Seed-mediated growth method to prepare cubic copper nanoparticles

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A new and simple method has been reported here which can be applied to control simultaneously the shape and size of the copper nanoparticles, without using any capping agent or template. By this method, cube-shaped copper nanoparticles in the size range ~ 75–250 nm were formed from smaller spherical copper particles. At the first stage, 5–6 nm spherical copper particles were prepared from aqueous copper sulphate solution by borohydride reduction. In the second stage, these small particles were mixed with appropriate amount of copper sulphate and sodium ascorbate, which resulted in the production of larger size cubic copper particles. In the latter step, the new grown larger particles acted as seed and grew larger due to the reduction of copper ions by ascorbate ion on their surfaces. Thus cubic copper nanoparticles of varied size regime were produced by ascorbate ion by varying the ratio of copper seed particles to copper ion concentrations in solution.

METAL nanoparticles, due to their special properties and also small dimensions, find important applications in optical, magnetic, thermal, electronic and sensoric devices, SERS (surface enhanced Raman scattering), catalysis, etc.[1]. Almost all properties of nanoparticles are due to their small sizes[1–6]. Of late, in addition to size effect, shape of the particles has also drawn special attention, mainly to explore the application of these particles in the field of nanotechnology. Therefore, attempts are being directed to gain precise control of the size and the shape of various types of nanoparticle systems during their syntheses[7–15]. The fact is that these syntheses result in a mixture of particles, in terms of both size and shape. The most common method employed for their preparation is the reduction of metal ions in solution, usually in the presence of a particle-stabilizer[2,3,7]. However, the control of size and, particularly, the shape at the nanometre level is a real problem, as the mechanism of size/shape control is still left largely unresolved[8]. There are few general methods available for size control, and for shape control, these are very few. These methods use either a capping agent or a template for the restricted growth of the particles. Some people used a seed-mediated controlled growth to prepare particles of different sizes[16–18]. We

exploited, for the first time, the seed-mediated method to prepare copper nanoparticles of cubic shape and variable size. To our knowledge, there is no simpler method of preparation reported that could yield simultaneously size- and shape-controlled nanoparticles at room temperature. Some reverse micelle-based template methods are available to control the copper particle size[19]. Reverse micelle has also been used to prepare nanosize rod-shaped copper particles[20]. Micrometre-size cubic copper particles were obtained by dissolving the spheres of basic copper carbonate which was formed by aging at 90°C a solution containing $Cu(NO_3)_2$ and urea, with the slow addition of $NH_2OH \cdot HCl$ into the solution[7].

An aliquot of 100 ml water solution of $CuSO_4$ (2×10^{-4} mol.dm^{-3}) was taken in a conical flask and purged with N_2 for 10 min to remove the dissolved oxygen. Then 1 ml ice-cold $NaBH_4$ (0.1 mol.dm^{-3}) solution was added into the $CuSO_4$ solution with stirring. The metal particles are formed immediately, visualized by the appearance of a yellow colour; for the quantitative confirmation, spectrophotometric investigation was made.

Appropriate amount (see Table 1 for conditions) of $CuSO_4$ was taken in water (final volume 100 ml) and the dissolved oxygen was removed by N_2 purging. The solution was then stirred with a magnetic stirrer. Then required amount of seed particles was mixed with this solution. Finally, ascorbic acid was added drop by drop. N_2 purging was continued until the addition of ascorbic acid was complete.

Table 1. Conditions for the preparation of cubic copper nanoparticles via seed (S) mediation

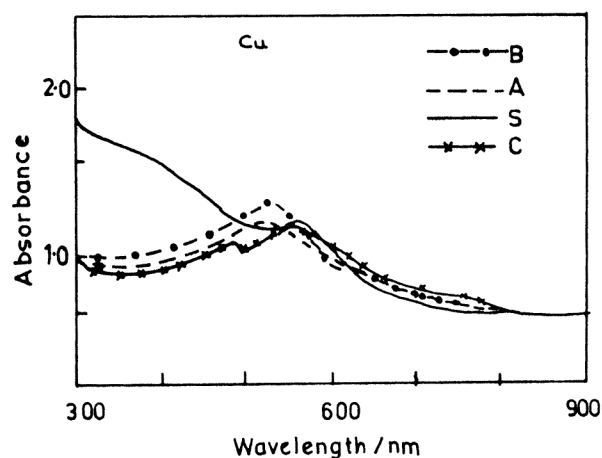| Sample set (prepared from)	$[M^0]/[M^+]$	$[M^0] + [M^+]$ (mol.dm^{-3})	Ascorbic acid (mol.dm^{-3})
A (from S)	1 : 99	2×10^{-4}	4×10^{-4}
B (from A)	1 : 8935	2×10^{-4}	4×10^{-4}
C (from B)	1 : 806360	2×10^{-4}	4×10^{-4}

Figure 1. UV-visible spectra of copper nanoparticles of various sizes. Size increases from seed particle 'S', through 'A', 'B' to 'C'. Conditions are given in Table 1.

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Copper nanoparticles were first produced by the sodium borohydride reduction of copper ions in aqueous solution, indicated by the appearance of a yellow colour. This is due to plasmon resonance, with a significant contribution from interband transition which produces yellow colour hydrosol having λ_{max} at 500 nm (Figure 1 'S'). TEM study (Figures 2 a and 3, (Cu-S)) showed that almost half of the population of the particles produced was of 4–6 nm and the rest of 9–12 nm in size. (TEM was carried at 400 kV using JEOL 4000 EX. Sample was prepared by placing a drop of solution containing nanoparticles on a carbon coated Cu grid.) And they were almost spherical in shape. $NaBH_4$ being a stronger reducing agent, can produce instantaneously large number of nucleation centres and hence smaller particles. These were used as seed particles (S) for further growth (i.e. growth centres). They are unstable to air in solution and the surface oxidation causes red shift of the plasmon band and ultimately black precipitate of copper oxide appeared within 30 min. This high reactivity of the particles (in solution) towards oxygen compared to bulk copper metal could be attributed to the effects of small size of the copper parti-

cles[2,3], and the adsorption of the highly electron injecting, excess BH_4^- ions onto the particle surface[2].

Sodium ascorbate (or ascorbic acid) could not reduce the copper ions in solution. This was checked by the addition of ascorbate ion in copper sulphate solution and in our experimental time scale, no plasmon band of copper appeared even after an hour. However, copper ion could be reduced by the ascorbate ion, if the copper seed particles are present in solution, i.e. an autocatalytic growth onto the preformed copper seed particles which takes ~ 5 min for the reduction of the adsorbed Cu^{2+} ion on the copper seed surfaces. This fact indicates the catalytic property of copper particles towards the copper ion reduction. This is often observed in solution phase metal particle synthesis[2,3]. This was further corroborated by UV–visible spectrophotometric and TEM studies (Figures 1 and 2, respectively). The plasmon λ_{max} shifts to longer wavelength with the increase in particle size (Figure 1 'A', 'B' and 'C'). This red shift is presumably due to the formation of large cube-shaped copper particles. TEM study showed only the presence of cube-shaped larger size particles instead of the original spherical seed particles. And the
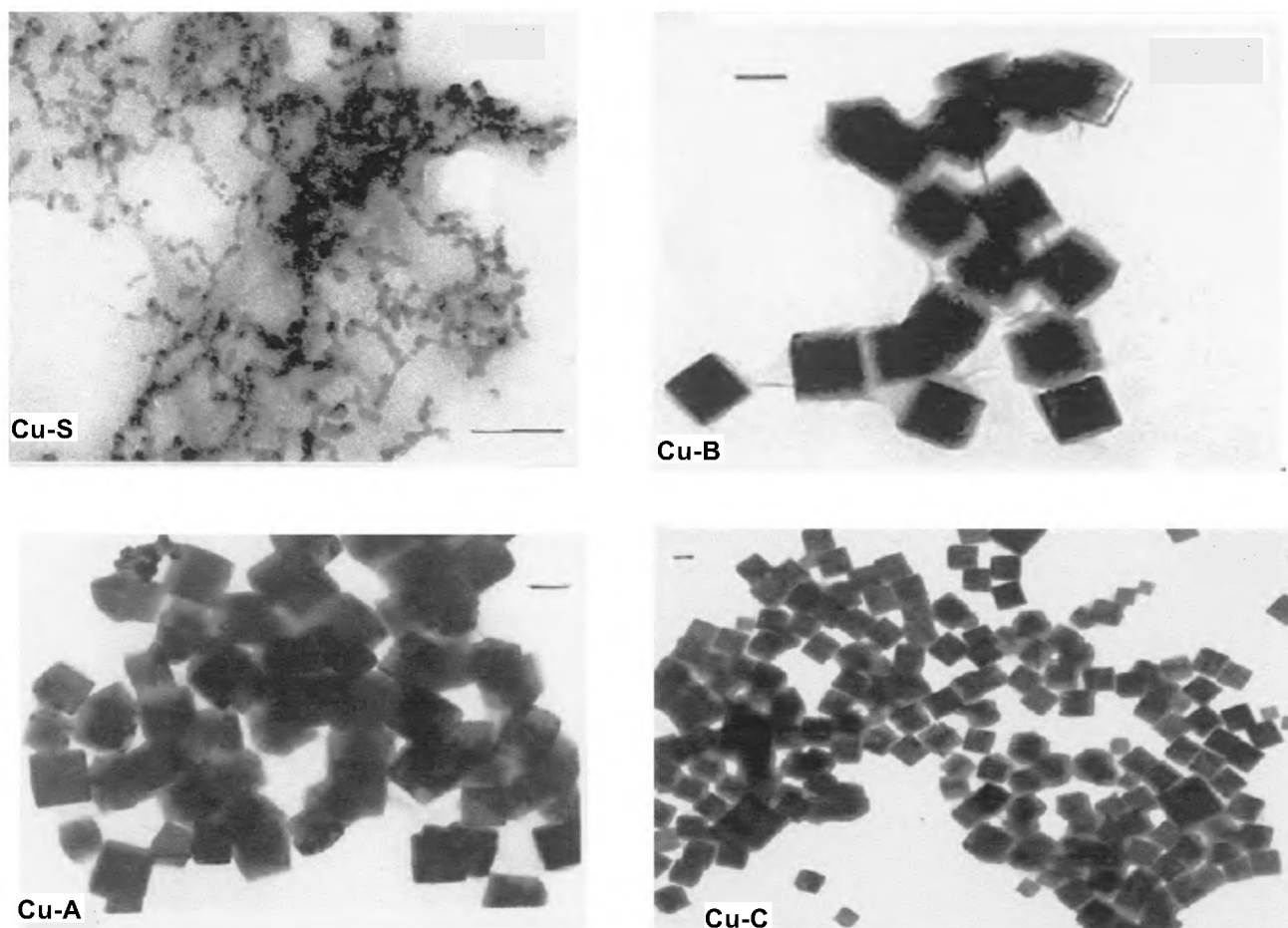

Figure 2. TEM pictures of copper nanoparticles. (Cu-S), (Cu-A), (Cu-B) and (Cu-C) corresponding to the samples 'S', 'A', 'B', and 'C', respectively, in Table 1. Bar indicates 100 nm.
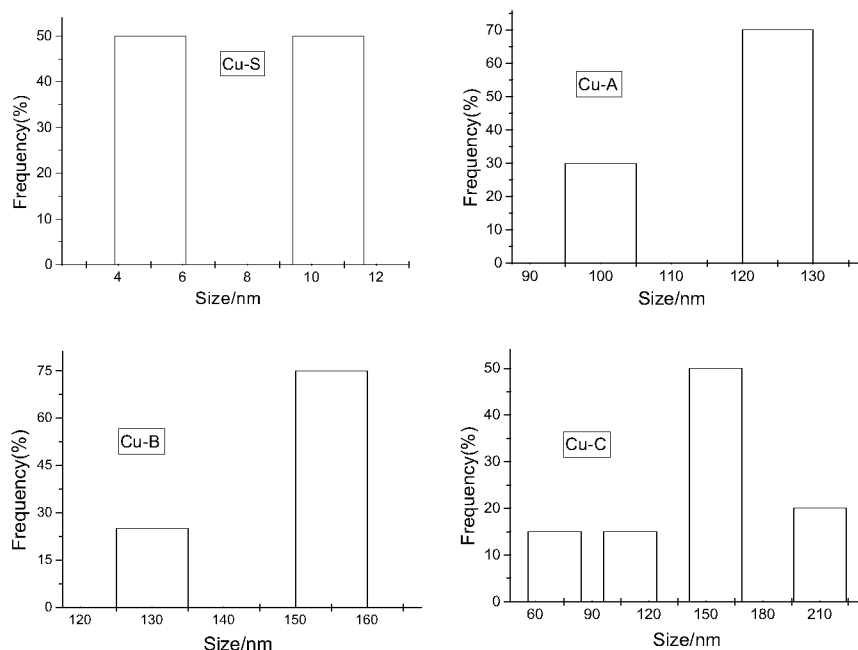
Figure 3. Histogram of the size distributions of copper particles: (Cu-S), (Cu-A), (Cu-B) and (Cu-C) corresponding to the samples 'S', 'A', 'B', and 'C', respectively. For cubic particles, 'size' means 'cube edge-length'.

particle size increases, as expected, with the increase in the size of the parent particles used and the amount of the copper ions added to the seed particles. Copper particles having the size range in the ~ 75 to 250 nm region were produced by varying the ratio of copper particle to ion concentration. The histogram of particle size distribution (Figure 3) revealed that seed particles grew to give two different batches of copper particles having sizes approximately around 100 nm and 125 nm. However, in Figure 3 (Cu-C) where the ratio of copper ion to copper particle concentration is reasonably high, particles of a varied range of sizes were observed. Time-dependent TEM studies of the sol solution revealed that particles in the size range of 150–200 nm remained stable for ~ 24 h and no significant oxidation was observed for the particles. Such larger size regular-shaped particle formation is indicative of a slow reduction of copper ions onto the particle surfaces. It is well known that small metal particles generally act as a relay system for the electron transfer from donor to acceptor. As a result, reduction of the copper ions could occur at the surface of the copper particles. The chance of formation of new nucleation centre is very rare because of the weak reducing character of the ascorbate ion, unlike BH_4^- ion, N_2H_4, etc. However, all the copper seed particles, which are of nearly spherical morphology, grow exclusively to cubic ones. Electron diffraction study showed that the particles were enclosed by six {100} faces and each particle was single crystalline. (High-resolution lattice image was rather difficult to record for the sample due to the large thickness of the particles.) The surface of the cubic nanoparticles was not quite smooth, but exhibited atomic scale roughness. The particles formed via seed mediation were stable for several days and showed a small fraction of surface oxidation. The selective growth to cubic shape of the spherical copper seed particles is not understood at this stage. Further work is under progress in an attempt to understand the mechanism of such shape-controlled growth. Under identical conditions, Ag, Au and Pd systems formed mostly spherical or hexagon-shaped nanoparticles.

In conclusion, the novelty of this two-step seed-mediated method for the generation of nanoparticles lies in its simplicity and simultaneous control of both size and shape of the particles, without using any capping agent or template. The seed-mediated technique or its modified version may be useful for other systems of nanoparticles for producing particles of desired sizes and shapes.

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Fluoride: Diffusive mobility in soil and some remedial measures to control its plant uptake

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Dietary (human) intake of fluoride (F) largely through consumption of agricultural produce grown in F contaminated environment, has recently been viewed as an important cause for several F related health problems in many parts of the world. Being a non-essential element, F is usually taken up by plants through passive uptake – a process which is dominantly diffusion controlled. Still very little is known regarding F diffusion in soil. In present study, diffusion of F in the alluvial soil (Entisol) of Dayalbagh (Agra) has been investigated as a function of soil water content (θ) and F concentration gradient. The data on F diffusion coefficients were recorded by determining the F concentration profile in horizontally incubated and homogenized soil columns, under varied experimental conditions ($\theta = 0.12$–0.25 cm cm^{-3}, pH = 7.3 ± 0.2, incubation time (t) = 96–384 h, temperature = 303 ± 1.2 K. The effects of aluminium and calcium, which are known to be strong binders for F in soil, on the F diffusion have also been investigated. The study, particularly, throws light on the possible dual role of aluminium in affecting the diffusion of F in soil which might prove critical in the ultimate uptake of F by plants in specific environmental conditions.

THE beneficial and harmful effects of fluoride (F) in the human body have been debated about a lot in recent times[1]. The widespread prevalence of fluorosis, a disease caused by excess intake of F, in parts of Rajasthan, Tamil Nadu, Uttar Pradesh, Delhi, Andhra Pradesh and Madhya Pradesh suggests that the aspects of excess F intake and their associated harmful effects are more relevant in the context of India compared to most Western countries where fluoridation of water is rather recommended to help prevent dental caries[2,3]. F is a naturally occurring pollutant, which is often released into the soil-environment through the use of phosphatic fertilizers and other pesticidal sprays, as well as through the disposal of industrial sludges[4]. The migration of F from such localized F-rich sources to adjoining top soil layers followed by its uptake by the plants, is a complicated but crucial process of high biological significance as it may decide the ultimate levels of dietary intake of F by animal and human populations in an area[5].

Studies on ion mobility in soil have so far recognized its importance in controlling the flow of nutrient ions/molecules and the toxic metals from the bulk of soil to roots. However, the observations are quite at variance. While mass flow reportedly plays an important role in the plant uptake of nitrates, diffusion supplies almost all the plant's phosphate and most of its potassium[6,7]. In a recent study[8], it has been shown that the uptake of Fe by rice is also largely diffusion controlled and the contribution of mass flow is limited to only 5–9%. Regarding F also, its diffusion in soil may be crucial in regulating its movement from the bulk of soil to root zone, particularly in plants grown in arid and semi-arid conditions. This contention is partly supported by F uptake values reported for certain plants grown in solution, sand and soil culture, where good correlation ($r = 0.99$) between the total F concentration in solution and F taken up by plants was found[5]. However, the phenomenon of F mobility in soil, particularly its diffusion aspect, is still not well studied and data in this regard are lacking. In this paper we are reporting the results of a study on diffusive mobility of F in an alluvial soil (Entisol) as a function of soil water content, F concentration gradient and soil amendment with aluminium and calcium.

Samples of soil (Entisol) were collected from open uncultivated fields spread all around Agra city ($27°10'$N, $78°05'$E, 168 m above sea level). The physico-chemical characteristics of the dried and sieved soil (S_1, particle size < 2 mm) were determined using standard methods[9,10]. S_1 soil taken in closed containers (700 g in each) was treated separately with 42, 35, 28, 21, 14 and 10.5 mg Al and Ca by adding 100 cm^3 of AlCl$_3$ and CaCl$_2$ solutions, respectively, of appropriate molarities, in small aliquots with thorough gentle mixing. Resulting soil-water slurries were incubated at 303 K for 25 days after which the dried soils were mildly crushed, sieved and used for diffusion studies.

Soil columns were prepared by packing soil in PVC pipes made of segmented cylindrical rings (inner diameter and length were 2.13 and 1 cm, respectively), at the bulk

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