A Simple H_2O_2-assisted Method for the Synthesis of Intestine-like SnO_2 Nanostructures at Room Temperature

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Highly crystalline intestine-like SnO_2 nanostructures with hollow interior have been synthesized by a one-step H_2O_2-assisted method at room temperature. A possible growth mechanism has been proposed. In the synthesis, H_2O_2 fulfills important functions in both forming the intestine-like morphology and promoting the formation of hollow structure.

During the past two decades, nanomaterials of unique structure, size, and shape have been designed and show their fascinating physicochemical properties for various potential applications.[1–3] SnO_2 is one of the most intensively studied materials owing to its myriad technological importance.[4–7] Recently, there has been an increasing interest in the preparation of hollow SnO_2 because of their wide potential uses in gas sensing, optoelectronics, lithium batteries, and energy conversion.[8–14] The preparation of hollow SnO_2 nanostructures generally involves the use of removable or sacrificial templates including hard templates such as monodispersed silica[15] and polymer–latex spheres,[16] as well as soft templates including emulsion droplets,[17] micelles,[18] and even gas bubbles.[19] However, hard-template routes usually suffer from the disadvantages of high cost and tedious synthetic procedures. On the other hand, soft templates such as surfactants or emulsion droplets are widely used in preparing special hierarchical structures. Yang and Zeng have successfully prepared intestine-like hollow nanostructure of anatase TiO_2 via a quasi-reverse emulsion solvothermal method.[17] However, this method used organic solvent at high temperature. Therefore, developing a facile, organic-free route to synthesize unique hollow nanostructures is still a challenge.

Herein, we report a one-step H_2O_2-assisted method to synthesize intestine-like SnO_2 nanostructures with nearly 100% morphological yield at room temperature. In the synthesis, H_2O_2 is a green and essential additive which not only induces the formation of intestine-like structures but also promotes their crystallization at room temperature.

In a typical synthesis, 50 μL H_2O_2 (30%) was added to 40 mL of distilled water in a 100 mL beaker and stirred for 10 min. Then 0.04 g of $SnSO_4$ was added to the above solution, and a white suspension gradually appeared under stirring. The suspension was continuously stirred for a period of 24 h at room temperature. After the reaction was completed, the white precipitates were collected from solution, washed with distilled water and absolute ethanol, and then dried under vacuum at 50 °C for 6 h.

XRD analysis was performed on a Philips X'Pert MPD Pro X-ray diffractometer, with graphite monochromatized Cu Kα radiation ($\lambda = 0.1541$ nm). TEM images were recorded on a JEM-100S electron microscope (JEOL). SEM images were taken on a LEO-1530 field emission scanning electron microscope.

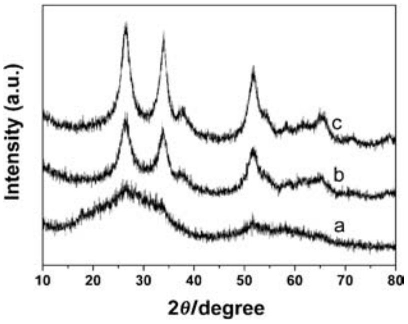

Figure 1. XRD patterns of samples reacted at room temperature (a) 1 h, (b) 12 h, and (c) 24 h, respectively.

The phase composition of the products was examined by X-ray powder diffraction (XRD). Figure 1 shows the XRD patterns of the samples obtained at different stages. Figure 1a shows the XRD pattern of the sample obtained in the initial stage of the reaction (1 h) at room temperature. The weak peaks shown in the pattern indicate that the sample is essentially amorphous. Figures 1b and 1c show the XRD patterns of crystalline SnO_2 with the reactions at 12 and 24 h, respectively. All the strong diffraction peaks could be readily indexed to the tetragonal phase (JCPDS card No. 41-1452) with the lattice constants of $a = 0.4738$ and $c = 0.3187$ nm. Both XRD patterns (Figure 1) and HRTEM image (not show) indicated that the SnO_2 nanoparticles are essentially crystalline. Figure 1 also shows that the crystallinity of product gradually increases with the extending reaction time.

Figure 2a shows the SEM image of the sample. A broken sphere is marked using a square, and the corresponding magnified image in inset clearly shows the hollow feature of the sample. The TEM images with low and high magnifications (Figures 2b and 2c) reveal the hollow nature of intestine-like nanostructures. Figure 2c further indicates the SnO_2 shell

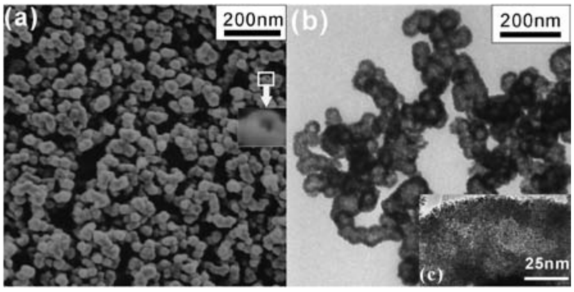

Figure 2. (a) SEM image (the inset is magnified SEM image of open hollow spheres of the square-marked area), (b) low-magnification TEM image, and (c) high-magnification TEM image of the intestine-like SnO_2 nanostructures.

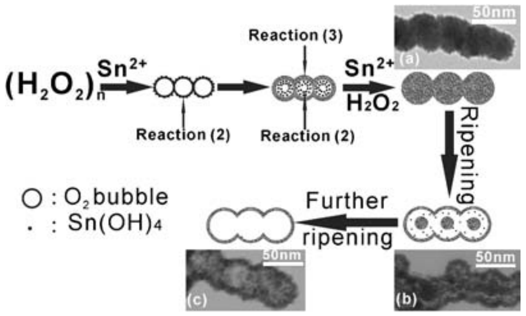

Figure 3. Schematic illustration of the evolution mechanism of intestine-like SnO_2. (a), (b), and (c) are the TEM images of the samples obtained after 1, 12, and 24 h, respectively.

comprises small-sized nanoparticles and is porous. The external diameter of the intestine-like nanostructure is in the range of 40–60 nm, and the shell thickness is ca. 10 nm.

A possible growth mechanism of the intestine-like SnO_2 nanostructures has been proposed and schematically showed in Figure 3. It is known that H_2O_2 molecules easily associated with each other via hydrogen bonds[20] and might form $(H_2O_2)_n$ aggregate. When portion of $(H_2O_2)_n$ decomposes under the synthetic conditions, conjoint O_2 bubbles are generated (reaction 1). In the reaction solution, $SnSO_4$ can be oxidized to $Sn(OH)_4$ by both O_2 and H_2O_2 via reactions 2 and 3:

$$2H_2O_2 \rightarrow 2H_2O + O_2\uparrow \tag{1}$$

$$2SnSO_4 + O_2 + 6H_2O \rightarrow 2Sn(OH)_4 + 2H_2SO_4 \tag{2}$$

$$SnSO_4 + H_2O_2 + 2H_2O \rightarrow Sn(OH)_4 + H_2SO_4 \tag{3}$$

The conjoint O_2 bubbles quickly react with $SnSO_4$ (reaction 2), and the generated $Sn(OH)_4$ can deposit on the surface of O_2 bubbles to form $Sn(OH)_4$ shells. The deposition of amorphous $Sn(OH)_4$ inside the shells may continue until the O_2 is completely consumed, which results in the formation of solid $Sn(OH)_4$ spheres. Simultaneously, the remaining H_2O_2 reacts with $SnSO_4$ in solution (reaction 3), and the $Sn(OH)_4$ is deposited on the outside of amorphous $Sn(OH)_4$ spheres, which makes the conjoint spheres evolve to the intestine-like conjunct aggregate. Additional experiments using $(NH_4)_2S_2O_8$ or $KClO_4$ rather than H_2O_2 were conducted. Note that in the reaction medium both $(NH_4)_2S_2O_8$ and $KClO_4$ can also generate oxygen, but they are free molecules rather than $(H_2O_2)_n$ aggregate. Therefore, there is no bulk intestine-like SnO_2 nanostructure formed in the cases of $(NH_4)_2S_2O_8$ and $KClO_4$, suggesting that the formation of bulk intestine-like SnO_2 is related to the conjoint O_2 bubbles from the decomposition of $(H_2O_2)_n$. The previous work indicated that O_2 bubbles can be served as soft templates to form hollow spheres.[21] However, the oxygen bubbles generated due to the in situ decomposition of $(H_2O_2)_n$ are very small in size and undergo the reaction rapidly, thus it is hard to experimentally capture them in our case.

According to the early work,[22] the intermediate compound originates from the reaction of $Sn(OH)_4$ with H_2O_2 may be metastable and easily dehydrates to produce SnO_2 under stirring at room temperature. The following involved Ostwald ripening process results in the evolution from solid intestine-like SnO_2 (obtained after 1 h, Figure 3a) to core–shell SnO_2 nanostructures (obtained after 12 h, Figure 3b) and finally to hollow intestine-like SnO_2 ones (obtained after 24 h, Figure 3c). This indicates that H_2O_2 also plays an important role in the evolution of hollow SnO_2 structure, in addition to forming the intestine-like morphology.

In conclusion, a simple and organic-free H_2O_2-assisted approach has been developed for synthesizing the intestine-like SnO_2 nanostructures at room temperature. The hollow SnO_2 may find potential applications in gas sensing due to their unique nanostructures. The possible growth mechanism has been illustrated. Our recent study showed that this method can also be applied to the synthesis of intestine-like TiO_2.

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