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ZnS nanoparticles for high-sensitive fluorescent detection of pyridine compounds

Zhe Li, Jiantao Ma, Yanqing Zong, Yi Men [*]

Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, PR China

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ABSTRACT

Water-soluble ZnS nanoparticles (NPs) capped with alpha-thioglycerol (TGO) have been synthesized through a chemical precipitation method. The nanoparticles were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), UV–Vis absorption spectroscopy, fluorescence spectroscopy, and fluorescence decay spectroscopy. Results showed that the TGO-capped ZnS NPs exhibited the cubic zinc blende structure, and the average size was found to be ~2.94 nm. Compared with the bulk ZnS, the band-gap energy of the nanoparticles (4.40 eV) rose significantly due to the strong quantum confinement. The TGO-capped ZnS NPs showed a characteristic blue luminescence corresponding to two emission peaks at 419 nm and 460 nm associated with the defect states of the nanoparticles. Such functionalized nanoparticles can be used as fluorescent sensor for the determination of pyridine compounds because they quenched the fluorescence of the nanoparticles effectively. The detection limit was 6.76×10^{-5} M for pyridine. The quenching mechanism was studied in detail, and the results demonstrated the existence of dynamic quenching processes. The proposed sensing method is not only sensitive, simple, fast and low cost, but also meaningful for practical applications.

1. Introduction

Nowadays, nanostructure materials are not only at the very frontier of fundamental materials research, but they have also entered into people's daily life step by step [1–3]. With the deteriorating trend of environmental pollution and the rising awareness of the public vulnerability to the chemical and biological threats, the detection techniques with both high sensitivity and reliability are demanded urgently. The application of nanostructure materials to the design of chemical sensors has attracted considerable attention due to their tremendous specific surface, high activity, excellent anti-photobleaching and tunable emission [4–6]. As a developing semiconductor material star, ZnS nanoparticles (NPs) are low toxicity materials with a wide band gap [7] of ~3.72 eV (cubic zinc blende structure) and ~3.78 eV (hexagonal wurtzite structure), exhibiting remarkable optical and electrical properties [8–11], which suggest that they may be particularly well-suited for the manufacture of novel sensor. At present, ZnS NPs can be used to detect the DNA molecular [12,13], protein [14], organic molecule [15–17], pH value [18,19], metal ion [20–23], etc.

Pyridine and its derivatives are important chemical raw materials, which are mainly used as solvent and intermediate in the production of agricultural chemicals, dyestuffs, additives, drugs, and others. However, this foul-smelling and toxic substance could intrude into the human living environment through the discharge of various industrial effluents and exhaust gases. Besides, pyridine and its derivatives are frequently found in the cigarette smoke [24], and also generated during the putrefaction processes of certain foodstuffs [25]. If inhaled, ingested or absorbed through skin, these chemicals can cause many potentially harmful effects on human body, which include nausea, vomiting, headaches, coughing, asthmatic breathing, laryngitis and even cancers [26]. Consequently, the detection of pyridine has become a heightened need for the health of human and the development of environment-friendly society. Various approaches have been established for the detection of pyridine, such as barbituric acid spectrophotometry [27], high-performance liquid chromatography [28,29], gas chromatography [30–32], liquid chromatography–mass spectrometry (LC–MS) [24], gas chromatography–mass spectrometry (GC–MS) [33,34], optical fiber sensing method [35], but the method based on the fluorescent of nanomaterials has not been reported so far.

Herein, we report a very simple method for the synthesis of TGO-capped ZnS NPs with a narrow size distribution and good optical properties. Compared with other traditional methods, the preparation is a one-step approach using non-toxic and low cost raw materials, and the obtained nanoparticles are water-soluble, which could expand their applying areas particularly in chemical and biological fields. When the pyridine is added to TGO-capped ZnS NPs aqueous solution, it could attach to the surface of ZnS NPs, and result in a significant fluorescence quenching. Based on this phenomenon, a novel fluorescent sensor for the determination

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[*] Corresponding author. Tel./fax: +86 010 58805186.
E-mail address: menyi@bnu.edu.cn (Y. Men).

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of pyridine compounds is proposed, and the performance of this ZnS NPs sensor exhibits high sensitivity, simple, fast and low detection limit. The possible mechanism of fluorescence quenching is also discussed.

2. Experimental

The TGO-capped ZnS NPs were synthesized by chemical precipitation method as follows: 1.00 g Zn $(CH_3COO)_2 \cdot 2H_2O$ (Tianjin Bodi Chemical Holding Co., Ltd.) and 1.20 g alpha-thioglycerol (TGO, Shanghai TCI Development Co., Ltd.) were dissolved in 285 mL secondary distilled water (homemade). The TGO acts as a capping agent to prevent the agglomeration of particles and stabilize the ZnS NPs. The pH value of the mixed solution was adjusted to 11.20 by 2 M NaOH solution. After about 30 min of bubbling nitrogen to drive off the oxygen from the reaction system, 10 ml of 0.214 M $Na_2S \cdot 9H_2O$ (Wako Pure Chemical Industries, Ltd.) solution was slowly injected to the above solution to yield a stoichiometric ratio of 0.47 for $[S^{2-}]/[Zn^{2+}]$. The mixture was heated to reflux for 18 h. After cooling down to the room temperature naturally, the colorless and transparent liquid was concentrated to 20 ml through the rotary evaporator, and 100 ml ethanol was then added to generate white precipitations, which was followed by centrifuging and washing with ethanol several times. Finally, the products were dried in vacuum for 24 h.

During the fluorescence measurement, the concentration of TGO-capped ZnS NPs aqueous solution was stabilized at 0.20 mg/ml, and 6.67×10^{-2} M Na_2HPO_4–KH_2PO_4 buffer solution (pH = 8.86) was chosen for the system to keep the pH value constant. A known concentration of pyridine solution was added into ZnS NPs solution and mixed entirely to monitor the change of fluorescence emission intensity.

High-resolution transmission electron microscope (HRTEM) images were observed on a JEOL JEM-2010 electron microscope operated at 200 kV, and Nano-Measurer 1.2 software was used to evaluate the size of each nanoparticle. The wide-angle X-ray diffraction (XRD) measurement was determined by a PAN-alytical X'Pert PRO MPD X-ray diffractometer using a Cu Kα radiation source. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet-380 FT-IR spectrometer. UV–Vis absorption measurement of TGO-capped ZnS NPs was carried out with a Purkinje General TU-1901 UV–Vis spectrometer. Fluorescence spectra were achieved by a Varian Cary Eclipse fluorescence spectrophotometer at the room temperature. Fluorescence decay behaviors were measured by an Edinburgh FLS920 transient/steady-state luminescence spectrometer using a nanosecond flash lamp as excitation sources.

3. Results and discussion

FT-IR spectra of TGO and TGO-capped ZnS NPs are shown in Fig. 1. A broad absorption band in the 3000–3696 cm^{-1}region is associated with the stretching vibrations of hydroxyl groups in bound water and TGO. The peaks at 2930 and 2879 cm^{-1} are assigned to the stretching vibrations of C–H groups of TGO on the surface of ZnS NPs. The deformation vibrations of the methine and methylene groups in TGO located at 1633 and 1417 cm^{-1} are also found. The characteristic vibrations at 1064 and 1035 cm^{-1} belong to the C–O group in TGO. Moreover, the absorption peak of the S–H vibration in TGO at about 2554 cm^{-1} cannot be observed, indicating that the sulfhydryl groups of the TGO have successfully attached to the surface of ZnS NPs [36], which leads the ZnS NPs to be water-soluble. Possible surface structure of TGO-capped ZnS NPs is shown in Scheme 1.

X-ray diffraction studies were carried out to establish the ZnS crystallite structure and obtain an approximate average size of the ZnS NPs, as shown in Fig. 2a. The three peaks appearing at about 28.6°, 47.8°, and 56.6° respectively correspond to the (1 1 1), (2 2 0), and (3 1 1) planes of zinc blende crystal structure, which match well with the standard card (JCPDS 05-0566) denoted in Fig. 2b. As expected, the XRD peaks of ZnS NPs are prominently broadened compared to the corresponding bulk form, which is the characteristic of nanosized particles. The average size of the crystallite (D) was estimated from the line broadening of the XRD peaks by using the Debeye–Scherrer equation [37],

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the wavelength of X-ray radiation (for Cu Kα1 radiation, λ = 1.5406 Å), β is the full-width at half-maximum (FWHM) of the diffraction peaks expressed in radians, and θ is the angle of diffraction. After the contribution from $K_\alpha 2$ radiation was removed by fitting a cubic spline via the MDI Jade 5.0 software, the calculated crystallite size is around 2.88 nm, and a comparison of this size with the size determined from HRTEM will be discussed later in the article.

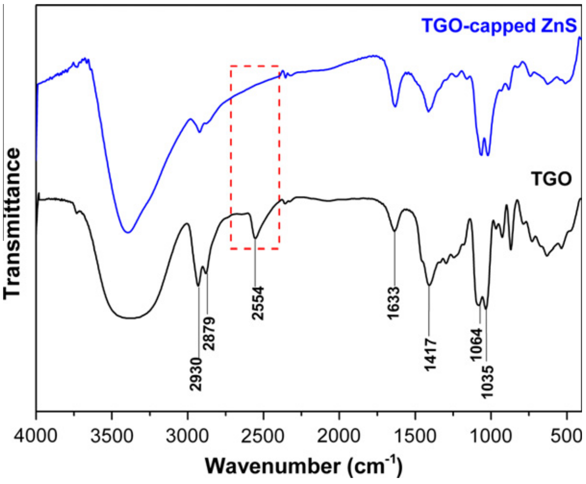
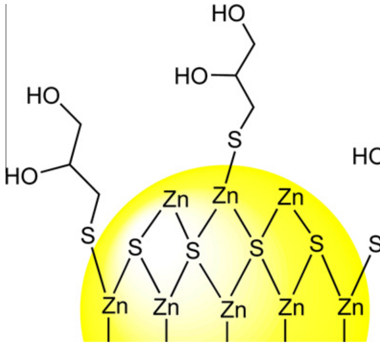


Fig. 1. FT-IR spectra of TGO and TGO-capped ZnS NPs.



Scheme 1. Possible surface structure of TGO-capped ZnS NPs.

Fig. 3a shows a high-resolution transmission electron microscopy (HRTEM) image of TGO-capped ZnS NPs, revealing that the

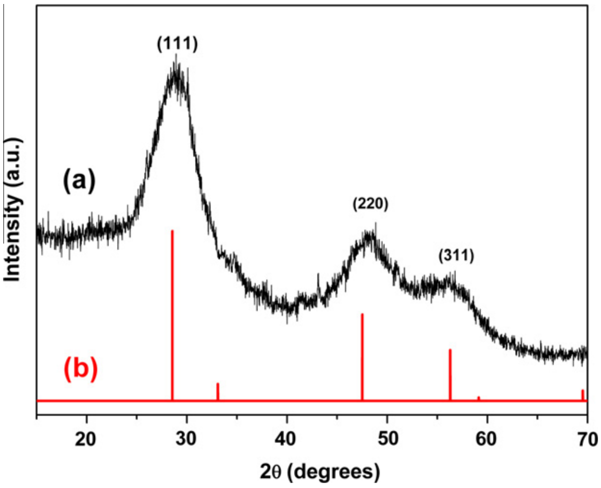


Fig. 2. (a) The wide-angle XRD pattern for TGO-capped ZnS NPs. (b) Standard XRD pattern of bulk ZnS with the zinc blende structure (JCPDS 05-0566).