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Structure and antibacterial property of nano-SiO_2 supported oxide ceramic

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Abstract

SiO_2 doped samples with different cobalt loading and pure SiO_2 and Co_3O_4 nanopowders were synthesized by the solvothermal method and their antibacterial activities were studied. The morphology and crystallinity of the powders were analyzed by scanning electron microscopy and X-ray diffractometry patterns, respectively. The increase of particle size with doping concentration was obtained for cobalt-doped samples. The optical properties were studied using UV–vis spectroscopy. Optical studies showed a blue shift in the absorbance spectrum with increasing the doping concentration. The antibacterial activities of undoped SiO_2, Co-doped SiO_2 and pure Co_3O_4 nanoparticles against a Gram-negative bacterium *Escherichia coli* (*E. coli*, ATCC 25922) and a Gram-positive bacterium *Staphylococcus aureus* (*S. aureus*, ATCC 29213) were investigated under UV illumination and in the dark condition. Bactericidal effects were determined by the minimum inhibitory concentration (MIC) method. There was no activity for pure SiO_2 and Co_3O_4, however, cobalt doping significantly improved antibacterial activity against both bacteria. Bacterial growth inhibition was observed under dark condition with lower efficiency than under UV illumination. The antibacterial efficiencies were affected by the physiological status of the bacterial cells, different morphologies, particle sizes and optical properties of samples.

Keywords: Nano-SiO_2 carrier; Co_3O_4 nanostructure; Solvothermal method; Antibacterial activity

1. Introduction

Bacterial contamination and growth in water are potential health hazards demanding disinfection. Moreover, the food-borne diseases still remain a universal problem [1] in spite of the rapid growth of nanotechnology as a possible approach to reduce the microbial contamination on food surfaces and in food preparation environments. The *Staphylococcus aureus* is a leading cause of gastroenteritis resulting from the consumption of contaminated food. On the other hand, certain types of *Escherichia coli* cause foodborne illness. The majority of bacteria recovered from different types of food and environmental sources have been found resistant to at least one antimicrobial drug [2]. Therefore, three types of antibacterials including metals, metal oxides and organic polymers were recently developed. However, new research has attracted interest in antibacterial nanomaterial containing various inorganic substances compared to the organics, due to their improved safety and stability [3,4]. Among these, ceramics with inherent bactericidal activity are convenient to use as they are insoluble.

Some antibacterial agents, when loaded onto inorganic carrier and released from it slowly by design, act as inorganic disinfectants, which are superior in terms of safety, durability and heat resistance compared with conventional organic ones [5]. As for inorganic carriers, some compounds such as zeolite [6], phosphate [7], titanium dioxide [8], activated carbon [9], montmorillonite [10], water-soluble glass [11] and mesoporous silica [12] have been investigated.

Nano-SiO_2 particles are expected to be one of the most promising carriers suitable for development of high performance antibacterial and bactericidal materials due to following reasons: (1) nano-SiO_2 particles are of extremely high surface activity and porous structure resulting to sufficient adsorption properties; (2) nanometric size particle metals/or metal oxides embedded in silica matrix have the lower tendency to agglomerate; (3) silica matrix is chemically inert,

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biocompatible and resistant to microbial attack both in vitro and in vivo and (4) controlled release of nanoparticles from SiO_2 matrix. These are the reasons why the development of inorganic bactericide and disinfectant prepared by loading antibacterial agents onto silica matrix carrier is receiving extensive attention for application in domestic and industrial fields [13,14].

The wide investigations on the antibacterial effect of various nanostructured systems including doped metal oxides [15], metal loaded silica [16] and composites [17] have been carried out. Nevertheless, the reports on the cobalt-included bactericides are limited to Co-doped nanoparticles [18,19], and cobalt coordination complexes in oxidation state 3+ [20]. As reported previously, no significant antibacterial activity was observed for cobalt oxides [21].

To our knowledge, for the first time we report the toxicity of Co-doped SiO_2 nanostuctures. This study examines the effects of Co-doping concentration and exposure time on the growth of the bacteria. In this paper, bactericidal nano-SiO_2 specimens were synthesized by solvothermal reaction. Among solution-based methods for tailored nanomaterials synthesis, solvothermal synthesis are related to homogeneous novel nucleation processes due to the elimination of the calcination step, producing very low grain sizes and high-purity powders [22]. The structure, morphologies and optical properties of the all samples were determined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV–vis spectroscopy. Chemical compositions of the prepared samples were estimated by chemical analysis. Their antibacterial properties were also examined against *Escherichia coli* (*E. coli*, ATCC 25922) and *Staphylococcus aureus* (*S. aureus*, ATCC 29213).

2. Materials and methods

2.1. SiO_2 supported oxide ceramic synthesis

Two sols were separately prepared using tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), and cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) as sources of Si and Co, respectively. For SiO_2 synthesis, TEOS and distilled water were mixed and stirred at room temperature. Then, 0.5 M HNO_3 solution was added as hydrolysis catalysis and to control the pH value at 3. $Co(NO_3)_2 \cdot 6H_2O$ was separately dissolved in 30 ml of H_2O and ethanol mixture with magnetic stirring for at least 30 min to form a red solution. One part of each set was left unmixed to prepare single component Co_3O_4 and SiO_2 powders. To the remaining Si sol, requisite amounts of Co sol prepared were added to obtain three sols at 10, 30 and 50% Co-doped SiO_2, individually. The sols were further stirred for 2 h at room temperature. Then, each sol was transferred into an individual 80 ml autoclave with a Teflon liner and heated at 180 °C for 20 h. The resulting products were filtered and washed several times with distilled water and ethanol, then, dried at 100 °C for 1 h, and finally annealed in the air atmosphere at 450 °C for 3 h.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were obtained by using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The size and morphology of all the catalysts were examined with a Philips, XL30 scanning electron microscope (SEM). The composition of the doped powders was analyzed by electron dispersive X-ray analysis (EDS). The optical properties were performed on a Shimadzu, MPC-2200 UV–vis spectrophotometer operated over the range of 200–800 nm at a resolution of 2.0 nm.

2.3. Antibacterial activity

The antibacterial activities of undoped SiO_2, Co-doped SiO_2 and Co_3O_4 nanoparticles were investigated against a Gram-negative bacterium *E. coli* and a Gram-positive bacterium *S. aureus* under UV illumination and in the dark condition. Nutrient broth (NB) was used as a growing medium for both the microorganisms at 37 °C for 20 h. The culture solution was centrifuged, and the cells were washed and suspended in distilled water, reaching a final concentration of 10^5 cells/ml *E. coli* or *S. aureus*. We used minimal inhibitory concentrations (MIC) method to test the antimicrobial activity. The MIC is the lowest concentration of an antimicrobial material that will inhibit the visible growth of a microorganism after incubation. Four different concentrations (0, 1, 3 and 6 μg/ml) of the Co-doped SiO_2 nanostructures have been used in the present study to determine the MIC. For single component SiO_2 and Co_3O_4 powders, the constant concentration of 6 μg/ml was used. The certain amounts of each sample were put into above suspended solution to keep in contact with *E. coli* or *S. aureus* respectively, and shaken at 37 °C (dark condition)/ or illuminated under four 8 W UV lamps (Philips UV-A, $\lambda_{max} = 365$ nm) for up to 56 h. Aliquots of 0.1 ml of each mixture (water+bacterium) were sampled every 4 h. These aliquots were diluted in distilled water. Each group of samples was spread on NB agar plates and incubated at 37 °C for 24 h, respectively. The number of viable cells in the each sample was determined by choosing the appropriate dilution of the sample onto NB agar plates and counting colonies that appeared on the plates.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows typical comparative X-ray diffraction patterns for single SiO_2, single Co_3O_4 and Co-doped samples, respectively. SiO_2 XRD pattern indicated amorphous phase. All the XRD patterns of Co-doped SiO_2 and single Co_3O_4 samples are commonly in good accord with those of cubic Co_3O_4. The (111), (220), (311), (400), (511) and (440) planes for Co_3O_4 are assigned on the peaks. At higher Co doping concentration, some new XRD peaks appear, possibly due to improved crystallinity. The particle size increases at higher Co doping concentration (table 1). The surface morphology of the samples was investigated by SEM as shown in Fig. 2. There