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A novel stellerite-based photocatalytic composite and its enhanced disinfection application

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ABSTRACT

The aim of this work was to prepare, characterize and evaluate the potential of novel ZnO/stellerite composite photocatalysts against *Staphylococcus aureus* (*S. aureus*). SEM/EDS studies employed to study the surface morphological properties revealed stellerite as the catalysts carrier played a role of dispersant for ZnO nanoparticles. The XRD patterns of the ZnO/stellerite indicated hexagonal crystal structure with 20–30 nm size. It was found that the crystallite size of ZnO/stellerite was much smaller as compared to pure ZnO and increased with increasing ZnO loading amount. The results of optical properties of ZnO/stellerite showed smaller band gap in contrast to pure ZnO, investigated by UV–vis absorption. Due to the optimum ZnO loading, the as-prepared ZnO-20 composite had the highest BET surface area and the pore volume. Using the TG-DSC measurement, the high thermal stability of the product was studied for different temperature values. Antibacterial activity of ZnO/stellerite affected by the ZnO loading, concentration of samples and light conditions (under dark and UV irradiation conditions) was examined by disinfection of *S. aureus*. The as-prepared ZnO-20 composite with 100 mg/L was found to exhibit excellent inactivation efficiencies (87.65% in the dark and 97.67% under UV illumination) towards *S. aureus*. Compared with pure ZnO, the obtained composite photocatalysts showed significantly better antibacterial performance by studying the disinfection kinetics of *S. aureus*. Thus, the present study reveals that the novel ZnO/stellerite shows great potential for its use in the targeted disinfection applications.

1. Introduction

Microbial contamination in water is always harmful to human health with the rapid development of human society. Many kinds of bacteria such as *Escherichia coli* (*E. coli*) and *S. aureus* can cause the mortality and morbidity for humans especially for multi-drug resistant microbe. *S. aureus* is a Gram-positive bacterium that is well known for its toxicity to humans. And it is proved that *S. aureus* is more resistant to bactericidal action than *E. coli* because of the differences in the cell wall structure inherent in gram-negative and gram-positive bacteria [1–4]. Many methods have been developed to disinfect various media of the microorganism considering their toxicities. However, traditional bacterial inactivation methods such as chlorination and UV disinfection chlorination were restricted because of their carcinogenic disinfection byproducts and ineffectiveness for resistant bacteria. Biocidal action of semiconductors has been emerged as a more reliable technique [5–9]. Most studies [3–5] suggest that these photocatalysts can absorb the light (ultraviolet or visible) and generate electron–hole pairs. Then electrons and holes react with water and dissolved oxygen respectively to generate reactive oxygen species (ROS) which subsequently inactivate microorganisms. To date, in most literatures [4,10,11] semiconductor-based photocatalyst was used under UV or visible light illumination and only in few studies [12] in the dark. It is reported that nano-ZnO powders can exhibit disinfection activity through damage the membrane and essential macromolecules of bacterial even under dark conditions [13]. However, the inactivation mechanism using nano-ZnO powders under dark condition is uncertain.

The antimicrobial efficiency of nano-ZnO depends on the particle size and illumination of UV light in assay [3]. The bare nano-ZnO particles suspended in water tend to aggregate with the active site significantly less than that of dry powder [2,7,13,14]. This results in poor photocatalytic activity and limits the use of nano-ZnO for photocatalytic inactivation of bacteria [15–17]. In order to avoid these issues, various supporters have been used such as alumina, zeolite, silica gel, fiber optic cable, glass beads, quartz, stainless steels, clays and activated carbon [8,18–20]. Among these catalyst supporters, natural zeolite is one of most attractive supports because of its abundance, high porosity, chemical stability and low costs [21]. Nevertheless, studies focused on water disinfection using ZnO supported onto natural stellerite are scarce. So far, no research on the bactericidal action using

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ZnO/stellerite has been reported. Therefore, it is necessary and meaningful to investigate the interaction between ZnO and natural stellerite to promote practical applications for environmental protection purpose.

In respect of the above considerations, the aim of this study is to prepare the novel stellerite-based photocatalyst through a facile hydrothermal-calcination method. The disinfection performance of ZnO/stellerite composites was evaluated by *S. aureus* as the target pollutant and the optimum loading of ZnO was obtained. Moreover, the bactericidal performance of ZnO/stellerite was compared to that of bare ZnO by the kinetic parameters of the bactericidal reaction. Hence, the ZnO/stellerite composite can be a promising degrader for bacteria as well as a potential material for super biomedical applications.

2. Experimental

2.1. Materials

Natural stellerite was used as the carrier of ZnO, which was purchased from Aiteli Materials Co., Ltd., Guilin, PRC. The raw stellerite was washed with deionized water and then dried at 80 °C for 24 h. The main chemical compositions of stellerite are listed in Supporting information (SI) Table S1 [22]. Zinc acetate ($Zn(CH_3COO)_2$), urea($CO(NH_2)_2$) and other chemicals used in the experiments were of analytical grade and were purchased from Beijing Chemical Reagent Plant. *S. aureus* (bacterium, AS1.89) were obtained from the Institute of Microbiology Chinese Academy of Science in form of slice packages according to international standard, with the bacteria number of 10^6 CFU /piece (CFU = colony forming units).

2.2. Preparation of ZnO/stellerite

The synthesis the ZnO/stellerite composite by a facile hydrothermal-calcination approach has been listed according to the literature [23]. 100 mL of aqueous solution with different dosages of zinc acetate and urea (The molar ratio of zinc acetate/urea is 1/5) were firstly added into the beaker, then 4 g of stellerite powders were added as well. Next, the mixture was stirred at 95 °C for 4 h. Secondly, the resulting mixture was vacuum-filtered and the pH value was adjusted to 7 by distilled water. The final powders were dried in an oven at 80 °C for 2 h. Finally, the filtered mixture was calcinated to 300 °C for 2 h in air at a heating rate of 2.5°/min to obtain ZnO/stellerite. For comparison, pure ZnO powder was also prepared by the same procedure without the addition of stellerite.

The ZnO/stellerite particles prepared with different ZnO theoretical loading amounts (10%, 20%, 30%, 40% and 50%) were denoted as ZnO-10, ZnO-20, ZnO-30, ZnO-40 and ZnO-50, respectively. Experimental solutions of the desired concentration were obtained by successive dilutions. The other reagents were of analytical grade and deionized water was used in this experiment.

2.3. Characterization

The morphology structure of ZnO/stellerite, stellerite and pure ZnO was examined via a scanning electron microscope (SEM Qua ta200, FEI, America) with attached energy-dispersive X- ray (EDX) detector. The nanoparticles were gold coated and observed under a condition of 30 kV. The crystal structure of the samples was characterized using a Bruker D8 Advance Powder X-ray diffractometer (Bruker, Germany) with Cu Kα-radiation (λ = 0.15406 nm), under the operation conditions of 20 mA and 40 kV. The range of 2θ values was from 5° to 70°, at a scanning speed of 4°/min. The Brunauer–Emmett–Teller (BET) specific surface area of samples was determined at liquid nitrogen temperature (77 K) via a volume adsorption apparatus (BET, JW-BK, China). The total pore volumes were calculated based on N_2 adsorption in the relative pressure (P/P_0) range of 0.05–0.99. Pore-size distributions were calculated from the adsorption branch of the isotherm, according to the Barrett–Joyner–Halenda (BJH) model [24]. Prior to N_2 adsorption process, the samples (ca. 0.5 g) were treated in a vacuum drying oven at 40 °C for 24 h. The UV–vis spectra of nanoparticles was measured on a UV-3150 (Shimadzu, Japan), at slit width of 5 nm and scanning wavenumber is 200–800 nm. $BaSO_4$ was used as the internal reflectance standard. The thermal stability of the ZnO/stellerite was performed on a thermal gravimetric analyzer (TGA-51, Shimadzu) and a differential scanning calorimeter (DSC-50, Shimadzu). The temperature was up to 600 °C at a heating rate of 10 °C /min under 40 mL/min nitrogen flow.

2.4. Bacterial culture and antibacterial experiments

S. aureus was selected as model bacteria. Bacterial cells were harvested at 37 °C in nutrient broth after an incubation time of approximately 12 h to yield a cell density of approximately 10^8 CFU/mL [25]. After centrifugation at 5000 rpm for 10 min, the collected bacterial pellets were then washed with sterile physiological water (NaCl, 9 g/L) three times. The cells were resuspended in a sterile saline solution to obtain 10^7CFU/mL.

The disinfection tests were assessed using an experimental apparatus. A quartz tube (100 mL) was used as a single liquid-phase photocatalytic reactor. Each tube contained 20 mL of bacterial solution (10^7CFU/mL) and different amounts of catalysts in a range from 25 to 100 mg/L. The mixtures of the bacteria solution with catalysts were agitated with a magnetic stirrer (170 r/min) to ensure adequate mixing of bacteria and catalysts. Meanwhile, UV irradiation (ca. 1600 μW/cm^2) started immediately for quartz tubes. The treatments performed within 30 min at 37 °C; other ones in the dark lasted for 2 h. After irradiation and for different time intervals, serial dilutions of cells were made in physiological water, and 100 μL of the final solutions were placed on NB-agar by the spread plate method. Each agar plate was cultured at 37 °C for 24 h, and loss of viability was determined by the cell viability on agar plates. All the disinfection experiments were performed in triplicates. The bactericidal efficiency of the catalyst against bacteria was calculated according to the following formula:

$$Rt = (N_0 - Nt)/N_0 \times 100\% \quad (1)$$

where N_0 and N_t is the survival number at initial time and at time t.

3. Results and discussion

3.1. SEM/EDS analysis

In this study, the ZnO/stellerite composites were denoted as ZnO-X. X means the loading of ZnO as 10%, 20%, 30%, 40% and 50%. Fig. 1 presents the SEM micrographs of stellerite (Fig. 1a and b), ZnO-20 (Fig. 1c and d) and pure ZnO (Fig. 1e). As can be observed from Fig. 1a, the stellerite with a large size of a few micrometer or so possesses a relatively smooth and flat surface. As shown in Fig. 1c and d, the surface of the ZnO-20 composites become rougher compared to the surface of stellerite due to the introduction of the ZnO particles. Pure ZnO particles with spherical like structures congregate together dramatically (Fig. 1f) because of the nanometer effect [9]. Compared with pure ZnO, it can be seen that the distribution of ZnO nanoparticles onto stellerite were relatively uniform. In addition, lesser ZnO particle size of ZnO-20 was obtained due to the immobilization of stellerite, compared to that of pure ZnO. Observed results were consistent with the results obtained by XRD analysis(SI Table S2) and S. Dinesh's reports [24]. It is clear from the XRD patterns that crystalline sizes make significant changes with addition of stellerite. The inset of Fig. 1d represents the distribution of Zn measuring by EDS under surface-distribution scanning. The EDS measurement confirmed the composition of the hybrids (Fig. 1i), which demonstrated the presence of Si, Zn and O. It clearly indicates the well distribution of ZnO nanoparticles onto surface of stellerite, although several of them tend to agglomerate. This result suggests that