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A general nonaqueous sonoelectrochemical approach to nanoporous Zn and Ni particles

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Abstract

For the first time nanoporous Zn and Ni particles were synthesized in dimethyl sulphoxide (DMSO) by a sonoelectrochemical method. The as-prepared samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen sorption. It was found that these nanopores were produced by the aggregation and/or melting of primary nanoparticles of about 4–5 nm in size under ultrasound irradiation after electrochemical reduction of metal ions. The utilization of nonaqueous solvent prevented the oxidation of these active metal nanoparticles, while the presence of poly-(vinylpyrrolidone) could inhibit the growth of the nanoparticles. This study provides a general method to continuously prepare nanoporous active metal particles from inorganic metal salts with high yields.

Keywords: Nanoporous particles; Zn; Ni; Sonoelectrochemical route; Nonaqueous electrolyte

1. Introduction

Nanoporous materials have attracted considerable interest in various chemical reactions for their high specific surface areas. Until now, there have been many researches on the synthesis of metal oxide [1–6]. But the study on nanoporous metals was limited. Recently, nanoporous metals have been synthesized by different routes, including chemical reduction by $NaBH_4$, electrodeposition of metal into the template and dealloying the less stable component in the alloys [7–9]. Among them, electrochemical method is an inexpensive and effective way since it directly uses electric current to reduce metal ions in solution. Moreover, some metal ions such as Zn^{2+}, which is difficult to be reduced by the chemical method, could easily be prepared by this method. Furthermore, if the anode material was used with the same as that of target metal, nanoporous metal particles could be produced continuously as long as the current flows through the solution. In the previous studies, nanoporous metals were usually prepared by electrodeposition into the template preformed on the surface of electrode [7], so it was difficult to release the products from the template to obtain nanoporous metal powders. Therefore, those methods could not meet the requirement for the continuous production of nanoporous metal powders with high yields.

Among the electrochemical routes to synthesize nanoporous metal, sonoelectrochemical reduction is a good candidate since the product can be separated from the cathode and easy to be collected by centrifugation. Metal ions were reduced on the surface of cathode and dispersed into the solution by the cavitation effect of the ultrasound. Reisse et al. first designed a device for the production of metal powders by the use of pulsed sonoelectrochemical reduction [10,11]. Since then, several kinds of metal and semiconductor nanoparticles have been prepared with this method [12–14]. For instance, Alex synthesized nanosized Zn particles in an aqueous system and studied the catalytic activity of the particles [15]. However, we found that nanosized Zn powder was highly active and easy to be oxidized in water under ultrasonic irradiation. As a result, most of the resulting Zn nanoparticles were oxidized into ZnO, resulting in low yield of Zn nanoparticles. Therefore, it is still a challenge to synthesize nanosized active metal particles with high yields.

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Here we report for the first time that nanoporous Zn and Ni particles could be synthesized in nonaqueous systems by a sonoelectrochemical method. Dimethyl sulphoxide (DMSO) was used as the solvent because of several reasons. These reasons include its good electric conductivity, high solubility for $ZnCl_2$, and prevention of the oxidation of Zn and Ni nanoparticles. The resulting metal particles were stable in the DMSO solution for several days. By adding poly-(vinylpyrrolidone) (PVP) into DMSO system, Zn and Ni particles with nanoporous structures could be obtained. Moreover, we found the electrical yields of nanoporous Zn and Ni particles were higher than 89%. A possible mechanism was presented to explain the formation of nanoporous structures.

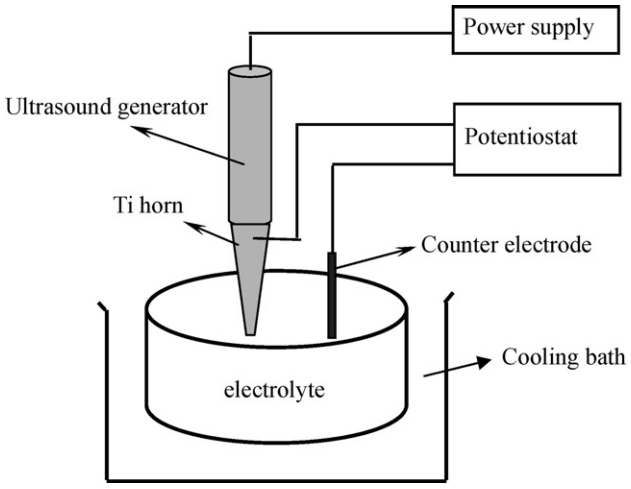
2. Experimental

2.1. Chemical reagents

All of the chemicals used in the experiment were of analytical grade. $ZnCl_2$, $NiCl_2$, DMSO (99.9%, water < 0.005%) and PVP (M_w = 40 000) were purchased from Shanghai Chemical Company.

2.2. Preparation of nanoporous Zn and Ni

The sonoelectrochemical instrument for synthesizing Zn and Ni nanoparticles was shown in Scheme 1. The cell was surrounded by a thermostat to control the temperature of electrolyte at required value. A JY92-2D ultrasonic processor (Ti horn, 6 mm in diameter, 20 kHz) worked as the ultrasound source and the Ti horn was immersed in the electrolyte as a cathode. Only the bottom of the Ti horn with the area of 0.28 cm^2 was exposed to the electrolyte, and other immersed part of the horn was covered with isolating material. Zn or Ni plate was used as the counter electrode in the electrolysis process. A potentiostat TD3691 acted as the current source and constant-current was applied to the cathode. The duration and off time of the ultrasonic pulse were respectively 2 and 0.5 s. The sonoelectrochemical experiments were carried out at an ultrasonic power intensity of 400 W and a current density of 10 mA cm^{-2}.



Scheme 1. Schematic diagram of the sonoelectrochemical instrument.

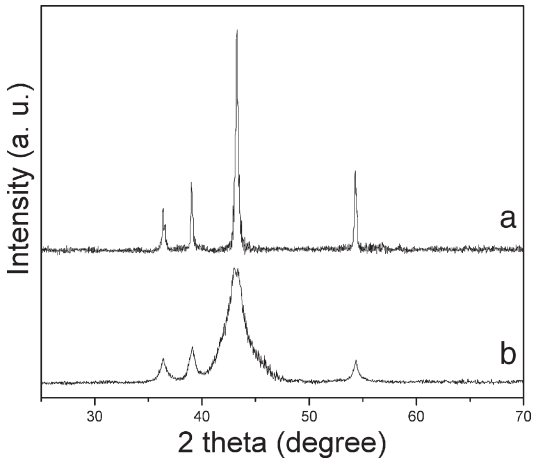


Fig. 1. XRD patterns of powders prepared in the DMSO electrolyte. (a) 20 mM $ZnCl_2$; (b) 20 mM $ZnCl_2$ and 50 g L^{-1} PVP.

In the experiments of producing Zn particles, the electrolyte was prepared by dissolving 20 mM $ZnCl_2$ in DMSO solvent with or without PVP. The volume of the electrolyte was 30 ml and all of the experiments were performed at 25 ± 5 °C. After reaction, the powder was collected by centrifugation, washed with ethanol twice and then dried in vacuum oven at room temperature for 24 h. The synthesis process of Ni was almost the same as that of Zn except for using the electrolyte containing 20 mM $NiCl_2 \cdot 6H_2O$.

2.3. Characterization

X-ray diffraction (XRD) patterns of the powders were recorded on a Philips MPD 18801 diffraction-meter (CuKα radiation, λ = 1.5418 Å, 20 kV, 150 mA). Scanning electron microscopy (SEM) imaging was performed using JSM-5600 SEM. Transmission electron microscopy (TEM) and high resolution transmission microscopy (HRTEM) images were analyzed by using JEM2010FEF TEM operating at a voltage of 200 kV. The sample was dispersed in ethanol and the mixture of dispersion was then dropped on carbon–copper grids for TEM analysis. Nitrogen adsorption and desorption isotherms at 77 K were measured by a Quantachrome NOVA2000e system.

3. Results and discussion

3.1. Zn particles

Our nonaqueous sonoelectrochemical routes mainly include two steps: electrodeposition of metals on the surface of Ti horn and subsequent dispersion of metal nuclei into the solution by ultrasonic cavitation. In the experiment, an ultrasonic processor worked as the ultrasound source and the Ti horn was immersed in the electrolyte as a cathode. After 30 min's electrolysis, the solution became black and the precipitate was centrifuged for analysis. Fig. 1 shows the X-ray diffraction (XRD) patterns of