



# Influence of copper doping on chlorine adsorption and antibacterial behavior of MgO prepared by co-precipitation method



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## ABSTRACT

Pure MgO and Cu-doped MgO nanopowders were obtained by a chemical co-precipitation process. The influence of copper doping on the crystal structure and particle morphology of MgO is discussed. The XPS results indicate that the Cu ion has been successfully incorporated into the MgO lattice. Adsorption tests show that the pseudo-second-order fitting equation is better for describing the adsorption kinetics of chlorine on MgO nanoparticles. The antibacterial properties of MgO nanopowders were investigated, as well as the influence of storage time on the adsorption and the antibacterial properties.

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## 1. Introduction

Magnesium oxide (MgO) is widely used for catalysis, toxic waste remediation and antibacterial action due to its well-defined surface defect structure, which includes low-coordinated ions and vacancies. MgO can absorb some ionic organic and waste gases [1–5] because of the large number of defects present on the surface. The novel and useful properties of MgO are further enhanced when the MgO particles are made smaller so as to contain more defects. The incorporation of another element into the oxide also is a very useful method to modify its physical and chemical properties [6,7]. Doping another metal ion into the oxide produces lattice defects such as vacancies, which play an important role in modifying the physical and chemical properties of the oxide to a certain extent [8–10]. For example, copper and iron doping influence the magnetic properties of ZnO powder [11]. In the case of metal doping in the MgO system, much research has been reported in recent years [12–15]. Wang et al. used the chemical co-precipitation method to prepare Ti-doped MgO powder, and studied the effects of Ti doping on its morphology and structure [16]. Trionfetti et al. investigated the inclusion of

lithium ions in the MgO lattice by using infrared spectroscopy to study the oxidative conversion of propane [17]. Balint et al. investigated the creation of specific defect sites by doping MgO with lithium and titanium [18]. Most of the previous studies investigated the influence of doping on the morphology and defect content of MgO, rather than the influence on adsorption and the antibacterial behavior of doping, especially with regard to copper doped MgO.

In this work, nano-sized Cu-doped MgO powder was prepared by a chemical co-precipitation process using magnesium nitrate hexahydrate, oxalic acid and copper acetate as precursors with ethanol as a solvent. The influence of copper doping on the crystal structure and particle morphology of magnesium oxide is discussed. The adsorption properties of Cu-doped MgO nano-powder were studied by measuring chlorine adsorption. The influence of storage time on adsorption was studied using an antibacterial test.

## 2. Experimental

### 2.1. Synthesis of Cu-doped MgO nanoparticles

All chemical reagents used were analytic grade and were used without further purification. In a typical synthesis of Cu-doped MgO nanoparticles, a quantity  $x$  mol of copper acetate was dissolved in ethanol.  $(0.2 - x)$  mol  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.2 mol  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$  were dissolved in ethanol separately and stirred to

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obtain two clear solutions. Then the three solutions were mixed together to yield a light green precursor solution, and stirring was continued for 30 min. Subsequently, the precursor was maintained undisturbed for 12 h, and the final light green precursor product was washed with ethanol, collected by filtration, and then dried at 80 °C in an oven. Nano-sized MgO was then prepared by calcination of the precursor in air at 500 °C at 10 °C min<sup>-1</sup> for 2 h.

## 2.2. Adsorption experiments

Adsorption experiments were carried out separately in a batch process in a homemade chlorine adsorption apparatus. In a typical test, a quantity  $a$  (about 0.5 g) of a freshly activated Cu-doped MgO sample was spread evenly on an agar plate, and then the weight of the dry Cu-doped MgO powder plus the agar plate was recorded and denoted as " $b_1$ ". The agar plate filled with Cu-doped MgO powder was placed in the dry chlorine adsorption device. The air was extracted from the adsorption device, chlorine was admitted into the apparatus to a pressure of 2 KPa, and the powder was allowed to adsorb the gas at about 25 °C until a steady state was reached. After adsorption, argon was back-filled into the apparatus to discharge any residual chlorine. The residual chlorine was absorbed with a sodium hydroxide solution. The weight of the resulting MgO-Cl<sub>2</sub> was denoted as " $b_2$ ", and the formula below was used to calculate the adsorption rate  $c$ :

$$c = 1000 \times \frac{(b_2 - b_1)}{a} \text{ mg/g} \quad (1)$$

Adsorption is a complex process, so understanding the kinetics is important for adsorption studies because it can be used to predict the rate at which an adsorbate is removed, and further provides valuable data for understanding the mechanism of sorption reactions [19–21]. For the physical adsorption process, pseudo-first-order and pseudo-second-order models are often used to describe and analyze the dynamics. The pseudo-first-order Lagergren rate equation is given by:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where  $q_e$  and  $q_t$  is the amounts of chlorine absorbed (mg/g) at equilibrium and at time  $t$  (min), respectively. The quantity  $k_1$  (min<sup>-1</sup>) is the pseudo first-order rate constant. Values of  $k_1$  were calculated from a plot of  $\ln(q_e - q_t)$  versus  $t$ .

The rate equation for the pseudo-second-order model is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where  $k_2$  (g/mg/min) is the pseudo-second-order rate constant, and its value was obtained from a plot of  $t/q_t$  versus  $t$ .

## 2.3. Test of antibacterial activity

Base on the existing literature [4], the inhibition zone was almost not observed for *E.coli*, so antibacterial tests were performed on *Escherichia coli* (*E. coli* ATCC 2385) to confirm the antimicrobial activity of the powder samples. Pure MgO, 1 mol% Cu-MgO, 2 mol% Cu-MgO, and 5 mol% Cu-MgO were used as the test materials. The bacteria were cultured in an agar nutrient medium at 37 °C for 24 h, and then their concentration was adjusted to 10<sup>5</sup> CFU/mL (CFU: colony-forming units) by diluting them with a sterile buffer. To evaluate the bactericidal efficacy of the samples, a sample (0.25 g) was added to 47.5 mL of buffer to achieve a suspension. A quantity of 2.5 mL of the bacterial solution with 10<sup>5</sup> CFU mL<sup>-3</sup> was added to each sample solution, and then

the mixture was incubated by shaking at 37 °C for 15 min and 24 h. An amount of 1 mL of the mixture solution was spread on the standard method agar plates. Then 1 mL of the mixture solution was added to 9 mL of the buffer (first dilution) and 1 mL of resulting the solution spread on standard method agar plates. A quantity of 1 mL of the first dilution mixture was added to 9 mL of the buffer (second dilution) and 1 mL of the resulting solution spread on standard method agar plates. The plates were then placed in an incubator and incubated at 37 °C for 48 h. The bactericidal rate ( $\rho$ ) was calculated according to the following equation [22]:

$$\rho(\%) = \frac{N_0 - N_1}{N_0} \times 100 \quad (4)$$

where  $N_0$  and  $N_1$  is the number of bacteria colonies corresponding to the positive control group and the sample group, respectively.

A quantity of 2% Cu-doped MgO and 2% Cu-doped MgO with chlorine adsorbed for a period of 24 h (and stored some time) were used as the test material. About 0.1 g of the powder samples were pressed into 10 mm diameter pieces. The antimicrobial effect of 2% Cu-doped MgO-Cl<sub>2</sub> samples were determined by means of disk diffusion assay using *E. coli* as a model bacterium. A quantity of about 20 mL of agar was poured into a sterilized dish, and solidified. The freshly prepared *E. coli* (0.1 mL) with a concentration of 10<sup>5</sup> CFU/mL was uniformly inoculated onto the solidified agar gel. Each sample was placed on the agar plate, and then incubated at 37 °C for 24 h. The antimicrobial activity was compared by measuring the diameters of the inhibition zone around each sample.

## 2.4. Characterization

The crystal structures of the as-prepared samples were characterized by X-ray diffraction (XRD). The size and morphology of the samples were examined by transmission electron microscopy (TEM). The data required for Brunauer-Emmett-Teller (BET) specific surface area analysis were measured on a Micromeritics ASAP 2010 physisorption analyzer. The existence of Cu in the MgO phase was further confirmed by X-ray photoelectron spectroscopy (XPS). The photoluminescence (PL) spectrum was measured at room temperature using a spectrophotometer (SPEX-1403) with an excitation wavelength of 325 nm.

## 3. Results and discussion

### 3.1. Structure and morphology

XRD patterns of pure MgO and Cu-doped MgO samples calcined at 500 °C for 2 h are shown in Fig. 1a, and the analytical data are listed in Table 1. All of the diffraction peaks are consistent with the cubic MgO structure (JCPDS 45-0946). The strong clear peaks reveal good crystallinity in the as-obtained product. No characteristic peaks from the cuprous or copper oxide phase were detected in the scanning range, nevertheless the peak intensity decreased with increasing Cu content. This result indicates that copper doping inhibits the crystallization of MgO. From Fig. 1b, it can be seen that the (200) diffraction peak shifts toward lower angles with increasing copper content. Also, the data in Table 1 clearly show that the lattice parameter  $a$  increases with increasing Cu content. These results all imply that the Cu has been incorporated into the MgO crystal lattice. Because the ionic radius of Cu (0.073 nm) is slightly larger than the ionic radius of Mg<sup>2+</sup> (0.066 nm), it is easy for Cu ions to be doped into the MgO crystal lattice and occupy substitutional sites. Moreover, the size discrepancy results in an increase in interplanar spacing. By considering Bragg's law:  $\lambda = 2d \sin \theta$ , it can be understood that

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