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ARTICLE TYPE

Morphology-controllable synthesis of carbon nanomaterials directly on Al$_2$O$_3$ substrates, and their photoluminescence

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Abstract: By controlling the growth temperature, different categories of carbon nanomaterials (CNMs) such as carbon nanocoils (CNCs) and chain-like carbon nanospheres (CNSs) can be synthesized directly over Al$_2$O$_3$ substrate without using any transition-metal catalysts. It is proposed that the Al$_2$O$_3$ particles play a key role in the CNM growth, and the reaction temperature has a great impact on the morphology of the obtained CNMs. Furthermore, the photoluminescence studies indicate that the obtained CNCs and chain-like CNSs
10 show different optical properties, which suggest that the optical properties of the obtained CNMs may be tuned by controlling their structures.
Keywords: Nanostructures; Chemical vapor decomposition; Optical properties characterization

1. Introduction

Owing to their peculiar properties and potential applications
15 such as field emission displays, hydrogen storage, micro-sensors and electromagnetic wave absorbers, different categories of carbon nanomaterials (CNMs) such as carbon nanotubes (CNTs), carbon nanocoils (CNCs), and carbon nanodots (CNDs) have gained much attention in the past decade.[1-6] In order to study their
20 properties and realize these applications, it is necessary to produce CNMs in high selectivity.[7-9] Besides the solution reaction process,[10,11] as we all know that the techniques for the production of CNMs can be classified roughly into three main categories: (i) laser ablation, (ii) arc discharge, and (iii) chemical
25 vapor deposition.[12,13] Common to these methods is the use of transition-metal catalysts, typically iron-group elements (Fe, Co and Ni) and their alloys. Because of the limitation of synthesis route and the understanding about catalyst, the growth of CNMs directly over substrate is thought to be impossible all the time,
30 which is the major obstacle for the development of CNM-based nanoelectronics.[12] Therefore, the role of catalyst and the growth of CNMs have attracted much attention in the past years, and many other metal and semiconductors nanoparticles such as Au, Ge and SiC, which were regarded as inactive catalysts for the
35 growth of CNMs in the past, have been proved to be active for CNM growth.[14-16] These findings challenge the traditional thinking about the growth of CNMs, and the increasing attention is being paid toward exploring new catalysts for the controllable and efficient growth of CNMs.
40 Recent experimental studies show that single-walled carbon nanotubes (SWCNTs) could growth directly over Si/SiO$_2$ substrate without using any transition-metal catalysts.[17-19] Enlightened by these ideas and based on our previous work,[20,21] in this study, we present a simple and efficient method for

45 realizing the selective growth of CNMs in high selectivity directly over Al$_2$O$_3$ substrate.

2. Experimental

2.1 Synthesis of Carbon Nanomaterials.

In a typical procedure, alumina (99.6% Al$_2$O$_3$, purchased from
50 Heifei Ke Jing Materials Technology Co., LTD) substrate was commercially available and analytically pure. After washed with ethanol and distilled water, Al$_2$O$_3$ substrate (**1cm^2 × 1cm^2**) was dispersed on a ceramic plate which was placed inside a quartz tube. With argon (99.999% Ar, purchased from Shen Jiang Gas
55 Company) flowing through (flow rata=0.03 L/min) the reaction tube, the temperature of furnace was raised from room temperature (RT) to a designed temperature. Then Ar was cut off and acetylene (dissolved C$_2$H$_2$, 99.999%, purchased from Shen Jiang Gas Company) was introduced into (flow rata=0.03 L/min)
60 the tube at 450, 600 and 650 °C for 1 h, respectively. After cooling to RT in Ar naturally, black samples could be observed clearly over the Al$_2$O$_3$ substrate. For easy description, the products generated at the decomposition temperature of 450, 600 and 650 °C are denoted hereinafter as C-450, C-600 and C-650,
65 respectively.

2.2 Characterization of products.

The samples were examined on an X-ray powder diffractometer (XRD) at RT for phase identification using CuKα radiation (model D/Max–RA, Rigaku). The morphologies of the
70 samples were examined using a transmission electron microscope (model JEM-2000EX, operated at an accelerating voltage of 200 kV), and a field emission scanning electron microscope (FE-SEM) (model FEI Sirion 200, operated at accelerating voltages of 5 kV). Raman spectroscopic investigations were performed using
75 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

3.1 Phase and microstructures of the substrate and samples.

In order to understand the growth of CNMs over Al_2O_3 substrate, Figure 1 gives the phase and microstructure of the raw substrate. As shown in Figure 1a, one can find that all the diffraction peaks can be indexed as the (012), (104), (110), (006), (113), (024), (116), (018), (214), (300) and (1010) crystal faces of rhomb centred hexagonal phase Al_2O_3, which is consistent with the reported data (JCPDS File No. 82-1467). No other peaks can be observed, indicating that the raw substrate is Al_2O_3 substrate. Figure 1b shows the FE-SEM image of the raw Al_2O_3 substrate. Different shapes and sizes of cavities can be observed frequently and clearly on the surface. The enlarged FE-SEM observation indicates some Al_2O_3 particles with different sizes (80-450 nm) appeared around these cavities.

For comparison, the microstructures of the annealed Al_2O_3 substrate and the obtained C-450 are shown in Figure 2. As shown in Figure 2a, many cavities can be seen obviously and the whole morphology of the substrate is almost unchanged. However, compared to the raw Al_2O_3 substrate, the high resolution FE-SEM investigation (as shown in Figure 2b) indicates that much more Al_2O_3 particles with different sizes can be observed around these cavities. In other words, the anneal process can make the formation of much more Al_2O_3 particles around the cavity. Figures 2c and d give the FE-SEM investigation of the obtained C-450. As shown in Figure 2c, large-scale of CNCs can be seen obviously around the cavities. The result indicates that the growth of CNMs should come from the area of Al_2O_3 particles, which is consistent with the growth of SWCNTs reported by Cheng and Huang et al., respectively.[17,19] Figure 2d shows the high resolution FE-SEM image of the obtained C-450. The closer investigation reveals that the diameters of the obtained CNCs are very uniform. The average diameter of CNCs is ca. 25 nm, which is much smaller than those of CNCs reported before.[22-24] In order to obtain high quality morphology images of C-450, the obtained sample was dispersed in ethanol and dropped on the copper screen for FE-SEM and TEM observations. As shown in Figures 3a and b, large scale and size uniform CNCs can be observed clearly. Moreover, as shown in Figures 3c and d, if acetylene was decomposed at 500 °C, the TEM and FESEM observations indicated that high selectivity of CNCs and carbon microcoils (CNMs) could be found in the obtained sample (C-500).[25]

3.2 Effect of temperature and possible formation mechanism of CNMs.

In order to investigate the effect of decomposition temperature, sample was synthesized at 600 °C (C-600). As shown in Figure 4a, the obtained C-600 is mainly made up of CNCs with different sizes and chain-like spheroidal carbon particles. The closer investigation (as shown in Figure 4b) shows that the morphology of some CNMs is very difficult to define as CNCs or chain-like CNSs. Based on the FE-SEM investigation of C-450 and C-600, we think that the morphology of CNMs involves the conversion from CNCs to chain-like CNSs with the increasing of decomposition temperature, and C-600 should be the interim of the transformation process. To prove the idea

further, C-650 was obtained through the decomposition of acetylene at 650 °C. Figure 4c shows the FE-SEM image of the obtained sample at the case, which reveals the obtained C-650 is chain-like spheroidal carbon particle, and the diameter ranges from 400 nm to 1 μm. According to the classification given by Serp et al.,[26] the obtained carbon material in the case is called chain-like CNSs. From the closer FE-SEM image (as shown in Figure 4d), it can be seen that no CNCs are observed at the case and the obtained chain-like CNSs show a large diameter distribution. In general, all the results show that CNMs can grow directly over the Al_2O_3 substrate and the morphology of CNMs can be tunable by controlling the decomposition temperature. Moreover, because no metal precursors were used over the Al_2O_3 substrate, the experiment here is much more simple and different from that reported by Liu et al.[27]

In comparison with the obtained results, we find that much more Al_2O_3 particles (as shown in Figures 2b, 4b and 4d) have formed on the substrate with the temperature increasing from 450 to 650 °C. Therefore, much larger scale of CNMs should be produced over the Al_2O_3 substrate, which is consistent with the obtained results (as shown in Figures 2c, 4a and 4c). Generally, all the obtained results show that different morphologies of CNMs can be synthesized directly over Al_2O_3 substrate. The growth of CNMs was proved by the fact that Al_2O_3 particles can serve catalytically as nucleation points, which was consistent with those of oxides such as SiO_2, TiO_2 for the SWCNT growth.[18,19] In order to confirm the point further, Al_2O_3 nanoparticles on Si substrate (Al_2O_3/Si) were prepared by the method reported elsewhere,[19] and the decomposition of acetylene was conducted over Al_2O_3/Si at 500 °C. As shown in Figures 5a and b, besides the observation of carbon nanofibers (CNFs) occasional, different sizes of CNCs/CNMs were seen in large-scale. Moreover, if the flat Al_2O_3 substrate was used to grow CNMs at 650 °C, as shown in Figures 5c and d, few of chain-like CNSs could be observed on the substrate, which may be caused by the thermal decomposition of C_2H_2 at the high temperature or the existence of few Al_2O_3 nanoparticles. Generally, combined with the aforementioned results, one can find that Al_2O_3 nanoparticles are very crucial for the growth of CNMs.

As reported before, some materials such as SiC, Al_2O_3, TiO_2 and SiO_2 were proved experimentally to be active for CNM growth.[28,29] Although, unlike metal catalyst, Al_2O_3 dose not have a catalytic function to decompose hydrocarbon molecules. The previous density functional theory calculations indicated that oxygen atoms in some oxides can improve the capture of $-CH_x$.[30] Based on these previous results, it is expected that the Al_2O_3 nanoparticles can capture the molecules of $-CH_x$ and give the formation of carbon atoms. The carbon atoms generated on the catalyst surface differ in mobility and assemble into hexagonal, pentagonal, and heptagonal rings.[31] As shown in Figure 6, a flat graphite layer is made up of hexagonal carbon rings. The introduction of pentagon and heptagon into the hexagonal carbon rings can make the curvature of the flat graphite flake. Moreover, it has been proved that the temperature has a great impact on the formation and creation rates of pentagonal or/and heptagonal carbon rings, and the formation of CNCs or CNSs can be attributed to the existence and creation rate of pentagonal-heptagonal carbon rings in the CNTs (as shown in Figure 6).[32-34]

Therefore, in our study, it is thought that the adsorption of –CH$_x$ is a first step toward the growth of CNMs, and the pyrolysis temperature is crucial for the structure of CNMs. Although the exact formation mechanism for CNMs cannot be given, the selective growth of CNCs and chain-like CNSs directly over Al$_2$O$_3$ substrate is not difficult to be understood in our study. More importantly, the method for the morphology-controllable synthesis of CNMs directly on Al$_2$O$_3$ substrates was not reported before, which may expand the utilization of CNMs in nanoelectronic effectively.

3.3 Optical and Raman spectrum analysis.

Figure 7 shows the Raman spectra of the obtained samples. All the Raman spectra exhibit two peaks of the D and G band. The D band in the Raman spectrum is associated with structural defect and partially disordered structures of sp^2 domains, while G band is an intrinsic property of the two-dimensional graphene lattice.[36,37] Generally, the intensity ratio of D band to G band (I$_D$/I$_G$) is used to estimate the disorder of graphene.[38] One can find that C-650 show higher I$_D$/I$_G$ value than C-600 and C-450, which indicates higher crystallinity of C-450 and C-600.

In order to explore the optical properties of the obtained samples, PL study was performed. Shown in Figure 8a are the PL spectra of C-450, C-600 and C-650 with an excitation wavelength of 280 nm. It can be seen that there are two weak emission peaks for the obtained C-450, one is in the UV region at ca. 362 nm and another is in blue region at ca. 465 nm, which is similar to the results of CNCs reported previously.[39,40] As reported previously by Shukla et al.,[41] the strong emissions in the UV region may be related to the effects of quantum confinement, and the blue emission may result from the recombination of electron-hole pairs, which originates from various structure-related defects.[42,43] Moreover, compared with C-450, two interesting phenomena can be observed clearly over the obtained C-600 and C-650: (i) the PL enhancement in both of the two peaks, and (ii) the appearance of new peak in the violet region at ca. 416 nm, which was not observed over other CNMs such as CNCs, CNTs or CNFs previously.[38-44] The observation of PL may imply the presence of a band gap in the electronic structure of some CNCs and CNSs in the obtained samples.[41] In comparison with the aforementioned results of the obtained samples, one can suggest that the peak enhancement and the appearance of new peak in the violet region should be related to the change of CNM morphology or structure. However, because of the complexity of CNM structure, further theoretical simulation is needed to explain the obtained experimental results clearly. Figures 8b-d gives the PL spectra of the obtained C-450, C-600 and C-650 with the different excitation wavelength. Common to these samples is the intensity of UV PL peak decreases rapidly with the excitation wavelength increasing from 220 to 300 nm, and the obtained samples exhibit an excitation-dependent PL behavior, which is consistent with carbon materials reported previously.[45] Interestingly, a clearly red shift of the UV PL peak can be observed over the obtained C-450 and C-600, while the UV PL peak of C-650 exhibits a obvious blue shift. In general, the obtained results suggest that the optical properties of the obtained CNMs may be tuned by controlling their structure, which may favor CNMs can be used in nanophotonics effectively.

4. Conclusions

In summary, without using any transition-metal catalysts, we have demonstrated that CNCs could be synthesized directly over Al$_2$O$_3$ substrate through the decomposition of acetylene at 450 °C. By controlling the reaction temperature, the morphology transformation of the obtained CNMs can be observed clearly. It is proposed that the Al$_2$O$_3$ particles play a key role in the CNM growth, and the Al$_2$O$_3$ particles show different catalytic activity at different growth temperature. Furthermore, the PL studies indicate that the obtained CNCs and chain-like CNSs show different optical properties, which suggest that the optical properties of the obtained CNMs may be tuned by controlling their structure.
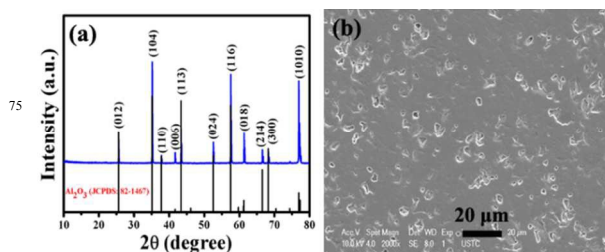

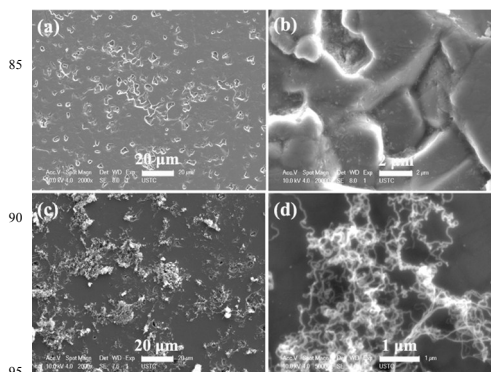Figure 1. (a) XRD pattern, and (b) FE-SEM images of the raw Al$_2$O$_3$ substrate.

Figure 2. FE-SEM images of (a,b) the annealed Al$_2$O$_3$ substrate, and (c,d) the as-synthesized C-450.
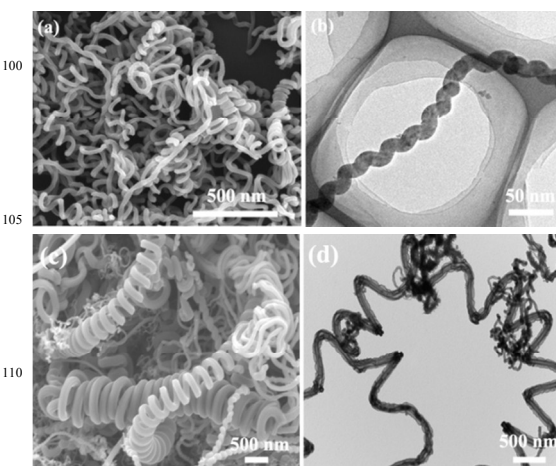

Figure 3. (a) FE-SEM and (b) TEM images of C-450; (c) FE-SEM and (d) TEM images C-500.
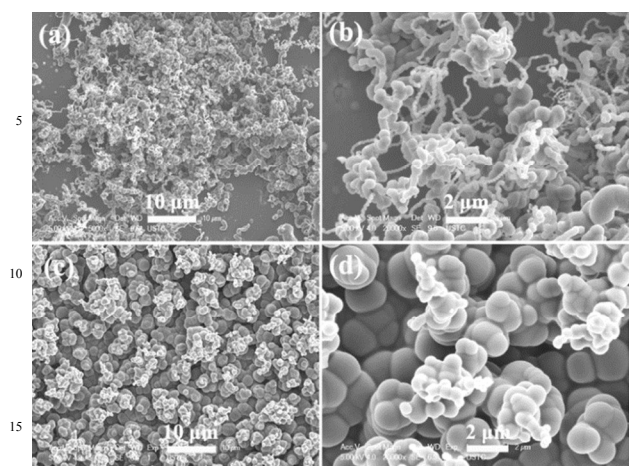
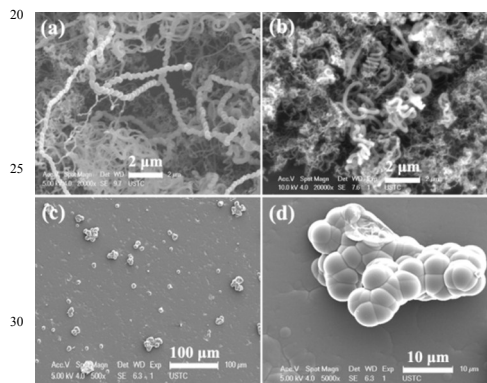Figure 4. FE-SEM images of the obtained (a,b) C-600, and (c,d) C-650.

Figure 5. FE-SEM images of the samples obtained over: (a,b) the Al_2O_3/Si substrate, and (c,d) the flat Al_2O_3 substrate
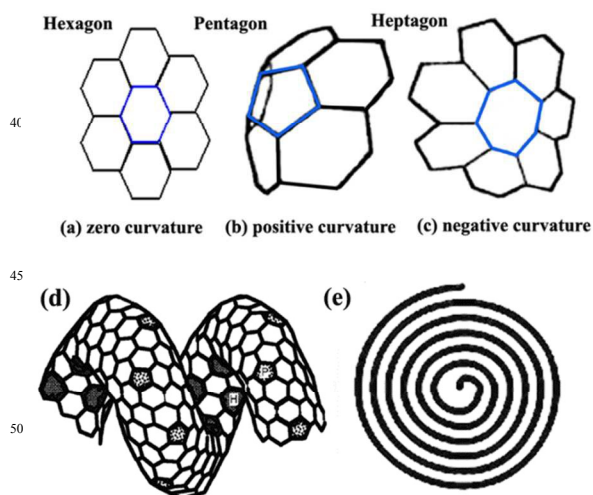

Figure 6. (a-c) the hexagonal, pentagonal and heptagonal carbon rings used to assemble the graphitic flakes; (d) formation of CNCs;[34] and (e) Schematic structural model of carbon spheres proposed by Kroto and Mckay.[35]
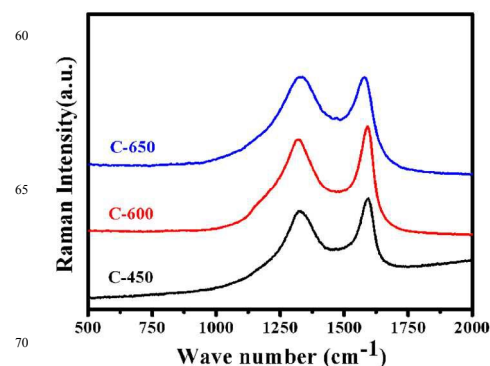

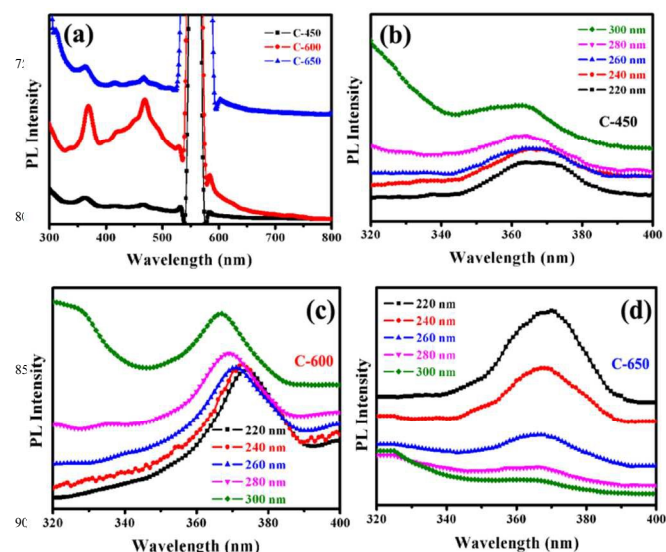Figure 7. Raman spectra of the obtained C-450, C-600 and C-650.

Figure 8. PL spectra of C-450, C-600 and C-650 with excitation wavelength (a) 280 nm, and (b-d) from 220 to 300 nm.

Acknowledgments

Notes and references

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