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Short communication

Effect of the addition of graphite oxide on the morphology of boehmite crystals

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ABSTRACT

Using graphene oxide (GO) as the additive, the boehmite (AlOOH) with various morphology including nanofibers, three-dimensional (3D)-microflowers and sea bile-like particles, can be easily synthesized by a two-stage hydrothermal method. The obtained products were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). It was put forward that GO acted as a template during forming boehmite crystals, and its detailed effect has been discussed.

1. Introduction

Nanomaterials have attracted much attention because of their unique physical and chemical properties [1,2]. Over the past decade, the researches focused on the morphology control of nanostructured functional materials because of the related relationship between the morphology and properties [3–5]. Recently, there are many reports on synthesizing inorganic nanomaterials with controlled shapes like nanotubes [6,7], nanowires [8], nanoribbons [9] and hollow structures [10–13]. Alumina, as one of the most important and widely used inorganic materials such as catalyst support, adsorbent, ceramic and abrasive [14–18], has attracted many researchers' attention because of its multiple crystal shapes. The conventional chemical method for synthesis of Al_2O_3 is boehmite (AlOOH) dehydrate with the original morphology remaining [19]. Thus, as the alumina-derived materials, boehmite has also attracted the attention of researchers [14,20]. Up to now, boehmite with numerous kinds of morphologies has been reported, such as nanorods, nanowires, nanofibers, nanotubes, nanodots, bunches of aligned nanowires, nanoplates, cantaloupe-like structures, flower-like structures and hollow spheres [21–23]. At the same time, synthesis methods of nanostructure boehmite have also been developed, such as sol-gel method, spray pyrolysis and hydrothermal treatment [24–27]. Bai and co-workers [28] synthesized porous microfibers of alumina in the presence of P123 as a template. Yu et al. [17] designed a three-step synthesis route to the preparation of flower-like mesoporous boehmite. Shen and co-workers [29] reported a steam-assisted synthesis method to prepare high-quality boehmite nanorods. Kim et al. [30] reported the synthesis of AlOOH with various morphologies including nanoleaves, nanofibers and hierarchically nanostructured microflowers by a two-step ionic liquid-assisted hydrothermal method using aluminum acetate hydroxide as the precursor. However, these synthetic methods usually need complicated procedures or accompany environmental pollution.

Graphene has attracted tremendous attentions as a novel nanostructured carbon material in the past few years. It is a one-atom-thick planar sheet formed by sp^2-bonded carbon atoms densely packed in a honeycomb crystal lattice. It is also the 2D building material for carbon materials of all other dimensionalities, and it can be wrapped up to 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphene materials. Graphene oxide (GO) was prepared based on the Hummers' method by oxidation of graphite flakes. Aqueous solution of graphene oxide occurs polymerization in hydrothermal condition. The polymerization way of GO is different with pH value [31,32]. Thus the different microenvironment for the growth of crystals can be obtained by addition of GO under different pH conditions, which may further induce boehmite with various morphologies. In this communication, we investigate the effect of GO on the growth of boehmite crystals under different pH values, and the growth mechanism is also discussed.

The synthesis steps of boehmite are as follows. GO was dissolved in deionized water and sonicated in an ultrasonic bath. Then, $AlCl_3 \cdot 6H_2O$ was added to the above solution and stirred to form uniform mixture solution. Diluted HCl and $NH_3 \cdot H_2O$ (1 mol/L) was used to adjust the pH of mixture solution. After that, the mixed solution was kept at 80 °C for 2 h. The resulting reaction mixture was transferred into Teflon-lined stainless-steel autoclave and cross-linked in an oven at 180 °C for 12 h. The product (gel) was washed with deionized water and

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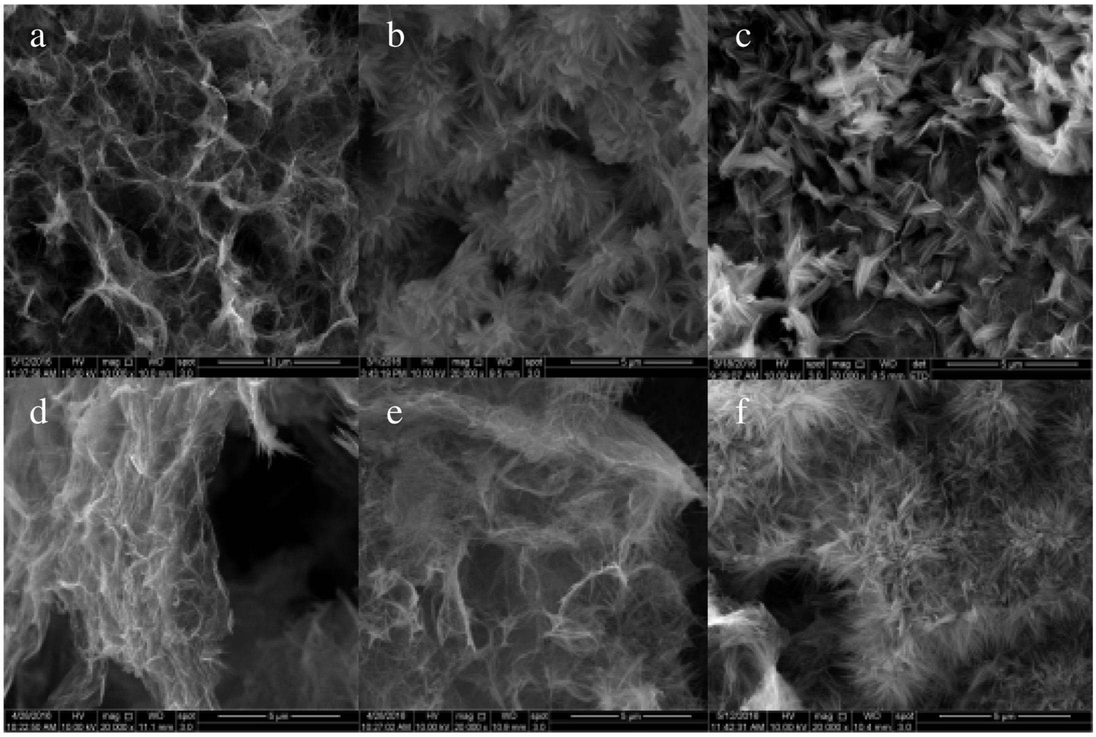

Fig. 1. SEM images of a typical as-synthesized sample at different pH. (a) pH = 2 (b) pH = 4 (c) pH = 6 (d) pH = 8 (e) pH = 9 (f) pH = 10.

freeze-dried for 12 h. The synthetic conditions for preparing samples kept the same except for the pH of final mixture. In order to obtain γ-Al_2O_3, the GO (template) was removed by calcination in air at 600 °C for 4 h with a heating rate of 3 °C·min^{-1}.

To investigate the formation process of the fiber-like nanostructures of boehmite, the morphology of the samples obtained under different reaction conditions was observed. Fig. 1 shows the SEM images of boehmite samples synthesized under different pH values with the addition of GO. From the images we can easily find that under the acidic conditions, when the pH value of solution is 2, the morphology of boehmite is observed as the 3D structure of the nanowires; when the pH value of the reaction mixture is 4, the 3D flowers architectures is obtained; when the pH value rises to 6, boehmite folded sheet of a length of 1 μm particles can be observed. While under the alkaline conditions, when the pH value of the reaction mixture is 8, boehmite whiskers form and integrate on the surface of GO sheets; when the pH value further rises to 9, the nanofibers can be observed; as the pH continually rises to 10, nanofibers will assemble into globular structure. These results hint that pH value plays an important role on the growth process of the boehmite nanostructures. It not only affects the hydrothermal process of aluminum chloride, but also affects GO surface chemical groups, which further limit the final morphology of boehmite. In the acidic range, the growth trend of boehmite is from the sheet to the sea bile-like particles; in the alkaline range, the growth trend of boehmite is from1D needle-like aggregates to 3D clusters which consist of numerous needle-like fibers. Under the acidic conditions, hydroxy aluminum

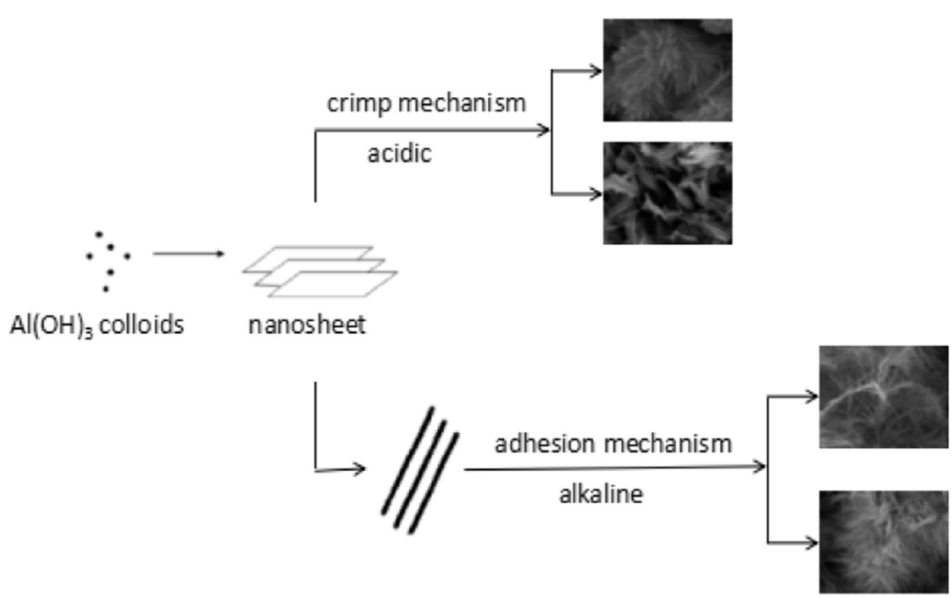

Fig. 2. Schematic illustration for the growth process of the precursor aluminum.