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Fabrication and performance of carbon coated copper nanoparticles

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Carbon coated copper nanoparticles were synthesized by the carbon arc discharge method using a powder mixture containing copper and carbon at the ratio different than in the raw material. The structure, topography, size distribution, phase composition and anti-oxidation property of the nanoparticles were characterized by X-ray diffraction, transmission electron microscopy, thermogravimetry and differential scanning calorimetry experiments. The results indicated that carbon coated copper nanoparticles had a clear core-shell structure, the core of the particles being copper single crystal, and the shell of the particles – a carbon layer with a graphite-like structure. Carbon coated copper nanoparticles had diameters of ca. 20–60 nm. As the copper content increased, the inner copper core became more crystallized. Copper promoted catalysis to the external carbon layers, the graphitization degree became more obvious as the content of copper increased. The outer graphitic carbon layers effectively prevented oxidation of the copper core inside. The oxidation resistance of carbon coated copper nanoparticles was superior to that of pure copper powder.

Keywords: *carbon coated; copper nanoparticles; carbon arc discharge; oxidation resistance*

1. Introduction

Compared with conventional materials, copper nanoparticles have some unusual properties, such as small dimensions, large specific surface area and low electric resistance. They display quantum size effect, macroscopic quantum tunnel effect. Therefore, copper nanoparticles have been the subject of much attention in recent years, due to their potential applications in several fields. Copper nanoparticles with low resistivity can be used for electronic connectivity, and this has aroused great interest in the field of electronics [1]. They are suitable for fabricating conductive paste, which can be applied to coating, electronic packaging in microelectronic industry [2]. Copper nanoparticles can be used as catalysts in metallurgical, petroleum and chemical indus-

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tries due to extremely high activity and selectivity in catalysis and hydrogenation of macromolecular polymers [3]. At the same time, owing to their low melting point, isotropy, weak shear strength and applicability over a wide temperature range, copper nanoparticles have been used as additives in lubricating oils, resulting in a very high quality of products [4–9]. Copper nanoparticles have anti-wear and anti-friction properties, are resistant to extreme pressure, are environment-friendly and also have self-repairing properties. Consequently they have become an indispensable and important, basic material for inorganic composites [10, 11].

Copper nanoparticles have a high activation state which is attributable to their special volume and surface properties. They are sensitive to various environmental factors such as instance, temperature and humidity, promoting strong interactions with substances exposed to air, thereby rendering the surfaces of copper nanoparticles vulnerable to oxidation. The chemical stability of nanoparticles decreases and their activity ceases, which makes copper nanoparticles inconvenient to store and use.

Carbon coating of metal nanoparticles can protect them from physicochemical changes. The technology can prevent metal particles from hydrolysis and oxidation. Carbon layers can improve the surface activity and electrical properties of the inner copper particles and effectively prevent their growth and agglomeration. Metal particles can be confined to a small place by the carbon shells, thereby preventing the metal particles from being oxidized. This solves the problem of how to make metal nanoparticles exist stably in air [12]. Carbon coated nanomaterials protection technology greatly extends the application range of metal nanomaterials in many fields such as chemistry, physics and materials science [13]. Many methods of fabrication of carbon coated metal nanoparticles have been reported, including arc discharging [14–17], ion beam method [18] and chemical vapour deposition [19, 20].

In the paper, we report on the preparation of carbon coated copper nanoparticles using dc carbon arc discharge under an argon atmosphere. The synthesized product is of high purity and has a small particle size the preparation route being rather simple.

2. Experimental

Micron size graphite powder (C, 98.0%) and micron copper powder (Cu, 99.8%) were used as staring materials. The powders in the weight ratio of graphite to copper 4:1 and 2:3 were mixed and pressed into a cylindrical sample of the diameter 24 mm, 20 mm high, which was placed at the bottom electrode of the reactor. The nanoparticle manufacturing apparatus consisted of the following parts: a stainless steel vacuum chamber cooled by circulating water; a water cooled copper anode on which the cylindrical metal to be evaporated is placed; a water cooled and moveable graphite cathode; a cold surface collector; a gas flow system; a two stage vacuum pump system; and a DC power supply. Before preparation, the chamber was vacuumed to 2–3 Pa by mechanical vacuum pump, pumped in argon to 1000 Pa and stopped, continued to vacuum to 2–3 Pa of the reactor, and then pumped in high purity argon. When the pressure

was 50 000 Pa, the distance of two electrodes for dc arc discharge was adjusted to 1–2 mm. When discharge current was 120 A, and discharge voltage was 22 V, the electrode began to discharge. The reaction caused ionization and a plasma fume was formed in the reaction chamber, which was deposited in the container wall and formed nanoparticles. After the reaction had finished, the product deposited on the container wall was collected, filtrated in toluene, and carbon coated copper nanoparticles were thus obtained.

Transmission electron microscopy (TEM; JEM-2000EX) and high-resolution transmission electron microscopy (HRTEM; JEM-2000EX) were applied to determine the morphologies and sizes of carbon coated copper particles. An X-ray diffractometer with CuK_α radiation under the applied power of 50 kV×30 mA was employed to detect phases and the crystal structure of the particles. The thermal effect and weight change analysis of the reaction were confirmed by differential thermal analysis (DTA) in the temperature range of 25–600 °C with the heating rate of 20 °C·min^{-1} was applied, under a nitrogen atmosphere.

3. Results and discussion

3.1. XRD analysis

Figure 1 shows X-ray diffraction profiles of carbon coated copper nanoparticles. Three sharp peaks at 2θ of 43.3°, 50.6° and 74.3° can be seen in the figure. The corresponding d value was 0.2087 nm, 0.1808 nm, 0.1278 nm, respectively. We consulted the PDF card (the PDF card number 04-0836), which corresponded to the (111), (200) and (220) plane of the face centred Cu, respectively. The carbon coated copper nanoparticles were found to match the diffraction peak characteristics of copper, whereas no peaks assigned to carbon were detected, suggesting that the carbon shell was amorphous.

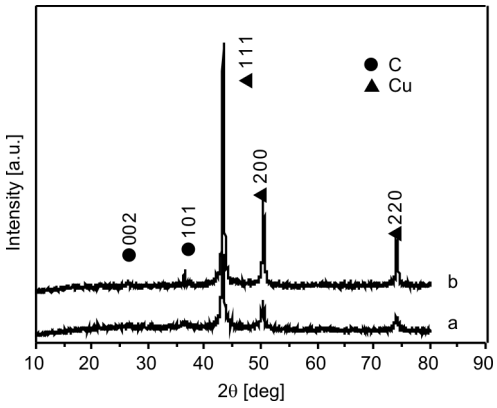

Fig. 1. X-ray diffraction patterns for carbon coated nanoparticles fabricated by using two different ratios of carbon to copper starting material: a) 4:1, b) 2:3

It is obvious from Fig. 1 that the increase in the copper content in the samples resulted in the marked increase in intensity of the copper diffraction peak. This indicated

that with an increase in the concentrations of copper nanoparticles, copper became more crystallized. At the same time, it can be seen that the carbon coated copper nanoparticles at 2θ of 36° are represented by a diffuse scattering peak in curve a, while at 2θ of 27° and 36° they are represented by a clear diffraction peak, for which the corresponding d values were 0.3364 nm and 0.2470 nm (the PDF card number 46-0945), which showed that the carbon of the former sample existed in amorphous form, while the surface of the latter sample of carbon coated copper nanoparticles changed to graphite state (a diffraction peak of graphite was present).

Obviously, carbon graphitization can be promoted by increasing the copper content, but XRD analysis of the powder did not reveal the presence of carbide or of copper oxide. During the preparation process, at first argon was ionized to form argon plasma and caused the release of electrons. The released electrons defined an electric field which caused the acceleration of Ar^+ ions from the anode, thereby producing a stream of high-speed ions. The ions bombarded the bottom electrode, so that their kinetic energy was converted to a thermal energy; the temperature of the reaction reached several thousand degrees, which enabled rapid gasification of copper and carbon atoms. The copper atoms agglomerated quickly, became radicals in container wall and left the discharge region. Since the diffusion rate of the copper atoms was larger than that of carbon, despite the role of surface tension, the copper atoms could spherodize and become spherical particles. At the same time, carbon atoms adhered to the molten Cu nanoparticles and eventually formed core-shell nanoparticles and were deposited on the container wall. As the copper content of the sample was increased, the quantity of copper atoms evaporating from the samples also increased, which led to an increase in the nanoparticle sizes. Therefore, the samples of higher Cu content exhibited stronger diffraction peaks of copper than those samples having a lower copper content.

3.2. TEM analysis

Typical TEM images for the obtained carbon-coated copper nanoparticles are shown in Fig. 2. The nanoparticles were spherical in shape (Fig. 2a), well dispersed, with the diameter of 50 nm. Particle surfaces were relatively smooth with no apparent traces of agglomeration.

According to HRTEM observation (Fig. 2b), we also found that these nanoparticles possessed a distinct core/shell structure. It was found that the carbon layers in carbon coated copper nanoparticles were 3–5 nm thick. The interlayer spacing of these graphitic planes was about 0.34 nm, therefore we can see that the shell of each nanoparticle possessed an ordered graphite structure.

The selected area electron diffraction (SAED) patterns of A and B areas from Fig. 2a are shown in Figs. 2c and 2d, respectively. According to the calculation of electron diffraction spots in Fig. 2c, it was revealed that the crystal plane spacing of the inner core region was 0.21 nm, which corresponded to the crystal plane distance of

the main diffraction peak of copper; the crystal plane is (111). It was proved to be the electron diffraction pattern of the face centred cubic single crystal copper. It is shown in Fig. 2d that the TEM diffraction pattern of B is an amorphous diffuse scattering ring. From the above analysis, we can see that the outer carbon layers were amorphous, which was consistent with the XRD spectrum.

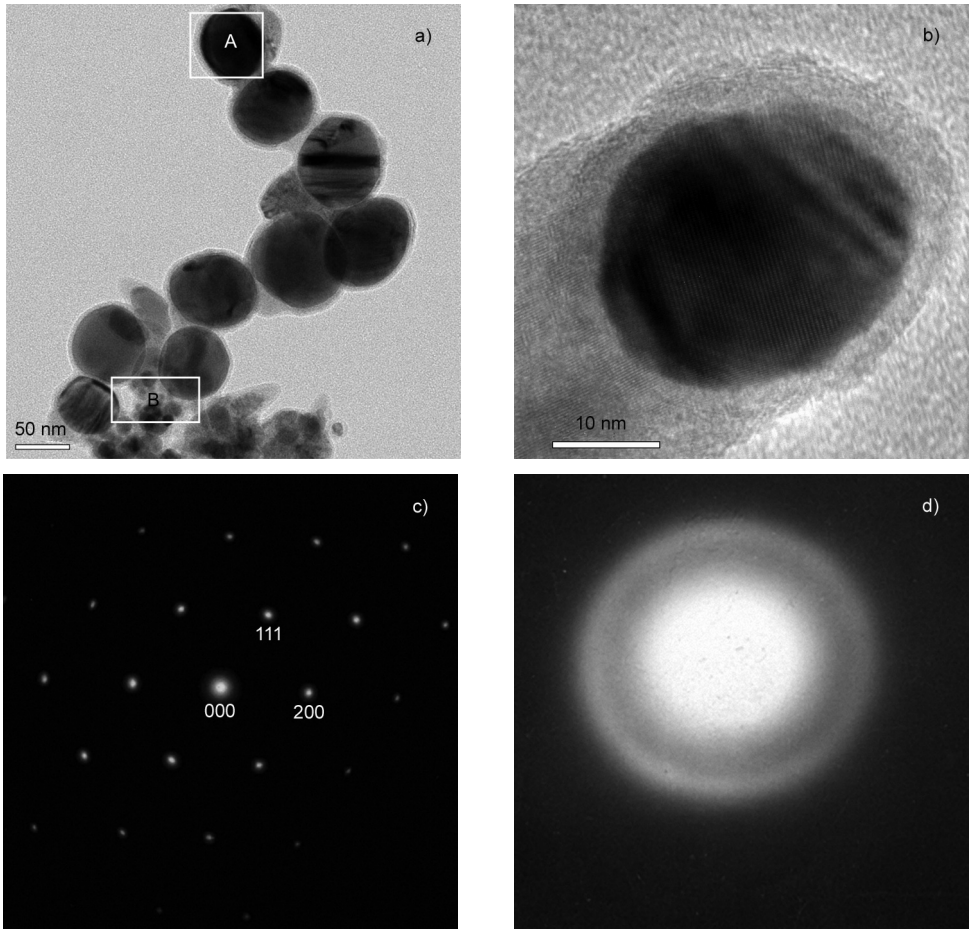

Fig. 2. TEM (a) and HRTEM (b) images of carbon coated copper nanoparticles as well SAED patterns of areas A (c) and B (d) in Fig. 2a

3.3. TGA-DSC analysis

The oxidation resistance of carbon coated copper nanoparticles was determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Figure 3a shows the TGA curves of the carbon coated copper nanoparticles. Between 35 °C and 293.9 °C, the mass of the sample slightly increased (ca. 1%) because at this

temperature the reaction of carbon with air occurred at a lower rate. This weight increase was attributed to the oxidation of the trace copper on the particle surface. From 293.9°C to 420.1° C, the outer amorphous carbon layer began to oxidize, which manifested in an exothermic peak at 321.5 °C with a radical weight loss. At 420.1 °C, the weight loss rate reached the maximum (weight loss rate of 1.5%). Upon increasing the temperature above 420.1 °C, due to the decrease of the outer carbon layer, a part of the copper nanoparticles exposed to air was oxidized, and thus the carbon coated copper nanoparticles had an obvious weight gain. From room temperature to 600 °C, the whole reaction caused a weight gain of 1.8 wt %.

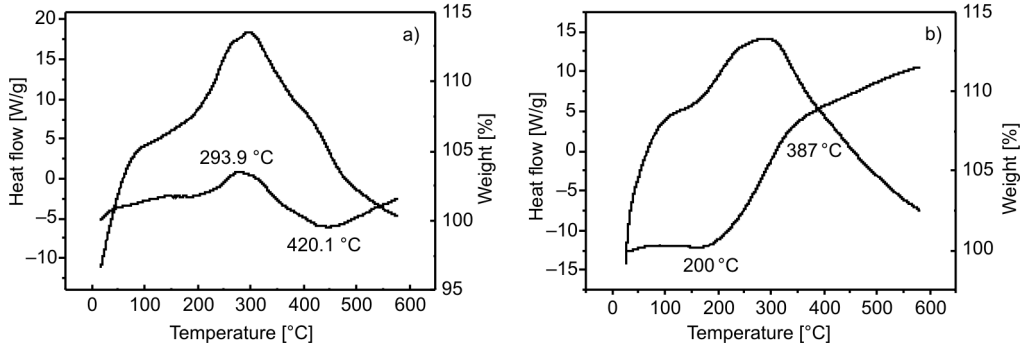

Fig. 3. TGA-DSC curves of carbon coated copper nanoparticles (a) and copper nanoparticles (b)

Figure 3b shows the TGA curves of copper nanoparticles. It was shown that the copper nanoparticles had an apparent weight gain at temperatures above 200 °C, there was an obvious exothermic peak associated with weight gain, which was observed at 310 °C. During the whole process, copper nanoparticles experienced a weight gain of 12%. The initial temperature of oxidation of carbon coated copper nanoparticles was superior to that of the copper nanoparticles.

From the above comparative analysis of both charts we can see that carbon coated copper nanoparticles have better oxidation resistance than that of copper nanoparticles. Copper nanoparticles experience very obvious weight gain, which revealed that they easily reacted with oxygen, while the weight gain of carbon coated copper nanoparticles was not obvious in the whole process, which demonstrates that carbon-coated copper nanoparticles have superior oxidation resistance. The carbon shell of graphite provides good protection for the copper particles in the core.

4. Conclusions

Carbon coated copper nanoparticles with the diameter of ca. 20–60 nm have been successfully fabricated by the carbon arc discharge method. The core shell nanoparticles had a graphitic carbon shell and face centred cubic copper core. The interlayer

spacing of the graphitic planes was about 0.34 nm. Copper catalyses graphitization of the external carbon layer, the higher the copper content, the more obvious the degree of graphitization is. The DSC experiments showed that the produced material exhibited an excellent oxidation resistance.

Acknowledgements

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