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Facile synthesis of novel nest-shaped Sb_2O_3 micro/nanostructures and their optical properties

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Supporting information

All of the chemicals were analytical grade and used without further purification. Distilled water was used throughout the experiments. Potassium antimonyl tartrate ($C_4H_4KO_7Sb$) was purchased from Xilong Chemical Industry Incorporated Co. Ltd. Urea (H_2NCONH_2) was purchased from Beijing Chemical Works. Didodecyldimethylammonium bromide (DDAB) was purchased from Aladdin Industrial (Shanghai) Co., Ltd.

The nest-shaped structures of self-assembly Sb_2O_3 micro/nano particles were synthesized *via* wet chemical method. In the typical reaction, a solution was prepared by adding 0.2313 g (0.5 mmol) DDAB to 30 mL of deionized water. After stirring for 1 h, 0.1808 g (0.1 mol/L) urea was added into the above solution under vigorous stirring for 0.5 h to form a homogeneous solution. Then, 0.2004 g (0.02 mol/L) $C_4H_4KO_7Sb$ as antimony source was added into the homogeneous solution and stirred for another 0.5 h. All of these above were done in room temperature and pressure. The mixture was stirred in an oil-bath and heated at 85 °C for 3 h. After the reaction, the resulting solution was cooled naturally to room temperature, and the product was washed several times with absolute ethanol before dried at 60 °C for 12 h, and collected for further characterization.

Controlled experiments were performed for comparison, such as changing the concentration of DDAB, urea, reaction temperature and time, while other conditions remained the same so as to find out the influences of each reaction parameters on sizes and morphologies.

The morphology and size of the as-synthesized product was observed directly by scanning electron microscopy (SEM, Quanta 250 FEG) and Ice emission scanning electron microscope (IESEM, JSM-7500F) equipped with energy-dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies were performed using JEOL JEM-2100F electron microscopes. The phase composition of the as-prepared product was determined using a Rigaku Dmax 2200 X-ray diffraction (XRD), equipped with Cu Kα radiation of 1.5406 Å. The patterns were recorded at a scanning rate of 6° min^{-1} from 10° up to 80° (2θ). The UV-vis diffusive reflectance spectrum was performed in a UV-3600 spectrophotometer at room temperature using barium sulfate as the reference. The groups on the samples were studied by Fourier transform infrared spectrometer (FT-IR, Nicolet, iN10MX). The Raman spectroscopy was performed on a laser Raman spectrometer (LabRAM HR800) using a visible laser (λ = 325 nm) at room temperature. The ability of emission excitation of Sb_2O_3 micro/nanosturctures was investigated using Cary Eclipse photoluminescence (PL) analyzer.

Influences of reaction parameters

The sizes and morphologies of the Sb_2O_3 products can be controlled by adjusting the concentration of DDAB, concentration of urea, reaction temperature and time. Among them, DDAB concentration is one of the most crucial factors according to our experimental data.

To ascertain the effect of the DDAB on the Sb_2O_3 morphologies, the SEM images of the Sb_2O_3 micro/nanostructures prepared with different DDAB concentrations at 85℃ for 3h with the addition of 0.1 mol/L urea are shown in Fig. S1. Only block polyhedron clusters were observed (Fig. S1a) and Sb_2O_3 nest-shaped structures could not be obtained without DDAB. In the system with 0.1 mmol DDAB, the product exhibiting with primary shape of flowers (Fig. S1b), and the flower-shaped Sb_2O_3 were grown bigger when 0.3 mmol DDAB were added (Fig. S1c). Further increasing the concentration to 0.5 mmol, a high yield of nest-shaped Sb_2O_3 micro/nanostructures were fabricated successfully (Fig. 2a). When the DDAB concentration increased to 0.6 mmol, the irregular nest-shaped with bigger size of Sb_2O_3 were formed (Fig. S1d).

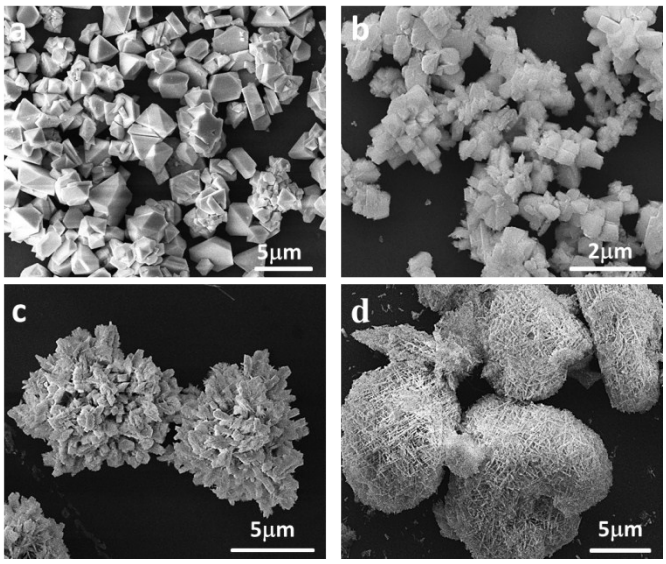

Fig. S1 SEM images of Sb_2O_3 nanorod-bundles synthesized with different DDAB concentrations at 85 ℃ for 3 h:(a) 0 mmol; (b) 0.1 mmol; (c) 0.3 mmol; (d) 0.6 mmol.

According to the experimental results, the concentration of urea also had significant effects on the morphologies and sizes of the final products. Sb_2O_3 micro/nanostructures were prepared with different urea concentrations while kept other conditions unchanged. Fig. S2 shows the SEM image of the as-synthesized products under the same reaction temperature of 85℃, at 3h and DDAB concentration of 0.5 mmol, but the urea concentrations were 0.02, 0.06, 0.16 and 0.2 mol/L, respectively. When 0.02 mol/L urea were added, most products exhibited an oriented micro sheet-flower structure(Fig. S2a). However, micro-sphere assembled by microwires was formed when the urea concentration was increased to 0.06 mol/L (Fig. S2a). With the increasing addition of 0.1 mol/L urea, unexceptionable structure of nest shape was obtained as shown in Fig. 2a. Further increasing the concentration, the morphology of nest shape was maintained, but nanorods that self-assembled into nest shape showed severe adhesion(Fig. S2c) and convert toward nanosheet (Fig. S2d). These results show that higher urea concentrations facilitate the formation of large and wide particles.

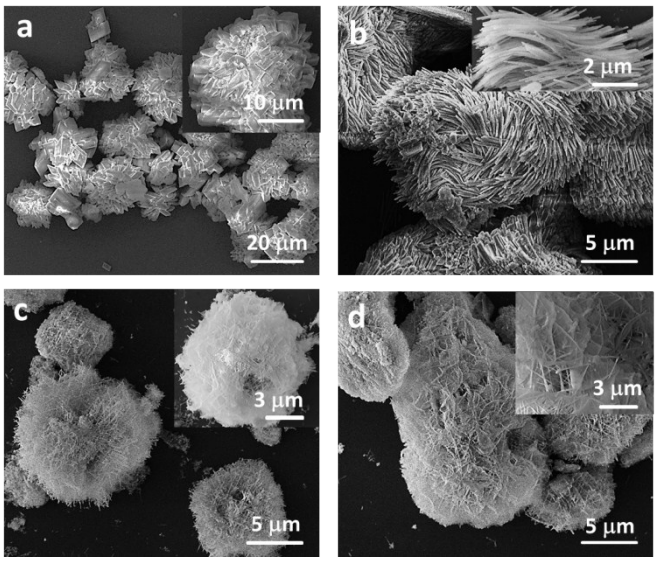

Fig. S2 SEM images of Sb_2O_3 micro/nanostructures synthesized with different concentrations of urea at 85 ℃ for 3 h with 0.5mmol DDAB:(a) 0.02 mol/L; (b) 0.06 mol/L; (c) 0.16 mol/L and (d)0.2 mol/L.

Fig. S3 shows the SEM images of the as-synthesized nest-shaped Sb_2O_3 after heating in an oil-bath at 75, 80, 90 and 95℃ for 3 h. Our studies indicated that urea scarcely decomposed below 75℃, but decomposed into cyanate above 100℃. Flower-like Sb_2O_3 with a hole in the middle were formed by oriented nanorods at 75℃, as shown in Fig. S3a. As the temperature increasing to 80℃, the lengths of these nanorods increased and diameters

decreased, and then assembled into nest shapes but with irregular shape and size (Fig. S3b). When the temperature increased to 85℃, the lengths and diameters of nanorods continuously change, homogeneous product with predominance of nest-shaped shapes were formed (Fig. 2a). Further increasing of the temperature, the same nest shapes were obtained, but with different diameters. The above facts indicate that temperature has a little effect on morphology.

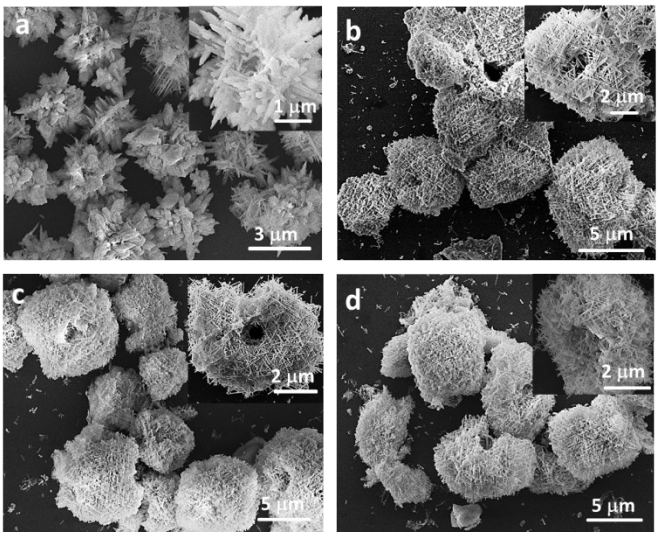

Fig. S3 SEM images of Sb_2O_3 micro/nanostructures synthesized with different reaction temperaturefor 3 h with 0.5 mmol DDAB: (a) 75 °C; (b) 80 °C; (c) 90°C; (d) 95°C.

In order to explore the shape developing process of the nest-shaped Sb_2O_3, a series of time-dependent morphologies can be observed in Fig. S4. After 0.5 h, the particles were formed (Fig. S4a). With the increase of reaction time, the particles grown along with the center axis orderly and aggregated at the same time as shown in Fig. S4b. When the reaction time was prolonged to 1.5 h, the particles began to form nanorods (Fig. S4c). With the further elongation of the reaction time to 2.5 h, the irregular nest-like morphology was obtained in Fig. S4d. The rods grown longer and finally formed nest-shaped structures (Fig. S4e) when the reaction time increased to 3h.

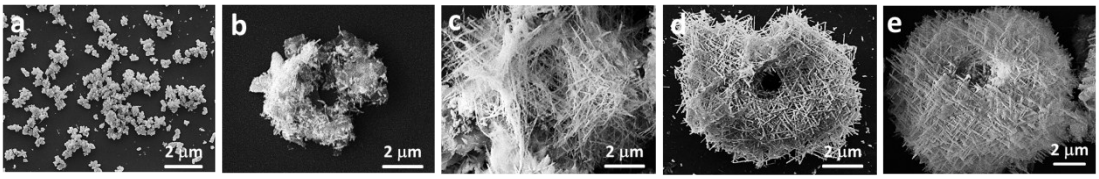

Fig. S4 FESEM images of the as-prepared products obtained at different time:(a) 0.5 h; (b) 1 h; (c) 1.5 h; (d) 2.5 h; (e)3 h.