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Sonoelectrochemical Synthesis of Metallic Aluminum Nanoparticles

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In this paper, we report for the first time on the room-temperature preparation of metallic aluminum nanoparticles by the pulsed sonoelectrochemical method. The prepared nanoparticles were characterized by X-ray diffraction (XRD), high-resolution scanning electron microscopy, transmission electron microscopy (TEM), and high-resolution transmission electron microscopy. TEM analysis shows that the prepared aluminum nanoparticles range from 10 to 20 nm in size. The XRD pattern confirms the formation of metallic aluminum nanoparticles. The results show that the sonoelectrochemical technique is a promising method for the fabrication of air-sensitive metallic nanoparticles that have a high, negative reduction potential.

Introduction

The development of metallic nanoparticles has gained increasing interest in recent years due to their fascinating properties when compared with bulk particles. The unique properties of nanostructures mainly depend upon the grain size of the particles, and hence, the preparation and exploitation of these nanoparticles becomes a challenge for the scientific community. Metallic nanoparticles have potential application in various fields such as sensing,[1–3] photonics[4,5] catalysis,[6,7] and device fabrication. Among the metals, aluminum plays a prominent role in the materials science world because of its unusual properties, such as its light weight, high strength, corrosion resistance, and high electrical and thermal conductivity. Therefore, it has been used in explosives, propellants,[8,9] and powder metallurgy parts for aircrafts[10,11] and automobiles,[12] and so on. To increase the utility of Al metals further, the particle size has to be minimized to reach the nanoscale.

Conventionally, Al metals have been prepared electrochemically by the Hall–Heroult process at 1233 K by using a carbon anode and an Al pool as the cathode. The main drawbacks to this process include high energy consumption, emission of greenhouse gases such as CO_2, CO, and CF_6, and stringent reaction conditions. Recently, different methods for the preparation of aluminum nanoparticles have been reported.[13–15] Pomfret et al.[16] reported on the synthesis of Al nanorods with a length of 2–4 µm and a width of 10–30 nm by the electrochemical template deposition method. Al particles 10–50 nm in size have also been prepared by using the laser ablation method.[17] Abedin et al.[18] synthesized nano- and microcrystalline aluminum particles in the size range 20–35 nm by using ionic liquids.

The above-mentioned methods have some drawbacks: (i) It is difficult to remove the template. (ii) A complicated experimental set up is required. (iii) Expensive water-stable ionic liquids must be used. The sizes of the aluminum particles prepared by the above-mentioned methods are very large. The preparation of aluminum nanoparticles with sizes ranging from 10 to 20 nm by using a simple preparation method at room temperature is still a challenge to the scientific community. This is especially true because there are no organic or inorganic chemicals that can reduce aluminum ions at room temperature, except for the alkaline metals.

Sonoelectrochemistry is an efficient technique for the preparation of nanometals,[19] metal sulfides,[20] nanoporous Zn and Ni particles,[21] polyaniline nanoparticles,[22] and so on. This technique was first introduced by Reisse et al.[23] and involved alternating sonic and electric pulses for the shape-controlled synthesis of nanostructured materials. The sonoelectrochemical formation of nanoscale metals was accomplished by applying an electric current pulse for electrodeposition, followed by a burst of ultrasonic energy that removes the particles from the sonotrode.[24,25] The ultrasonic waves do not play a chemical role here, but rather a mechanical one. Herein, we report for the first time, on the pulsed sonoelectrochemical synthesis of aluminum nanoparticles. We have recently employed sonoelectrochemistry for the preparation of nanosized Mg.[26] The current paper extends the previous study to a commercially more important metal.

Results and Discussion

The X-ray diffraction (XRD) pattern of the deposited nanoparticles is shown in Figure 1. The sharp and well-de-

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fined peaks are observed at 2θ values of 38.6, 44.6, 65.3, and 78.3° corresponding to planes of (111), (200), (220), and (311), respectively, which confirm the formation of face-centered cubic aluminum (JCPDS No. 004-0787). No other diffraction peaks are observed in the pattern that reveals the single-phase formation of Al. A first indication of the presence of nanoparticles was observed from the width of the diffraction peaks. The application of the Debye–Scherrer formula to the strongest diffraction peaks at 38.6° gives a crystallite size of 25.0 nm.

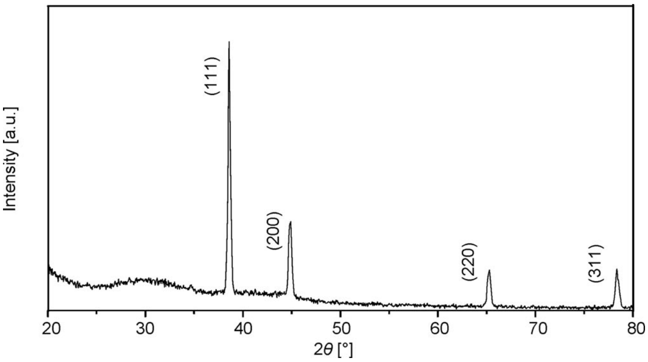

Figure 1. XRD pattern of Al nanoparticles.

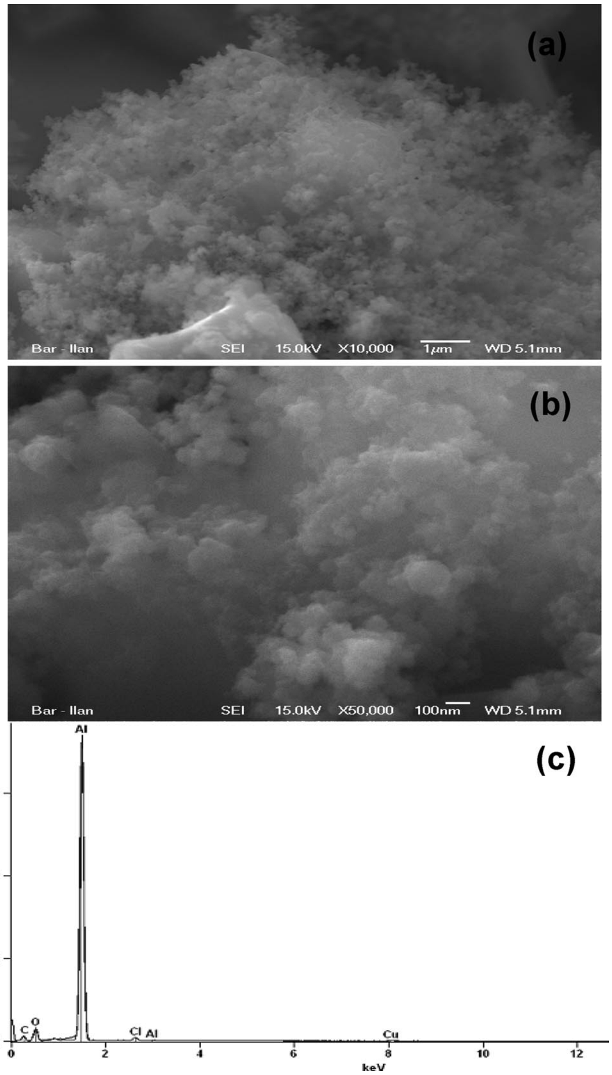

Figure 2. HRSEM images (a, b) and EDX pattern (c) of Al nanoparticles.

Further support for the morphology of the product was obtained from high-resolution scanning electron microscopy (HRSEM; Figure 2) and transmission electron microscopy (TEM), and from high-resolution transmission electron microscopy (HRTEM) for identification of the product as aluminum (Figure 3). The as-prepared sample was mounted on top of carbon tape, which was attached to the copper plate for SEM analysis. Figure 2 depicts two different HRSEM magnifications (×10000, ×50000) of the aluminum nanoparticles, demonstrating that the aggregates are composed of very small particles. However, as a result of the limited magnification of the instrument, the smallest particles, identified by SEM, are 25 ± 8 nm, which can be further resolved into smaller particles with a better magnifying SEM. The SEM measurements led to the conclusion that the Al nanoparticles are aggregated. Energy-dispersive X-ray (EDX; Figure 2c) analysis shows that the surface of the material is mainly composed of aluminum, and the small peaks observed for oxygen show that the surface of the aluminum is oxidized. Trace amounts of chlorine are

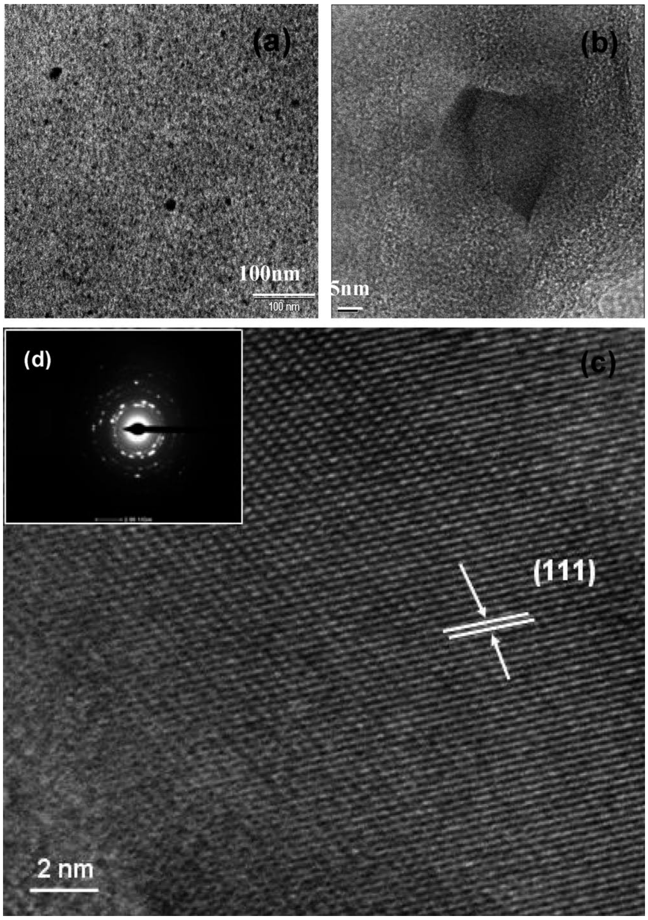

Figure 3. TEM (a), HRTEM (b and c) and SAED (d) images of Al nanoparticles with different magnifications.

also observed but we attribute it to surface adsorption of chloride ions on aluminum, as this is a well-known phenomenon that has been studied in detail previously.[27]

Samples for TEM and HRTEM were prepared by ultrasonically dispersing the product into absolute ethanol, then by placing a drop of this suspension onto a copper grid coated with an amorphous carbon film supported by filter paper, and by drying in air. Figure 3a presents the images of TEM measurements of the products obtained in THF. The obtained images show the formation of small and aggregated particles in the range 10–20 nm. Figure 3c presents the HRTEM images of Al nanoparticles. It illustrates the well-defined lattice fringes, indicating the crystalline nature of the Al nanoparticles. The measured interplanar spacing d value is 2.35 Å, which corresponds to the lattice plane of (111). These values are in agreement with the reported JCPDS value of d_{111} = 2.33 Å (JCPDS No. 004-0787). The selected area electron diffraction (SAED) pattern (Figure 3d) shows the formation of ring patterns, which infer the polycrystalline behavior of the materials and confirms that the metal is Al.

Conclusions

In conclusion, a sonoelectrochemical technique was presented herein for the preparation of metallic aluminum nanoparticles. This method is demonstrated for a very reactive metal, Al, whose standard reduction potential is –1.66 V. No active reducing agents are known to reduce such an active metal. The only way to chemically reduce Al ions is to use another metal with a more negative reduction potential, such as Na or Li. It is therefore clear that only electrolytic methods could lead to the reduction of Al ions. Sonoelectrochemistry is such a technique, which, in addition, produces the metal as a powder composed of nanoparticles. Moreover, the present method is considered a promising technique for the fabrication of metal nanoparticles on a large scale.

Experimental Section

Anhydrous $AlCl_3$ (99.99%) and a 1 M $LiAlH_4$ solution in THF (tetrahydrofuran) were obtained from Aldrich and used as received. The detailed experimental set up and the procedure are given elsewhere.[26] In brief, all the sonoelectrochemical measurements were carried out under a pure argon atmosphere in a glove bag (Aldrich). An ultrasound horn (ultrasonic liquid processor VC-600, 20 kHz, Sonics & Materials) acts both as the cathode and as the ultrasound emitter. The electroactive part of the sonoelectrode is the planar circular surface at the bottom of the horn. The immersed cylindrical part is covered by three layers, an isolating plastic jacket, a gold crucible, and another isolating plastic jacket. All electrochemical reactions were carried out by using an EG&G. Inc. 273 potentiostat. This sonoelectrode produces a sonic pulse that is triggered immediately following the current pulse.

The sonoelectrochemical synthesis was performed in one-compartment, three-electrode cells consisting of an aluminum metal (40 mm × 20 mm) counter electrode, an aluminum metal (40 mm × 5 mm) reference electrode, and an ultrasonic tip as a working electrode. In the synthesis, a cathodic current density of 100 mA cm^{-2} was applied to a solution of 4 g of $AlCl_3$ dissolved in 80 mL of a 1.0 M solution of $LiAlH_4$ in THF for 4 h. The duration of the current pulse was 600 s, and the off time of the current pulse was 60 s. The duration of the ultrasonic pulse was 240 ms. The ultrasound power intensity was 76 W. The resulting metallic aluminum product was washed several times with THF and dried under vacuum. The need for such a long duration for the electric pulse was dictated by the low current. The yield of the product is 53.0%, measured in respect to the total number of coulombs passed through the solution.

The product was deposited on the cathode and was characterized as aluminum by XRD measurements. The particle morphology was studied with HRSEM, TEM (JEOL-2010), and HRTEM (JSM-7000F HR).

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