Synthesis and Photocatalytic Activity of Superfine Cu$_2$O Sphere with Smooth Surface on Degradation of Methyl Orange

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Abstract. Superfine cuprous oxide (Cu$_2$O) spheres with smooth surface have been successfully synthesized by using gelatin as template. The possible mechanism for the formation of superfine Cu$_2$O sphere is revealed. The results of X-ray diffraction (XRD), scanning electron microscopy (SEM) and Transmission electron microscope (TEM) indicated that the as-obtained powder was cubic structure, pure, uniform, monodispersed Cu$_2$O spherical polycrystalline with smooth surface. What’s more, the photocatalytic activity of the superfine Cu$_2$O spherical polycrystalline is investigated under visible light irradiation. It is worth noting that the superfine Cu$_2$O microspheres have a highly selective adsorption for anionic dyes, such as methyl orange, and the mechanisms of absorption were mainly attributed to electrostatic adsorption.

1. Introduction
Cuprous oxide, an important p-type semiconductor with the narrow direct band gap of 2.0-2.2 eV, has attracted great interest of researches, because it has many potential applications in solar energy conversion [1], photocatalytic degradation of organic pollutants [2], marine antifouling coating [3], lithium ion batteries [4], carbon dioxide [5], gas sensors for NO$_2$[6], and so on.

Compared with some conventional photocatalyst, such as ZnO and TiO$_2$, the electrons of cuprous oxide at band gap are more easily excited under visible light irradiation. The suitable position of its energy levels which make it a more suitable visible photocatalyst. Meanwhile, cuprous oxide is non-toxic, has low preparation cost, so it is an ideal semiconductor for water decomposition under visible light and degradation of dye contaminants. However, it is disadvantageous that the easy recombination of electron and hole results in low catalytic activity of Cu$_2$O. In order to control the rate of recombination, the semiconductor materials possessing different morphology were prepared and found to be able to suppress the electron-hole recombination, resulting in the better catalytic performance. As known, morphology is an important factor in determining the physical and chemical properties of particles. Therefore morphology-controlled synthesis has become a focus. The different morphologies of cuprous oxide were studied intensively by changing the reaction conditions and processes in the experiment. Up to now, cuprous oxide has been prepared by several different methods, such as electrodeposition, thermal relaxation, sonar-chemical methods, γ-irradiation, vacuum evaporation, and the liquid-phase reduction of a metal salt [7-9]. Moreover, these various morphologies of Cu$_2$O, such as octahedrons [10-11], nano-cube, nanocages [12-15], nanowire [16-17], solid and hollow spheres
[18-19], double tower-like tip nanostructures, and multi pods [20] have been synthesized by the method mentioned above. Recently, it has been reported in the previous literature that inorganic hollow spheres are prepared using microorganisms or gelatins as templates. Zhou et al [21] reported that ZnO hollow spheres by employing lactobacillus as template. Yang et al [18] fabricated hollow spheres Cu$_2$O by a reaction between CuO suspension and NH$_2$OH in the presence of gelatin. In this paper, we reported the preparation approach of Cu$_2$O possessing ultrafine, uniform, monodispersed and spherical polycrystalline using gelatin as template and their characterizations by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Transmission electron microscope (TEM). Moreover, the photocatalytic activity of synthesized superfine spherical Cu$_2$O was studied.

2. Experimental details

2.1. Chemicals
CuSO$_4$·5H$_2$O (≥99.7%, AR), NaOH (≥99.7%, AR), Polyethylene glycol (PEG, ≥99.7%, CP), and glucose were purchased from XiLong Scientific Co. LTD. Gelatin was supplied from Shanghai Jinsui Biotechnology Co., Ltd.

2.2. Synthesized of superfine Cu$_2$O sphere
The Cu$_2$O spherical polycrystalline were prepared by the following procedure. First, solutions of 1g gelatin in 100ml deionized water were prepared, and then sonicated for 30 min, labeled as A solution. A set of solutions were prepared by adding 0.2mol/l Copper sulfate pentahydrate (Cu (SO$_4$)$_2$·5H$_2$O) to 100ml deionized water, in which a certain amount of polyethylene glycol (PEG) as surfactant, labeled as B solution, Second, B solutions were added to A solutions drop by drop, and then heated at 50℃ in a water bath and stirred continuously. Third, 100ml 0.1mol/l aqueous glucose solution was added to the above mixture drop by drop. And then 100ml 3mol/l NaOH solution was added to the mixture drop by drop. And the mixture was kept at 50℃ for another 30 min. Magnetic stirring was continuously applied throughout the entire process of reduction and particle growth. The Cu$_2$O particles were separated from the solution by centrifugation at 2000rpm for 5 min. They were then suspended again in hot water and the centrifugation was repeated twice so as to remove the surfactant. After the Cu$_2$O particles were filtered and washed with hot deionized another two times, the Cu$_2$O ultrafine microspheres by using gelatin as templated were obtained. For comparison, the Cu$_2$O was synthesized with the same parameters without using gelatin as templated.

2.3. Characterization
The structure of the prepared powders was characterized by X-ray diffraction (XRD) with Cu Kα radiation (λ=1.5418 Å) (Philips, PANalytical X’pert). The morphology of powders was examined using a field mission scanning electron microscope (SEM) (Hitachi S4800, Japan) and transmission electron microscopy (TEM) (FEI Talos, F200S, American).

2.4. Photocatalytic activities
Adsorption performance of the synthesized Cu$_2$O microsphere was assessed by organic dye, such as rhodamine B, methylene blue and methyl orange. 100mg of catalyst was dispersed in 100mL of a 10mg/L simulated pollutants solutions in a quartz tube under the irradiation of visible light (PLS-SXE300C, 300W, λ≥420nm) with ultrasonication during reaction. Before irradiation, the mixture was magnetically stirred for 30 min in the dark to establish adsorption-desorption equilibrium between the dye and the catalyst. During illumination, at given time intervals (30min), 12ml solution was sampled for photocatalytic examination by absorption band maximum. The curves of absorbance vs wavelength for organic dye solutions were recorded using a UV-vis spectrophotometer (UV-9000A, Metash).
3. Results and Discussion

Figure 1 shows typical XRD patterns of the synthesized Cu$_2$O. There are five peaks with 20 values of 29.58, 36.48, 42.39, 52.61, 73.71 and 77.59, corresponding to (110), (111), (200), (211), (220), (311) and (222) crystal planes of Cu$_2$O with cubic structure (standard JCPDS file no. 99-0041). The lattice constant calculated from this pattern was 4.2623Å, which is in agreement with the standard value 4.269 Å. And the XRD pattern of the as-synthesized powders in Figure 1 shows the sharp peak shape, indicating that the powders obtained by the current one-pot synthetic approach were well-crystallized. No characteristic peaks of CuO and Cu are observed in XRD patterns, indicating high-purity Cu$_2$O crystalline is successfully synthesized by this method. The pure crystal phase is attributed to the existence of glucose in the process of preparation. Because glucose is a weak reducing agent, only in a strongly basic solution can the Cu$^{2+}$ be reduced to Cu$^+$. 

![Figure 1. Powder x-ray diffraction pattern of the Cu$_2$O sphere.](image)

Figure 2 (a)-(b) show the SEM images of as-synthetic Cu$_2$O particles under different magnifications. Figure 2 (c) is the TEM images of as-synthetic Cu$_2$O. It can be clearly seen that the powders have uniform, monodispersed and spherical particle with the crystal size of 200-500 nm, because of PEG as surfactant. When the micrograph of microsphere is further enlarged to high magnification (Figure 2 (b)), it is found the surface of microsphere is very smooth, this is different from other literature [13, 19], which the surface of the reported Cu$_2$O particles is very rough, with small flakes and large particles of irregular morphology, or composed of abundant nanoparticles. In addition, its selected area electron diffraction (SAED) pattern is shown in Figure 2(d), the as-synthetic Cu$_2$O is polycrystalline rather than amorphous, because the XRD of as-prepared Cu$_2$O shows crystal material (as shown in Figure 1).

![Figure 2. (a)-(b) SEM image of as-synthesized Cu$_2$O microsphere using gelatin as templated, (c) TEM image of Cu$_2$O microsphere using gelatin as templated, (d) Selected area electron diffraction (SAED) pattern of the Cu$_2$O.](image)

For comparison, Cu$_2$O was synthesized without using gelatin as templated, the SEM image of Cu$_2$O was shown in Figure 3. From the Figure 3, it can be seen that Cu$_2$O particles exhibit octahedral-like morphology, and aggregation. According to the Figure 2 and Figure 3, the two above mentioned samples indicates that gelatin play important roles in the formation of Cu$_2$O sphere. The mechanism of formation of Cu$_2$O sphere was analyzed as follows. When the temperature is relatively high (50°C), the gelatin sol can exist in the form of droplets in the solution. These droplets should serve as
templates for the development of spherical structures. The gelatin contain large amounts of carboxyl and ammonia, the positive Cu$^{2+}$ is easily absorbed on the surface of the gelatin droplets, due to electrostatic interaction. The reduction of Cu$^{2+}$ by glucose makes Cu$^{+}$ to nucleate at the appropriate position and isotropic grow into polycrystalline structure. The mechanism of formation of Cu$_2$O spherical polycrystalline was shown in Figure 4.

Figure 3. (a)-(b) SEM image of Cu$_2$O without using gelatin as templated.

Figure 4. Schematic illustration of the formation of Cu$_2$O spherical polycrystalline.

Cuprous oxide is an important P-type semiconductor with a band gap of 2.0-2.2eV and has important applications in photocatalytic degradation of organic pollutants, lithium ion batteries, gas sensors for NO$_2$ [2,4,6,13]. Especially, cuprous oxide is a promising material with potential applications in catalytic degradation of organic pollutants under visible light [2,13]. Recently, Xu et al [22] reported that the adsorption and photodegradation of methyl orange with octahedral Cu$_2$O was more that of cubic Cu$_2$O. In addition, Huan et al [13] demonstrated that nanostructure Cu$_2$O shows a highly selective adsorption for anionic dyes. Herein, this phenomenon with selective adsorption for anionic dyes for as-synthesized Cu$_2$O polycrystalline was also found. Figure 5 (a)-(c) show the absorption spectra of different organic dye solutions after photodegradation for various durations over prepared Cu$_2$O polycrystalline microsphere. Figure 5 (d) gives the degradation ration of different organic dye at 120min. The degradation ratio is calculated using the relationship: $1 - A/A_0$, where $A_0$ is the initial absorbance of the organic dye, and A is the residual absorbance after an irradiation time. Under visible light, as shown in Figure 5 (a)-(c), the absorption peak of rhodamine B (RB), methylene blue (MB) and methyl orange (MO) located at 553nm, 664nm and 460nm, respectively. the absorption peak of RB located at 553nm almost unchanged, and the absorption peak of MB located at 664nm weaken slightly. However, the absorption peak of MO located at 460nm weaken gradually as the illumination time increase. From recorded absorption spectra, we have calculated the residual absorbance of organic dye as a function of irradiation time, the results are presented in Figure 5 (d). It is obvious from Figure 5(d) that the photodegradation of RB is very low (~ 0.15%) after 120min of visible light irradiation. This indicated the degradation of RB dye is not so easy under visible light in the presence of the as-synthesized Cu$_2$O photocatalyst. The photodegradation rate of MB dye is also low (~ 12%) after 120min of visible light irradiation. This exhibits that the as-synthesized Cu$_2$O microsphere has very low photocatalytic activity towards MB dye. However, the photodegradation rate of MO dye in presence of as-synthesized Cu$_2$O microsphere is calculated to be ~84.89% during the same time duration of visible light irradiation. We presume that the smooth surface of the prepared
Cu$_2$O polycrystalline microsphere can increase the multiple reflections to improve the visible light utilization, and smooth spherical structure has good dispersion and fluidity, which will also help to improve the photocatalytic effect. All the results certified that the prepared Cu$_2$O microspheres show a highly selective adsorption for anionic dyes, such as methyl orange. Similar phenomena were also observed in previous studies, and the mechanisms of adsorption mainly attribute to electrostatic adsorption [14]. It surmises that as-synthesized superfine Cu$_2$O spherical polycrystalline may have potential application in degradation of anionic organic dye by visible light driven photocatalysis.

4. Conclusions
We have successfully fabricated the superfine phase-pure Cu$_2$O by using gelatin as template. As-synthesized Cu$_2$O is cubic structure, pure phase, uniform, monodispersed and spherical polycrystalline with smooth surface. The diameter of sphere is about 200-500nm. Generated gelatin droplets, serving as template, play a key role in the formation of microspheres. As-prepared superfine Cu$_2$O sphere has been verified to have a highly selective adsorption for anionic dyes, such as methyl orange, and the mechanisms of absorption were mainly awe to electrostatic adsorption. This suggests that superfine Cu$_2$O spherical polycrystalline are promising and interesting materials with potential applications in adsorption and photocatalytic degradation of anionic organic dye.

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References
[1] Briskman R N. 1992 Sol Energy Mater Sol Cells, 273 361
[2] Jongh P E, Vanmaekelbergh D and Kelly J J. 1999 Chem Commun, 12 1069
[3] Elsaeed A M, Abd EI-Fattah M, Azzam A M and Dardir M M. 2016 Inter J Biological Macromolecules, 89 190
[4] Fu L J, Gao J, Zhang T, Cao Q, Yang L C, Wu Y P, Holze R and Wu H Q. 2007 J Power Sources, 174 1197
[5] Samarasekara P, Yapa N U S, Kumara N T R N and Perera M V K. 2007 CO2 Bulletin Mater Sci, 30 113
[6] Deng S Z, Verawati T, Hai M F, Tan H R, Sayle D C, Olivo M, Mhaisalkar S, Wei J and Sow C H. 2012 Journal of the American Chemical Society, 134 4905
[7] Lu C, Qi L, Yang J, Wang X, Zhang D, Xie J and Ma J. 2005 Adv Mater, 17 2562
[8] Yin M M, Wu C K, Lou Y, Burda C, Koberstein J T and Zhu Y. 2005 J.Am. Chem.Soc., 127 9506
[9] Siegfried M J and Choi K S. 2006 J American Chemical Society, 128 10356
[10] Wei X F, Pan J Q, Mei J, Chen Y Y, Cui C and Li C R. 2018 Photonics and Nanostructures Fundamentals and Applications, 30 20
[11] He P, Shen X H and Gao H C. 2006 J. colloid and interface science, 284 510
[12] Kuo C H and Huang M H. 2008 J.American Chemical Society, 130 12815
[13] Huang L, Peng F, Yu H and Wang H J. 2008 Materials Research Bulletin, 43 3047
[14] Yang Z, Chiang C K and Chang H T. 2008 Nanotechnology, 19 025604
[15] Hong X, Wang G Z, Wei Z, Shen X S and Wang Y. 2009 J phys chem C, 113 14172
[16] Das K and De S K. 2009 Journal of Luminescence, 129 1015
[17] Sui Y M, Zhang Y Y, Fu W Y, Yang H B, Zhao Q, Sun P, Ma D, Yuan M X, Li Y X and Zou G T. 2009 J.Crystal Growth, 311 2285
[18] Yang M M and Zhu J J. 2003 J. Crystal growth, 256 14
[19] Zhang H W, Zhang X, Li H Y, Z K. Qiu, Fan S and Ji M Y. 2007 Cryst Growth Des, 7 820
[20] Zhang L and Wang H. 2011 ACS Nano, 5 3257
[21] Zhou H, Fan T and Zhang D. 2007 Microporous and mesoporous materials, 100 322
[22] Xu H L, Wang W Z and Zhu W. 2006 The Journal of Physical Chemistry B, 110 13829