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Structure and magnetic properties of flower-like α-NiS nanostructures

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ABSTRACT

In this paper we report the structure and magnetic properties of flower-like α-NiS nanostructure prepared by a facile one-step hydrothermal method. The flowers consist of polycrystalline nanoflakes, and the nanoflakes are composed of single crystalline nanocrystals with an average size of about 15 nm. The α-NiS flowers exhibit the transition from paramagnetism to ferromagnetism with the blocking temperature of about 12 K. The field dependences of the magnetization prove that these flowers demonstrate a coexistence of antiferromagnetism and ferromagnetism at 5 K, and exhibit a strong paramagnetic response at temperature higher than 100 K.

1. Introduction

Magnetic nanostructures, such as nanoparticles, nanowires, multilayers and nanojunctions, are especially important for studying nanomagnetism and for technological applications. The 20 nm nanoparticle is usually in a single domain state with all spins align in one direction [1,2]. In a strict sense, ferromagnetism is limited to infinite magnets, because thermal excitations in finite magnets cause the net moment to fluctuate between opposite directions. In practice, it is difficult to distinguish the magnetism of particles larger than about 1 nm from true ferromagnetism, because interatomic exchange ensures well-developed ferromagnetic correlations inside the particles [1]. The surfaces and interfaces have a strong impact on nanomagnetism.

Transition metal Ni sulfides represented by NiS and NiS_2 are important materials to study the physics of a system with strong electron correlation involving, for instance, the metal–insulator transition, in which elucidation of the mechanism responsible for the magnetism and electric transport has been a subject of great interest [3–5]. NiS has two polymorphs of the low-temperature rhombohedral (β-NiS) and high-temperature hexagonal (α-NiS) crystal structures. The high-temperature α-NiS phase is antiferromagnetic and exhibits a metal–insulator transition with an abrupt change in magnetic susceptibility when it is cooled below a transition temperature, i.e. Neel temperature $T_N = 271$ K. Below transition temperature α-NiS has a magnetic moments of about $1.7\mu_B$; however, above the transition the moment appears negligibly small [6,7], and Neel suggested that some small antiferromagnetic particles, due to the uncompensated number of spins on two sublattices, should exhibit superparamagnetism and weak ferromagnetism [8].

α-NiS is a well studied traditional material with potential application as hydro-desulphurization catalyst, cathodic material and solar storage. α-NiS nanostructured materials with different morphologies have been reported, such as nanoparticles [9,10], hollow nanospheres [11], nanorods [12,13], nanotubes [14] and urchin-like nanostructures [15–17]. Anomalous properties have been observed in those nanoscale nickel sulfides due to size effect compared to its bulk counterpart, which is significant for basic research and technical applications. In this paper, the magnetic properties of flower-like α-NiS nanostructures were reported, and it was found that the flowers show a coexistence of antiferromagnetism and ferromagnetism at 5 K, and exhibit a strong paramagnetic response at temperature higher than 100 K.

2. Experimental

Flower-like α-NiS nanostructures were prepared by a hydrothermal method. In a typical preparation process, 1 mmol allyl thiourea and 1 mmol $NiSO_4$ were added to 50 ml deionized water and stirred vigorously for 10 min. Then the solution was

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transferred into a Teflon-lined stainless steel autoclave of 65 ml capacity. The system was maintained at 170 °C for 10 h and then cooled to room temperature naturally. The precipitate was washed with deionized water and absolute ethanol for several times, and finally was dried at 60 °C for 3 h.

The structure of the as-prepared product was determined by X-ray powder diffraction (XRD) using a Philips X'Pert diffractometer with the Cu Kα line. The morphology was characterized by field emission scanning electron microscope (SEM) (Sirion 200 FEG), transmission electronic microscope (TEM, JEM-2010) and high resolution transmission electron microscope (HRTEM, JEOL 2010). X-ray photoelectron spectroscopy (XPS, VG ESCALAB MK II, Mg Kα) was used to determine the chemical bonding states and composition of the flowers. The magnetic measurements were examined on a superconducting quantum interference device (SQUID).

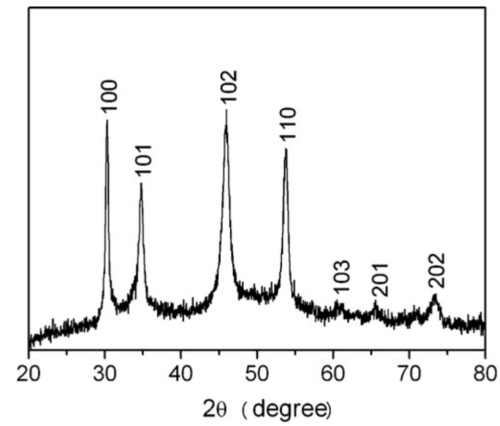

Fig. 1. XRD pattern of the as-prepared product.

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared product. One can see that all the diffraction peaks can be indexed to hexagonal NiAs-type α-NiS phase with unit cell parameters of a = 3.420 Å and c = 5.300 Å (JCPDS Card 75-0613), conforming the overall phase composition and purity of the product. The crystallite size in the growth direction, D, can be estimated from XRD patterns using the Scherrer relationship:

$$D = \frac{0.94\lambda}{(\beta \cos\theta)} \tag{1}$$

where β is the full width at half maximum (FWHM) of a diffraction peak at 2θ corrected for instrumental broadening. From Eq. (1), the estimated crystallite size is about 9–18 nm. Fig. 2a and b shows SEM images of the as-prepared products. It can be seen clearly that there are many flower-like α-NiS nanostructures with the size about 1 μm. The flowers are composed of nanoflakes, as shown in Fig. 2b at high magnification. The nanoflakes are as thin as about 20 nm and interconnect with each other. Fig. 2c shows the TEM image of a single α-NiS flower, in which the layer feature can be seen clearly, the corresponding selective area electron diffraction further proves the hexagonal polycrystalline structure of the flowers. HRTEM observations demonstrate that the nanoflakes are composed of nanocrystals with an average size of about 15 nm, and the nanocrystals are single crystalline, as shown in the marked area

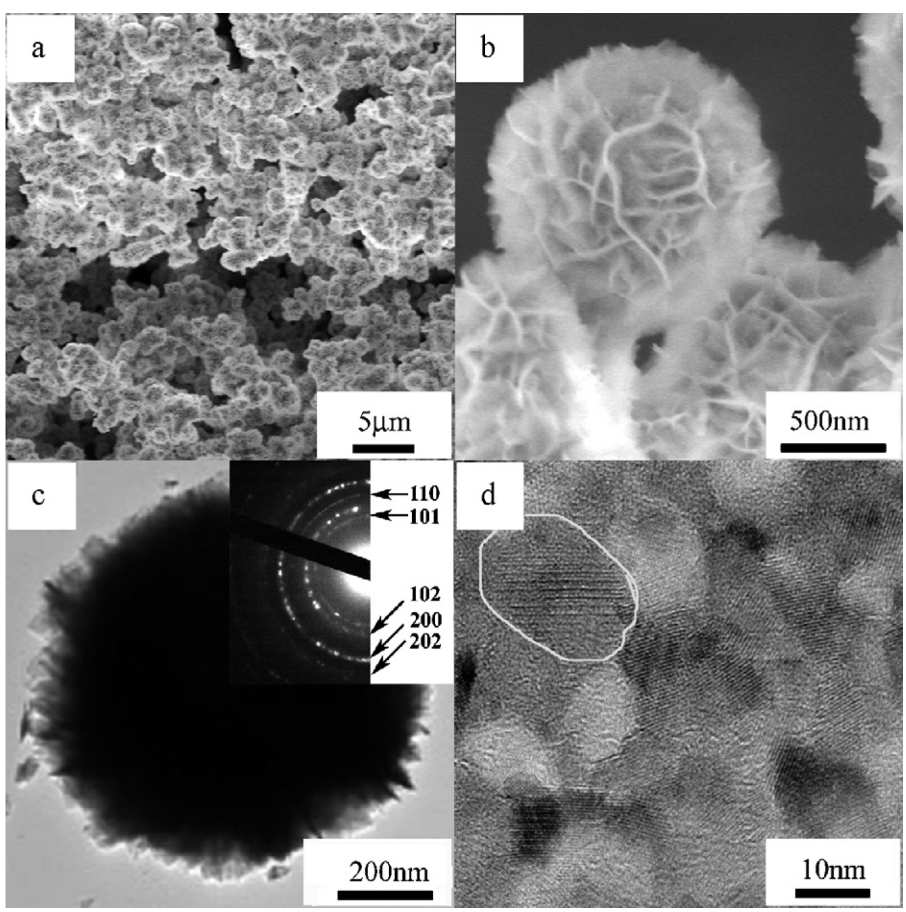

Fig. 2. (a and b) Typical SEM images of the α-NiS flowers at different magnifications, (c) TEM images of a α-NiS flower and the corresponding SAED and (d) HRTEM image of a nanoflake.