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Synthesis of micro-sized Sb_2O_3 hierarchical structures by carbothermal reduction method

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ABSTRACT

Micro-sized Sb_2O_3 hierarchical structures were prepared by carbothermal reduction method, using antimony doped tin oxide (ATO) nanoparticles and graphite powder as source materials. The products were characterized by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and field-emission scanning electron microscopy (FE-SEM). Furthermore, the possible growth mechanism of the as-synthesized samples was discussed. The room-temperature photoluminescence (PL) measurement exhibited one relatively strong violet emission peak at about 420 nm under the 325 nm excitation wavelength and another violet emission peak, about three times stronger in intensity than the former, at about 435 nm under the 365 nm excitation wavelength. In addition, the optimal excitation wavelength of 363 nm was obtained and the luminescence causes were speculated.

1. Introduction

With the rapid development of micro/nano technology, micro/nano-scale structures have aroused intense interest due to their novel properties and potential applications in many realms [1]. So far, the means of synthesizing micro/nano-scale structures have been very plentiful. Thereinto, carbothermal reduction is a common method, and varieties of micro/nano materials with different morphologies have been prepared such as metal, metal oxide, nonmetal oxide, composite, etc. [2–6].

Antimony trioxide (Sb_2O_3), an important member of V–VI main group compounds, has been widely used as flame retardants, catalyst agents, covering agents, functional fillers and so on [7,8]. In recent years, more attention has been paid to Sb_2O_3 nano- or microstructures because of their unique optical and optoelectronic properties, as well as the potential applications in the micro/nano-scale electronic and optoelectronic devices. So far, various strategies have been reported on synthesis of Sb_2O_3 materials such as microemulsion method [9], hydrolysis–precipitation approach [10], vapor condensation method [11], solvothermal process [7,12], hydrothermal route [13,14], aqueous solution strategy [15,16], electrochemical preparation [17], biosynthesis [18] etc. In this letter, a simple and facile route for micro-sized Sb_2O_3 hierarchical structures by carbothermal reduction method was reported and their characteristics were discussed.

2. Experimental section

The products were fabricated in the tube furnace. First, the source materials consisting of ATO nanoparticles and graphite powder (3 g, 6:1 in mass ratio) were located at the central of an alumina tube with 100 cm in length and 3 cm in inside diameter, and a silicon wafer was put at downstream of the tube furnace being 13 cm away from source materials. For the purpose of air removal, Ar gas was pumped into the furnace at the rate of 200 standard cubic centimeters per minute (sccm) for 2 h, and then the tube furnace was started and, meanwhile, the rate of Ar gas was changed into 100 sccm. After the furnace was heated to the setting temperature of 1150 °C, O_2 was pumped into at the rate of 1 sccm for 2 h. Then, the rate of Ar gas was kept and O_2 was terminated until the system was cooled to the room temperature naturally. Finally, grey samples were obtained on the silicon wafer.

The as-synthesized products were characterized by X-ray powder diffraction (XRD, Philips PW 1710 with Cu Kα radiation, $\lambda = 1.5406$ Å), X-ray photoelectron spectroscopy (XPS, ESCALAB-250) and field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700 F). Also, room-temperature photoluminescence spectra (PL, Edinburgh luminescence spectrometer FLS 920, NEXUS) were tested with the excitation wavelength of 325 nm

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and 365 nm by the Xe lamp, and excitation spectrum was recorded as well.

3. Results and discussion

Powder XRD pattern of the as-prepared samples is shown in Fig. 1(a). All the peaks can be indexed to orthorhombic phase of Sb_2O_3 with the cell parameters of a = 4.914 Å, b = 12.460 Å, c = 5.240 Å (JCPDS card NO. 011-0691). No peaks of metal Sb or any other phases were detected, demonstrating that the products are very high purity, single-phase samples. In addition, the intense and sharp diffraction peaks suggest the products are well crystallized. XPS spectra in Fig. 1(b) and (c) further confirm the Sb_2O_3 compositions of the samples. Fig. 1(b) is the typical survey spectrum, indicating the presence of Sb and O elements. The appearance of C impurities peaks is due to graphite powder in source materials. Fig. 1(c), the core level spectrum, displays that the two strong peaks at 530.5 eV and 539.7 eV correspond to $Sb3d_{5/2}$ and $Sb3d_{3/2}$ binding energy respectively, which coincides with the reported values in the literature [19], and the peak at 532.1 eV corresponds to O1s binding energy.

Fig. 2(a)–(d) represents the FE-SEM images of the products. From Fig. 2(a), it can be seen that some complicated hierarchical structures distribute dispersedly on the silicon wafer. Fig. 2(b)–(d), high-magnification images of the hierarchical structures, reveals that the samples consist of trunks (thick and long rod-like structures) and lateral branches (sheets and short rods). In accordance with the analysis of these images: the sheets were about 4–5 μm in length, 1.8 μm in width, 200–300 nm in thickness; the short rods were about 2 μm in diameter, 4–5 μm in length; most angles between trunks and their lateral branches were nearly 90°.

A small number of cylindrical particles and rod-grown particles, as shown in Fig. 3(a) and (b), exist around the hierarchical structures. These particles can be considered as the intermediates of the hierarchical structures. From the HRTEM of the cylindrical particle (inset in Fig. 3(a)), the possible preferential growth direction of [101] could be speculated. Combined with Fig. 3(a) and (b), the forming process of hierarchical structures can be proposed and the schematic diagram of the forming process is exhibited in Fig. 4. When Sb_2O_3 monomer concentration is relatively low at the initial reaction stage, spherical particles are favored to form according to Ostwald ripening and the particles tend to grow up continuously (Fig. 4(a)) [20,21]. Along with the reaction going on, the higher Sb_2O_3 monomer concentration leads to different growth rates for different faces [22]. The spherical particles grow along the preferential growth direction of [101] and the cylindrical particles begin to form (Fig. 4(b)). When some defects formed on the surface of the previously formed crystals, the defects would serve as secondary nuclei for the growth of sub-arms of the crystals [23,24]. And generally the sub-arms are perpendicular to the main branches due to the crystals with orthorhombic structure (Fig. 4(c)). The size of the defects would finally determine the diameter of the sub-arms. In addition, the mass transfer rate in different position would also influence the size of the arms, which have been observed in the current work, and the sub-arms were only formed at a relative high evaporation rate. So, as the Sb_2O_3 monomer concentration gradually decreases, the sub-arms will stop growing. Eventually, the hierarchical structures in Fig. 4(d) were formed.

Room-temperature PL spectra shown in Fig. 5 present that the micro-sized Sb_2O_3 hierarchical structures have very obvious photoluminescence properties. Fig. 5(a), the emission spectrum, reveals two strong violet emission peaks: the one is at about 420 nm under the 325 nm excitation wavelength; the other, about three times stronger in intensity than the former, is at about 435 nm under the 365 nm excitation wavelength. Fig. 5(b) is the excitation spectrum, displaying that the optimal excitation wavelength is at about 363 nm, which proved the accuracy that the peak intensity under

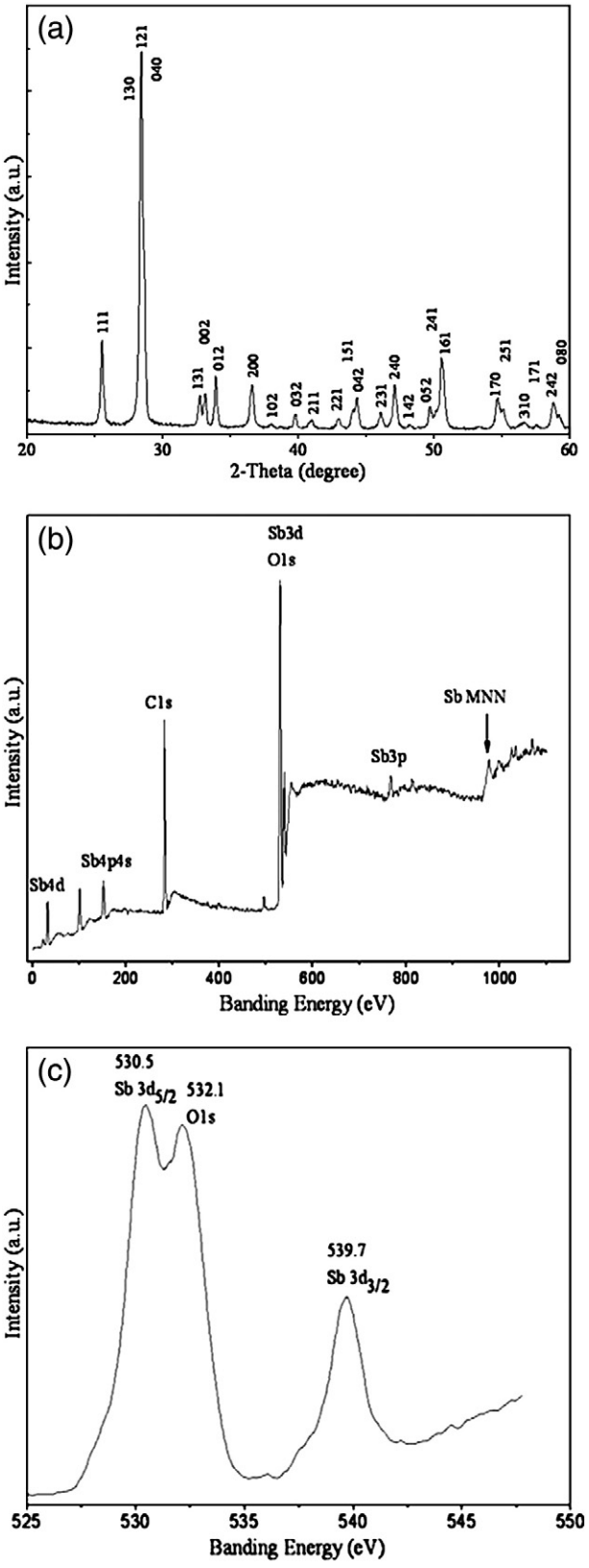

Fig. 1. Powder XRD and XPS patterns of the as-prepared samples. (a) powder XRD; (b) typical survey spectrum and (c) core level spectrum of XPS.