

Electro-reduction of cuprous chloride powder to copper nanoparticles in an ionic liquid

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Abstract

Cyclic voltammetry of the CuCl powder in a cavity microelectrode revealed direct electro-reduction in solid state in 1-butyl-3-methylimidazolium hexafluorophosphate. Potentiostatic electrolysis of the salt powder (attached to a current collector) in the ionic liquid produced Cu nanoparticles as confirmed by X-ray diffraction, energy dispersive X-ray analysis, scanning and transmission electron microscopy. The particle size decreased down to 10 nm when the electrode potential was shifted from -0.9 V to -1.8 V (versus Ag/Ag⁺). The electro-reduction and the nanoparticle formation mechanisms were investigated in the ionic liquid and also in aqueous 0.1 mol L⁻¹ KClO₄ in which larger Cu particles were obtained.

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1. Introduction

Metallic nanoparticles, particularly copper nanoparticles, are multi-functional and capable of, for example, catalysing the oxidation of CO at mild temperatures [1], improving the thermal stability of phenolic resins [2], and assisting the detection of nitrate in natural mineral water with a limit of detection as low as 1.5 μ mol L⁻¹ [3]. Various methods have been developed for preparation of metal nanoparticles, in which metal compounds are usually reduced by a reductant at elevated temperatures or under hydrothermal conditions, and formation of the nanoparticles is assisted by templates or in a stabilising medium [4–6]. These pro-

cesses are usually operated in the batch or non-continuous mode, and separation of the nanoparticles from the reductant and reaction medium is often complicated.

Using electrons as the “green” reductant, electrochemical processes involve fewer chemicals and impose a lower environmental impact. Particularly, copper nanoparticles were prepared in aqueous electrolytes by electro-deposition [3]. Following the success of electro-reduction of solid oxides to metals in molten salts [7,8], solid CuO were electro-reduced to copper nanoparticles in an aqueous electrolyte [9]. Nevertheless, although being readily available and environmentally clean, water offers a narrow potential window and reacts with some metals and their compounds.

Room temperature ionic liquids (ILs) are generally considered as “green” reaction media and were used in catalytic synthesis [10], electroplating [11] and many other chemical processes [12,13]. Using ILs for preparation of metallic nanoparticles was also recently demonstrated [14–17]. In these cases, the ILs can function as the stabilising agent to prevent the kinetically unstable nanoparticles

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from agglomeration. Electro-deposition of nanostructured metals and semiconductors were also reported [3,18–20], taking advantage of the wide electrochemical windows of ILs.

Considering the capability of some ILs for transferring chloride ions [21,22], we have attempted direct electro-reduction of solid cuprous chloride powder in an IL to produce copper nanoparticles. This communication reports our preliminary findings from this investigation. Our aim is to develop a simple but generic IL electrolysis method for preparation of metallic nanoparticles from convenient inorganic metal compound precursors.

2. Experimental

Preparation and characterisation of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl, viscous liquid as-synthesised) and hexafluorophosphate ([BMIM]PF₆, liquid) followed the literature [21,23]. Metal chlorides (Cu₂Cl₂ or CuCl: >97%; CuCl₂: 99%, Acros Organics; NiCl₂·6H₂O: >98%, Sinopharm Chemical Reagent Co. Ltd; CrCl₃: 98%, Alfa Aesar) were thermally dried in vacuum.

Viscosity was measured using a rotational rheometer (HAAKE Reho Stress 600, Thermo Scientific). For [BMIM]PF₆, the viscosity decreased with increasing temperature: 125 mPa s, 89 mPa s, 68 mPa s and 53 mPa s at 308 K, 318 K, 328 K and 338 K, respectively. The as-synthesised [BMIM]Cl remained visually viscous, but did not give a stable viscosity value. The variation was beyond reasonable experimental errors. The liquid turned into solid after long-time storage or addition of a few crystals, suggesting a metastable or supercooled state [21].

The solubility of these salts in [BMIM]PF₆ was measured as follow. The IL was first saturated with an excess amount of the salt at 80 °C under stirring for 48 h. After standing still for over 24 h, the clear solution was sampled at different temperatures (80 °C, 60 °C, 40 °C, 28 °C). The sample was treated with concentrated H₂SO₄ and H₂O₂ and then diluted in double-distilled water before analysis by atomic absorption spectrometry (AAAnalyst800, Perkin–Elmer).

The electrochemical property of the CuCl powder was investigated by cyclic voltammetry using a cavity micro-electrode (CME) [24]. It was fabricated by first sealing a Pt wire (100 μm in diameter) in a glass tube on a gas flame. The end of the sealed tube was then ground and polished to expose the Pt wire as a microdisc. This Pt-disc was either directly used as the working electrode for studying species dissolved in the IL, or it was converted to the CME. In the latter case, a small length of the Pt wire in the glass tube was dissolved in *aqua regia*, resulting in a cylindrical cavity of about 100 μm in diameter and 50 μm in depth. The salt powder was loaded into the cavity by repetitive manual pressing the cavity's open end on a small pile of the salt powder on a glass slide.

In potentiostatic electrolysis, several electrodes were fabricated. When the silver foil was used as the current

collector, the CuCl powder was first dispersed in acetone (~50 mg in ~5 mL) in an ultrasonic bath. The silver foil was then dipped in and removed from the mixture. Upon evaporation of acetone, a thin layer CuCl coating (≤100 μm thickness) was formed on the Ag foil. When the current collector was replaced by a molybdenum mesh disc (3 mm in diameter, attached to a Pt wire), the CuCl powder (~2 mg) was pressed (10 MPa) directly onto the substrate to form an assembled working electrode (cathode). The experiment was also repeated on a nickel foam strip (50 mm length, 6 mm width, immersion depth 4 mm) on which the salt powder was manually pressed into the end of the porous strip. These electrodes are each termed as CuCl–Ag, CuCl–Mo and CuCl–Ni in the following text.

All experiments in the ionic liquid were carried out in a glove-box that was dried by P₂O₅ and continuously purged with argon at room temperature. The aqueous solution of 0.1 mol L⁻¹ KClO₄ was used in ambient air, but argon was applied to deaerate and blanket the solution before and during electrochemical measurements. Two reference electrodes were used in this work: the Ag/Ag⁺ electrode (a silver wire in 0.01 mol L⁻¹ AgNO₃ in acetonitrile, connected to the electrolyte via a [BMIM]PF₆ bridge and porous alumina frits) and the saturated calomel electrode (SCE) in water. More details on the electrochemical experiments were previously described [21].

The electrolytic products from the IL were washed with acetonitrile twice, dried in vacuum and analysed directly by X-ray diffraction spectroscopy (XRD, SHIMADZU X-ray 6000 with Cu-Kα), energy dispersive X-ray analysis and scanning electron microscopy (SEM, SIRION-FEG). Samples for transmission electron microscopy (TEM, JEM-2010, 200 kV) were first dispersed in acetone by ultrasonication for 10 min, and then loaded on a carbon-film-coated copper grid (diameter: 3 mm).

3. Results and discussion

3.1. Solubility of transition metal chlorides in [BMIM]PF₆

Between 28 °C and 80 °C, the solubility of some chloride salts in [BMIM]PF₆ was measured. In accordance with the convention of reporting solubility, the solubility data are presented below as the mass of solute in 100 g solution: 1.02–1.13 mg, 13.4–16.4 mg, 99.6–119 mg, and 162–164 mg for CrCl₃, NiCl₂, CuCl and CuCl₂, respectively. On the other hand, simply adding excess CuCl to pure [BMIM]PF₆, and stirring for over 12 h at room temperature did not change the cyclic voltammogram (CV) of the IL using the Pt-disc electrode, implying that the dissolution of CuCl may also be kinetically difficult.

It was thought that the solubility of transition metal chlorides would increase in the presence of Cl⁻ ions due to formation of complex species [20,25]. Fig. 1a presents the CV measured in mixed [BMIM]Cl and [BMIM]PF₆ (1/20, v/v), showing the characteristic irreversible

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