Cu nanorods and nanospheres and their excellent catalytic activity in chemoselective reduction of nitrobenzenes

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ABSTRACT

Highly selective chemical route for the hydrothermal synthesis of Cu^0 nanorods and nanospheres using a long chain saturated fatty acid, viz. lauric acid as template is reported. Our experimental results revealed Cu nanorods are of *ca*. 14 nm diameters and 100–235 nm length, whereas the nanospheres are of dimensions 2–15 nm diameter. Cu nanospheres show much enhanced catalytic activity over the nanorods for the chemoselective reduction of 4-nitrophenol and 5-nitroisophthalic acid to respective substituted anilines in one pot at room temperature, suggesting the role of particle size and shape in catalytic reduction.

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1. Introduction

Experimental methods in designing metal nanoparticles of definite size and shape are area of major research interest due to the fact that these metals have different optical, electrical, catalytic, magnetic, and/or electronic properties compared to their bulk counterpart [1–5]. Different synthetic routes for nanoscale particles of metallic copper of various size and shapes have been reported in recent times [6–8]. Of them the thermal, photochemical or sonochemical reduction of copper(II) salts/complexes are convenient process for the synthesis of copper nanoparticles of various shapes. Often these syntheses yielded low valence cuprous oxide (Cu_2O) along with metallic copper in the product [8], which hinders the potential applications responsible solely for metallic nanoparticles. Thus selective synthetic route for high purity metallic Cu nanoparticles is highly desirable. Vazquez–Vazquez et al. have observed the crucial role played by the amount of the reducing agent in size and optical properties of Cu nanoparticles [9].

Although there are intensive research works on stabilized nanoparticles in colloidal or solution phase [10,11], relatively little attention has been focused on their existence as a solid phase. For the fruitful utilization of tiny nanoparticles in heterogeneous catalysis and their easy separation from the reaction mixture, stabilization of these metallic nanoparticles in solid phase is crucial. Nanoparticles of copper and nickel are grown in thermally evaporated stearic acid films [12]. Lisiecki et al. have used sodium dodecyl sulfate as surfactant and sodium borohydride or hydrazine as reducing agent to synthesize metallic Cu nanoparticles at or above the critical micelle concentration [13]. Anionic surfactants like $C_{11–17}$–COOH or SDS can stabilize Cu^{2+} in the solution phase through electrostatic interactions and thus their *in situ* reduction in the presence of reducing agent like $LiAlH_4$ can promote the formation of Cu nanoparticles of definite size and shape. Electrochemical methods are often found very selective for the synthesis of organized Cu nanostructures [14].

In this context preparation and study of supported copper catalysts over silica [15,16], zeolites [17], zirconia, alumina [18], etc. have also attracted much attention in recent times. Their use in the technologically important methanol synthesis through reverse water gas-shift reaction [19] is also noteworthy. In addition, the nanocatalysts are often used for the complete oxidation of light paraffins (methane, propane) into carbon dioxide and water or reduction of nitrogen oxides [20,21]. Small copper nanoparticles also show excellent catalytic activity in Ullmann reaction for the condensation (homocoupling) of aryl halides [22], and O-arylation of phenols [23] or "click" 1,3-dipolar cycloaddition between azides and terminal alkynes [24]. Herein, we report a simple and generalized method to prepare Cu nanospheres and nanorods hydrothermally utilizing the templating property of a long chain fatty acid with or without the addition of ethylenediamine. The catalytic activities of these Cu nanoparticles are studied in the chemoselective reduction of nitrobenzenes to their respective anilines at room temperature.

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2. Experimental section

Synthesis: In a typical synthesis of the copper nanospheres, 2.003 g lauric acid ($C_{12}H_{24}O_2$, Loba Chemie, 99%) was dissolved in an aqueous solution (20 g distilled water) of 1.2 g ethylenediamine (Merck, 99%). The solution was stirred for 30 min, 1.705 g $CuCl_2\cdot 2H_2O$ (Loba Chemie, GR) dissolved in 5 g distilled water and slowly added to the above solution. The solution became deep blue in color (pH 9). Then the pH of the solution was adjusted by addition of aqueous NaOH (Merck, 98%) upto pH 12–13. Again the solution was stirred for 15 min and then the solution was hydrothermally treated in Teflon-lined stainless steel autoclave at 443 K for 24 h. After the hydrothermal treatment the reaction mixture composed of Cu nanoparticles, residual lauric acid and ethylenediamine was taken into 100 ml beaker and 20 ml ethanol was added onto it. Then the content was sonicated about 10 min. to dissolve the residual lauric acid and ethylenediamine. Then the mixture was allowed to settle for 15 min. during which the all Cu nanoparticles precipitated and then it was filtered. This process was repeated 10 more times to obtain pure copper nanoparticle sample. The copper nanorods are synthesized by taking 2.003 g lauric acid dissolved in the mixture of 20 g distilled water and 1.2 g ethylenediamine. The solution was stirred for 30 min, 1.705 g $CuCl_2\cdot 2H_2O$ and 1.333 g $AlCl_3$ (Merck, anhydrous powder) taken in 5 g distilled water and mixed together. The mixed solution was slowly added to the surfactant solution. The solution became deep blue in color (pH 6). The pH of solution was adjusted by addition of aqueous NaOH upto pH 12–13. Again the solution was stirred for 30 min and then the solution was hydrothermally treated in Teflon-lined stainless steel autoclave at 443 K for 24 h. The copper nanorods are collected by sonication followed by filtration.

Characterization techniques: Powder X-ray diffraction patterns are recorded on a Bruker D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current and calibrated with a standard silicon sample, using Ni-filtered Cu Kα ($\lambda = 0.15406$ nm) radiation. Transmission electron microscopic images are recorded in a JEOL 2010 TEM operated at 200 kV. For the TEM analysis samples are dispersed in ethanol and then a droplet of the solution is spread onto a carbon-coated copper grid with 300 messes. BET surface area of the Cu nanoparticles were obtained from nitrogen adsorption/desorption isotherms by using a Beckman Coulter SA3100 at 77 K. Prior to gas adsorption measurements, all samples were degassed for 4 h at 423 K. A JEOL JEM 6700F field emission scanning electron microscope was used for the determination of morphology of the particles. For the catalytic reactions 4-nitrophenol (Loba Chemie, 98%) and 5-nitroisophthalic acid (Sigma Aldrich, 98%) are used as reactants and sodium borohydride (Merck, 95%) was used as reducing agent. For a typical reaction 10 ml 1 mM aqueous solution of 4-nitrophenol was taken in a 50 ml beaker. Then 10 ml 10 mM aqueous solution of sodium borohydride ($NaBH_4$) and 10 mg copper nanoparticles are added to it. After addition, the solution was stirred vigorously and 0.5 ml aliquot was taken for UV–vis spectra at different time interval. The progress of the reactions was studied by using a Shimadzu 2401PC UV–vis spectrophotometer. Finally the reaction mixture was filtered to separate the 4-aminophenol product and the copper nanoparticles. Product 4-aminophenol has been identified by capillary column gas chromatography (Agilent 4890), and ^1H NMR spectroscopy (Bruker DPX-300 MHz).

3. Results and discussion

The powder XRD pattern of copper nanospheres and nanorods are shown in Fig. 1. The wide angle XRD pattern of the nanospheres and nanorods shows that the materials are highly crystalline in

nature and planes corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) are clearly observed (JCPDS PDF No. 03-065-9743). For both these Cu nanoparticles these peaks could be assigned to
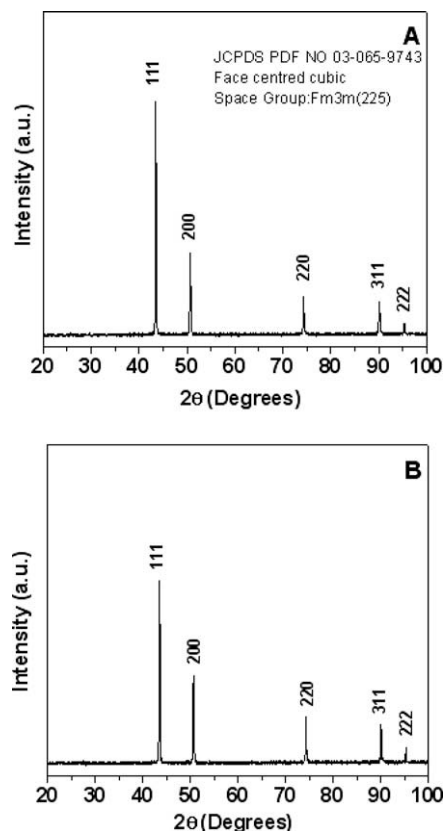

Fig. 1. XRD pattern of the Cu nanospheres (A) and nanorods (B).
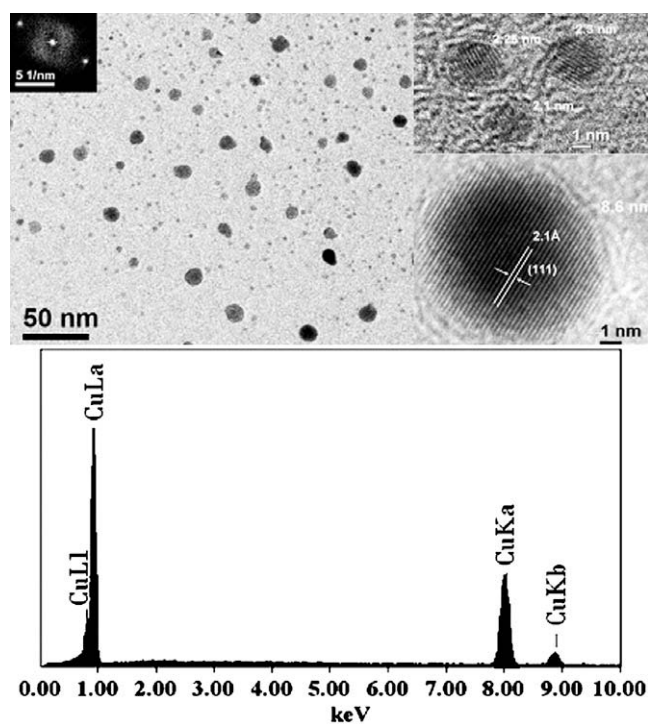

Fig. 2. HR TEM of the Cu nanospheres (up). SAED pattern and enlarged nanospheres with (1 1 1) planes are shown in the insets. EDS pattern of the selected area is shown at the bottom.

the face centered cubic with space group Fm3m and $a = 0.36078$ nm. Thus these powder XRD results revealed that we have synthesized highly stable and pure Cu nanospheres and nanorods through a new hydrothermal synthesis method. The observed intensity ratios of (1 1 1) to (2 0 0) peaks for the Cu nanospheres and nanorods are 2.69 and 2.02, respectively. Thus for the Cu nanospheres the (1 1 1) facets are more exposed to the crystal surface [25] and show relatively stronger diffraction intensity vis-à-vis the Cu nanorods. These variations of the intensity ratio suggest anisotropic growth of these planes during the growing processes and this has been reflected from their spherical and rod-like shapes. In Figs. 2 and 3 HR TEM images of Cu nanospheres and nanorods at different magnifications are shown. The sizes of Cu nanospheres are 2–15 nm in diameter and the Cu nanorods are *ca.* 100–235 nm long, which are clearly seen in these TEM images (Figs. 2 and 3). *d*-Spacing as observed for the (1 1 1) plane from the electron diffraction pattern of these HR TEM images agree well with the powder XRD results. HR TEM image also shows well resolved (1 1 1) cubic lattice fringes, suggesting that the nanocrystals are highly crystalline in nature. Energy dispersive X-ray (EDX) analysis (Fig. 2, bottom) suggested the presence of highly pure Cu, K and L signals devoid of any other metal or oxygen impurity. For Cu nanorods and nanospheres have BET surface areas 1.5 and 6.1 $m^2 g^{-1}$, respectively.

Mechanism of Cu nanosphere and nanorod formation: Cu nanospheres are synthesized by hydrothermal treatment of lauric acid and $CuCl_2$ in presence of ethylenediamine and NaOH. Here NaOH is used for adjusting the pH (pH 12–13) of the solution and ethylenediamine is used for dissolving the lauric acid and act as a capping agent for copper nanoparticles. We have carried out
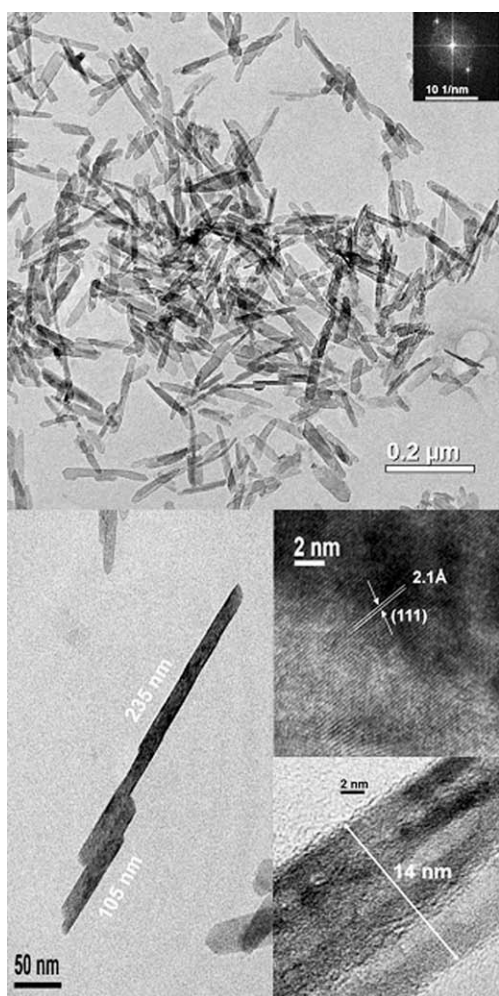

Fig. 4. Reduction of 4-nitrophenol over Cu nanospheres (A), nanorods (B) and in absence of any catalyst (C).

Fig. 3. HR TEM of the Cu nanorods. SAED pattern is shown in the inset.

one set of synthesis in the absence of lauric acid. In that case no Cu nanoparticles are formed (no reduction occurred) after hydrothermal treatment and the synthesis gel remained as blue colored solution as it was before hydrothermal treatment. This result suggested that lauric acid can reduce the Cu^{2+} to copper atom, which are highly unstable and form copper nanoparticle. When the copper nanoparticles are capped by ethylenediamine, further growth of the nanoparticles is not possible. The same reaction has been carried out without the addition of ethylenediamine in the synthesis mixture and there we got the copper nanorods only. So this reaction proves that ethylenediamine act as capping agent. In the absence of the capping agent copper nanoparticles are grown in one direction and formed nanorods. For better understanding of this phenomenon we have added $AlCl_3$ in the former reaction, where $AlCl_3$ act as a complexion agent with ethylenediamine [26,27]. In this reaction Cu^{2+} and Al^{3+} both form complexes with

ethylenediamine but Cu^{2+} only reduced in this medium because standard oxidation potential of aluminium ($Al^{3+}/Al = -1.66$ V) is too high which can not overcome by lauric acid. So when lauric acid reduce Cu^{2+} ($Cu^{2+}/Cu = +0.34$) to Cu, where formal oxidation potential of copper is different from standard value. On the other hand Al^{3+} forms complex with ethylenediamine and thus no free ethylenediamine is present in the reaction medium to act as capping agent of Cu^{2+} during hydrothermal reduction. Hence we got copper nanorods only in the presence of Al^{3+} containing system.

The catalytic reduction of nitro group of 4-nitrophenol and 5-nitroisophthalic acid has been studied over copper nanoparticles. Aqueous solution of 4-nitrophenol shows absorption maxima at 317 nm. With the addition of sodium borohydride solution the peak has been shifted to 400 nm. This peak has been assigned due to formation of 4-nitrophenolate ion in the basic condition for sodium borohydride [28]. Under this condition the nitropheno-
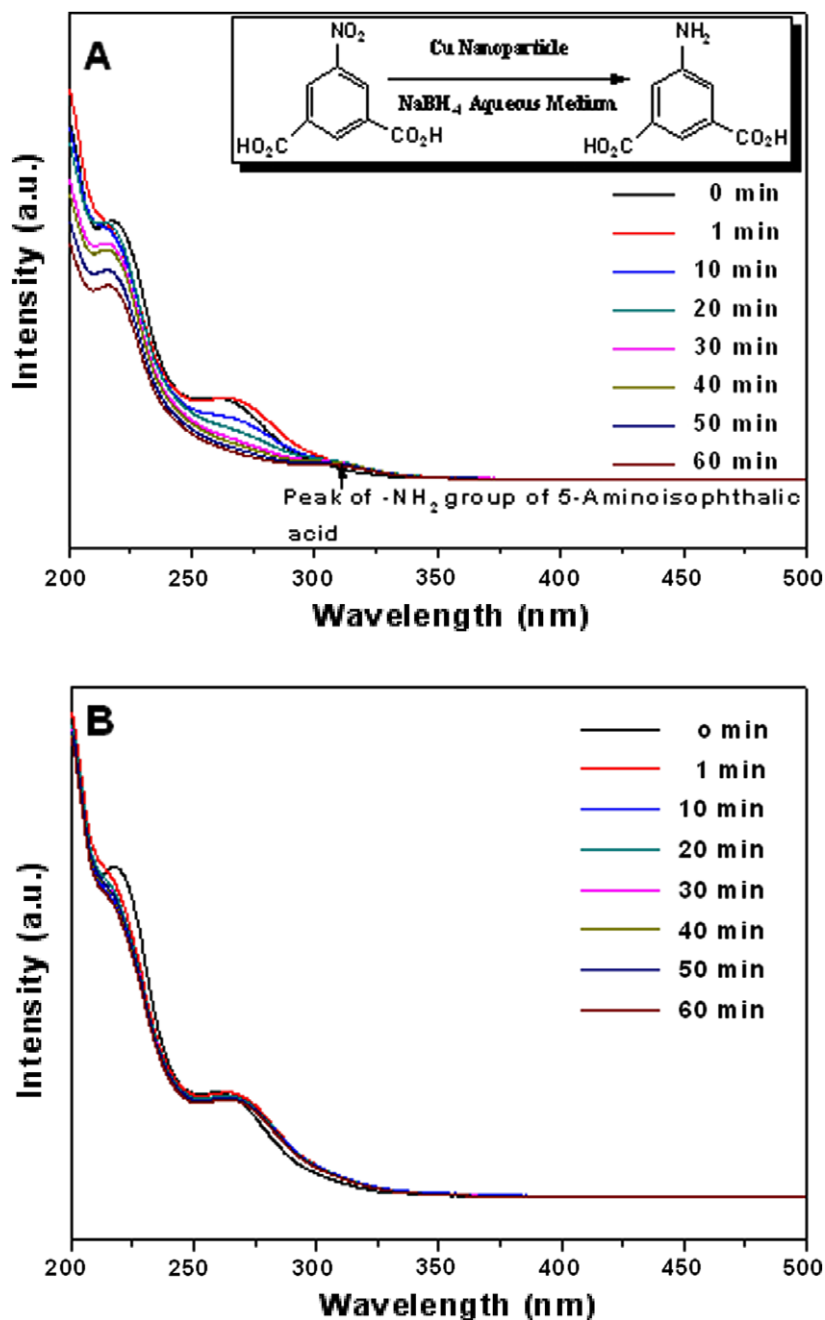

Fig. 5. (A) Reduction of 5-nitroisophthalic acid over Cu nanospheres. (B) Reduction of 5-nitroisophthalic acid in absence of any catalyst.

late was reduced to aminophenolate. In absence of any catalyst, $NaBH_4$ reduce the 4-nitrophnolate moiety to a very small extent (shown in Fig. 4C). On the other hand commercial Cu nanopowder (Sigma–Aldrich, particle size <100 nm) catalyzes this reduction to 47.2 mol% in 1 h reaction time. Hence copper nanoparticles synthesized herein, acting as efficient catalysts for reduction to occur. From the UV–vis plots in Fig. 4A and B it is further revealed that for the Cu nanospheres (spherical particles of size 2–15 nm) within 1 h reaction reaches maximum conversion level (*ca.* 94%), whereas for Cu nanorods (14 nm × 100–235 nm) it reaches much lower conversion level (*ca.* 76%) even after 1.5 h reaction time. This result suggests that Cu nanosphere is more efficient catalyst than Cu nanorod in this reduction reaction. Smaller size of the particles together with greater BET surface area (6.1 vis-à-vis 1.5 $m^2\,g^{-1}$) could be responsible for higher catalytic activity of the former. For the reduction of 4-nitrophenol the intensity of the peak at 400 nm has been gradually decreased with time and a new peak appeared at 295 nm indicating the formation of 4-aminophenol. Furthermore, the UV–vis absorption profiles suggests that the reduction of 4-nitrophenol gives only one product, 4-aminophenol. This has been further confirmed from ^{1}H NMR and gas chromatographic analysis with the authentic 4-aminophenol. For 5-nitroisophthalic acid, aqueous solution of 5-nitroisophthalic acid shows absorption maxima at 261 nm (Fig. 5). Now with the addition of sodium borohydride solution the peak has been shifted to 266 nm. The peak shift occurred due to formation of 5-nitroisophthalate ions in the basic condition. Under this condition the nitroisophthalate has been reduced to aminoisophthalate. As seen from Fig. 5 that the intensity of the peak at 266 nm has been gradually decreased with time and a new peak appeared at 309 nm indicating the formation of 5-aminoisophthalic acid. Fig. 5 further revealed that $NaBH_4$ in absence of any catalyst is not capable for this reduction at all.

4. Conclusions

From the above experimental results we can conclude that Cu nanospheres and nanorods can be very efficiently synthesized hydrothermally by using the long chain fatty acids as templates and the nanospheres show much enhanced catalytic activity over the nanorods for the chemoselective reduction of 4-nitrophenol and 5-nitroisophthalic acid to respective substituted anilines in one pot at room temperature, suggesting the role of particle size and shape in catalytic reduction.

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