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Solvent-Dependent, Low-Temperature Solution Phase Synthesis of FePt Nanowires

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Preparation of FePt nanowires by thermal decomposition of the solution mixture of equimolar $Fe(CO)_5$ and $Pt(acac)_2$ in *n*-octylamine will be presented in this account. The nanowires with the average diameter about 2 nm and the length of several hundred nanometers were characterized by TEM, EDS, XRD. It is believed that FePt nanowires were generated via the catalytic solution-liquid-solid (S-L-S) synthetic approach. This process is strongly dependent on the solvent and barely on the reaction temperature and the concentrations of precursors.

Keywords: FePt Nanowires, Alkylamine, Transmission Electron Microscopy, Fcc Crystallinity, Magnetism Measurement.

1. INTRODUCTION

Nanostructured materials are attracting great research interest due to their applications as catalysts of organic reactions, as gas sensors and as advanced materials in the future optic, electronic and magnetic devices.[1–3] Since Sun and coworkers first reported the preparation of ferromagnetic FePt nanoparticles in 2000,[4a] a great deal of the research has been focused on size-tunable and shape-controlled fabrication,[4–16] structural and magnetic properties studies,[17] self-assembly,[18] as well as the potential biological applications[19] of FePt nanoparticles. Polyol reduction of $Fe(CO)_5$ and $Pt(acac)_2$ at 297 °C initially reported by Sun et al. provides a general route to monodispersed FePt nanoparticles.[4a,b] Instead of $Fe(CO)_5$, several other iron precursors such as $Fe(OEt)_3$,[11] $Fe(acac)_3$,[12] $Fe(acac)_2$,[8] $FeCl_2$,[4d] and $Na_2Fe(CO)_4$ (Ref. [10]) have been used to conduct the preparation. On the other hands, there are only few examples of FePt 1-D nanostructures reported in the literature.[20] These preparations required either biological virus-based template,[20a] or hard alumina template[20b,c] or solvothermal reaction[20d] to accomplish the growth of FePt nanowires or nanotubes. Sun's group reported the preparation of FePt nanowires and nanorods in a recent communication.[4h] In this report, we present a simple solution-phase fabrication of FePt nanowires by thermal decomposition of pentacarbonyliron, $Fe(CO)_5$ and bis(acetylacetonato)platinum, $Pt(acac)_2$ in *n*-octylamine at relatively low temperature and under an atmospheric pressure. The systematic studies in the effects of solvent, precursor concentration, and reaction temperature on the generation of FePt nanowires have also been explored. The FePt nanoproducts were characterized by TEM, EDS, XRD, AA, as well as magnetism measurement.

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2. EXPERIMENTAL DETAILS

2.1. General Procedure

All preparative operations were carried out under an atmosphere of nitrogen purified by passage through columns of activated BASF catalyst and molecular sieves and using standard Schlenk techniques or in a glove box under N_2. The solvents, *N*,*N*-dimethyl formamide (DMF), *n*-hexylamine, *n*-octylamine, *n*-decylamine, *n*-octanol and *n*-decanol were purchased from Aldrich Chemical Co. and purified by distillation before use. The precursors, pentacarbonyliron, $Fe(CO)_5$ and bis(acetylacetonato)platinum, $Pt(acac)_2$ were purchased from Strem Chemicals Co. and used without further purification.

2.2. Preparation of FePt Nanowires and Nanoparticles

A typical example of the preparation of sample **3** is described as follow. 50 mg (0.255 mmol) of $Fe(CO)_5$ and 100 mg (0.254 mmol) of $Pt(acac)_2$ were placed in a 100-mL flask attached with condenser in the glove box. Addition of 40 mL of *n*-octylamine to the flask to dissolve the precursors under nitrogen atmosphere gave a light

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Table I. Reaction conditions and experimental results for preparation of FePt nanostructures.

No.	Precursors concentration (mM)	Solvent	Reaction temperature (°C)	Experimental result
1	2.550	*n*-octylamine	175	nanowires (width: 2.0±0.6 nm) and nanoparticles (diameter: 5.6±1.1 nm)
2	1.275	*n*-octylamine	175	nanowires (width: 1.7±0.4 nm) and nanoparticles (diameter: 4.8±0.7 nm)
3	0.638	*n*-octylamine	175	nanowires (width: 2.3±0.4 nm) and nanoparticles (diameter: 5.5±0.7 nm)
4	0.319	*n*-octylamine	175	nanowires (width: 2.4±0.5 nm) and nanoparticles (diameter: 6.2±1.5 nm)
5	0.212	*n*-octylamine	175	nanowires (width: 1.6±0.4 nm) and nanoparticles (diameter: 4.4±0.7 nm)
6	0.638	*n*-octylamine	130	nanowires (width: 1.7±0.4 nm) and nanoparticles (diameter: 4.9±1.0 nm)
7	0.638	*n*-octylamine	90	nanowires (width: 1.0±0.3 nm) and nanoparticles (diameter: 3.5±0.7 nm)
8	0.638	*n*-hexylamine	132	nanowires (width: 1.4±0.2 nm) and nanoparticles (diameter: 3.4±0.5 nm)
9	0.638	*n*-decylamine	218	nanowires (width: 1.9±0.3 nm) and nanoparticles (diameter: 2.5±0.7 nm)
10	0.638	*n*-octanol	195	nanoparticles (diameter: 2.2±0.5 nm)
11	0.638	*n*-decanol	231	nanoparticles (diameter: 3.2±0.6 nm)
12	0.638	DMF	150	nanoparticles (diameter: 3.5±0.7 nm)

yellow solution. After the solution mixture was heated at 175 °C for 3 h, the color of the solution gradually turned to black. After cooling the resulting black mixture to room temperature, the black powder product containing nanoparticles and nanowires was collected by centrifugation and washing with acetone. Nanowires were precipitated by addition of *n*-hexane/ethanol (volume ratio = 5:1) to the powder and nanoparticles remained in the solution. Other samples listed in Table I were prepared in the similar way by changing the concentrations of precursors, the reaction temperature or the solvent.

2.3. Characterization of FePt Nanoproducts

The nanoproducts have been characterized by transmission electron microscopy (TEM, Hitachi H-700H or JEOL JEM-1200CX II), energy dispersive spectroscopy (EDS, Noran Voyager 1000), electron diffraction (Hitachi HF-2000), atomic absorption spectroscopy (AAS, PE Atomic Absorption Spectrometer 3110), and X-ray powder diffraction (XRD, Shimadzu XRD-6000 with Cu Kα radiation, $\lambda = 1.5045$ Å) analyses. TEM sample was prepared by placing a drop of the resulting solution onto a carbon-coated copper grid (200 mesh) and followed by naturally evaporating the solvent. The sizes of the particles are estimated from TEM images by Sigma Scan-Pro software. XRD sample was prepared by adhesion of powders on a glass substrate. Magnetism measurement of FePt nanowires was conducted by a superconducting quantum interference device (SQUID, Oxford MagLab 2000).

3. RESULTS AND DISCUSSION

3.1. Preparation of FePt Nanowires in *n*-Octylamine

The preparative procedure for FePt nanowires summarized in Scheme 1 is simplified from the method to generate FePt nanoparticles originally reported by Sun et al.[4a] After being heated at 175 °C for about 15 min, the reaction solution became darker and opaque. Continuously heating the solution for 3 h, a black solution containing nanoparticles and nanowires was formed. Separation of nanowires and nanoparticles can be achieved by addition of *n*-hexane/ethanol (volume ratio = 5:1) to the crude product.

Step (i) reflux in *n*-octylamine at 175 °C, 3 h

Step (ii) (a) centrifugation; (b) washing with acetone; (c) dry under vacuum

Step (iii) (a) addition of hexane/ethanol; (b) separation by precipitation

Scheme 1. Synthetic procedure for FePt nanowires.

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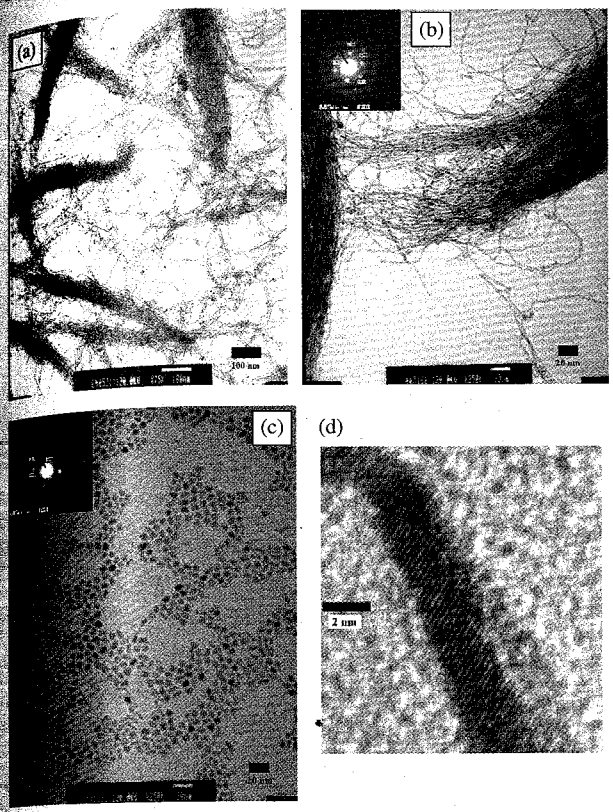

Fig. 1. Transmission electron micrographs for (a) the as-prepared products in *n*-octylamine, (b) the FePt nanowires after separation (inset: electron diffraction pattern), (c) the FePt nanoparticles after separation (inset: electron diffraction pattern), and (d) high-resolution TEM for the FePt nanowire.

Both nanowires and nanoparticles can be re-dispersed in *n*-octylamine. A similar result was reported in Sun's recent communication report.[4h]

3.2. Characterization of FePt Nanowires

Transmission electron microscopy examinations revealed that the majority of the crude products (Fig. 1(a)) were nanowires with the diameter of 2.3 ± 0.6 nm and the length of several hundred nanometers. TEM image of FePt nanowires obtained after separation is shown in Figure 1(b) and the electron diffraction pattern exhibited the fcc FePt crystallinity of the nanowires. A HRTEM image of a single wire (Fig. 1(d)) also demonstrated the crystalline nature of the nanowire with an inter-fringe distance of 0.223 nm, close to the lattice spacing of the {111} planes in the fcc structured FePt. The supernatant contains nanoparticles of irregular shape (Fig. 1(c)) and the average size of the particles is 5.5 ± 0.7 nm. The compositions of the wires and particles characterized by atomic absorption spectroscopy are $Fe_{49}Pt_{51}$ and $Fe_{48}Pt_{52}$, respectively. X-ray powder diffraction analysis (Fig. 2) of as-prepared FePt nanowires exhibited the fcc crystal structure pattern and the strongest (111) peak is consistent with

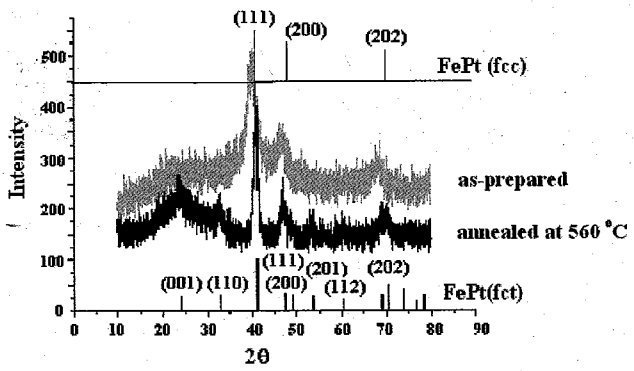

Fig. 2. XRD patterns for the as-prepared FePt nanowires and the sample after annealing at 560 °C.

the observed crystalline feature in TEM image. The XRD broad peaks are likely resulted from the small diameter of the nanowires and the chemically disordered fcc structure. After annealed at 560 °C under nitrogen atmosphere, the sample changed the crystallinity to fct structure. However, aggregation of the nanowires to bulk material was observed during the annealing process.

3.3. Concentration, and Reaction Temperature Have No Significant Effects on FePt Nanowires Preparation

Samples **1**–**5** containing FePt nanowires and nanoparticles with similar size were prepared by the experiments of varying the concentrations of precursors in *n*-octylamine. TEM images of sample **1** and **5** are shown in Figure 3 and the results indicate that no significant effect of the concentration on the generation of FePt nanostructures was observed. Preparation reactions conducted in *n*-octylamine at 175, 130, 90 °C (samples **3**, **6**, and **7**) afforded FePt nanowires and nanoparticles with slight size change. The results demonstrated in Figure 4 revealed that the widths

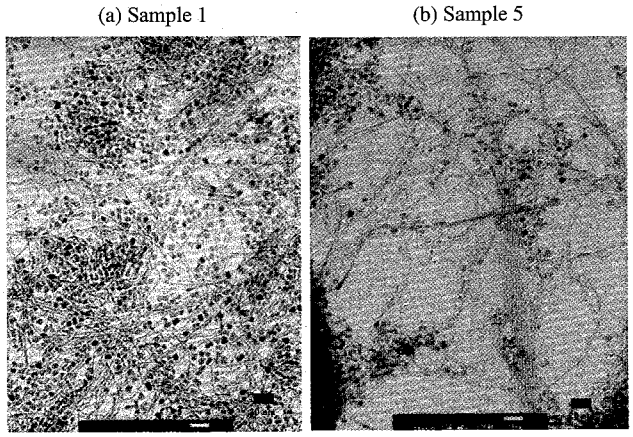

Fig. 3. Transmission electron micrographs for the FePt nanostructures prepared in *n*-octylamine with different precursor concentrations: (a) 1.024 mM, and (b) 0.085 mM.

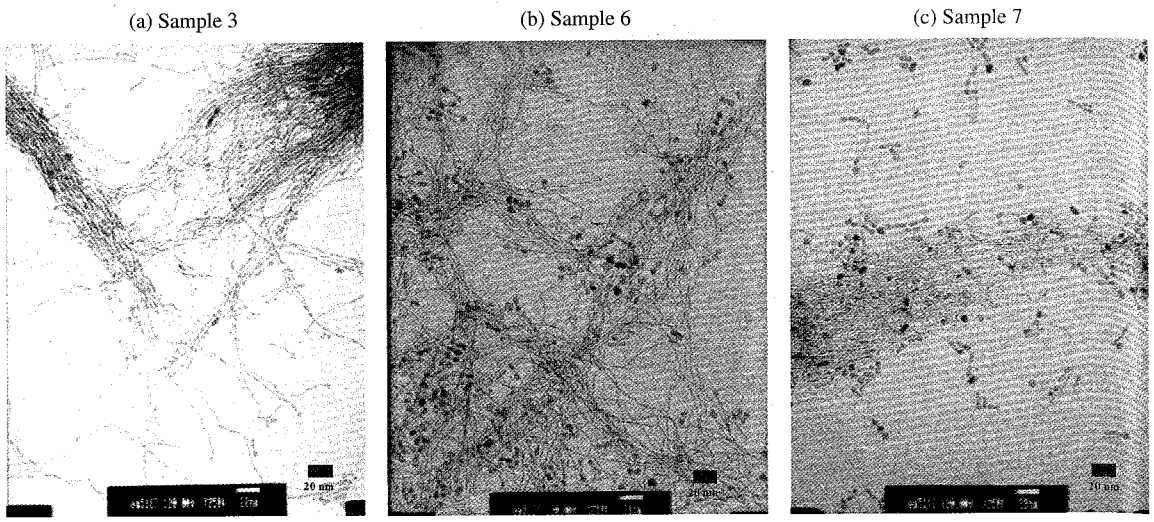

Fig. 4. Transmission electron micrographs for the FePt nanostructures prepared in *n*-octylamine at different temperatures: (a) 175 °C, (b) 130 °C, and (c) 90 °C.

of FePt nanowires slightly decrease with decreasing the reaction temperatures. Higher reaction temperature led to greater generation rate of metal atoms and resulted in the greater crystal growth rate and the formation of larger FePt nanowires.

3.4. Growth Mechanism Study—Solvent Dependence of the Preparation of FePt Nanowires

We proposed that thermal decomposition of $Fe(CO)_5$ firs produced Fe nanoparticles and iron catalytically assiste

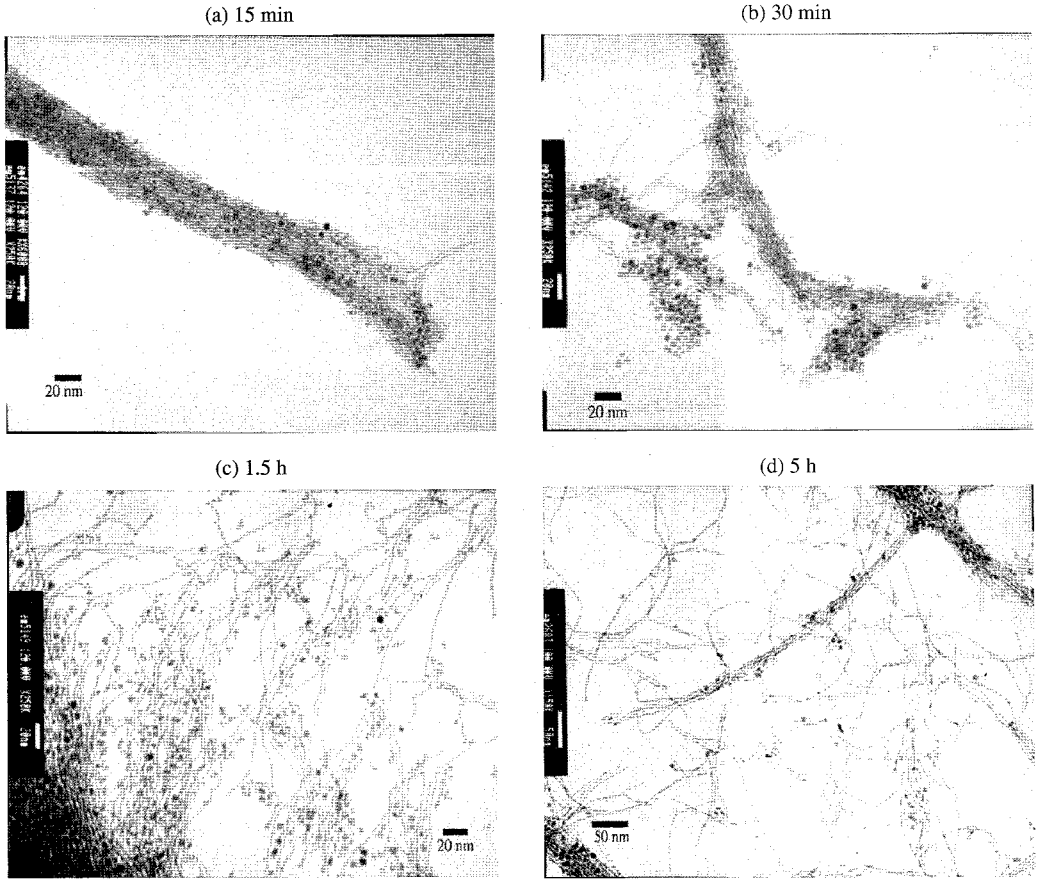

Fig. 5. TEM images of *in-situ* monitoring FePt nanowires growth for sample **3**. Reaction time: (a) 15 min, (b) 30 min, (c) 1.5 h, and (d) 5 h.

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Fig. 6. Transm
(c) *n*-octanol, (d

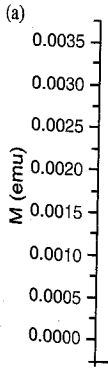

Fig. 7. (a) ZFC
K for the FePt na

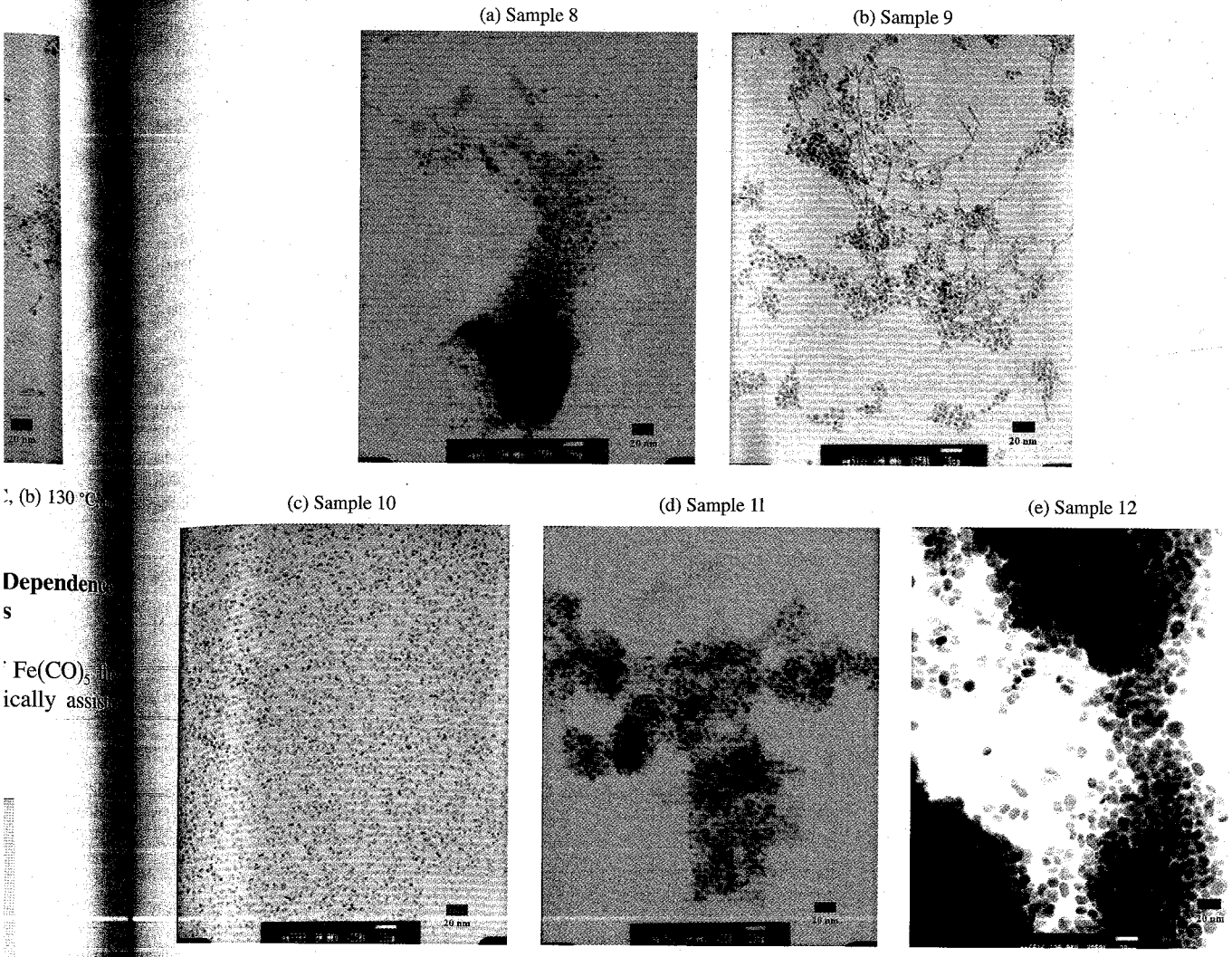

Fig. 6. Transmission electron micrograph for the FePt nanostructures prepared in different solvent systems: (a) *n*-hexylamin, (b) *n*-decylamine, (c) *n*-octanol, (d) *n*-decanol, and (e) DMF.

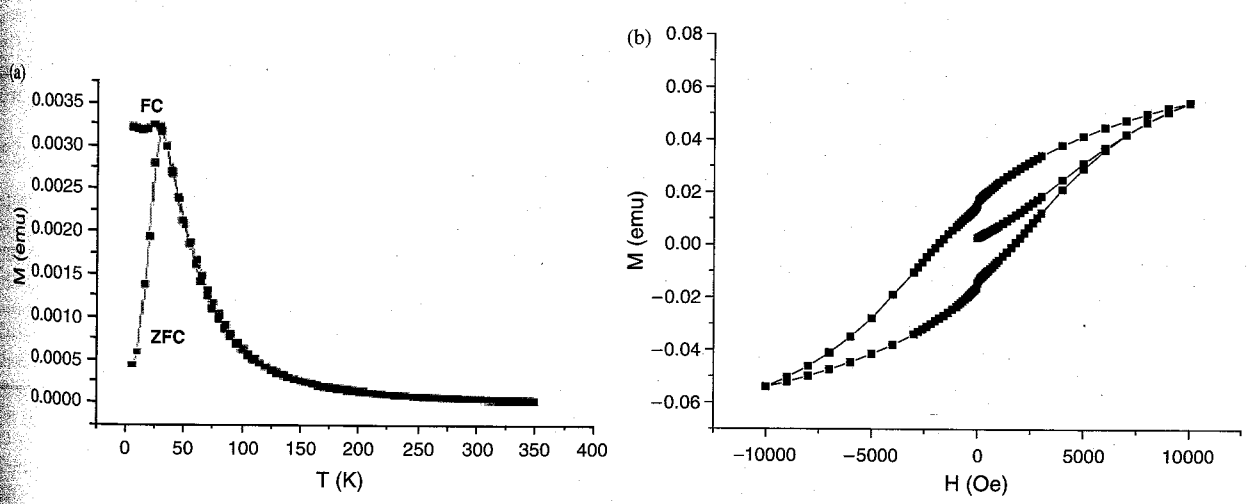

Fig. 7. (a) ZFC and FC magnetization versus temperature at applied magnetic field of 1000 Oe, and (b) magnetization hysteresis loop recorded at 6 K for the FePt nanowires fabricated in *n*-octylamine.

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the reduction of $Pt(acac)_2$ to form Pt atoms. The FePt nanowires were believed to be generated via the solution-liquid-solid (S-L-S) mechanism which originally suggested for the growth of 1-D semiconductor nanostructures by Buhro.[21] *In-situ* monitoring of the preparation of sample **3** has been conducted and TEM images are shown in Figure 5. However, this preparation seems to be a very fast reaction so that the monitoring did not provide much information about the growth of nanowires. FePt nanowires were already formed after heating the reaction solution for 15 min. The morphology of the products did not show significant change when the reaction was continued up to 5 h. The comparing experiments conducted in the solutions of other alkylamines such as *n*-hexylamine, *n*-decylamine also gave the mixed products of nanowires and nanoparticles whose TEM images shown in Figures 6(a and b), respectively. On the other hand, reflux of the precursors in *n*-octanol, *n*-decanol or DMF only afforded FePt nanoparticles. TEM images (Figs. 6(c–e)) of the products fabricated in these solvents showed that irregular shape particles were formed. This reveals that the fabrication of FePt nanowires is strongly solvent-dependent and organic amine plays an important but unknown role in the reaction.

3.5. Magnetism Study of FePt Nanowires

Magnetic property of FePt nanowires prepared in *n*-octylamine has been investigated. The temperature dependence of magnetization was measured in an applied magnetic field of 100 Oe between 2 and 350 K using zero-field cooling (ZFC) and field-cooling (FC) procedures. The blocking temperature of 27.6 K and irreversibility temperature of 125 K were observed in this measurement shown in Figure 7(a). Those are probably caused by high aspect ratio (length/width) and more thermal energy is needed to align the disordering spin. The magnetization hysteresis loop at 6 K is shown in Figure 7(b) and exhibits a coercivity of about 1750 Oe and no saturation up to a magnetic field of 1 T.

4. CONCLUSION

This work demonstrates that FePt nanowires can be prepared by thermal decomposition of $Fe(CO)_5$ and $Pt(acac)_2$ at the temperature as low as 90 °C in the organic amine solution. Fabrication of FePt nanowires is a strongly solvent-dependent reaction. The FePt nanowires exhibit face-centered cubic crystallinity and superparamagnetic property. Detailed study in the formation mechanism of metal alloy nanowires is underway.

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