

An improved pretreatment method for the fabrication of Cu-Ag core-shell nanoparticles

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Abstract. A pretreatment method of nitric acid pickling is applied in the fabrication of Cu-Ag core-shell nanoparticles. By tuning the pH value and the concentration of Cu ions after acid pickling, the cleaning and separation process can be eliminated. This simplified pretreatment process can prevent the oxidation and particle loss. The as-prepared Cu@Ag nanoparticles show promising coating quality, oxidation resistance and quasi-spherical core-shell microstructure. Such a pretreatment method provided by this study could be promising in further rapid fabrication of Cu-Ag core-shell nanoparticles.

1. Introduction

With the development of the third generation of semiconductor power device, the copper nanoparticles have attracted wide attention due to their excellent electronic/thermal conductivity, mechanical properties, low sintering temperature, high temperature stability and low cost[1]. However, the poor oxidation resistance of copper nanoparticles is still an main restriction for their further application[2]. Fabrication of copper nanoparticles with Ag shell becomes a feasible solution to overcome such a problem[3].

At present, a main fabrication method for Cu-Ag core-shell nanoparticles is wet chemical reduction, in which the original Cu particles is mixed in Ag solution [4,5]. The Ag is coated onto the Cu particles through reduction reaction. In this method, the size of the Cu@Ag nanoparticles can be tuned by the size of the original Cu nanoparticles[6]. Consider that the original Cu nanoparticles have been partly oxidized, a pretreatment of acid pickling is required to remove the oxide layer on the Cu nanoparticles[5]. Dilute sulfuric acid is conventionally used in different studies. However, some drawbacks should also be considered for its application in the fabrication of Cu nanoparticle. The sulfate and Ag ions can form the less soluble Ag_2SO_4 , which will influence the coating quality. After the acid pickling, the nanoparticles should be separated from the solution and cleaned by deionized water, which will also introduce oxidation and particle loss.

In this study, consider the good compatibility between the nitrate and silver ion, we applied another nitric acid to the pretreatment process in the fabrication of Cu-Ag core-shell nanoparticles. By tuning the pH value and the concentration of Cu ions in the solution after acid pickling, the particle cleaning and separation process can be eliminated. And the chemical coating process can proceed directly. The results show good coating quality of the as-prepared Cu-Ag core-shell nanoparticles. The study provides a promising pretreatment method for the rapid fabrication of Cu-Ag core-shell nanoparticles.



2. METHODS

Cu nanoparticles (the preparation method is shown in Ref.[7]) with an average diameter of 55 nm are dispersed in deionized water, and then mixed with dilute nitric acid for acid pickling. KOH is dripped into the solution to tune the pH to the range of 8~11. Then the solution is mixed with ammonia. Another solution of silver nitrate and ammonia is prepared and mixed with the original solution for chemical coating. Ultrasonic agitation is applied during the whole process. After the chemical coating, nanoparticles are separated from the solution by centrifugation and cleaned by deionized water for 3 times and alcohol for 3 times. The morphology, composition and element distribution of the as-prepared nanoparticles are inspected through scanning electron microscope (SEM), X-Ray Diffraction (XRD) and energy dispersive spectrometer (EDS), respectively.

3. RESULTS AND DISCUSSIONS

Figure 1 and Figure 2 show the morphologies of the original Cu nanoparticles and the as-prepared Cu@Ag nanoparticles. Both the two kinds of nanoparticles are in globular shape. The morphologies of the nanoparticles before and after the chemical coating are very similar. The Cu@Ag nanoparticles are slightly smaller than the original Cu nanoparticles, which probably results from the surface dissolution of Cu nanoparticles during the acid pickling process. Size distribution of the nanoparticles are analyzed by ImageJ software. It shows that the size of the Cu nanoparticles are in the range of 26~102 nm, with an average diameter of 55nm. The size of the Cu@Ag nanoparticles are in the range of 21~89nm, with an average diameter of 50nm.

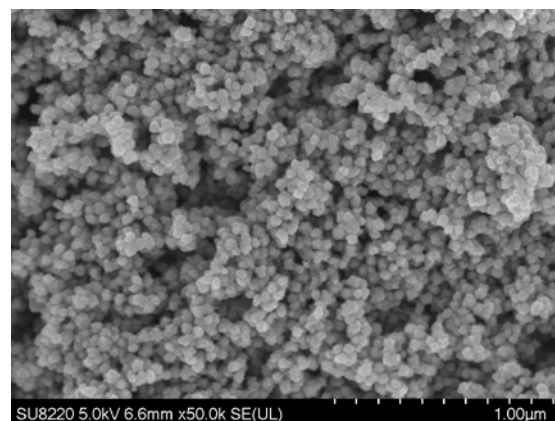


Figure 1. SEM image of the original Cu nanoparticles.

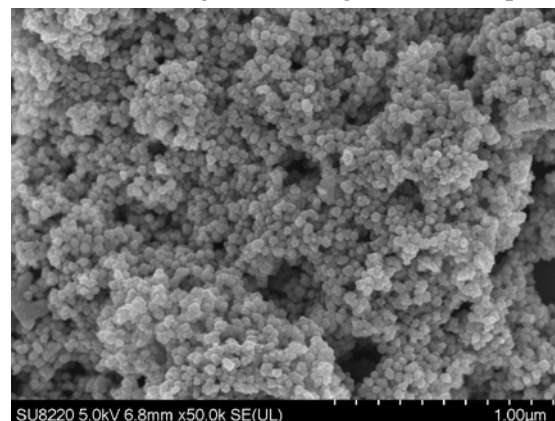


Figure 2. SEM image of the as-prepared Cu@Ag nanoparticles.

Figure 3 shows the XRD spectra of the as-prepared Cu@Ag nanoparticles and the nanoparticles after exposure in air for 24 days. Sharp peaks of face-centered-cubic (FCC) Cu crystals can be observed at the positions of $2\theta=43.3^\circ$, 50.4° , and 74.1° , which relate to the crystal planes of {111}, {200}, and {220}, respectively. Sharp peaks of FCC Ag crystals can be observed at the positions of $2\theta=38.1^\circ$, 44.3° , 64.4° , and 77.4° , which relate to the crystal planes of {111}, {200}, {220}, and {311}, respectively. No peak of oxide can be detected on the spectra. The spectrum of the nanoparticles exposed in air for 24 days barely shows any difference compared to that of the as-prepared nanoparticles, demonstrating a promising oxidation resistance of the Cu@Ag nanoparticles fabricated by this method.

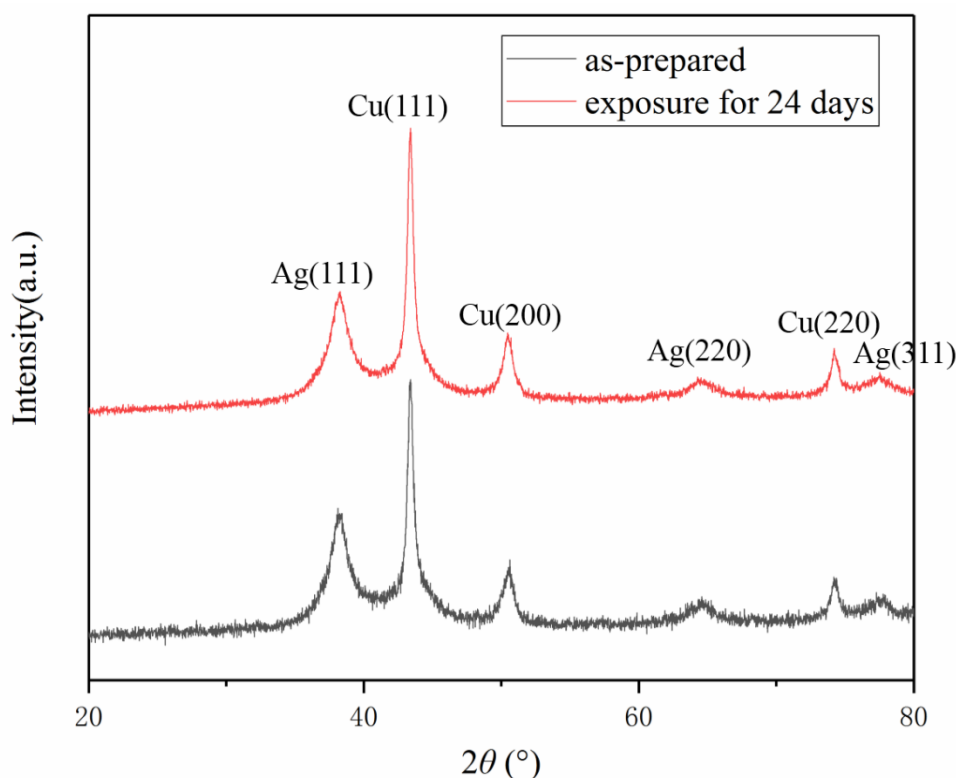


Figure 3. XRD spectra of the as-prepared Cu@Ag nanoparticles and the nanoparticles after exposure in air for 24 days.

To confirm the core-shell microstructure of the as-prepared Cu@Ag nanoparticles, the element distributions of the nanoparticle are inspected by EDS. Figure 4 shows the element distribution of an as-prepared Cu@Ag nanoparticle along its diameter direction, obtained by line sweeping of EDS. The signal intensity of Cu reaches the maximum at the center of the particle, and decreases dramatically near the edge of the particle. The signal intensity of Ag is high near the edge of the particle and is relatively stable in the positions inside the particle. The results certificate that the Cu@Ag nanoparticles are in core-shell microstructure.

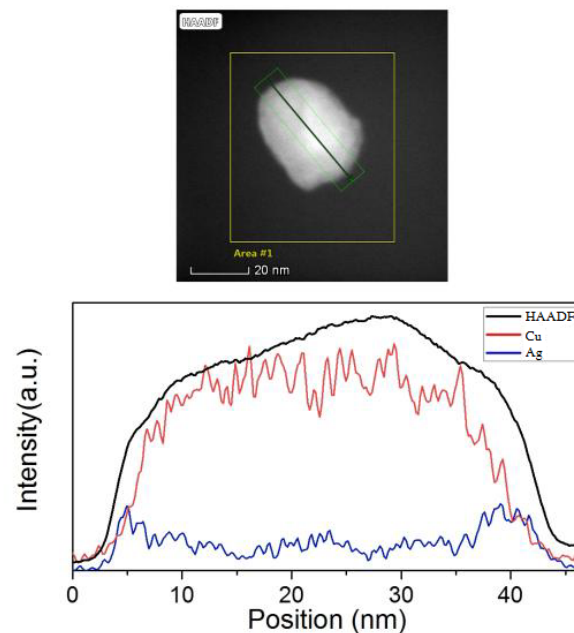


Figure 4. The element distribution of an as-prepared Cu@Ag nanoparticle along its diameter direction, obtain by line sweeping of EDS.

4. CONCLUSIONS

This study applied nitric acid to the acid pickling pretreatment process in the fabrication of Cu@Ag nanoparticles. Compared to the conventional pretreatment using sulfuric acid, the substitution of nitric acid simplifies the pretreatment process by eliminating the cleaning and separation process after acid pickling, and therefore can prevent oxidation and particle loss. The morphologies of the nanoparticles before and after the chemical coating are well consistent. The as-prepared Cu@Ag nanoparticles show promising coating quality, oxidation resistance and quasi-spherical core-shell microstructure. The pretreatment method provided by this study could be applied in the rapid fabrication of Cu@Ag core-shell nanoparticles in the future.

5. References

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