Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 121 (2014) 350–354

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Preparation of ZnS:Ni/ZnS quantum dots with core/shell structure and application for detecting cefoperazone–sulbactam

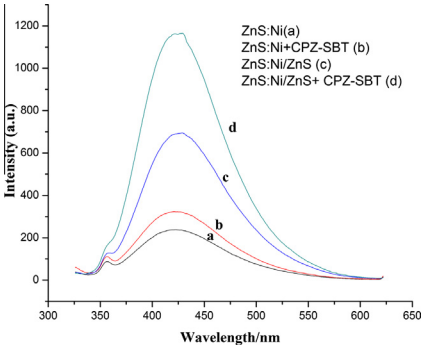
Jianying Qu [a,*], Zhuanying Zhu [a], Changda Wu [a], Lianjie Zhang [a], Jianhang Qu [b]

[a] Institute of Environmental and Analytical Sciences, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, PR China
[b] College of Bioengineering, Henan University of Technology, Zhengzhou, Henan 450000, PR China

HIGHLIGHTS

- ZnS:Ni/Zn**S** QDs were synthesized easily with nontoxic.
- It shows fluorescent characteristic with good water-solubility and stability.
- ZnS:Ni/Zn**S** QDs was firstly used as fluorescent probe to detect CPZ–SBT.
- This novel method is sensitive with good selectivity and a low detection limit.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 August 2013
Received in revised form 25 October 2013
Accepted 31 October 2013
Available online 7 November 2013

Keywords:
Cefoperazone
Sulbactam
Quantum dots

ABSTRACT

ZnS:Ni quantum dots (QDs) have been synthesized via a water-soluble route, which were coated by ZnS shell through surface modification to give ZnS:Ni/ZnS QDs. The QDs were characterized by atomic force microscope, X-ray diffraction, infrared spectrometry and fluorescent spectrometry. Then, a novel method for the determination of cefoperazone–sulbactam (CPZ–SBT) in aqueous solutions has been developed based on the enhancement of fluorescence of ZnS:Ni/ZnS QDs in the presence of CPZ–SBT. Under the optimal conditions, the enhanced fluorescence intensity (ΔF) was proportional to CPZ–SBT concentration in the range of 8.0×10^{-6}–1.0×10^{-4} g/L with a detection limit of 1.0×10^{-7} g/L. The method was employed for the determination of CPZ–SBT in sample to give satisfactory result. Compared with others, this method was more sensitive, fast and simple with low limit detection.

Introduction

Cefoperazone–sulbactam (CPZ–SBT) is a combination of antibiotics and enzyme inhibitor. Cefoperazone has B-lactam structure and sulbactam has semi-synthetic B-lactamase inhibitors, when used in combination, it can enhance antibacterial effect and antibacterial spectrum. And it has strong inhibitory effect against staphylococcus, β-lactamase, which were used for the treatment of various diseases [1,2]. At present, a few methods to determine CPZ–SBT have been reported mainly by high performance liquid chromatography (HPLC) [3–5] and ultra performance liquid chromatography (UPLC) [6].

Quantum dots (QDs) have attracted great interest due to their unique properties and potential applications in the past few decades. Recently, the applications of QDs in fluorescent probes [7], analysis and the detection [8], optical device [9] and fingerprint collection [10,11] are studied. Research showed that core/shell structure and alloy structure QDs could both significantly change the optical and electrical properties [12], which have attracted more and more attention.

Here, ZnS:Ni/ZnS QDs with core/shell structure were prepared successfully. And based on the enhancement of fluorescence of ZnS:Ni/ZnS QDs in the presence of CPZ–SBT, a novel method to

* Corresponding author. Tel./fax: +86 0378 3881589.
E-mail addresses: qujy@henu.edu.cn, lilyqujy@126.com (J. Qu).

1386-1425/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2013.10.096

detect CPZ–SBT was established. Compared with other reports [3,4,6], this method was more simple, sensitive and rapid with low limit detection with potential prospect for practical applications.

Experimental

Apparatus

SPA400 scanning probe microscope (Japan's seiko), F-7000 spectrofluorometer (Japan's Hitachi), VATAR360 type Fourier transformed infrared spectrometer (the United States, high-power company), UV-5400 UV spectrophotometer (American thermoelectric company), X-PertPro type X-ray diffraction (Dutch Philips), Phs-3 CT pH meter (Shanghai, Dapu instrument Co.), DF-101 Z water bath pot and DZF-250 vacuum drying oven (Zhengzhou, the Great Wall traded Co.) were used for experiments.

Materials and reagents

$HSCH_2COOH$, NaOH (Tianjin Kemiou chemical reagent Co.), $Zn(Ac)_2{\cdot}2H_2O$, $Ni(Ac)_2{\cdot}4H_2O$, $Na_2S{\cdot}9H_2O$ (Tianjin chemical reagent Co.), CPZ–SBT (Shandong runze pharmaceutical Co.), KH_2PO_4-K_2HPO_4, KH_2PO_4-sodium citric, citric acid-sodium citric, and all other materials were analytical reagent grade. Doubly distilled water was used throughout.

Synthesis of ZnS:Ni/ZnS QDs

By modifying the synthesis methods reported [13], core/shell structure ZnS:Ni/ZnS QDs were obtained according to the following steps: 20 mL 0.1 mol/L of $Zn(CH_3COO)_2$, 2 mL 0.005 mol/L of $Ni(CH_3COO)_2$, 0.28 mL $HSCH_2COOH$ and 68 mL doubly distilled water were added into the three neck flask in turn and pH was adjusted to 11 with NaOH solution. The mixture was purged with N_2 for 30 min. After being heated to 80 °C, 10 mL 0.1 mol/L of Na_2S solution was added into the solution quickly with stirred magnetically and the mixture was stirred at 80 °C for 2 h. Then, 100 μL 1 mol/L of $Zn(CH_3COO)_2$, 12 μL $HSCH_2COOH$, 25 μL 8 mol/L of NaOH and 25 μL 2 mol/L of Na_2S were added respectively with stirred for 2 min. The above steps were repeated for 5 times.

After 5 min, the proper amount of ethanol was added until a homogeneous solution was obtained. The obtained dispersions were washed respectively by water and ethanol, and centrifuged. This operation was repeated for several times to remove impurities. Then the products were dried in a hot air oven at 65 °C for 5 h to obtain functionalized ZnS:Ni/ZnS QDs with approximate same size.

Results and discussions

Characterization of the ZnS:Ni/ZnS QDs

Dynamic force microscope (DFM) characteristic

Fig. 1a and b was DFM images of ZnS:Ni/ZnS QDs without and with CPZ–SBT. It was obviously that the synthetic ZnS:Ni/ZnS QDs were uniform with the average size of 60 nm. After interacting with CPZ–SBT, the diameter of ZnS:Ni/ZnS QDs became larger with the average size of about 70 nm.

X-ray diffraction (XRD) characterization

The XRD figures of ZnS, ZnS:Ni and ZnS:Ni/ZnS were obtained and shown in Fig. 2. It was clear that the three diffraction peaks for the three samples were appeared at the same positions, which were corresponding with the three peaks of ZnS (3 1 1), (2 2 0) and (1 1 1), respectively. Through comparison, Doping with Ni and further coating with ZnS shell did not change peak positions, intensity and number of ZnS, which demonstrated that ZnS:Ni/ZnS has the same crystal structure with ZnS [13].

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) characteristic

ICP-AES was employed to test whether Ni existed in ZnS:Ni/ZnS QDs. The experimental results showed that Ni was doped into ZnS:Ni/ZnS successfully and the concentration of Ni in synthetic QDs was 0.301 mg/L. Therefore, the doping percentage of Ni in ZnS:Ni/ZnS was calculated of 1.0%.

Infrared radiation (IR) characterization

The IR spectra of CHCOOHSH (TGA) and ZnS:Ni/ZnS were shown in Fig. 3. Through comparing Fig. 3a and b, the peak of S—H of TGA at 2568 cm^{-1} disappear for ZnS:Mn QDs, while peaks for C═O at 1581 cm^{-1} and 1386 cm^{-1} appeared. This demonstrated that TGA have combined with the surface of ZnS:Ni/ZnS QDs successfully through sulfydryl. Peak of C═O of ZnS:Ni/ZnS had a little hypochromatic shift due to substituent of C═O made change.

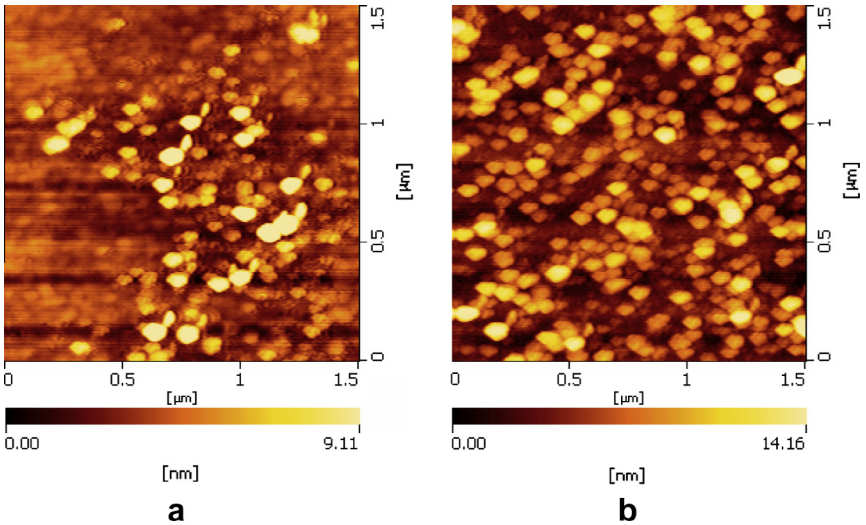


Fig. 1. DFM images of ZnS:Ni/ZnS QDs (a) and ZnS:Ni/ZnS QDs + CPZ–SBT (b).