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Cu-doped zinc oxide and its polythiophene composites: Preparation and antibacterial properties

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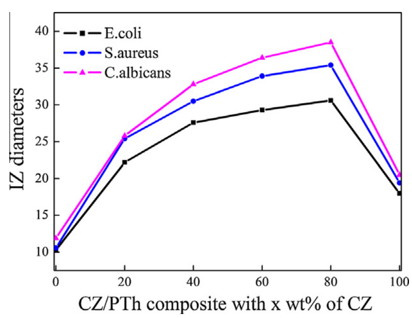
HIGHLIGHTS

- Cu-doped zinc oxide and its polythiophene nanocomposites were prepared successfully.
- There exists some synergistic effect between components in the ternary composites.
- The ternary composites present excellent antibacterial properties on three types species of bacteria.
- The antibacterial mechanisms of the samples were discussed in detail.

GRAPHICAL ABSTRACT



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ABSTRACT

Cu-doped zinc oxide and its polythiophene nanocomposites were prepared by the Sol–Gel and in situ polymerization methods, respectively. The structures, morphologies and compositions of the samples were characterized. The antibacterial properties of the samples on three kinds of strains were determined by using powder inhibition zones, minimum inhibitory concentrations and minimal bactericidal concentrations. The study confirmed that the antibacterial activities of the composites were better than those of their each component. The antibacterial mechanisms of the samples were discussed further.

1. Introduction

The conductive polymers with a large π conjugation system, such as polythiophene (PTh), polypyrrole and polyaniline have made considerable progress for their easy polymerization, good thermal stability and low cost since they were discovered (Soares et al., 2012; Yslasa et al., 2012). As one of the most potential conducting polymers, PTh and its derivatives have attracted researchers' great interests. However, the conductivity of pure PTh is very low because of the wide energy gap and no electrons in its antibonding orbitals. To expand the application scope of PTh, the doped PTh and its composites, especially PTh composites embedded with inorganic nanoparticles, are researched widely (Číka et al., 2006; Zhang et al., 2006; Wang et al., 2007; Lanzi and Paganin, 2010; Gao et al., 2012; Guo et al., 2012; Higashihara et al., 2013). The composites can not only improve the properties of PTh itself but also reveal some new performances that a single component does not possess due to the synergistic effect among components. Some efforts have been paid to study the composites for catalyst (Wang et al., 2008), solar cells (Lanzi and Paganin, 2010; Higashihara et al., 2013), low-temperature NO_2 sensors (Guo et al., 2012), molecular recognition system (Zhang et al., 2006), etc.

Zinc oxide (ZnO), a kind of vital multifunctional semiconductor material, possesses broad forbidden band. Its unique properties in

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optics, electrics, magnetism and antimicrobial activity can be improved obviously through doping ions, coating rare metals or metallic oxide on its surface (Ba-Abbada et al., 2013). It was reported that nano-ZnO was toxic to bacteria, copepods, microalgae, mammalian cells, etc. (Wiench et al., 2009; Wang et al., 2011, 2012; Saifa et al., 2013). And its antibacterial activity for many pathogens under the ultraviolet radiation is higher than that of nano-TiO_2 (Kasemets et al., 2009; Wang et al., 2009). Besides nano-sized ZnO, CuO nanoparticles are also an excellent antimicrobial material with broad foreground for application (Heinlaan et al., 2008; Karlsson et al., 2008; Perelshtein et al., 2009). As is well known, photoinduced carriers can be generated when PTh is exposed in the sunlight. But no report was available on the preparation and evaluation of antimicrobial activity of the PTh nanocomposites with Cu doped ZnO nanoparticles.

Based on our previous work, the antibacterial activities of a series of Cu-doped zinc oxide ($Cu_xZn_{1-x}O$) nanocomposites were evaluated (Liang et al., 2011). Considering both the antibacterial property and doped content of Cu^{2+} in ZnO, $Cu_{0.05}Zn_{0.95}O$ (CZ) is the optimal composition in the series samples. Herein, we report our recent efforts on the preparation and characterization of CZ/PTh nanocomposites. The antibacterial performance of the samples were evaluated by the experiments of powder inhibition zone (IZ), minimal inhibitory concentration (MIC) and minimal bactericidal concentration (MBC) under the irradiation of sunlight against *Escherichia coli* (*E. coli*), *Staphylococcus aureus* (*S. aureus*) and *Candida albicans* (*C. albicans*). And the antibacterial mechanisms of the samples were discussed in detail.

2. Experimental

2.1. Materials

Zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$), copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$), citric acid, thiophene (Th), trichloromethane ($CHCl_3$), ferric chloride anhydrous ($FeCl_3$), aqueous ammonia ($NH_3{\cdot}H_2O$, 25–28%), poly vinyl alcohol (PVA) and methanol were all purchased from SCRC, China. All chemical reagents were of analytical grade and used without purification.

2.2. Preparation of CZ/PTh

CZ was prepared by the Sol–Gel method, as reported in the literature (Liang et al., 2012). 2.82 g of zinc nitrate and 0.07 g of copper nitrate were dissolved in appropriate content distilled water to form a transparent solution. And then 2.16 g of citric acid was added to the above solution with stirring. The pH value of the mixed solution was adjusted to 8 with $NH_3{\cdot}H_2O$. It was maintained at 80 °C with constant stirring to form a sol and then dried further at 80 °C to form a solid precursor. Finally, the CZ powder was obtained after sintering the precursor for 2 h at 500 °C.

CZ/PTh nanocomposites were prepared by in situ polymerization method. The procedure of CZ/PTh nanocomposite with 20 wt% of CZ was as follows: 50 mL of $CHCl_3$ and 1 g of Th were mixed in three-necked flask with magnetic stirring. And 0.25 g of as-prepared CZ was added into the mixture above and dispersed with ultrasonication for 30 min at room temperature. 3 g of $FeCl_3$ was dispersed in 150 mL of $CHCl_3$ and added into the flask with mechanical raking. As Th began to be polymerized, the solution turned to dark from yellow gradually. The reaction was performed for 12 h in ice water bath. Finally, the filtered product was washed with methanol and $CHCl_3$ several times respectively until the filtrate became colorless, and dried in vacuum for 24 h at 50 °C. The CZ/PTh nanocomposite with 20 wt% of CZ was obtained. A series of CZ/PTh nanocomposites with 40 wt%, 60 wt%, 80 wt% of CZ and pure PTh were prepared according to the condition and procedure above-mentioned.

2.3. Characterizations

The element content in CZ and CZ/PTh nanocomposites was confirmed by chemical analysis methods, i.e., the content of Cu^{2+} was determined by iodometry method; the content of Zn^{2+} was carried out by disodium ethylenediamine tetra-acetate titration method used xylenol orange as indicator.

The X-ray diffraction (XRD) patterns of the samples were characterized using an X-ray diffractometer (Philips-PW3040/60) with Cu Kα radiation. The microstructures of the samples were observed by a scanning electron microscope (SEM, Hitachi S-4800) and a transmission electron microscope (TEM, JEOL-2010), respectively. The FT-IR spectra were recorded in KBr on a FT-IR spectrometer (Nicolet-Avatar 360). UV–Vis spectra were studied by a UV–visible spectrophotometer (Shimadzu-UV-2501PC). The thermogravimetric curves were recorded by a thermal analyzer (Mettler Toledo-TGA/SDTA 851) under air atmosphere, the heating rate was 10 °C min^{-1} and the flow rate was 40 mL min^{-1}. The electrical conductivities were carried out on a four-probe resistivity instrument (SDY-4) at room temperature (The tested samples mixed as-prepared samples with PVA (adhesive) in the mass rate of 3:1 were pressed to a column with the thickness of 3.30 mm under the pressure of 3 MPa). The growth of bacterial strains was monitored by UV–visible spectrophotometer. The concentrations Zn^{2+} and Cu^{2+} released from the CZ/PTh composite suspension were determined by an atomic absorption spectrometer (PE, AA800).

2.4. The evaluation of antibacterial performance

E. coli (ATCC25922), *S. aureus* (ATCC25923) and *C. albicans* (ATCC10231) were used as test strains. All the strains were purchased from WKZ, China. The antibacterial properties of the samples were measured by IZ, MIC and MBC against the three strains above.

2.4.1. Preparation of media

Beef peptone (bacterial culture): beef extract 0.13 g, peptone 1 g, NaCl 0.15 g, agar 115–210 g, deionized water 100 mL, pH 7.10–7.12; Sabouraud agar medium (fungal culture): peptone 1 g, glucose 4 g, agar 118 g, deionized water 100 mL, pH 5.60.

2.4.2. Preparation of bacterial suspension

The test strains inoculated to the sterilized fluid medium in a incubator shaker with constant temperature of 37 °C, and oscillated for 24 h at the rate of 100 r min^{-1}. Concentration of the inoculums was controlled in the range of $1 \times 10^5 \sim 9 \times 10^5$ cfu mL^{-1} with the sterile saline. Bacterial suspension was prepared for using by shaking uniformly.

2.4.3. Antibacterial property test

Antibacterial properties (IZ, MIC and MIC) of samples against E. coli, S. aureus and C. albicans were measured according to the literature (Liang et al., 2012).

3. Results and discussion

3.1. Chemical composition and XRD

The chemical compositions of CZ and CZ/PTh nanocomposites confirmed by chemical analysis method are given in Table S1 in Supplementary materials. The measured values of metal ions are consistent well with theoretical value for the samples, which