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Synthesis and characterization of metallic copper nanoparticles via thermal decomposition

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ABSTRACT

Copper oxalate was used as a precursor to prepare metallic copper nanoparticles by thermal decomposition. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy and UV-Vis spectroscopy. XRD analysis revealed broad pattern for fcc crystal structure of copper metal. The particle size by use of Debye-Scherrer's equation was calculated to be about 40 nm.

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1. Introduction

In recent years, synthesis of transition metal nanoparticles is a growing research field in chemical science [1–3]. Nanoparticles which are ultra fine particles have the diameter from 1 to 100 nm and their properties are different form bulk materials. As the metal particles are reduced in size, the bulk properties of the particles disappear to be substituted to that of a "quantum dot", following quantum mechanical rules. It can thus be easily understood that metal nanoparticles' chemistry differs from that of the bulk materials [4]. Since with size reduction, the high surface area to volume ratio lead to enhanced catalytic activity [5].

Among various metal particles, copper nanoparticles have attracted considerable attention because copper is one of the most important metals in modern technologies [6]. Considerable interest has been focused on copper nanoparticles due to their optical, catalytic, mechanical and electrical properties [7-12]. Since late 1980s, copper nano particles have attracted much attention of researchers because of their applications in catalysis [13]. The advantages of Cu nanoparticles are being cheap, high yields in mild reaction conditions and having short reaction times as compared to traditional catalysts [14,15]. Cu nanoparticles have been synthesized through different methods such as thermal decomposition [16-19], metal salt reduction [20], microwave heating [21], radiation methods [22], micro emulsion techniques [23], super critical

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techniques [24], laser ablation [25], polyol method [26], solvothermal method [27], DC arc discharge method [28], thermal and sonochemical reduction [29].

Among various techniques for synthesis of inorganic nanoparticles, thermal decomposition is one of the most common to produce stable monodisperse suspensions with the ability of self-assembly. Nucleation occurs when the metal precursor is added into a heated solution in the presence of surfactant, while the growth state take place at a higher reaction temperature [30]. Recently Zheng and coworkers reported synthesis of nanosized CuO via thermal decomposition of copper oxalate [31], but up to now there has not been any report about synthesis of metallic copper nanoparticles with this precursor.

Very recently, our group reported the synthesis of uniformsized nanoparticles of various transition metal oxides from thermal decomposition of metal-oleate complexes which were prepared from the reaction of some organometallic complexes [32,33]. In the continuation of the development of simple synthesis of nanosized nanoparticles, we herein report on the synthesis of metallic copper nanoparticles from a simple, green, low-cost, and reproducible process from copper oxalate as precursor. In this process, oleylamine was used as both the medium and the stabilizing reagent.

2. Experimental

2.1. Materials

All the chemicals reagents used in our experiments were of analytical grade and were used as received without further





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purification. Copper oxalate precursor was synthesized according to this procedure: the Cu(OOCCH₃)₂ · H₂O (2 mmol) was dissolved into 10 mL of distilled water to form a homogeneous solution. A stoichiometric amount of potassium oxalate dissolved in an equal volume of distilled water was dropwise added into the above solution under magnetic stirring. The solution was stirred for about 15 min and a blue precipitate was centrifuged and washed with ethanol several times. The product was dried at 50 °C. The copper oxalate, Cu(O₄C₂), was characterized by elemental analyses, powder X-ray diffraction (XRD) and thermo gravimetric analysis (TGA) [31,34]. *Anal.* Calc. for [Cu(O₄C₂)]: C, 15.84; Cu, 41.93. Found: C, 15.75; Cu, 41.84%.

2.2. Characterization

XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K α radiation. Elemental analyses were obtained from Carlo ERBA Model EA 1108 analyzer. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscopy. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. Thermogravimetric-differential thermal analysis (TG-DTA) were carried out using a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a flow rate of 20.0 mL min⁻¹ and a heating rate of 10 °C min⁻¹. The electronic spectra of the complexes were taken on a Shimadzu UV–Vis scanning spectrometer (Model 2101 PC).

2.3. Synthesis of Cu nanoparticles

The current synthetic procedure is a modified version of the method developed by Hyeon and others for the synthesis of metal nanoparticles which employs the thermal decomposition of transition metal complexes [32,33,35]. The synthetic pathway is shown in Scheme 1. In this synthesis Cu nanoparticles were prepared by the thermal decomposition of copper oxalate, $[Cu(O_4C_2)]$ -oleyl-amine complex as precursor. First, the $[Cu(O_4C_2)]$ -oleylamine complex was prepared by reaction 0.6 g of $Cu(O_4C_2)$ and 5 mL of oleylamine. The mixed solution was placed in a 50 mL three-neck distillation flask and heated up to 140 °C for 60 min under an argon atmosphere. The resulting metal-complex solution was injected into 5 g of triphenylphosphine (TPP) at 240 °C. As the thermal decomposition proceeded, the azury solution turned to red, indicating the formation of metallic copper. The reddish solution was

aged at 240 °C for 45 min, and was then cooled to room temperature. The reddish nanoparticles were precipitated by adding excess ethanol to the solution. The final product was washed with ethanol several times to remove excessive surfactant. This product could easily be re-dispersed in nonpolar organic solvents, such as hexane or toluene (Scheme 1).

3. Results and discussion

The TGA curve of the as-prepared precursor is shown in Fig. 1. There is only one weight loss step in the temperature range 250–310 °C. The weight loss at 250–315 °C may be ascribed to the decomposition of the oxalate. The weight loss is about 43.23%, which is close to the theoretical value.

X-ray powder diffraction (XRD) patterns of Cu nanoparticles at room temperature shows in Fig. 2. The XRD pattern is consistent with the spectrum of copper, and no peak attributable to possible impurities is observed. The peak positions are consistent with metallic copper. All possible peaks of copper are observed, which indicates the polycrystalline nature of the product. Bragg's reflections for Cu nanoparticles are observed in XRD pattern at 2θ value of 43.6°, 50.7° and 74.45° representing [111], [200] and [220] planes of fcc structure of copper with the space group of *Fm3m*



Fig. 1. TGA of the copper oxalate precursor, $Cu(O_4C_2)$.



Metallic Cu nanoparticles



Fig. 2. XRD pattern of the copper nanoparticles.

(JCPDS No. 4–0836). The size of the crystallites was estimated from Debye–Scherrer equation is about 40 nm.

FT-IR spectroscopy is a useful tool to understand the functional group of any organic molecule. The infrared spectra of free TPP, oleylamine and copper nanoparticles coated with oleylamine and TPP are shown in Fig. 3. By comparing the infrared spectra of the nanoparticles with free surfactants in Fig. 3 we can see that the organic molecules have indeed become a part of the nanoparticles. As shown in Fig. 3a and b, peaks corresponding to P–ph stretching at 1710 cm⁻¹, rocking and bending mode of the methylene group ω (CH₂) at 1270 cm⁻¹, bending mode of the phenyl group γ (=CH) at 742 cm⁻¹ and v (benzene ring) at 697 cm⁻¹ can be seen clearly. The only difference among these characteristic peaks is either the peak intensity or a slight shift in the peak position. For example, the peak position of the longitudinal modes of oleylamine and TPP shifts to lower wavenumbers after TPP and oleylamine are ad-

sorbed on the surface of the copper nanoparticles. The FT-IR of the copper nanoparticles shows the intense adsorption peaks at 2920 and 2850 cm⁻¹ attributed to the alkyl chains of oleylamine. The bands attributed to the antisymmetric and symmetric vibration modes of –N–H are observed at 3437 and 3232 cm⁻¹, respectively (Fig. 3c). Due to the coordination of the unpaired electron couple of the nitrogen atom, the vibration bands are observed in lower values than those expected for the free amine group, i.e., 3500 and 3300 cm⁻¹, respectively. This indicates that oleylamine is bound on the surface through the unpaired electron couple of the amine group [36]. From these results, a chemical bond can be formed between N and Cu atoms and a coordinate bond between P and Cu atoms on the surface of the nanoparticles. Thus, the phenyl stretching mode v(P-ph) at 1430 cm⁻¹ is still visible in Fig. 3c. So the oleylamine and TPP serves as the capping ligand that controls growth. Triphenylphosphine (TPP) was widely used in the synthesis of phosphine-stabilized cobalt or other metal nanoparticles



Fig. 3. FT-IR spectra of (a) free TPP absorption, (b) free oleylamine and (c) Cu nanoparticles coated by oleylamine and TPP.



Fig. 4. SEM image of Cu nanoparticles.



Fig. 5. TEM images of Cu nanoparticles.

[37]. The phenyl groups in TPP can provide greater steric hindrance than straight-chained alkyl groups such as tributyl and trioctyl to control the size of nonmagnetic metal nanoparticles and to stabilize efficiently the magnetic nanoparticles.

The morphology of the Cu nanoparticles is examined by SEM (Fig. 4). From the micrograph, it was observed that the nanoparticles were agglomerated. The TEM image (Fig. 5) shows the presence of dense agglomerates. The particles have an irregular shape, and their distribution, likewise, is not uniform (30–80 nm).

The growth mechanism could be well understood on the basis of the following reactions and the crystal habits of Cu. In the presence of oleylamine as solvent $[Cu(O_4C_2)]$ -oleylamine were synthesized. After addition of TPP to these solutions at high temperature the complexes were decomposed. TPP is a high-boiling point surfactant with a patulous long-chain structure providing great steric hindrance. The addition of TPP into the mixture of oleylamine and complex as an additional surfactant reduced the particle size much further and resulted in nanoparticles with very thin arrays. Olevlamine is known as a ligand that binds tightly to the metal nanoparticles surface. The combined effects of TPP and oleylamine were much more profound than those of individual contributions. On the other hand these complexes transform to Cu under an argon atmosphere. When the triphenylphopsphine (TPP) was used as the complexing agent, the spherical nanoparticles capped by this surfactant were obtained. The growth of the Cu nanoparticles can be explained on the basis of the schematic view presented in Scheme 1. The Cu nanoparticles agglomerated together to form a spherical structure. In this synthetic rout oleylamine acts not only as the reaction solution but also as the stabilizer, which prevents the nanoparticles from oxidizing. Recently, copper oxalate was used as precursor for synthesizing CuO. In that method copper oxalate was calcined at 400 °C for 4 h [31] or 350 °C for 10 h [34] without any capping agent and argon atmosphere. So, metal oxide nanoparticles obtained. But here with use of capping agent, metallic nanoparticles obtained. We believe that capping agents used here help to the formation of metal rather than metal oxide.

Nanosized particles exhibit unique optical properties with an exponential-decay Mie scattering profile with decreasing photon energy. Some transition metal nanoparticles show a distinct surface-plasmon resonance (SPR). The SPR is very sensitive to metal size, dielectric constant of metal and embedding medium (here is oleylamine) [20,29]. For instance, Cu nanoparticles typically exhibit SPR at around 600 nm [38]. However, for the fresh Cu nanoparticles synthesized here show an absorption peak at around 572 nm (Fig. 6). This peak can be assigned to the absorption of nanoparticles of copper [38]. A modest blue shift (about 28 nm) of the absorption edge relative to that of the bulk copper powder is



Fig. 6. UV-Vis absorption of the Cu nanoparticles.

observed. This observation alludes to the size effect to the Cu nanoparticles. The synthesized particles were stable for \sim 6 days. This kind of stabilization of Cu nanoparticles was due to the capping of particles by oleylamine in thermal treatment. The arrangement of capping agent, oleylamine surrounding the nanoparticles is size dependent. After a few days, slow oxidation of copper particles sets in with the disappearance of absorption peaks [39] and finally the as-synthesized product becomes black. This indicated that the sample was oxidized.

4. Conclusion

In summary, Cu nanoparticles with diameters from 30 to 80 nm have been successfully synthesized via thermal decomposition of $[Cu(O_4C_2)]$ -oleylamine complex. This method employed an inexpensive, reproducible process for the large-scale synthesis of copper nanoparticles.

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