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Preparation and Photocatalytic Performance of Cu_2O Nanopowders Using Liquid Phase Method†

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Cu_2O nanopowders were prepared by liquid phase reduction method by which $CuSO_4$ and Na_2SO_3 were used as raw materials and the preparation solution pH value was adjusted by NaOH. The nanopowders were charactered by XRD and SEM. According to the XRD results, the nanopowders prove to be Cu_2O. The SEM results show that powders were of uniform morphology. The main factors that effect on nanoparticle size of Cu_2O were followings: pH, raw materials concentration and reaction time. The Cu_2O nanopowders were used as photocatalyst to degrade methyl orange in water solution when photodegradation experiments were carried out. According to the results of photodegradation, the dosage of Cu_2O powders, the pH value of methyl orange solution were of obvious effect on photocatalysis efficiency.

Key Words: Cu_2O, Nanopowders, Liquid phase method, Photocatalytic, Methyl orange.

INTRODUCTION

To date, semiconductor-based photocatalysis has attracted more and more attention as a kind of "green" technology for air and water purification with solar energy. Among them, TiO_2 has proved to be an excellent photocatalyst for the oxidative decomposition of many organic compounds[1]. However, the relatively wide bandgap (3.2 eV) limits its further application in the visible region (λ = 390-780 nm)[2]. In this regard, semiconductors with narrow band gap have received more and more interest for photocatalysis under visible light[3]. Cuprous oxide (Cu_2O), is one of the most important semiconductor materials with a narrow band gap (E_g = 2.17 eV), widely used as gas sensors, solar cells and photocatalysis[4]. The successful application of Cu_2O photodegradation technique to remove methyl orange from dyeing wastewater has been reported[5]. Today, there were many methods to prepare Cu_2O nanopowders[6]. In this work, well defined Cu_2O nano-powder with unique morphologies have been fabricated simply by using aqueous solution containing copper sulfate and sodium sulfite instead of any expensive reagents *via* a low-temperature and environment-friendly soft chemical method.

EXPERIMENTAL

Preparation of Cu_2O powder: All reagents were of analytical grade and used without further purification. Cu_2O powder was precipitated from a solution containing $CuSO_4$ and Na_2SO_3 which were raised to a predetermined pH value by adding 10 mol/L NaOH solution under constant stirring. Precipitation reaction temperature, time was 100 ºC[7] and 1 h, respectively. After 1 h, the precipitation system was cooled and aged in air at room temperature for 0.5 h. And then, Cu_2O precipitation was separated from solution by centrifugal separation (10000 r/min, 10 min). After washed by absolute ethyl alcohol, the precipitation was dried in air at 120 ºC for 2 h. The preparation of Cu_2O powder was completed.

In this paper, a series of experiments at different process conditions was carried out when Cu_2O powder was prepared. The process conditions were listed following:

Series of solution pH: After mixing 36 mL Na_2SO_3 (1 mol/L) and 20 mL $CuSO_4$ (1 mol/L), the solution was diluted with deionized water till solution volume was raised to 50 mL. By adding 10 mol/L NaOH, the solutions pH value was adjusted to 7, 8, 9, 10, 11, 12 and 13 respectively.

Series of Na_2SO_3 concentration: The solutions were made by mixing 20 mL $CuSO_4$ (1 mol/L) and 30, 33, 36, 39, 42 and 45 mL Na_2SO_3 (1 mol/L), respectively. (*i.e.* the overdose Na_2SO_3 were 0, 10, 20, 30, 40 and 50 %, respectively). By adding NaOH, the solutions pH value was adjusted to 8.

Series of $CuSO_4$ congcntration: The solutions were made by mixing 9, 18, 27, 36, 45, 54 mL Na_2SO_3 (1 mol/L) and 5,

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10, 15, 20, 25, 30 mL $CuSO_4$ (1 mol/L), respectively. The solutions pH value were also adjusted to 8.

Photodegradation experiments: The Cu_2O nanopowders prepared as mentioned above were used for photocatalyst. A methyl orange solution was chosen for photodegradation. Different amount of Cu_2O nanopowders and methyl orange solution with different concentration were mixed in photodegradation reactor-a glass culture dish which diameter and height were 12.0 cm and 1.8 cm, respectively. A 70 W iodine-tungsten lamp (Z30RR25) was used as the solar simulator. The distance between the bottom of the lamp and the top of the solution is 18 cm. The photodegradation reactor was gently shaken on the platform of a horizontal shaking table at room temperature when photodegradation experiments were carried out. The factors that effect on photodegradation, such as methyl orange solution pH value, original methyl orange concentration and the dosage of Cu_2O nanopowders were investigated in this paper and the best photodegradation conditions were obtained also.

Characterization of photodegradation performance: A 7230 G ultaviolet-visible spectrometer was used to record the change of the absorbency of the methyl orange solution after the irradiation. The degradation rate (h) was replaced by the decolour rate (D)[8] and was calculated by the following formula:

$$D = (A_0 - A_t)/A_0 \times 100\ \% \quad (1)$$

The "A_0" and "A_t" in the formula present the absorbency values of the methyl orange solution at maximum absorption wavelength (470 nm) before and after photodegradation, respectively.

RESULTS AND DISCUSSION

Cu_2O nanopowders preparation and XRD characterization

Effect of precipitation solution pH value on nanoparticle size of Cu_2O: The X-ray diffraction patterns of Cu_2O nanopowders were investigated by a X-ray diffractometer (Y-2000, Dandong Radiative Instrument Group Co. Ltd., Liaoning, PRC) with CuK_α radiation. The XRD parameters: tube voltage was 30 kV, tube current was 20 mA, scan step length was 0.06º and scan speed was 3.600º/min. Fig. 1 shows the X-ray diffraction patterns of the different Cu_2O nanopowders which were precipitated in the solutions with different pH value. According to Scherrer formula[9], the nanoparticle sizes of Cu_2O precipitated from the solutions with different pH value were estimated and showed in Fig. 1 (d is average diameter, similarly hereafter).

When pH were 8 and 9, the XRD powders patterns were consistent with the Cu_2O powder standard card: PDF # 05-5667 and the powders can be perfectly indexed as cubic structures which lattice parameter a is 0.4269 nm.

Effect of Na_2SO_3 over-dose on nanoparticle size of Cu_2O: Fig. 2 shows that nanoparticle size of Cu_2O became small when Na_2SO_3 over-dose increased. The smaller nanoparticle size of Cu_2O would be helpful in photocatalysis.

Effect of $CuSO_4$ concentration on nanoparticle size of Cu_2O: Fig. 3 shows that nanoparticle size of Cu_2O became small slightly when $CuSO_4$ concentration increased. The smaller nanoparticle size of Cu_2O would be helpful in photocatalysis.

Given the above, the optimal Cu_2O nanopowder preparation conditions were followings: Na_2SO_3 over-dose is 20 %; $CuSO_4$ concentration is 0.20 mol/L; solution pH value is 8; precipitation reaction temperature, time are 100 ºC and 1 h, respectively.

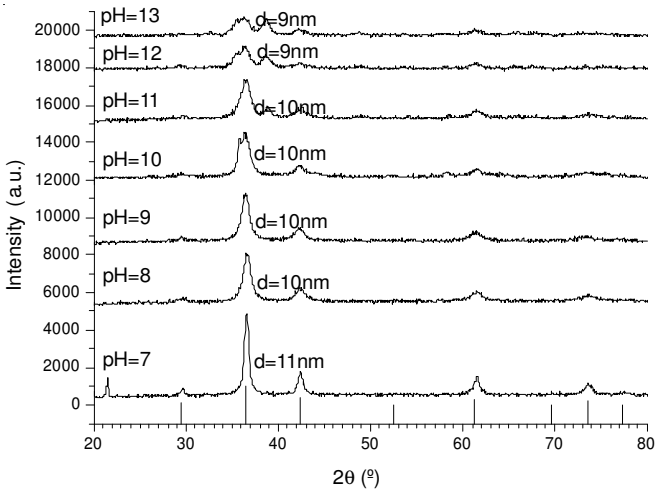

Fig. 1. Effect of precipitation solution pH value on nanoparticle size of Cu_2O

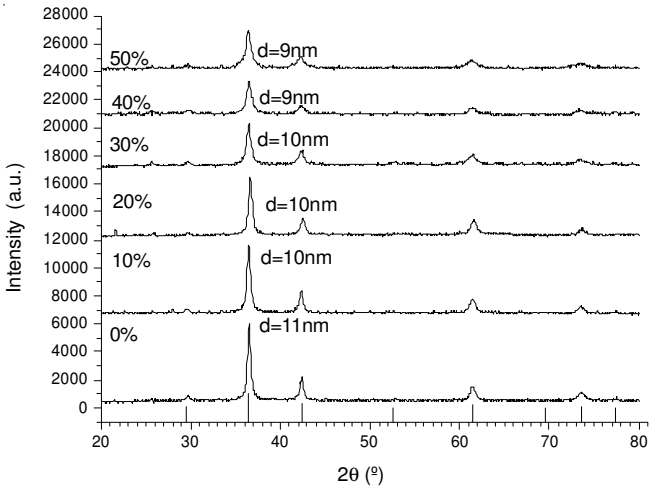

Fig. 2. Effect of Na_2SO_3 over-dose (%) on nanoparticle size of Cu_2O

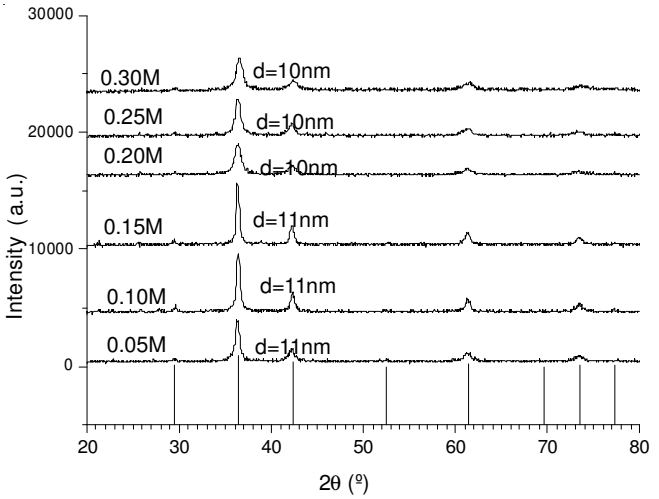

Fig. 3. Effect of $CuSO_4$ concentration on nanoparticle size of Cu_2O

Fig. 4 shows XRD pattern of the Cu_2O nanopowder obtained at the optimal preparation conditions. From Fig. 4, strong reflections which 2θ value are 36.48, 42.29, 61.44 and 73.65º corresponding to (111), (200), (220) and (222) planes are observed. The most strong peak is (111), indicating the powder is polycrystalline with obvious (111) preferred orientation. The other peaks are obviously weaker than (111) peak, indicating the preparation conditions were not conducive to the growth of other orientation.

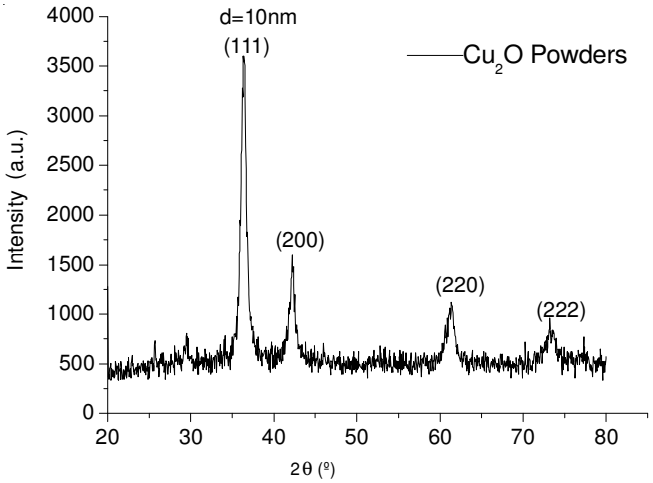

Fig. 4. XRD pattern of the Cu_2O nanopowder obtained at the optimal preparation conditions

Morphology of Cu_2O nanopowder: Fig. 5 shows the top-view SEM images (Sirion 200, FEI Company, USA) of the powders obtained at the optimal preparation conditions. Image (a) and (b) were obtained at magnification 50000 and 200000, respectively. Fig. 5 shows the crystal grains are of uniform shape and like diamond flowers. There are much spaces among the grains which are helpful in photocatalysis. The Cu_2O nanopowder is cubic crystals with preferred (111) growth orientation, which is consistent with the XRD pattern in Fig. 4.

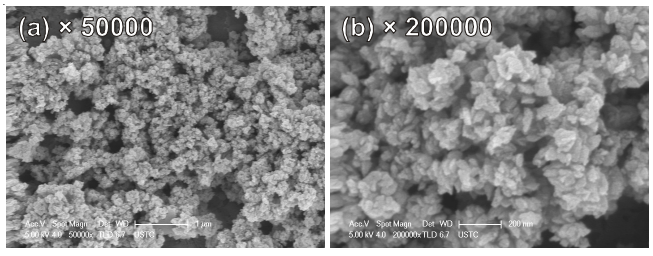

Fig. 5. SEM images of the Cu_2O nanopowder obtained at the optimal preparation conditions

Photodegradation of methyl orange using Cu_2O nanopowders

Effect of Cu_2O nanopowders dosage on photodegradation performance: Fig. 6 shows the effect of Cu_2O nanopowders dosage on photodegradation performance. The solution concentration of methyl orange and volume were 50 mg/L and 100 mL. The black, red, blue and magenta lines represent the methyl orange degradation rate of the solution mixed with 0.1, 0.2, 0.3 and 0.0 g Cu_2O nanopowders, respectively. The magenta line shows photodegradation speed of methyl orange was very slow when the Cu_2O dosage was 0.0 g. The other lines show the photodegradation was obviously speeded up when the Cu_2O nanopowders added in the methyl orange solution. The black, red and blue lines in Fig. 6 show that photodegradation speed became slow when Cu_2O nanopowders dosage increased, from 0.1 g to 0.3 g, therefore, the best Cu_2O dosage was 0.1 g.

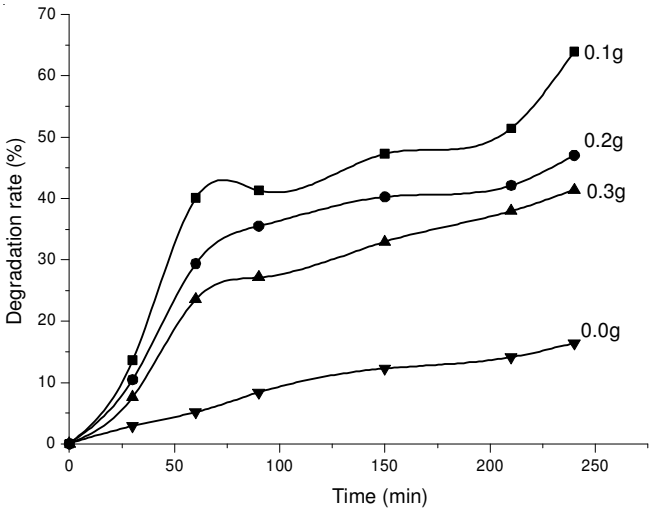

Fig. 6. Effect of Cu_2O nanopowders dosage on photodegradation performance

Effect of solution pH on photodegradation performance: Fig. 7 shows that photodegradation was slowed down when solution pH increased, from 3 to 11. Cu_2O powder would be dissolved in acid methyl orange solution and could be stable on neutral or alkaline condition, so the optimal methyl orange solution pH was 7.

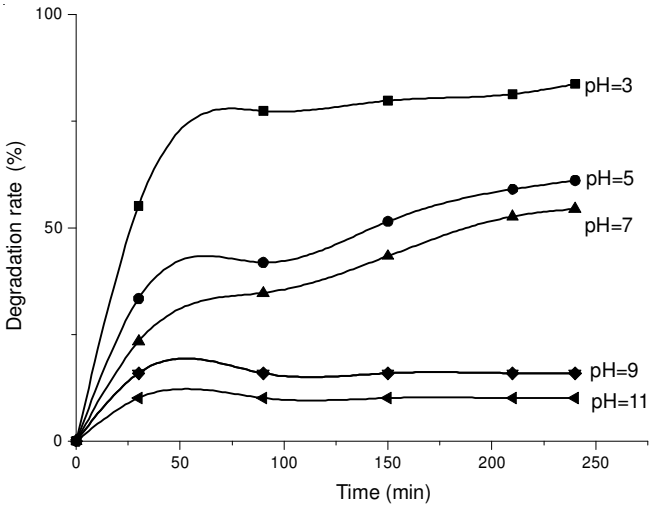

Fig. 7. Effect of solution pH on photodegradation performance

Conclusion

The Cu_2O nanopowders were prepared by liquid phase reduction method by which $CuSO_4$ was raw material and Na_2SO_3 was reductant. The optimal preparation conditions were followings: Na_2SO_3 over-dose was 20 %; $CuSO_4$ concentration was 0.20 mol/L; solution pH value was 8; precipitation

reaction temperature, time were 100 ºC and 1 h, respectively. The Cu_2O nanopowders were effective photocatalyst on methyl orange solution photodegradation. The optimal photodegradation conditions were followings: solution pH value was 7 and Cu_2O nanopowders dosage was 0.1 g/L, respectively.

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