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The shape dependence of magnetic and microwave properties for Ni nanoparticles

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ABSTRACT

The magnetic and microwave properties of Ni nanospheres and conical nanorods have been investigated through experimental and theoretical methods. Ni nanospheres and conical nanorods have the same crystal structure and close particle size, whereas the remanence ratio, coercivity, dynamic permeability and microwave absorbing properties show great dependence on their shape. Ni conical nanorods self-assembled into urchin-like structure have higher natural resonance frequency due to the large shape anisotropy compared to the Ni nanospheres. Supposing random spatial distribution of magnetic easy axes and using the Landau–Lifshitz–Gilbert equation associated with the Bruggeman's effective medium theory, we simulate the complex permeability of Ni nanoparticles, which agrees well with the experimental results.

Ferromagnetic metals have been paid much attention in microwave application due to their higher saturation magnetization and permeability compared to ferrite. Such materials which were expected as high density recording media, magnetic field sensor or electromagnetic wave absorption material should have high value of complex permeability, tunable resonance frequency and low eddy current loss in microwave range [1–5]. Considerable works have investigated the complex permeability of metal-based magnetic material through experimental or theoretical method. It is widely proved that the magnetic properties and microwave properties of ferromagnetic nanoparticles are related to their size and shapes [6–8]. As the particle size decreases, eddy current loss can be considerably suppressed and when it comes into nanometer scale, surface effect [9], size effect [10,11] combined with shape anisotropic effect [12–14] become dominant in the magnetic and microwave properties. The behavior of the complex permeability in microwave frequency should ascribe to such mixed effect to clarify which we should find a proper way to separate the size, surface and shape effect. In our present work, we compared Ni nanospheres with Ni conical nanorods to research the shape effect on the static magnetic properties (coercivity and remanence ratio), complex permeability and microwave absorbing properties. Landau–Lifshitz–Gilbert equation associated with the Bruggeman's effective medium theory were used to simulate the complex permeabilities of Ni nanospheres and conical nanorods supposing random spatial distribution of magnetic easy axes.

To prepare Ni nanospheres, 25 ml alcoholic solution of 0.1 M $NiCl_2 \cdot 6H_2O$, 25 ml alcoholic solution with 0.2 g polyvinyl pyrrolidone (PVP, $K=30$), 50 ml alcoholic solution of 0.5 M NaOH and 6 ml hydrate hydrazine ($N_2H_4 \cdot H_2O$ 80%) were mixed together. Then, the mixed solution was heated to 80 °C for 3 h. After washing and desiccation, the spherical Ni nanoparticles were obtained. To prepare Ni conical nanorods, 25 ml alcoholic solution of 0.1 M $NiCl_2 \cdot 6H_2O$ and 25 ml alcoholic solution with 0.2 g PVP were mixed, and 6 ml hydrate hydrazine was added into the above solution dropwise at 70 °C. A pink suspension was obtained immediately. The as-prepared suspension was added dropwise into a mixed solution with 50 ml alcoholic solution of 0.5 M NaOH and 10 ml hydrate hydrazine in a three-necked flask at 80 °C. Then, the solution was refluxed for 3 h. After washing and desiccation, Ni conical nanorods self-assembled into urchin-like structure were obtained.

The scanning electron microscopy (SEM) observations were carried out to investigate the morphology of Ni nanoparticles. Ni nanospheres with a mean diameter of 30–50 nm are shown in Fig. 1(a) while conical nanorods radially growing from one center into urchin-like architectures are shown in Fig. 1(b). The nanorods have diameters in the range of 25–50 nm and lengths up to 500 nm. Fig. 1(c) shows the X-ray diffraction (XRD) patterns of the as-prepared Ni nanospheres and conical nanorods. All diffraction peaks can be indexed with the face-centered cubic (fcc) Ni. No additional diffraction peaks from the impurities such as nickel oxide or hydroxide were detected. The broad diffraction peaks, which are quantified by the full-width at half-maximum (FWHM) are indicative of the ultrafine Ni particles. Furthermore, the average grain dimensions are estimated to be 30 nm for nanospheres and 35 nm

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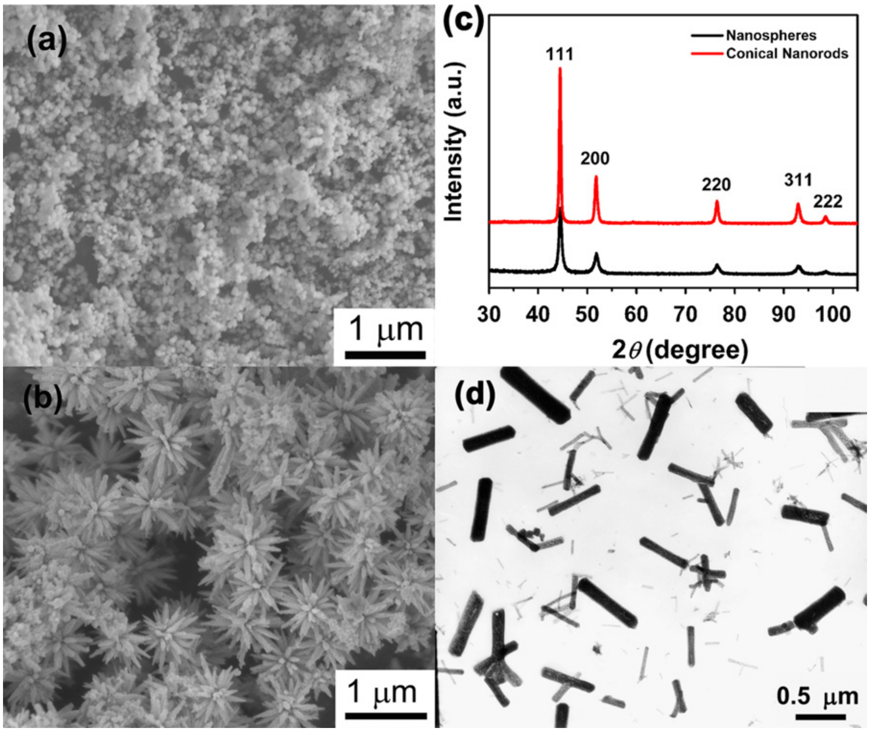

Fig. 1. The SEM micrographs of Ni nanoshperes (a) and conical nanorods (b); XRD patterns of the Ni nanospheres and conical nanorods (c); TEM micrograph of the as-synthesized coordination compound (d).

for conical nanorods with the FWHM (with the instrumental peak width eliminated) of the (111), (200) and (220) crystallographic planes according to the Scherrer equation. The calculated grain sizes are consistent with the diameters of nanospheres and nanorods, which suggests that both the Ni nanospheres and the conical nanorods obtained by wet chemical methods are single crystal.

It was found that the adding sequence of the reactants plays a dominant role in the control of crystal morphology. The adding sequence of the reactants dominated the formation of intermediates in the reduction procedure. Conical rods were not obtained unless the intermediate known as coordination compound $Ni(N_2H_4)_xCl_2$ was formed through the reduction reaction. To research the mechanism of the formation of conical nanorods, we investigated the morphology and composition of the intermediate. It is found that the probable chemical formula is $Ni(N_2H_4)_3Cl_2$ based on the weight percentages of 26.17, 37.44 and 5.34 wt% for Ni, N and H, respectively, by atomic emission spectrometer and elemental analysis. Fig. 1(d) shows the transmission electron microscopy (TEM) observations of the $Ni(N_2H_4)_3Cl_2$ synthesized at 70 °C. All particles are rod-like maintaining diameters about 100–300 nm and lengths up to 400–600 nm. The formation of coordination compound is probably attributed to the nature of the electrostatic attraction. As we know, each nitrogen in hydrazine has a couple of unbonded electrons, so that hydrazine is eager to absorb positive charged ions such as Ni^{2+}. It is reasonable to conclude that such rod-like coordination compound can serve as an in-situ template resulting in the Ni conical nanorods. However, the bond energy of OH^- and Ni^{2+} is larger than that of N_2H_4 and Ni^{2+} so that the rod-like coordination compound can only be ensured by adding $N_2H_4 \cdot H_2O$ first into the $NiCl_2$ solution, and without the rod-like coordination compound as the precursor, Ni conical nanorods cannot be synthesized.

The M–H hysteresis loops of the Ni nanospheres and nanorods are illustrated in Fig. 2(a). It can be seen that they are both ferromagnetic and their coercivity (H_c) and remanence ratio (M_r/M_s) are 134 Oe, 0.32 and 279 Oe, 0.38, respectively. The H_c and M_r/M_s of the Ni conical nanorods are both higher than that of the Ni nanospheres. Considering that the nanospheres and conical nanorods have close grain size and particle diameter, such discrepancy in H_c and M_r/M_s is probably due to the effect of shape anisotropy. As we know, the effective anisotropy, which is the sum of magnetocrystalline and shape anisotropy, is directly proportional to the coercivity. Along long axis of the nanorods the demagnetizing field is much smaller compared to that of short axis, which means the pinning of the magnetization in the long axis direction. Such pinning effect usually makes the magnetization harder to reverse so that higher H_c and M_r/M_s compared to isotropic structures. This is why the H_c and M_r/M_s of Ni conical nanorods is higher than that of Ni nanospheres.

The saturation magnetization of the bulk Ni at 300 K is 55.0 emu/g [15]. Both of the saturation magnetizations of nanospheres (45.02 emu/g) and nanorods (43.77 emu/g) are smaller than that of bulk Ni. There are several reasons for the decrease in M_s such as the surface oxidation, the nonmagnetic or weakly magnetic interfaces [16], the ligand effect on the particle surface, etc. It was inevitable to have oxidation layers for ultra fine nanoparticles in our present work. The oxide layer of the Ni particle is an antiferromagnet, so that the presence of such layers usually has no contribution to the M_s and lowers the magnetic moment per unit mass, and the spin of nickel which is close to the oxide layer is pinned due to the exchange anisotropy interaction between the antiferromagnetic layer of NiO and the ferromagnetic core of Ni [17]. Furthermore, poor magnetic properties found for nanoparticles were usually related to the presence of precursor residues coordinated on the surface. It is well known that strong π–acceptor ligands, such as carbon monoxide, induce a dramatic collapse of the saturation magnetization [18,19]. In our experimental system, PVP which is a widely used surfactant serves as a dispersant. It usually absorbs on the surface of Ni nanoparticles, so that the saturation magnetization might also decrease through the ligand effect of carbonyl groups in PVP.