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Mineral wool fibers incorporated with cuprous oxide for visible light photocatalytic inactivation of *Escherichia coli*

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Abstract

Mineral wool fibers (MWF) commonly used in building insulation and decoration are incorporated with cuprous oxide particles at room temperature to inactivate *Escherichia coli* (*E. coli*). X-ray diffraction (XRD), scanning electron microscopy (SEM), and ultraviolet–visible diffuse reflection absorption spectroscopy (UV–vis/DRS) are employed to characterize the photocatalytic composites and the bactericidal effects are assessed by UV–visible spectrophotometry. Cuprous oxide particles with a size of 100 nm can be immobilized effectively on the surface of the MWF. The MWF improves the optical properties of cuprous oxide and red-shifts the band gap thereby enhancing the utilization efficiency of visible light. The Cu_2O/MWF composites deliver excellent photocatalytic performance in the inactivation of *E. coli*. After illumination for 24 h, more than 95% of the bacteria are inactivated and the materials are suitable for indoor antibacterial applications.

Keywords: Photocatalysis; Cuprous oxide; Inactivation; Mineral wool fibers; Building materials

1. Introduction

Indoor air contamination by microbial pollutants has been increasingly recognized as a public health problem and may be responsible for building-related illnesses such as allergic responses, infectious diseases, hypersensitivity reactions, and asthma [1–3]. Hence, methods capable of controlling the spreading and/or eradicating microorganisms are urgently needed. Many techniques such as purging with outdoor air, filtration of microbial species, isolation by pressurization control, ultraviolet germicidal irradiation, ozone disinfection, and chemical oxidation have been proposed [4–6]. Unfortunately, these methods suffer from some inherent limitations, for instance, high energy consumption and low efficiency and many biological species are seldom thoroughly destroyed [7]. Moreover, many of these techniques are not environmentally benign and ineffective for long-term applications [8,9]. As a result, an alternative sterilization approach involving photocatalysis has been developed [6,10–13] but the technology has not been used in indoor applications.

Photocatalysis which has many industrial applications including mineralization of organic pollutants, production of renewable fuels, organic synthesis, and sterilization is normally environmentally green. Unfortunately, the wide band gaps of some photocatalysts like TiO_2 and ZnO have hampered wider utilization of visible light [12–15]. Cuprous oxide, a semiconductor with a relatively narrow band gap (2.2 eV), is a promising photocatalyst [16–18] and measures like loading and recombination have been adopted to improve the optical property and photocatalytic performance [19–21].

In this work, mineral wool fibers (MWF) used commonly in building insulation and decoration and manufactured from metallurgical slag are used as the carrier to immobilize cuprous oxide particles. The structure, optical properties, photocatalytic performance against *Escherichia coli* (*E. coli*) [4,9,10] of the Cu_2O/MWF composites are determined.

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2. Experimental details

2.1. Preparation of photocatalyst composites

Mineral wool fibers (MWF) manufactured by Beijing New Building Materials Public Limited Company were washed with deionized water and 50% ethanol to get rid of surface dusts and particles. The chemical reagents used in the experiments including copper sulfate, sodium hydroxide, hydrazine hydrate, polyvinyl pyrrolidone (average molecular weight = 27,000–33,000, PK30) were used without further purification. Copper sulfate and sodium hydroxide were purchased from Beijing Chemical Works and hydrazine hydrate and PK30 were produced by XiLong Chemical CO., LTD.

The Cu_2O/MWF samples were prepared as follows. 10.0 g of the scoured mineral wool fibers were soaked in solutions containing 500.0 mL of copper sulfate with different concentrations of 2–6 mM and 5.0 mL of 3% (W/V) PK30. The blend was ultrasonicated for 1 h to impregnate Cu^{2+} into the MWF. Appropriate amounts (2.0, 3.0, 4.0, 5.0, and 6.0 mL) of 0.1 M hydrate hydrazine were added as reducing agents following the ultrasonic treatment. A 1.0 M sodium hydroxide solution was dropped to the above mixture under vigorous stirring until a pH of about 11 was reached. The reaction proceeded for 15 min at room temperature under violent stirring and red precipitates were produced. The unwanted impurities were removed by filtration and rinsing with deionized water and absolute ethanol several times. The products were acquired after drying in a vacuum desiccator at 85 °C for 2 h. The samples with different cuprous oxide concentrations were labeled as CM-1, CM-2, CM-3, CM-4, and CM-5 (Table 1).

2.2. Characterization of photocatalysts

The crystalline structure and phases were determined on a D/MAX-RC X-ray diffractometer (XRD, Rigaku, Japan) employing 1.5406 Å Cu *K*α radiation at a scanning rate of 8°/min. The scanning range was between 10 and 90°. The microstructure and morphology of the composites were examined by scanning electron microscopy (SEM, LEO1450) and the ultraviolet–visible diffuse reflection absorption spectra (UV–vis/DRS) were acquired on a Lambda-900 UV/vis/NIR spectrometer (Perkin Elmer, USA) at room temperature.

Table 1
The photocatalytic inactivation rate and the physical properties of different Cu_2O/MWF samples.

Sample	CM-1	CM-2	CM-3	CM-4	CM-5	MWF
C_{Cu_2O} (mmol/g)	0.050	0.075	0.100	0.125	0.150	0
[a]BG (eV)	2.40	2.26	2.23	2.18	2.31	–
[b]PIR (%)	87	92	94	95	91	13

[a] BG: band of gaps.

[b] PSR: photocatalytic inactivation rate.

2.3. Preparation of culture media

Meat extract, peptone, and sodium chloride were used to prepare the culture media for *E. coli.* 18.0 g of the nutrient broth (NB) composed of 3.0 g of meat extract, 10.0 g of peptone, and 5.0 g of sodium chloride were dissolved in 1.0 L of boiled deionized water and sterilized in an autoclave at 121 °C to obtain the culture medium. The pH of the medium was adjusted between 7.2 and 7.4 using 1.0 M sodium hydroxide and/or 1.0 M hydrochloric acid.

2.4. Photocatalytic bacteria inactivation

Photocatalytic inactivation of *E. coli* was investigated using a constant temperature rotary bath. The visible light was provided by a 20 W fluorescent lamp (Philips, China) with a wavelength range of 545 to 610 nm positioned about 25 cm above the solution surface. Fig. 1 shows the wavelength range of the lamp obtained by S2000-VIS (Seeman technology, China). To prevent contamination from other bacterial phages, the glass apparatus was disinfected thoroughly in an autoclave at 121 °C for 20 min prior to the experiments.

E. coli was cultured by the standard laboratory culture method [10]. In a typical photocatalytic experiment, 150 mL of NB were incubated in the bath at 37 °C for 24 h in the presence of 1.0 g of immobilized photocatalysts and agitated at 160 rpm under irradiation of visible light. About 1 g of the non-ionic surfactant Tween-100 was employed to disperse the bacteria ahead of photocatalytic experiments. After irradiation for 24 h, the bacterial suspension was centrifugated at 2000 rpm and the absorption spectra were acquired on the TU-1810 ultraviolet–visible spectrophotometer (Purkinje General, China). Suspensions with different bacteria contents showed different absorbance values and the photocatalytic inactivation efficiency was assessed by the contrast between the absorbance values of the bacteria suspension with and without the photocatalysts [23]. Two control experiments were arranged, one conducted in darkness with the photocatalysts and the other under light irradiation without the photocatalysts.

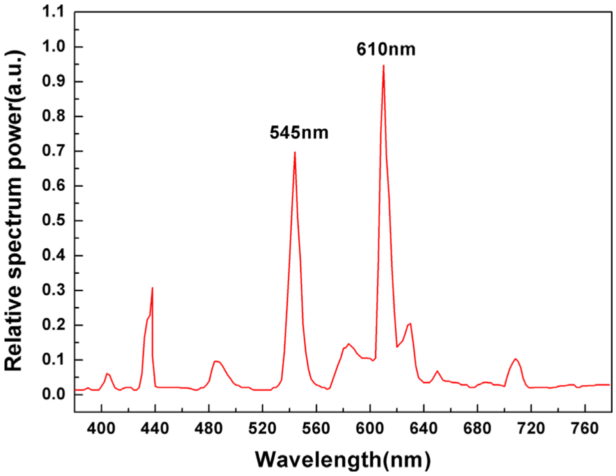

Fig. 1. Emission spectrum of the fluorescent lamp.