



# A highly-efficient route to three-dimensional nanoporous copper leaves with high surface enhanced Raman scattering properties



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## HIGHLIGHTS

- Three-dimensional (3D) nanoporous Cu leaves was prepared using single-step redox colloidal route.
- SERS performance of the Cu leaves was induced by the porous 3D structure and synergistic effect of organic ligands.
- Growth Mechanism for the 3D nanoporous Cu leaves was proposed.

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## ABSTRACT

Copper nanostructures have aroused extensive research interests due to their large number of applications in phonology, electronics, catalysis, etc. Here, we have developed a novel single-step redox colloidal route to construct three-dimensional (3D) nanoporous Cu leaves. By tuning the surface chemistry of copper nuclei, the morphology of as-prepared copper nanocrystals can be adjusted from nanoparticles to leaves. The 3D Cu leaves own anisotropic nanoporous structure and exhibit surface-enhanced Raman scattering (SERS) performance with an enhancement factor of  $\sim 10^6$ . The present facile and low-cost route to develop 3D nanoporous Cu leaves provides an efficient platform for achieving high-performance nanostructures for next generation photocathode applications.

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## 1. Introduction

The research on metal nanostructures is mainly centered on their nanofabrication both by physical and chemical methodologies, especially for catalysis, optical imaging, plasmon resonance, etc. Metal nanostructures have a capability to dramatically enhance the local electrical field by concentrating electromagnetic energies into subwavelength volumes [1]. This could lead towards their wide applications in various fields including cancer diagnostics [2–5], optical bioimaging [6–8], single molecule Raman scattering [9–11], etc. Among these, surface-enhanced Raman scattering (SERS) is of particular research interest to detect and identify the adsorbate down to the limit of single molecule detection using the enhanced Raman signal [9]. Various metal nanostructures including Au, Ag and Cu and their hybrids have been

employed in SERS [10]. To achieve high identification and sensitivity of SERS, hybrids have been taken under consideration. For instance, Jin et al. developed a Ag-Au-Ag structure with controllable plasmonic nanogaps to enhance the SERS performance, which is attributed to the strongly enhanced electric field within such nanogaps [11]. Shin et al. reported that 200 nm platinum nanoparticles on macroscopically smooth Pt substrates present a higher SERS intensity than those on Ag and Au substrates [12]. However, Yang et al. synthesized hollow copper microcages via a template method by reducing 26-facet  $\text{Cu}_2\text{O}$ , and the hollow Cu microcages with rough surfaces showed good performances as SERS substrate [10]. Copper is proposed for SERS applications owing to its unprecedented advantage of low cost, low toxicity [13,14], good optical characteristics, and promising stability [15]. Up to date, several approaches have been developed to prepare Cu with SERS activities. For instance, ultrafast laser ablation technique is applied to obtain SERS-active copper nanostructure from copper targets [16]. Kowalska et al. developed a high pressure method to synthesize copper nanocrystals through the decomposition of copper hybrid, and showed good SERS performances with enhancement

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factors ranging between  $1.5 \times 10^6$  and  $4.6 \times 10^7$  [17]. Colloidal copper nanoparticles were synthesized by Mao et al. using a chemical reduction method and delivered an SERS enhancement factor of  $10^3$  [18]. Recently, Tan et al. developed three-dimensional (3D) sub-micrometer Cu structures with an excellent SERS enhancement effect due to higher hotspot density compared with plain 2D Cu structures [19]. However, 3D structure typically provides a long diffusion path for analyte molecules through the structure. Porous structure was designed to overcome the shortcoming since that metal cluster is open to the surrounding environment through highly porous surfaces, promoting the diffusion of analyte molecules [20]. Chen et al. conducted SERS experiments *via* nanoporous copper and achieved an enhancement factor of  $\sim 1.85 \times 10^5$  [21]. Similarly, Yang et al. fabricated 3D hierarchical nanoporous Cu films *via* an *in-situ* electrochemical approach [19]. Further, Chen et al. prepared Cu structures with tunable nanoporosity by de-alloying Cu-Mn alloy, but the process required hazardous solution such as concentrated hydrochloric acid [21].

In this study, a novel single-step redox colloidal route is developed to prepare 3D nanoporous Cu leaves with excellent SERS activities at a lower cost compared with noble metals (Au, Ag, etc.). The SERS enhancement factor (EF) reaches  $\sim 10^6$ , showing a larger EF value compared to previously-reported copper nanomaterials [21,22]. We believe that the present work will facilitate the development of SERS-based sensitive devices with high performance at low cost for photocathode applications.

## 2. Experimental section

### 2.1. Materials

Starting materials including cupric tartrate obtained from 1 M mixed solution of  $\text{CuSO}_4$  and potassium sodium tartrate, isooctane, polyethylene glycol (PEG 200) and hydrazine hydrate were purchased from Chengdu Changzheng Glass Co. Ltd in Chengdu, China. All the reagents were analytical grade and used without further purification.

### 2.2. Synthesis

Cupric tartrate was used as copper precursor in the reduction of hydrazine hydrate. Isooctane, PEG, deionized water and their mixture were chosen as reaction solution. Copper nanocrystals were prepared using a micro-emulsion redox method in Schlenk line. Initially, 1 g of cupric tartrate was added into 26 mL mixed solution of isooctane: PEG: deionized water with a volume ratio of 20:3:3. Then, 20 mL hydrazine hydrate was added into the mixed solution to reduce cupric tartrate into Cu nanocrystals. The entire process was carried out inside the Schlenk line under vacuum. The Schlenk line was pumped for 45 min and then nitrogen was introduced for the reaction to occur in an oxygen-free atmosphere. The as-prepared copper nanocrystals were named as sample S1. Reaction systems were conducted in the mixture of isooctane: PEG: deionized water with volume ratios of 20:3:0 (23 mL in total), 20:0:3 (23 mL in total), 0:3:3 (6 mL in total), 0:0:0 and y:1:1 (y = 2, 4, 6, 8, 10, 26 mL in total).

### 2.3. Characterization

The morphology was characterized with field emission scanning electron microscope (FESEM, Fei, Inspect-F, Hillsboro, OR, USA) and transmission electron microscope (TEM, JEOL JEM-2100F, Ltd, Tokyo, Japan). Energy Dispersive X-ray spectrometer (EDS) and SEM-mapping were employed to analyze the elements of samples. X-ray diffraction (XRD, XRD-7000; Shimadzu, Japan,

Cu  $K\alpha$ ,  $\lambda = 0.154178$  nm) was performed to examine the crystallinity and purity of copper nanocrystals. Ultraviolet-visible spectroscopy (UV-Vis, PerkinElmer Lambda 950, USA) and infrared spectroscopy (IR, PerkinElmer, USA) were also taken. Zeta potential analysis was performed to study the stability of the copper suspension. The samples were also analyzed with Raman spectroscopy (Renishaw, inVia, Derbyshire, England) in surface-enhanced Raman scattering (SERS) experiments by using 4-mercaptobenzoic acid (4-MBA) and Rhodamine 6G (R6G) as probe shown in Fig. S1.

## 3. Results and discussion

Copper nanocrystals were synthesized through the reduction of copper precursor (copper tartrate) using a different reaction approach compared with previous methods [23]. The growth of Cu nanocrystals followed a redox process based on a bottom-up approach. We designed different solutions to tune the Cu nanocrystal growth. Fig. 1(a) shows the typical colloidal solution of 3D Cu porous leaves in ethanol, which exhibited pronounced stability due to a zeta potential of  $-74.36$  mV. Fig. 1(b–f) show the field emission scanning electron microscopic (FESEM) images of copper particles as synthesized in solutions of (i) isooctane/PEG, (ii) isooctane/deionized water, (iii) PEG/deionized water, (iv) pure deionized water from the reduction of cupric tartrate precursor by hydrazine hydrate, and (v) mixed solution of isooctane: PEG: deionized water with volume ratio of 20:3:3, respectively. The SEM images delineate that the morphology of as-prepared Cu crystals can be adjusted from 3D leaves to spherical particles. The as-synthesized spherical Cu particles in pure deionized water are  $\sim 800$  nm in size as shown in Fig. 1(e). The mixed solutions of (i) isooctane/PEG, (ii) isooctane/deionized water, and (iii) PEG/deionized water are effective for the growth of Cu leaves, as shown in the Fig. 1(b–d), respectively. The formation mechanism is attributed to the soft template with leaf-shape in the dynamic growth process. The average size of the as-obtained Cu leaves can be tuned in different solutions and the corresponding size of Cu leaves decreases in the sequence of mixed solutions of (i), (ii) and (iii). Considering a series of mixed solutions, the optimal volume ratio for the mixture of isooctane: PEG: deionized water of 20:3:3 is efficient for the growth of uniform Cu leaves with pronounced reproducibility. The uniform 3D Cu leaves own a width of  $\sim 400$  nm and a length of  $\sim 2$   $\mu\text{m}$ , as shown in Fig. 1(f). The difference in morphologies indicates great influence of agent (*e.g.* PEG and isooctane) on the colloidal model during Cu crystal growth. These solutions are typical dispersant and tend to form 3D leaf soft template [24–28]. PEG can attach active copper crystal planes *via* hydrogen bond, which leads to the anisotropic growth of Cu crystal with 3D leaf morphology. Isooctane serves not only as dispersant but also as oil phase to protect air-sensitive metal crystals. Without the introduction of dispersant, Cu grows into relatively large irregular particles as shown in Fig. 1(e). In the self-assembly, dispersant could effectively mitigate the aggregation of colloidal copper nanocrystals and facilitate the formation of micelles with 3D leaf structure. Isooctane is applied as oil phase in the mixed solution since that isooctane provides repulsion to water to ensure the stability of Cu in the reaction system [29]. For the mixed solution of isooctane and PEG, copper crystals own a sheet shape with a wide size distribution, as shown in Fig. 1 (b). As a frequently used dispersant, PEG is well dissolved in isooctane solution. In such a miscible organic solution, the length of PEG 200 is three times above than that of isooctane. It is proposed that several micelles self-assembled in the mixed solution to form Cu crystals with a wide size distribution. In the isooctane/water system gave rise to more regular sheets compared with the isooctane/PEG system, as shown in Fig. 1 (c). Isooctane and water are two immiscible fluids and form

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