



Optimal synthesis and magnetic properties of size-controlled nickel phosphide nanoparticles



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ABSTRACT

Pulse discharge method was used in liquid phase to prepare nickel phosphide nanoparticles. The size and morphology of the as-prepared nanoparticles were found to be easily controlled through changing reaction parameters such as temperature, reactants concentration, reactants molar ratio, pulse discharge number, and pulse discharge voltage. The optimal reaction parameters have been obtained by single-factor experiments. X-ray diffraction, X-ray absorption fine structure spectra, Field Emission Scanning Electron Microscope, and Energy Dispersive X-ray Spectrum were used to characterize the as-prepared Ni–P nanoparticles. Vibrating Sample Magnetometer was used as magnetic measurements of the Ni–P nanoparticles. The results demonstrate that the as-prepared Ni–P nanoparticles are in amorphous phase, and consist of Ni and P elements. The P-content in the as-prepared Ni–P nanoparticles increases with the increasing of Ni–P particle size, and is independent on the initial concentration of P-concentration in the reaction solution. The Ni–P nanoparticles have totally about 12 near-neighbors of Ni–Ni and Ni–P around center Ni. The Ni–Ni distance increases with the increasing particle size. The as-prepared Ni–P nanoparticles present paramagnetic nature. Their saturated magnetizations are also size-dependent. The larger Ni–P particles has lower saturated magnetization, which can be attributed to the entrance of P into Ni lattice, causing a larger Ni–Ni separation and a looser, distorted local atomic structure.

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1. Introduction

Nickel phosphides are a class of compounds that have properties similar to those of ordinary metallic compounds such as carbides, nitrides, borides and silicides. They are good conductors of heat and electricity and they have high thermal and chemical stability. Due to their properties of fundamental and commercial interest, transition metal phosphides have been used as excellent catalysts for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) [1], electrocatalysts for hydrogen evolution reaction (HER) [2], magnetic storage for their magnetic properties [3], and electrode materials for Li batteries [4,5]. Therefore, the synthesis of nickel phosphides has attracted extensive attention since several decades. Multiple synthesis routes, for example, the solid phase reaction [6], the solution-phase reaction [7–10], the decomposition of single source precursors [11], the thermolysis of nickel

compounds [12], and relatively inexpensive synthesis method [13], have been reported for the preparation of nickel phosphides with different shapes (solid particles, core–shell particles, rods, and wires) in recent years. Synthesis methods of amorphous nickel phosphide nanoparticles have also been developed [14,15]. However, the report about size-controllable synthesis of Ni–P nanoparticles is scarce. Little is known about their local ordering and the implications of their structure on their novel properties due to the limitation of X-ray diffraction (XRD) and transmission electron microscope (TEM) techniques [16].

Although techniques that enable the structure characterization of bulk material have been well-developed, the characterization of material at the nanoscale still presents significant challenges. The dominance of surface facets, small size and poor crystalline order makes characterization of nanoparticles difficult. X-ray absorption spectroscopy (XAS) is a method that has been used to resolve the structure of colloidal nanocrystals. With the use of the X-ray beam available through synchrotron radiation facility, XAS spectra can be obtained and used to gain insight into material structural

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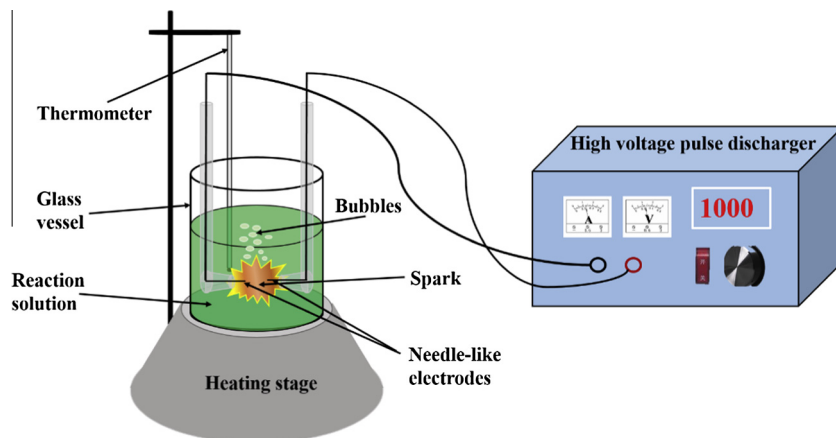


Fig. 1. Schematic map of synthesizing Ni-P nanoparticles with pulse-discharge appliance.

properties [17,18]. The structures of amorphous and crystalline phases can be determined through both X-ray-absorption near-edge-structure (XANES) spectrum to resolve geometric configuration, and extended X-ray-absorption fine-structure (EXAFS) to resolve radial structure, including interatomic distances, coordination numbers, and mean-squared disorder [19].

In this paper, a size-controllable preparation of nickel phosphide nanoparticles was performed through pulse discharge method. Reaction conditions such as temperature, solution concentration, reactants molar ratio, pulse number and pulse voltage were adjusted to obtain nanoparticles with different size distributions. Field Emission Scanning Electron Microscope (FESEM) pictures and Energy Dispersive X-ray Spectrum (EDS) spectra were collected through traditional laboratory experiments to determine morphology and composition of the as-prepared nanoparticles. XRD patterns and X-ray-absorption fine-structure (XAFS) spectra from both Ni K-edge and P K-edge were collected at Beijing Synchrotron Radiation Facility (BSRF) to resolve phase and atomic ordering. Size-dependent magnetic property was also measured through Vibrating Sample Magnetometer (VSM).

2. Experiments

2.1. Preparation of samples

A pulsed-discharge method was used to prepare the Ni-P nanoparticles. The pulse discharge generator is home-made with a peak voltage of 1200 V and a peak current of 6 A. The schematic map of this one-step pulsed-discharge appliance is described in Fig. 1. Two commercially available reagents, i.e. nickel-sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) and sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), were directly used as the raw materials without further purification. The preparation detail of the reaction solution is described as follows: firstly, 262.8 g of nickel-sulfate hexahydrate was dissolved into distilled water to get the nickel-sulfate solution with concentration of 1 mol/L, and 211.8 g of sodium hypophosphite was also dissolved into distilled water to get the sodium hypophosphite solution with concentration of 2 mol/L. 20 ml of the nickel-sulfate solution and 20 ml of the sodium hypophosphite were mixed to get a 40 ml mixture solution of nickel-sulfate and sodium hypophosphite. Then, the mixture solution was stirred and heated on a magnetic stirring and heating stage. The solution temperature was monitored with a thermometer. A pair of needle-like electrodes about 3 mm apart were immersed into the mixture solution. This mixture solution was heated to a certain temperature with a heating rate of $10^\circ\text{C min}^{-1}$. During the heating process, the dark green¹ mixture solution was gradually faded to light green. When the solution temperature reached to given temperature, several pulse discharges were applied to the solution, appearing bright yellow and/or white light simultaneously. These pulse discharges triggered the formation process of Ni-P nanoparticles. Almost at the same time, the solution around the electrodes turned turbid and black, indicating the formation of nickel phosphide

nanoparticles. The formation rate of nickel phosphide nanoparticles can be controlled by simply changing the solution temperature. When the reaction solution was poured into freezing ice water, further reaction was sharply slowed up or even stopped. Finally, the black Ni-P nanoparticles were separated and collected from the solution by centrifugation after the solution was washed, respectively, by distilled water and ethanol three times. Black nickel phosphide nanoparticles were obtained after the deposit was dried at 45°C in a furnace for 4 h.

2.2. Characterization methods

The particle size and morphology were observed by the Zeiss SUPRA 55 FESEM, and the composition was measured by EDS. In addition, the XRD patterns of nickel phosphide nanoparticles were collected at Beamline 4B9A in BSRF with an X-ray wavelength of $\lambda = 1.5406 \text{ \AA}$.

XAFS measurements at Ni K-edge were also performed in transmission mode at Beamline 4B9A in BSRF. The storage ring of BSRF was operated at 2.5 GeV with a maximum current of 250 mA. An approximate X-ray photon flux of $10^{11} \text{ photons s}^{-1}$ was monochromatized using a double-crystal Si (111) monochromator to choose the incident X-ray energy from 8133 to 9133 eV with an energy resolution ($\Delta E/E$) of about 2×10^{-4} . The incident and transmission X-ray intensities were collected with ion chambers. P K-edge XAFS data were collected at Beamline 4B7A also in BSRF. The incident X-ray energy was also chosen by a double-crystal Si (111) monochromator. The Ni-P powder samples were smeared on a carbon adhesive tape, which was mounted into a vacuum chamber for XAFS measurements. The P K-edge XAFS spectra were collected in fluorescence mode with a scanning energy range from 2100 to 2754 eV. The fluorescence signal was collected with a Si (Li) detector.

3. Results and discussion

3.1. Effects of reaction parameters on particle size distribution and morphology

In order to control the particle size of the as-prepared Ni-P nanoparticles, five groups of single-factor experiment were carried out under different temperatures, reactant concentrations, reactant ratios, pulse numbers and pulse voltages. Each impact of the five reaction parameters on the size-distribution and morphology of Ni-P nanoparticles were investigated. In these experiments, only one of the reaction parameters was variable at each time, while the others were kept constant. The detailed preparation conditions for each group were listed in Table 1. The as-prepared Ni-P nanoparticles' sizes were counted based on the FESEM micrographs. In some cases, the particles are easy to aggregate together, which increases the difficulty to count the particle size. However, after enlarging the FESEM pictures, the outlines of these aggregated particles are enough visible to measure the particle sizes. The particle-size distributions and the counting numbers of particles are shown in Fig. 2. The size distributions and morphologies of the as-prepared Ni-P nanoparticles changed with reaction temper-

¹ For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

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