

Preparation of monodisperse Ni nanoparticles and their assembly into 3D nanoparticle superlattices



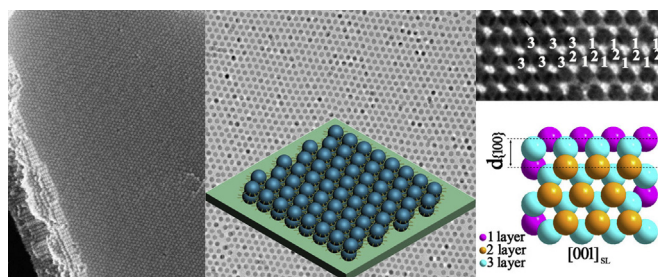
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HIGHLIGHTS

- A facile solution route to monodisperse Ni nanoparticles with tunable sizes.
- 3D Ni nanoparticle superlattices are formed on different substrates.
- A dominant large-scale hcp symmetry is observed on carbon film substrate.
- Typical structural parameters are obtained on the 3D nanoparticle superlattices.
- The demonstrated method gives a convenient access to study collective properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Monodisperse Ni nanoparticles with sizes varying from 4.8 to 11.3 nm are prepared via a one-pot reaction that involves the reduction of nickel(II) acetylacetonate in oleylamine in the presence of trioctylphosphine and 1,2-hexadecanediol. Reaction parameters such as temperature and the concentration of capping agent and metal precursor are critical for the adjustment of particle size. The decrease of crystallinity is observed for the samples with smaller particle sizes, which significantly affects the magnetic properties. Three-dimensional (3D) superlattices that are composed of Ni nanoparticles with different sizes are obtained on different substrates by a facile self-assembly process, and are characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and small-angle X-ray diffraction (SAXRD). The Ni nanoparticle superlattices formed on carbon-coated TEM copper grids exhibit a dominant hexagonal close-packed (hcp) symmetry, although local fcc packing is also occasionally observed. The formation of 3D nanoparticle superlattice structures on Si substrates is confirmed from the SAXRD measurements. The method revealed in this study for the preparation of 3D superlattices composed of Ni nanoparticles with tunable sizes offers the potential to explore their interesting collective properties for multiple applications.

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1. Introduction

Ni nanoparticles represent an important transition metal nanomaterial that has widely practical applications because of their

valuable catalytic, magnetic and electronic properties. Up to now, many synthetic methods have been developed to prepare Ni nanoparticles with a broad size range [1–21]. Aqueous methods that involve the reduction of Ni inorganic salts by boron hydrides or hydrazine can easily generate Ni nanoparticles [2–4]; however, the control over particle size and morphology cannot be easily achieved. Polyol synthesis is another route for the synthesis Ni nanoparticles with highly uniform sizes in large scale [7–9]. The major

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limitation of polyol synthesis is that it is not easy to obtain nanoparticles with small sizes (e.g. <10 nm) even through heterogeneous nucleation using noble metal seeds or fast nucleation using strong reducing agents. The robust method for the preparation of Ni nanoparticles with highly narrow size distribution and high crystallinity is the nonaqueous synthetic route in which Ni precursors such as Ni acetylacetonate or acetate form metal-surfactant complexes with certain chemical compounds (e.g. oleylamine and trioctylphosphine) at first, then they are reduced in high-boiling-point organic solvents at an elevated temperature to generate metallic nanoparticles [1,10–21]. This nonaqueous synthetic approach usually can generate nanoparticles with a narrow size distribution and high crystallinity, and is especially suitable for the synthesis of monodisperse nanoparticles. However, it is still needed to explore simple but effective methods that are capable of producing monodisperse Ni nanoparticles having tunable sizes without changing the nature of capping ligands or the reducing agents.

Monodisperse Ni nanoparticles with a highly narrow size distribution are not only meaningful for their existing technique applications, but also they can be used as building blocks for the construction of self-assembled superlattices that may exhibit new collective properties arising from interactions between neighboring nanoparticles. The nanoparticle superlattices that consist of ordered arrays of one or more types of nanoparticle units represent a new type of artificial solid materials that have properties determined by both individual nanoparticle units and their collective interactions. They have been used for the fabrication of diverse nanoparticle-based devices [22,23]. The self-assembly of Ni nanoparticles into three-dimensional (3D) superlattices arouse intensive interests from the perspectives of both fundamental research and application purpose. Since the magnetic behaviors of 3D Ni nanoparticle superlattices are affected by the dipole–dipole interactions that vary with different crystalline structures, it is important to build specific 3D superlattices which can be used to clarify the relationship between the structure and magnetic properties. Besides, 3D Ni nanoparticle superlattices may also find potential applications such as high-density magnetic storage media. However, compared to numerous reports on the preparation of the 3D nanoparticle superlattices such as GdSe [24,25], Au [26–29], Ag [30–34] and Co [35,36], reports on the preparation of Ni nanoparticle superlattices are not common. Very limited information is available on the self-assembly methods and structural information of Ni nanoparticle superlattices formed under different experimental conditions.

In this study, we have synthesized monodisperse Ni nanoparticles with tunable sizes using a simple one-pot reaction. The important reaction parameters on the control of particle size have been identified, and the structure and magnetic properties of the prepared Ni nanoparticles have been characterized. We also demonstrate that the as-prepared Ni nanoparticles can self-assemble into 3D superlattices on carbon-coated copper grids and Si substrates by a facile self-assembling process. The structures of the superlattices assembled using Ni nanoparticles with different sizes have been investigated. The methods revealed in this study for the synthesis and self-assembly of Ni nanoparticles also give a convenient access to the further study of their interesting collective properties.

2. Experimental

2.1. Synthesis of monodisperse Ni nanoparticles

The synthesis of Ni nanoparticles is based on the methods reported in previous studies [13–15]. For the synthesis of 11.3 nm Ni nanoparticles, 1 mmol of nickel(II) acetylacetonate ($\text{Ni}(\text{acac})_2$, 96%, J&K), 2 mmol of 1,2-hexadecanediol (>98%, TCI) and 21 mmol of oleylamine (80–90%, Acros) were mixed together and stirred

magnetically at 65 °C in a flow of high-purity argon gas. When the mixture was completely dissolved, ~1.5 mmol of trioctylphosphine (TOP, 97%, Strem) was injected into the flask, followed by resetting the temperature to 120 °C and kept for 10 min. Then the mixture was rapidly heated to 210 °C for nucleation and ripening. After 45 min, the synthesis was halted and cooled to room temperature. 80 mL of hexane along with 100 μL of oleic acid was added into the flask. After ultrasonication for 10 min, acetone was added into the dispersion and the nanoparticles were precipitated by centrifugation. For the synthesis of 6.4 nm Ni nanoparticles, the molar quantity of the $\text{Ni}(\text{acac})_2$ was reduced to 0.25 mmol while the volume of the oleylamine was reduced to 6 mmol. Other parameters and processing procedures were kept the same as those for 11.3 nm Ni nanoparticles. For the synthesis of 4.8 nm Ni nanoparticles, the amount of TOP was increased to 4 mmol, and the reaction temperature decreased from 210 to 195 °C, while other parameters were kept fixed. The nanoparticles were harvested through the same way as that for 6.4 nm Ni nanoparticles after synthesis.

2.2. Self-assembly of Ni nanoparticles

For the self-assembly of 3D Ni nanoparticle superlattices, 300–400 μL of the toluene dispersion containing Ni nanoparticles (typically ~7 mg mL^{-1}) and oleic acid (~1.7 $\mu\text{L mL}^{-1}$) was transferred into a small glass vial in which a treated Si substrate had been placed flatly on the bottom. The Si substrate for supporting nanoparticles was washed by ultrasonication in acetone and ethanol alternately for four times. Then it was immersed in HF solution under ultrasonication for 2 min, picked out and washed with ethanol. The vial was sealed with a matched cap with a pore diameter of 0.5 mm as an outlet. The setup was left undisturbed in ambient temperature (24 ± 2 °C) until the solvent volatilized completely. To obtain the superlattices on the carbon-coated copper grid for transmission electron microscopy (TEM) measurement, much less (~60 μL) of the above toluene dispersion was transferred into the glass vial, and other procedures are the same as those mentioned above.

2.3. Characterization

TEM images of the Ni nanoparticle superlattice samples deposited on carbon-coated TEM copper grids were taken with a JEM 1400 and a JEM 2100 transmission electron microscopes. The averaged particle sizes were obtained from measuring the diameters of about 100 particles shown in the TEM images. The scanning electron microscopy (SEM) images of Ni nanoparticle superlattice samples deposited on Si substrates were acquired using a LEO 1530 scanning electron microscope. Small-angle X-ray diffraction (SAXRD) operated by a Panalytical X'pert PRO X-ray diffractometer with $\text{Cu K}\alpha$ radiation was used to inspect the long-range ordered structure of the samples deposited on Si substrates. The measurement angles ranged from 0.4 to 3° at a step size of 0.02°.

3. Results and discussion

The employed synthetic method utilizes oleylamine both as the solvent and the reducing agent, and no additional reducing agent such as NaBH_4 and hydrazine are needed to reduce Ni precursors. Although TOP also has a reducing effect, the relatively fast reduction of $\text{Ni}(\text{acac})_2$ by oleylamine was confirmed in a recent study [15]. TOP mainly serves as a capping agent for the control of particle size. This has been demonstrated in several previous studies [1,10,13–15]. However when TOP is subjected to partial oxidation

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