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Growth of Pt–Ni Nanoparticles of Different Composition using Electrodeposition and Characterization of Their Magnetic Properties

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We prepared Pt₃Ni and PtNi₃ nanoparticles of various sizes on conductive and atomically smooth highly oriented pyrolytic graphite surfaces using potentiostatic electrodeposition. We can control the size of electrodeposited nanoparticles and their density on the surface by changing the deposition time. The morphology of nanoparticles was determined by scanning electron microscopy. PtNi₃ particles have spherical shape, while Pt₃Ni particles have more irregular shape. Composition of particles was confirmed by energy dispersive spectroscopy. We have measured magnetic properties of both systems with 100 s preparation time, superparamagnetic behavior was observed in PtNi₃ nanoparticles with blocking temperature $T_B = 225$ K.

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1. Introduction

Interest in nanotechnology and nanoparticle science has enhanced internationally over the past 20 years. Typical size of magnetic nanoparticles is in the range from 1 to 100 nm. These length scales provide their unique properties. Magnetic nanoparticles have a wide range of various applications. These applications use magnetic nanoparticles in a variety of forms, e.g. in solution as ferrofluids for audio speakers, as particle arrays in magnetic storage media [1], as surface, functionalized particles for biosensing applications [2], as powder compacts for power generation, conditioning and conversion, as contrasting agents in magnetic resonance imaging, in medical applications including magnetic targeted drug delivery, and alternatives to radioactive materials as tracers. Magnetic nanoparticles also provide an attractive alternative to conventional bulk magnetocaloric effect materials [3]. Electrodeposition is a simple, reproducible, and scalable approach for producing of thin films. The alloy composition is a monotonic function of deposition potential, with chemically homogeneous films being obtained by potentiostatic deposition at room temperature. Given a suitable conductive support, thin alloy catalyst films can be synthesized in a matter of seconds to minutes [4]. We have investigated this preparation technique to produce Pt-Ni nanoparticles with different composition.

2. Experimental methods

Two types of Pt-Ni alloy nanoparticles with different composition were prepared using electrodeposition

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technique under potentiostatic conditions. The composition of $Pt_{100-x}Ni_x$ alloy was controlled by the potential applied during deposition to obtain particles with chemical composition Pt₃Ni and PtNi₃ (Fig. 1). Pt₃Ni nanoparticles were electrodeposited at -0.300 V and PtNi₃ nanoparticles at -0.600 V versus a saturated calomel electrode (SCE) on highly oriented pyrolytic graphite (HOPG). Deposition time of 100 s was used. Nanoparticles were grown from solution consisting of 0.003 mol/l K₂PtCl₄, 0.1 mol/l NiCl₂, and 0.5 mol/l NaCl with pH adjusted to 2.5 by addition of HCl and/or NaOH. All solutions were prepared using ultrapure deionized water with electrical conductivity 18 M Ω cm. The electroplating cell consisted of closed glass beaker containing 50 ml of the plating solution. We used Ag/AgCl reference electrode (RE), platinum wire as a counter electrode (CE) and HOPG substrate connected to a platinum wire using a carbon paste as a working electrode (WE) (see Fig. 2).

In order to reduce the influence of surface contaminants, the top layer of HOPG was peeled off before each experiment using plastic tape. Pt-Ni nanoparticles were electrodeposited by immersion of the WE into electrolyte at controlled potential. Growth of nanoparticles was terminated by removing WE from plating solution after predetermined time followed by rinsing the deposit with ultrapure deionized water. Performing the rinsing step promptly helped to minimize galvanic displacement of deposited Ni component by residual Pt^{2+} in the hanging meniscus.

Magnetic properties of selected nanoparticles were studied using a Quantum Design SQUID magnetometer in the temperature range from 5 K to 300 K. The sample with area of $5 \times 5 \text{ mm}^2$ was held in the plastic straw and the magnetic moment was measured with the magnetic field of 50 Oe applied parallel to the deposition surface along one of 5 mm sides.

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Fig. 1. Potential dependence of the composition of the electrodeposited $Pt_{100-x}Ni_x$ alloy films. Reprinted with permission from [4]. Copyright (2016) by American Chemical Society.



Fig. 2. Schematic representation of: (a) electrical circuit of a typical three-electrode cell in potentiostat, (b) experimental setup for the three-electrode cell.

3. Results and discussion

 Pt_3Ni and $PtNi_3$ nanoparticles were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The morphology of Pt–Ni nanoparticles grown for 100 s at different potentials was examined (see Fig. 3 and Fig. 4). As one can see, Pt_3Ni nanoparticles have irregular thorn-like shape with average size approximately 164 nm and wide particle size distribution (Fig. 5), while $PtNi_3$ nanoparticles have spherical shape with diameter of around 133 nm with narrow particle size distribution (Fig. 6).

Composition of prepared nanoparticles was characterized by EDS and experimental results showed good agreement with the required chemical composition of Pt_3Ni and $PtNi_3$ nanoparticles.

Magnetic measurements were performed to probe possible particle size effect in nanoparticles grown for 100 s. The temperature dependence of magnetic moment of both Pt_3Ni and $PtNi_3$ nanoparticles on HOPG measured in zero-field cooled (ZFC) and field-cooled (FC) mode is shown in Fig. 7. For comparison, the magnetic moment of pure HOPG substrate was also measured. Only a small diamagnetic contribution from Pt_3Ni nanoparticles was observed in addition to magnetic moment of HOPG substrate. This was expected since bulk Pt_3Ni alloys have no net magnetic moment in comparison to $PtNi_3$ [5]. It should be noted that a small difference between ZFC and FC data measured on HOPG (and Pt_3Ni nanoparticles on HOPG) is an evidence of already well-known defectinduced ferromagnetism observed in several carbon-based materials [6].



Fig. 3. SEM image of $\rm Pt_3Ni$ nanoparticles electrode-posited at -0.300 V on HOPG.



Fig. 4. SEM image of $PtNi_3$ nanoparticles electrodeposited at -0.600 V on HOPG.

Although, only about 3 μ g of the alloy (as estimated from the particle size distribution and density of deposited nanoparticles) is contributing to the total magnetic moment, a clear evidence of dominant magnetic moment of nanoparticles was obtained for PtNi₃ sample. The temperature dependence of the magnetic moment of PtNi₃ nanoparticles exhibits features of superparamagnetic systems [7]: a difference between ZFC and FC measurements and a round maximum in ZFC curve. The position of maximum in ZFC magnetic moment was taken as the blocking temperature $T_B \approx 225$ K. Due to the relatively large average size of nanoparticles (133 nm) we expect that the resulting magnetic properties cannot be described only by a simple model of single-domain super-



Fig. 5. Histogram of size distribution of Pt_3Ni nanoparticles on HOPG substrate.



Fig. 6. Histogram of size distribution of $PtNi_3$ nanoparticles on HOPG substrate.



Fig. 7. Temperature dependence of magnetic moment of Pt_3Ni and $PtNi_3$ nanoparticles on HOPG substrate and pure HOPG measured in applied magnetic field of 50 Oe. Different scale is used to show the details of HOPG and Pt_3Ni nanoparticles magnetic moment. Both ZFC and FC data are measured during the temperature increase.

paramagnetic particles (e.g. reported critical size of Ni nanoparticles is 24 nm [8]). Also the influence of the substrate on inter-particle interaction needs to be elucidated in further studies [9].

4. Conclusion

We have grown Pt_3Ni and $PtNi_3$ alloy nanoparticles on HOPG using potentiostatic electrodeposition technique. We successfully demonstrated that this technique could be used to produce not only thin films, but also nanoparticles. Composition of nanoparticles could be varied by adjusting the deposition potential. The particle size and their density on surface of HOPG substrates can be controlled by changing the deposition time. The nanoparticles were characterized by SEM and EDS. Electrodeposition allows tuning the size and composition of $Pt_{100-x}Ni_x$ nanoparticles, which affects their magnetic behavior. Magnetic studies revealed that Pt_3Ni system is diamagnetic and $PtNi_3$ nanoparticles grown for 100 s exhibit a superparamagnetic behavior with the blocking temperature 225 K.

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