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\textsubscript{2}O/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.

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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\textsubscript{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\textsubscript{2}O/MWF composites are determined.
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\(_2\)O/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\(\alpha\) 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.

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 centrifuged 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.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>CM-1</th>
<th>CM-2</th>
<th>CM-3</th>
<th>CM-4</th>
<th>CM-5</th>
<th>MWF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{\text{Cu}_2\text{O}}) (mmol/g)</td>
<td>0.050</td>
<td>0.075</td>
<td>0.100</td>
<td>0.125</td>
<td>0.150</td>
<td>0</td>
</tr>
<tr>
<td>(^a)BG (eV)</td>
<td>2.40</td>
<td>2.26</td>
<td>2.23</td>
<td>2.18</td>
<td>2.31</td>
<td>–</td>
</tr>
<tr>
<td>(^b)PIR (%)</td>
<td>87</td>
<td>92</td>
<td>94</td>
<td>95</td>
<td>91</td>
<td>13</td>
</tr>
</tbody>
</table>

\(^a\)BG: band of gaps.

\(^b\)PSR: photocatalytic inactivation rate.
3. Results and discussion

3.1. XRD patterns of photocatalyst composites

The crystal phase of the mineral wool fibers (MWF) incorporated with different amounts of cuprous oxide is determined by X-ray diffraction (XRD) and Fig. 2 shows the XRD patterns acquired from the Cu$_2$O/MWF composites and MWF from 10 to 70$^\circ$. As the amount of the photocatalyst goes up, the peaks at 36.4, 42.3, and 61.3$^\circ$ corresponding to the crystal planes of (1 1 1), (2 0 0), and (2 2 0) of cuprous oxide according to the JCPDS card No. 34-1354 become progressively more intense, furnishing proof that more cuprous oxide is incorporated into the mineral wool fibers using a higher concentration of the raw materials. The peaks corresponding to the crystal planes of (1 1 1), (2 0 0), and (2 2 0) of cuprous oxide crystals in Fig. 2(b) and (c) are indiscernible due to insufficient cuprous oxide crystals in the MWF. The ridge-like peak near 30$^\circ$ illustrates that the MWF is amorphous silicate. No other impurity peaks are observed from the patterns indicating the absence of impurity crystals in the MWF. The as-prepared cuprous oxide crystals have high purity. A slight shift towards the low angle is observed as a result of the (1 1 0) plane of crystalline cuprous oxide corresponding to 2$\theta$ = 29.6$^\circ$ again suggesting the interaction between MWF and cuprous oxide. The mean size of the cuprous oxide crystals is about 50 nm calculated from the Scherrer equation.

3.2. SEM images of photocatalyst composites

The morphology of the cuprous oxide loaded MWF is examined by scanning electron microscopy (SEM). Fig. 3 reveals that the MWF has a perfect fibrous structure and the octahedral cuprous oxide particles are immobilized on the surface of the mineral wool fibers (Fig. 3f). There are scarcely discrete particles. The crystal size measured by SEM agrees to that derived by XRD. Different amounts of cuprous oxide particles with nanometer scale loaded stably on MWF are widely scattered. The photocatalysts are dispersed effectively in the MWF thereby enhance the utilization efficiency of visible lights.

3.3. UV–vis/DRS and band gaps of photocatalyst composites

The ultraviolet–visible diffuse reflection absorption spectra (UV–vis/DRS) are employed to analyze the optical performance and to estimate the band gap of the Cu$_2$O/MWF composites. The absorption spectra acquired from samples containing different amounts of cuprous oxide are displayed in Fig. 4. All the Cu$_2$O/MWF composites exhibit a clear absorption edge at a wavelength larger than 600 nm while the host MWF shows an absorption edge at a wavelength of less than 400 nm. The intensity increases as the amount of cuprous oxide is increased, except CM-5. CM-1 shows weaker absorbance due to the small photocatalyst concentration. CM-5 also shows lower absorbance than CM-4 because of excessive accumulation of cuprous oxide particles consequently reducing the utilization of visible light. All of the Cu$_2$O/MWF samples exhibit strong absorbance at about 500 nm where the wavelength is very close to that of the visible light emitted by the fluorescent lamp used in our experiments.

To further investigate the optical performance of the photocatalysts, the band gaps are estimated. Cuprous oxide is a direct gap semiconductor boasting efficient light absorption. The band gap of the Cu$_2$O/MWF composites is estimated by the following equation [16].

$$\alpha h\nu = C(h\nu - E_g)^{1/2}$$

where, C is a constant which does not depend on the photon energy and $E_g$ is the band gap energy. The band gap is calculated from the intercept of the tangent in the $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ plot. The plots of $(\alpha h\nu)^2$ versus $h\nu$ for different Cu$_2$O/MWF samples are depicted in Fig. 5 and the direct band gaps of CM-1, CM-2, CM-3, CM-4, and CM-5 are calculated to be 2.40, 2.26, 2.23, 2.18, and 2.31 eV, respectively. The red shift in the direct band gap occurs as the cuprous oxide concentration is larger than 0.125 mmol/g, but the band gap of CM-5 (0.15 mmol/g) widens again due to the excessive amount of cuprous oxide particles. Our results disclose there is an optimal range of concentration.

3.4. Photocatalytic inactivation of E. coli

The photocatalytic inactivation of E. coli is assessed by monitoring the UV–vis absorption spectra of the bacteria suspensions. For comparison, control experiments are performed under visible light irradiation for 24 h at 37 °C without the photocatalysts. There is only a small difference between Curve (1) (nothing) and Curve (8) (MWF) (Fig. 6a). Only a small amount of E. coli can be inactivated when there are no cuprous oxide particles in the MWF, suggesting that inactivation effectiveness rendered by the pure MWF is negligible. Another control experiment is conducted on CM-4 but without light irradiation. A small amount of E. coli is inhibited after 24 h at 37 °C in darkness, implying that Cu$_2$O/MWF works poorly without light irradiation (Fig. 7).
The UV–vis absorption spectra of bacteria suspensions with different Cu$_2$O/MWF samples after incubation for 24 h at 37 °C are depicted in Fig. 6a which shows obvious differences among the samples. The inactivation efficacy is enhanced with a larger amount of cuprous oxide, although CM-5 is an exception as aforementioned. CM-4 exhibits the optimal photocatalytic inactivation activity and the results are consistent with the ultraviolet–visible diffuse reflection absorption spectra (Fig. 4). The bacteria concentrations are derived from the optical density readings at 600 nm (OD$_{600}$). The converting factor is calculated from the plot of OD$_{600}$ values versus logarithmic bacteria concentrations [22,23]. The bacteria culture is diluted sequentially with the culture medium by factors of $10^{-1}$ to $10^{-7}$, and the OD$_{600}$ value of the diluted samples are measured. The bacteria concentrations in the diluted samples are determined by the standard plating method. The OD$_{600}$ values are plotted against the log bacteria concentrations to obtain the conversion factors. The inactivated bacteria percentage is determined by the following equation:

$$S(\%) = \frac{C_0 - C_s}{C_0} \times 100\%$$

where, $S(\%)$ is the inactivation rate of *E. coli* and $C_0$ and $C_s$ are the concentrations of the bacterial suspension based on...
OD600 after incubation for 24 h in the absence and presence of photocatalyst composites, respectively. The photocatalytic inactivation rates of *E. coli* for CM-1, CM-2, CM-3, CM-4, CM-5, and MWF are 87, 92, 94, 95, 91, and 13%, respectively (Fig. 6b and Table 1). CM-4 shows the best inactivation. Our data reveal that *E. coli* can be effectively inactivated by mineral wool composites containing 0.125 mmol/g of the photocatalyst under irradiation of visible light and the materials have large potential in indoor antibacterial applications.

4. Conclusion

Cuprous oxide is incorporated into mineral wool fibers to achieve photocatalytic inactivation of *E. coli*. Red shift in the band gap is observed from the composite materials and the optical property and photocatalytic performance are enhanced. The optimal cuprous oxide concentration is 0.125 mmol/g and at this concentration, 95% of *E. coli* can be inactivated under 20 W visible light illumination for 24 h at 37°C. The materials have high efficiency, low energy consumption, and slight pollution and are promising in indoor antibacterial applications.
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