

Convenient and green soft chemical route to cuprous oxide films and their visible-light photocatalytic properties

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Cuprous oxide (Cu_2O) films have been synthesised by a convenient and green soft chemical route at room temperature. The films were obtained through the chemical reduction of copper acetate by ascorbic acid in solutions with ethylene glycol and deionised water. X-ray diffraction, energy-dispersive X-ray spectrometry, scanning electron microscopy (SEM), atomic force microscopy, as well as UV-Vis spectroscopy (UV-Vis) were used to characterise the resulting films. It was obvious from the SEM image that the obtained films were composed of nanosphere particles with a size of 100–400 nm. The photocatalytic activity of degradation of methyl orange (MO) of the obtained Cu_2O films, H_2O_2 and $\text{H}_2\text{O}_2/\text{Cu}_2\text{O}$ films system under visible light irradiation was also investigated. The results have shown that the system exhibits high catalytic ability under visible light irradiation. Also, there was a strong synergistic effect between the obtained Cu_2O films and H_2O_2 when the system was used to degrade MO.

1. Introduction: Semiconductor nanomaterials have attracted considerable attention in recent years, especially the optically active semiconductors [1, 2]. Among them, cuprous oxide (Cu_2O) has become more and more important with the increase in environmental pollution, which can be used as a photocatalyst in the visible region [3]. Among the different morphologies of Cu_2O , films should have a high surface area to obtain an efficient light harvesting [4].

Many efforts also have been devoted to the research of Cu_2O films, which have potential applications in solar cells [5], photocatalysis [6, 7], electrochromic devices [8], and in oxygen and humidity sensors [9]. Various methods have been used in attempts to obtain thin films of Cu_2O , such as sputtering [10, 11], electrodeposition [12], sol-gel [13], spin coating [14], thermal oxidation of Cu [15] and pulsed laser deposition [16]. In the work reported in this Letter, Cu_2O films were prepared by a chemical route at room temperature. A series of characterisation methods were used to investigate the resulting films. The photocatalytic degradation of methyl orange (MO) over the obtained Cu_2O films with H_2O_2 is discussed. A strong synergistic effect between the resulting Cu_2O films and H_2O_2 in degradation was obtained.

2. Experimental: The Cu_2O films were deposited on the polished side of silicon substrates by the chemical route. In a typical experiment, the silicon substrates were adhered to the bottom of the beaker (200 ml) which was used as the reaction vessel. Then 40 ml ethylene glycol was added into the vessel under slow stirring. After that, a copper acetate solution (0.2 g of copper acetate was added into a glass beaker containing 10 ml of deionised water) and an ascorbic acid solution (0.528 g of ascorbic acid was dissolved in 10 ml of deionised water) were prepared. Finally, the two solutions were simultaneously added into the reaction vessel at room temperature. The mixture turned black at once and then became yellow, indicating the formation of Cu_2O . After stirring for 1 h, the mixture was put aside for another 1 h. Lastly, the silicon substrates were taken out and washed by absolute ethanol softly.

The crystallographic structure of the obtained films was analysed with an X-ray diffractometer (XD-3 system, Beijing Purkinje General Instrument Co. Ltd) with Cu-K α radiation ($\lambda = 0.154178$ nm) at a scanning rate of 0.02°s^{-1} in the 2θ range from 20° to 80° . The scanning electron microscopy (SEM) and energy-

dispersive X-ray spectroscopy (EDX) were measured with a FEI Quanta 250 emission SEM equipped with an energy spectrum analytical system. Atomic force microscopy (AFM) was employed with CSPM5500 scanning probe microscope. The Brunauer-Emmett-Teller (BET) specific surface area of the samples was analysed by nitrogen (N_2) adsorption-desorption in a Quantachrome 2QDS-MP-30. UV-Vis absorption spectra were recorded using a Hitachi U-3310 spectrophotometer.

To investigate the photocatalytic property, MO was chosen for photodegradation. Cu_2O films deposited for 2 h with the size of 1×1 cm were used for the photocatalytic investigation. First of all, three pieces of Cu_2O films, 3 ml 2 wt% H_2O_2 and three pieces of Cu_2O films, 3 ml 2 wt% H_2O_2 were added into a 45 ml 20 mg/l aqueous MO solution. Then the mixture was placed in the dark for 45 min under constant stirring in order to make the molecules achieve the balance of adsorption and desorption onto the surfaces of the catalyst. After that, the beaker was irradiated under a Xenon lamp with two fans blowing the air to keep a constant temperature. A measure of 3 ml of the mixtures at irradiation intervals of 20 min was withdrawn and characterised by UV-Vis absorption spectroscopy.

3. Results and discussion: Fig. 1 shows the X-ray diffraction (XRD) pattern of the Cu_2O powder which resulted from peeling-off Cu_2O films from the silicon substrates. All of the

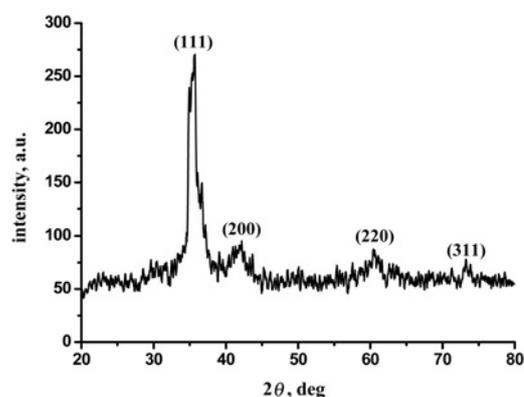


Figure 1 XRD spectra of the obtained Cu_2O powder

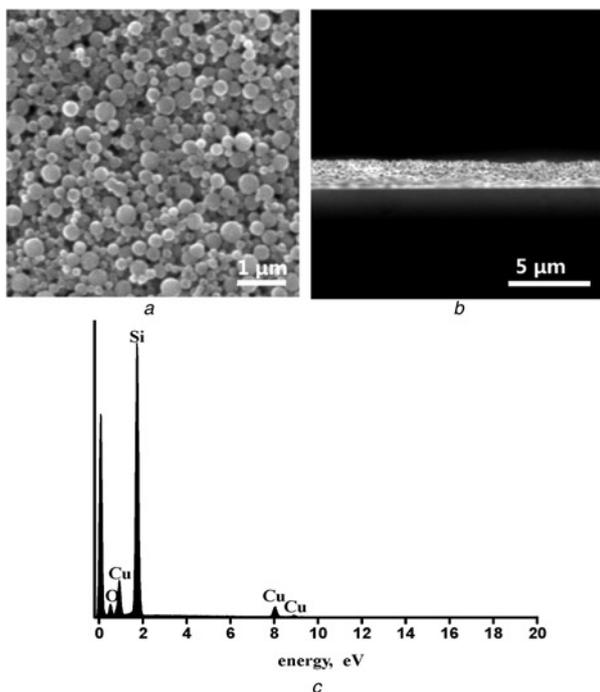


Figure 2 SEM image of surface view (Fig. 2a) and of cross-sectional view (Fig. 2b), and EDX spectrum of the obtained Cu_2O film (Fig. 2c)

peaks can be indexed to a standard cubic structure of Cu_2O (JCPDS No. 05-0667). No diffraction peaks from other species could be observed, which indicates that the powder was pure Cu_2O . The crystallite size of the sample was calculated using the Scherrer formula for the (111) facet diffraction peak, which was 14.6 nm.

The morphology of the as-obtained Cu_2O films was characterised by SEM. Figs. 2a and b are the SEM images of the plain view and the cross-sectional view of Cu_2O film. It is obvious that the Cu_2O film is composed of nanoparticles of size 100–400 nm as shown in Fig. 2a. The result is larger than the size calculated using the Scherrer formula, as the XRD analysis provides information on the crystallite size while electron microscopy provides particle size analysis from individual particles (particles could be formed of several crystallite grains) [17]. The thickness of the film is about 1.7 μm after deposition for 2 h (Fig. 2b). From the cross-sectional view, it can be found that the film surface is smooth. Fig. 2c is the corresponding EDX spectrum taken from the plain view of the SEM image. It is obvious that only Cu, O and Si signals, which come from the substrate, are found in the spectrum. The result is in good agreement with the XRD and further demonstrates that the products are pure Cu_2O crystals.

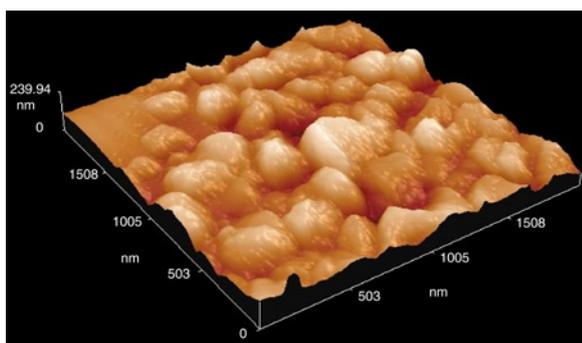


Figure 3 AFM image of the obtained Cu_2O film

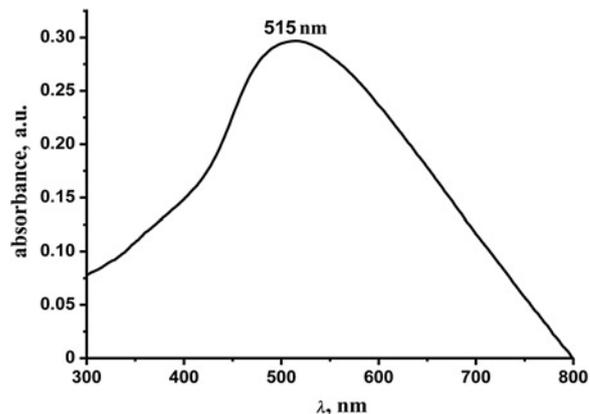


Figure 4 UV-Vis absorption spectrum of Cu_2O films

To gain more insight into the morphology of the obtained Cu_2O films, the sample reaction for 1 h and that deposited for 1 h was examined by atomic force microscopy. Fig. 3 shows the AFM image of the film surface. It can be seen that the surface of the film is smooth. Also, the size of the particles is in agreement with the SEM image of the film.

The increasing interest in the fabrication of optical devices and their application in photocatalysis have created a new demand for techniques to determine the optical constants of thin films of semiconducting materials [18]. The UV-Vis absorption spectrum

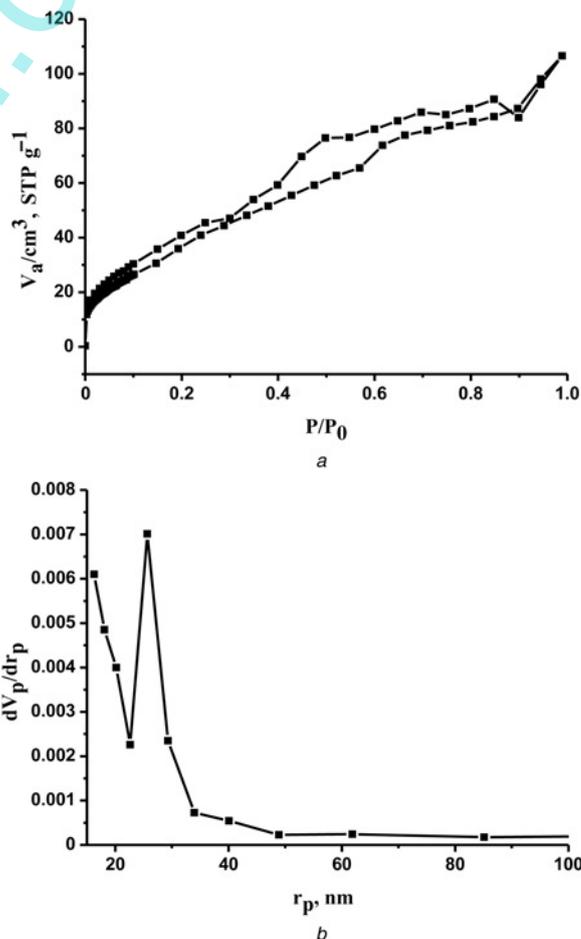


Figure 5 BET adsorption-desorption analysis of as-prepared sample (Fig. 5a), and pore size distribution curve of as-prepared nanoparticles (Fig. 5b)

of Cu_2O which was peeled from the Si substrate and dispersed in ethanol is shown in Fig. 4. It can be seen that there is a broad peak centred at 515 nm in the range of 300–800 nm. According to the equation $\alpha E_p = K(E_p - E_g)^{-2}$ (α is the absorption coefficient, K represents a constant, E_p stands for the discrete photoenergy and E_g is the bandgap energy) [19], the bandgap energy of the as-obtained Cu_2O film is calculated to be 2.41 eV. The evaluated bandgap is larger than the reported value of bulk Cu_2O ($E_g = 2.0\text{--}2.17$ eV) [20]. The reason for the increasing of the bandgap may be due to the quantum confinement effect [21]. Usually, the quantum confinement effect occurred in the small particles and the threshold of the quantum confinement effect was once deduced to be 14 nm for Cu_2O nanoparticles [22]. He *et al.* [23] reported that the absorption peak of the octahedral Cu_2O with a size of 95 nm was at 482 nm. Also, the morphology and crystallinity of Cu_2O crystals has had important influences on optical absorption [24].

On the basis of the result of the UV–Vis absorption spectrum, Cu_2O can be used as a photocatalyst. To evaluate its activity, the active surface area of the nanoparticles was analysed. Fig. 5a shows the nitrogen adsorption–desorption isotherms. The surface area of the nanoparticles is about $158.111 \text{ m}^2 \text{ g}^{-1}$. The pore size distribution of the sample (Fig. 5b) suggests a narrow pore size range with a maximum pore diameter of around 25 nm.

Up to now, many kinds of nanosized semiconductors have been used for photocatalytic applications, including TiO_2 ($E_g = 3.2$ eV) [25], ZnO ($E_g = 3.2$ eV) [26], WO_3 ($E_g = 2.6$ eV) [25], CdS ($E_g = 2.46$ eV) [27], ZnS ($E_g = 3.6$ eV) [28] and so on. Compared with these semiconductors, Cu_2O has a narrower energy band. The photocatalytic degradation of MO over the Cu_2O films and H_2O_2

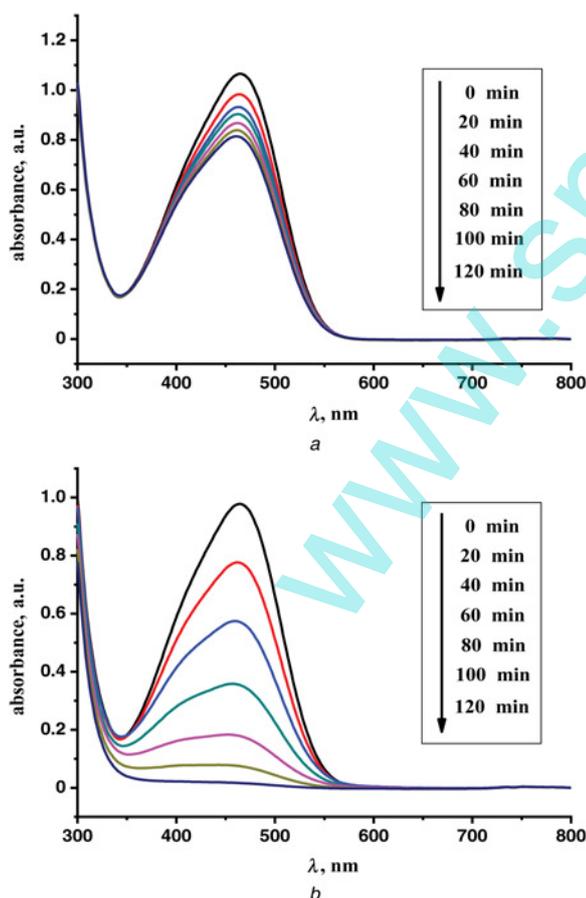


Figure 6 Absorbance of the different additives aqueous solution of MO at different irradiation times
a 3 ml 2 wt% H_2O_2
b Cu_2O films/ H_2O_2

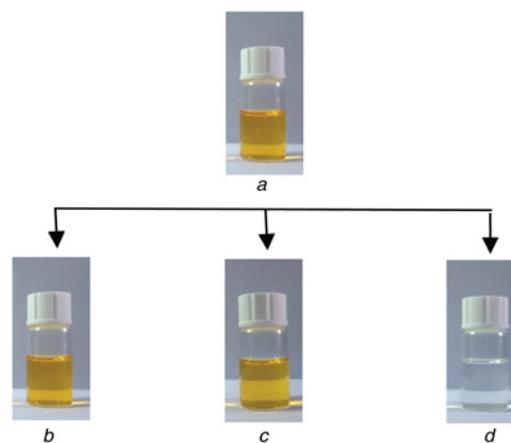


Figure 7 Colour change of solutions
a MO solution
b Solutions under visible light irradiation for 2 h with Cu_2O films
c Solutions under visible light irradiation for 2 h with 3 ml H_2O_2
d Solutions under visible light irradiation for 2 h with Cu_2O films/ H_2O_2

was then investigated. When three pieces of Cu_2O films were added in the MO solution, there was no change in the absorbance of the solution after irradiation for 2 h. Fig. 6a shows the photocatalytic degradation of MO in the presence of H_2O_2 . It can be seen that the intensity of absorbance is decreased with the prolongation time and the degradation rate 23.6% is reached after irradiated for 2 h. The photocatalytic degradation of the MO solution in the presence of $\text{Cu}_2\text{O}/\text{H}_2\text{O}_2$ is shown in Fig. 6b. It is obvious that the change in the intensity of absorbance is remarkable. The notable finding from Fig. 6b is that the degradation rate reached 100% after 120 min irradiation, which is more than four times the total value of the degradation rate of MO on pure Cu_2O films and pure H_2O_2 solution. The colour change of the solutions is shown in Fig. 7. It can be seen that the colour of the solution in Fig. 7b has almost no change. The colour of the solution in Fig. 7c becomes a little lighter than that in Fig. 7a. The interesting phenomenon is that the colour of the solution in Fig. 7d is transparent and looks like clean tap water after irradiation for 2 h under visible light. It can be inferred that there is a strong synergistic effect between Cu_2O films and H_2O_2 of degradation.

When Cu_2O , a semiconductor material, was irradiated by visible light, it would create pairs of electrons and holes. On one hand, the photogenerated holes had a strong ability to attract the electron. The OH^- and H_2O adsorbed on the surface of Cu_2O can be oxidised into $\cdot\text{OH}$ free radical [29]. On the other hand, H_2O_2 accepted the photo-generated electron from the conduction band of Cu_2O and inhibited electron–hole recombination. Electron transfer from the photo-generated electron to these acceptors gave rise to reactive oxygen species $\cdot\text{OH}$ free radical. Then, it can be inferred that the strong synergistic effect between Cu_2O films and H_2O_2 should be due to the narrow bandgap of Cu_2O , which can produce electrons under solar light.

4. Conclusion: We have presented a simple and green soft chemical route to obtain Cu_2O films. The obtained films were composed of nanosphere particles with the size of 100–400 nm. The photocatalytic activity of Cu_2O films, H_2O_2 , Cu_2O films H_2O_2 system is discussed. A strong synergistic effect was found between Cu_2O films and H_2O_2 . Taking the method and cost into consideration, the Cu_2O films have more advantages over the existing ones for environmental remediation.

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