

Cu@Ag core-shell nanoparticle with multiple morphologies: a simple surfactant-free synthesis and finite element simulation

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Cu@Ag nanoparticles with multiple morphologies were prepared using the galvanic exchange method with surfactant-free in air. The thermal stability of as-prepared nanoparticles was evaluated by thermo-gravimetric analysis and the morphology evolution of the sample as conductive ink was investigated by using a scanning electron microscope. In the meantime, the optical properties of synthesised nanoparticles were simulated by the finite-element method. It is feasible for Cu@Ag nanoparticles to be applied as a conductive.

1. Introduction: The core-shell structure has drawn increasing attention due to its unique surface construction between the core and shell. Various core-shell structures have been reported in recent years, such as oxide, semiconductor, organic, and metallic. The bimetallic core-shell nanoparticles (NPs) have drawn intensive attention for potential applications such as conductive inks, catalysts, and solar cells. For technology, core-shell means that the cheaper metal at the core of the bimetallic system, meanwhile the outer shell (a more expensive one) as the protective material to passivate the core-metal, generally oxidation. Copper NPs were widely used in optical, catalytic, and electrical fields because of their low cost and high conductivity. However, Cu NP is very sensitive to oxygen, which greatly limited the application in practical production. There is a new approach to enhance the oxidation stability of Cu NPs by the formation of a Cu core-Ag shell (Cu@Ag) structure. Recently, Cu@Ag particles were prepared using organic solvent [1, 2], a combination of electro-spinning and chemical reduction [3], galvanic replacement-free [4], NaOH assisted [5], epitaxial growth [6], and chemical dealloying [7] methods. Although Cu@Ag NPs were also prepared by using galvanic exchange [8], they have not been obtained using a surfactant-free and protective gas-free in the process [9–17].

Here, we prepared Cu@Ag NPs with multiple morphologies by using a facile galvanic exchange and surfactant-free method. The formation of the structure was confirmed by transmission electron microscopy (TEM)–energy dispersive X-ray spectroscopy (EDS), and the result showed that the inoxidisability of Cu@Ag NPs can be increased by Ag shell coatings. Moreover, the distinction between spherical and non-spherical Cu@Ag NPs was evaluated by using the finite-element method (FEM).

2. Experiment and simulation section: Experimentally, 2 mmol of Cu(OAc)₂ was dissolved in 45 ml of oleylamine (OAm) with stirring in a 100 ml three-necked flask, then, continuous stirring at 85°C for 10 min to make the mixed solution fully dissolved, and the blue solution formed. Then, the solution was heated to 185°C for 1.5 h to prepare the metal core. After the red dark solution formed and return to room temperature, 2 mmol of AgNO₃ (completed dissolved in 45 ml of OAm) was added drop wise into the above solution at 90°C for 1 h to prepare Ag coating. Finally, the grey/red-coloured dispersion was obtained. Note that no surfactant or protective gas was employed in synthetic processes. A scanning electron microscope (LEO 1530VP) and a transmission electron microscope (FEI Tecnai 20) were used to obtain the morphologies of the synthesised sample. EDS (EDX, JEM-2100) was employed

to analyse the element contents of samples. X-ray diffraction (XRD; Bruker AXS D8) measurements have been made on Cu k_{α} radiation. Absorption spectra of samples were measured by using a spectrophotometer (ultraviolet–visible, Varian Cary 5000). The mass change of as-prepared NPs was measured by thermogravimetry analysis (TGA) under air with a heating rate of 10°C/min (TGA–differential scanning calorimetry, Setaram LabSys evo). For FEM simulation, the electric field distribution and main parameters are based on the quasi-static approximation. The out-of-plane and plane wave-vector were set to ensure the matching of the port. Moreover, for fully absorbing, the scattering boundary condition and perfectly matched layer were considered.

3. Results and discussion: Fig. 1*a* shows the XRD pattern of Cu@Ag NPs. It is found that as-prepared samples are well crystallised, and these diffraction peaks can be fully indexed to face-centred cubic (fcc) Ag (JCPDS Card No. 65-2871) and fcc Cu (04-0836). It is interesting that the characteristic peaks from Cu@Ag NPs of Ag are stronger than that of Cu, which is due to the formation of Ag shell. Moreover, the crystallite size of the NPs was calculated as 125 nm by the Debye–Scherrer equation [18, 19]. No peaks for other impurities are found in Fig. 1*a* revealing the high purity of all samples [20–22]. Fig. 1*b* shows the optical spectrum of Cu@Ag NPs. It can be seen that a broad band at $\lambda = 397$ nm corresponding to the localised surface plasmon resonance (LSPR) of Ag [23], however, the LSPR of Cu did not appear. Osowiecki *et al.* [1] reported that the Cu feature peak (about 570 nm) gradually fade and eventually become completely invisible as the introduction of Ag into the Cu NPs to form the core-shell structure. It is well supported by our experiment.

Fig. 2*a* shows the TEM image of Cu@Ag NPs, it can be found that the size of Cu@Ag NP distributed is about 100 nm in the presence of non-regular shapes, such as spherical, rod-like, hexagonal, and trilateral structures. The result shows that the silver shell was coated on the copper core by a diffusion control process rather than a thermodynamic control process [24]. Fig. 2*b* shows a high resolution TEM (HRTEM) image of a white area in Fig. 2*a*, the interplanar d spacing of Cu and Ag is 0.208 and 0.236 nm, which correspond to the spacing of (111) plane of fcc Cu and (111) plane of fcc Ag, respectively. The results indicated that bimetallic crystal was formed without a noticeable sign of an oxide shell. The red line in Fig. 2*c* shows the scanning area, which corresponds to the element contents and EDS line (inset) of Fig. 2*d*. This data imply that the uniform Ag shell was successfully coated onto the surface of the Cu core.

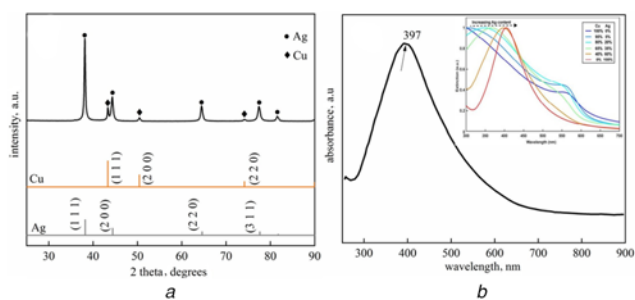


Fig. 1 Chemical analysis of Cu@Ag NPs

a XRD pattern of Cu@Ag NPs

b Optical spectrum of Cu@Ag NPs, the control spectra [1] are in the inset

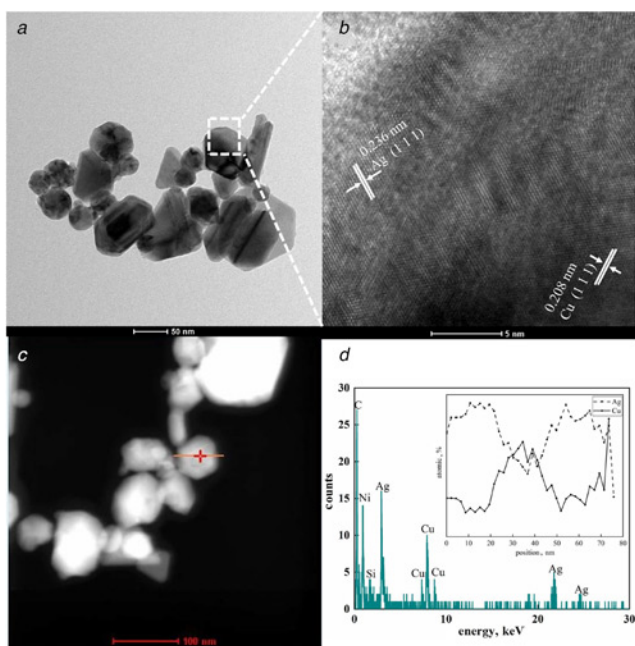


Fig. 2 Micro-morphology of Cu@Ag NPs

a TEM image

b HRTEM image

c Line scanning area

d Element contents and distribution of Cu and Ag (inset) components of Cu@Ag NPs

Fig. 3a shows the thermogravimetry (TG) curves of the as-prepared Cu@Ag NPs in air, there is a slight decrease on the curve below 150°C, which comes from the loss of OAm on the surface of NPs [25]. It can be seen that NPs exhibit a weight gain around 220°C, which indicated that Cu@Ag NPs have better thermal stability in air. The oxidation behaviour of NPs occurred at 220–380°C, at the same time, the mass change was 14.6%. For the application of as-prepared Cu@Ag NPs as printed electronics, the coated NPs film was prepared by the same as the previous work [26]. Pastes containing the fabricated Cu@Ag NPs were heated to 220°C in a vacuum (50 mTorr). Figs. 3b and c show the scanning electron microscopy (SEM) images of the conductive ink before and after sintering. It can be found the formation of necks between adjacent particles at 220°C. Moreover, after sintering, the size distribution and geometry of the Cu@Ag NPs exhibited more irregular aggregation.

The Cu–Ag bimetallic system exhibits the potential application in the optical field because both Cu and Ag feature plasmonic responses. The distinction between spherical and non-spherical Cu@Ag NPs for optical absorption was investigated by using

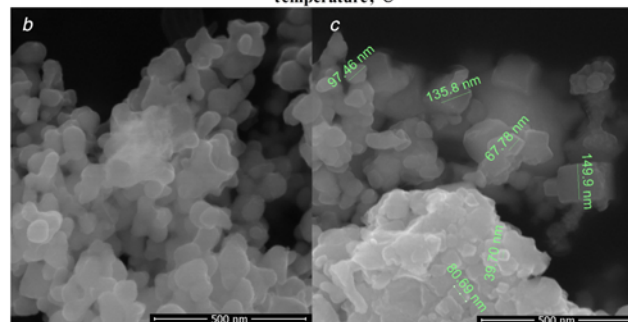
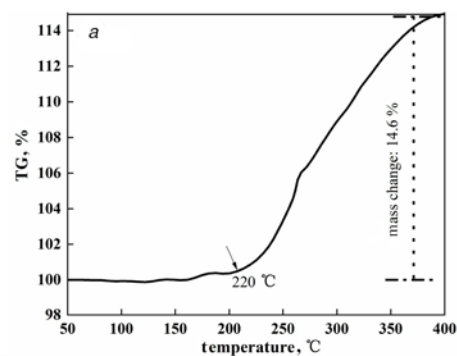


Fig. 3 Thermodynamics action of Cu@Ag NPs

a TG curve of Cu@Ag NPs with a heating rate of 10°C/min

b SEM images of the conductive ink before sintering

c Sintered at 220°C

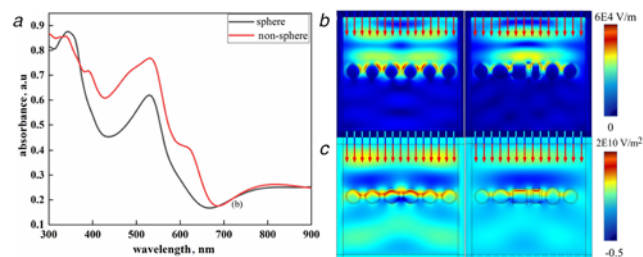


Fig. 4 Finite element modelling of Cu@Ag NPs

a Optical absorption of Cu@Ag NPs measured using FEM simulation

b Normalised-electric field surface charge

c Distribution for TM waves of Cu@Ag NPs, which correspond to the maximum in the absorption of (a), respectively

FEM simulation, as shown in Fig. 4a. As non-spherical-shaped Cu@Ag NPs are introduced into the spherical system, a strong resonance feature appears and broadened at about 520 nm. At the same time, the Cu feature (about 620 nm) appears. Compared with the experimental result in Fig. 1b, the resonance features red-shifted. It can be attributed to the difference of refractive index between in air (experiment) and in a vacuum (simulation). The results showed that the Cu@Ag NPs with multiple morphologies exhibit better optical properties than spherical Cu@Ag NPs. Figs. 4b and c show the normalised-electric field and surface charges distribution for transverse mode (TM; p-pol) waves of Cu@Ag NPs at the maximum absorption of Fig. 4a. It can be found that there was not a clean distinction between the spherical Cu@Ag system and the non-spherical Cu@Ag system.

4. Conclusion: The Cu–Ag core–shell structure with multiple morphologies was successfully prepared using the galvanic exchange and surfactant-free method. Cu core with uniform Ag coating could be obtained in our synthetic processes.

Moreover, the optical properties of as-prepared Cu@Ag NPs were simulated by the FEM. Thus, it shows that Cu@Ag NPs with multiple morphologies have higher oxidation resistibility and well optical properties, and they have the potential to be applied in optical and electronic fields.

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6 References

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