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Optical and photocatalytic properties of *Corymbia citriodora* leaf extract synthesized ZnS nanoparticles

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HIGHLIGHTS

- ZnS nanoparticles were first time synthesized using *Corymbia citriodora* leaf extract.
- Quantum confinement effects was observed in biosynthesized ZnS nanoparticles.
- Biosynthesized ZnS was used for photodegradation of methylene blue.

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ABSTRACT

ZnS nanoparticles were biosynthesized via a green and simple method using *Corymbia citriodora* leaf extract as reducing and stabilizing agent. The biosynthesized ZnS nanoparticles were in the size range of 45 nm with a surface plasmon resonance band at 325 nm. XRD analysis revealed that the nanoparticles were in the sphalerite phase. Quantum confinement effects of biosynthesized ZnS nanoparticles were observed using photoluminescence spectroscopy. The photocatalytic activity of the ZnS nanoparticles has been investigated by degradation methylene blue under UV light irradiation. Due to the smaller size and excellent dispersicity, the biosynthesized ZnS nanoparticles showed a superior photocatalytic performance compared with that of chemical synthesize ZnS nanoparticles.

1. Introduction

Nanomaterials have wide-ranging applications and implications in a variety of areas, including physics, chemistry, electronics, optics, materials science and biomedical sciences. The biologically diverse plant environment has a great promise for nanotechnology. Biosynthetic and environment friendly technology for the synthesis of nanomaterials are believed to be nontoxic, bio-safe, and biocompatible and have been used as drug carriers, cosmetics and fillings in medical materials [1–3].

Zinc sulfide (ZnS) is group II–IV binary compound semiconductor and it has traditionally shown exceptional physical and chemical properties and a promise for novel diverse applications, such as electroluminescence, sensors, lasers, and so on [4–7]. Recent research mainly focused on the various physical and chemical methods to synthesize ZnS nanoparticles. However, physical and chemical approaches often utilize toxic chemicals not only causing environmental concerns but also limiting clinical applications. This has prompted researchers to seek the use of biological systems to produce ZnS nanoparticles in an ecofriendly way [8–11]. Recently, Mala and Rose [12] reported the biosynthesis of ZnS nanoparticle by a yeast sp. ZnS nanoparticles also have been synthesized by different bacterial sp. such as the *Desulfobacteriaceae* family [13], *Rhodobacter sphaeroides* [14] and *Serratia nematodiphila* [15]. The main problem about above methods is the extreme low yield. Therefore, we attempt to synthesize ZnS nanoparticles through plant. *Corymbia citriodora* a tall tree have been found growing widely in temperate and tropical north eastern Australia and recently introduce to China. Citronellal is the major chemical component existed in the *C. citriodora*, which may produce a reducing effect to certain chemical [1]. In this study, we report for the first time synthesis ZnS nanoparticles using *C. citriodora* leaf extract as reducing agent. The optical property and photocatalytic activity of biosynthesized ZnS nanoparticles also been investigated.

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2. Experimental

C. citriodora plants were collected from Kaifeng forest botanic garden and the leaf extract was prepared based on the biosynthesis method [16]. Typically, 20 g of *C. citriodora* leaves were washed with water and cut into small pieces. The leaves then boiled in 100 mL of water for 15 min. After cooling, the leaf extract was filtered, centrifuged and stored in refrigerator. Zinc sulfate and methylene blue (MB) were purchased from Sigma-Aldrich. All other chemicals used were analytical grade reagents without further purification.

The *C. citriodora* leaf extract was added into 1 M zinc sulfate solution (3:1 wt%) and kept under continuous stirring at 60 °C for 2 days. The pale white precipitate was obtained through centrifugation and washed with methanol and water. The ZnS nanoparticles were than collected after dried at an oven for 12 h.

X-ray diffraction patterns were collected from 20° to 90° in 2θ by a XRD with Cu Kα radiation (D8-Advanced, Bruker, Germany). Surface morphology of samples were analyzed by scanning electron microscope (SEM, S-4700, HITACHI, Japan). The photoluminescence (PL) emission curves were obtained by a fluorescence spectrophotometer using the intracellular sample at excitation wavelengths of 280 nm and 325 nm. The emission spectra were recorded between 300 and 600 nm. The Fourier-transform infrared spectra (FT-IR) of the samples were recorded using a Bruker Equinox 55. X-ray photoelectron spectrum was obtained for the sample at $\sim 2 \times 10^{-8}$ Torr, 15 kV, 150 W with a non-monochromatized Al K_α X-ray source and a hemispherical sector analyzer capable of 25 meV resolution. The UV–visible spectral analysis was carried out to monitor the surface plasmon resonance band typical of ZnS nanoparticles in solution using a Shimadzu spectrophotometer.

The photocatalytic activity of the samples were compared by monitoring the discoloration of heterocyclic dye MB under visible light irradiation. In a typical process, 20 mg of sample were added into a quartz tube containing a MB solution (50 mL, 20 mg/L), which was placed with a 15 cm distance from the lamp. Prior to the illumination, the suspension was magnetically stirred in the dark for 30 min to reach the adsorption–desorption equilibrium. At given time intervals, 2 mL of suspension was sampled and centrifuged, the supernatant was collected for absorption analysis on a UV–vis spectrophotometer. The absorbance of MB at 664 nm was used for measure the residual dye concentration.

3. Results and discussion

Fig. 1A shows the typical SEM image of biosynthesized ZnS nanoparticles. It can be clearly observed that the ZnS nanocrystals display a sphere like nanostructure with very uniform size. This regular shape of ZnS nanoparticles is rare reported in the literature from biosynthesis method. The cause of this uniform formation of ZnS nano-sphere could ascribe to the bio-molecules in the *C. citriodora* leaf extract, which not only act as a reducing agent but also as capping agent. Moreover, the ZnS nanoparticle did not show strong aggregation after formation, indicating the bio-molecules in the *C. citriodora* leaf extract further act as a stabilizing agent. Fig. 1B displays the size distribution of ZnS nanoparticles. The average size of ZnS nanoparticle formed via biosynthesis method is calculated as 45 nm.

The composition and purity of the biosynthesized ZnS nanoparticles were investigated by XPS. The photoelectron spectroscopy of the sample over a wide range from 0 to 1150 eV was collected. As shown in Fig. 2A, sharp peaks of Zn, S, O, N and C were observed. The peaks locate at 1024.3 eV and 1048.2 eV are corresponding to Zn ($2p_{3/2}$) and Zn ($2p_{1/2}$), respectively. The difference between these two peaks is 23.9 eV, which confirms the presence of ZnS phase formation. This difference is due to spin–orbit splitting. S 2p and 2s were observed at 165.8 eV, and 231.1 eV, respectively. The spectrum indicates the presence of ZnS and also impurities like C 1s (284.6 eV), and O 1s (533.2 eV) due to adsorbed gaseous molecule such as CO_2. Moreover, N 1s also observed in the survey, which could ascribe to the bio-molecules from *C. citriodora* leaf extract attached on the ZnS nanoparticles.

XRD was used for analyzing the crystal information of biosynthesized ZnS nanoparticles. Fig. 2B shows the wide angle X-ray diffraction pattern of ZnS nanoparticles. The diffraction peaks at 28.8°, 47.8° and 56.9° are assigned to (111), (220) and (311) planes of the zinc blende (cubic) phase of ZnS which are in good agreement with the literature values [JCPDS no: 5-0566]. The mean grain size was estimated to be 4 nm from the width of the XRD peak broadening, using the Scherrer equation [17].

In order to further confirm the formation of ZnS nanoparticles and investigate the interactions between bio-molecules and ZnS nanoparticles, FTIR spectrum of biosynthesized ZnS nanoparticles was recorded. As shown in Fig. 3C, the stretching mode of amino group $V_{NH}(–NH_2)$ at 3310 cm^{-1} and rocking modes of δ_{NH} $(–NH_2)$ at 1570 cm^{-1} for oleylamine related groups. Furthermore, the peaks at 2920 cm^{-1} and 2850 cm^{-1}correspond to C–H asymmetric ($V_{as}(–CH_2–)$) and symmetric stretching modes ($V_s(–CH_2–)$) of the methylene group. These peaks indicate the presence of biomolecules on the ZnS nanoparticle surface, which could act as a stabilizing agent for preventing aggregation.

UV–visible absorption spectrum of biosynthesized ZnS nanoparticles is shown in Fig. 3A. The optical absorption edges and well-defined excitonic features indicate that the synthesized particles have relatively narrow size distribution [18]. The band gap energy (E_g) of ZnS nanoparticles can be evaluated from the UV–vis spectra by Tauc plot of $(h\nu\alpha)^2$ versus $(h\nu)$ and extrapolation of the linear portions of the curves to the energy axis according to

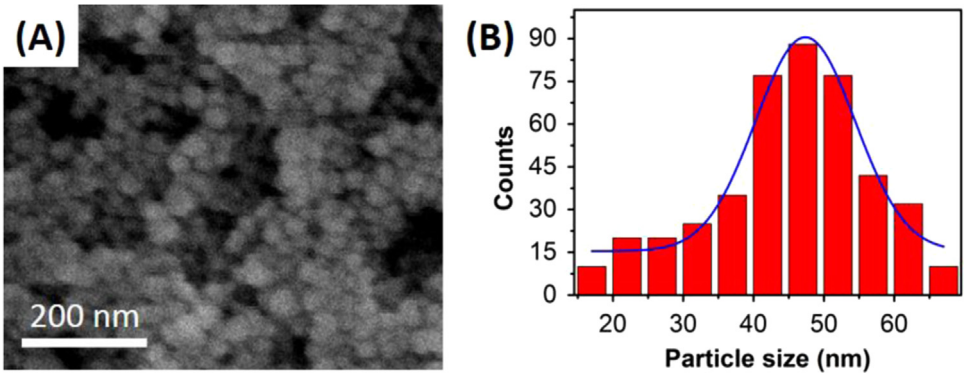

Fig. 1. (A) SEM image and (B) particle size distribution of biosynthesized ZnS nanoparticles.