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Application of functionalized ZnS nanoparticles to determinate uracil and thymine as a fluorescence probe

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ABSTRACT

ZnS nanoparticles were prepared by hydrothermal method and modified with mercaptoacetic acid in this paper. The functionalized nanoparticles were characterized using transmission electron microscopy (TEM), X-ray diffractometer (XRD) and photoluminescence spectroscopy. They were used as fluorescence probes in the determination of uracil and thymine. Under the optimum conditions, the fluorescence of functionalized ZnS nanoparticles was quenched by uracil and thymine, respectively. The responses are linearly proportional to the concentrations of uracil and thymine both between 0.8×10^{-5} and 9.6×10^{-5} mol L^{-1} and the limits of detection are 0.9×10^{-6} and 0.4×10^{-5} mol L^{-1} for uracil and thymine, respectively.

1. Introduction

In recent years, the newly developed semiconductor nanoparticles have attached most important application in clinical diagnostics, biomedical research, and studies in life sciences because these nanoparticles can work as fluorescence probes which have narrow, tunable, symmetric emission spectrum, and are more stable against photobleaching, and do not suffer from blinking in comparison with the conventional fluorophores [1]. Various functionalized nanoparticles have been prepared to determinate biological materials, such as nucleic acids [2,3] and proteins [4,5] and the like.

Uracil and thymine are one of the important bases of RNA and DNA, respectively. They are frequent models of theoretical studies due to their considerable importance from biological and clinical points of view [6–9]. The quantitative analysis of uracil and thymine is very essential and medically significant in some instances. For example, for the patients with dihydropyrimidine dehydrogenase (DPD) deficiency, the determination of the concentrations of uracil and thymine in blood and/or in urine is very significant to diagnose the patients prior to 5-fluorouracil treatment [10]. Because dihydropyrimidine dehydrogenase is the rate-limiting enzyme in the pathway of uracil and thymine catabolism [11], whose deficiency inhibits the metabolization of uracil and thymine, which consequently results in large amounts of uracil and thymine in urine and/or blood [12,13]. And besides abnormally a high urinary level of uracil has been in some defects of urea cycle [14].

To date, different techniques have been reported to detect uracil and thymine. The concentrations of uracil and thymine are measured with monoclonal antibodies [15,10], high-performance liquid chromatography [16,17], voltammetric determination [18], capillary electrophoresis [19], gas chromatography–tandem mass spectrometry [20], and capillary zone electrophoresis [14] and so on. However, the detection method of uracil and thymine with nanoparticles as fluorescence probes has not been reported until now. Compared with the methods mentioned above, the fluorescent probes method is obviously simpler and rapider in the experimental processes and more sensitive for different fluorescent emission wavelengths corresponding to different molecular structures.

In this paper, ZnS nanoparticles were synthesized and functionalized with mercaptoacetic acid. The combination of functionalized ZnS nanoparticles with different bio-molecules can make some differences in fluorescent intensity and/or fluorescent emission wavelength between each other. Under the optimum conditions in our study, the fluorescence of functionalized ZnS nanoparticles can be quenched by uracil and thymine, respectively, and the extent of the fluorescence intensity quenchment is proportional to the concentrations of the analytes. The two analytes were distinguished and determined according to the different fluorescent emission wavelengths. The proposed method leads to a particularly sensitive and quantitative assay, permitting limits of 0.9×10^{-6} and 0.4×10^{-5} mol L^{-1} for uracil and thymine, respectively. This method is simple, rapid and sensitive.

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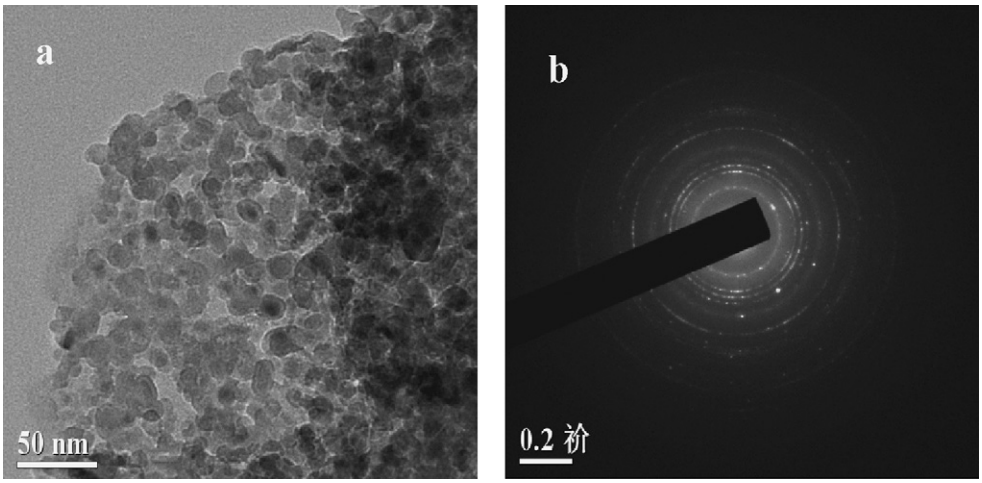

Fig. 1. (a) TEM images of ZnS nanoparticles and (b) SAED pattern of ZnS nanoparticles.

2. Experiments

2.1. Apparatus

TEM images and electron diffraction spectra were generated on a Hitachi model-800 transmission electron microscopy (TEM). High-resolution transmission electron microscopy (HRTEM) analyses were performed using JEM-2010F. Powder X-ray diffraction (XRD) patterns of the samples were measured on a rigaku D/max 2550 X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.15418 nm) (Japan). Fluorescence measurements were performed using a RF-5301PC spectrofluorometer (Shimadzu, Japan) with a 1 cm quartz cell. DZ-1 titration equipment and 2# magnetic stirrer (The Second Analytical Instruments Co., Shanghai, China) were used. All pH measurements were made with a pHS-3C pH meter (Analytical Instruments Co., Shanghai, China).

2.2. Reagents

All chemicals used were of analytical grade or of the highest purity available. All solutions were prepared with double distilled water. Mercaptoacetic acid was purchased from Shanghai Lingfeng Chemical Reagent Co. (China). Uracil, thymine, sodium carbonate, sodium bicarbonate and zinc powder were acquired from Shanghai Sinopharm Chemical Reagent Co. Ltd. (China) and used as received.

2.3. The preparation of nano-ZnS fluorescence probe

In a typical procedure, the mixture of 0.4062 g Zn powder (99.95%) and 0.1154 g S powder (99.95%) was put into a Teflon lined autoclave with 30 mL capacity. And then 20 mL 3 mol L^{-1} NaOH solution was added into the autoclave. The autoclave was sealed, maintained at 180 °C for 24 h, and then cooled to room temperature naturally. At last, the white product of ZnS solid powder was collected by filtration, washed with distilled water and ethanol, and then dried at 80 °C in vacuum.

At room temperature (around 25 °C), under vigorous stirring, 5 mL 0.10 mol L^{-1} mercaptoacetic acid solution was added into 50 mL solution containing 0.01 mol L^{-1} ZnS nanoparticles drop by drop in the circumstances of buffer solution of sodium carbonate and sodium bicarbonate at pH 9–10 for 3 h. The relative concentration of ZnS nanoparticles and mercaptoacetic acid was 1:1. Lightproofly sealing the colloidal solution for one night. Taking 6 mL functionalized nanoparticles solution into a 500 mL brown jar and then storing mixture in buffer solution of sodium carbonate and sodium bicarbonate at room temperature. The obtained solution was ready for the following experiment.

2.4. Determination of uracil and thymine with functionalized nano-ZnS fluorescence probe

The functionalized nanoparticles solution was used to detect uracil and thymine with the following procedure. 20 mL of functionalized nanoparticles solution and a series of known volumes of uracil or thymine standard solution were added into a dry 25 mL calibrated flask. The solution was diluted to volume with double distilled water, and then the fluorescence intensity was measured at 262 and 275 nm for uracil and thymine, respectively.

3. Results and discussion

3.1. TEM and XRD images of the prepared ZnS nanoparticles

The morphologies and structures of products were investigated by TEM and powder XRD. Fig. 1a shows that monodisperse ZnS nanoparticles with defined shape and diameter about 14 nm could be obtained via hydrothermal process. Fig. 1b shows the typical electron diffraction pattern of nanoparticles, which indicates that they are poly-crystal.

HRTEM images of the Nps clearly demonstrate the lattice fringes (see Fig. 2). From this image, it is very clear that the nanoparticle is a single crystal and the measured *d* spacing along the [1 1 1] direction is 3.0470 Å, the measured *d* spacing along the [3 1 1] direction is 1.6119 Å, which is in good agreement with the lattice constant of cubic ZnS.

Fig. 3 shows powder XRD patterns of ZnS nanoparticles. It is obvious that all of the XRD peaks of the ZnS nanoparticles correspond to the (1 1 1), (2 2 0), and (3 1 1) planes of cubic ZnS structure, which is consistent with the values in the stand card (JCPDS No. 50566). According to the Debye–Scherrer equation: $D = 0.89\lambda/\beta\cos\theta$, the average crystallite size is 14.11 nm through calculating, which is in good agreement with the particle size estimate from the TEM images.

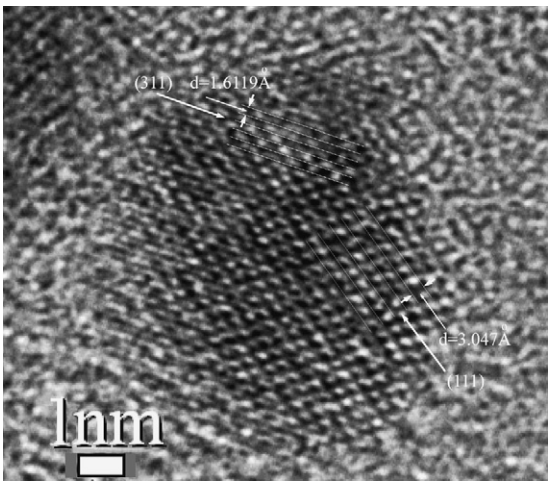

Fig. 2. HRTEM pattern of ZnS nanoparticle.