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Designed synthesis of tunable amorphous carbon nanotubes (a-CNTs) by a novel route and their oxidation resistance properties

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Abstract. Tunable amorphous carbon nanotubes (a-CNTs) were successfully synthesized using $V_3O_7{\cdot}H_2O$ and glucose solution as the starting materials by a novel route for the first time. The as-obtained samples were separately characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), energy-dispersive spectrometer (EDS), elemental analysis (EA), Fourier transform infrared spectroscopy (FT–IR) and Raman spectrum. The results showed that the as-obtained a-CNTs had uniform diameters with outer diameter ranging from 140 to 250 nm and inner diameter about 28 nm on an average, and their length was up to several micrometres. No VO_x residues remaining in a-CNTs showed the as-obtained a-CNTs with high purity. The as-prepared a-CNTs were a kind of hydrogenated a-CNTs containing both the sp^3- and sp^2-type carbons. Furthermore, the thermal stability of the as-obtained a-CNTs in the air atmosphere were investigated by thermo-gravimetric/differential thermal analyser (TG-DTA), revealing that the as-obtained a-CNTs had good thermal stability and oxidation resistance below 300 °C in air.

Keywords. Amorphous carbon nanotubes; chemical synthesis; structures; oxidation resistance properties.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 (Iijima 1991), CNTs have promptly attracted much attention owing to their extraordinary mechanical, chemical and electrical properties as well as their potential applications (Lehman *et al* 2011; Ionescu *et al* 2012; Nanot *et al* 2012). Previous works were mostly focused on either multi-walled CNTs or single-walled CNTs. In recent years, amorphous carbon nanotubes (a-CNTs) have attracted increasing attention because of their amorphous structure being different from crystalline carbon nanotubes. The walls of a-CNTs are composed of many carbon clusters, whose characteristic is of short-distance order and long-distance disorder (Zhao *et al* 2006). The properties of a-CNTs are different from single-walled and multi-walled CNTs (Nishino *et al* 2003; Zhao *et al* 2006, 2009; Lonappan *et al* 2011; Song *et al* 2011). The a-CNTs are favourable for certain applications such as in some nanoelectronics and sensor devices (Zhao *et al* 2009). Thus, a-CNTs become another focus of research. So far, some methods including CVD, arc discharge, anodic aluminium oxide (AAO) template, solvothermal method, etc., have been developed to synthesize a-CNTs (Ci *et al* 2001, 2003; Nishino *et al* 2003; Zhao *et al* 2005, 2006, 2009; Chen *et al* 2006; Luo *et al* 2006; Liu *et al* 2004, 2007a,b). However, requirements of high synthesis temperature and pressure, poisonous reagents, catalyst supports, complicated processing steps, longer synthesis period or expensive costs may still be the major drawbacks arising from the above-mentioned techniques (Tan *et al* 2012). Therefore, it is necessary and meaningful to explore new processes for the preparation of a-CNTs, which could overcome the disadvantages of these techniques, and is crucially important to the future application of a-CNTs. In our previous report, a-CNTs were synthesized using vanadium dioxide as the template (Zhang *et al* 2013c). Herein, we have designed and developed a novel route for the synthesis of a-CNTs using $V_3O_7{\cdot}H_2O$ and glucose solution as the starting materials. The as-obtained a-CNTs have high purity and a kind of hydrogenated a-CNTs containing both the sp^3- and sp^2-type carbons. Besides, the as-synthesized a-CNTs have good thermal stability and oxidation resistance below 300 °C in air.

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2. Experimental

All reagents used in the experiments were of analytical grade and used without any further purification. The synthetic route for a-CNTs was schematically described as follows

$$V_2O_5 \xrightarrow[\text{Hydrothermal}]{\text{EtOH, } H_2O} V_3O_7{\cdot}H_2O \xrightarrow[\text{Hydrothermal}]{\text{Glucose solution}}$$

$$V_3O_7{\cdot}H_2O@C \xrightarrow[\text{Inert gas}]{\text{Thermal}} VO_x@C \xrightarrow{\text{HCl}} \text{a-CNTs}.$$

The synthesis of $V_3O_7{\cdot}H_2O$ and $V_3O_7{\cdot}H_2O$@C was based on previous reports (Zhang *et al* 2010, 2011a,c). For the preparation of a-CNTs, $V_3O_7{\cdot}H_2O$@C was first heated in a tube furnace with 5 °C/min heating rate under a flow of argon (99·999%) gas at a given temperature for a given time. The purpose of this step is to stabilize the framework of carbon. After the heating treatment, the above products were treated by dilute HCl solution to remove VO_x in the a-CNTs, and high purity a-CNTs were obtained.

The morphology of the products was observed by the scanning electron microscopy (SEM, Quanta 200) and transmission electron microscopy (TEM, JEM-2100 HR). X-ray powder diffraction (XRD) was carried out on D8 X-ray diffractometer equipment with Cu$K\alpha$ radiation, λ = 1·54060 Å. The elemental analysis (EA) of the sample was carried out using a Vario EL III equipment (Germany). Raman spectrum was taken on an RM-1000 spectrometer (confocal Raman microspectroscopy) with an argon-ion laser at an excitation wavelength of 514·5 nm. Fourier transform infrared spectroscopy (FT–IR) was recorded on a Nicolet 60-SXB spectrometer from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. Energy-dispersive

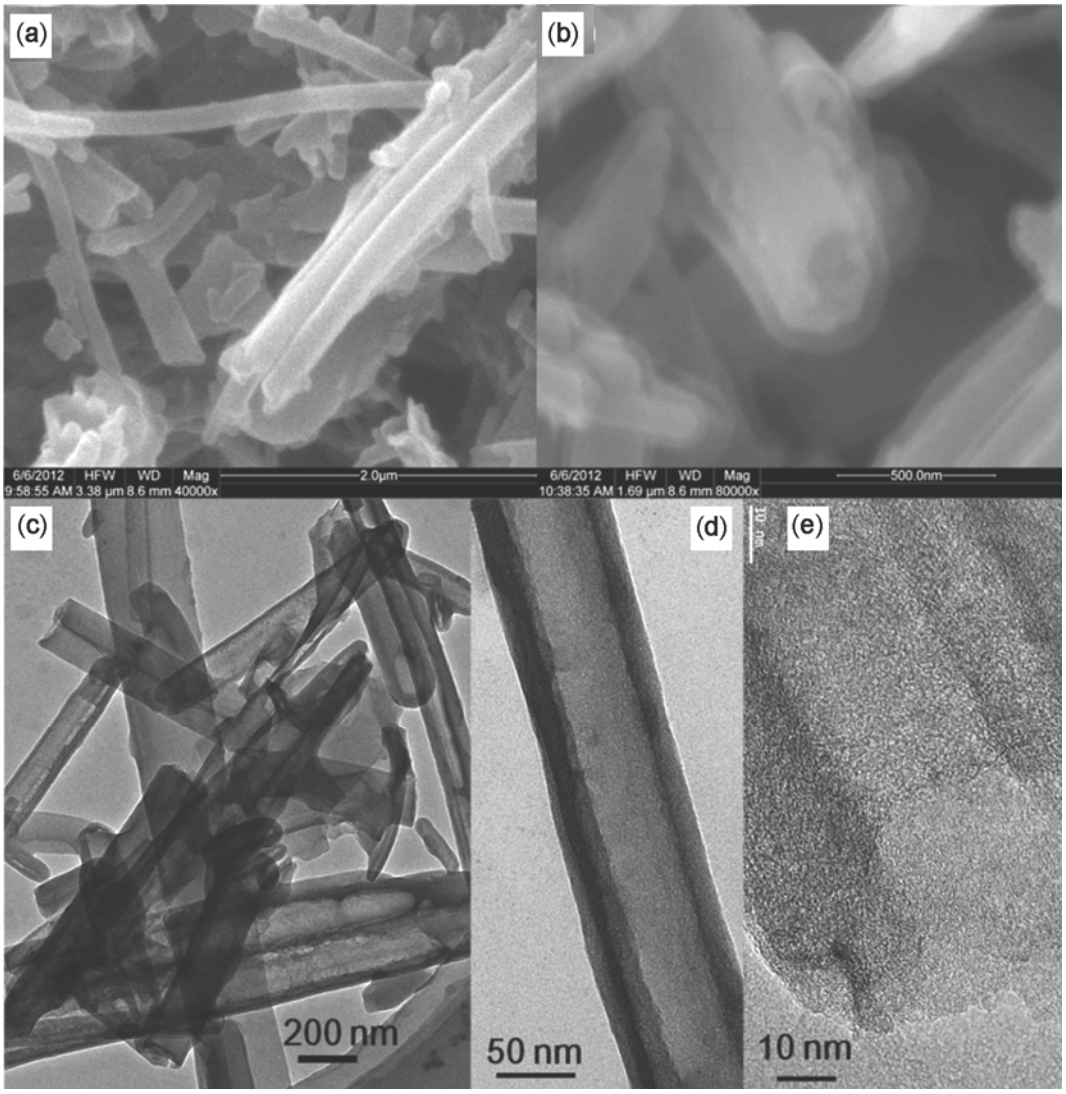

Figure 1. Morphology of the as-obtained a-CNTs: (**a** and **b**) SEM images; (**c** and **d**) TEM images and (**e**) HRTEM image.

spectrometer (EDS) was carried out on the equipment Quanta 200. Thermo-gravimetric/differential thermal analysis (TG/DTA) was performed on SETSYS-1750 (AETARAM Instruments). About 5 mg of the as-obtained sample was heated in an Al_2O_3 crucible in air atmosphere from ambient temperature to 600 °C at a constant rise of temperature (10 °C/min).

3. Results and discussion

The morphology and structure of the as-obtained sample were evaluated by SEM and TEM, as shown in figure 1. It can be observed that the sample consists of wire-like shape with length up to several micrometres in figure 1(a) and tubular shape with open end is clearly seen in figure 1(b). The TEM images give the clear insight into the core–shell structure of the as-obtained sample, as shown in figure 1(c–f). The contrast grade between core and shell also indicates that the sample consists of large-scale nanotubes (figure 1c), in good agreement with the SEM observation. A typical TEM image of one single nanotube is provided in figure 1(d), and the dark area in the image corresponds to the wall of the nanotube. The nanotubes have uniform diameters, with outer diameter ranging from 140 to 250 nm and inner diameter about 28 nm on average. The higher magnification TEM image (figure 1f) reveals that the nanotube is completely amorphous, which agrees well with the XRD patterns presented in figure 2. According to our designed route, the a-CNTs are probably synthesized. Further information about the composition of the amorphous nanotube was collected from the XRD, EA, EDS, FT–IR and Raman tests.

Figure 2(a) shows the XRD pattern of the as-obtained nanotubes. Only a broadened peak ranging from 15 to 25° can be detected, which reveals that the as-prepared nanotube is amorphous carbon (Zhang *et al* 2012b,c, 2013a,b). The EDS spectrum (figure 3a) reveals that the as-synthesized a-CNTs consist of C and O elements. Both XRD and EDS manifest that no residual reactant of VO_x remains within the sample.

The result of EA shows that the prepared a-CNTs contain 86·22 wt% of C and 2·287 wt% of H, and the atomic ratio of C and H is 3·142 : 1. High C/H atomic ratio and relatively high H content indicate that this solid might be a kind of hydrogenated a-CNTs, which can be further

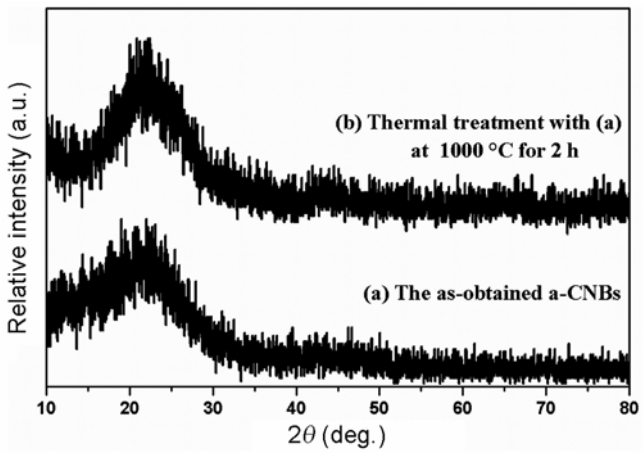

Figure 2. XRD patterns of the as-obtained a-CNTs.

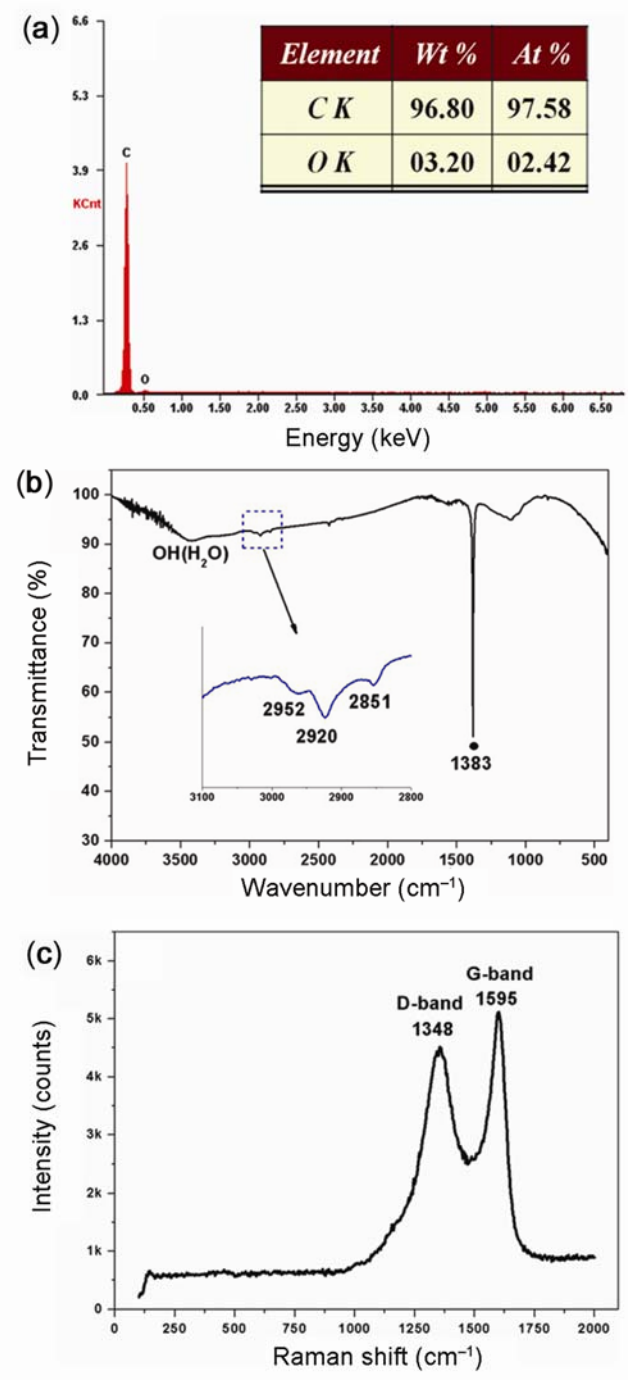

Figure 3. Composition of the as-obtained a-CNTs: (**a**) EDS spectrum; (**b**) IR spectrum and (**c**) Raman spectrum.

proved by FT–IR. FT–IR spectrum of the as-obtained a-CNTs shows the characteristic C–H stretching vibration bands, as depicted in figure 3(b). The absorption bands located at 2851 and 2920 cm^{-1} can be assigned to sp^3 CH_2-symmetric and (-)asymmetric bands, respectively. The peak at 2952 cm^{-1} is the characteristic sp^2 CH_2-symmetric band, although its asymmetric band at about 3080 cm^{-1} is not observed, because it is a weak absorption band. Besides, the absorptions at 3425 and 1383 cm^{-1} are due to water and nitrate (NO_3^-) adsorbed on the KBr and can be disregarded (Ros *et al* 2002; Zhang *et al* 2012a,f).

Important information of the structure of the as-obtained a-CNTs could be provided by Raman spectrum. Figure 3(c) represents a typical Raman spectrum of a-CNTs, which is characteristic for amorphous carbon because of the presence of the D- (1348 cm^{-1}) and G-bands (1595 cm^{-1}) (Ilie *et al* 2002; Odani *et al* 2006). It was reported that the D-band (1348 cm^{-1}) is usually associated with the vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered graphite, and the G-band (corresponding to the E_{2g} mode) is closely related to the vibration in all sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphitic layer, corresponding to the E_{2g} mode (Dresselhaus *et al* 1999; llie *et al* 2002; Odani *et al* 2006; Sun *et al* 2006; Zhang *et al* 2012d,e). These two peaks are broad in figure 3(c), indicating that the carbon in the as-prepared a-CNTs is of poor crystallinity, corresponding to the previous report (Sun and Li 2004; Zhang *et al* 2011b, 2012b). The intensity ratio of the G- and D-bands was $I_G/I_D = 1{\cdot}15$ for the as-obtained a-CNTs. The relatively high intensity of the D-peak further proves that the as-synthesized a-CNTs comprise disordered carbon. Therefore, Raman spectrum further confirms that the carbon in the as-obtained a-CNTs is disordered, which is well consistent with the HRTEM and XRD observations.

On the basis of the above results, hydrogenated a-CNTs are successfully synthesized at the current conditions, and the as-obtained a-CNTs contain both the sp^3- and sp^2-type carbons. The thickness of the walls of a-CNTs can be changed within a certain range. If the carbon thickness coating on the precursor is higher (Zhang *et al* 2011a), a thick amorphous carbon wall will be obtained. This kind of a-CNTs is expected to find potential applications since the outer surface of a-CNTs is very reactive toward functionalization by chemical or physical methods due to its amorphous nature. However, the as-obtained a-CNTs cannot be transformed to CNTs at 1000 °C, as shown in figure 2(b).

Therefore, a-CNTs were successfully synthesized using $V_3O_7{\cdot}H_2O$ and glucose solution as the starting materials by a novel route. Table 1 lists the synthetic methods of a-CNTs in the literatures and our results. The requirements

Table 1. Summary of the synthetic methods of amorphous carbon nanotubes (a-CNTs) in the literatures.

Serial	Carbon source	Catalyst	Method	Description and reference
1	Polytetrafluoroethylene	Ferrous chloride	Thermal under vacuum	The product has impurity, containing very minor amount of Fe and Cl (Nishino *et al* 2003)
2	Citric acid	Porous anodic aluminium oxide (AAO) membrane as template	Thermal	Zhao *et al* (2009)
3	Ferrocene and chloride find powders	–	Thermal	Liu *et al* (2007a)
4	Polyacrylonitrile (PAN) and polystyrene-*block*-polyacrylonitrile (PS-*b*-PAN)	Porous (AAO) membrane as template	Casting and pyrolysis	Chen *et al* (2006)
5	Methane	Ni/Al	Chemical vapour deposition (CVD)	The product has impurity, containing a little of Al and Ni (Zhao *et al* 2006)
6	Mixed CH_4/H_2	Ni thin film	Radio frequency plasma-enhanced CVD	Liu *et al* (2007b)
7	Benzene and ferrocene	–	CVD	Benzene solution with a given content of ferrocene and a small amount of thiophene was used (Ci *et al* 2001)
8	Graphite powders	Co/Ni alloy	Modified arc discharge	Precision instrument and hydrogen gas atmosphere (Zhao *et al* 2005)
9	Graphite powders	FeS	Temperature-controlled DC arc discharge	Liu *et al* (2004)
10	Glucose	Vanadium oxide as template		Our work

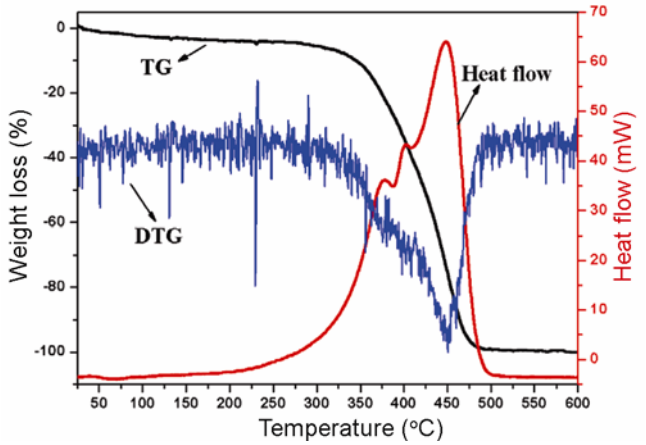

Figure 4. Thermal stability of the as-obtained a-CNTs in the air atmosphere.

of precision instrument, poisonous reagents, catalyst supports, complicated processing steps, longer synthesis period or expensive costs may be the major drawbacks arising from the above-mentioned techniques. To synthesize a-CNTs, we only used glucose (which is very cheap and easily obtained) as the carbon source and vanadium oxide as the template by the hydrothermal route and thermal treatment, which shows our method is very convenient for preparing a-CNTs. Therefore, a novel route was explored to successfully synthesize a-CNTs using $V_3O_7{\cdot}H_2O$ and glucose solution as the starting materials.

Furthermore, the thermal stability of the as-obtained a-CNTs in the air atmosphere was investigated by TG-DTA, as shown in figure 4. The weight loss *ca* 2·4% below 120 °C in the TG curve can be due to the release of water absorbed on the surface of a-CNTs. The weight loss starting at about 300 °C and finishing at about 490 °C is associated with a-CNTs reacting with O_2. There is no residue after the TG test, indicating that the as-obtained a-CNTs have high purity, in agreement with XRD and EDS observations. Both DTG and heat flow curves reveal the fierce oxidation of a-CNTs is located at 450 °C and the oxidation process finishes at 490 °C. Therefore, the as-obtained a-CNTs have good thermal stability and oxidation resistance below 300 °C in air.

4. Conclusions

In conclusion, a novel route was explored to successfully synthesize a-CNTs using $V_3O_7{\cdot}H_2O$ and glucose solution as the starting materials. The as-obtained a-CNTs were separately characterized by SEM, TEM, HRTEM, XRD, EDS, EA, FT–IR and Raman. The as-prepared a-CNTs have uniform diameters, with outer diameter ranging from 140 to 250 nm and inner diameter about 28 nm on average, and their length is up to several micrometres. No VO_x residues remaining in a-CNTs reveal that the as-obtained a-CNTs are of high purity, and the as-prepared a-CNTs are a kind of hydrogenated a-CNTs containing both the sp^3- and sp^2-type carbons. The thickness of the walls of a-CNTs can be changed within a certain range. The as-obtained a-CNTs cannot be transformed to CNTs at 1000 °C. Furthermore, the thermal stability of the as-obtained a-CNTs in the air atmosphere was investigated by TG–DTA, revealing that the a-CNTs have good thermal stability and oxidation resistance below 300 °C in air.

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Electronic Supplementary Material

Supplementary material pertaining to this article is available on the Bulletin of Materials Science website (www.ias.ac.in/matersci).

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