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Preparation and Characteristics of α-Fe_2O_3 Nanocrystalline/Block Copolymer Heterostructure Composite

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α-Fe_2O_3 nanocrystalline was encapsulated by block copolymer, hydroxylated poly(styrene-b-butadiene-b-styrene) (HO-SBS), and formed α-Fe_2O_3/HO-SBS heterostructure composite consisting of nanocrystalline core and copolymer shell. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) are used to investigate the structure of the composite. And the results show that α-Fe_2O_3 core is 45nm in diameter and copolymer shell is 10nm. Cyclic voltammetry demonstrated copolymer shells can act as potential barriers, while electric field introduced surface photovoltage spectroscopy (EFISPS) testifies that charges can be introduced to penetrate through the shell under external electronic field.

Keywords: α-Fe_2O_3; block copolymer; heterostructure; nanocomposite

INTRODUCTION

Current interest in metal and semiconductor nanocrystals is intensely increasing, because their size-tunable properties render them practical and potential application in nanoelectronics, nonlinear optics, catalysis and high-density information storage.[1] For electronic device application, surface

passivation and ordered assembly must be considered.[2] This is always realized via separating nanocrystals by potential barrier of materials with wide energy band gap. In this paper, we prepared α-Fe_2O_3 nanocrystalline/ HO-SBS heterostructure composite and studied its properties.

EXPERIMENTAL SECTION

α-Fe_2O_3 single crystalline was prepared by forced hydrolysis of acidified $FeCl_3$ aqueous solution.[3] TEM micrograph of α-Fe_2O_3 shows that mono-dispersed particles are in the average size of 45nm. Commercial SBS was hydroxylated in a typical hydroxylation run.[4] The hydroxyl value was measured to be about 0.36 by acidation method. α-Fe_2O_3 nanocrystalline was added to the HO-SBS/toluene solution to form suspension, facilitated by the means of ultrasound. After centrifugalized and filtered to remove unsoluble α-Fe_2O_3, a brick red transparent solution was obtained.

The assembly properties and topography of the resulting product was investigated by TEM (HITACHI, H-8100IV) and AFM (PSI Model AP-0190). respectively. The absorption spectra were measured with a spectrophotometer(Shimadzu UV-365). Electrochemical measurements were performed by potentiostat-galvanostat (EG&G PAR Model 273), and EFISPS was measured by a home-made instrument.

RESULTS AND DISCUSSION

The TEM micrograph of the resulting solution (Figure 1a) shows that dark spheres are in a hexagon array, which corresponds to the lowest free energy.[5] Their average size is about 45nm, coincident with that of α-Fe_2O_3 nanocrystalline. In the AFM topography (Figure 1b), microspheres distribute

equally on the substrate. Their average diameter approximates to 65nm. It can be determined that α-Fe_2O_3 nanocrystalline has been encapsulated by HO-SBS and forms α-Fe_2O_3 nanocrystalline/HO-SBS heterostructure composite consisting of nanoparticle core and copolymer shell. The outer dimension of copolymer is calculated to be 10nm. These heterostructure composite can assembly orderly on the substrate.

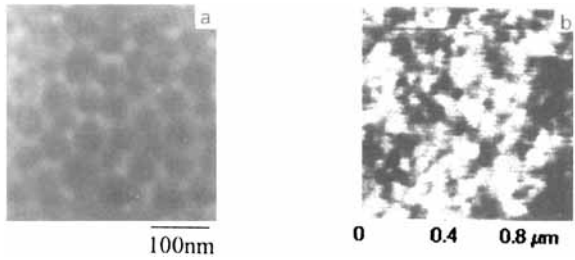

FIGURE 1 (a) TEM micrograph and (b) AFM image of α-Fe_2O_3 nanocrystalline/HO-SBS heterostructure composite
See Color Plate VI at the back of this issue

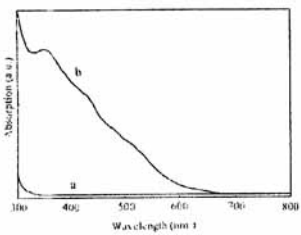

FIGURE 2 The UV-vis spectra of (a)HO-SBS(b)α-Fe_2O_3/HO-SBS nanocomposite.

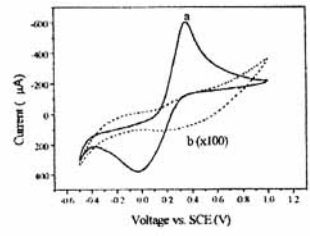

FIGURE 3 Cyclic voltammetry of (a) α-Fe_2O_3 (b)α-Fe_2O_3/HO-SBS nanocomposite.

Figure 2 is UV-vis spectra of HO-SBS and α-Fe_2O_3 nanocrystalline/ HO-SBS composite. The copolymer has absorption before 300nm(Figure 3a). In the case of the composite(Figure 2b), three absorption bands appear near 350nm, 430nm and 540nm, respectively, which correspond to the absorption

of α-Fe_2O_3.[6]

In cyclic voltammetry measurement, anodic and cathodic current peaks of α-Fe_2O_3/HO-SBS composite (Figure 3b) are much weaker than that of α-Fe_2O_3(Figure 3a). This suggests the copolymer shell act as a potential barrier and restrict the anodic and cathodic reactions on electrode.

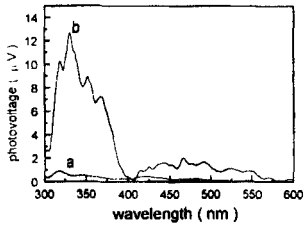

FIGURE 4 EFISPS of α-Fe_2O_3/HO-SBS nanocomposite(a)0V (b) +0.7V.

In EFISPS of the composite, there is no apparent photovoltage response without electric field (Figure 4a). While under +0.7V electronic field, peaks at 340 and 470nm corresponding to the electron transition of α-Fe_2O_3 were observed (Figure 4b). It shows that external electric field can introduce photo-generated charges of α- Fe_2O_3 to penetrate through barriers of the copolymer shell.

Acknowledgements

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