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Sonoelectrochemistry of Cu^{2+} in the Presence of Cetyltrimethylammonium Bromide: Obtaining CuBr Instead of Copper

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The sonoelectrochemistry of Cu^{2+} ions which yields metallic copper with surfactants such as poly(*N*-vinyl-2-pyrrolidone) and poly(vinyl alcohol) or without any surfactant produced nanocrystalline CuBr (95 wt %) and 5% of metallic copper in the presence of cetyltrimethylammonium bromide. A sonoelectrochemical mechanism explaining the different behaviors for the various surfactants is proposed.

Introduction

The synthesis of nanosized particles is a growing research field in chemical science, in accordance with the extensive development of nanotechnology. Metals and, moreover, nanometallic particles will play a major role in the sustainable growth of industries such as chemical, automotive ,and pharmaceutical. This is due to the fact that metallic nanoparticles offer improved properties in comparison to bulk metallic materials that are currently in use.[1−3]

Several synthetic techniques have been employed in the preparation of copper nanoparticles. The various methods include reverse micelles,[4] the reduction of copper(II) acetate in water, and 2-ethoxyethanol using hydrazine under reflux,[5] reduction of aqueous copper chloride solution using $NaBH_4$ in the nonionic water-in-oil (w/o) microemulsions,[6] sonochemical synthesis,[7] gamma radiolysis method,[8] using carbon nanotubes as a template,[9] the electro-exploding wire process,[10] chemical reduction of Cu^{2+}, ions dissolved in the water core of a water-in-supercritical CO_2 microemulsion,[11] photochemistry,[12] metal vapor synthesis,[13] microwave irradiation,[14] laser ablation,[15] and so forth.

The electroreduction of a copper salt (or other metallic salts) on a cathode leads to metal deposition. Electrometallurgy is indeed the classical method for copper preparation. However, only quite recently has the potential benefit of combining sonochemistry with electrochemistry been studied. These beneficial effects include acceleration of mass transport, cleaning and degassing of the electrode surface, and an increased reaction rate. Drake[16] found that, during electrodeposition of Cu, 1.2 MHz and 20 kHz ultrasound radiation reduced the diffusion layer from 200 μm to about 20−30 μm and 3.4 μm, respectively.

The discovery that the application of ultrasonic energy can increase the rate of electrolytic water cleavage was reported as early as 1934.[17] Afterward there was a period of neglect until the early 1980s when there was again an upsurge of interest in the field. At present, ultrasound is used in a wide range of electrochemical processes such as metal plating, deposition of polymers, electrogeneration of gases and solids, and electrochemical waste processing. Ultrasound and electrochemistry provide a powerful combination for several reasons. Ultrasound is well-known for its capacity to promote heterogeneous reactions, mainly through increased mass transport, interfacial cleaning, and thermal effects. Effects of ultrasound in electrochemistry may be divided into several important branches: (1) Ultrasound greatly enhances mass transport, thereby altering the rate, and sometimes the mechanism, of the electrochemical reactions. (2) Ultrasound is known to affect surface morphology through cavitation jets at the electrode−electrolyte interface, which usually acts to increase the surface area. (3) Ultrasound reduces the diffusion layer thickness and, therefore, ion depletion. A comprehensive review of the field has recently been given by Compton et al.[18]

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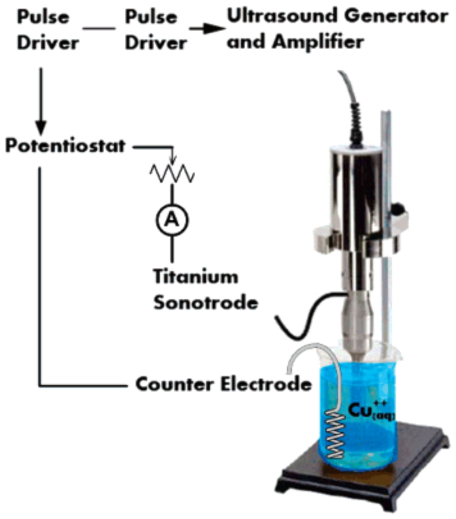
Reisse and co-workers[19−21] were the first to describe a novel device for the production of nanometallic powders using pulsed sonoelectrochemical reduction. This device exposes only the flat circular area at the end of the sonic tip to the electrodeposition solution. The exposed area acts as both a cathode and an ultrasound emitter, termed by Reisse et al as a "sonoelectrode". A pulse of electric current produces a high density of fine metal nuclei. This is immediately followed by a burst of ultrasonic energy that removes the metal particles from the cathode, cleans the surface of the cathode, and replenishes the double layer with metal cations by stirring the solution. The advantages of the sonoelectrochemical method are its low cost, safety, environmental friendliness, and versatility, as well as the use of water as a solvent.

An early list of the materials synthesized by the sonoelectrochemical method is given by Reisse.[19,20,22] It consists mostly of metals or metallic alloys with particle size varying between 10 and 100 nm depending on deposition conditions.[23] Silver,[24] palladium,[25] zinc,[20] and copper[19] are the nanometals prepared by this method. More recently the sonoelectrochemistry synthesis was extended to the preparation of nanosized semiconductors.[23,26,27]

In the present paper, we describe the use of the sonoelectrochemical method for the preparation of nanosized copper particles. The reason for preparing this material sonoelectrochemically, despite Reisse's study, is to get a better understanding of the parameters that affect the particle size. We realized that to get good information on the size and size distribution of the copper nanoparticles, a colloidal solution of the product has to be prepared. Otherwise, the copper nanoparticles are highly aggregated. The sonoelectrochemical reduction of the aqueous solution containing the Cu^{2+} ions was conducted in the presence of a surfactant, CTAB (cetyltrimethylammonium bromide).[28] The nanosized product was capped by the CTAB, and a stable colloidal solution was formed. However, to our surprise, the major product was nanosized CuBr. The copper was a minor component, and its percentage was dependent on the surfactant concentration. When CTAB was replaced by poly(*N*-vinyl-2-pyrrolidone) (PVP) and poly(vinyl alcohol) (PVA) as the capping agents, metallic copper nanoparticles were obtained as expected.

Scheme 1. Schematic of the Sonoelectrochemical Deposition Setup



Experimental Section

Sonoelectrochemical Method. The sonoelectrochemical device employed in these experiments has been described elsewhere[23−27] and is similar to Reisse's instrument.[19,20] Our experiment is based on the electroreduction of $CuSO_4$ in an acidic aqueous solution. The as-prepared copper and copper bromide nanoparticles are characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), dynamic light scattering (DLS), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

Experimental Setup. A titanium horn (Ultrasonic liquid processor VC-600, 20 kHz, Sonics&Materials) acts both as the cathode and as the ultrasound emitter (Scheme 1). The electroactive part of the sonoelectrode is the planar circular surface, of area 1.23 cm^2, at the bottom of the horn. The immersed cylindrical part is covered by an isolating plastic jacket. This sonoelectrode produces a sonic pulse that is triggered immediately following a current pulse. Our pulse driver (General Valve) is used to control a potentiostat, and a second pulser (Wavetek function generator 164) controls the ultrasonic processor, which is adapted to work in the pulse mode. The home-built potentiostat is operated in the constant current regime (without using the reference electrode). A platinum wire spiral (0.5 mm diameter and 15 cm long) is used as the counter electrode. In the first experiment the cathodic current density pulse (at the ultrasonic horn) was 480 mA/cm^2. The duration of the current pulse was 900 ms. The off time of the current pulse was 900 ms. The duration of the ultrasonic pulse was 600 ms. The off time of the ultrasonic pulse was 300 ms. In the second experiment the cathodic current density pulse was 440 mA/cm^2. The duration of the current pulse was 250 ms. The off time of the current pulse was 250 ms. The duration of the ultrasonic pulse was 100 ms. The off time of the ultrasonic pulse was 150 ms. The experiments were carried out at an ultrasound power intensity of about 76 W. Prior to electrodeposition, the sonoelectrode was sonicated in 50:50 acetone−distilled water solution for 5 min at an ultrasound power intensity of about 76 W.

Synthetic Procedure. The electrolyte in the first experiment was identical to that used by Reisse et al.:[19] an aqueous solution of copper(II) sulfate pentahydrate (40 g/L) and sulfuric acid (180 g/L). The electrolyte volume was 50 mL. In the second experiment the molar ratio of $CuSO_4$/CTAB was 3:1. All the other parameters remained the same as in the first experiment. The electrolyte volume was 60 mL. The pH of the solution was 0.5. The copper deposition

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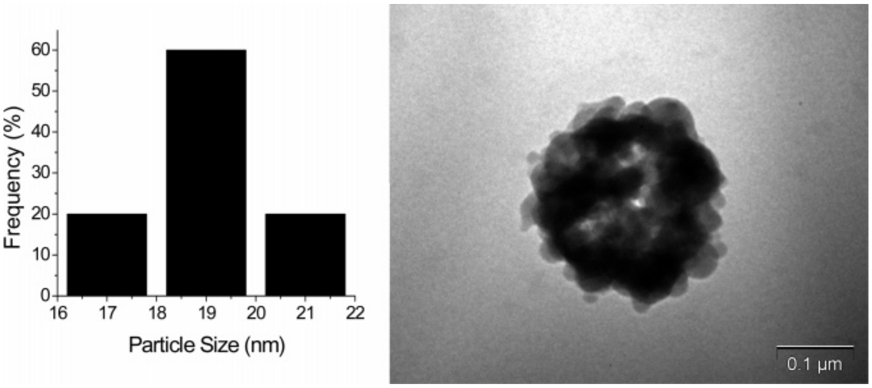

Figure 1. Right: TEM picture of fcc copper particles. Left: A histogram of the sizes of individual copper particles.

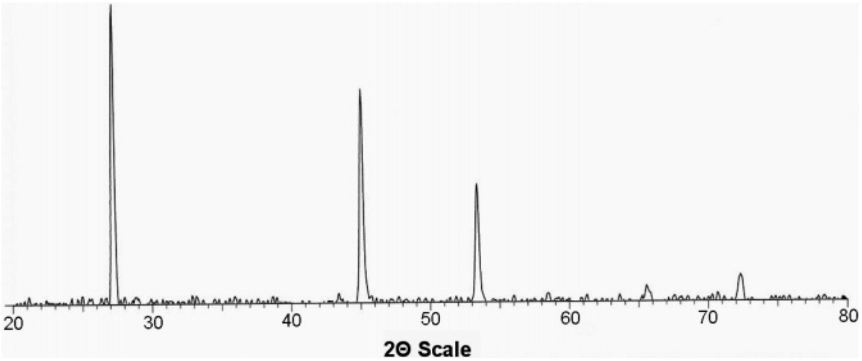

Figure 2. XRD diffractions of the sonoelectrochemical product obtained in the presence of CTAB.

was carried out in the electrochemical cell for typically 30 min. In the early experiments the reaction was conducted in a beaker containing the electrodes. Later we used a cell with a sintered glass separating between the anode and the cathode. At the end of the reaction, the precipitate was washed repeatedly with distilled water and dried under a vacuum overnight.

Characterization Methods. *TEM.* A Phillips EM-400T electron microscope operating at 100 kV was used for TEM and electron diffraction.

XRD. XRD spectra of the powders were obtained using a Rigaku RU-200 B Rotaflex diffractometer operating in the Bragg configuration using Cu Ka radiation. Data were collected with a counting rate of 0.25 deg min^{-1} and sampling interval of 0.002°. The accelerating voltage was set at 50 kV with a 150 mA flux. Scatter and diffraction collection slits of 0.3 and 0.5 mm were used. The crystal size (coherence length) was estimated from the width of the diffraction peaks using the Debye–Scherrer relationship.

DLS. The mean particle size and the particle size distribution were determined by DLS. The suspension of particles in the aqueous solution was measured by a Coulter N-4 partical size analyzer. The measurements were conducted 10 min after the completion of the sonoelectrochemical process. The sample was examined in a quartz cuvette at room temperature without diluting the final solution.

DSC. The DSC measurements were performed on a Mettler Toledo DSC 25 (TC 15 TA controller). The DSC analysis was conducted on a sample that was dried overnight at room temperature. The heating rate of the first cycle was 1 °C/min. The sample was cooled at 10 °C/min and reheated at 10 °C/min.

TGA. TGA measurements were carried out on a Mettler TC11TA. The sample was heated under nitrogen at a rate of 3 °C/min.

Results and Discussion

1. Cu^0. In the first experiments we succeeded in reproducing the results obtained by Reisse et al.[19] The sonoelectrolytic process yielded a reddish precipitate at the bottom of the cell that was identified by XRD as fcc Cu^0. The TEM image of the product is depicted in Figure 1. The picture shows a highly aggregated product having a diameter of about 200 nm. A histogram of the sizes of individual particles observed at the edges of the aggregate is also provided, and the particle sizes are calculated to be 19.0 ± 2.0 nm. The histogram is based on counting 70 nanoparticles. It is clear, however, that it would be impossible from such an aggregated form to study the dependence of the size on parameters such as the temperature. We have, therefore, conducted the sonoelectrochemical experiment in the presence of a surfactant or a polymer to form a colloidal solution of the copper to get a more exact description of the particles sizes and their distribution.

2. Colloidal Solution of Cu^0 Particles. Previous reports[28] have documented that CTAB forms a stable colloidal solution of copper particles in an aqueous medium. Indeed, when the sonoelectrochemical process was conducted in the presence of CTAB a gray solution was formed at the end of the sonoelectrochemical process. The solution was stable for 1 h, and by that time a gray precipitate was detected at the bottom of the flask. The XRD pattern of the precipitated solid is presented in Figure 2. The material is identified as CuBr. The diffraction peaks match well those of JCPDS card no. 01-077-1997. The major peaks are detected at $2\theta = 27.2$, 45.0, 53.4, 65.7, and 72.4. They are assigned to the (111), (220), (311), (400), and (331) CuBr planes, respectively. We could not detect any diffraction peaks of metallic Cu^0.

TGA measurements have indicated that the amount of the second component, amorphous copper, is about 5%. This was the amount of the residue left after heating the sample

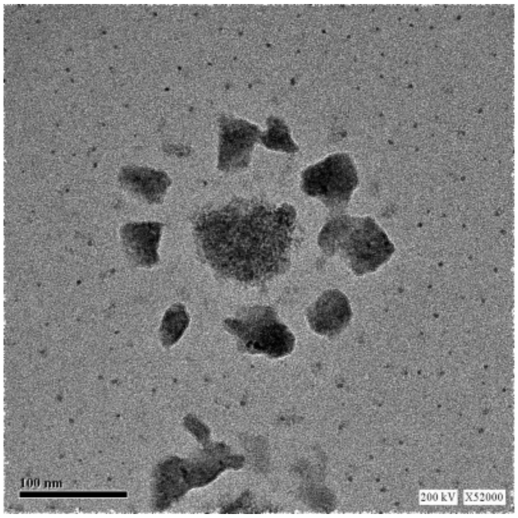

Figure 3. HRTEM images of the as-prepared sample.

to 850 °C. The major product, 95%, is CuBr. These results are supported by the energy-dispersive analysis of X-rays where 50.4 Cu and 49.6 Br (atomic percent) were found in the analysis of the as-prepared product. The absorption of the colloidal solution obtained at the end of the electrolysis was measured to detect the well-known copper plasmon peak at 600 nm.[29] This was done because of the small amount of copper (less than 5%) that is obtained in the process. We could not detect any absorption at 600 nm. On the other hand, a sonoelectrochemical process performed on an aqueous Cu^{2+} solution reduced in the presence of PVP, instead of CTAB, yielded a colloidal solution of copper nanoparticles for which the plasmon peak was observed. All these experiments point to CuBr being the major product (95%) and amorphous Cu as a very minor component (less than 5%). A control experiment in which the electrolysis of the same components of the sonoelectrochemical process in the absence of ultrasound yields nanocrystalline copper. It is, therefore, concluded that the introduction of the sono pulses alter considerably the nature of the product. On the other hand, a control experiment, in which only the sonochemical pulse was employed, did not yield any products.

Particle Size and Size Distribution. Obtaining a stable colloidal solution for about 1 h has enabled the CuBr and Cu^0 particle size and their distribution to be measured. The size and its distribution are determined by DLS measurements. Two populations of different sizes were found: the first with an average diameter of 3 nm (77.8%) and the second with an average size 3.8 nm (22%). A very narrow size distribution is obtained, but we cannot assign the larger size, 3.8 nm, to the copper population.

In addition, we have also carried out high-resolution TEM (HRTEM) measurements which have provided more information on the morphology and particle size. Figure 3 presents the TEM image of the as-prepared particles. The organization observed in this picture, namely, a central aggregated particle of 80 nm surrounded by about 10−12 particles whose diameter is 50 ± 20 nm, is typical for the whole grid. Many more of this kind of arrangement are spread all over the grid. In addition, very small, 3 ± 1 nm, monodispersed nanoparticles are found in this picture. We assigned the particles as "stars" arranged around the central "sun" of CuBr particles. Both the central "sun" and the surrounding "stars" are aggregates of small particles. The assignment of this structure ("sun" and "stars") to CuBr is based on the analysis of the distances between the fringes (Figure 4, left panel) and their comparison to the *d* values of CuBr. The measured distance is 0.328 nm which corresponds well with the *d* value of the (111) plane of CuBr (0.328 nm according to PDF file number 01-077-1997). The monodispersed nanoparticles, 3 ± 1 nm, which are spread all over the grid are assigned to amorphous metallic copper particles. Most of the particles did not show fringes in accordance with our interpretation. However, a small percentage of particles (2%) revealed fringes that could indeed help to confirm their assignment to metallic copper. In Figure 4, right panel, we depict an example of such a particle. Fringes are detected only in the left part of the particle, and the distances between the fringes are 0.208 nm in good agreement with the *d* value of the (111) plane of Cu^0 (0.208 nm according to PDF file number 4-836).

Figure 5 depicts the image of one copper particle. However, its size, ≈10 nm, is larger that the rest of the small particles (3 ± 1 nm). The reason it is presented is that it showed two interesting and different features from the other copper particles. First, it is a crystalline product, revealing fringes that fit perfectly the (111) plane of Cu (measured distance 0.208 nm literature, PDF file 4-836, 0.208 nm). The second feature is the observation of a 2 nm layer surrounding the copper core. One possibility is to identify this as a carbon layer because the distances between adjacent fringes are 0.385 nm which we assign to extended graphitic layers which are expected at 0.34 nm. We will reiterate again that the crystalline copper particles constitute less than 5% of all the small Cu particles, which are only 5−10% of the total products. The other 95% are amorphous copper and have a smaller size.

The surrounding 2 nm layer results from the CTAB, and it is observed as a result of the image of the heavy atom, bromine, of the CTAB, because the light carbon atoms would not have been observed in the TEM image. The width of the weak ring around the particle, about 2 nm, would fit well the length of CTAB, 1.9 nm,[30] which contains 18 carbons and a large bromine atom.

Finally, the use of CTAB as a surfactant is unique. Replacing the CTAB by polymeric surfactants such as PVP and PVA leads to the full reduction of Cu^{2+} ions to metallic copper and the formation of a stable colloidal solution of metallic copper. At this point we have decided to investigate why CuBr is obtained instead of Cu; namely, we are trying to understand the sonoelectrochemical mechanism for preparing CuBr in the presence of CTAB.

Mechanism. Our proposed mechanism assumes the reduction of Cu^{2+} ions to copper as the first stage. In the second stage the Cu reacts with OH radicals or H_2O_2 formed by the

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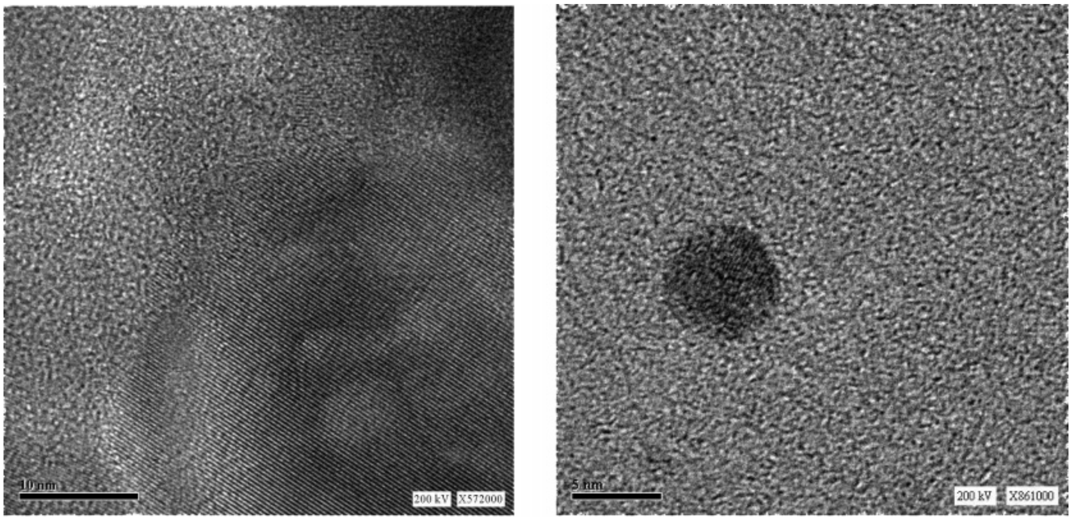

Figure 4. Left: An image of a CuBr particle taken for one of the “star” particles surrounding the central “sun”. Right: A HRTEM picture of one of the monodispersed Cu^0 particles.

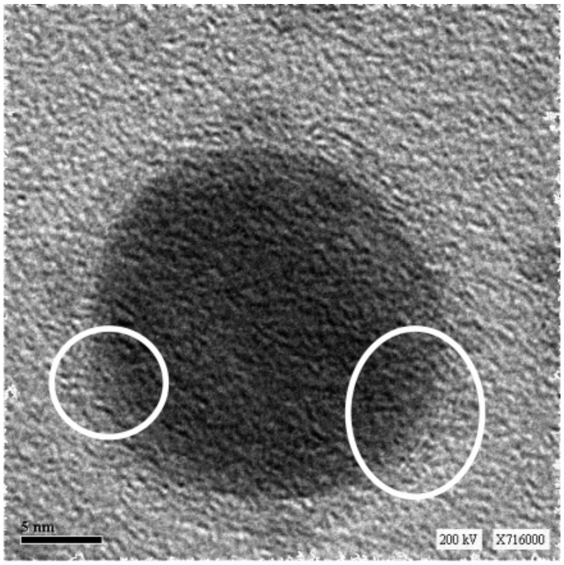

Figure 5. HRTEM picture of a Cu^0 particle.

sonochemistry of water according to

$$Cu^0 + OH \rightarrow Cu^+ + OH^- \qquad (1)$$

The reducing agent can also be H_2O_2 as presented in a previous sonochemical paper (see eq 5 in ref 7). The Cu precipitates because of the small value[31] of the K_{sp} of CuBr, 6.27×10^{-9}. Palladium which has a soluble bromide does not react this way. To support our assumption concerning the importance of the sonochemical pulse in the formation of the CuBr, we have carried out the reaction varying only the sonochemical intensity and leaving all the other parameters constant. The ultrasonic intensity was varied from 50 to 35 and to 15 W. An increase in the amount of metallic copper is clearly observed upon reducing the ultrasonic intensity. The increase in the amount of copper is due to the higher amount of Cu^0 that is obtained. In other words, the importance of the sonochemistry and the percent of OH radicals formed is smaller when measured in respect to the amount of metallic copper. Thus, reaction 1 occurs less and the amount of copper remaining is higher. The amount of Cu^0 is determined from TGA. We measure the weight of the material remaining at 850 °C and assign it to metallic copper. The remaining question is why Cu^+ ions are not detected in the presence of the polymers PVA and PVP. According to our explanation Cu core particles are oxidized by the OH radicals on its surface. The presence of Br^- ions shift the equilibrium constant toward the formation of CuBr and the removal of the Cu^0 from the surface to further oxidation. This does not happen in the presence of the polymers, and a Cu_2O layer protects the Cu^0 from further oxidation. Another explanation for the reason that reaction 1 does not occur with PVP and PVA is their strong complexation with H_2O_2 and OH, respectively.[32,33] An IR absorption spectrum of the metallic copper product obtained in the presence of PVP has revealed a peak at 1656 cm^{-1}. Panarin et al.[32] have assigned this peak to the H_2O_2−PVP complex.

A control reaction in which the CTAB underwent a sonoelectrochemical process without the Cu^{2+} ions in the solution was also carried out. The only reaction observed at the cathode was the release of hydrogen.

Another possible mechanism is based on the direct reaction

$$Cu^+ + CTAB \rightarrow CuBr + CTA^+ \qquad (2)$$

Conclusion

We have presented a sonoelectrochemical method for the preparation of nanosized copper particles. Sonoelectrochemistry is combining electrochemistry with ultrasound radiation which serves only as a mechanical shaker. The mode of sonoelectrochemistry used in the current experiments is that the cathode, or the so-called sonotrode, provides both electric and sono pulses. We consider this technique as a unique

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method for the preparation of nanometals having negative reduction potential, larger than −1 V. This is because the reduction is carried out by the electric current, and metals that cannot be reduced by chemical means will undergo the process because the voltage exceeds the standard reduction potential plus the over-potential. In the current process we have reduced copper ions and used a well-known surfactant, CTAB, for isolating the metallic copper nanoparticles. We have unexpectedly obtained CuBr nanoparticles, instead of copper. The particle size of the CuBr is found to be 50−80 nm. Ninety five percent of the solid product was identified as CuBr, and the rest was identified as metallic copper. A Sonoelectrochemical mechanism is proposed to explain this phenomenon.

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