



# Silk sericin-assisted synthesis of architected porous copper@cuprous oxide hybrid microspheres with enhanced visible light photocatalytic activity

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## ABSTRACT

Novel architected porous Cu@Cu<sub>2</sub>O hybrid microspheres were successfully designed and synthesized using silk sericin (SS) as structure-director to firstly form the hierarchical Cu<sub>2</sub>O/SS microspheres by self-assembly, followed by a calcination process. A possible mechanism has been proposed based on the results of FESEM, TEM and XRD analysis. The photocatalytic performance of obtained porous Cu@Cu<sub>2</sub>O hybrid microspheres was investigated, and the synergistic effect of Cu and Cu<sub>2</sub>O phases contributed to improving the light absorption ability, electron-hole separation and transfer compared with pure Cu<sub>2</sub>O. Importantly, the photo-degradation ratio of Cu@Cu<sub>2</sub>O hybrid microspheres for methyl orange (MO) reached up to 99.9% after 110 min visible light irradiation, which is almost 1.3 times than that of pure Cu<sub>2</sub>O. Furthermore, Cu@Cu<sub>2</sub>O hybrid microspheres also exhibited outstanding reusability and stability because that its degradation efficiency for MO still maintained at 93.5% after five cycles.

## 1. Introduction

With the fast development of modern industry, persistent organic dye pollutants in the aquatic ecosystem have become a worldwide and serious environmental issue due to their high toxicity and carcinogenicity. Photocatalytic degradation under sun light and visible light is believed as one of the most promising approaches to eliminate these toxic and carcinogenic organic dyes [1–3]. Cuprous oxide (Cu<sub>2</sub>O), a p-type semiconductor with direct band gap of 2.0–2.2 eV, has been extensively investigated because it can absorb visible light and generate electron-hole pairs which can initiate a series of photo-degradation reactions [4]. Therefore, Cu<sub>2</sub>O exhibits potential applications in the field of photocatalysis.

It is well known that physical and chemical properties of inorganic materials depend significantly on its morphology and particle size [5]. Thus, many efforts have been done to control the morphology and the size of the Cu<sub>2</sub>O particles, and a variety of Cu<sub>2</sub>O with different micro/nanostructures have been obtained, such as cube [6], octahedrons [7], thin film [8], nanowire [9], hollow sphere [10], flowerlike [11], nanocage [12], etc. However, there are many factors limiting the wide application of traditional Cu<sub>2</sub>O particles, such as the rapid recombination of photo-excited electrons and holes, poor stability in oxidizing environments, and transformation of crystal planes under

reaction process [13–15]. To address this issue, one effective strategy is to construct the Cu<sub>2</sub>O-based heterojunction structure to improve the photocatalytic activity. Various Cu<sub>2</sub>O compounds containing metals or metal oxides, such as Cu-Cu<sub>2</sub>O [16–18], Ag-Cu<sub>2</sub>O [19], Au-Cu<sub>2</sub>O [20], TiO<sub>2</sub>-Cu<sub>2</sub>O [21,22], ZnO-Cu<sub>2</sub>O [23], and CuO-Cu<sub>2</sub>O [24,25], have been reported, and their photocatalytic performance has improved to some extent. For instance, Liu et al. [17] and Kou et al. [18] synthesized core-shell Cu@Cu<sub>2</sub>O photocatalysts by oxidation-assisted dealloying in alkaline media and presented good photocatalytic activity for methyl orange degradation. Those cases on Cu<sub>2</sub>O-based heterojunction structure have frequently focused on the micro/nano-scale particles. However, the porous Cu<sub>2</sub>O-based nanostructures are few reported, which exhibit wide application in catalysis owing to their unique physical and chemical properties associated with their high specific surface area and fast mass transfer channel [26,27].

Nowadays, the concept of green chemistry and cleaner production has attracted wide attention in the fabrication of nanomaterials, and green synthetic techniques using nontoxic and eco-friendly natural materials are developed. Silk protein sericin, a water soluble globular protein, is usually discarded as a waste product during the degumming process in raw silk production [28–30]. In our previous work, smart silk sericin micro/nanostructures with different morphologies (discoidal, biconcave, cocoon-like) have been prepared through protein self-

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assembly in aqueous solution [31,32].

Inspired by its assembly method, a novel architected porous Cu@Cu<sub>2</sub>O hybrid microspheres were successfully designed and prepared using silk sericin (SS) as the template. Hierarchical architecture of cuprous oxide/silk sericin (Cu<sub>2</sub>O/SS) microspheres were firstly formed by aqueous-phase synthetic route using silk sericin as structure-director and dispersant. Subsequently, calcination led to the formation of porous Cu@Cu<sub>2</sub>O hybrid microspheres. Based on their unique hierarchical architectures, the porous Cu@Cu<sub>2</sub>O hybrid microspheres were employed in the photocatalytic degradation of organic dye, methyl orange (MO). In comparison to the octahedral pure Cu<sub>2</sub>O particles with equal size, the as-synthesized hierarchical architectures of porous Cu@Cu<sub>2</sub>O hybrid microspheres show much better catalytic efficiency and recyclability.

## 2. Experimental

### 2.1. Materials

Copper acetate monohydrate (Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O), methyl orange (MO), sodium hydroxide (NaOH) and glucose were purchased from Aladdin Reagent Co. Ltd.. Silk sericin (SS, 8 kD) were acquired from Xintiansi Bio-Tech Co. Ltd., Huzhou, China.

### 2.2. Preparation of porous Cu@Cu<sub>2</sub>O microspheres

Hierarchical porous copper@cuprous oxide (Cu@Cu<sub>2</sub>O) hybrid microspheres were prepared via the combination of chemical reduction of Cu<sup>2+</sup> in SS media with subsequent annealing in nitrogen atmosphere. In brief, desired amount of SS was dissolved in 50 mL deionized water under vigorous stirring at 60 °C. 4 mM of Cu(CH<sub>3</sub>COO)<sub>2</sub> solution (50 mL) was added into the SS solution with stirring, then adjusting solution pH to 12 by adding NaOH solution (1 M). Subsequently, 7.2 mg of glucose was added into the blue reaction solution. After 2 h reaction, the resultant precipitates were harvested by centrifugation, then washed three times with both deionized water and ethanol, and finally dried at 60 °C for 6 h in a vacuum oven. The as-prepared products were denoted as Cu<sub>2</sub>O/SS microspheres. In order to detect the self-assembly process of Cu<sub>2</sub>O/SS microspheres, the dosage of SS was controlled in reaction system. For comparison, pure Cu<sub>2</sub>O was prepared as reference under the same conditions as those of Cu<sub>2</sub>O/SS microspheres except that SS solution was replaced by deionized water.

Finally, porous copper@cuprous oxide (Cu@Cu<sub>2</sub>O) microspheres were obtained via calcining the as-prepared Cu<sub>2</sub>O/SS microspheres at 350 °C for 2 h with a heating rate of 5 °C min<sup>-1</sup> under nitrogen atmosphere.

### 2.3. Characterization

Thermogravimetric analysis (TGA) was performed under N<sub>2</sub> stream at a heating rate of 5 °C min<sup>-1</sup> using a PYRIS 1 thermal analyzer (PerkinElmer, USA). The crystal structures of the samples were determined by a D8 discover X-ray diffractometer (XRD, Bruker, Germany) with Cu Kα radiation. The surface chemical compositions of the samples were analyzed by K-Alpha X-ray photoelectron spectroscopy (XPS, Thermo Electron Corp., USA). The morphologies of the samples were observed by S-4800 field emission scanning electron microscopy (FESEM, Hitachi, Japan) after sputtering with gold, as well as by a JEM-2100 transmission electron microscopy (TEM, JEOL, Japan). UV–Vis diffuse reflectance spectra (DRS) of the samples were measured on a UH4150 UV–Vis spectrometer (Hitachi, Japan) using BaSO<sub>4</sub> as the reference standard. Photoluminescence emission (PL) spectra of the samples were obtained by F-4600 fluorescence spectrophotometer (Hitachi, Japan) with an excitation wavelength of 370 nm at room temperature. The surface area of the samples was measured using Brunauer-Emmett-Teller (BET) methods based on the 3H-2000PS1

nitrogen adsorption-desorption isotherms (Micromeritics Instrument Corporation, USA).

### 2.4. Photocatalytic properties

The photocatalytic activity of the as-prepared samples was evaluated through the photo-degradation of methyl orange (MO) under visible light irradiation. 30 mg of samples were dispersed in 10 mg L<sup>-1</sup> of MO aqueous solution (100 mL), and then were stored in the dark under magnetic stirring for 30 min to reach absorption–desorption equilibrium. The photocatalytic reaction was performed by exposing the suspension to a 350 W xenon lamp coupled with a UV cut-off filter ( $\lambda > 400$  nm). The concentration change of MO was monitored by recording a U2900 UV–Vis absorption spectra (Hitachi, Japan) at 463 nm at given time intervals. For comparison, the photocatalytic activities of pure Cu<sub>2</sub>O and Cu<sub>2</sub>O/SS microspheres were also studied under the same experimental conditions, respectively. The photo-degradation ratio (R) was calculated according to the following equation:

$$R = (C_0 - C)/C_0 \times 100\%$$

where C<sub>0</sub> and C is the original concentration and the concentration of MO after different degradation durations, respectively. Three replicates were tested for each sample.

## 3. Results and discussion

### 3.1. Fabrication and characterization of Cu@Cu<sub>2</sub>O microspheres

The typical strategy to fabricate hierarchical-structured porous Cu@Cu<sub>2</sub>O microspheres are schematically depicted in Scheme 1. First, hierarchical Cu<sub>2</sub>O/SS microspheres are synthesized via chemical deposition using globular silk sericin (Fig. S1) as structure-director and dispersant. During the formation process, adding Cu(CH<sub>3</sub>COO)<sub>2</sub> solution into SS solution, Cu<sup>2+</sup> ions are chelated with the carboxyl groups and amino groups along the molecular chains of SS, and the SS-Cu<sup>2+</sup> complex is formed. The addition of NaOH solution not only completes the requirement of an alkaline environment for the subsequent reduction reaction, but also facilitates the transformation of Cu<sup>2+</sup> ions into Cu(OH)<sub>2</sub> [33]. Afterwards, the SS molecular chains with Cu(OH)<sub>2</sub> began to self-assemble to form a primary spherical structure. Then the complex compounds of copper are reduced by glucose, and in situ transform to Cu<sub>2</sub>O nanoparticles. The acting force of the Cu<sub>2</sub>O and the active groups of SS result in the local collapse and condensation of SS chains, which prompts the adjacent nanoparticles to gather into the hierarchical architectures. Furthermore, the thermolysis was accompanied by the decomposition of SS, as well as the release of gaseous products and moisture, consequently generating highly porous structures with unchanged spherical structures. Meanwhile the formed Cu<sub>2</sub>O and/or Cu(OH)<sub>2</sub> nanoparticles are partly reduced to elemental Cu. Finally, these factors together induced the formation of the hierarchical porous Cu@Cu<sub>2</sub>O hybrid structure.

Assumptive growth mechanism of the hierarchical Cu<sub>2</sub>O/SS microspheres is supported by investigating the morphological evolution of Cu<sub>2</sub>O/SS microspheres with the change of SS additive amount. Figs. 1 and 2 exhibit the morphology change of the samples and their corresponding XRD patterns. As shown in Fig. 1a, the pure Cu<sub>2</sub>O samples displayed typical truncated octahedral architecture with an edge size of 200 nm and smooth surface. XRD pattern reveals phase-pure Cu<sub>2</sub>O without any impurity phases (Fig. 2a). After addition of SS, truncated octahedral pure Cu<sub>2</sub>O nanoparticles gradually disappeared accompanied with the formation of hierarchical spherical structures (Fig. 1b–d). Increasing SS dosage from 0.05% to 0.2% in reaction system, more homogeneous Cu<sub>2</sub>O/SS microspheres with average size of 450–700 nm were observed. From the magnified FESEM image (inset in Fig. 1d), it can be seen that the Cu<sub>2</sub>O/SS samples are hierarchical and composed of numerous small nanocrystals, which provides some insights into the

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