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High yield synthesis and photoluminescence properties of carbon coils over Al_2O_3 substrates

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ABSTRACT

Using acetylene as carbon source, high yield of carbon coils could be synthesized directly over Al_2O_3 substrate through the decomposition of acetylene at 500 °C. The microstructure and photoluminescence (PL) properties of the obtained carbon coils were investigated in detail. The results demonstrate that the as-synthesized carbon coils exhibit a strong ultraviolet (UV) PL peak at 365 nm and a sideband peak at 465 nm. By increasing the excitation wavelength from 220 to 300 nm, the UV PL could be enhanced. Because of the as-synthesized carbon coils directly growing over Al_2O_3 substrate, the proposed route for the synthesis of carbon nanomaterials may expand their utilization in electronics effectively.

1. Introduction

Due to their unique shape and potential applications such as nanosprings, electromagnetic wave absorbers and micro-sensors, carbon nanocoils/microcoils (CNCs/CMCs) have attracted much interest in the past years [1–3]. In order to realize these applications, it is necessary to produce high yield of CNCs/CMCs. It is recognized that the quality of CNCs/CMCs is mainly determined by structure and composition of the used catalysts [4–8]. For example, by introducing H_2S, Motojima et al. produced CMCs over a Ni powder catalyst at 770 °C [9]. Bajpai et al. reported the synthesis of aligned CNCs by co-pyrolysis of $Fe(CO)_5$ and pyridine at 900–1100 °C [10]. Wang et al. presented the rational synthesis of CNCs and helically coiled carbon nanowires through the use of In and Sn catalysts at 800 °C [11]. Using activated carbon nanotube (CNT) supported Ni as catalyst, Liu et al. prepared CMCs and CNCs at 750 °C [12]. Over Fe–Sn based catalyst, Li et al. reported that CNCs could be produced at a lower temperature (700–770 °C) [13]. Recently, Hirahara et al. found that the efficiency in the growth of CNCs could be significantly improved by introducing a SnO_2 buffer layer into the Fe–Mg–Co/Al_2O_3 catalyst [14]. Generally, common to all the reported synthesis routes for CNC/CMC growth is the necessity of transition-metal catalysts and high pyrolysis temperature (>700 °C), and adding the impurity such as tin or sulfur, or using a specific substrate such as ceramics could improve their yield effectively [15,16]. In recent years, Huang [17] and Liu et al. [18] reported the growth of single-walled carbon nanotubes (SWCNTs) directly over Si/SiO_2 substrate without using any transition-metal catalysts, respectively. However, up to now, there is no report on the growth of CNCs/CMCs directly on a substrate.

Enlightened by these ideas and based on our previous works [19,20], in the study, we investigate the synthesis of carbon nanomaterials (CNMs) over Al_2O_3 substrate without using transition-metal catalysts. And the result indicated that high yield of carbon coils could grow directly over Al_2O_3 substrate, and the PL properties of the obtained carbon coils were also investigated in detail.

2. Experimental

In a typical procedure, Al_2O_3 substrate was dispersed on a ceramic plate which was placed inside a quartz tube. With argon (Ar) flowing through the reaction tube, the temperature of the furnace was raised from room temperature (RT) to 500 °C. Then Ar was cut off and acetylene was introduced into the tube at 500 °C for 1 h. After cooling to RT in Ar naturally, voluminous black floccules could be observed clearly over the Al_2O_3 substrate. In order to understand the growth of carbon coils over Al_2O_3 substrate, an Al_2O_3 substrate was annealed at 500 °C for 0.5 h with the introduction of Ar into the tube all the time.

The samples were examined on an X-ray powder diffractometer (XRD) at RT for phase identification using CuK_α radiation (model D/Max-RA, Rigaku). The morphologies of the samples were examined using a transmission electron microscope (TEM) (model H-7650, operated at an accelerating voltage of 100 kV), field emission scanning electron microscope (FE-SEM) (model FEI Sirion 200, operated at accelerating voltages of 5 kV). Raman spectroscopic investigations were performed

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using a Jobin-Yvon Labram HR800 instrument with 532 nm laser excitation. The photoluminescence (PL) spectra of the obtained sample were obtained at RT by a spectrofluorophotometer using Xe lamp as the light source.

3. Results and discussion

The microstructures of the annealed Al_2O_3 substrate and the sample obtained over Al_2O_3 substrate are shown in Fig. 1. As shown in Fig. 1a, one can find that the surface of the annealed Al_2O_3 is relatively smooth and contains many cavities on the surface. The enlarged FE-SEM image (as shown in Fig. 1b) indicates many Al_2O_3 particles (as indicated by the arrows in Fig. 1b) with different sizes that could be observed clearly. And the surface EDX analysis of the substrate indicates the presence of the elements Al and O, no other elements such as Fe, Co or Ni could be detected (not shown here). As shown in Fig. 1c, the low magnified FE-SEM image indicates that the major morphology in the obtained sample is carbon coils. And the yield, defined as the ratio of the number of carbon coils to the total carbon products, is ca. 90%. Fig. 1d gives a closer FE-SEM observation, which reveals that the obtained carbon coils have a fiber diameter of 50–300 nm, a coil diameter of 0.2–2 μm and a length of 50–120 μm. The enlarged FE-SEM image (as indicated by the arrow in the inset image of Fig. 1d) indicated that the size of a single CMC is very uniform and the fiber diameter is ca. 260 nm. Generally, as shown in Table 1, the previous reports indicate that transition-metal catalyst and high temperature are necessary to obtain high yield of CNCs/CMCs [21–24]. Herein, high yield of carbon coils can be obtained directly over Al_2O_3 substrate at a relative low temperature (500 °C) without using any transition-metal catalysts, which was not reported before.

Fig. 2 displays some typical TEM images of the as-synthesized carbon coils. As shown in Fig. 2a and b, there are no particles that could be observed from the top to root of CMC. As revealed by the FE-SEM investigation, the typical CNC is uniform in size and the diameter is ca. 75 nm. Fig. 2c and d shows the low and high resolution TEM of a typical CNC. Fig. 2c indicates that the obtained CNC is uniform (average diameter: 70 nm), and no particles could be seen in the middle of CNC. The high resolution for the top of the typical CNC is shown in Fig. 2d. One can find that there is no particle at the top of CNC. In order to confirm the CNC yield obtained by the FE-SEM investigation, based on the statistical TEM observation, the morphology distribution histogram is shown in the inset of Fig. 2d. One can find that high yield of carbon coils could be really synthesized over Al_2O_3 substrate without using any transition-metal catalysts. Although the exact CNC/CMC formation mechanism is still unclear, as mentioned by the previous results [17,25], some oxide particles including SiO_2, Al_2O_3 and TiO_2 have been proved to be active for the growth of SWCNTs. Based on the obtained results, we think that the catalysis of Al_2O_3 particles and the high temperature cause the decomposition of active C_2H_2 molecule and the CNC/CMC growth.

Fig. 3 shows the XRD pattern and Raman spectrum of the obtained carbon coils. As shown in Fig. 3a, all the diffraction peaks correspond to the phases of C and Al_2O_3, and no other peaks can be observed. Fig. 3b displays the Raman spectrum of the as-synthesized carbon coils. Two peaks are observed clearly in Raman spectrum: the one at ca. 1324 cm^{-1} (called D-band) is associated with structural defects or disorders in CNMs. The other one at ca. 1592 cm^{-1} (called G-band) originates from graphite structure. The D-band to G-band intensity ratio (I_D/I_G) is commonly used to characterize the crystallinity of carbon

Table 1
The typical synthesis routes for the growth of CNCs/CMCs in high yield.

Catalyst	Temperature (°C)	Statistical yield	Reference
Fe	900–1100	ca. 90%	[10]
Fe–In–Sn	700	ca. 90%	[11]
Fe–Sn	700–770	ca. 90%	[13]
Fe–Mg–Co/SnO_2/Al_2O_3	700	ca. 90%	[14]
Stainless steel substrate	700	ca. 90%	[21]
Cu	250	ca. 90%	[22]
Fe–In–Sn–O	700	ca. 90%	[23]
Fe–Sn	700	ca. 90%	[24]
Al_2O_3 substrate	500	ca. 90%	This work

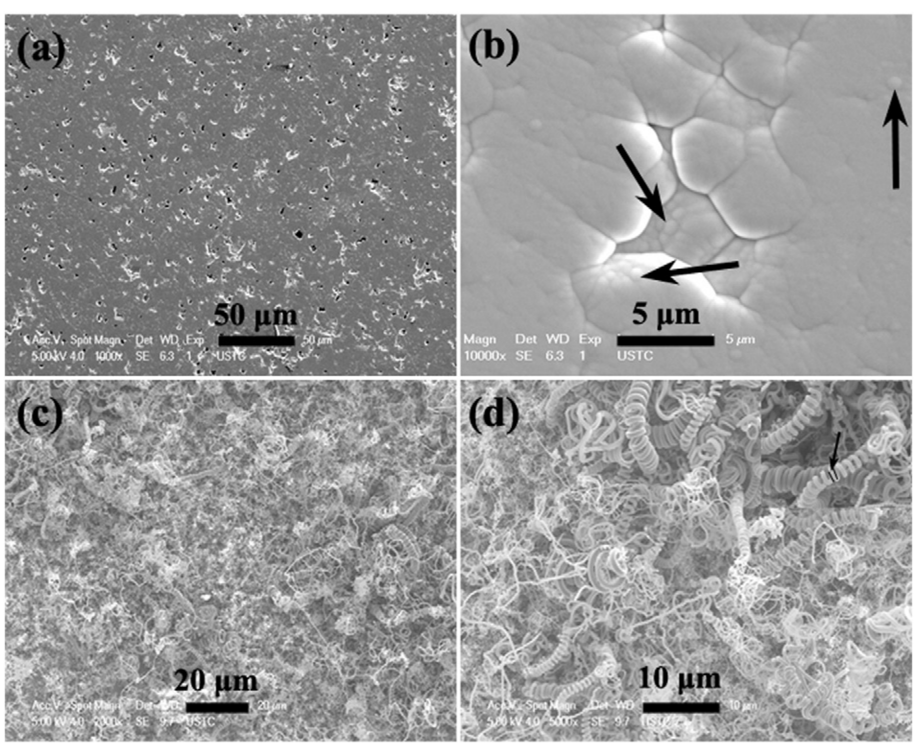

Fig. 1. FE-SEM images of (a, b) the annealed Al_2O_3 substrate, and (c, d) the as-synthesized obtained carbon coils over Al_2O_3 substrate (inset: the enlarged FE-SEM image of the obtained CMCs).