

Enhancement of structural stability of nanosized amorphous Fe_2O_3 powders by surface modification

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Abstract

The surface of low-dimensional solids plays a key role in their phase transition. In the present study, to enhance the structural stability of nanosized amorphous Fe_2O_3 powders their surfaces were modified by employing NaOH solution, which leads to an increase in both the crystallization temperature from 364 °C to 411 °C and the crystallization activation energy from 81.5 kJ/mol to 156.8 kJ/mol. The surface-modified amorphous Fe_2O_3 powders show an entirely different crystallization behavior as compared with the as-prepared amorphous powders. The enhanced structural stability is attributed to the increase of the amount of hydroxide groupings at the surfaces of amorphous powders, which lowers their surface energy.

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1. Introduction

Nanosized amorphous iron and manganese oxides are potential candidates as cathode materials with a high specific capacity and energy for the application of rechargeable lithium and lithium-ion batteries [1,2]. The high specific capacity of the oxides is attributed to their amorphous structure with structural free volumes, which can potentially yield fast lithium conduction and can also accommodate large amount of lithium without structural changes. The shorter diffusion lengths due to the nanosized morphology of the materials also lead to a better utilization of the active electrode material and a high intercalation capacity. These nanosized amorphous oxides possess a lot of surfaces which can provide heterogeneous nucleation sites for phase formation and thus lower the phase transition (i.e., crystallization) temperature. Moreover, from the thermodynamic point of view, the amorphous structure is metastable and has a potential to transform into a crystal structure. The nanosized

amorphous iron and manganese oxides have, therefore, a considerably poor structural stability. Their excellent electrochemical properties will disappear once the crystallization transition occurs. The study of the structural stability against crystallization transition is, therefore, of particular interest for practical applications of these low-dimensional amorphous materials. The studies of superheating of metal nanoparticles show that [3–5] the solid–liquid phase transition initiates by melt nucleation at a solid surface or at a solid–solid interface. A low surface or interface energy will suppress the heterogeneous nucleation of melt and thus enhance the structural stability of nanoparticles against melting. The surface structure of iron oxides, e.g., $\alpha\text{-Fe}_2\text{O}_3$, has been studied in detail due to its effects on chemical and physical properties of the compounds [6–8]. The surface energy of iron oxides can be altered by surface termination with different atoms [9,10]. It is, therefore, expected that the surface energy of amorphous iron oxides can also be significantly changed by surface modification since they have more dangling bonds at surfaces than corresponding crystal oxides, which may provide us a possibility to enhance the structural stability of nanosized amorphous iron oxides against crystallization transition.

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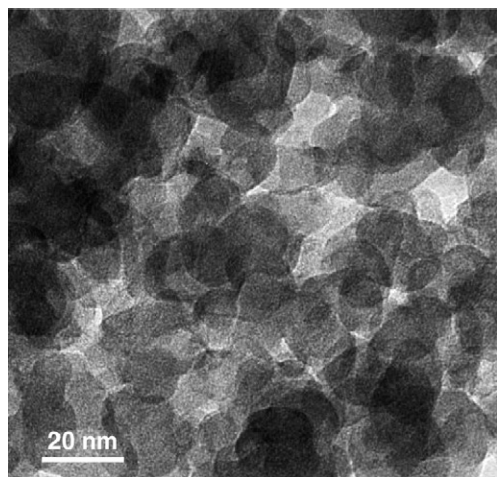


Fig. 1. TEM image of the as-prepared iron oxide powders.

In the present study, the structural stability of nanosized amorphous Fe_2O_3 powders has been considerably enhanced by employing surface modification using NaOH solution. This is of wide interest for technological applications and for the enhancement of structure stability of low-dimensional amorphous materials against phase transition.

2. Experimental

Nanosized amorphous iron oxide powders were synthesized by dropping $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution (6 mol/L) into $\text{Fe}(\text{NO}_3)_3$ solution (1 mol/L), which produced iron oxide precipitates. The precipitated iron oxide powders were dried at room temperature for 3 days, and then some of the iron oxide powders were dipped into the NaOH solution (1 mol/L) for 20 min for a surface chemical modification processing. Both the as-prepared and the surface-modified iron oxide powders were dried in a drying box at a temperature of 80 °C for 3 h. The microstructure

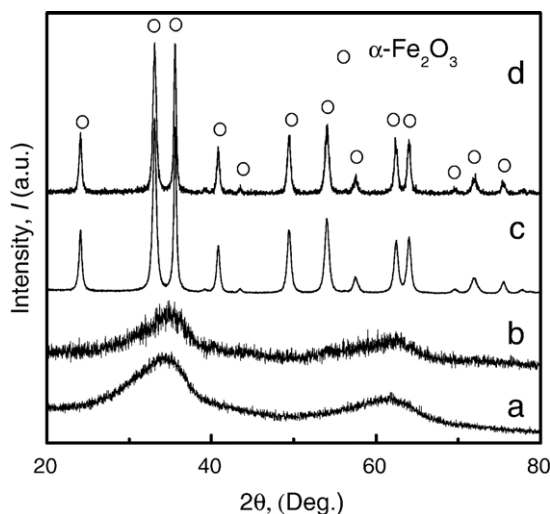


Fig. 2. XRD spectra of (a) as-prepared nanosized amorphous iron oxide powders and (b) after surface modification in NaOH solution, (c) as-prepared amorphous iron oxide powders after annealing at 400 °C for 2 h, and (d) surface-modified amorphous iron oxide powders after annealing at 400 °C for 2 h.

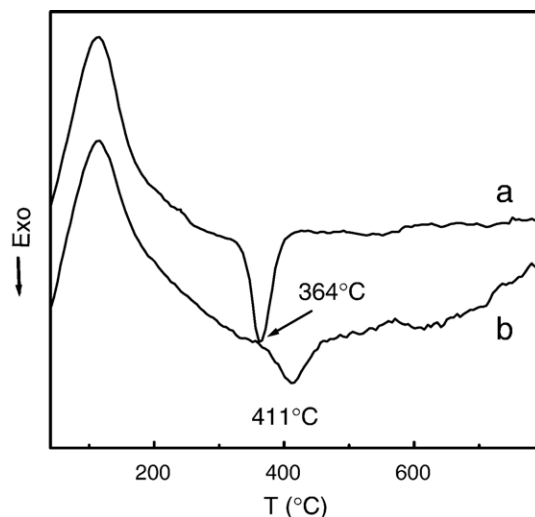


Fig. 3. DSC curves of (a) as-prepared amorphous Fe_2O_3 powders and (b) surface-modified amorphous Fe_2O_3 powders by NaOH solution at a heating rate of 10 °C/min.

of the as-prepared and surface-modified iron oxide powders was investigated by employing an X-ray diffractometer (XRD) with $\text{Cu } K\alpha$ irradiation and a transmission electron microscopy (TEM). The crystallization transformation of these amorphous iron oxide powders was studied by XRD and differential scanning calorimetry (DSC) measurements. The X-ray photoelectron spectroscopy (XPS) with $\text{Mg } K\alpha$ irradiation ($E=1253.6$ eV) was employed for a surface analysis of the as-prepared and surface-modified iron oxide powders.

3. Results and discussions

TEM observations show that the as-prepared iron oxide powders have a particle size of about 20 nm (see Fig. 1). XRD measurements show that both the as-prepared and surface-modified iron oxide powders by NaOH solution have an amorphous nature (see Fig. 2a and b), and they transform exclusively into $\alpha\text{-Fe}_2\text{O}_3$ crystals after annealing

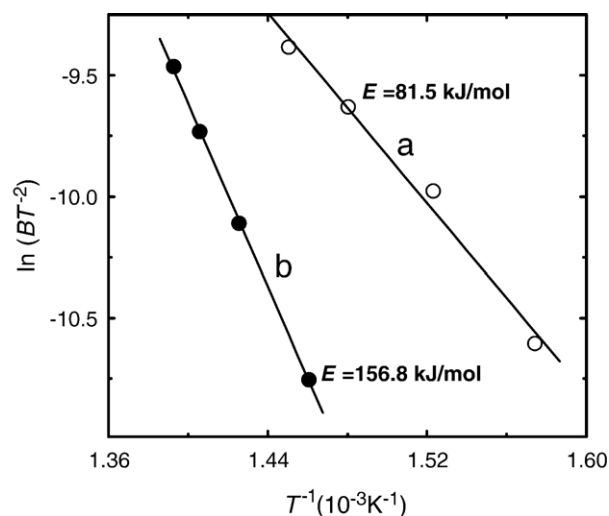


Fig. 4. Plots of $\ln(BT^{-2})$ vs T^{-1} of crystallization temperatures T at different heating rate B : (a) as-prepared amorphous Fe_2O_3 powders and (b) surface-modified amorphous Fe_2O_3 powders by NaOH solution.

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