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SYNTHESIS AND PHOTOCATALYSIS OF CUPROUS OXIDE NANO-SPHERES IN AQUEOUS

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ABSTRACT

Cuprous oxide (Cu_2O) nanocrystallites were successfully prepared by using hydrazine hydrate as reducing agent and polyvinyl pyrrolidone (PVP) as the capping agent in aqueous phase, which was proved to be a green and convenient method for the synthesis of Cu_2O Nano-spheres. Photocatalytic decolorization of Methyl Orange in aqueous Cu_2O suspensions was investigated. Using X-ray diffraction, scanning electron microscope, High Resolution Transmission Electron Microscopy characterized the samples and UV–vis Spectroscopy was employed to investigate the photocatalysis behavior of the Cu_2O samples.

KEYWORDS

nanocrystallites, cuprous oxide, photocatalysis.

1. INTRODUCTION

Based on a study, approximately 80% of world energy consumption is derived from fossil fuels [1]. However, reserves of fossil fuel are not abundant and have posed significant concerns regarding widespread environmental pollution [2]. For addressing these problems, many proposals have been studied for the clean energy developments in which the fossil fuels are replaced by solar cells, secondary cells and photoelectron-chemical cells [3-5]. Over the past few years, semiconductor photocatalysts have attracted considerable attention due to their challenging potential for resolving the current energy and environmental problems [6]. According to a study, cuprous oxide (Cu_2O) is an attractive alternative for widespread use in future photovoltaic devices owing to its direct band gap of approximately 2.2 eV, a high optical absorption coefficient, and its earth abundant, nontoxic constituents [7-10]. Cu_2O, a p-type semiconductor metal oxide, has received extensive attention owing to its remarkable cost advantage compared to noble metals, as well as its suitable properties in photocatalysis, solar energy conversion, and catalysis [11-13]. The synthesis of Cu_2O has attracted much attention in recent years. To the best of our knowledge, a large number of syntheses of Cu_2O with various morphologies had been reported. In this work, we reported an easier, more convenient and nontoxic method to preparing Cu_2O in water by used hydrazine hydrate as reducing agent. The concentration of hydrazine hydrate effect the synthesis of Cu_2O, and polyvinyl pyrrolidone (PVP) as the capping agent influent the morphologies. Moreover, photocatalytic activities of the resulted Cu_2O could be used to photodegrade methyl orange (MO).

2. EXPERIMENTAL DETAILS

2.1 Materials

$CuSO_4{\cdot}5H_2O$ and hydrazine hydrate (85%) were purchased from Tianjin, China. PVP and MO were acquired from Shanghai, China. All chemicals were used without further purification.

2.2 Synthesis of cuprous oxide (Cu_2O) nanocrystals

In a typical procedure, 0.04g $CuSO_4{\cdot}5H_2O$, 0.5g PVP were dissolved in 50 mL H_2O under stirring, then 100~310 μl hydrazine hydrate was poured under the same constraints, respectively. The mixture was continued stirring for 30 minutes. After centrifuging, the precipitate was filtered with ethanol then dried in vacuum drying chamber.

2.3 Characterization of cuprous oxide (Cu_2O) nanocrystals

The samples were characterized for their phase purity and crystallinity by X-ray diffractometer with angles ranging from 20 to 80°, and the operating current and voltage were maintained at 40 mA and 30 kV, respectively. The size and morphology of the Cu_2O nanocrystals were analyzed via TEM and SEM.

2.4 Photocatalytic decolorization of MO

Photocatalytic decolorization of MO was carried out in glass vial with cycled cool water under 300 W mercury lamp, the degradating percentage of MO was calculated by absorption maxima (λ=463 nm), obtained using PE Lambda 750 spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Characterization

The XRD spectra of the samples displayed they were cuprous oxide (Cu_2O) when the hydrazine hydrate was poured 100-290 μl, and according to the Scherrer formula, we can draw a conclusion that the diameters of cuprous oxide (Cu_2O) are about 10 nm. But the samples were reduced to Cu directly (Figure 1d when the hydrazine hydrate was poured more than 290 μl.

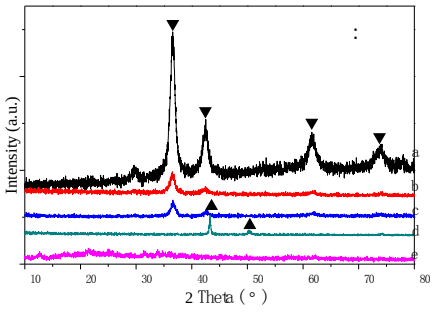

Figure 1: XRD pattern of Cu_2O prepared with different hydrazine hydrate. (a: 100, b: 200, c: 290, d: 300 μl, e: after photocatalytic decolorized 20 cycles of sample a)

From SEM image (fig 2a), the Cu_2O spherical particles with a diameter of about 0.5 μm can be observed. The results had significant differences with the calculation from XRD, maybe caused by PVP encapsulated a large number of Cu_2O nanoparticles. The HRTEM images of Cu_2O showed the sample has a grave adhesion phenomenon due to the presence of PVP, whereas it has a good lattice (Figure 2b).

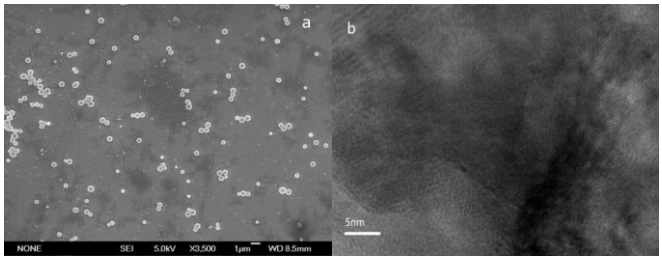

Figure 2: SEM (a) and HRTEM (b) images of Cu_2O.

The survey spectra showed Cu 2p electrons can be identified at the twin peaks of 933 eV and 953 eV, the C1s electrons at about 284 eV and the O1s electrons can be readily found at around 530 eV (Figure 3a). High-resolution scans of the Cu2p electrons are depicted in figure 3b, from which two main peaks may be identified at around 933 and 953 eV. These may be assigned to the Cu2p3/2 and Cu2p1/2 electrons, respectively, which are consistent with cuprous oxide.

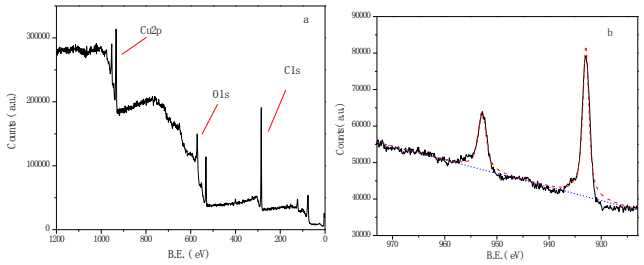

Figure 3: Survey (a) and Cu 2p (b) XPS spectra of Cu_2O.

3.2 Photocatalytic properties

Different Cu_2O (10, 20, 30mg) were added to 10^{-4} mol/L MO respectively. Figure 3 shows the dosage effect of Cu_2O. The more dosage of Cu_2O we added the shorter time was used.

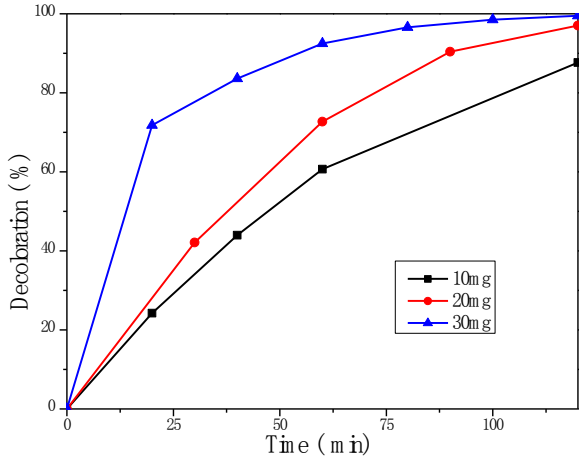

Figure 4: Photo decoloration Catalytic efficiency of 10, 20, 30 mg Cu_2O.

30 mg Cu_2O was added into 10^{-3}, 10^{-4}, 10^{-5} mol/L MO, respectively. Figure 4 shows the effect of MO. The lower density of MO result the higher catalytic efficiency.

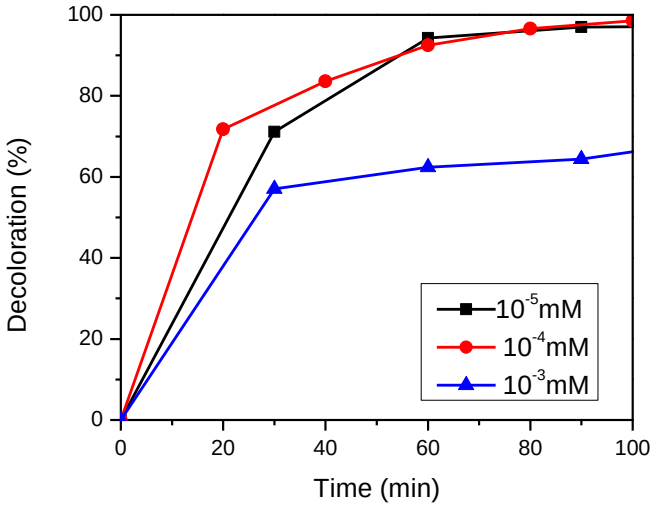

Figure 5: Catalytic efficiency of 10^{-3}, 10^{-4}, 10^{-5} mol/L MO.

We used 10^{-4} mol/L MO and added Cu_2O to test the catalysis life of catalyst. The decoloration was near 90% after the catalyst catalysis 24 cycles (Fig. 6)

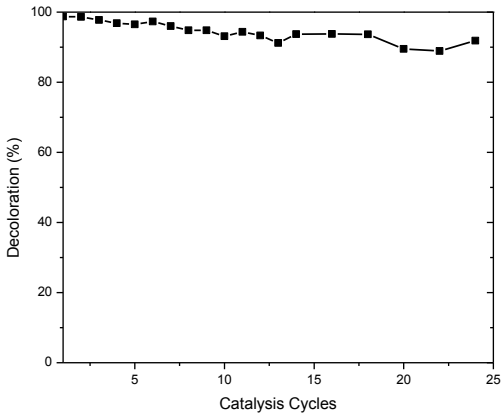

Figure 6: The catalysis life of Cu_2O

4. CONCLUSIONS

In this work, Cu_2O was prepared when the hydrazine hydrate was added 100-290 μl, and Cu was obtained when the hydrazine hydrate was added more. The Cu_2O particles had good lattice and the diameters were less than 100 nm and had good catalytic activity and could be used more than 24 cycles.

ACKNOWLEDGEMENTS

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