One-step in-situ fabrication of silver-modified Cu_2O crystals with enhanced visible photocatalytic activity

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Silver-modified cuprous oxide (Cu_2O) crystals (SMCCs) were successfully created by a facile one-step in-situ Ag-loading reaction under room temperature. The samples were studied by X-ray diffraction, scanning electron microscopy, UV-vis diffuse reflectance spectra and transmission electron microscopy. The photocatalytic performance of the SMCCs were estimated by using methyl orange aqueous solution as a standard pollutant under visible light irradiation. As a result, the SMCCs show a higher photocatalytic activity than the pure phase Cu_2O. The silver nanoparticles which adhered on the surface of Cu_2O of different size and content can greatly effects the photocatalytic efficiency. The enhanced photocatalytic activity owed to the effective charge transfer of excited electron-hole pairs by loading Ag.

1. Introduction: Cuprous oxide (Cu_2O), as a significant and typical p-type semiconductor with a direct band gap of 2.0–2.2 eV [1], has attracted much more attention due to its superior physical and chemical performance, which are widely applied in photocatalysis, photovoltaic devices [2, 3], magnetic storage media [4–6], gas sensors [7] etc. However, the high electron-hole pairs recombination rate of pure Cu_2O limits its application in the field of photocatalysis.

Thus, some strategies, such as loading some noble metals [8, 9], combination of Cu_2O with another semiconductor, have been employed to solve these problems. Compared with Pt and Au, Ag is considered as a relatively cheap noble metal, especially Ag nanoparticles can act as electron traps to accelerate the separation of photogenerated electron-hole and facilitate the electron excitation by creating a local electrical field. The Ag-Cu_2O crystals can also exhibit excellent absorption and photoresponse in the visible light region [10], due to its excellent surface plasmon resonance effect of Ag nanoparticles. Furthermore, the relatively low cost and special behaviour for oxygen adsorption also make silver to become a better choice for modification Cu_2O to enhance the photocatalytic activities.

Several methods have been used to synthesize Ag-Cu_2O crystals as visible light catalyst, including by preparing Cu_2O particles or films first, and then followed by the addition of Ag^+ solution or electrodepositing Ag particles onto it. Yang *et al.* [11] fabricated the Ag-Cu_2O nanocorncobs by a traditional preparation method which prepared the Cu_2O particles first and then soaked these particles into the $AgNO_3$ solution, the Ag-Cu_2O composite shows enhanced photocatalytic activity under visible light. However, these approach require complex operations and high energy consumption. Herein, we fabricated the Ag-Cu_2O crystals by a one-step in-situ Ag-loading method, the silver nanoparticles directed growth on the surface of cubic Cu_2O. The structure and photocatalytic properties of as-prepared silver-modified Cu_2O crystals (SMCCs) were also investigated.

2. Experimental

2.1. *In-situ* synthesis of silver-modified Cu_2O crystals: In a typical procedure, 0.01 mol of $CuCl_2{\cdot}2H_2O$ (Tianli Chemical Reagent Co., Ltd., China) were dissolved in 100 ml deionised water under magnetic stirring at 55°C for 0.5 h, we can obtain a homogenous transparent light green solution. Then, 10.0 mL of 2.0 M NaOH (Hongyan Chemical Reagent Co., Ltd., China) aqueous solution was added dropwise into the above solution, a blue precipitate was formed immediately and then stirred for 30 min. During the process, the colour of the solution turned into light blue, turbid blue-green, and dark brown. 10.0 ml of 0.60 M ascorbic acid (Tianli Chemical Reagent Co., Ltd., China) solution was added dropwise into the mixture and stirred for another 30 min, a turbid red suspension was obtained. It was followed by the addition of desired amounts of $AgNO_3$ (Guanghua Chemical Reagent Co., Ltd., China) solution with continuous stirring for 20 min, then the mixture was aged for 3 h. The precipitate was collected by centrifugation and decanting, washing with deionised water and absolute ethanol (Xi'an Chemical Reagent Co., China) for several times to remove the residual inorganic ions and polymer, finally dried at 60°C for 12 h in a vacuum oven.

2.2. Characterisation: The structure of the products was analysed by X-ray diffraction (XRD, D/max-2200) using Cu Kα radiation (λ = 0.154 nm). The morphology and microstructure were performed by field emission scanning electron microscopy (Hitachi S-4800 & Hiroba EDX electron microscopy). Transmission electron microscopy (TEM) images were taken on JEM 3010 (JEOL, Tokyo, Japan) operated at 200 kV. The UV–vis absorbance spectra were recorded on an American PerkinElmer Corporation Lambda-950 using $BaSO_4$ as reference.

2.3. Measurements of photocatalytic activity: The photocatalytic activities of the as prepared samples were monitored through the degradation of methyl orange (MO) aqueous solution. In the

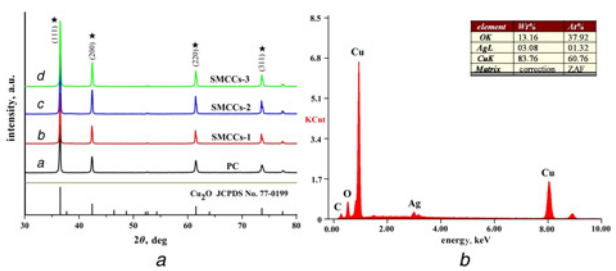

Fig. 1 *XRD patterns of pure Cu_2O (PC) and SMCCs: (b) EDX spectroscopy of SMCCs. (SMCCs-1 defined as the addition of $AgNO_3$ is 1 mg; SMCCs-2, 5 mg; SMCCs-3, 10 mg)*

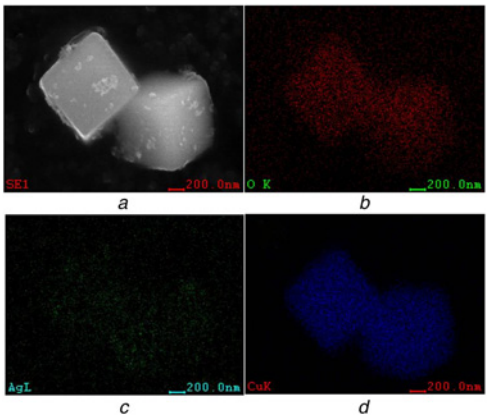

Fig. 2 *EDX elemental mapping of SMCCs-2*

photocatalytic experiments, 10 mg of the photocatalysts was added into 10 ml MO solution with a concentration of 10 mg/l, the mixture was stirred for 30 min in the dark to reach the adsorption-desorption equilibrium. A 500 W Xe lamp (100 Mw cm^2 illumination, equipped with a 420 nm cut off filter) was used as a light source to trigger the photocatalytic reaction. After the photocatalytic reaction, the mixed solution was centrifuged immediately and the supernatant was used to analyse.

3. Results and discussion: Fig. 1*a* shows the crystal structure of the pure Cu_2O (PC) and SMCCs. The major diffraction peaks of Cu_2O are observed clearly with 2θ at 36.5, 42.4, 61.5, and 73.7° in Fig. 1*a*, which are consistent with the basis of Cu_2O (JCPDS

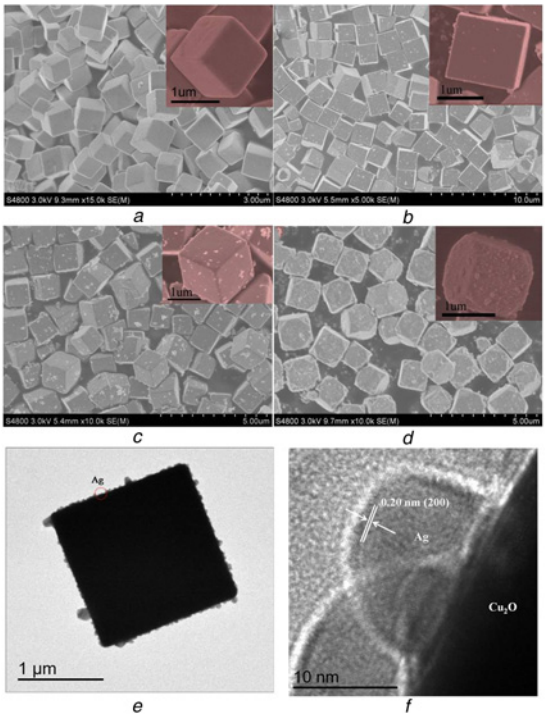

Fig. 3 *SEM images of PC and SMCCs samples, illustrations are higher magnification image of the samples*
a PC
b SMCCs-1
c SMCCs-2
d SMCCs-3
e TEM images of SMCCs
f HRTEM images

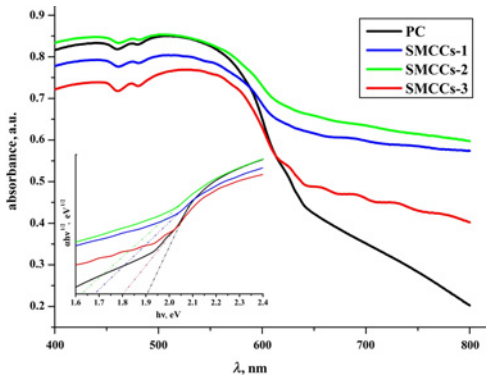

Fig. 4 *UV-vis absorption spectrum of PC and SMCCs*

Card No. 77-0199). There was no apparent diffraction peaks of Ag could be found in all XRD patterns of SMCCs, which could be attributed to their low contents. In addition, the EDX analysis in Fig. 1*b* confirms the presence of Cu, Ag, O elements of the SMCCs, and the SMCCs-2 has about 3.08% Ag content (table in Fig. 1*b*). Fig. 2 shows the EDX elemental mapping of SMCCs-2, it can be seen clearly that the O, Ag, Cu elements distribution within the selected area, and Ag lies in the area of both Cu and O.

Fig. 3*a* displays a typical SEM image of the as-prepared Cu_2O cubes. Without the addition of $AgNO_3$, the sample is dispersed with smooth surface and relative uniform cubic shape with an average edge length of about 1.2 μm. Figs. 3*b–d* shows the SEM image of SMCCs with the different content of $AgNO_3$, which clearly demonstrated that Ag particles uniform dispersed on the smooth surface of Cu_2O cube, and the SMCCs show a similar geometrics and dimensions of the PC. With the content of $AgNO_3$ increase, the homogeneously dispersed Ag nanoparticles grow gradually, gather together with each other and finally covered the Cu_2O surface (Figs. 3*b–d*). Fig. 3*e* shows the TEM image of SMCCs, it can be observed that SMCCs with defined cubic shapes were distinctly decorated by Ag nanoparticles. Furthermore, HRTEM image (Fig. 3*f*) clearly shows that Ag nanoparticles homogeneously distribute on the surface of Cu_2O cubes with a size about 10 nm. It is observed that the spacing of marked adjacent lattice fringes is 0.20 nm, which is consistent with the standard value of Ag (200).

The diffuse reflectance spectra of the as-prepared cubic Cu_2O and SMCCs are shown in Fig. 4, we can see that the Cu_2O has a high absorption coefficient in the visible region. The greater absorbance of the SMCCs in the range of 460–800 nm possibly attribute to the absorption of Ag nanoparticles on the surface of Cu_2O crystals. In addition, a little shift of band gap absorption edges observes after Ag loaded, and obvious band gap absorption edge shift maybe owing to its close connection between the Ag and Cu_2O. Furthermore, the Ag loading can obviously enhance the photoabsorption in the visible light region. For the study of the crystals' band gaps, the value of the band gap energies of the as-prepared Cu_2O, SMCCs are based on the empirical formula $\alpha hv = A(hv - Eg)1/2$ (where α is the absorption coefficient, hv is the photo energy, A is the constant, and Eg is the band gap energy). The illustration in Fig. 4 shows that band gap energies of the PC and SMCCs are estimated to be 1.91, 1.78, 1.68, 1.62 eV, respectively. It is found that the band gap of SMCCs is much reduced than that of the PC.

The photocatalytic activities of the as-prepared PC and SMCCs are tested by detecting the degradation of MO in an aqueous solution under visible-light irradiation ($\lambda > 420$ nm). Fig. 5*a* shows the photocatalytic efficiency of PC and SMCCs of MO in an aqueous solution. After 150 min visible-light irradiation, the photocatalytic efficiency of PC, SMCCs-1, SMCCs-2, SMCCs-3 was about 10.8, 43.5, 60.5 and 52.6%, respectively. All the SMCCs show higher photodegradation efficiency than that of the PC, SMCCs-2

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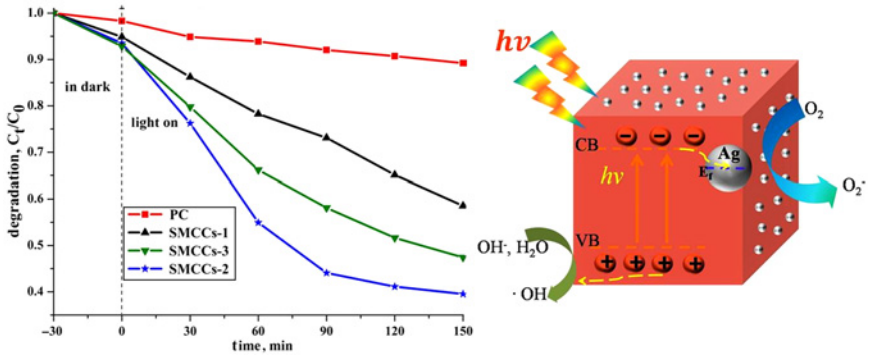

Fig. 5 *Photocatalytic activities of PC and SMCCs for the degradation rate of MO under visible light (a) and proposed photocatalytic mechanism of SMCCs (b)*

displays the highest photodegradation efficiency while SMCCs-3 becomes lower. This may attribute to the excess Ag loading, which impedes the activity. Compared with the PC, The enhanced photocatalytic activity of the SMCCs can be attributed to the efficient charge separation when Ag nanoparticles loaded on the Cu_2O crystal facets.

The Ag nanoparticles were observed to be closely adhered to the surface of Cu_2O crystals, electron can transfer from the Cu_2O conduction band to silver particles is thermodynamically possible because the Fermi level of Cu_2O is higher than that of silver. This may cause the formation of Schottky barriers at the metal-semiconductor contact region, which was thought to facilitate the transfer of photogenerated charges, shift of light absorption was also increased into the visible-light range due to plasmon formation and thus enhance the photocatalytic activity [12]. When the content of Ag is over-loading, more Cu_2O surface is covered by larger size Ag nanoparticles decreasing the reach of light on its surface (Fig. 3*d*), and the excess Ag nanoparticles can also occupy the Cu_2O surface active centres, hence the photocatalytic effect was limited. Hence, the content of Ag nanoparticles on Cu_2O surface played an important role in the formation of Schottky barriers. On the other hand, it can influence the light efficiency that reached the surface of photocatalysts. From the above all, we can come to the conclusion that the suitable content of Ag can effectively improve the photocatalytic performance.

On the basis of the experimental results and discussion, a possible mechanism for dye degradation under visible light irradiation is proposed in Fig. 5*b*. When the as-prepared SMCCs are irradiated by visible light, the excited Cu_2O can easily generate electron-hole pairs, and the photogenerated electrons of the Cu_2O are easily transferred from the VB ($E_{VB} = 1.92$ eV) to the CB ($E_{CB} = -0.28$ eV). Because the work function of Cu_2O (4.2 eV) is lower than Ag (4.6 eV), the electrons can be transferred to the silver nanoparticles easily, and the silver nanoparticles act as traps level of electrons to promote the reaction. So that the recombination rate of electron-hole pairs can be reduced to a large extent and improve the degradation process of organic pollutant.

4. Conclusions: SMCCs have been fabricated successfully via a one-step in-situ Ag-loading method. The photocatalytic experiments proved that suitable content of Ag species loading with intimate contact can effectively enhance the photocatalytic activity of Cu_2O in the visible-light region, and the different content of Ag nanoparticles is a key factor in the formation of Schottky barriers as well as the light efficiency to influence the photocatalytic performance during the degradation reaction. This synthesis strategy could be generalised to the fabrication of the same noble metal modified semiconductors with enhanced physicochemical properties to be used in many fields.

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6 References

[1] Xu H.L., Wang W.Z., Zhu W., *ET AL.*: 'Shape evolution and size-controllable synthesis of Cu_2O octahedral and their morphology-dependent photocatalytic properties', *Chem. B.*, 2006, **110**, pp. 13829–13834

[2] Kloppel A., Kriegseis W., Meyer B.K., *ET AL.*: 'Dependence of the electrical and optical behaviour of ITO-silver-ITO multilayers on the silver properties', *Thin Solid Films*, 2000, **365**, pp. 139–146

[3] Li X.D., Gao H.S., Murphy C.J., *ET AL.*: 'Nanoindentation of Cu_2O nanocubes', *Nano Lett.*, 2004, **4**, pp. 1903–1909

[4] Zhang J., Liu J., Peng Q., *ET AL.*: 'Nearly monodisperse Cu_2O and CuO nanospheres: preparation and applications for sensitive gas sensors', *Chem. Mater.*, 2006, **18**, pp. 867–871

[5] Huang W.C., Lyu L.M., Yang Y.C., *ET AL.*: 'Synthesis of Cu_2O nanocrystals from cubic to rhombic dodecahedral structures and their comparative photocatalytic activity', *J. Am. Chem. Soc.*, 2012, **134**, pp. 1261–1267

[6] Wang Y.Q., Nikitin K., McComb D.W.: 'Fabrication of Au–Cu_2O core–shell nanocube heterostructures', *Chem. Phys. Lett.*, 2008, **456**, pp. 202–205

[7] Pierson J.F., Rolin E., Petitjean C., *ET AL.*: 'Effect of the oxygen flow rate on the structure and the properties of Ag–Cu–O sputtered films deposited using a Ag/Cu target with eutectic composition', *Appl. Surf. Sci.*, 2008, **254**, pp. 6590–6594

[8] Tseng C.C., Hsieh J.H., Wu W.: 'Microstructural analysis and optoelectrical properties of Cu_2O, Cu_2O–Ag, and Cu_2O/Ag_2O multilayered nanocomposite thin films', *Thin Solid Films*, 2011, **519**, pp. 5169–5173

[9] Liu H., Dong X.N., Liu T.T., *ET AL.*: 'Silver-modified colloidal-aggregated TiO_2 microstructures with enhanced visible photocatalytic activities', *Mater. Lett.*, 2014, **115**, pp. 219–221

[10] Zheng Z., Huang B., Qin X., *ET AL.*: 'Facile in situ synthesis of visible-light plasmonic photocatalysts M@TiO_2(M=Au, Pt, Ag) and evaluation of their photocatalytic oxidation of benzene to phenol', *J. Mater. Chem.*, 2011, **21**, pp. 9079–9087

[11] Yang S.Y., Zhang S.S., Wang H.J., *ET AL.*: 'Controlled preparation of Ag-Cu_2O nanocorncobs and their enhanced photocatalytic activity under visible light', *Mater. Res. Bull.*, 2015, **70**, pp. 296–302

[12] Pulido Melian E., Gonzalez Diaza O., Dona Rodriguez J.M.: 'Effect of deposition of silver on structural characteristics and photoactivity of TiO_2-based photocatalysts', *Appl. Catal. B.*, 2012, **127**, pp. 112–120