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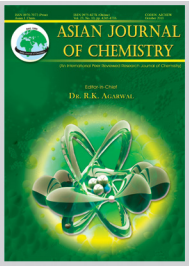

Photocatalytic Properties of Cupric Oxide Nanosheets Prepared by a Low-Temperature Soft Solution Processing†

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Cupric oxide nanosheets with uniform thickness less than 20 nm have been prepared by a low-temperature soft solution processing simply using $Cu(NO_3)_2$, NH_4Cl and ammonia instead of any toxic and dangerous reagents. The results illustrate that well defined CuO nanosheets can be obtained at 80 ºC for 1 h with pH of 10. The prepared CuO nanosheets show quite good photocatalytic activity under irradiation of solar simulator lamp. The photocatalytic degradation is strongly dependent on solution pH, and H_2O_2 is quite favorable for degradation of methyl orange in CuO nanosheets photocatalytic system.

Key Words: CuO, Nanosheets, Visible light, Photocatalytic, Soft solution processing.

INTRODUCTION

Cupric oxide (CuO) has the unique property of being intrinsically *p*-type and with a low band gap (1.2-2.0 eV) making it the lowest bandgap metal oxide available semiconductor[1]. The low band gap of CuO could prove it useful in photodetection and optical switching applications in the visible range where other metal oxides with their larger band gaps fail to perform[2]. It is a promising semiconductor for solar cell fabrication due to its suitable optical properties[3]. It also attractive as a selective solar absorber since it has a high solar absorbency and a low thermal emittance[4]. Furthermore, it is possesses unusual photocatalytic degradation properties of organic substances under visible light irradiation. The photocatalytic degradation is generally dependent on morphology and size of photocatalysts. Nanosized photocatalysts with unique morphologies such as core-shell structures, nanosheets and nanotubes show enhanced photocatalytic properties[5].

In this work, well defined cupric oxide nanosheets have been fabricated simply by using $Cu(NO_3)_2$, NH_4Cl and $NH_3{\cdot}H_2O$ instead of any toxic and dangerous reagents *via* a low-temperature and environment-friendly soft solution processing. The photocatalytic degradation properties have been investigated.

EXPERIMENTAL

Material and general procedure: All reagents were of analytical grade and used without further purification. Under continuous stirring, 2 mL NH_4Cl (0.04 M) was added into $Cu(NO_3)_2$ solution (0.01 mol/L), the pH value of the mixed solution was adjusted to 10.0 by ammonia (30 %). The beakers containing the solution were maintained at 80 ºC for 1 h. After cooling to room temperature, the precipitates were collected, washed with deionized water and dried at 100 ºC for 2 h.

Detection method: The structure and overall crystallinity in the powders were characterized through θ-2θ scans obtained on a Y-2000 X-ray diffractometer (XRD) with CuK_α radiation. Morphology and size were monitored through scanning electron microscopy (SEM) on a Sirion 200 field-emission SEM operated in a 5-10 kV voltage range.

The photocatalytic property of the products was tested in our home-made instruments. At first, the product was dispersed into the culture dish filled with 100 mL 10 mg/L methyl orange solution. The suspensions was put onto velocity-modulated oscillator and irradiated under the light. The applied light source was solar simulation lamp (80 W) with whole emission wavelength range.

The concentrations of methyl orange solution were determined by measuring the absorbance at 470 nm with the UV spectrophotometer (721) and the degradation ratio was calculated by the following formula:

$$\text{Degradation ratio} = \frac{(A_0 - A_1)}{A_0} \times 100\ \%$$

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where, A_0 and A_1 represent the absorbance values at 470 nm of methyl orange solution before and after photocatalytic degradation, respectively.

RESULTS AND DISCUSSION

Fig. 1 shows XRD pattern of the obtained powder. All peaks on XRD pattern are corresponding to that of monoclinic CuO (PDF card No. 72-629), which indicates that the powder is phase-pure monoclinic CuO in good crystallinity.

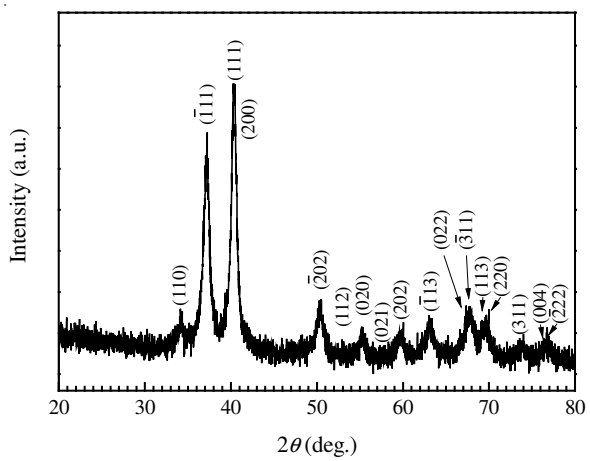

Fig. 1. XRD pattern of the obtained powders

Morphology and size of the prepared powder were characterized by SEM shown in Fig. 2. It indicates that the obtained CuO powder is consisted of nanosheets with uniform thickness less than 20 nm.

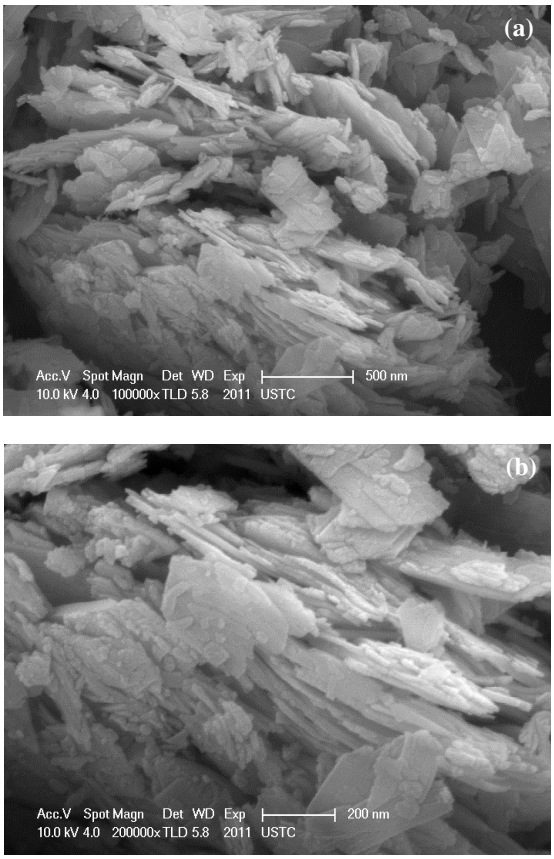

Fig. 2. SEM images of the obtained powder, (a) 100000×, (b) 200000×

The influence of parameters including H_2O_2, pH and the usage amount of CuO nanosheets on photocatalytic degradation efficiency has been investigated. Fig. 3 shows the influence of usage amount of H_2O_2 on photocatalytic degradation of methyl orange with the prepared CuO nanosheets (0.3 g) under daylight lamp irradiation for 2 h. The degradation ratio increases with enhancing the volume of H_2O_2. The degradation ratio of methyl orange by CuO nanosheets without using H_2O_2 is only 32 %. With 15 mL H_2O_2 (3 %) assisted, the degradation ratio increases to 74 %. However, further enhancing H_2O_2 (20 mL) causes the degradation decrease slightly. Here, H_2O_2 plays two important roles in photocatalytic processing, on one hand it can produce $OH^{\cdot}$, which helps the degradation of methyl orange; on the other hand, it can capture photons, which decreases the number of electrons and holes in CuO nanosheets generated by photons[6]. Therefore, the volume of H_2O_2 in CuO nanosheets photocatalytic system should be controlled.

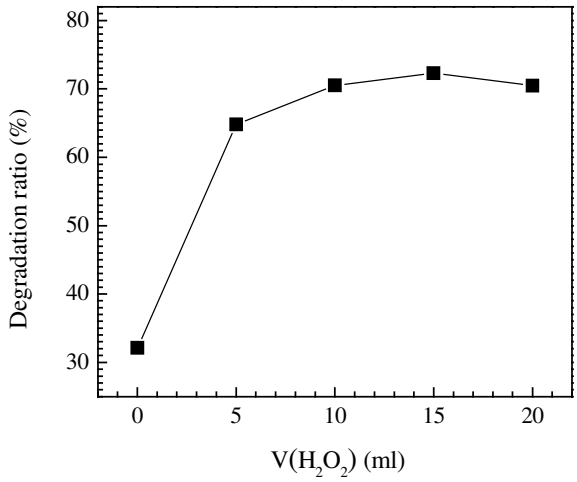

Fig. 3. Photocatalytic degradation of methyl orange assisted with H_2O_2

The influence of pH on degradation shows in Fig. 4. It indicates that the degradation effect is strongly dependent on pH of the solution reaction media in CuO nanosheets photocatalytic system assisted by H_2O_2. The degradation ratio decreases with enhancing solution pH, which means the degradation is high under neutral condition.

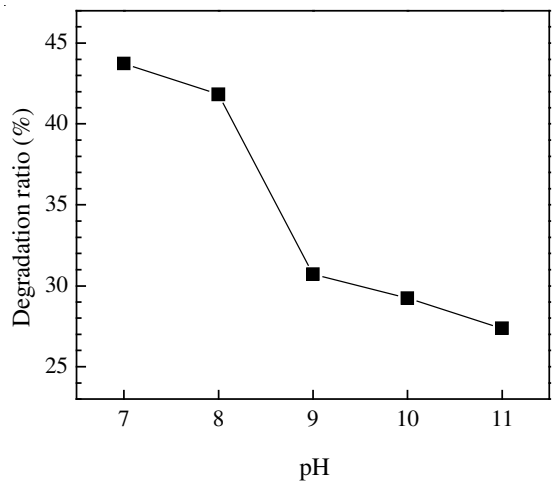

Fig. 4. Photocatalytic degradation of methyl orange at different pH values

Fig. 5 shows the influence of the usage amount of photocatalyst CuO nanosheets on the degradation of methyl orange with H_2O_2 assisted. The degradation ratio enhances gradually with increasing the usage amount of CuO nanosheets. As CuO increases to 0.5 g, the degradation ratio reaches maximum. Further increase the concentration of CuO, the degradation ratio reduces, because the transmittance of solution decreases with increase of the usage amount of photocatalyst in the solid-solution two phases catalytic reaction system. The photocatalyst particles scatter irradiation light resulting in reduction of the effective utilization rate of light, which causes lower degradation[7].

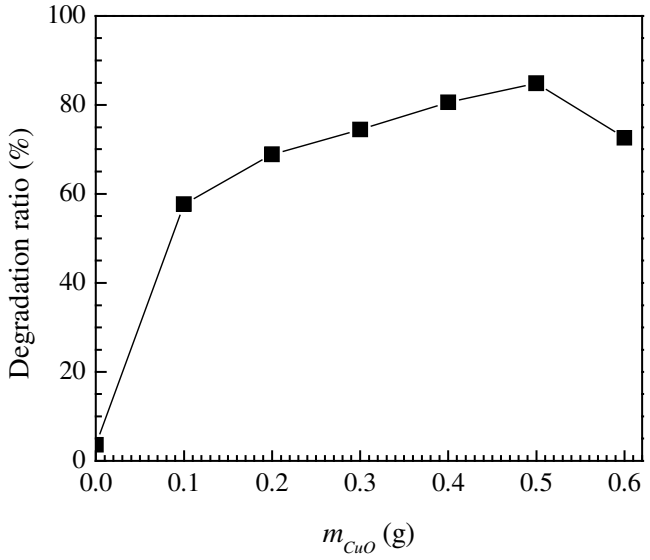

Fig. 5. Degradation ratio varies with amount of CuO nanosheets

Conclusion

A low-temperature and environment-friendly soft solution processing has been successfully applied to fabricate CuO nanosheets. The results show that CuO nanosheets with uniform thickness less than 20 nm could be obtained using $Cu(NO_3)_2$ as Cu^{2+} ion source, NH_4Cl as buffer solution and ammonia as complexing agent as well as pH adjustment agent with pH of 10 at 80 ºC for 1 h. The investigation on photocatalytic degradation of methyl orange indicates that the prepared CuO nanosheets show good photocatalytic activity under irradiation of solar simulator lamp. The photocatalytic degradation is strongly dependent on solution pH and H_2O_2 is quite favourable for degradation of methyl orange in CuO nanosheets photocatalytic system.

ACKNOWLEDGEMENTS

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