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Colloids and Surfaces A: Physicochem. Eng. Aspects 312 (2008) 73–78
COLLOIDS AND SURFACES A
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Phase transfer catalysis: Synthesis of monodispersed FePt nanoparticles and its electrocatalytic activity

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Received 10 May 2007; received in revised form 26 June 2007; accepted 3 July 2007
Available online 7 July 2007

Abstract

Using dibenzo-24-crown-8-ether (DB24C8) as phase transfer catalyst, the monodispersed iron–platinum (FePt) alloy nanoparticles with size of ~17 nm were synthesized by reduction of $H_2PtCl_6{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ in the solvothermal system. The structure, magnetic property and electrocatalytic activity of FePt nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffraction system (XRD), vibration sample magnetometer (VSM) and CHI 820 electrochemical analyser (three electrodes system, the reference electrode is saturated calomel electrode (SCE), the counter electrode is platinum electrode and the glassy carbon electrode is used as working electrode (GCE)), respectively. The results show that the as-synthesized FePt nanoparticles have a chemically disordered fcc structure and can be transformed into chemically ordered fct structure after annealing treatment above 400 °C, simultaneously accompanying with the coercivity changed from 5 to 2400 Oe. CVs of 0.5 M H_2SO_4/0.5 M CH_3OH on GCE modified with FePt nanoparticles monolayer illustrate that the as-synthesized FePt nanoparticles have strong electrocatalytic activity toward the oxidation of CH_3OH in aqueous solution.

Keywords: FePt nanoparticles; Monodispersed; Phase transfer catalysis; Electrochemical activity

1. Introduction

Structure, electrochemical, catalytic and magnetic properties of many materials are strongly size-dependent in the nanometer scale [1,2]. New approaches for preparing nanoparticles with controlled size and composition are important in improving the science and technology [3–7]. Preparation of high quality nanocrystals with a desired dimension is the precondition to investigate and utilize their size-determined properties. Thus the control of the nanocrystal size and monodispersity is essential in the formation of multi-dimensional self-assembled structure, in which an individual nanocrystal plays an important role in building blocks-artificial atoms in the next level of the material hierarchy [8]. In data storage density, as an important candidate storage media, FePt nanoparticles have been researched extensively recent years due to their $L1_0$ phase with large uniaxial magnetocrystalline anisotropy [$Ku \approx 7 \times 10^6$ J/m^3] and good chemical stability [9–13]. Solution phase chemical method is known as a superior way for the preparation of monodispersed metal nanoparticles. There are some reported synthesis of monodispersed FePt nanoparticles based on the reduction of $Pt(acac)_2$ and decomposition of $Fe(CO)_5$ or reduction of $Fe(acac)_3$, $FeCl_2$ salts in high temperature solution [14–24]. Long chain diol and polyalcohol (e.g., 1,2-hexadecanediol and glycerol) are always employed to reduce metallic salts to metal particles in the above reports.

In this work, we developed a new simpler approach "phase transfer catalysis synthesis" for synthesizing monodispersed FePt nanoparticles with controlled size and composition. Using DB24C8 as phase transfer catalyst, the synthesis proceeded on the reduction of $H_2PtCl_6{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ by propylene glycol involving oleic acid as stabilizer in the solvent-thermal system. DB24C8 is a macrocyclic polyether whose structure contains 32 hydrogen, 24 carbon and eight oxygen atoms. Each oxygen atom is confined between two carbon atoms and exhibits a conformation with a 24-member hole to offer various ionic species. The structure, electrocatalytic activity and magnetic property of as-synthesized FePt nanoparticles will be discussed in detail later. The as-synthesized monodispersed FePt nanoparticles size was in the range of 15–18 nm with narrow deviation,

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doi:10.1016/j.colsurfa.2007.07.001

and the structure changed from disordered fcc to ordered fct after proper annealing treatment, accompanying with the coercivity varying from 5 up to 2400 Oe. Furthermore, because Pt catalysts can catalyse the redox reaction in H_2SO_4/CH_3OH system [25]. We here keep on studying on the electrocatalytic activity of FePt alloy nanoparticles film in H_2SO_4/CH_3OH system. It will be meaningful for the development of new kind electrochemical sensors.

2. Experiment section

2.1. Chemicals

Dihydrogen hexachloroplatinate ($H_2PtCl_6{\cdot}6H_2O$, 99%), ferrous chloride ($FeCl_2{\cdot}4H_2O$, 99%), oleic acid ($C_{18}H_{34}O_2$, 99%), sodium hydroxide (NaOH, 99%), hexane (C_6H_{14}, 99%), ethyl alcohol absolute (C_2H_5OH, 99%), trichloromethane ($CHCl_3$, 99%), propylene glycol ($C_3H_8O_2$, 99%) were all purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC), dibenzo-24-crown 8-ether ($C_{24}H_{32}O_8$, Tokyo Chemical Industry Co., Ltd. 99%). All the reagents were used without further purification.

2.2. Synthesis of monodispersed FePt alloy nanoparticles

Before the synthesis of FePt alloy nanoparticles, sodium oleate was prepared via 15 ml oleic acid reacting with 7 g sodium hydroxide under 100 °C water condition for about 2 h, ivory-white product dried in the air.

Monodispersed FePt nanoparticles were prepared with a series $FeCl_2{\cdot}4H_2O/H_2PtCl_6{\cdot}6H_2O$ at 76/24 (S1), 60/40 (S2), 56/44 (S3), 50/50 (S4) and 40/60 (S5). As far as S3 was concerned, 3 ml ethyl alcohol absolute solution containing 0.0124 g of $FeCl_2{\cdot}4H_2O$ and 0.0253 g of $H_2PtCl_6{\cdot}6H_2O$ was mixed well by ultrasonic, 0.02 g sodium oleate, 0.005 g DB24C8, 4 ml propylene glycol and 3 ml oleic acid were added to a 12 ml autoclave tube under agitation. The reaction system was sealed and treated at 150 °C for 10 h. After the reaction was cooled to room temperature, the FePt (S3) nanoparticles can be easily collected at the bottom of the container. The as-synthesis products were washed out from the autoclave tube by ethanol. The product was then centrifuged at 5000 rpm for 10 min. The FePt nanoparticles precipitate was washed by centrifuged thrice, finally the particles redispersed and stored in 5 ml of chloroform. The other products of differ-

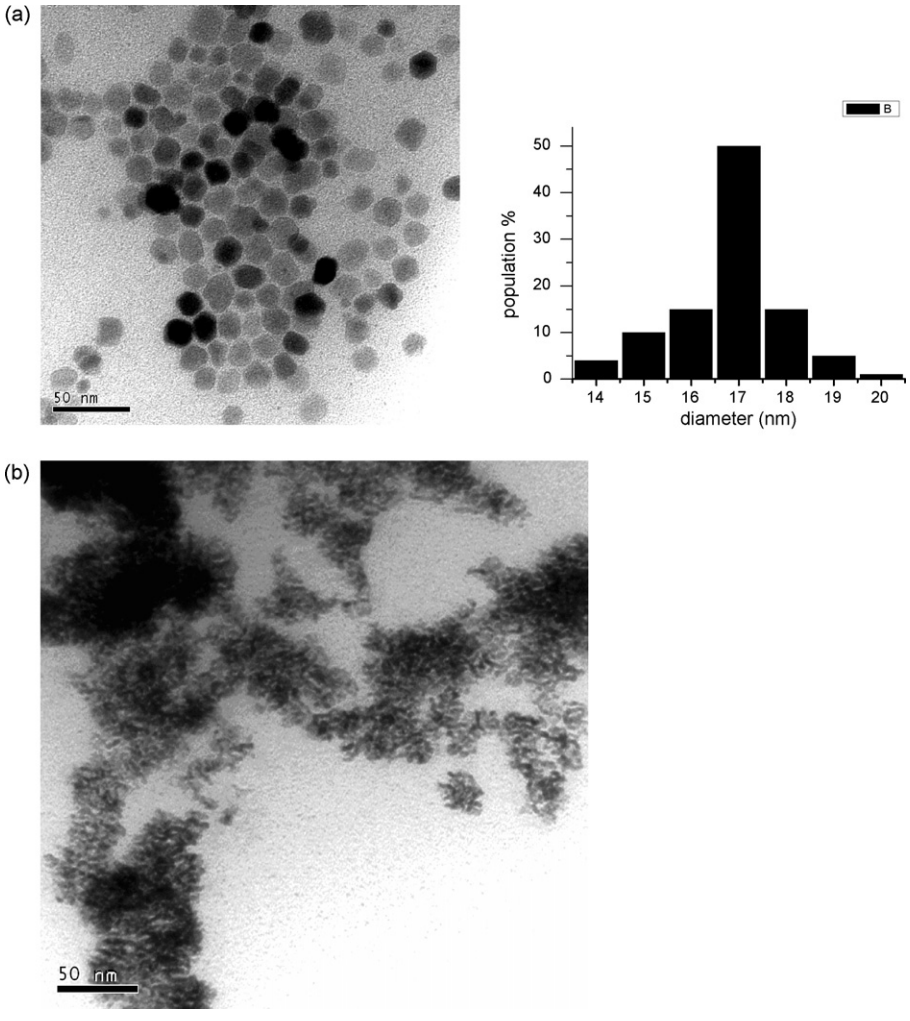

Fig. 1. TEM images of FePt nanoparticles. (a) as-synthesized FePt(S3) nanoparticles with distribution of particle size. (b) The FePt particles prepared without DB24C8.