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# Hollow copper micro-amygdalae with porous shells

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Compared with dispersed nanoparticles, stable hollow porous microspheres can obtain more extensive applications [1–6]. They can be used as filters, functional materials, and catalysts, and easily recycled [7–10]. Even new catalytic properties can be induced due to this special structure [11]. Recently, spherical polystyrene and silica particles were widely used as a template to synthesize such microspheres [5, 6, 8, 12], but systematic manipulation of their shapes was still a significant challenge. In contrast to spherical microspheres, there was great interest in making desired structures with control over shapes and sizes [13]. Self-assembly through noncovalent interactions has proven successful in forming different nanoparticle assembly motifs [14]. In this paper, we describe a simple method to prepare stable hollow copper micro-amygdalas with porous shells using polystyrene particles as a template and copper oxalate as a precursor.

In this study, negatively charged, sulfate stabilized polystyrene latex particles with an average sphere diameter of 1 μm, were used as a template. To prepare the hollow copper micro-amygdalas, 0.2 g of polystyrene particles and 0.61 g of dodecyl benzene sulfonic acid sodium (DBS) were added to 100 mL of 0.1 mol/L copper dichloride aqueous solution. A stable suspension was obtained after the polystyrene particles were dispersed by ultrasonic vibration for 30 min. Then 50 mL of 0.2 mol/L sodium oxalate aqueous solution was slowly added to the suspension with stirring using a magneton stirrer for 30 min. Light blue copper oxalate-coated polystyrene particles were formed. After vacuum filtration and drying at 60 °C for 10 hrs, they were calcined at 300 °C for 20 hrs in vacuum.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to examine the morphology of the obtained sample. As shown in Fig. 1A, SEM investigations reveal that all these copper assemblies uniformly show a micro-amygdala shape instead of replicating the spherical shape of the polystyrene particles used as a template. These copper amygdalae have a diameter of 1 to 4 μm, slightly larger than that of the polystyrene particles. On an average, their diameters are twice as long as their thickness. It must be noticed that there is an eyelet in the middle of one side of the amygdalae obviously indicating that they are hollow. Some of them even have two eyelets, as indicated by an arrow in Fig. 1A. The diameter of these eyelets ranges from 200 to 500 nm. Fig. 1B and C clearly show two copper micro-amygdalae with eyelets imaged at higher magnification in different orientations. It can be known that the surface of these hollow micro-amygdalae is not perfectly smooth.

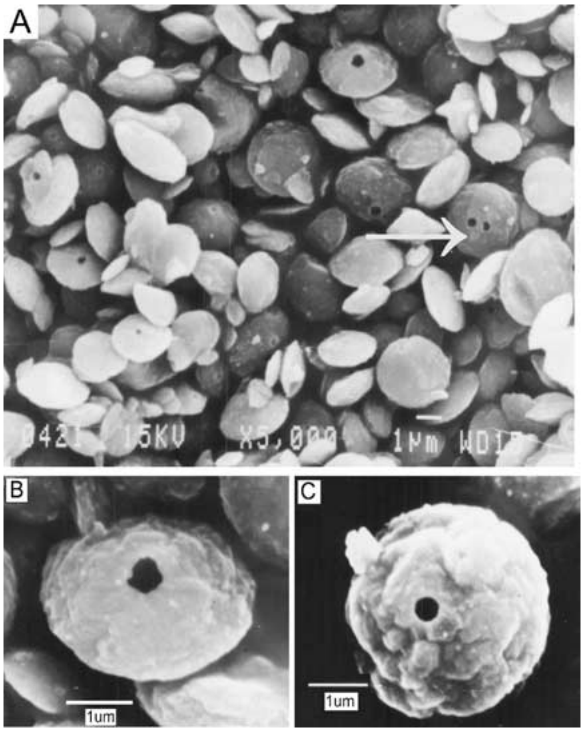

*Figure 1* (A) SEM image of the obtained copper micro-amygdalae. (B and C) High-magnification SEM images of two copper micro-amygdalae with eyelets.

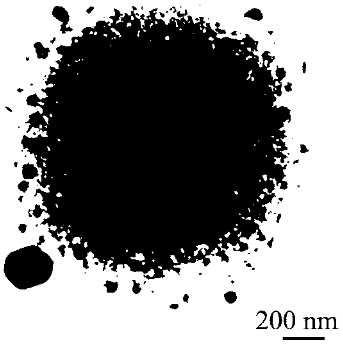

*Figure 2* TEM image of a representative porous copper micro-amygdala.

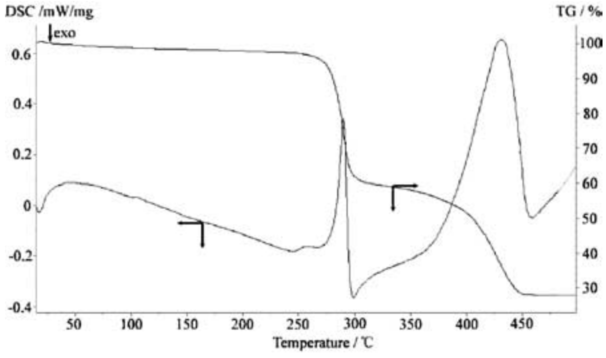

*Figure 3* Differential scanning calorimetry and thermogravimetric analysis of the copper oxalate-coated polystyrene particles.

Fig. 2 shows a representative TEM image of the hollow copper micro-amygdalae, revealing that the shell of the hollow copper micro-amygdala is composed of copper nanoparticles. These copper nanoparticles with a grain size of 10–30 nm are loosely aggregated, resulting in a porous structure in the shell. The TEM image also shows that the edge of the shell of the copper amygdala is thin and the middle of the shell is thick, further verifying the amygdala-like shape.

Differential scanning calorimetry and thermogravimetric analysis of the copper oxalate-coated polystyrene particles are shown in Fig. 3. The weight loss at 250–300 and 350–450 °C are ascribed to the decomposition of copper oxalate [15] and the pyrolysis of polystyrene [16], respectively. After the copper oxalate-coated polystyrene particles are calcined at 300 °C for 20 hrs in vacuum, metallic copper shells are obtained, ascertained by XRD (Fig. 4). The broad peak at 20–30 °C corresponds to the residue of polystyrene after pyrolysis.

As for the formation of the hollow copper micro-amygdalae, the roles of the template and the precursor must be taken into account. In the preparation, when sodium oxalate aqueous solution was slowly added to the template suspension, copper oxalate particles with low solubility in water self-assembled into a particulate shell on the surface of polystyrene particles because of the existence of DBS. Copper oxalate was converted into metallic copper and polystyrene was decomposed into $CH_4$, $H_2$ and so on when calcined at 300 °C, so porous metallic copper nanocrystal shell was obtained. Polystyrene melted and shape changes took place due to the gravity during the process of heating. This led to the formation of copper micro-amygdalae instead of copper micro-spheres.

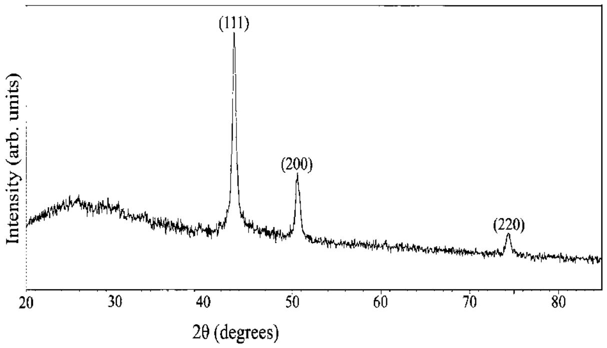

*Figure 4* XRD patterns of the obtained copper micro-amygdalae.

In summary, we have succeeded in synthesizing the hollow copper micro-amygdalae with porous shells. These copper amygdalae have a diameter of 1 to 4 $\mu$m and the diameters of these eyelets range from 200 to 500 nm. The shells are composed of copper nanoparticles with a grain size of 10–30 nm. The porous structures add the potential applications to the hollow copper micro-amygdalae.

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