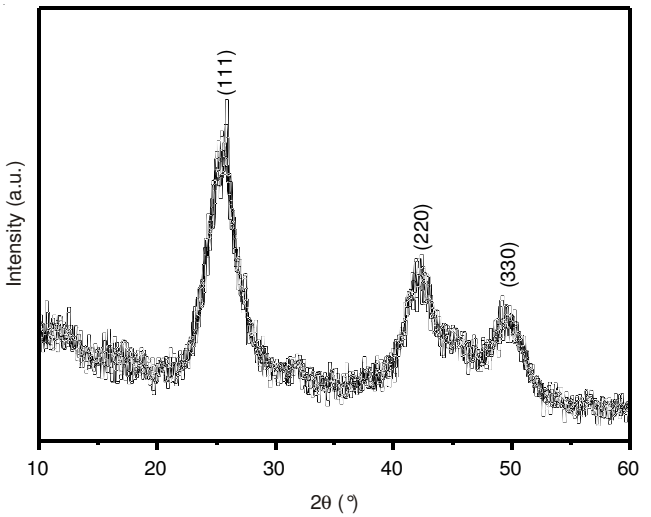

Fig. 3. XRD pattern of CdSe quantum dots synthesized by the optimum process

The glutathione modified CdSe quantum dots synthesized by the optimum process is used to detect Hg^{2+} ions. Fig. 4 shows fluorescence spectra of CdSe quantum dots in the presence of various concentration of Hg^{2+} ions in deionized

water. As the concentration of Hg^{2+} ions is increased, the fluorescence intensity of glutathione modified CdSe quantum dots is significantly decreased. The low fluorescence intensity is due to the quenching effect of the fluorescence. The fluorescent properties of quantum dots are sensitive to their surface states. The fluorescence quenching phenomenon can be understood due to facilitating non-radiative e^-/h^+ recombination annihilation on the surface of glutathione modified CdSe quantum dots resulting from an effective electron transfer process between the surface functional groups and Hg^{2+} ions base on the strong affinity with the functionalized CdSe quantum dots[18]. A linear relationship between $\Delta F/F_0$ (F and F_0 are the fluorescence intensities of glutathione modified CdSe quantum dots at given Hg^{2+} ions concentration and Hg^{2+}-free solution, respectively and then $\Delta F = F_0$-F) and the concentration of Hg^{2+} ions in the range from 0.3 to 15 μg/L (shown in the inset of Fig. 4) is found, which can be defined approximately by the relation $\Delta F/F_0 = 0.04513C + 0.1682$.

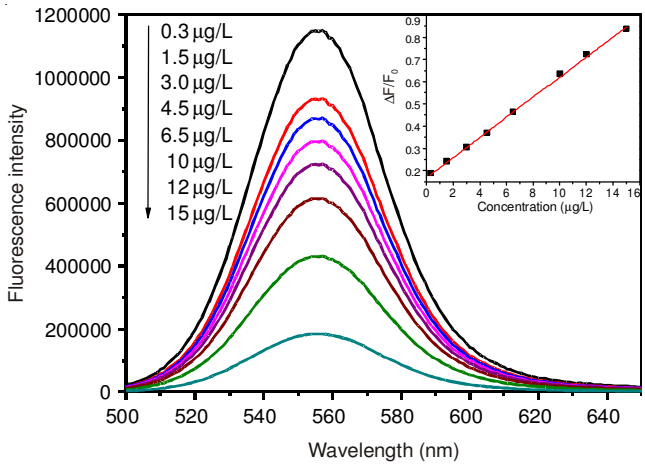

Fig. 4. Fluorescence spectra of CdSe quantum dots in the presence of various concentration of Hg^{2+} ions in deionized water. Inset show relationship between $\Delta F/F_0$ and the concentration of Hg^{2+} ions in deionized water.

Conclusion

A simple and environmentally benign process has been developed to synthesize water-soluble glutathione modified CdSe quantum dots. As the concentration of $NaBH_4$ is increased, the fluorescence is firstly enhanced and then quenched. On the other hand, the fluorescence is quenched with increasing the concentration of glutathione. Finally, the optimum $NaBH_4$:Se:Cd^{2+}:GSH molar ratio is obtained to be 3:1:3:9. The fluorescence quenching occurred when Hg^{2+} ions interact with glutathione modified CdSe quantum dots. Hg^{2+} ions can be determined in the concentration range of 0.3-15 μg/L.

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