

2006, *110*, 17711–17714 Published on Web 08/22/2006

Carbon-Coated Core Shell Structured Copper and Nickel Nanoparticles Synthesized in an Ionic Liquid

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Received: June 20, 2006; In Final Form: August 8, 2006

A simple synthetic route to prepare carbon-coated copper or nickel nanoparticles is developed in an ionic liquid under microwave heating. The obtained products are characterized by XRD, UV-spectroscopy, and Raman spectroscopy. The morphologies are studied with the help of TEM, HRSEM, and HRTEM. A bulk transport property for carbon coated nickel is reported in this letter.

Introduction

Nanoparticles have properties intermediate between those of bulk and single particles.¹ Carbon-coated nanomaterials, especially metals, are of great interest due to their stable nature toward oxidation and degradation, and they show potential applications.^{2–8} Whereas bare metal nanoparticles can be easily oxidized in an oxidizing medium, it is well known that an outer layer or a carbon shell coated on a nanomaterial provides excellent protection against air oxidation.³ There are various known methods for obtaining carbon coating on metal nanoparticles, the most popular being the arc-discharge technique.⁹ In general, the various methods for obtaining carbon-coated metal nanomaterials are very chaotic, and closed systems with very harsh conditions, such as high pressure, are required to attain the desired products.^{10,11}

In this paper we describe a simple reaction, which combines the use of an ionic liquid (IL) and microwave irradiation to obtain metal nanoparticles coated with carbon in an IL solvent.

Room temperature ionic liquids (RTILs) are known as "green" solvents due to their unusual extreme physical properties. In the literature they are well-known solvents, mostly used as solvents for organic synthesis, separation techniques, and electrochemistry.¹²⁻¹⁴ Recently, RTILs have been gaining increasingly more importance in inorganic chemistry. There are reports of the synthesis of inorganic nanometals in IL. For example, Mu et al. report on a general ethanol reduction method for the preparation of PVP-stabilized noble metal nanoparticles in RTIL.¹⁵ Nanoparticles of metals such as platinum, palladium, and rhodium, were synthesized in RTIL.^{15,16} Tellurium nanowires have been prepared in an IL where NaBH4 was used as a reducing agent and PVP acts as a stabilizer.¹⁷ Ir and Rh nanoparticles have been synthesized in ILs by a chemical reduction.¹⁸ Anisotropic gold nanoparticles have been synthesized by photochemical reduction in an ionogel template.¹⁹ CoPt alloy nanorods have been synthesized in an IL using CTAB

(cetyltrimethylammonium bromide) as a surfactant.²⁰ The precursors used for CoPt alloy preparation were the metal acetates, whereas the metal acetates on thermal decomposition yield the respective metal.²¹ Recently, it has been reported that a large-scale synthesis of single-crystal gold nanosheets in an IL is accomplished without any additional template agent.²² Ni nanoparticles were synthesized in IL via the thermolysis of nickel formate, which undergoes a self-redox reaction.²³

High-speed synthesis using microwave (MW) radiation has attracted a considerable amount of attention in recent years.²⁴ The efficient in-core volumetric heating with the help of MW radiation has helped to reduce chemical reaction times from hours to minutes, and it is also known to reduce side reactions, increase yields, and improve reproducibility.²⁵ The observed rate enhancement is a purely thermal/kinetic effect, i.e., a consequence of the high reaction temperatures (superheated solvents above their boiling temperature) that can rapidly be attained by irradiating polar materials in a MW field. The ionic nature and thermal stability of the RTIL make them very good susceptors of MW radiation. This gives RTILs an advantage over other solvents in the synthesis of inorganic nanomaterials.^{15–23,26}

This combination effect of an IL and MW radiation has a unique advantage for our research on the fabrication of metal nanoparticles, as well as for the synthesis of metallic nanoparticles with a coating of a carbon shell.

Experimental Section

1-Butyl-3-methylimidazolium tetrafluoroborate (BMIBF₄), (10 g, 44.2mM, for each reaction) IL solvent and the metal precursors copper (3.38mM) or nickel nitrate (3.43mM) salts (1 g) were heated for 10 min in a domestic microwave oven (2.45 GHz, Kenwood Microwave 900 W). After completion of the reaction time the products were washed with acetone and ethanol for several times to remove the IL and other organic impurities and centrifuged for 10 min at 9000 rpm. The washed products were dried under vacuum and used for further investigations. The quantitative yields of the products obtained after drying are in the range of 80–95%.

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Figure 1. XRD patterns of (a) nickel nanoparticles (b) copper nanoparticles.

Results and Discussion

The products were characterized by XRD measurements on a Bruker AXSD advanced powder X-ray diffractometer using Cu K α radiation at 40 kV. The XRD patterns of the desired products are given in Figures 1a and 1b. The crystalline XRD patterns of the products (Figure 1a) fit well with that of nickel (hexagonal, PDF-45–1027), and the patterns in Figure 1b match that of copper nanoparticles (face-centered cubic, PDF-1–85– 1326).

The structural morphology was studied with HRSEM (high resolution scanning electron microscope) using a JEOL JSM-7000F field emission scanning electron microscope with an accelerating voltage of 15 kV. TEM (transmission electron microscopy) measurements were conducted on a JEOL-TEM 100SX microscope and the HRTEM (high resolution transmission electron microscopy) on a JEOL-2010, using an accelerating voltage of 200 kV. Samples for HRTEM measurements were prepared by ultrasonically dispersing the products into absolute ethanol, then placing a drop of this suspension onto a copper grid coated with an amorphous carbon film and then drying in air. The HRSEM images of copper and nickel nanoparticles are shown in Figures 2a and 2b, respectively. The HRSEM images illustrate that both the copper and nickel nanoparticles are in the size range of 100 nm and show aggregation. The regular TEM images are shown in Figures 3a and 3b, where we see that the metal nanoparticles are embedded in a matrix of carbon. The carbon layer is indicated by an arrow. The HRTEM images for copper and nickel nanoparticles are depicted in

Figures 3c-f, respectively. The HRTEM images show that the copper and the nickel nanoparticles are coated with an amorphous carbon layer on their surface and are shown by an arrow. The Fourier transform image also confirms the carbon layer, which shows a d spacing of 3.3 Å. The observed spacing of the fringes detected in the HRTEM images is well matched with the d value (2.08 Å, Cu) and (2.03 Å, Ni) of the respective metals. The UV-vis spectrum of the sample is recorded on a Perkin-Elmer UV-visible spectrophotometer. The surface plasmon band around 570 nm is characteristic of copper nanoparticles (10 nm).^{27,28} The shifts in plasmon band depend on the size and shape of the nanoparticles. Copper nanoparticles with 30-50 nm diameter show plasmon band at 579 nm, whereas nanorods with 50-70 nm size show a plasmon band at 586 nm.²⁹ The individual isolated nanoparticles and aggregated nanoparticles also affect the absorption spectra.²⁷ As we can see in Figure 4a the UV-vis plasmon band for carbon coated copper nanoparticles shows a broad band that is red shifted to higher wavelengths (608 nm). This is due to an increase in the particle size to 100 nm. The red shift is expected in comparison with refs 27 and 29. The broadening of the plasmon band results also from the particle size. Raman spectrum is recorded on a Jobin Yvon Horiba Raman system. The 524 nm line of an Ar⁺ laser was used as the excitation source. The Raman spectra are shown (Figure 4b) to confirm the presence of a carbon coating on the copper and nickel nanoparticles.¹¹ The Raman spectra show the characteristic bands at 1354 cm⁻¹ for disordered D-band carbon and at 1589 cm^{-1} graphitic G-band carbon.

The transport properties of the carbon-coated nickel nanoparticles were studied using the Van der Pauw method³⁰ on a pellet sample ($\Theta 6$ mm, h1.5 mm). The resistivity, measured between 12 and 300 K, exhibits strong temperature dependence and it diverges as the temperature is decreased (see Supporting Information, Figure S7).

The results of XRD and the HRTEM indicate that the metal ions undergo a reduction to the metallic state. The presence of the amorphous carbon observed clearly in the HRTEM images suggests that the reduction of the metal ions is, perhaps, assisted by the amorphous carbon. The remaining question is how is the amorphous carbon formed? We attribute this formation to the decomposition of the IL, which absorbs the MW radiation



Figure 2. HRSEM images of (a) copper nanoparticles (b) nickel nanoparticles.



Figure 3. TEM images of (a) copper nanoparticles (b) nickel nanoparticles, HRTEM images of (c) and (d) carbon coated copper, and (e) and (f) carbon coated nickel nanoparticles. The inset shows the electron diffraction scattering and the Fourier transform image of the copper and nickel, respectively. In all the TEM and HRTEM images the carbon coating is indicated with the arrow in the pictures.



Figure 4. (a) Surface plasmon band of Cu, (b) Raman spectra for Cu and Ni particles (D band-disordered carbon, G band-graphitic carbon).

and reaches its decomposition temperature³¹ in the presence of a metal salt within a short period. This is confirmed by the control MW irradiations of the pristine ionic liquid without metal salt leading to its decomposition to yield carbon particles. Superheated solvents are a known phenomenon under MW radiation, especially in our case where the solvent is an IL that absorbs the MW radiation. At this high temperature, once the decomposition occurs the formed carbon reduces the metallic ions. This reduction process is strongly dependent on irradiation time. A short, 5 min MW irradiation of copper nitrate in an IL solvent yields a mixture of Cu₂O and copper. The HRTEM images of this reaction also show wrapping of carbon on the Cu₂O and copper particles (see Supporting Information). The complete reduction of Cu^{2+} ions to copper occurs within a 10 min MW irradiation of the IL. The percentage of carbon formed in a 5 min MW reaction of copper salt is less (11% mole) than that of 10 min MW reaction (16% mole).

We also carried out MW irradiation in the same IL of the same precursor with the addition of water. There was no other byproduct as the time duration remains the same for all the reactions. It was found that the formation of metals is unaffected by the addition of water. To be sure that the reduction of metal ions is due to the presence of carbon, which is the decomposition product of IL, and not due to water or to a MW heating effect, we have carried out MW reaction in the presence of distilled water (10 mL) and metals salts (1 g) without IL. The XRD results show no evidence of metals or metal oxides (see Supporting Information). We have also examined the possibility of reducing the solid metal salts under MW. No metallic products are detected. It can be stated and confirmed with the results obtained (HRTEM) that during the reaction a decomposition temperature is reached for the IL, which decomposes to obtain carbon, which absorbs microwave energy³² and acts as a reducing agent³³ forming a shell around the nanoparticles. These synthesized carbon-coated metal nanoparticles are stable in air atmosphere but are oxidized in acidic medium. The acid treated product may be of great importance in attaining carboncage types of materials.34

Conclusion

In conclusion, we are able to synthesize copper and nickel nanoparticles coated with carbon. It was also found that in our reactions carried out in an IL under microwave heating, the decomposition of this liquid takes place to form carbon. This carbon acts as a reducing agent for the copper and nickel ions to get pure metal nanoparticles and also forms a layer structure over the metal nanoparticles.

Supporting Information Available: Raman spectrum, XRD patterns, HRTEM images, and resistance measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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