Cu_2O Nanocrystals: Study on Hydrothermal Morphology-Modulated Synthesis and Photodegradation of Organic Pollutants

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Abstract. We report a facile method for the synthesis of cuprous oxide nanocrystals with three different structure. High surface roughness spheres, self-assembly layered Cubic and snowflake nanocrystals can be synthesized directly by hydrothermal method. F127, CTAB and EDTA was used to be a precise control of the nanocrystal morphology. Different proportions of water and ethanol mixed together was used as solvent. All three samples displayed activity toward photodegradationof rhodamine B molecules, self-assembly layered Cubic nanocrystal exhibited a higher extent of the photodecomposition reaction. We inferred that the {111} faces Cu_2O nanostructures are catalytically more active. These nanocrystals provide a comparing in various properties as a function of the crystal structures. The photocatalytic properties of the prepared nanocrystals are studied showing enhanced photocatalytic activities. The improced activities are considered to be related to the special structure and edge sites on the particles.

Introduction

During the past few decades, special attention has been focused on the synthesis of inorganic nanocrystals with tailored shapes owingto their intrinsic shape-dependent properties. Cu_2O nanostructures have been demonstrated to be used for photodegradation[1], CO oxidation[2] and gas sensing[3]. A varity of Cu_2Onanostructres such as nanoplates[1], octahedra[4], nanocages[5], nanowires[6] and other structures[7-10] have been synthesized in recent years. Though Cu_2O crystals with various morphologies have been synthesized[11-12], the reports about the preparation of Cu_2O and the properties are limited. Developing facile and effective methods for the controlled synthesis of special Cu_2O as photocatalysts are still necessary.

Herein we report a facile route for the controlled synthesis of Cu_2O special structures with high surface roughness sphere, self-assembly layered Cubic and snowflake. The systematic variation in the product morphology can be controlled by changing the amount and variety of additive. The formation mechanism of special structured Cu_2O was investigated and proposed based on the scanning electron microscope analysis. The photodegradation ability were studied with the comparison of three kinds of Cu_2O.

Experimental section

Materials

$Cu(NO_3)_2 \cdot 3H_2O$, Formic acid(HCOOH), Ethylenediaminetetraacetic acid(EDTA), Hexadecyl trimethyl ammonium Bromide(CTAB), F127($EO_{96}PO_{70}EO_{96}$,MW=12 000 g/mol) and ethanol from Shanghai Chemical Co. All materials were used as received without furtherpurification.

Synthesis

3.76g of copper nitrate was dissolved in a solution with 190mL deionized water and 20mL ethanol,then 19.3g EDTA as additive was added, and sonication to get a clear solution. Subsequently, 8.28g formic acid was added to the solution, stir for some minutes to mix well. The solution was then transferred into an autoclave, and hydrothermal treated at 150˚C for 4h. The resulting solution was centrifuge at speed of 8000rpm/min, then washing with deionized water till the pH value of washing out reach to 7,further dried at 60 ˚C to obtained the cuprous oxide micro-nanoparticles with a surface roughness spheric. By replacing the additive with F127and CTAB mixture consisting of EDTA to obtain the cuprous oxide with snowflake and layered cubic morphology, respectively.

Photocatalysis

150mg catalyst was dispersed in 30ml 2mg/L aqueous rhodamine B solution. The solution was irradiated with light from a 150 w mercury lamp. The solution was constantly stirred during photoirradiation. UV-vis absorption spectra of these samples were taken before and after every 30min of irradiation for up to 150 min. Scheme illustrating in Fig 1.

Characterization

Scanning electron microscopy (SEM)imageswere taken by a Hitachi S3400 scanning electron microscope. X-ray scattering (XRD) measurements were taken on a PANalyticalX'Pertdiffractometer using Cu Ka radiation (40 kV, 40 mA).

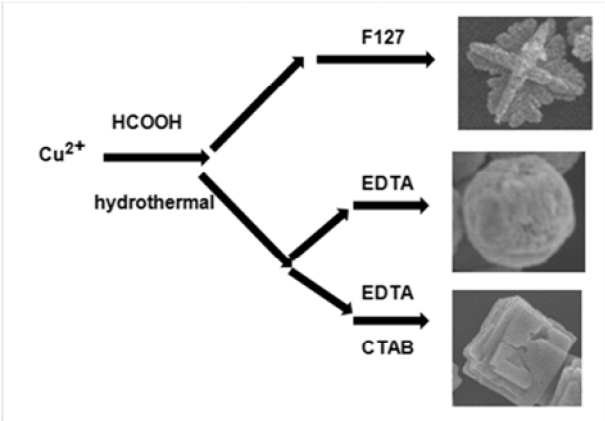

Fig. 1. Scheme illustrating three different conditions to control the crystal growth of Cu_2O and the corresponding SEM images of different morphologies. This suggests the controlled synthesis of Cu_2O high surface roughness spheres, self-assembly lamelleted cube and snowflake.

Results and discussion

The higher magnification SEM image in Fig. 2A clearly manifests the products'high surface roughness spheres. When Formic acid was used as reductant, EDTA controlled the growth direction ofCu_2O and The conformational regularity of spheres were very high. It was also found that Cu_2O self-assembly layered Cubic could be generated when EDTA and CTAB was adopted together as directing agent in the hydrothermal reaction(Fig. 2B). Interestingly, the self-assembly layered Cubic could not be synthesized when the amount of CTAB is decreased half with other conditions remaining unchanged. The SEM image of Cu_2O (Fig. 2C) shows the morphology ofsnowflake. Investigation of replacement for directing agent in Cu_2O Morphology growth could be studied by comparing with threedifferent morphology. The successful preparation of the above Cu_2O morphologies in this work suggests that the additive is a key to the structure growth.

Wide angle XRD patterns ofself-assembly layered CubicCu_2O are shown in Fig. 3B. Seen from the Fig. 3B, there arefive typical diffraction peaks of Cu_2O. No other diffration peaks arising from possible impurities such as Cu and $Cu(OH)_2$ are found, indicating the Cu_2O is very pure.

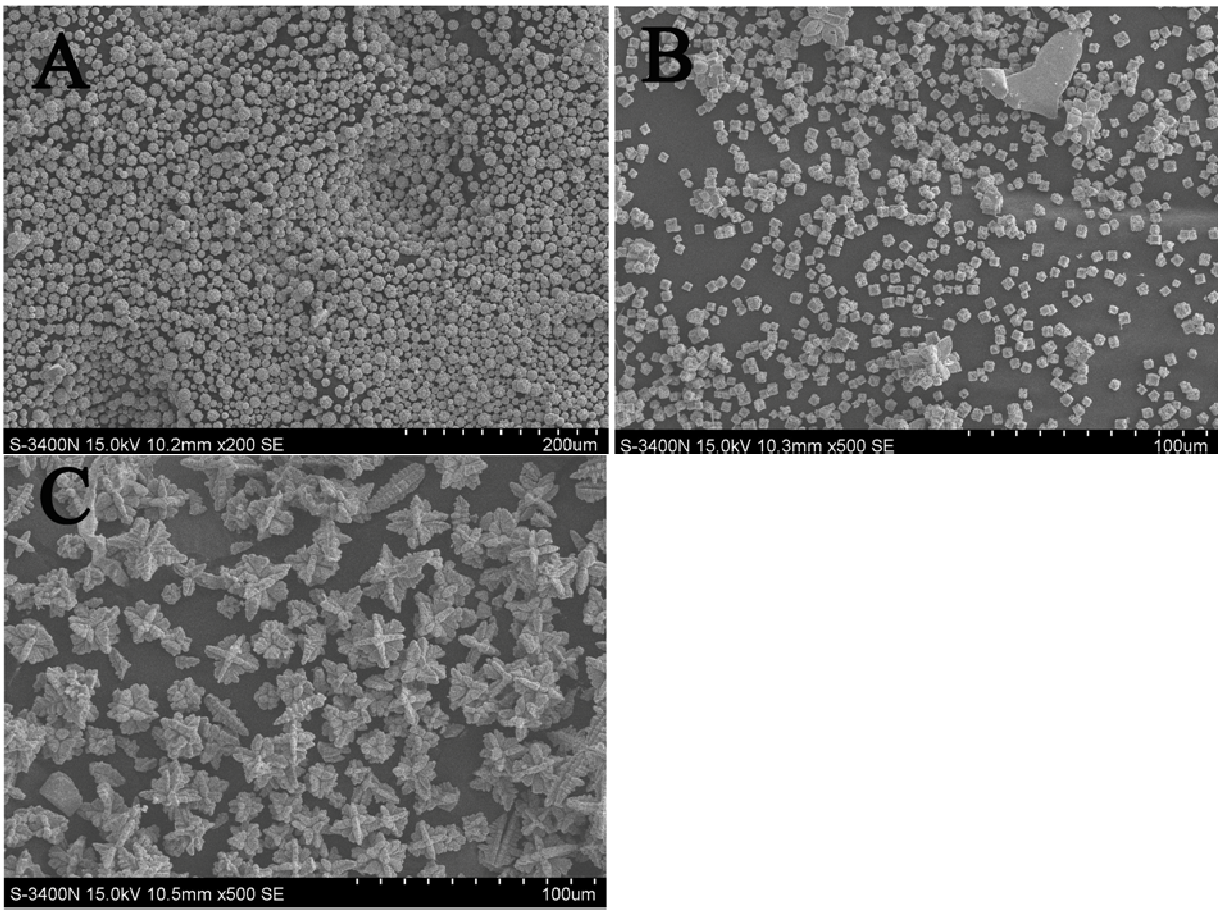

Fig. 2. (A-C) Respective SEM images of the Cu_2O nanocrystals with different sturctures. The particle morphologies are (A) high surface roughness spheres, (B) self-assembly layered Cubic, (C) snowflake.

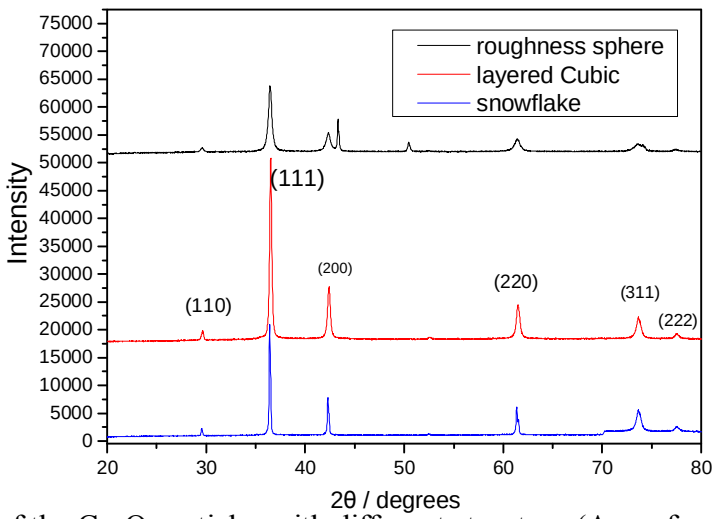

Fig. 3. XRD pattern of the Cu_2O particles with diffenent structure (A: surface roughness spheres, B:self-assembly layered Cubic, C:snowflake).

The relative photocatalytic activity toward the degradation of dve molecules provides a opportunity to demonstrate the systematic shape ability. Fig. 4 is a plot of the extent of photodecomposition of rhodamine B as a function of the irradiation time for the blank and the three samples with different

shape. After irradiation for 3 h, the fraction of remaining absorption of rhodamine B was 0.94 for the blank sample, 0.6 for high surface roughness spheres, 0.47 for self-assembly layered Cubic and 0.66 for snowflake. It suggests that layered Cubic Cu_2O nanoparticles are most effective photocatalysts. High surface roughness spheres Cu_2O showed a higher photodegradation extent than snowflake Cu_2O particles presumably because High surface roughness provides more reaction field. The results serve as a obvious comparison of the photocatalytic activities of the different crystal structure of Cu_2O.

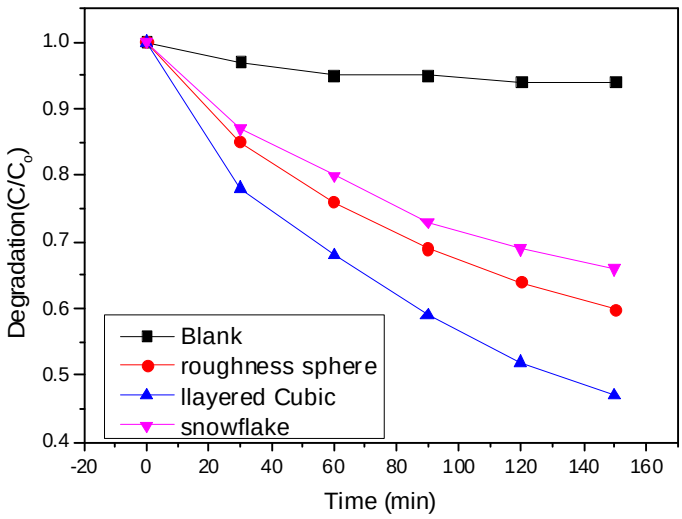

Fig. 4. Photodegradation of rhodamine B molecules as a function of the blank, high surface roughness spheres, self-assembly layered Cubic and snowflake samples. The blank sample did not use any catalyst nanoparticles.

Conclusions

Using a simplehydrothermal method to synthesis special particle shape.All three samples displayed activity toward photodegradation of rhodaine B molecules, self-assembly layered Cubic nanocrystal exhibited a higher extent of the photodecomposition reaction. These nanocrystals may find more applications in photocatalysis and organic synthsis. It is exected that the nanocrystals with different shapes may exhibit different catalytic activities.

Acknowledgments

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