Synthesis of novel hexagon SnO$_2$ nanosheets in ethanol/water solution by hydrothermal process

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Abstract

The novel hexagon SnO$_2$ nanosheets are successfully synthesized in ethanol/water solution by hydrothermal process. The samples are characterized by X-ray diffraction (XRD), infrared ray (IR) and transmission electron microscopy (TEM). By changing the reaction conditions, the size and the morphology can be controlled. Comparison experiments show that when the temperature increased from 140 °C to 180 °C, the edge length of the hexagon nanoparticles increases from 300–450 nm to 700–900 nm. On the other hand, by adjusting the ratios of water to ethanol from 2 to 0.5, SnO$_2$ nanoparticles with different morphologies of triangle and sphere are obtained. When the concentration of NaOH is increased from 0.15 M to 0.30 M, a hollow ring structure can be obtained.

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1. Introduction

Shape- and size-controlled dispersible inorganic nanocrystals such as metals, semiconductors, and metal oxides have attracted considerable interests because of both their unique material properties compared with their bulk counterparts, and their corresponding theoretical and practical applications in chemistry, physics, material science, biology, and medicine [1–3]. Relative to size control, morphology control is more demanding to achieve by means of classical chemical approaches [4]. So far, several major pathways including vapor-based [5], ionic liquid-crystal [6], microemulsion-based and template-assisted methods [7,8] have been widely applied to synthesize various materials with diverse structures.

Semiconductor particles have attracted more interests because of their size-dependent optical and electrical properties. Among such oxide nano- or microcrystals, SnO$_2$ is an $n$-type semiconductor with a direct band gap of 3.6 eV between the full oxygen 2p valence band and the tin states at the bottom of the conduction band. It has received intensive interests for its applications in solar cells [9,10], catalysis [11], and transparent electrodes [12], especially in combustible and toxic gas detection devices (gas sensors) [13]. For most of these applications, using nanocrystalline SnO$_2$ with high stability against sintering/aging during heat-treatment steps or during their use at high temperatures is regarded as a promising way to fabricate the catalytic and electronic devices (such as gas sensors) with superior performance. Several methods have been employed to prepare SnO$_2$ nanocrystals, such as hydrothermal methods [14], evaporating metal oxide powders [15], microemulsion technology [16], chemical deposition [17,18], solid-state reactions [19], and laser ablation [20]. To date, various nanostructures of SnO$_2$, such as nanoparticles [21], nanorods [22], nanobelts [23], nanoarrays [24], nanotubes [25], nanodisks [26], nanoboxes [27], hollow spheres [28], and mesoporous structures [29] have been prepared.

Hydrothermal techniques have found their places in several branches of modern science and technology. Owing to their
specific physical properties, particularly high salvation power, high compressibility and mass transport of the solvent, one can also expect the occurrence of many novel reactions [14]. In this report, we first synthesize hexagon SnO₂ nanosheets in ethanol/water solution with hydrothermal treatment. To the best of our knowledge, such hexagon nanosheet SnO₂ crystals have not been reported previously.

2. Experimental

Analytical grade 0.105 g of SnCl₄·5H₂O (0.01 M), 0.180 g of NaOH (0.15 M) and 0.315 g of hexadecyltrimethyl ammonium bromide (CTAB, 0.03 M) are mixed in 30 ml distilled water and ethanol (1:1) at room temperature. About 30 min later, the homogeneous solution is transferred into a 50 ml stainless Teflon-lined autoclave and heated at 140 °C for 24 h. Thereafter, the solution containing the products is centrifugally separated, and washed in turn with absolute ethanol and distilled water for several times to obtain SnO₂ products, and then dried in vacuum at 100 °C for 3 h.

3. Results and discussions

The structure and chemical composition of all SnO₂ samples synthesized in this work are confirmed with XRD and IR spectra, and all of the products obtained give the similar results. The typical XRD pattern of as synthesized SnO₂ samples is shown in Fig. 1a. All diffraction peaks can be indexed to tetragonal unit cell with lattice constant \( a=4.737 \text{ nm} \) and \( c=3.185 \text{ nm} \). Six slightly broadened diffraction peaks with \( d \) spacings of 3.35, 2.641, 1.765, 1.674 and 1.436 nm can be readily indexed as (110), (101), (200), (211), (220) and (112) respectively (JCPDS 72-1147). Fig. 1b shows the IR spectra recorded for SnO₂ samples. Peaks at 500–700 cm⁻¹ correspond to Sn–O and SnO₂ stretching [30].

By examining numerous TEM images of the sample, we find that almost all the products are hexagon with 300–450 nm in edge length synthesized at 140 °C [Fig. 2(a)]. Surprisingly, we find stripes on the surface of the sheet, which confirms that the sheet is very thin. Through increasing reaction temperature, the thickness and edge length of SnO₂ nanosheets grow larger. We can get different sizes of SnO₂ by controlling temperature. Fig. 2b presents the SnO₂ sample at 180 °C, which looks much larger and thicker than the sample at 140 °C. The sample is 700–900 nm in edge length. We can not find stripes on the surface, which testifies it is thicker. The exact growth process of the large-sized SnO₂ plates has not yet been established, although some groups have presented the growth mechanism for anisotropic nanostructures synthesized by solution phase methods. The standard explanation for the formation of nanosheet usually involves the role of preformed “seed” and the appropriate capping reagents used to control the growth rate of various facets of the preformed seeds. In the literature, surfactants are often used to prepare metal oxide nanoparticles, in which the polar groups directly interact with the particle surface and strongly influence the particle shape. CTAB is a cation surfactant, which can be absorbed on the surface of Sn(OH)₆²⁻ and lead the growth of SnO₂ crystal. On the other hand, high temperature and high pressure of hydrothermal treatment must have led to the formation of sheet-like micelles, and make nanocrystals grow along sheet-like template which serves as the nuclei for the crystal growth [31]. Successfully controlled growth of SnO₂ hexagon sheets in this article is important both for the fundamental understanding of new nanostructures and for the creation of novel functional devices. One of the attractive features of these hexagon sheet structures is that their thickness is tunable from nano- to microscale by adjusting the reaction temperature.

Fig. 3a, b shows TEM images of SnO₂ at different ratios of water to ethanol. When the ratio is 2, the final product has triangular structure with 300–450 nm in edge length [Fig. 3(a)]. When the ratio is 1, the morphology exhibits hexagon structure [Fig. 2(a)]. When the ratio is 0.5, the final product shows sphere with massif-like structure on the surface [Fig. 3(b)]. It is well known that the surface tension of distilled water is up to \( 73 \times 10^{-3} \text{ N m}^{-1} \) and ethanol is only \( 23 \times 10^{-3} \text{ N m}^{-1} \) at 20 °C. In such reaction situation, the final morphology is easy to change owing to the surface tension at different ratios of water to ethanol. On the other hand, the concentration of NaOH also has a great influence on the final products. When the concentration is 0.30 M, we

![Fig. 1. (a) XRD pattern of SnO₂ samples; (b) IR pattern of SnO₂ samples.](image)

![Fig. 2. TEM images of the SnO₂ nanosheets prepared at different reaction temperatures. (a) \( T=140 \text{ °C} \); (b) \( T=180 \text{ °C} \).](image)
obtain SnO$_2$ hollow ring structure with a hole at the center [Fig. 3(c)]. Surprisingly, under ultrasonic condition, many hollow rings broke up. We think overabundant OH$^-$ can dissolve the SnO$_2$ crystals. To the best of our knowledge, such ring-like morphology has not been reported too.

4. Conclusions

In summary, we find an economical and efficient process for synthesizing large scale hexagon SnO$_2$ nanosheets via a one-step solution-based route. Through controlled temperature, we can get different scales of SnO$_2$ nanosheets. The concentration of NaOH and the ratio of water and ethanol are important to synthesize various morphologies of SnO$_2$ crystals.

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References