

Preparation and self-assembly of copper nanoparticles via discharge of copper rod electrodes in a surfactant solution: a combination of physical and chemical processes

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Abstract

Cu nanoparticles with a mean diameter of 10–15 nm were prepared and self-assembled via discharge of bulk copper rods in a cetyltrimethylammonium bromide (CTAB)/ascorbic acid solution. Ascorbic acid was used as a protective agent to prevent the nascent Cu nanoparticles from oxidation in the solution; otherwise spindle-like $\text{Cu}_2\text{O}/\text{CuO}$ structures, with a lateral dimension of 30–50 nm and length of up to 100 nm, were formed in pure deionized water. The surfactant CTAB had a critical influence on self-assembly of spherical Cu nanostructures (with diameter of 700 nm–1 μm). Such a low-temperature and non-vacuum method, exhibiting the characters of both physical and chemical processes, provides a versatile choice for economical preparation and assembly of various metal nanostructures.

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1. Introduction

The study of metal nanoparticles has been an extremely active area in recent years because of their interesting properties different from those of bulk substances [1,2]. A number of methods for metal nanoparticles preparation have been developed and they can be mainly classified into two kinds of processes, i.e., physical and chemical [2,3]. The physical approach is versatile towards a wide range of metal nanoparticles with high quality, but it usually calls for expensive vacuum systems to generate plasmas. The chemical route appears to be suitable for experiments performed in laboratories and capable of controlling growth and

assembly of metal nanoparticles by optimizing reaction parameters (e.g., surfactant, capping agent, solvent, precursor concentration and temperature), but is mainly employed to synthesize nanomaterials of noble metals such as Ag and Au [4–8], and far from a versatile method for the non-noble metals. Therefore, combination of physical and chemical processes should be realized to develop a new flexible method for the preparation and assembly of different metal nanoparticles. The arc-discharge in liquid phase (i.e., the discharged electrodes are submerged into liquid) could be a hopeful candidate for such an application owing to the simultaneous co-existence of both physical process (arc-discharge) and chemical process (solution reaction).

Arc-discharge in the gas phase has been utilized in the synthetic field for many years. An example is the graphite discharge in low-pressure inert gas to produce carbon materials such as fullerenes [9] and carbon nanotubes [10]. Submerging metal electrodes into liquid

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phase, e.g. liquid nitrogen [11], liquid ammonia [12,13] and hydrocarbon [14], a number of nano/micro-particles of metals (e.g. alpha-Ti, gamma-Fe) or metal nitrides/carbides (e.g. TiN, AlN, Cr₂N, TiC, Al₄C₃, Fe₂C and Cr₇C₃) were produced. More recently, spherical carbon nano-anions of 25–30 nm were produced from the arc-discharge between two graphite electrodes submerged in water [15,16]. Closed-cage fullerene-like MoS₂ nanoparticles with diameters of 5–15 nm were obtained via an arc-discharge between a graphite cathode and a molybdenum anode filled with microscopic MoS₂ powder submerged in deionized water [17]. Carbon nanotubes with high yield were fabricated from the graphite discharge in liquid nitrogen or water [18,19]. Ag nanowire/particles were formed in a discharge between silver nitrate solution and silver electrode placed slightly above the liquid surface [20]. Carbon nanohorns with one Ni-contained in its center are produced by submerged arc in liquid nitrogen using Ni-contained graphite anode [21]. Most of the previous studies usually stopped when any monodispersed colloids were obtained, and emphasized the advantages originated from physical discharge process, e.g., versatile, environmentally benign and uncontaminated productions. In this article, regarding the formation of 10–15 nm Cu particles from the discharge of bulk rod in water or aqueous cetyltrimethylammonium bromide(CTAB)/ascorbic acid solution, the method of discharge in liquid is found not only useful for economical preparation of Cu and its oxide nanomaterials, but also capable of self-assembling the nanoparticles to spindle-like or spherical nanostructures in selected solutions. The advantages originating from both physical and chemical aspects in the discharge process might be promising for opening a new pathway versatile enough to synthesize various metal nanostructures.

2. Experimental section

The arc-discharge experiment was performed in a three-necked flask under non-vacuum conditions. Two copper rod electrodes with 3 mm diameter were placed in two side-necks of the flask, in which one end of the copper rod was submerged into 40 ml liquid and the gap between the ends of the two rods was about 2 mm. When an alternating electrical source (with voltage of about 1.5 kV, discharge current of 10 A, pulsing frequency of 50 Hz, and input power of ca. 10 kW) was supplied to the electrodes, pulsed arc-discharge was observed at the gap in the liquid phase. Here we carried out three types of experiments in three kinds of liquid phases, i.e., deionized water, boiling 0.025 mol/L ascorbic acid aqueous solution, and boiling 0.025 mol/L ascorbic acid mixed with 0.005 mol/L CTAB aqueous solution, respectively. After discharge reaction for several min-

utes, part of the copper tips was consumed to form Cu or CuO/Cu₂O nanomaterials in the solution, giving a black (in the case of deionized water) or red (in the presence of ascorbic acid) colloid. The consumption rate of the electrodes was about 0.05 g/min, which also reflects the production rate of the nanomaterials because the conversions of Cu from the rods (electrodes) to the products (Cu or CuO/Cu₂O nanomaterials) were almost 100% in each condition.

The micrographs of the products were taken by a JEM-100CXII transmission electron microscopy (TEM) and a LEO1530 scanning electron microscopy (SEM): The nascent colloidal products were stirred by ultrasonic treatment to disperse the nanoparticles at room temperature prior to the TEM or SEM analyses. 30–50 μL of the stirred colloid was dropped onto copper grids covered with collodion/carbon film and dried in the air for TEM observations; specimens for the SEM were prepared in the same procedure but the collodion/carbon film was replaced by a black substrate. The composition and crystallinity was characterized by a Rigaku DMAX/RC X-ray diffractometer (XRD) using CuK_α radiation ($\lambda = 0.154178$ nm). All the SEM, TEM and XRD analyses were carried out within a few days after the preparation of the products.

3. Results and discussion

In the primary experiment, we tried to develop the method of discharge in liquid, which had been successfully applied to the synthesis of carbon-rich clusters in our previous studies [22], for a novel application to fabricating metal materials in nanometer scale. A bulk copper rod was chosen as electrode and reactant for the production of its allotrope nanomaterials, which could be potentially applied in nano-technique fields. As shown in Fig. 1, the TEM and SEM images of the products from Cu discharge in deionized water, spindle-like nanostructures with a central lateral dimension of 30–50 nm and length of up to 100 nm dominate the products. XRD analysis (see Fig. 2) revealed that the as-prepared nanostructures were a mixture of Cu₂O and CuO, rather than the expected pure Cu species. The XRD peaks closely matched with those of cubic Cu₂O (JCPDS 05-0667) and monoclinic CuO (JCPDS 45-0937).

Further insight into the spindle-like nanostructures subunit particles, could be observed as shown in the insets to Fig. 1a and b. Based on the XRD pattern, the average size of the particles was estimated by the Scherrer formula to be about 10–15 nm. Copper has a melting point of 1083 °C, but it is indeed interesting that this metal could be transformed from bulk to nanometer scale in the pure water under room temperature. We suppose that the bulk copper undergoes a top-down

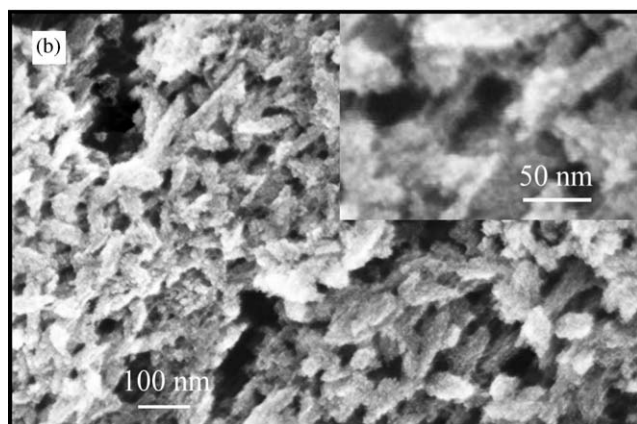
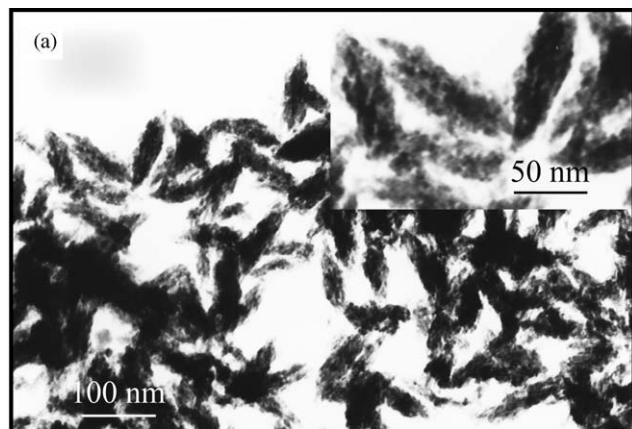


Fig. 1. TEM (a) and SEM (b) images of the spindle-like nanostructures produced from Cu arc-discharge in deionized water

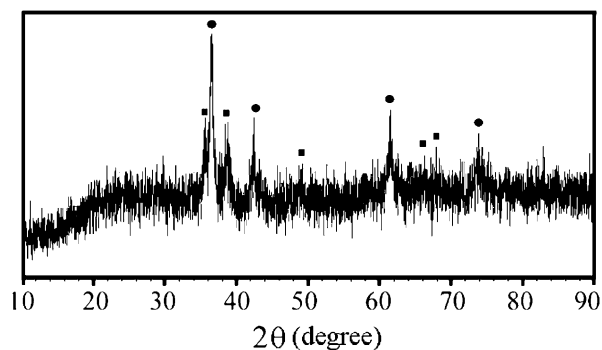


Fig. 2. XRD pattern of the spindle-like $\text{Cu}_2\text{O}/\text{CuO}$ nanostructures (●- Cu_2O , ■- CuO).

route to form nanoparticle. Forced by the arc-discharge some kinds of copper clusters were deviated from the tips of the copper rods, and followed immediately by cooling by the water surrounding the electrode/reactant to form Cu nanoclusters. The surfaces of the nascent Cu nanoclusters would be reactive and subject to oxidation and self-assembly in the water to form spindle-like nanostructures of $\text{CuO}/\text{Cu}_2\text{O}$.

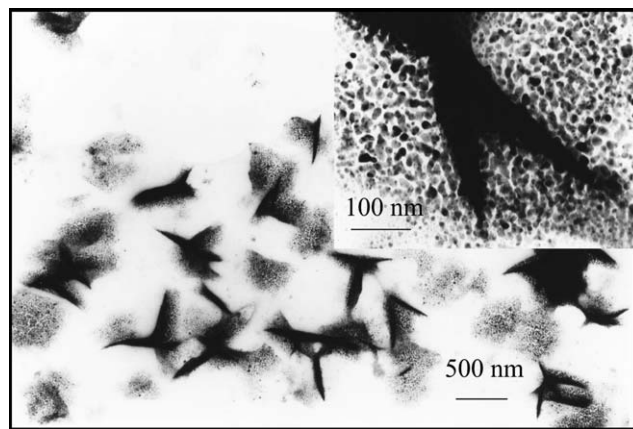


Fig. 3. TEM image of the products from discharge of Cu in the presence of ascorbic acid.

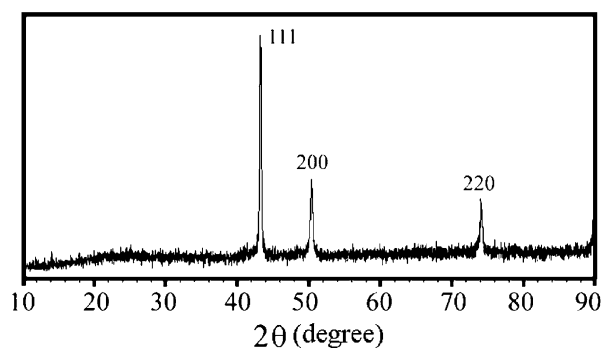


Fig. 4. XRD pattern of the products from discharge of Cu in ascorbic acid solution.

To prevent the nascent Cu clusters from oxidation reaction, ascorbic acid was added as protective agent into the solution. Fig. 3 shows the typical TEM images of the products in the presence of 0.025 mol/L ascorbic acid, in which the products with non-uniform nanostructures are observed. These products appear to be horned structures but surrounded with nanoparticles of 10–15 nm. The XRD pattern (Fig. 4) shows that the as-prepared nanostructures were pure Cu, and the peaks are in agreement with those of crystalline cubic Cu (JCPDS 04-0836). The red-colored colloidal of the end products from the Cu discharge in the presence of ascorbic acid also provides evidence of the existence of pure Cu. By increasing aging time (e.g., up to 10 days) in the air, however, the colloidal color of the end products would change from red to black, implying that the Cu particles (red color) would be slowly oxidized to form their oxides (black color) during the aging process. Note that it is difficult to distinguish a small amount of carbonaceous by-products, possibly produced from organic compound added (e.g., ascorbic acid), from the main products (Cu) by the techniques of X-ray diffraction and electronic microscopies, whereby the purity of the products could not be well quantified.

The experiment of Cu discharge in the presence of ascorbic acid, in which the nascent Cu nanoparticles had been partly dispersed and prevented from the oxidation reaction, encouraged us to further develop this kind of non-vacuum method for the preparation and self-assembly of pure Cu particles. We assumed the aggregate shape of the Cu particles was pertinent to the composition of the liquid-phase, and hoped to further investigate this kind of self-assemble process through replacing the pure deionized water by a traditional surfactant such as CTAB, which has been widely used for controllable growth of metal nanomaterials with different shapes [23–28]. As shown in the SEM images (see Fig. 5), spherical structures with diameters ranging from 700 nm to 1 μm , sufficiently stable in the solution, were formed in the presence of CTAB (0.005 mol/L) /ascorbic acid (0.025 mol/L). Fig. 6 shows the typical TEM image of an individual nanostructure. Of particular interest is that the self-assembled structure is made of nanoparticles of 5–35 nm

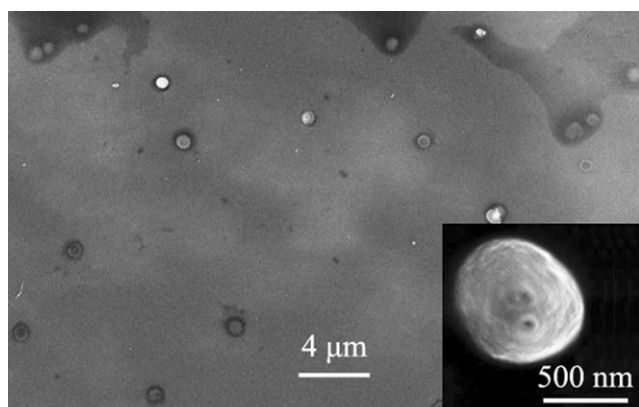


Fig. 5. SEM image of the products from Cu discharge in CTAB/ascorbic acid solution.

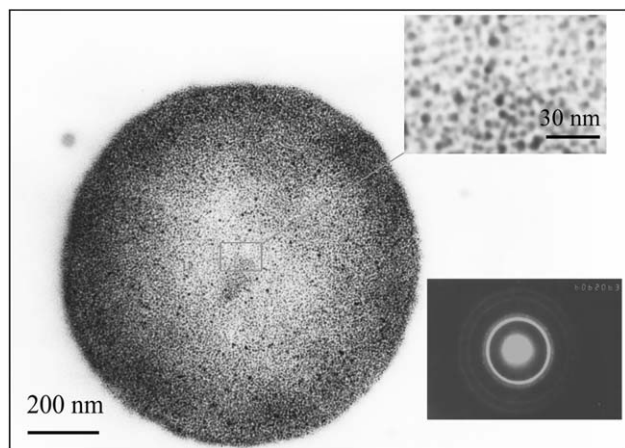


Fig. 6. TEM image of an individual spherical nanostructure self-assembled from Cu nanoparticles.

(mean 10–15 nm). The electron diffraction pattern (the inset to Fig. 6) supports that the as-prepared nanostructure is composed of Cu nanoparticles with symmetrical decentralization.

The spherical nanostructure grown in the chemical environment of CTAB/ascorbic acid, apparently differed from those obtained in the presence of only ascorbic acid (or pure water), showing that the applied surfactant CTAB plays a critical role in regulating the organization shapes of the end products. The roles of the CTAB on micelle and nanostructure formation in solution process have been previously discussed extensively in scientific literature [23–28], and most of the prior studies [23–26] emphasized the rod-like micellar template of the CTAB for synthesizing one-dimensional nanomaterials. Since discharge of Cu in the presence of CTAB/ascorbic acid results in spherical structures, a rod-like micellar templating mechanism is less likely in the current process. Considering that the building blocks for the spherical aggregates were fabricated from Cu discharge, a physical top-down process rather than the previously reported chemical bottom-up process [23–28]; it is thus deemed that the CTAB is irrelevant to the formation of the Cu nanoparticles but contributes to their self-assembly.

Under the discharge condition, nanoparticles are grown in the plasma zone between the electrodes gap surrounded by gas bubbles [16]. This kind of gas bubble is formed due to the liquid vaporization under arc-discharge high temperature (around 4000 K) condition, and serves as a microwater-cooling reaction chamber that enables rapid quenching of the Cu plasma vapor produced in the arc-discharge to form nanoparticles. The nascent Cu nanoclusters from the discharge of Cu rods are reactive and subject to coalescence due to their unsaturated valences on the surfaces, e.g., forming the horned structures in Fig. 4. In the presence of CTAB, however, the nascent nanoclusters from the arc-discharge of Cu rods are covered with CTAB layer so as to lower the surface tension and stabilize the otherwise unstable nanoclusters [27,28]. As shown in the inset in Fig. 6, there are gaps of 3–5 nm between the packed neighboring nanoparticles. Because the average molecular length of the C16 chain in CTAB is about 1.8–1.9 nm [29], the gap distance is almost double the length of the CTAB long alkyl chain. This suggests that the surface of each nanoparticle may be covered with a monolayer of CTAB molecules, most likely, with its $\text{CH}_3\text{-N}^+$ headgroup bound to the Cu surface and its long alkyl hydrophobic chain outward. It is the strong hydrophobic interactions between long alkyl chains on neighboring particles that causes stacking of the nanoparticles. The similar double alkyl layer structures for CTAB have already been suggested on Au nanorod [30] and Ag nanodisk [28] surfaces.

Building metal nanoparticles into organized structures is of importance for the applications in nanotechnology involving a host of unusual properties [31,32], and a number of approaches have been developed in synthesis and self-assembly of three-dimensional (3D) structures of noble metal nanoparticles via chemical bottom-up route [33–35]. In the present experiment, the 3D metal nanostructures (i.e., Cu spherical structures) can be manufactured by means of Cu arc-discharge in liquid, a top-down approach in which the properties from both physical arc-discharge and chemical solution reaction were combined. Our ongoing researches show that the proposed method involving discharge in liquid is also applicable to preparation and self-assembly of other metals (e.g., Ag, W and Ni) nanoparticles in deionized water or liquid nitrogen. Therefore, this kind of non-vacuum and low-temperature method, bearing both physical and chemical processes, provides an alternative choice for the preparation and self-assembly of various metal nanoparticles.

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