Solution-phase synthesis of single-crystalline magnetic nanowires with high aspect ratio and uniformity†

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Single-crystalline Fe_3O_4 nanowires with uniform diameters and the largest aspect ratio (>500) were prepared by a one-step sol–gel process in the presence of ethylene glycol and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly-(ethylene glycol).

There is no doubt that nanowires have drawn a special attention because of their properties quite different from the bulk, resulting from their nanometer-scale one-dimensional (1D) structure and their potential applicability to engineer a variety of state-of-the-art nanodevices.[1] To date, various approaches such as the hard-template[2] or soft-template process[3] have been developed for the preparation of 1 D magnetic materials including magnetic metals, alloys, and metal oxides. However, these processes tend to yield polycrystalline nanowires or nanorods, and their aspect ratios are low due to the size of the template pores.

To obtain single-crystalline magnetic nanowires, Wang *et al,*[4] used an external magnetic field during a hydrothermal process, but the aspect ratio of the product is only 40. In other aqueous systems with an induced magnetic field only arborescent aggregates were easily obtained without significant oriented 1 D growth.[5] So far, the diameters of the produced magnetic nanowires are not uniform in an aqueous system. According to Tanase's report,[6] ferromagnetic nanowires with high aspect ratio can be bound to mammalian cells and the technique has the potential for controlled assembly of cell populations in specific geometries. Additionally, to the best of our knowledge, high aspect ratio and uniform Fe_3O_4 nanowires have not been prepared.

In this paper, we report a novel one-step sol–gel route to prepare single-crystalline magnetic nanowires with uniform diameters and the largest aspect ratio (more than 500), and propose a plausible mechanism for the formation of these nanowires. Our experiments have used a mixed solvent (ethylene glycol (EG) and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123)) that is commonly used by many groups for the preparation of various nanostructures.[7] We have shown here that PEG segments in P123 may passivate the surface of the nanocrystals.

In a typical experiment, 2.0 g of P123 and 5 ml of EG (96%) were dissolved in ethanol, and then added into 250 ml deoxygenated water and heated to a desired temperature (80 °C) with stirring under N_2. Next 20 ml of a stock solution 1 (prepared from 0.4 g $FeCl_2{\cdot}2H_2O$ and 0.4 g $FeCl_3$ dissolved in 20 ml deoxygenated water) and 10 ml of stock solution 2 (prepared from 2.5 g hexamethylenetetramine dissolved in 10 ml deoxygenated water) were quickly injected into this stirred, hot polyol–water solution. The temperature was kept constant at 80 °C for 2 h, then the system was cooled to room temperature. The product was precipitated, cleaned with distilled water several times and then dried in an oven.

Fig. 1 shows TEM images of representative samples prepared in polyol–water solution, which clearly reveal the effect of the polyol during the synthesis process. As shown in Fig. 1(a) and (b), nanorods and nanowires with uniform diameter of about 30 and 10 nm, respectively, can be prepared. Interestingly, the length of the nanorods increases with increase of P123, while the diameter remains essentially unchanged. Nanowires with length up to a few microns (aspect ratio >500) can be prepared by multiple injections. From SEM images of nanowires (ESI†), we see that these nanowires are composed of several relatively finer nanowires, whose diameters are about 10 nm.

The result of EDX analysis (ESI†) showed that the nanowires were mainly Fe_3O_4; the excess amount of oxide should come from the amorphous layer on the surface, most likely the polyol

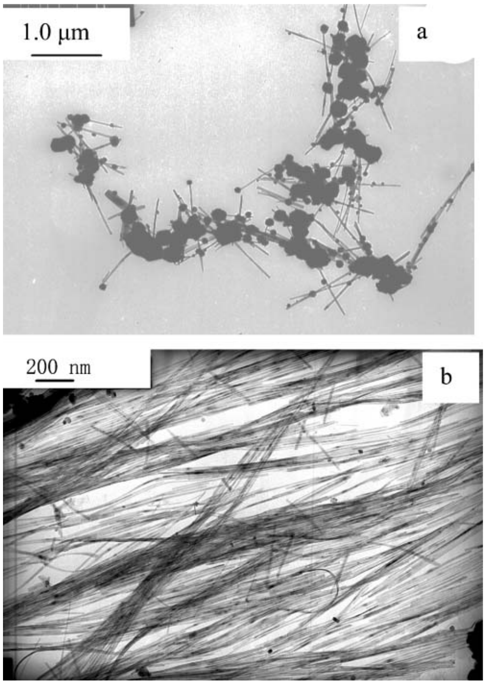

Fig. 1 TEM images of the magnetic nanowires prepared for different ratios of P123 and EG: (a) 10; (b) 50 wt%.

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† Electronic supplementary information (ESI) available: Experimental details. Fig. S1: TEM images. Fig. S2: SEM images. Fig. S3: EDX spectrum. Fig. S4: Electron diffraction pattern. See http://www.rsc.org/suppdata/cc/b4/b410463c/
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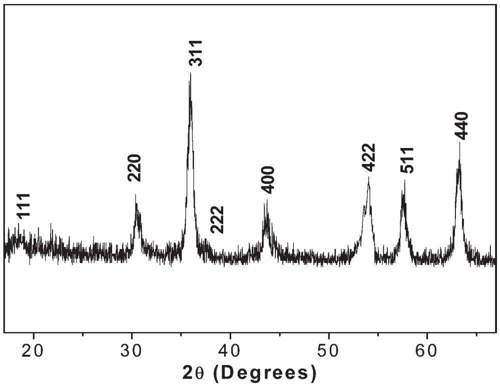

Fig. 2 XRD diffraction patterns of Fe_3O_4 nanowires assembles.

polymer. As shown in Fig. 2, the sample is pure Fe_3O_4 without other crystals; the broadening of reflection peaks is obvious, indicating the formation of ultrafine particles.

HRTEM and electron diffraction patterns further confirmed that the produced nanowires were single-crystalline Fe_3O_4 nanowires. An electron diffraction pattern (ESI†) was taken on Fe_3O_4 nanowires. The space between (311) planes measured from Fig. 3(a) is 2.48 Å, which is close to the result from the electron diffraction pattern. Fig. 3(b) is an HRTEM image of two nanowires adhering to each other, showing that these nanowires are composed of 10 nm nanowires, which is in accordance with the result of the SEM images of the nanowires (ESI†). In addition, the wires are usually covered with a thin layer of amorphous coating.

We have performed a series of experiments, finding that such nanostructures can only be prepared in P123. When no P123 was used, only spherical Fe_3O_4 nanopartices and a few uneven nanorods were prepared under identical reaction conditions. Obviously, the P123 in the mixture has the function as a surfactant for growth of 1 D nanowires. However, to grow long and uniform nanowires, the ratio between EG and P123 is very important. Although Fe_3O_4 nanorods can be prepared without P123, the diameter distribution is much broader and the aspect ratio is lower. At lower P123 concentration, although the diameters are uniform, the lengths are usually only hundreds of nanometers. The optimal ratio of EG/P123 is about 50 wt% (Fig. 1(b)) to obtain uniform single-crystal nanowires.

Obviously, the concentration of P123 in our system is very important for causing a large difference among the growth rates of various crystallographic surfaces. Several recent studies have showed that the existence of an appropriate amount of capping reagents can alter the surface energies of various crystallographic surfaces to promote selective anisotropic growth of nanocrystals.[8] Fe_3O_4 nanoparticles with a bimodal size distribution were generated during heterogeneous nucleation processes, then the larger Fe_3O_4 nanoparticles were able to grow into nanorods at the expense of smaller ones through Ostwald ripening.[9] The newly formed side surfaces of Fe_3O_4 nanocrystals must be stabilized through chemical interactions with the oxygen atoms of P123. In comparison, the interaction between P123 and the two ends of nanorods should be much weaker to enable these ends to grow continuously. Once the rod-shaped structure has been formed, it can readily grow into a longer nanowires[10] because its side surfaces are tightly passivated by P123 and its ends are largely uncovered and remain to be attractive (or reactive) toward new mental atoms. The presence of hydroxide and ether groups of P123 on the surface of nanowires was also verified by IR spectra in the OH or –O– stretching region. A broad absorption band centered at *ca.* 3400 cm^{-1} and a small absorption peak at 1080 cm^{-1} were observed for all of the materials (data not shown). Without P123, the produced nanocrystals were a mixture of nanorods and nanoparticles.

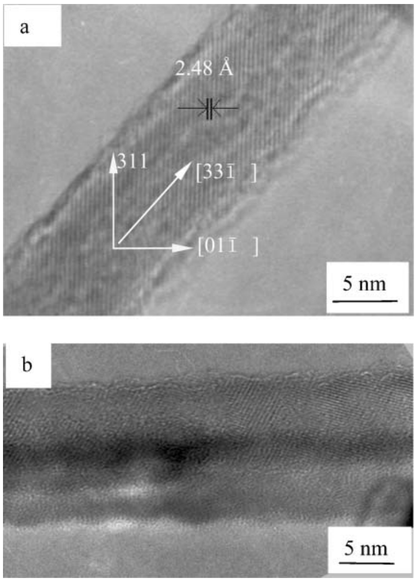

Fig. 3 HRTEM image of an Fe_3O_4 nanowire (a) and two nanowires (b).

Fig. 4 shows magnetic hysteresis curves for the samples measured at room temperature. It shows that sample A (mixture of particles and nanowires) (Fig. 4(a)) and sample B (nanowires) (Fig. 4(b)) have saturation magnetization of 37.8 and 34.5 emu g^{-1}, respectively. The high shape anisotropy of the nanowires preventing them from magnetizing in directions other than along their easy magnetic axes, might be a major reason for these low values. With a random orientation of nanowires, the projection of the magnetization vectors along the field direction will be lower than that for a collection of nanoparticles without a large shape anisotropy effect. On the other hand, pinning of the magnetic

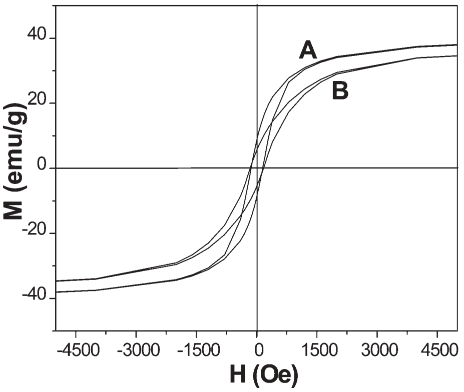

Fig. 4 Magnetic hysteresis curves measured at room temperature for the samples prepared by a polyol process with ratio of P123/EG of (A) 0.20 and (B) 0.50.

domains in Fe_3O_4 nanowires might also be responsible for the low saturation magnetization.

In summary, high aspect ratio and uniform Fe_3O_4 nanowires have been synthesized in EG/P123 polyol–water systems *via* a simple one-step solution-phase route. A lower saturation magnetization was observed in the sample, which was explained in terms of the pinning of antiparallel magnetic domains in Fe_3O_4 nanowires. It is expected that this process could be a promising technique to synthesize 1D nanostructures of other magnetic materials. The PEG-modified nanowires are suited to conjugating to target cells or enzymes for the preparation of the artificial organs.

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