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Surfactant-mediated low-temperature synthesis of phase pure multiply twinned copper nanoparticles under non-inert condition via thermal decomposition of copper malonate

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ABSTRACT

Multiply twinned phase pure copper nanoparticles were successfully synthesized without any inert gas protection via a low-temperature thermal decomposition of a new precursor copper malonate, $[CuCH_2C_2O_4]\cdot 2H_2O$ in the presence of surfactant stabilizers oleylamine ($C_{18}H_{35}NH_2$) and triphenylphosphine ($(C_6H_5)_3P$). The synthesized nanoparticles were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), FT-IR and UV–vis spectroscopy. Freshly prepared copper nanoparticles showed surface plasmon resonance (SPR) around 574 nm. TEM studies revealed a five-fold multiply twinned morphology of decahedral shape for the copper nanoparticles. Powder XRD pattern furnished evidence for a face-centered cubic crystal structure of pure metallic copper having an average crystallite size of about 35 nm.

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1. Introduction

In recent years, copper nanoparticles have attracted enormous attention due to their excellent catalytic, optical and conducting properties [1–3]. Compared to other noble metals, copper possess high electrical conductivity and is substantially cheaper. However, metallic copper is extremely susceptible to oxidation [4]. Anchoring suitable surfactant at the outer surface can offer protection from surface oxidation and also control the nucleation of particles by serving as a particle growth terminator. Copper nanoparticles have been synthesized via various routes such as the microemulsion technique [5], thermal decomposition [6], chemical reduction [7], polyol method [8], etc. As compared to conventional methods, the thermal decomposition method is much faster, cleaner and economical. Devising strategic synthetic protocol for preparing copper nanoparticles with controllable size and shape is anticipated to extend the application areas and also augment fundamental research in the field. Recently chemical synthesis of metallic copper and copper oxide nanoparticles via thermal decomposition of copper complexes was described [6,9]. However, the difficulty of copper reduction under mild reaction conditions or the easy oxidation of copper nanoparticles in air under ambient conditions in sharp contrast to noble metals like Au and Ag poses great challenges to afford pure metallic copper devoid of any oxide impurities. In order to protect copper nanoparticles against oxidation during preparation and storage, the reactions are often performed in non-aqueous media, at low precursor concentration, and in an inert atmosphere [10]. Very recently, we reported low-temperature surfactant-assisted synthesis of ZnO and Co_3O_4 nanomaterials via thermal decomposition of zinc and cobalt malonates [11,12]. Besides nanoparticle size and composition, particle shape also plays a crucial role in achieving different applications. Multiply twinned particles (MTPs) are the naturally abundant seed morphology and this twin defect is often attributed to their higher reactivity trend [13,14]. Though leaving aside oxalates, thermal decomposition of various other metal dicarboxylates (malonates/succinates) were studied earlier [15–17], but till date there has not been any report on the preparation of metal nanoparticles from such precursors. Accordingly, we report herein the synthesis of multiply twinned, phase pure copper nanoparticles capped with surfactants oleylamine and triphenylphosphine (TPP) by thermal decomposition of a new precursor, copper malonate.

2. Experimental

Materials and physical measurements: All chemicals were of analytical grade and used without further purification. Oleylamine, TPP, n-hexane and ethanol were purchased from Aldrich. The precursor copper malonate, $[CuCH_2C_2O_4]\cdot 2H_2O$ was prepared according to the literature procedure [16]. FT-IR spectra were recorded on Shimadzu Varian 4300 spectrometer on KBr pellets. Elemental analyses were performed on a Heraeus Vario EL III

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Carlo Erba 1108 elemental analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris Diamond thermal analyzer maintaining flow rate of 20 mL/min and heating rate of 10 °C/min in air. Powder X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu-Kα radiation (λ=1.5418 Å) with a scan speed 2°/min. Transmission electron microscopy (TEM) images were obtained on a JEOL, JEM2100 transmission electron microscope with an accelerating voltage of 200 kV. The sample powders were dispersed in *n*-hexane, under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air. Electronic spectrum was taken on a Shimadzu 1601 PC UV–vis scanning spectrophotometer.

Synthesis of copper nanoparticles: 0.6 g of $[CuCH_2C_2O_4]\cdot 2H_2O$ was taken in a round bottomed flask and 5 ml of oleylamine was added to it and heated for 1 h at 140 °C on an oil bath to get $[CuCH_2C_2O_4]$–oleylamine complex. Triphenylphosphine (5 g) was then added to the resultant solution and temperature was raised to 240 °C. The green solution changed to red, indicating the formation of metallic copper. The reddish solution was aged at 240 °C for 1 h and cooled to room temperature. The reddish products were precipitated by adding excess ethanol to the solution. The products were washed with ethanol several times. These products could be easily re-dispersed in nonpolar organic solvents like n-hexane or toluene (Scheme 1).

3. Results and discussion

The principle of synthesis is based on a modified procedure developed by Hyeon and others for the synthesis of metal and oxide nanocrystals [6,9,18]. In the current synthesis (Scheme 1), copper nanoparticles were prepared by the thermal decomposition of copper malonate, $[CuCH_2C_2O_4]\cdot 2H_2O$ as precursor in the presence of surfactants oleylamine and triphenylphosphine. The as-synthesized nanoparticles were characterized by XRD, TEM, FT-IR, and UV–vis studies. In order to ascertain the precursor composition, elemental analysis was performed. The thermal decomposition behavior of the neat precursor (Fig. S1 in ESI) revealed that copper malonate undergoes decomposition in two steps. The first step is dehydration which commences at 100 °C and is completed at 150 °C as indicated by a weight loss of 16%. The anhydrous compound remains stable up to 225 °C and then undergoes rapid oxidative pyrolysis till a weight loss of 64.5% at 250 °C suggesting the formation of Cu_2O. However, Cu_2O formed underwent oxidation up to 315 °C accompanied by an increase of weight approximately 4% suggesting the formation of CuO. However, use of surfactant molecules like oleylamine and TPP as capping ligands lowered the decomposition temperature of copper malonate to 240 °C yielding copper nanoparticles.

The powder XRD pattern (Fig. 1) shows the material to be face-centered cubic Cu (space group Fm3m, JCPDS File no.89-2838). No peak attributable to possible impurities such as Cu_2O/CuO were observed indicating the formation of phase pure metallic Cu. The average crystallite size estimated using the Debye–Scherrer formula was found to be about 35 nm.

The TEM images (Fig. 2) show typically multiply twinned copper nanoparticles. A multiply twinned boundary at the center of copper nanoparticles can be clearly observed from different angles; the lattice plane is separated by a twin boundary indicated as a line on the image. Formation of multiply twinned copper nanoparticles has been documented earlier [19,20]. Initially, copper ions (Cu^{2+}) are reduced to metallic copper (Cu^0), which assemble together to form nuclei. At this point the available thermal energy causes the structure of the nuclei—a miniscule cluster of few metal atoms to fluctuate, allowing defects to form or be removed depending upon their energetic favorability [21]. It has been argued that most copper nuclei incorporate twin boundary defects because such defects enable a lower surface energy [22]. As the nuclei grow into a seed, changes in the defect structure become too costly relative to the available thermal energy which confines the particles to a fixed morphology. This process results in a Boltzmann-like distribution of multiply twinned, singly twinned, and single-crystal seeds, with the five-fold twinned decahedron being the lowest in free energy thus constituting the most dominant morphology [23]. In summary, the growth of a copper nanocrystal during the synthesis involves three distinct stages: nucleation (reduction of metal ions to zerovalent atoms), seeding (evolution from nuclei to seeds), and growth (evolution from seeds to nanocrystals) [19]. Bigger particle sizes obtained from TEM (40–120 nm) as compared to the average crystallite size from XRD is attributed to the polycrystalline nature of the nanoparticles. From HRTEM image (Fig. 2(c)) two types of lattice fringes were observed having interplanar distance of 0.18 nm and 0.21 nm which correspond to (200) and (111) planes of fcc-copper, respectively. The electron diffraction (ED) pattern (Fig. 2(d)) indicated the polycrystalline nature of the nanoparticles.

FT-IR spectrum (Fig. S2 in ESI) shows bands attributed to the asymmetric and symmetric vibrational modes of –N–H around 3489 and 3257 cm^{-1}, respectively. The peaks between 1000–1400 cm^{-1} and 2800–3000 cm^{-1} arose due to the symmetric and asymmetric

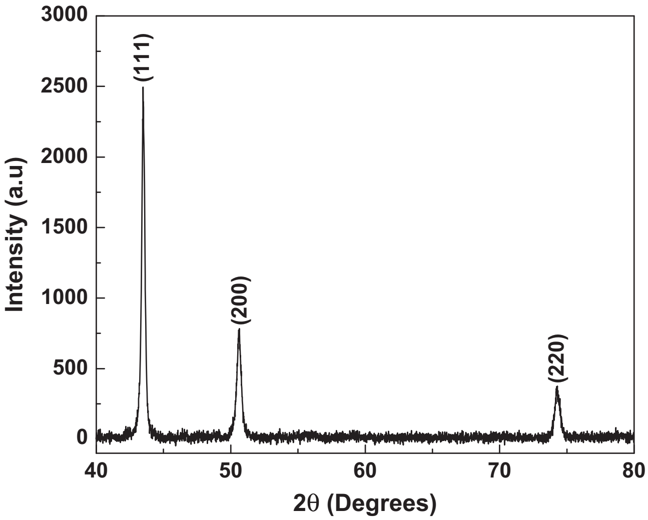
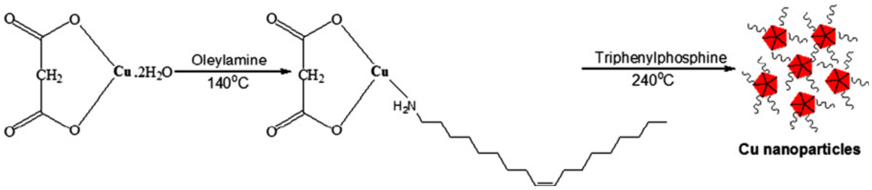


Fig. 1. XRD pattern of copper nanoparticles.



Scheme 1. Illustration of the formation of copper nanoparticles.

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