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Effect of metal ion doping on ZnO nanopowders for bacterial inactivation under visible-light irradiation

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ABSTRACT

Among metal oxide photocatalysts, zinc oxide (ZnO) has attracted extensive attention due to its advantages of low toxicity and relatively low cost of production. In this work, ZnO nanopowders doped with different metal ions (Li^{+}, Mg^{2+}, Al^{3+} and Ti^{4+}) were synthesized by a sol-gel method. Multiple techniques such as X-ray diffraction (XRD), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), UV-vis diffused reflectance spectra (UV-vis DRS), photoluminescence (PL) spectra and Brunauer-Emmett-Teller (BET) measurements were employed to study the structures, morphologies and physicochemical properties of the photocatalysts. The influence of metal ion doping on the photocatalytic activity of ZnO was assessed by inactivating a typical Gram-negative bacterium, *Escherichia coli* K-12 under visible-light irradiation. It was found that Al doping and Ti doping could promote the photocatalytic bacterial inactivation activity of ZnO, while Li doping and Mg doping hindered the bacterial inactivation activity of ZnO photocatalysts. Moreover, Al-doped ZnO exhibited the best visible-light-driven (VLD) photocatalytic activity among these samples, with 7-log of *E. coli* K-12 cells being completely inactivated within 4 h. The large percentage of absorbed oxygen, narrow band gap and extended visible light absorption were considered to contribute to the powerful VLD photocatalytic activity of Al-doped ZnO.

1. Introduction

Our society is now troubled with environmental issues due to the aggravation of ecological damage. As a result, water sources are contaminated by pathogenic bacteria, which causes diseases even death in human beings [1]. Thus, it is necessary to develop efficient disinfection techniques for inactivation of infectious pathogens to improve environmental sanitation [2]. Compared with traditional disinfection methods, such as ozone and chlorination, which have the drawbacks of high cost and carcinogenicity, semiconductor photocatalysis has been regarded as a promising water purification approach to remove pathogenic microorganisms [3,4]. Zinc oxide (ZnO) has been one of the most widely used photocatalysts due to the advantages of low toxicity and relatively low cost of production [5–9]. Moreover, it is well established that reactive oxygen species (ROS) play a significant role in the photocatalytic activity of ZnO during photoexcitation [10,11], which can lead to the decomposition of bacteria cells through various actions [4].

Nevertheless, pure ZnO as a photocatalyst has some practical problems including irradiation by UV light, undesired recombination of photogenerated electron-hole pair and photocorrosion effect [12]. Thus, much attention has been drawn on improving the photocatalytic activity of ZnO by suitable modification, among which metal ion doping is considered to be an effective method. Ganesh et al. [13] proposed that Li doping could significantly improve the photocatalytic activity of ZnO nanopowders for methylene blue degradation. Etacheri et al. [14] reported that Mg-doped ZnO had enhanced sunlight-driven photocatalytic activity, owing to the combined effect of superior textural properties and more efficient electron-hole separation. Ahmadet et al. [15] concluded that the enhanced photocatalytic activity of Al-doped ZnO was due to the extended visible light absorption and enhanced adsorption of methyl orange (MO) dye molecule on the surface of Al-doped ZnO nanopowders. Blohet et al. [16] studied the effect of Ti doping on the photocatalytic activity of ZnO and gave the optimal doping ratio to maximize the photonic efficiency for acetaldehyde degradation under UV-light illumination. However, the preparation processes and conditions of these doped ZnO were different from each other, which may affect the physical and chemical properties of final products. To the best of our knowledge, a systematic study on the influence of different metal ion doping on the visible-light-driven (VLD) photocatalytic activity of

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ZnO has never been explored. Moreover, most previous studies about the photocatalytic performance of doped ZnO mainly focused on dye degradation and hydrogen production, there were few studies involving VLD photocatalytic bacterial inactivation by doped ZnO.

In this work, the different metal ions of Li^+, Mg^{2+}, Al^{3+} and Ti^{4+} were selected to incorporate into ZnO crystal lattice. These four metal ions with different valence states had close ionic radius with that of Zn^{2+} ($R_{Li}^{+} = 0.076$ nm, $R_{Mg}^{2+} = 0.072$ nm, $R_{Al}^{3+} = 0.054$ nm, $R_{Ti}^{4+} = 0.060$ nm and $R_{Zn}^{2+} = 0.074$ nm), so they were considered to be easily doped into the ZnO matrix, resulting in the substitutional doping to generate different types of defect sites (oxygen vacancies, substitutional ions and metal vacancies). Photocatalytic activity of the doped ZnO samples was assessed by inactivating a typical Gram-negative bacterium, *Escherichia coli* K-12 under visible-light irradiation. Also, the influence of different metal ion doping on the structures, morphologies and physicochemical properties of ZnO was explored in the study.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), tetrabutyl titanate ($Ti(OC_4H_9)_4$) and citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Lithium nitrate ($LiNO_3$) was bought from Aladdin Chemistry Reagent Chemistry Co., Ltd. Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) was obtained from Shanghai Experimental Reagent Co., Ltd. All the chemical reagents were of analytical grade and used without further purification in this study.

2.2. Synthesis of the doped ZnO samples

A citric acid-assist sol-gel method was applied for the preparation of the doped ZnO samples, and the molar ratios of doped metals to zinc were controlled at 5 mol%. Firstly, 0.019 mol of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.001 mol of the dopant ($LiNO_3$, $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ or $Ti(OC_4H_9)_4$) were dissolved in 20 mL of distilled water. At the same time, 0.02 mol of $C_6H_8O_7 \cdot H_2O$ was dissolved in 20 mL of distilled water, and subsequently added to the above solution under stirring until a homogeneous solution was obtained. Secondly, the mixed solution was placed in a water bath of 80 °C under continuous stirring. After a period of time, the mixture turned into a gel, which was then put in a drying oven at 150 °C to obtain a fluffy precursor. At last, the dried precursor was heated from room temperature to 600 °C in 5 h and held at 600 °C for 1 h to get the doped ZnO samples. For comparison, the undoped ZnO sample was also prepared using a similar procedure as mentioned above, without the addition of any metal ion dopant.

2.3. Characterizations

The crystal structure of the as-prepared samples was characterized by X-ray diffraction (XRD) (Philips/X' Pert PRO). Morphology of the samples was observed using transmission electron microscope (TEM) (FEI Tecnai G220) with an acceleration voltage of 200 kV. The samples were suspended in ethanol and placed a drop on a carbon-coated Cu TEM grid for observation. Brunauer-Emmett-Teller (BET) surface area measurement was carried out on a Micromeritics ASAP 2020M surface area analyzer with nitrogen adsorption at 77 K. X-ray photoelectron spectroscopy (XPS) analysis was acquired on a Kratos/Axis Ultra DLD-600W spectrometer, and the spectra were calibrated referring to the C 1s peak (284.6 eV). UV-vis diffuse reflectance spectra (UV-vis DRS) was conducted on a Varian Cary 500 UV-vis spectrophotometer equipped with a Labsphere diffuse reflectance accessory. Room temperature photoluminescence (PL) spectra were recorded using a fluorescence spectrometer (Jasco, Japan). The excitation source was a Xe lamp and the excitation wavelength was 325 nm. Besides, the leakage of metal ions from the samples during bacterial inactivation was also determined by microwave plasma-atomic emission spectrometry (4100 MP-AES, Agilent Technologies).

2.4. Photocatalytic bacterial inactivation

The photocatalytic bacterial inactivation performance of as-prepared doped ZnO samples was evaluated by the inactivation of the representative Gram-negative bacterium *Escherichia coli* K-12 (*E. coli*). A 300 W xenon lamp with a UV cutoff filter ($\lambda < 400$ nm) was used as the visible light source, and the light intensity was fixed at ~200 mw/cm^2. Firstly, *E. coli* K-12 was cultured in 50 mL of nutrient broth at 37 °C for 15 h in a shaking incubator. The bacteria cells were harvested by centrifugation for 1 min and washed twice with sterilized saline (0.9 wt% NaCl) solution and then resuspended in sterilized saline solution. The suspension (50 mL) containing ~10^7 colony forming unit (cfu) mL^{-1} of *E. coli* K-12 and 25 mg of photocatalyst was stirred for 30 min in dark to reach the adsorption equilibrium before light irradiation. Then the xenon lamp was turned on to start the photocatalytic reaction. At different time intervals, an aliquot of reaction solution was sampled and spread on Nutrient Agar (Oxoid, England) plates after a series of 10-fold dilution. The survival number of cells was determined after incubating at 37 °C for 24 h. For comparison, dark control (photocatalysts and bacterial cells without light irradiation) and light

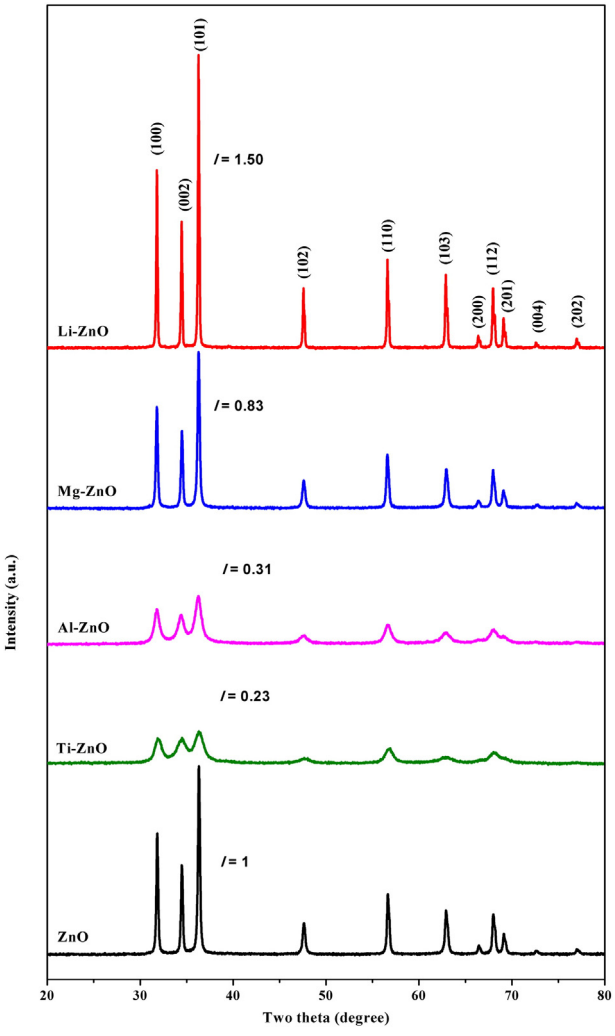

Fig. 1. XRD spectra of the ZnO and doped ZnO samples.