CHEMISTRY OF MATERIALS

VOLUME 19, NUMBER 17 AUGUST 21, 2007

Communications

On the Graphitization Nature of Oxides for the Formation of Carbon Nanostructures

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Received May 7, 2007
Revised Manuscript Received July 5, 2007

Despite enormous strides in the synthesis of carbon nanostructures, carbon nanotubes (CNT) in particular, our understanding of the mechanisms regarding their nucleation and growth is still developing. The hydrocarbon chemical vapor deposition (CVD) process is the most studied of all the synthesis routes because of its superior potential for mass production with economic effectiveness as compared to the other mainstream synthesis routes. In the CVD synthesis of CNT, metal catalyst particles are accepted as fulfilling two key roles, namely, catalytic decomposition of the carbon feedstock (hydrocarbon) and catalytic nucleation/growth of the emerging CNT. However, there are several inconsistencies in the commonly held arguments that are only now beginning to be questioned. For example, it is often argued that the termination (or even prevention) of nanotube growth is caused by the catalyst particle being poisoned.[1] How this poisoning actually occurs has not been demonstrated and has recently been questioned by Reilly and Whitten.[2] They also point out the contradiction in the argument that an amorphous carbon coating on the catalyst particle halts growth, yet bewilderingly, they are able to grow nanotubes (ordered carbon) or even carbon nanofibres (disordered carbon). Reilly and Whitten argue that a more likely scenario is that a free radical condensate (FRC) provides carbon species through a leaving group such as hydrogen (or oxygen). In this scenario, the catalyst particle's role is to simply provide an interface where carbon rearrangement can occur. The FRC model has significant strengths and merits serious consideration. The FRC model is strengthened by CVD-synthesized CNT in which no catalyst particles are used.[3,4] In this so-called "catalyst free" synthesis route graphitic tubular structures, i.e., CNT are templated by a porous Al_2O_3 structure. Clearly the argument that catalyst particles in CVD are necessary to decompose the hydrocarbon is redundant (even if they can decompose the hydrocarbon). The FRC model neatly explains this. On the other hand, the requirement that the catalyst particle provide an interface for (ordered) carbon structuring is obviously not a prerequisite. This does not mean the catalyst structuring role is lost. Far from it. The "catalyst-free" studies simply point to Al_2O_3 being able to fulfill the role of providing an interface for ordered carbon formation, viz. the substrate is the catalyst for graphitic formation. In fact, the catalytic graphitization of carbon by metal oxides has been known for some time.[5,6] In this communication, we explore the graphitization role of various oxides under typical carbon nanotube CVD synthesis conditions and interpret the data in terms of their implications to CNT synthesis and primary soot particle formation.

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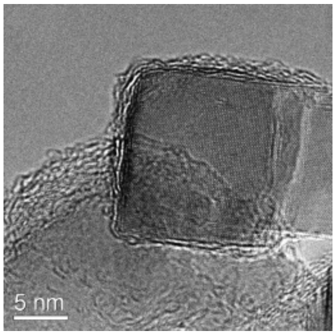

Figure 1. TEM image of a MgO nanocrystal coated in a few graphitic layers.

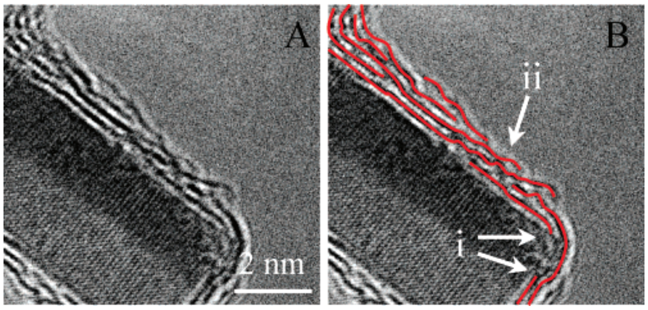

Figure 2. (A, B) TEM images of a MgO crystal coated in graphene layers. Graphene layers are highlighted in image B. (i) Graphene layer roots on the MgO crystal. (ii) Wrinkle formation due to growth process.

In the present study, a horizontal tube CVD reactor was used. Two carbon feedstocks, ethanol and methane, were explored with a temperature of 850 °C. The following nanopowdered oxides were investigated; SiO_2, Al_2O_3, MgO, Ga_2O_3, and ZrO. Thin films of SiO_2 and SiO_2/Al_2O_3 on Si substrates were also used.

We begin by looking at the thin film substrates after the CVD reaction. Visual inspection of the surfaces show no apparent change, i.e., no carbon coating. Raman spectroscopic studies on the substrate confirm no changes, with the spectra being identical before and after the reaction. However, in the case of nano-oxide powders, very obvious changes are observed. All powders, upon removal from the reactor, were black in color, hinting at carbon formation. Transmission electron microscopy (TEM) studies of the material showed the oxide crystals to be coated with a few layers of material with a spacing around 0.34−0.36 nm, which is the typical graphene spacing found in graphitic nanostructures.

Figure 1 shows a typical example of a MgO nanocrystal coated in a few graphitic layers. Energy-dispersive X-ray (EDX) analysis confirmed the presence of carbon in the samples. Raman spectroscopy is a powerful tool to detect the presence of sp^2 hybridized carbon through the E_{2g} mode or G band (stretching vibrations in the basal plane of crystalline graphite) and the so-called D band (indicating the level of defects in the graphitic material). All samples had very similar Raman responses, with a G/D ratio of ca. 0.6 (see the Supporting Information). This confirms the formation of graphitic layers in the CVD reaction. Changing the carbon feedstock, oxide, crystal size, or increasing the reaction time (10−90 min) does not alter the number of graphitic walls nor the Raman response. A statistical analysis of the number of walls always showed between 1 and 8 walls (most between 2 and 5). The permeable nature of the graphitic coating encasing the nano crystals is highlighted in these samples by the ease with which they can be dissolved out of their graphitic casing via diluted acid treatment. After acid treatment, the shape of the nanostructures are the same shape as the initial crystals around which the graphite layers form (see the Supporting Information), i.e., they encapsulate the nanoparticles. This is highlighted by comparing the templated carbon nanostructures from a different MgO powder in which the crystals are smaller and mostly round in shape (see the Supporting Information). When using Ga_2O_3 nanocrystalline powders in the reaction, most of the templated nanostructures are empty. This is more noticeable for samples prepared with long reaction times. In rare cases, some material remains inside the shell-like structures. In addition, large pieces of material (50−300 μm) could also be seen in the sample. Local EDX analysis of these large pieces and the residual pieces inside the shell structures showed them to be Ga and Ga_2O_3, respectively. This points to the Ga_2O_3 being reduced in the reaction and easily diffusing out of the templated carbon nanostructures during the reaction itself. Presumably, hydrogen from the decomposed hydrocarbon (feedstock) diffuses into the shells, which can then decompose the Ga_2O_3. One can then also expect carbon species to be able to diffuse into the shell structure and feed the growth of the graphene sheets. This then raises two questions: (1) Is the carbon addition to the growing graphene layers taking place at their free exposed ends, viz. in the vapor region, or does growth occur at the interface of the graphene layer and the oxide? (2) Why are the number of graphene layers formed always limited regardless of the reaction conditions or oxide used? These questions can be answered by closer inspections of the graphene layers on the oxide particles themselves. Images a and b of Figure 2 are high-magnification TEM images showing how the graphene layers form on the surface of MgO. In Figure 2b, the graphene layers have been highlighted for easy viewing. Typically, all the layers can be traced to the surface of the oxide (e.g., Figure 4b, label i). In addition many graphene sheets have wrinkles in them, which occurs where individual sheets overlap (Figure 2b, label ii). This can be explained by the sheets meeting each other during growth and then having to crease in order to overlap an opposing graphene layer. Obviously, the process of growing graphene layers having to squeeze in between each other gets progressively more difficult, and eventually, no further growth can take place. This explains why the number of walls is limited regardless of the reaction conditions and why the walls are so readily permeated. More importantly, the results clearly show that oxides are exceedingly good at promoting ordered carbon (graphene) growth under CVD conditions typically used for CNT synthesis. Clearly, this has important implications for CVD-based CNT synthesis. Normally, it is argued that the role of the oxide support is to merely stabilize the metal catalyst particles via the strong metal/support interaction. In addition, no observations of carbon formation on single-crystal substrates (e.g., Si/SiO_2) are reported. This is in keeping with our results. However, when using nanopowders one easily obtains graphitic layers stemming from the oxide surface. We attribute this difference to the presence of surface defect sites on the powdered oxides. It is then entirely conceivable that in substrate-based CNT synthesis routes, the interface between the catalyst particle and the substrate (particle circumference) behaves as a circular defect site. This would then promote cylindrical graphene structures growing upward, in other words, nanotube growth. It is well-known that there is a strong correlation between the catalyst diameter and that of the resultant nanotube.[7,8] This is in agreement with the above proposed mechanism. In addition, this growth route would allow the catalyst particle to detach from the substrate surface and be lifted off as the tube grows. This is often referred to as top growth; however, in our proposed mechanism, there is no distinction between top growth and base growth, because growth is always at the base on the substrate. Hence, the metal catalyst still serves as an interface for ordered carbon structuring for the embryonic cap formation. We propose that carbon would add directly at the root of a growing tube, coming from the gas phase and/or via surface diffusion of adsorbed carbon species. At this point it is worth noting that surface diffusion of adsorbed carbon species as well as the active catalysis site occurring at the metal/support interface are commonly argued processes for the catalytic chemistry of Au nanoparticles on metal oxide supports.[9−11] In addition, previous studies have suggested a substrate role in the synthesis of carbon nanotubes[12] and O playing a role at the root of a growing nanotube.[13]

It is also interesting to note that the same mechanisms could explain the formation of primary soot particles produced in hydrocarbon flames. Typically, spherical primary soot particles range between 10 and 50 nm and show no dependence on fuel type. The formation of primary soot particles are mostly accepted as stemming from mass accumulation of polycyclic aromatic hydrocarbons (PAH), which provide the nuclei for soot formation.[14] PAHs are ideal initiators for the nucleation of FRCs.[2] Further, studies on the early stages of soot formation show they contain high levels of free radicals and that although early soot formation is fuel specific, the resultant mature soot particles are the same regardless of fuel type.[15] The same study also showed O chemically bound to carbon species. The accepted mechanism for the growth of primary soot particles is via surface accumulation of species; however, this cannot explain the diameter limitation of primary soot particles, regardless of which hydrocarbon is used. It is our contention that the initial nucleus of a soot particle, namely, accumulated PAHs, provide the means for FRC formation and the root for carbonaceous growth via O species (cf. oxides). As the carbonaceous species grow from the nucleus, they will progressively entangle, which will ultimately limit growth exactly as the graphitic layers do when forming via oxides. This can explain the size limitations of primary soot particles and the presence of O chemically bound to C. Furthermore, this points to a common growth process for both soot and carbon nanotube formation in which O plays a key role at the root of carbon species formation in the presence of a FRC. Moreover, the use of H_2O or O in the "super growth" of CNT is argued to reduce the formation of amorphous carbon and thus prevent catalyst passivation.[16] Although amorphous carbon production may well be reduced by the addition of nominal amounts of H_2O or O, these studies hint that their role may also include the provision of a steady supply of O at the root of growing nanotube and/or promote the formation of carbonaceous species by building up (and maintaining) the radical supply.[14]

In summary, we have shown the ability of various pure oxides to grow graphitic sheets under typical CVD conditions for CNT synthesis. The synthesis route leads to encapsulating graphitic nanostructures and can easily be scaled up for mass production. The high surface density and permeability of these nanostructures makes them ideal for use in electrochemical applications such as lead-acid batteries, electric double-layer capacitors, and fuel cells. Our findings suggest that carbon nanotube growth may occur via the oxide support, such that the root of a carbon nanotube lies at the interface of the metal catalyst/support. Bearing in mind the demonstrated graphitization ability of oxides, the simplistic view of the support playing a catalytically passive role can no longer be taken for granted. The proposed mechanisms can also explain the formation of primary soot particles pointing to a common growth mechanism for both primary soot particles and carbon nanotubes synthesized from hydrocarbons.

Acknowledgment. M.H.R. thanks the DFG PI 440/3−/4, C.K. thanks the International Max Planck Research School "Dynamical Processes in Atoms, Molecules and Solids" for a fellowship, and A.G. acknowledges the EU for an MC fellowship.

Supporting Information Available: Experimental details, Raman spectra, and EDX data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0712220

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