Synthesis of Carbon Nanofibers by Chemical Vapor Deposition Using Polyoxometalates as Catalysts

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ABSTRACT

This work reports a new approach to synthesize carbon nanostructures by the Chemical Vapor Deposition (CVD) technique using Polyoxometalates (POMs) as catalysts. POMs are anionic metal-oxygen complex nanoclusters, which can be synthesized by aqueous chemical processes. Hydrogen and acetylene were used as the carrier gas and the carbon precursor, respectively, for the CVD growth at 700°C. Two methods for the preparation of POM catalysts have been explored: (1) the solution was drop-cast directly onto Si substrates; or (2) the POM solutions were blended with polyvinyl alcohol (PVA) and spin-coated on the substrates. Morphologies and structures of synthesized carbon nanomaterials were examined by the Scanning Electron Microscopy (SEM), the Transmission Electron Microscopy (TEM) and the X-Ray Diffraction (XRD). The results showed that the polyoxomatelates containing cobalt yielded mostly cup-stacked carbon nanofibers (CNFs) with diameter in the range of 10-100 nm, whereas other polyoxomatelates did not seem suitable for carbon nanostructure syntheses. The uniformity, in terms of both the fiber size and the coverage on the substrates, was found to be improved in the case of the spin-coated POM catalysts, compared to the drop-casting method. The XRD results also revealed the remnants of POM catalysts in the synthesized CNFs, mostly in the form of tungsten and tungsten carbide. Future applications of the synthesized CNFs include electrodes for dye-sensitized solar cells, patterned electrodes and gas-sensing materials.

Key words: Carbon nanotubes (CNTs), Polyoxometalates (POMs), Chemical vapor deposition (CVD)

INTRODUCTION

Carbon nanostructures are a fascinating model system for nanomaterials and nanoelectronics research. The most outstanding forms of carbon nanostructures are fullerenes and carbon nanotubes (CNTs). Since the first discovery of CNTs (Ijima, 1991 and Ijima & Ichihara, 1993), CNTs have generated a new field of science and technology. With their unique structures, CNTs have many special intrinsic properties such as high tensile strength, high surface area, high thermal and electrical conductivity (Meyyappan, 2005). Their potential industrial applications have been demonstrated, for example, in CNT composite materials (Coleman et al., 2006), field-emission devices (Zhi et al., 2002), molecular sensing materials (Su et al., 2006), Atomic Force Microscope (AFM) probes (Solares et al., 2005) and nanoscale electronic devices (Yao et al., 1999).

A variety of carbon nanostructure synthesis methods have been explored, for example by arc discharge, laser ablation, and catalytic chemical vapour deposition (CVD). Amongst them, CVD is the most promising method for the industrial scale production because of its simple design and low construction cost (Meyyappan, 2005). The growth of carbon nanostructures by the CVD methods utilizes powder catalysts. The most common catalysts are the transition metals, such as Fe, Ni, and Co or their alloys such as Ni-Co alloy (Dai et al, 1996), Fe-Co alloy (Maruyama et al., 2002), and Fe-Ni alloy (Yang et al., 2003). Recently, other types of catalysts have also come into the spotlight. For example, the synthesis of single-walled CNTs have been achieved by using Cu, Ag and Au catalysts with particle sizes less than 3 nm (Takagi et al., 2006).

Polyoxometalates (POMs) are anionic metal oxide complex nanoclusters, which can be synthesized by relatively simple aqueous chemical processes (Fukaya and Yamase, 2007). POMs have attracted large research interest for both their intriguing complex structures and their applications in medicine, biology, pharmacy and catalysis (Muller et al., 1999). For their applications on carbon nanostructures, POMs have been used to functionalize carbon nanostructures, such as carbon nanosheets (Zhang et al., 2005) and CNTs (Fei et al., 2006 and Kang et al., 2004). Nevertheless, uses of POMs for the CVD synthesis of carbon nanostructure have never been reported.

This work focuses on the CVD syntheses of carbon nanostructures using POMs as a new catalyst material. The POMs have been obtained in aqueous solutions. Methods to disperse POMs uniformly on Si substrates has also been investigated by spin-coating the mixture of POM solution and polyvinyl alcohol) (PVA), in comparison to the drop-casting technique. Morphologies and structures of as-synthesized carbon nanostructures were investigated by the Scanning Electron Microscopy (SEM), the Transmission Electron Microscopy (TEM) and the X-Ray Diffraction (XRD).

MATERIALS AND METHODS

Silicon wafer substrates, used as the support for POM catalysts, were cleaned by the Piranha solution (3:1 by Vol. of H_2SO_4:H_2O_2) and rinsed by deionized water. The synthesis of POMs is described elsewhere (Fukaya and Yamase, 2007). Three types of POM solutions were prepared for the CVD synthesis:

Solution (1), $Na_{17}[Co_6(H_2O)_2(AsW_9O_{34})(AsW_6O_{26})].41H_2O$ (30mg) in water (2ml);

Solution (2), $Na_{17}[Mn_6(H_2O)_2(AsW_9O_{34})(AsW_6O_{26})].41H_2O$ (30mg) in water (2ml); and

Solution (3), $Na_{17}[Co_6(H_2O)_2(AsW_9O_{34})(AsW_6O_{26})].41H_2O$ (30mg) with Polyvinyl alcohol (10mg) in water (2ml).

Solutions (1) and (2) were dispersed on Si substrates by drop-casting. In order to improve the uniformity of the dispersion, Solution (3) contains polyvinyl alcohol (PVA). The PVA addition adjusted the viscosity of Solution (3) to be suitable for the spin-coating process (WS-400B-6TFM-Lite Spincoaters, Laurell Technology), which was conducted at the spin speed of 1000, 2000, and 3000 rpm for 45 seconds.

All catalyst samples were baked in air at 80°C for 10 minutes prior to the CVD processes. Figure 1 shows the schematics of the CVD system. The samples were put onto an alumina holder and placed at the centre of the CVD tube furnace. The system was then pumped down to ~2 mtorr. Acetylene was used as the carbon source, while hydrogen was a diluting gas. The hydrogen gas was flowed through the furnace at a rate of 800 sccm, controlled by the mass flow controller (5850E, Brooks Instrument PA, USA). When the temperature reached 700°C, acetylene was introduced into the furnace at a flow rate of 200 sccm for 10 minute. After that, both the acetylene gas supply and the heating element were turned off. At the end of the process, the hydrogen supply was turned off when the furnace temperature fell below 200°C.

The uniformity and the topography of the as-synthesized carbon nanostructure films on Si substrates were observed by an optical microscope. The structure and the morphology of the carbon nanostructures themselves were then characterized by XRD (D8 Discover, Bruker AXS GmbH, Karlsruhe, Germany), SEM (S-3400N, Hitachi High Technology, Tokyo, Japan) and TEM (JEM-2010, Jeol Ltd., Tokyo, Japan). For the TEM measurements, powder samples were removed from the Si support and dispersed in ethanol by ultrasonication. The colloidal samples were then dropped onto TEM grids and allowed to dry.

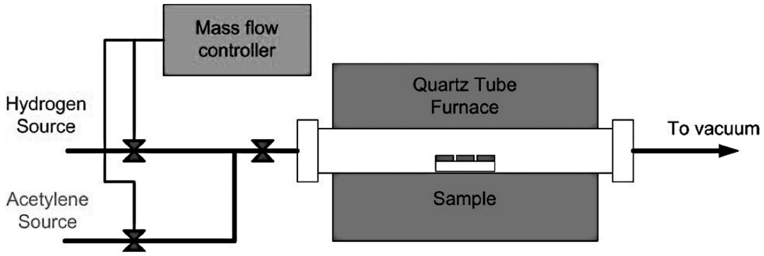


Figure 1. Schematics of the Chemical Vapour Deposition system.

RESULTS AND DISCUSSION

Figure 2 compares the distribution of the synthesized carbon materials on Si substrates for the drop-casting and the spin-coating methods. In Figure 2(a), the carbon materials synthesized from Solution (1), appearing in black, are randomly distributed. This is expected for the drop-casting method. On the other hand, in Figure 2(b-d) the carbon materials obtained by spin-coating exhibit a uniform distribution with regular patterns. The results therefore demonstrate that our method of PVA addition into the POM solutions was able to improve the material dispersion on the substrate. The dispersion also depends on the spin speed, which should match the viscosity and the concentration of the solutions. Here, at the spin speed of 2000 rpm, coarse patterns no longer appear in the synthesized carbon films, indicating a highly uniform distribution of the carbon materials within the films.

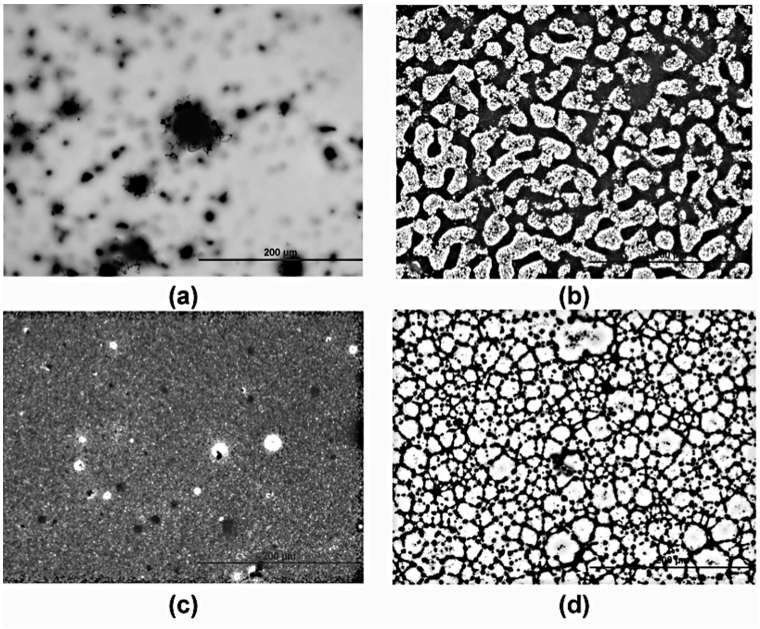


Figure 2. Optical micrographs of synthesized carbon fibers on silicion prepared by (a) drop-casting from Solution (1) and by spin-coating from Solution (3) (b) with spin speed (b) 1000, (c) 2000, and (d) 3000 rpm.

Figure 2 depicts SEM images of as-synthesized carbon nanostructures from Solutions (1), (2) and (3). The difference between the synthesized materials for Solution (2) and the other two is evident. In Figure 3(a), the morphology of the carbon materials was found to be of a fibre form throughout the Si support. A similar morphology is also observed for Solution (3) in Figure 3(c). In contrast, Figure 3(b), which displays the synthesized materials from Solution (2), does not show any fibrous structures on the support. A possible explanation is that both Solutions (1) and (3) contain Co, which is known to be an excellent catalyst for syntheses of CNTs (Dupuis, 2005), whereas, in Solution (2), Co was replaced by Mn, which may not be suitable for the carbon nanostructure synthesis. Note also that the SEM images indicate that the diameter of the fibres synthesized from Solutions (1) and (3) was below 100 nm, which may be termed ‘carbon nanofibers’ (CNFs). In addition, the CNFs obtained by the spin-coated Solution (3) appear more regular in size than those obtained by the drop-casting Solution (1).

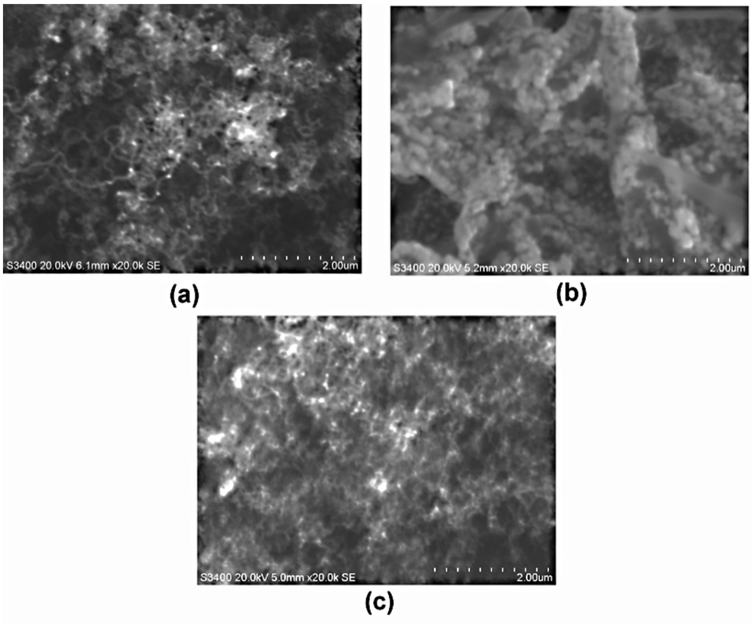
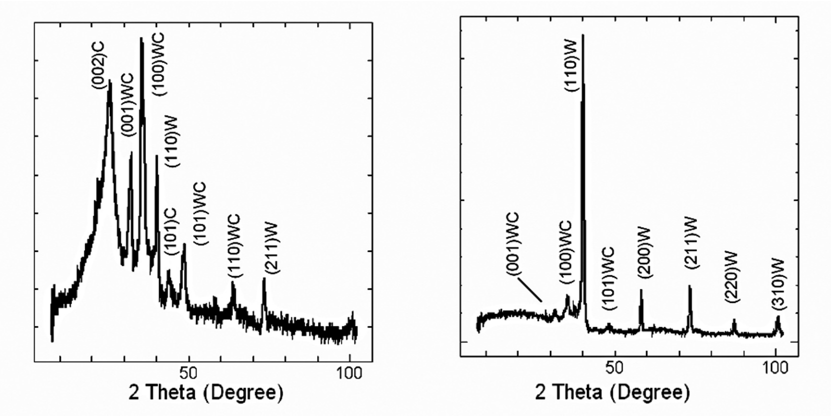


Figure 3. SEM images of as-synthesized CNF prepared by drop-casting from (a) Solution (1) and (b) from Solution (2), and (c) by spin- coating from Solution (3).

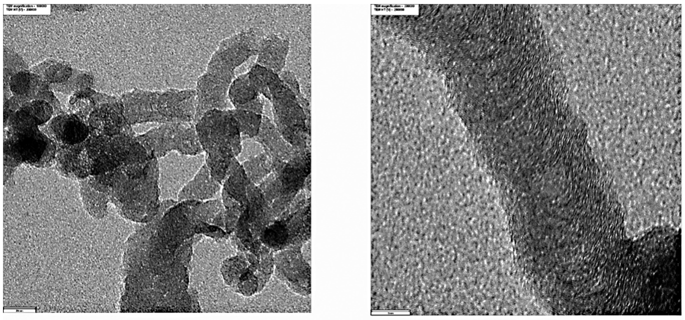
The structure of the synthesized carbon materials was further probed by the XRD measurements. Figure 4 compares the XRD patterns of the synthesized materials from Solutions (1) and (2), which exhibit an apparent difference of the two samples. The remnants of the POM catalysts in the carbon materials can be observed for both Solutions (1) and (2), in which the characteristic peaks of W and WC appear in the XRD patterns. However, the XRD peaks corresponding to graphitic carbons were only observed in the materials synthesized by Solution (1). This confirms the SEM results that Solution (2) did not yield any carbon nanostructures, or perhaps produced only some amorphous carbon. Furthermore, the XRD graphite peaks for Solution (1) suggest some atomic ordering inside the CNFs, rather than a completely amorphous structure. Note also that the predominant presence of W and WC in the synthesized materials suggests that the POMs decomposed during the high temperature processes of the CVD growth. The mechanisms for the CNF growth should occur in two steps. First, the Co in the POMs decomposed and formed particles. Then, CNFs grew via the catalytic CVD processes from these Co particles.



(a) (b)

Figure 4. XRD patterns of the as- synthesized CNF prepared by drop-casting from (a) Solution (1) and (b) Solution (2).

The structural analysis of the CNFs by direct imaging was achieved by the Transmission Electron Microscopy. Figure 5 displays TEM images of the CNFs obtained from Solution (3). The results reveal that the CNFs have mostly the structure of a hollow tube. The tube diameter was measured to be between 15-30 nm. However, although the XRD measurements indicate graphitic structures inside these tubes, the high-resolution image in Figure 5(b) shows that they possessed a difference structure from the multi-walled CNTs. The shell of the synthesized CNFs is composed of short pieces of multi-walled carbon cones, connected along the fibre length. This nanofiber structure, which may be termed 'cup-stacked' carbon nanofibers, has been previously observed for the CVD method using different catalysts (Endo et al, 1995). In future work, the CVD methods should be optimized to produce other carbon nanostructures, in particular single-walled and multi-walled CNTs. As discussed previously, the growth mechanisms should occur first via the decomposition and aggregation of Co particles. Controlling these Co particles via the catalyst preparation or by using other types of POMs should lead to a better yield of CNT structures.



(a) (b)

Figure 5. TEM images of carbon nanofibers prepared by spin-coating from Solution (3).

CONCLUSION

The polyoxometalates (POMs) have been used as catalysts in the carbon nanostructure synthesis by the CVD method. The cup-stacked carbon nanofibers (CNFs) have been obtained with the process by using the POMs containing cobalt. In addition, uniformly dispersed CNFs on the Si support have been achieved by using the spin-coating method to prepare POM catalysts from the solution containing polyvinyl alcohol (PVA). The distribution of as-synthesized CNF on the support can also be tuned by the spin speed. The XRD and TEM results suggest also that possible mechanisms for the carbon nanostructure growth may occur first via the decomposition and aggregation of Co nanoparticles from the POMs. Future work should improve the control of the POM catalyst preparation to enhance the yield of CNTs or lead to other carbon nanostructures.

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