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Synthesis and characterization of Cu nanoparticles and studying of their catalytic properties

ABSTRACT

A. Nasirian*

*Iran University of Science and
Technology, Tehran, Iran.*

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In this paper, we report on the synthesis of Cu nanoparticles through a single-precursor route by controlling the growth temperature. Selective adsorption of oleylamine on various crystal planes may play an important role in the growth process. The understanding of this self-assembling process will help us develop reliable and reproducible methods to synthesis other three dimensional nanostructured architectures and increase the knowledge of self-assembly. The catalytic activities of these nanoparticles of different sizes have been tested on the yield of production of biphenyl from the iodobenzene in reaction. The as synthesized products were characterized by powder X-Ray diffraction (XRD), Scanning electron microscopy (SEM), Energy-dispersive X-ray (EDX) analysis and UV-vis spectra.

Keywords: *Cu nanoparticles; Oleyl amine; Single precursor; Biphenyl.*

INTRODUCTION

In recent years, controlled synthesis of monodisperse inorganic nanocrystals with different sizes and shapes has been strongly motivated by the requirement to uncover and map their size and shape-properties and to achieve their applications [1–3]. Nanoparticles, acting as nanoscale building blocks, can self-assemble into different ordered superstructures with a range of practical applications [4-5]. Therefore, the development of uniform nanoparticles has been intensively pursued [6–10]. But the methods usually offer materials with poor optical and physical properties, as the nanocrystals can continue to grow slowly at now temperature via coarsening or epitaxial attachment because of the absence of a strong repelling reaction between the particles. For the preparation of nanoparticles with desired properties, it remains a challenge to explore robust pathway and purify principles towards the systematic manipulation of their size and shape.

* Corresponding author:

Azam Nasirian

Iran University of Science and
Technology, Tehran, Postal Code:
16846-13114, Islamic Republic of
Iran.

Tel +98 9171903016

Fax +98 7914442524

Email a.nasirian@sci.ui.ac.ir

Nowadays the method of thermal decomposition of organometallic precursors in coordinating solvents is used more frequently, which results in relatively stable nanoparticles for organic monolayer protection.

Synthesis of Cu nanostructures has been actively researched for many decades because Cu is an important industrial material due to its novel physical and chemical properties. Among all metals used in modern electronic circuits, Cu is the most common one because of its excellent electrical conductivity and low cost. Logically, Cu is expected to be an essential component of nanodevices developed in future [5]. Therefore, nanoscale copper is of particular interest for the applications mentioned above. To date, several synthetic approaches- the microwave-induced method, the electrochemical synthetic method, the vapor deposition method [8], the sonochemical method [9], the solution-phase synthesis method, and so on [8-19], have been developed for the preparation of nanosized Cu. Cu is one of the most normal conductors in modern technologies and could be used widely in nanodevice. Many methods have been devoted to the shape controlled synthesis of Cu nanocrystals, nanoparticles, nanowires and nanorods [19-23].

In this paper, we have reported the synthesis of copper nanoparticles through a single-precursor route by controlling the growth temperature. The catalytic activities of these nanoparticles have been tested on synthesis of biphenyl from iodobenzene.

EXPERIMENTAL

Materials

Copper (II) acetylacetonate ($\text{Cu}(\text{acac})_2$, 99.99%), oleylamine (OA, 80–90%), DMSO, CH_2Cl_2 were purchased from Aldrich and iodobenzene was purchased from merck.

Preparation of Cu nanoparticles

In a typical synthesis, about 0.001 mol $\text{Cu}(\text{acac})_2$ was added to the three necked flask, which contained 8ml oleylamine (OA) under Ar. The solution was heated to certain temperatures for the synthesis of Cu nanoparticles, the temperature is 220°C in a few minutes, and kept at those temperatures for 6 hours. After the

solutions were cooled to room temperature, nanoparticles were obtained by centrifugation and washing. The as-prepared nanoparticles were dried in vacuum at 60°C for 12 hours for following characterization.

Preparation of biphenyl

Iodobenzene was purchased from Merck. The copper nanoparticles prepared through the above-said method were used for catalytic testing without further activation.

In a typical reaction, 50 mg of copper nanoparticles were added to 1 ml of DMSO solution containing 100 mg of iodobenzene and the mixture was refluxed at 200°C for 5 h. After the required time the reaction system was cooled rapidly to room temperature and the product was separated by thoroughly mixing with 2 ml of saturated ammonium chloride followed by 2.5 ml of dichloromethane which separated two layers with the upper layer containing the product dissolved in dichloromethane. The product was extracted three times by solvent evaporation method to get the pure compound.

RESULTS AND DISCUSSION

Figure 1 illustrates the XRD pattern of copper nanoparticles for the freshly prepared sample at 300°C . The peak positions coincide with those of metallic copper with a specific structure and broadening of the peaks due to crystallites with sizes in the nanometer scale is also observed. The Peaks are very sharp due to the high nano crystalline nature of copper.

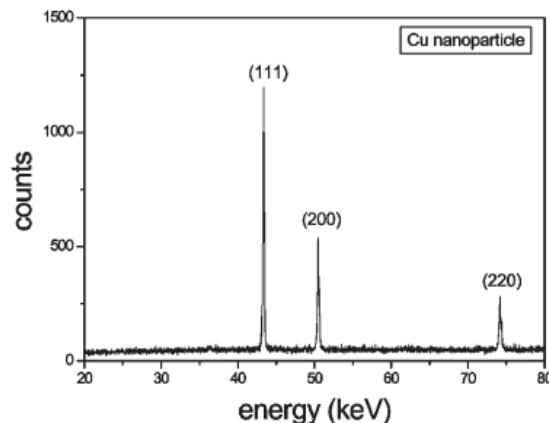


Fig. 1. X-ray diffraction pattern (Cu K α -radiation) of copper nanoparticles.

Figure 1 shows three peaks at 2θ values of 43.3° , 50.4° , and 74.1° , corresponding to (111), (200), and (220) planes of copper, respectively. No impurity peak is observed in the X-ray diffraction pattern. Peaks corresponding to copper oxide were absent from this spectra.

Figure 2 shows SEM images of Cu nanoparticles. Copper nanoparticles by this method show the monodispersed distribution of particle sizes. The average particle sizes of the Cu nanoparticles were obtained around 50 nm with spherical shape.

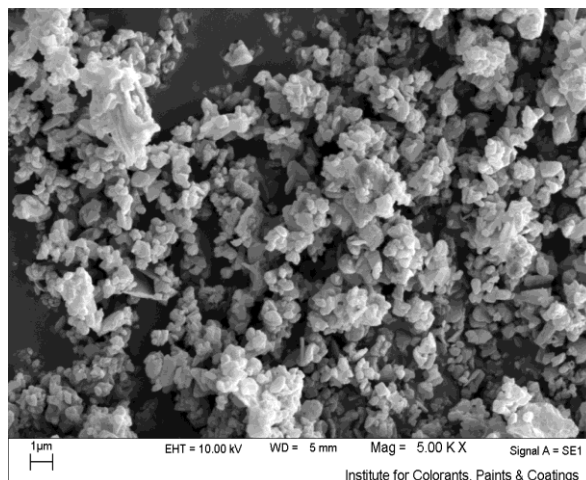
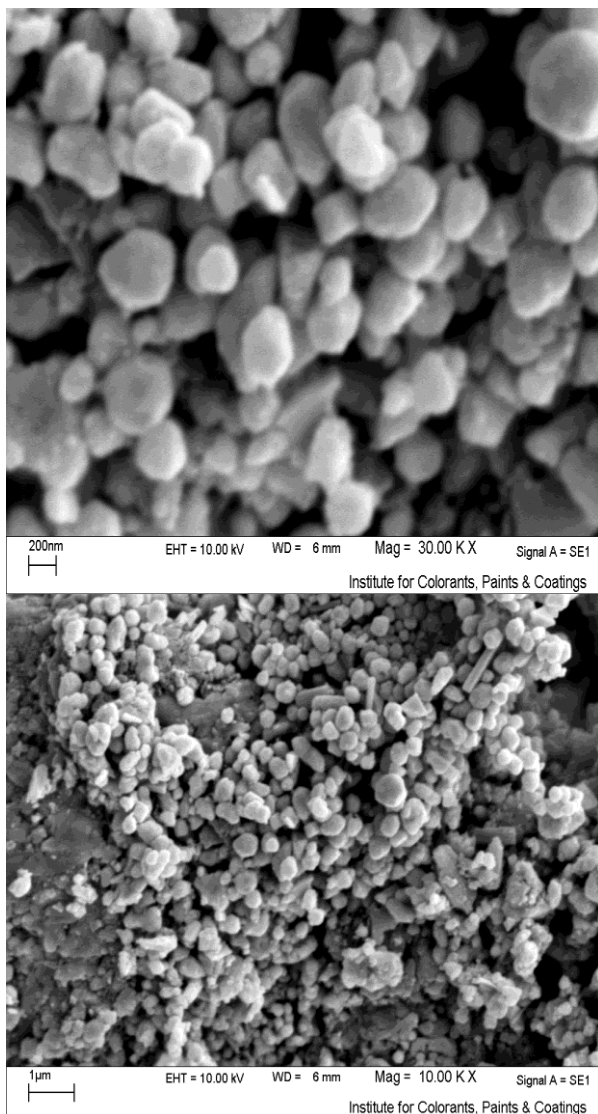


Fig. 2. SEM images of Cu nanoparticles

The composition of copper nanoparticles was further probed by energy-dispersive X-ray (EDX) analysis (Figure 3). In this spectra there are number of sharp peaks that indicate that copper nanoparticles were prepared.

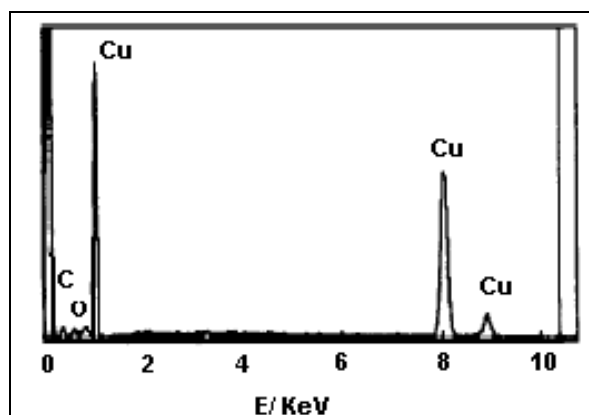


Fig. 3. EDX spectra of cu nanoparticles

Figure 4 shows the absorption spectrum of the copper nanoparticles. The copper nanoparticles prepared display an absorption peak at around 570 nm. This peak can be assigned to the absorption of nanoparticles of copper. A modest blue shift (20-30 nm) of the absorption edge relative to that of the bulk copper powder (600 nm) is observed. This observation alludes to the size effect of the copper nanocrystallites. On the other hand, the thermally prepared copper nanoparticles display a broad absorption from 550 to 700 nm. The broadness of the absorption peak probably stems from the wide size distribution [20].

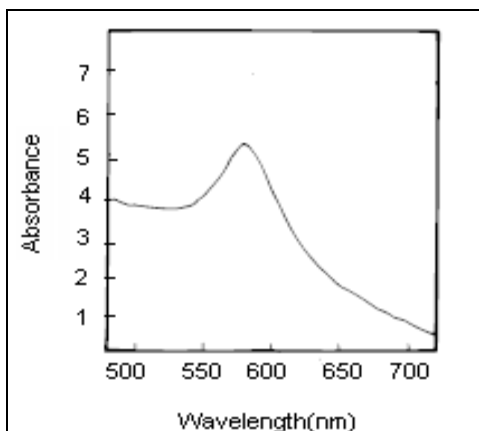


Fig. 4. UV-visible spectra of copper nanoparticles

The condensation of iodobenzene to biphenyl was chosen as the model reaction for catalytic activity due to its significant role in organic synthesis. As shown in Figure 5, when iodobenzene is heated at 200°C in presence of copper powder it forms diphenyl. Aryl halides couple among themselves to form diaryl derivatives, an important drug intermediate, in presence of copper catalyst [20-23].

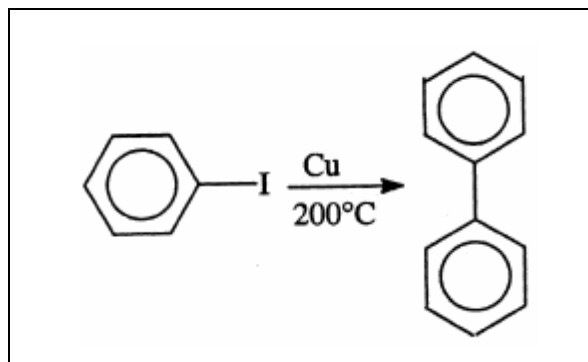


Fig. 5. Iodobenzene in presence of copper nanoparticles

Figure 6 shows the IR spectra of biphenyl that is prepared by reaction of iodobenzene as the precursor and copper nanoparticles as a catalyst. But unfortunately the yield of the reaction is mostly affected by the large size and coating of copper metal by hard material like copper oxide or other strongly adsorbed compounds. As a result, the total exposed surface area of the catalyst is significantly reduced. This is more true when the nanoparticles are prepared in surfactant solution e.g. in reverse

micellar system, the surface is further complicated by the strong adsorption of the surfactant molecules. Some studies have reported heating of the particles at high temperature for removal of adsorbed materials. This creates an additional complication of converting the catalyst surface into irremovable metal oxide, nitride or sulphide. As a result, the catalytic efficiency is drastically reduced [20-23].

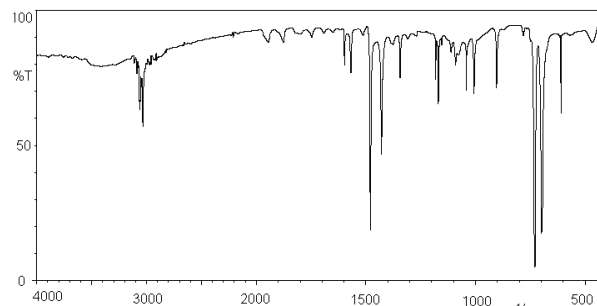


Fig. 6. IR spectra of the biphenyl

The total yields of biphenyl in the condensation of iodobenzene for different copper powders are summarized in Table 1. The particle size of different copper powders was included in the table for comparison. The uncapped and undefined macro sized copper powder showed a 43% conversion of iodobenzene to biphenyl in 5 h under our experimental conditions. Same amount of copper nanoparticles (size, ~ 50 nm diameter) showed 88% conversion of iodobenzene to biphenyl, which increased to about 95% when 8 nm diameter capped copper nanoparticles are used. Surprisingly, 5 nm size copper nanoparticles showed no change in the yield of about 95% [20].

The higher catalytic activity towards the condensation of iodobenzene could be due to the higher catalytic surface area of small nanoparticles. It is presumed that the electrophilic nature of the catalyst surface renders a weak bond between the π -system of benzene ring and vacant d system of copper atoms, which gives slightly positive charge over iodine atom. The whole complex reacts with another molecule of iodobenzene to produce biphenyl and cuprous iodide. The electrophilic nature of copper surface obviates that when the particles are extremely small in size, the electrons are pumped into copper by the benzene π -system, which usually reduces the band gap between Fermi

level and conduction band considerably so that the catalytic activity is also expected to be reduced. However, copper has d-bands well below the Fermi level and the antibonding stage at the top of the d bands end up below the Fermi level and are filled. As a result, the catalytic activity did not decrease rather it remained constant. Any aggregation of the particles in aqueous dispersion leads to lower efficiency. The freshly prepared and capped Cu nanoparticles also showed good activity for this reaction type of condensation indicating that any oxide layer formation on the particle surface perhaps inhibits the catalytic activity [20-23].

Table 1. Dependence of yield of iodobenzene (%) on size of the copper nanoparticles

Particles size (nm)	Approximate yield (%)
90	80
67	88
35	92
8	95
5	95
Uncapped copper particles of undefined large sizes and broad polydispersity	43

CONCLUSION

In summary, Cu nanoparticles have been selectively synthesized by using $\text{Cu}(\text{acac})_2$ as precursor by controlling the growth temperature. Selective adsorption of OA on various crystal planes may play an important role in the growth process. Furthermore, the understanding of this self-assembling process will help us develop reliable and reproducible methods to synthesis other 3D nanostructured architectures and increase the knowledge of selfassembly. Moreover, the synthesis route is mild and environmentally friendly. It is believed that this method will be re-considered toward the research in the nanometer regime. Also their chemical reactivity in the reaction of synthesis of biphenyl is proportional to their surface area, and their reactivity.

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