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Single step hydrothermal synthesis of 3D urchin like structures of AACH and aluminum oxide with thin nano-spikes

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Abstract

3D urchins like ammonium aluminum carbonate hydroxide (AACH) nanostructures with nano-spikes of dia. 20–30 nm were synthesized by a simple, single step hydrothermal technique by using aluminum nitrate and urea as precursor materials. It was found that morphology of the produced structure strongly depends upon the urea concentration. With increasing the amount of urea, the AACH particles having embedded rods like surface features transformed into 3D urchins. The added urea decomposed during hydrothermal treatment and increased the pH of the solution, which affected the morphology of the produced nanostructures. SEM, XRD, FTIR and TGA were employed to characterize the produced structures. On heating, the volatile ingredients of AACH were removed, leaving behind the alumina urchins.

Keywords: A. Calcination; B. Electron microscopy; B. Whiskers; D. Al_2O_3

1. Introduction

Due to wide range of applications the metal oxides with controlled nanostructured morphologies have drawn considerable attention in the fields of gas-sensing [1], photocatalysis [2], magnetism and energy storage [3,4], high strength composites [5,6], etc. To fabricate nanostructures of various morphologies, numerous techniques have been reported including vapor–liquid–solid (VLS) methods, thermal evaporation, thermal decomposition, chemical vapor deposition (CVD), template-confined and solution-phase methods [7], etc. However, out of these, the solution phase technique is the more promising to obtain nanostructures including nanorods, wires, sheets, flakes, networks, etc. to meet different applications [8]. Out of the other metal oxides, the alumina has a unique position due to its utilization as catalyst, sensor and membrane material [9,10]. Moreover, nano-aluminum hydroxide is further useful due to its sorption–desorption and flame retardation characteristics [11,12].

Presently, a lot of work has been reported on the production of 1D and 2D aluminum hydroxide and alumina nanostructures including nanowhiskers [5,6], nanoflakes [13], nanowires [14], nanofibers [15], nanorods and nanotubes [16], etc. However, the work on 3D nanostructures requires further investigation. Due to their importance 3D nanostructures are also designated as next generation nanostructures [17]. These structures have potential applications in the areas of electronic and optoelectronics [18]. To the best of the authors' knowledge no work on the production of 3D urchin like AACH and aluminum oxide nanostructures synthesized through simple solution based approach has been ever published. Therefore, a facial single-step solution based (hydrothermal) technique to synthesize 3D urchin like AACH and aluminum oxide nanostructures which are composed of fine 20–30 nm spikes, is being reported. Moreover, the possible mechanism for the formation of this nanostructure has also been discussed in this article.

2. Experimental procedures

For the present study, the chemical used were Aluminum Nitrate and Urea. All the chemicals were of analytical grade and were used without any further purification. Series of hydrothermal runs were conducted in which 25 g of aluminum

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Table 1
Synthesized samples, their identification codes and amount of urea used.

S. no.	Sample designation	Urea amount (g)	pH of the filtrate after hydrothermal treatment
1.	U6	6	7.4
2.	U8	8	7.9
3.	U10	10	8.3

nitrate and varying amounts of urea (as mentioned in Table 1) were mixed in 70 ml of distilled water with the help of magnetic stirrer.

After 30 min of stirring, the solution was transferred into the autoclave reactor (by Buchi Glas Uster, Model ''Limbo 350''). The autoclave was sealed and heated up to 120 °C for 24 h. After 24 h, the autoclave was switched OFF and was allowed to cool with the help of installed automatic water circulation system. At room temperature the product was collected carefully. It was filtered using a filter paper, washed repeatedly with distilled water and then dried in an oven for 24 h at 80–85 °C in air. The samples were characterized through SEM, XRD, TGA and FTIR.

3. Results and discussion

Fig. 1(a–d) shows morphologies of the produced nanostructures in the samples (6U and 8U) containing 6 and 8 g urea. Fig. 1(a and b), SEM images of 6U, shows the particles/clusters with 300–500 nm diameter and length up to 3 μm having rod like surface features joined together longitudinally. These features can be ascribed as the initiation point of the spikes of the urchin. By increasing the amount of urea up to 8 g (Fig. 1c and d) these features become more prominent with separation of their surfaces at the interface. By further increasing the amount of urea up to 10 g (Fig. 2a and b), the formation of complete urchin like morphology having size up to 4 μm with diameter of individual spike as 20–30 nm is observed.

These results suggest that the urea has played a vital role in defining the morphology of the produced AACH nanostructure. Urea is an organic compound that decomposes thermally into ammonia and carbon dioxide [19] at 70–100 °C, the chemical reaction is given in Eq. (1) below,

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2 \quad (1)$$

This ammonia then reacts with the aluminum ions (produced due to hydrolysis of aluminum nitrate) in presence of water vapors and forms AACH ($NH_4Al(OH)_2CO_3$) according to the given below chemical reaction (2),

$$CO_2 + H_2O + NH_4^+ + Al^+ + OH^- \rightarrow NH_4Al(OH)_2CO_3 + H_2O \quad (2)$$

By increasing the amount of urea, the number of produced OH^- ions and the pH of the solution increases [20], as shown in Table 1. This increase in the pH results in increasing the number of nucleation sites and ultimately the particle size decreases. Also in accordance with Von Weimarn's theory, the particle size increases as the concentration of the precipitating agent

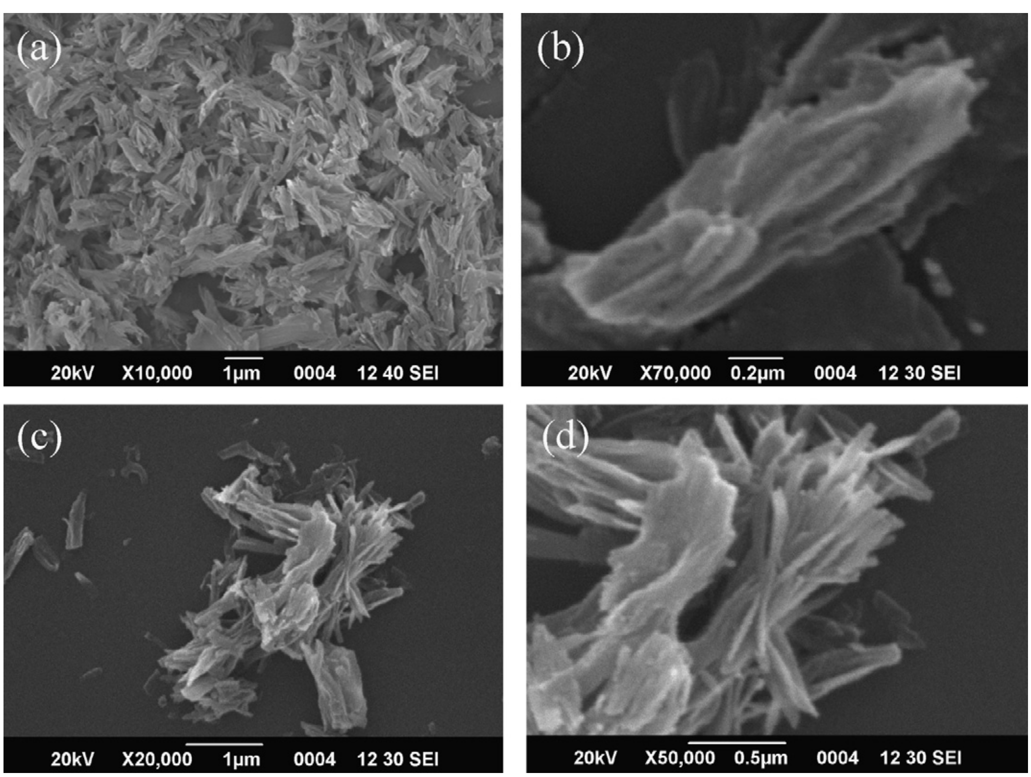

Fig. 1. SEM images of hydrothermally synthesized AACH urchins (a) *U6* low magnification; (b) *U6* high magnification image of individual particle; (c) *U8* low magnification image; (d) *U8* high magnification individual particle.