Synthesis and photoluminescence properties of SnO₂/ZnO hierarchical nanostructures
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A B S T R A C T
SnO₂/ZnO hierarchical nanostructures were synthesized by a two-step carbon assisted thermal evaporation method. SnO₂ nanowires were synthesized in the first step and were then used as substrates for the following growth of ZnO nanowires in the second step. Sn metal droplets were formed at the surfaces of the SnO₂ nanowires during the second step and were acted as catalyst to facilitate the growth of ZnO nanowires via vapor–liquid–solid mechanism. Room temperature photoluminescence measurements showed that the SnO₂/ZnO hierarchical nanostructures exhibited a strong green emission centered at about 520 nm and a weak emission centered at about 380 nm. The emissions from the SnO₂ were drastically constrained due to screen effect caused by the ZnO layer.

1. Introduction
One-dimensional (1D) nanostructures, such as nanowires, nanorods, nanotubes, and nanobelts, have attracted intensive interest due to their special physical, chemical properties, and potential applications as building blocks for nanodevices, such as lasers, sensors, transistors, and generators [1–7]. It is a crucial step toward the realization of functional nanosystems by assembling 1D nanoscale building blocks into two- and three-dimensional ordered superstructures or complex functional architectures. Hierarchical nanostructures are composed of trunks and branches, which consist of the same or different materials. This special structures show some novel properties resulting from their multi-dimensional shape and the combination of both micrometer-scale and nanometer-scale building blocks and thus have attracted much attention recently [8–16]. A variety of hierarchical nanostructures, such as ZnO [11], ZnS [8], SnO₂ [17], Ga₂O₃/In₂O₃ [18], ZnS/ZnO [19], ZnS/CdS [20], In₂O₃/ZnO [21], and CuO/ZnO [13], have been reported recently. However, the controlled synthesis of the hierarchical structures is still a challenge.

A rational way to synthesize hierarchical nanostructures is a two-step method: Trunks are synthesized in the first step. Then a thin layer of Au film is deposited on the trunk to act as catalyst to synthesize branches via vapor–liquid–solid (VLS) mechanism in the second step. This method is simple and effective. Many hierarchical nanostructures, such as ZnO [11], ZnS [9], CdSe [12], ZnS/CdS [20], have been successfully synthesized by this method. Consistent with Au droplets, Sn droplets can also act as catalyst to facilitate the formation of nanowires or nanobelts via VLS mechanism, such as ZnO nanowires/nanobelts [22], ZnS nanowires [23], and Ga₂O₃ nanobelts [24]. Although the synthesis of SnO₂/ZnO hierarchical nanostructures has been reported [25,26], developing new method to synthesis such nanostructure is still needed. In this paper, we report the synthesis of SnO₂/ZnO hierarchical nanostructures by a two-step carbon assisted thermal evaporation method. Sn droplets were formed on the surface of SnO₂ trunks during the second step. Then the Sn droplets acted as catalyst to facilitate the formation of ZnO nanowires via VLS mechanism. The room temperature photoluminescence (PL) properties of the SnO₂/ZnO have also been discussed. This method is simple, cost effective, and highly reproducible.

2. Experimental details
SnO₂/ZnO hierarchical nanostructures were synthesized by a two-step carbon assisted thermal evaporation method. SnO₂ nanowires were synthesized in the first step. A mixture of SnO₂ and C powder (molar ratio: 1:1) was placed in the center of a ceramic boat. A piece of Au (10 nm) coated Si wafer was covered on the top of the ceramic boat to collect SnO₂ nanowires. The distance between the mixture and the wafer was about 4 mm. Then the ceramic boat was placed in the center of a quartz tube. The quartz tube was inserted in a horizontal tube furnace. The pressure inside the system was adjusted to 1 Pa. A gas mixture containing Ar and O₂ (Ar:O₂=100:1 by volume) was passed...
through it at a flow rate of 20 sccm for the entire process. The furnace was raised to 800 °C at a rate of 50 °C min⁻¹ and kept at that temperature for 30 min. After the furnace was cooled to room temperature, a layer of white wool-like product was found on the surface of the Si wafer. In the second step, the SnO₂ nanowires obtained in the first step was placed 11 cm away from the center of the tube downstream. A mixture of ZnO and C powder (molar ratio: 1:1) was placed in the center of a ceramic boat. The boat was placed in the center of the tube. The pressure inside the system was adjusted to 1 Pa. Ar gas was passed through it at a flow rate of 20 sccm for the entire process. The furnace was raised to 850 °C at a rate of 50 °C min⁻¹ and kept at that temperature for 1 h. After the furnace was cooled to room temperature, a layer of black wool-like product was found on the Si wafer.

X-ray diffraction (XRD) patterns were collected using a Philips X’Pert diffractometer with Cu Kα irradiation at room temperature. Scanning electron microscopy (SEM) images and Energy dispersive X-ray spectroscopy (EDS) spectra were obtained in a Hitachi-S-3400 N II instrument. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were obtained in a Philips Tecnai F20 instrument, operating at 200 kV. The PL

![Figure 1](image-url)
measurements were carried out on an ultraviolet-visible spectrophotometer (Labram HR800) with a 325 nm He–Cd laser and a 514 nm Ar ion laser as the excitation sources.

3. Results and discussion

The SnO₂ nanowires obtained in the first step were characterized by SEM. A typical low magnification SEM image is shown in Fig. 1a. As can be seen, a large quantity of nanowires with typical lengths in the range of several to several tens of micrometers was obtained. A high magnification SEM image is shown in Fig. 1b. Each nanowire has a uniform width along its length. The average diameter of the nanowires is about 200 nm. Au particle is observed at the tip of each SnO₂ nanowire as shown in the inset of Fig. 1b, which indicates SnO₂ nanowires were formed via VLS mechanism. EDS spectrum of the SnO₂ nanowires is shown in Fig. 1c. Besides Au element, peaks belonging to O and Sn are observed. Fig. 1d shows the XRD pattern of the SnO₂ nanowires. All the peaks can be indexed to the tetragonal rutile structure of SnO₂, with lattice constants of \( a = 0.4738 \) nm and \( c = 0.3187 \) nm (JCPDS NO.: 41–1445), which indicates phase pure SnO₂ nanowires were obtained. The nanowires were further characterized by TEM. Fig. 1e shows a typical TEM image of a single nanowire. The diameter of the nanowire is about 200 nm, which is consistent with the SEM result. The HRTEM image taken from the single nanowire is shown in Fig. 1f. Clear lattice fringes are observed, which indicates the high crystallinity of the nanowire. The lattice spacing of the crystallographic planes is 0.47 nm, which corresponds to the (1\( \overline{1} \)0) or (0\( \overline{1} \)0) lattice plane of rutile SnO₂ crystal. The corresponding fast Fourier transformation (FFT) pattern of Fig. 1f is shown in the inset of Fig. 1f. From the HRTEM and FFT images, the growth direction of this nanowire is determined to be (1\( \overline{0} \)0).

SnO₂/ZnO hierarchical nanostructures would form after the second step. Fig. 2a shows a low magnification SEM image. A large quantity of nanowires with wool-like surfaces is observed. The high magnification SEM image (see Fig. 2b) shows that a large quantity of thin ZnO nanowires is grown on the surfaces of the SnO₂ nanowire. The diameters of the newly formed ZnO nanowires range from 15 to 50 nm. The lengths of the ZnO nanowires are in the range of several tens nanometers to several micrometers. Sn particle is observed at the tip of each ZnO nanowire as shown in the inset of Fig. 2b. Thus the growth mechanism of ZnO branches is VLS. The EDS spectrum of the hierarchical nanostructures is shown in Fig. 2c. Peaks belonging to Zn, Sn, and O elements are observed. The XRD pattern of the SnO₂/ZnO hierarchical nanostructures is shown in Fig. 2d. Peaks belonging to hexagonal ZnO (JCPDS NO.: 80–0075), metallic \( \beta \)-Sn (JCPDS NO.: 04–0673), and tetragonal SnO₂ (JCPDS NO.: 41–1445) are observed in the XRD pattern. No other phases are observed in the XRD pattern.

The SnO₂/ZnO hierarchical nanostructures were further characterized by TEM. Fig. 3a shows a typical TEM image of the hierarchical nanostructures. Sn particle is observed at the tip of each branch nanowire, which is consistent with the SEM result. The HRTEM image of the Sn particle is shown in Fig. 3b. Lattice spacing of 0.29 nm is determined from Fig. 3b, which is in good agreement with the \( d \)-value of 0.2915 nm for the (1\( \overline{0} \)0)\(_{\text{Sn}}\) set of planes, confirming that the particle is pure metallic tin. As can be seen the particle shows a core/shell structure. The lattice spacing of the shell is about 0.26 nm, which is consistent with the lattice spacing of (0\( \overline{0} \)1) planes of hexagonal ZnO. The ZnO shell might be formed during the cooling process. The crystal lattice curves in the surface part may provide some information for the understanding the growth of nanobubbles [27] and need further investigation. Two kinds of ZnO nanowires are found from HRTEM measurements. Fig. 3c and d show the typical HRTEM images of the two kinds of nanowires. The clear lattice fringes observed in Fig. 3c and d indicate that the ZnO nanowires have good crystallinity. Lattice spacing of 0.248 nm is determined from Fig. 3c,
which can be ascribed to the (−1 0 1) or (1−1 1) planes of hexagonal ZnO (JCPDS: 80–0075). The corresponding FFT pattern of Fig. 3c is shown in the inset of Fig. 3c. The diffraction spots can be indexed to the (−1 0 1) or (1−1 1) planes of hexagonal ZnO. Lattice spacing of 0.28 nm is determined from Fig. 3d, which can be ascribed to the (1 0 0) planes of hexagonal ZnO. The corresponding FFT pattern is shown in the inset of Fig. 3d. (100) and (1−1 0) diffraction spots are observed.

A simple model is proposed to explain the formation of the SnO$_2$/ZnO hierarchical nanostructures. Fig. 4 shows the schematic diagram to explain the growth mechanism. First, SnO$_2$ nanowires were formed in the first step (Fig. 4a). The as-synthesized SnO$_2$ nanowires were placed downstream of the tube furnace. In the second step, ZnO reacted with C to generate Zn vapor and CO vapor. The Zn and CO vapor would be transported to the downstream side by the carrier gas Ar. Then two possible reactions will happen on the surfaces of SnO$_2$ nanowires to form Sn droplets (Fig. 4b):

\[
2\text{Zn}(g) + \text{SnO}_2(s) \rightarrow 2\text{ZnO}(s) + \text{Sn}(l)
\]

(1)

\[
2\text{CO}(g) + \text{SnO}_2(s) \rightarrow 2\text{CO}_2(g) + \text{Sn}(l)
\]

(2)

The Zn vapor transported to the SnO$_2$ would be absorbed by Sn droplets. When the droplets became supersaturated, ZnO nanowires would be formed, possibly by the reaction between Zn and CO$_2$.

The room temperature PL spectra of SnO$_2$ nanowires and SnO$_2$/ZnO hierarchical nanostructures were investigated. Fig. 5a shows the PL spectra of the two samples excited by a He–Cd laser (325 nm). Two emission peaks centered at ~585 and ~615 nm are observed in the PL spectrum of the SnO$_2$ nanowires. According to previous reports [28–30], both of the two emission peaks are attributed to oxygen vacancies. No ultraviolet (UV) luminescence is observed. The direct band gap of SnO$_2$ is 3.6 eV, which is dipole forbidden [31,32]. The direct gap luminescence can be observed in ultrathin nanowires [28,33,34]. Because the SnO$_2$ nanowires we obtained are not thin enough, the band gap related UV luminescence cannot be observed [28]. Two emission peaks centered at ~380 (see the inset of Fig. 5a) and 520 nm are observed in the PL spectrum of the SnO$_2$/ZnO hierarchical nanostructures. The UV emission (380 nm) is attributed to free-exciton recombination at the near-band edge of ZnO [35]. The green emission (520 nm) is due to the radiative recombination of the photo-generated holes with electrons belonging to the oxygen vacancy of the surface [36]. Compared with the PL spectrum of the SnO$_2$ nanowires, the oxygen vacancies related emissions of SnO$_2$ are drastically constrained, which is attributed to the screen effect caused by ZnO nanowires. The result is consistent with previous reports [25,26]. Because a large quantity of the ZnO nanowires was formed on the surfaces of SnO$_2$ nanowires, the UV light (325 nm) was hard to
SnO2/ZnO hierarchical nanostructures show a broad emission consistent with the PL spectrum excited by a He–Cd laser. The about 640 nm and a weak peak centered at 580 nm, which is electronic devices.

As long wavelength laser can penetrate deeper than short wavelength laser, the screen effect should be vanished if we excited the SnO2/ZnO hierarchical nanostructures with a long wavelength laser. Thus we measured the PL spectra of SnO2 nanowires and SnO2/ZnO hierarchical nanostructures excited by an Ar ion laser with a wavelength of 514 nm, which are shown in Fig. 5b. The SnO2 nanowires show a broad emission centered about 640 nm and a weak peak centered at 580 nm, which is consistent with the PL spectrum excited by a He–Cd laser. The SnO2/ZnO hierarchical nanostructures show a broad emission centered at about 670 nm and a weak peak centered at 590 nm. The emission centered at 670 nm can be attributed to SnO2 nanowires. Compared with SnO2 nanowires, this emission of the SnO2/ZnO hierarchical nanostructures is broader and has a red shift. This phenomenon might be attributed to the defects introduced into SnO2 nanowires during the growth of ZnO branches. The weak peak centered at 590 nm is the combination of the emissions from ZnO nanowires and SnO2 trunk nanowires. From those results, we can conclude that the screen effect is indeed vanished when excited by an Ar ion laser (514 nm).

4. Conclusions

In summary, SnO2/ZnO hierarchical nanostructures were successfully synthesized by a two-step carbon assisted thermal evaporation method. The ZnO branches were formed on the surfaces of SnO2 nanowires via VLS mechanism using Sn droplets as catalyst. The diameters of the ZnO branches were in the range of 15–50 nm, while the lengths could be up to several micrometers. The SnO2/ZnO hierarchical nanostructures showed a strong green emission centered at about 520 nm and a weak emission centered at about 380 nm when excited by a 325 nm laser. Due to the screen effect caused by ZnO branches, the emissions of SnO2 nanowires were drastically constrained. The PL spectra excited by a 514 nm laser confirmed the screen effect. This novel structure may find applications in nanoscale optoelectronic devices.

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