# SYNTHESIS AND CHARACTERIZATION OF SPHERICAL HOLLOW ASSEMBLY COMPOSED OF Cu NANOPARTICLES

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Hollow spheres of Cu nanoparticles with an average diameter of 300–500 nm have been prepared by a simple reaction of CuCl and hydrazine in suspension in the presence of gelatin at 60 °C. Gelatin played a decisive role as an inhibitor of the direct attack of hydrazine on CuCl surfaces and in coagulation of the growing Cu producing the hollow spheres. The products were characterized by X-ray powder diffraction, transmission electron microscopy, UV-VIS absorption spectroscopy and X-ray photoelectron spectrometry.

**Keywords**: Copper; Nanostructures; Morphology control; Sol–gel processes; Hollow materials synthesis; X-ray powder diffraction; X-ray spectroscopy.

Hollow spheres of nanometer to micrometer dimensions are pursued with great interest because of possible technical applications in catalysis, solar cells, drug delivery systems, separation techniques, photonics as well as piezoelectric and other dielectric devices[1,2]. Of all metals, copper is one of the most common materials due to its high electric conductivity. In the past two decades, copper nanomaterials have received considerable attention because of their unusual properties in nanodesigns, thermal conducting, lubrication, nanofluids, and catalysts[3–8]. Copper nanoparticles have been prepared by several different methods, such as radiation methods[9], microemulsion techniques[10–12], supercritical techniques[13,14], thermal reduction[15], sonochemical reduction[16], laser ablation[17], metal vapor synthesis[18], vacuum vapor deposition[19], and chemical reduction[20,21]. Gelatin is a natural biopolymer with wide-ranging applications and it has been used as a protective medium for synthesizing nanoparticles[22] and porous composite microspheres[23]. Spherical Ag particles, Au and AuNi nanocomposites were prepared by chemical reduction processes with hydrazine as a reductant and gelatin as a protective agent[24,25]. In this paper, we report a method of

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synthesis of Cu nanoparticles by a very simple reaction of CuCl suspension and hydrazine in the presence of gelatin agents. The hollow Cu spheres were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-VIS absorption spectroscopy and X-ray photoelectron spectra (XPS).

## EXPERIMENTAL

### Materials

All the reagents used in the experiment were of analytical purity. $CuSO_4$, $NH_2OH·HCl$, HCl, NaOH, hydrazine hydrate and gelatin were purchased from Shanghai Chemical Reagent Factory (China). Distilled water was used throughout.

### Instruments

Powder XRD patterns were recorded on a Shimadzu X-ray diffractometer XD-3A (CuKα radiation, $\lambda = 0.15418$ nm). TEM was performed using a JEOL-JEM 200CX instrument. The samples used for TEM observations were prepared by dispersing some products in ethanol followed by sonication for 5 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. A Shimadzu UV-3100 photospectrometer was used to record the UV-VIS absorption spectra of the as-prepared Cu. XPS were recorded on ESCALAB MKII instrument.

### Standard Procedure for Preparation of Cu Particles

The standard procedure for the synthesis of Cu is as follows. First, CuCl powder was prepared by adding 50 ml of 0.1 M $NH_2OH·HCl$ to the same volume of 0.1 M $CuSO_4$, aging the precipitated CuCl gel at room temperature for 4 h in a laboratory oven, washing with doubly distilled water. The CuCl product was separated using a centrifuge. Then 0.1 M CuCl suspension and 0.1 M hydrazine were prepared both containing 2% of deionized gelatin. 50 ml of 0.1 M hydrazine was slowly added to 100 ml of 0.1 M CuCl suspension stabilized by stirring at 60 °C for 3 h. pH was adjusted to 10–11 with NaOH in the course of the reaction. The products obtained were washed thoroughly with doubly distilled water in an inert glove box ($O_2 < 2$ ppm) and vacuum-dried at room temperature overnight.

## RESULTS AND DISCUSSION

### *XRD Study*

An XRD pattern of the Cu particles is given in Fig. 1. The peaks of XRD spectrum are clearly distinguishable. All of them can be perfectly assigned to crystalline Cu, not only in the peak position, but also in their relative intensity. The peak positions are in good agreement with those for Cu powder obtained from the International Center of Diffraction Data (ICDD, formerly JCPDS, 04-0836).

### *TEM Measurements*

The morphology of the as-prepared Cu was studied by TEM. Figures 2a, 2b show the hollow spherical structure of Cu with average dimensions ca. 300–500 nm. The TEM image exhibits a clear porous structure on the spherical surface and the hollow inside can also be observed.

### *Optical Properties*

The as-prepared Cu was well dispersed in ethanol to form a transparent solution by sonication for 10 min. UV-VIS absorption spectrum of Cu shows one absorption peak in Fig. 3. The peak of the hollow spheres of Cu nanoparticles at 586 nm is in good agreement with the reported value for Cu nanoparticles[26]. No characteristic absorption bands for copper(II) oxide around 800 nm and copper(I) oxide around 510 nm were observed[27,28].

### *XPS Measurements*

The high-resolution XPS spectrum for the $Cu_{2p}$ region of the as-prepared Cu hollow spheres is shown in Fig. 4. The peaks at 932.6 and 952.3 eV cor-

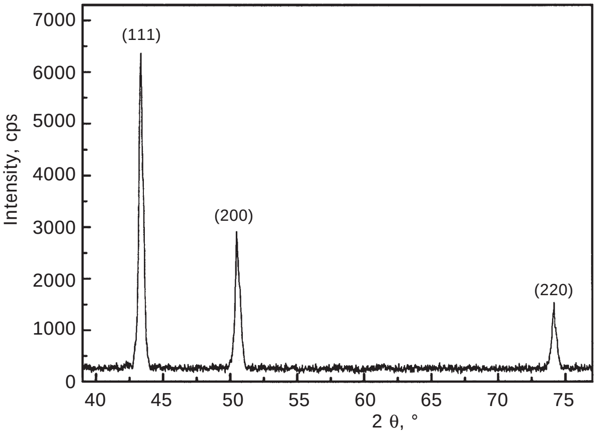

FIG. 1
Powder X-ray diffraction pattern of Cu hollow spheres

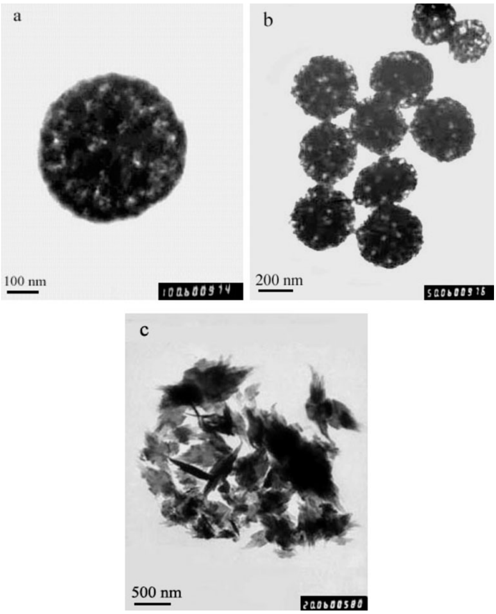

FIG. 2
TEM micrograph of: a single Cu hollow sphere (a), Cu hollow spheres prepared under standard procedure (b), the CuCl as intermediate products (c)

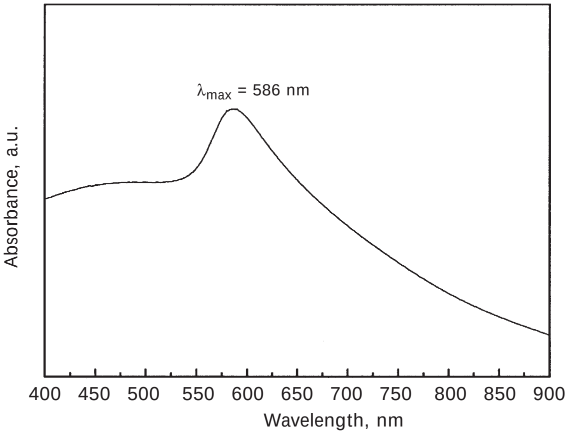

FIG. 3
The UV-VIS absorption spectrum of the as-prepared hollow spherical assembly composed of Cu nanoparticles

responding to the binding energy of $Cu_{2p}^{3/2}$ and $Cu_{2p}^{1/2}$ are in good agreement with the data observed for Cu [29]. Thus, the XPS results prove that the sample is composed of Cu. This result is in good agreement with XRD result.

### *Proposed Reaction Path*

Based on the investigation of the formation of Cu hollow spheres, a possible mechanism has been summarized:

$$2\ CuSO_4 + 2\ NH_2OH{\cdot}HCl \longrightarrow 2\ CuCl + N_2 + 2\ H_2SO_4 + 2\ H_2O$$

$$4\ CuCl + H_2NNH_2 + 4\ NaOH \longrightarrow 4\ Cu + N_2 + 4\ NaCl + 4\ H_2O$$

In the experiment, we employed hydroxylamine hydrochloride and hydrazine as reducing agents. The gelatin acts as an inhibitor of the direct reaction of hydrazine with CuCl and coagulation of the produced Cu hollow spheres.

### *Roles of Gelatin*

Gelatin plays decisive key roles in producing hollow spherical Cu nanoparticles. In the absence of gelatin, the reaction may take place on the solid

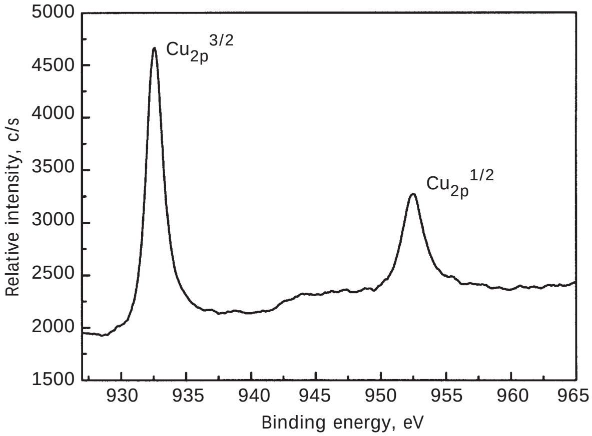

FIG. 4
High-resolution XPS spectrum of the $Cu_{2p}$ region of the as-prepared Cu hollow spheres

precursor surface because of the too rapid diffusion of the reagent. Irregular large Cu particles were observed. We employed CuCl as the solid precursor (TEM micrograph of the CuCl is shown in Fig. 2c). CuCl particles were used as a source of $Cu^+$ ions. As gelatin is in aqueous reaction medium, the gelatin in the bulk and on the surface of CuCl particles in the form of an adsorption layer may control the diffusion of $Cu^+$ ions and hydrazine. As a result, the reaction may occur mainly in a balanced region of the reagent flux and counter-flux of the released metal ions, more or less away from the surface of each solid precursor particle. The total reaction is slower. The rate-determining step of the total reaction is the dissolution process of CuCl particles under the standard procedure. The gelation acts as an inhibitor of the direct reaction of hydrazine with CuCl and coagulation of the produced Cu particles. Cu hollow spheres were prepared under standard procedure due to the retarded nucleation and gelatin-controlled growth of Cu nanoparticles during the nucleation period. Hence, gelatin plays key role in producing hollow spherical Cu nanoparticles. The formation process of Cu hollow sphere was studied by TEM. The nucleation period of spherical hollow assembly composed of Cu nanoparticles is shown in Fig. 5.

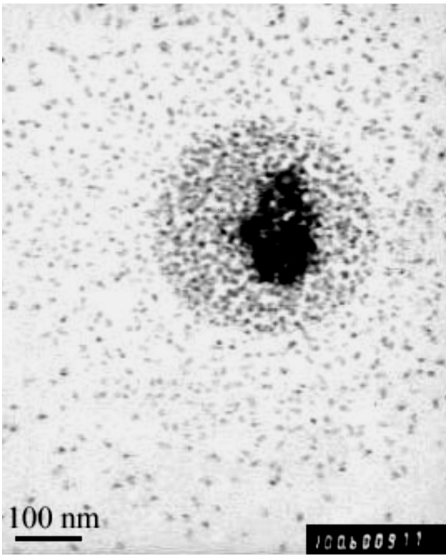

FIG. 5
TEM micrograph of formation process of Cu hollow sphere

## CONCLUSIONS

Hollow Cu nanoparticle spheres have been successfully prepared by the sol–gel/emulsion technique. The role of gelatin in growing Cu hollow spheres was discussed. It is expected that the method can be extended to prepare other hollow spheres.

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