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New insight in magnetic saturation behavior of nickel hierarchical structures

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It is unanimously accepted that non-ferromagnetic inclusions in a ferromagnetic system will lower down total saturation magnetization in unit of emu/g. In this study, "lattice strain" was found to be another key factor to have critical impact on magnetic saturation behavior of the system. The lattice strain determined assembling patterns of primary nanoparticles in hierarchical structures and was intimately related with the formation process of these architectures. Therefore, flower-necklace-like and cauliflower-like nickel hierarchical structures were used as prototype systems to evidence the relationship between assembling patterns of primary nanoparticles and magnetic saturation behaviors of these architectures. It was found that the influence of lattice strain on saturation magnetization outperformed that of non-ferromagnetic inclusions in these hierarchical structures. This will enable new insights into fundamental understanding of related magnetic effects.

1. Introduction

In recent years, large-scale self-assembled hierarchical structures with highly specific morphologies and novel properties are of great interest in the area of materials synthesis and device fabrication [1–3]. These hierarchical and repetitive architectures not only offer insight into how complex forms can emerge from simple starting materials [1,2], but also provide promising complex functions and direct bridges between nanoscale objects and the macroscale world [4]. Up to now, many of research activities have been devoted to the invention and development of synthetic routes to obtain desired hierarchical structures, and investigations of their current and foreseen applications in various fields [5–11]. As a result, a substantial amount of information is now available on crystallography [2], structural evolution [12], morphological controls [13], and surface properties [14] of final architectures. Compared to the above topical areas, nonetheless, much less attention has been paid to the relationship between assembling patterns of primary nanoparticles and the electrical, optical, magnetic and mechanical properties in final self-assembled hierarchical structures, although it has been well conceived that novel properties are always desirable and can be really realized during nano-assembling process.

In this work, therefore, we report our recent effort in the syntheses of flower-necklace-like and cauliflower-like nickel hierarchical microstructures, and theoretically unravel the relationship between assembling patterns of primary nanoparticles and magnetic saturation behaviors of these architectures. Although the underlying rule is complex and poorly understood, we believe the lattice strain, varying for different assembling patterns, is of fundamental importance to understand magnetic behaviors of hierarchical structures.

2. Experimental

2.1. Synthesis of nickel hierarchical structures

All reagents in experiments were used as received without further purification. Typically, 0.2 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ and 0.779 g of Cetyltrimethyl Ammonium Bromide (CTAB) were dissolved into 50 mL of de-ionized water. After stirring for 30 minutes, 6 mL of hydrazine hydrate ($N_2H_4 \cdot H_2O$) was added dropwise into the above solution and mechanically stirred for another 30 minutes. The resultant stock solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed and heated at 140 °C for 5 h to obtain flower-necklace-like nickel hierarchical structures. Separately, the previous stock solution was heated in water bath and maintained at 80 °C for 5 h under vigorously mechanical stirring to obtain cauliflower-like nickel hierarchical structures. After cooling down to room temperature naturally, these two

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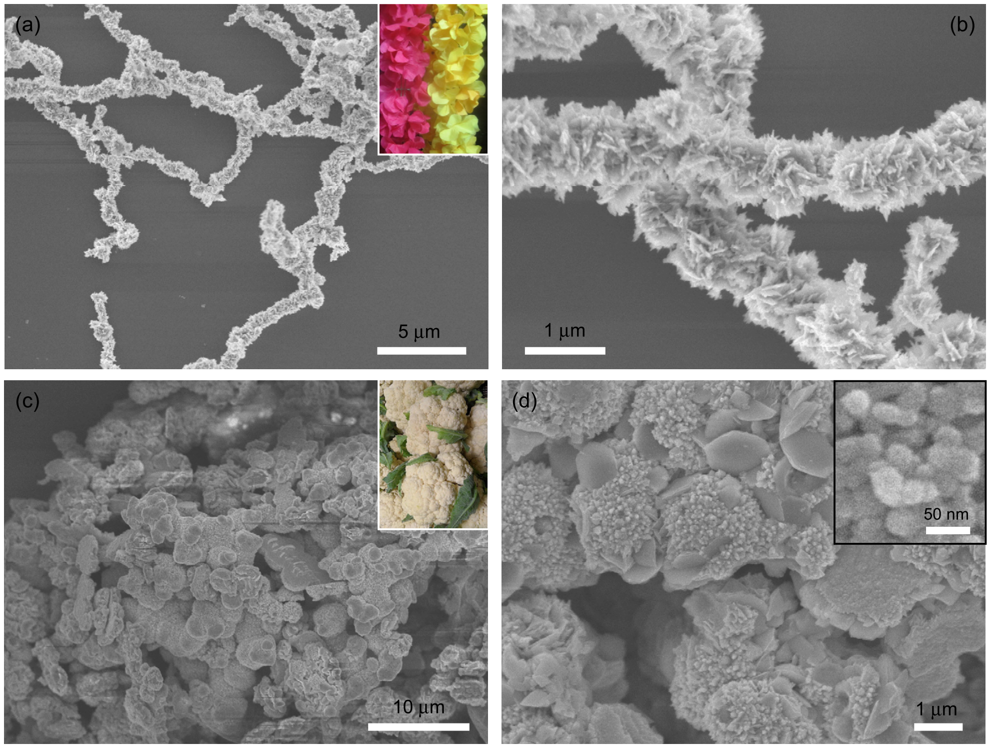

Fig. 1. SEM images of (a, b) flower-necklace-like and (c, d) cauliflower-like hierarchical structures with low- and high-magnifications. Digital photographs of flower necklaces and cauliflowers in daily life are shown as insets in panel a and c, respectively. The zoom-in view of nanoparticles in panel d is shown as its inset.

kinds of precipitates were magnetically separated from solution, repeatedly washed with de-ionized water and absolute ethanol, and finally dried in the air at 60 °C for 4 h.

2.2. Characterization

The XRD patterns were recorded on a powder X-ray diffractometer (Rigaku D/max-rA; Japan) equipped with a rotating anode and a Cu-$K_{\alpha 1}$ radiation source ($\lambda = 1.5406$ Å) at a step width of 0.02°. Scanning electron microscope (SEM) images were collected on a field-emission scanning electron microscope (JEOL JSM-6700F, Japan). The high-resolution transmission-electron microscope (HRTEM) experiments were conducted using a Field Emission Gun (FEG) JEOL 2010F microscope (Japan) with a point resolution of 0.19 nm. X-ray photoelectron spectroscopy (XPS) was performed on VG ESCALAB 220i-XL system equipped with a monochromatic X-ray source in an ultra-high-vacuum chamber at a pressure lower than 1.0×10^{-9} Torr. Peak positions were referenced to the adventitious C 1s peak taken to be 284.8 eV. Magnetic measurements were carried out using a commercial superconducting quantum interference device magnetometer (SQUID MPMS-XL5, USA).

3. Results and discussion

The morphologies of end products obtained from hydrothermal reaction and water-bath route (Fig. 1a and 1c) bear striking similarities with common flower necklace (inset of Fig. 1a) and cauliflower (inset of Fig. 1c), respectively, in our daily life. The zoom-in view in Fig. 1b shows every single "flower" in the "necklace" is of an open-up network structure with a size of ca. 1 µm assembled by tens of intertwined curving two-dimensional nanosheets. In contrast, the geometry architecture of "cauliflower" in Fig. 1d is much more complicated. The particle surface is rough in texture which, upon closer scrutiny, reveals an intricate assembly of nanoparticles with a size of ca. 50 nm (inset of Fig. 1d) and interconnected smooth hexagonal nanosheets with an edge length of ca. 1 µm and a thickness of about 30 nm. The XRD patterns of these hierarchical structures are shown in Fig. 2, in which the diffraction peaks at 44.5°, 51.8°, 76.4° can be unambiguously indexed to the cubic structure of Ni ($Fm\bar{3}m$, JCPDS No. 87-0712) and the diffraction peaks at 19.2°, 33.0°, 38.5°, 59.0° can be indexed to hexagonal structure of $Ni(OH)_2$ ($P\bar{3}m1$, JCPDS No. 74-2075). The presence of $Ni(OH)_2$ impurity phase in cauliflower-like hierarchical structure is presumably because of low reaction temperature and inadequate reaction time in water bath. Considering the hexagonal structure and crystalline characteristic of $Ni(OH)_2$, the observed hexagonal nanosheets in Fig. 1d may well be $Ni(OH)_2$ phase [15–17], which will be further validated and discussed in the following section.

The Ni 2p survey scan spectrum of XPS in Fig. 2c demonstrates the peak types of $Ni2p_{3/2}$ and $Ni2p_{1/2}$ are located at around 855.7 and 873.3 eV with a spin-energy separation of 17.6 eV, which is consistent with $Ni(OH)_2$ phase [18]. A sharp peak at 852.4 eV can be attributed to metallic Ni and two shake up satellites peaks of $Ni2p_{3/2}$ and $Ni2p_{1/2}$ are located at around 861.35 eV and 879.6 eV. These results demonstrate that the cauliflower-like structure is mainly composed of Ni and $Ni(OH)_2$ phases.

It is generally the case that the presence of non-ferromagnetic impurity phase can compromise the ferromagnetic performance of the system [19–21]. In this regard, the saturation magnetization (M_S), being one of the most important magnetic characteristic of a ferromagnet, should be adversely affected by the hybrid non-ferromagnetic $Ni(OH)_2$ phase in cauliflower-like hierarchical structure. Interestingly enough, the reverse is the case in this work. The magnetization curves in Fig. 3 clearly demonstrate that the M_S values of cauliflower-like structure are ca. 4.1% and 3.6% higher than those of its flower-necklace-like counterpart at 300 and 5 K, respectively. Moreover, the zero field-cooled (ZFC) and field-cooled (FC) thermomagnetic curves measured at 100 Oe in Fig. 4 further evidence such magnetization deviation. The shape and vari-

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