

Synthesis of sp^2 carbon nano- and microrods with novel structure and morphology

Yu-Hsu Chang,^a Hsin-Tien Chiu,^{*a} Lung-Shen Wang,^a Cheng-Yu Wan,^a
 Chih-Wei Peng^a and Chi-Young Lee^{*b}

^aDepartment of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050, R.O.C. E-mail: htchiu@cc.nctu.edu.tw

^bMaterials Science Center, National Tsing Hua University, Hsinchu, Taiwan 30043, R.O.C.

Received 12th December 2002, Accepted 6th March 2003

First published as an Advance Article on the web 18th March 2003

A unique form of carbon rods has been synthesized by reacting C_6Cl_6 with Li at 523 K. TEM images show that the structure is graphite-like, with the layers arranged perpendicular to the long axis of the rods. The average rod size is $0.3 \times 5 \mu m$. The larger ones are $1 \times 10 \mu m$. The ratio of graphite-like to disordered carbon atoms, determined by solid-state ^{13}C NMR, is 1 : 1.

The multiplicity of carbon shows various allotropic morphologies and physical characters.^{1–3} Studies of graphite fibers,⁴ filaments⁵ and whiskers⁶ have attracted much attention in the past. In recent years, two major breakthroughs in the field of carbon materials, buckminsterfullerene^{7,8} and carbon nanotubes (CNTs),⁹ have greatly influenced the current research and development in this important area. The parallel layers of sp^2 carbon atoms in CNTs are arranged such that the long axis of the rolled-up cylinders is parallel to the layers. Here, we wish to report a rare form of carbon rods with a unique morphology and structure. Previously, we have demonstrated that C_6Cl_6 and C_5Cl_6 react with Na metal to form nano-sized graphite and graphite onion powders, respectively, via a Wurtz-type reaction.¹⁰ In this report, we demonstrate that by employing C_6Cl_6 as the building block and Li as the coupling reagent, carbon rods with graphite layers perpendicular to the long axis can be synthesized.

C_6Cl_6 was reacted with a stoichiometric amount of Li metal at 523 K in a Pyrex tube sealed under vacuum.¹¹ The black powder formed was washed with 2-propanol to remove the residual Li and the byproduct, LiCl. A scanning electron microscopy (SEM) image of the sample is shown in Fig. 1. The material shows a rod-like morphology with dimensions of 0.1–0.5 μm width and 3.0–15 μm length. The average rod size is ca. $0.3 \times 5.0 \mu m$. In addition, a powder with spherical grain morphology is a minor component in the solid. Transmission electron microscopy (TEM) images of a carbon rod are shown in Fig. 2. The low magnification TEM image, Fig. 2(a), shows an overall morphology consistent with the SEM observations.

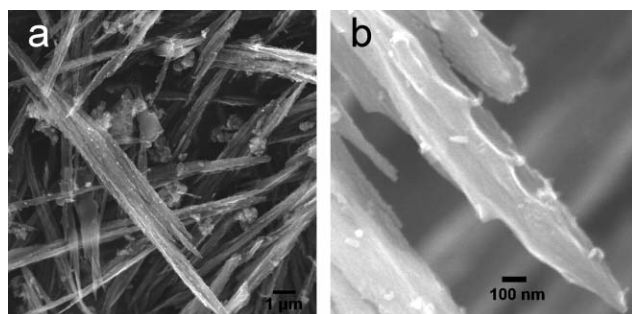


Fig. 1 SEM images of carbon rods: (a) low and (b) high magnification.

Fig. 2(b), the high-resolution TEM (HRTEM) image, shows that a branch on the rod has a disordered layer structure. Even though the structure is not well ordered, the interlayer distance can still be estimated to be 0.33–0.40 nm from the image.¹² This value is typical for turbostratic graphite layered structures. From Fig. 2(b), it is clear that the layer stack is perpendicular to the long growth axis of the branch on the rod. Another area of the sample, shown in Fig. 3(a), reveals some individual carbon rods. The carbon layers in these rods are also perpendicular to the long axis [Fig. 3(b)]. The arc pattern observed by electron diffraction (ED), shown in the inset in Fig. 3(b), is assigned to the (002) reflection of the highly textured graphene layers.^{13–15} Due to the small grains, no significant structural information was obtained from X-ray diffraction studies. For an as-prepared sample, 7Li solid-state NMR spectroscopy showed only one major signal at 0 ppm before the byproduct LiCl was removed. No other signal assignable to intercalated Li was observed.

From solid-state ^{13}C NMR data, the ratio of graphite-like carbon atoms (130 ppm) to disordered carbon atoms (178 ppm)¹⁶ is estimated to be nearly 1 : 1. A Raman spectrum

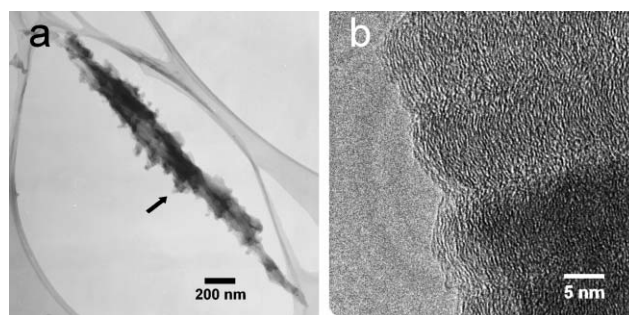


Fig. 2 TEM images of a carbon rod: (a) TEM image and (b) HRTEM image of the selected area shown in (a).

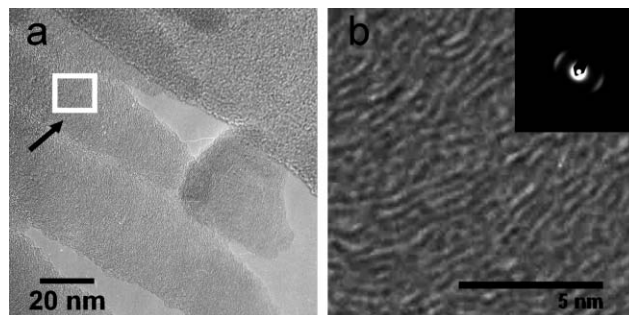


Fig. 3 TEM images of individual carbon rods: (a) TEM image and (b) HRTEM image and ED pattern (inset) of the selected area shown in (a).

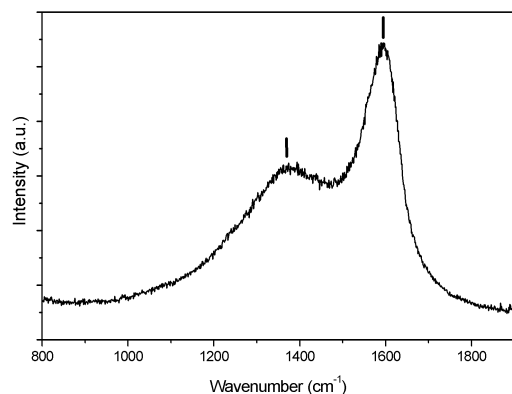
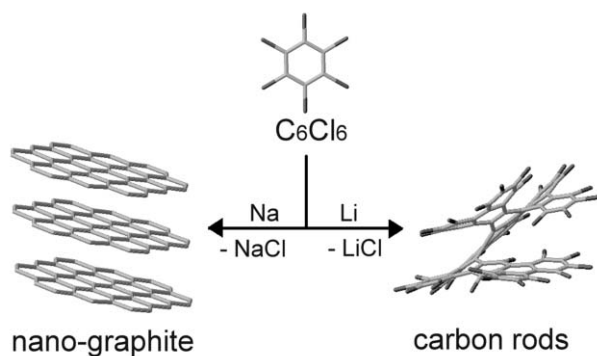


Fig. 4 Raman spectrum of the carbon material.

of the sample is shown in Fig. 4. The peaks at 1592 and 1370 cm^{-1} are assigned to the G and D bands, respectively, of a graphitic carbon material.¹⁷ The ratio I_D/I_G is estimated to be 1.2, reflecting the relative disorder of the rod.¹⁸ The elemental composition of the sample was characterized by X-ray photoelectron spectroscopy (XPS). On the surface, the composition is 95% C, 2% Cl and 3% O. The binding energy (B.E.) of C 1s electrons was observed at 284.3 eV, which is close to the values reported for graphite-like materials.¹⁹ The B.E. of Cl 2p electrons was observed at 200.0 eV and attributed to Cl atoms covalently bonded to carbon atoms. After heat treatment of the sample at 1273 K in Ar for 10 h, the Cl concentration on the surface of the rods decreased to below the XPS detection limit, *i.e.* less than 1%, and the composition became 97% C and 3% O. The morphology and the nanostructure of the material did not appear to change significantly as a result of this process, according to TEM and SEM studies.

The cause of the growth of the graphene layers perpendicular to the rods' long axis is unclear. The presence of residual Cl atoms in the rods may be significant. This suggests that the $\text{C}_6\text{-C}_6$ coupling reaction assisted by Li, a milder reducing agent than Na, was less efficient than the coupling promoted by Na.²⁰ Molecular models are proposed in Scheme 1 to demonstrate the difference. Using Na, flat graphene layers can be formed due to the more effective removal of the Cl atoms. Formation of well-ordered nano-graphite crystals has been observed experimentally.¹⁰ On the other hand, when Li is used, the coupling is less efficient, so that the removal of Cl atoms from the C_6 ring is incomplete. These residual Cl atoms may have two effects. The first is that they terminate the coupling process and limit the expansion of the graphene layers. Secondly, they



Scheme 1

also cause the graphene layers to bend and curl. Propagation of the process may lead the layer growth to spiral into a one-dimensional graphite material with many defects within the structure. Apparently, the rods show that the layers are perpendicular to the long axis of the rods.

Our studies have provided a method to generate a unique carbon material. Taking C_6Cl_6 as the building block and Li as the coupling reagent, carbon rods with the graphene sheets perpendicular to the long axis can be synthesized. The morphology of the rods is very different from that of the nano-graphite reported previously, produced by employing Na as the reducing agent. The process is a low temperature route and does not involve transition metal catalysts. Potential applications of the carbon rods, such as hydrogen storage, will be investigated in the near future.

Acknowledgement

We thank the National Science Council of Taiwan, Republic of China (NSC-90-2113-M-009-022 and NSC-90-2218-E-007-063), for financial support.

Notes and references

- W. N. Reynolds, in *Chemistry and Physics of Carbon*, ed. P. L. Walker, Marcel Dekker, New York, 1973, vol. 11, p. 1.
- I. S. McLintock and J. C. Orr, in *Chemistry and Physics of Carbon*, ed. P. L. Walker, Marcel Dekker, New York, 1973, vol. 11, p. 243.
- B. T. Kelly, *Physics of Graphite*, Applied Science Publishers, London, 1988.
- M. S. Dresselhaus, G. Dresselhaus, K. Sugihara, I. L. Spain and H. A. Goldberg, *Graphite Fibers and Filaments*, Springer-Verlag, Berlin, 1988, vol. 5 and references therein.
- R. Iley and H. L. Riley, *J. Chem. Soc.*, 1948, 1362.
- R. Bacon, *J. Appl. Phys.*, 1960, **31**, 283.
- W. Kratschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354.
- H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
- S. Iijima, *Nature*, 1991, **354**, 56.
- C.-Y. Lee, H.-T. Chiu, C.-W. Peng, M.-Y. Yen, Y.-H. Chang and C.-S. Liu, *Adv. Mater.*, 2001, **13**, 1105.
- In general, 1.0 g (3.5 mmol) C_6Cl_6 was allowed to react with 0.15 g (22 mmol) Li at 523 K in a Pyrex tube (70 ml) sealed under vacuum. A black powder was formed from the highly exothermic reaction. After the reaction ceased, the byproduct, LiCl, was removed by refluxing with 200 ml 2-propanol overnight. The black powder, composed of carbon and trace amounts of oxygen and chlorine, as indicated by XPS and ED, was isolated in nearly quantitative yield. Solid-state ^7Li and ^{13}C NMR spectra were obtained using a Bruker DSX-400WB spectrometer. SEM images were obtained using a Hitachi S-4000 instrument. TEM and ED data collection were accomplished on a Philips Technai-20 operating at 200 keV. Raman data were collected using a Renishaw-1000 Ramanscope instrument.
- S. Iijima, *Chem. Scr.*, 1979, **14**, 117.
- T. Hayashi, M. Endo and M. S. Dresselhaus, *Appl. Phys. Lett.*, 2000, **77**, 1141.
- B. Reznik and K. J. Hüttinger, *Carbon*, 2002, **40**, 617.
- De Pauw, B. Reznik, S. Kalhöfer, D. Gerthsen, Z. J. Hu and K. J. Hüttinger, *Carbon*, 2003, **41**, 71.
- H. Darmstadt, C. Roy, S. Kaliaguine, G. Xu, M. Auger, A. Tuel and V. Ramaswamy, *Carbon*, 2000, **38**, 1279.
- R. J. Nemanich and S. A. Solin, *Phys. Rev. B*, 1979, **20**, 392.
- D. S. Knight and W. B. White, *J. Mater. Res.*, 1989, **4**, 385.
- E. Papirer, R. Lacroix, J.-B. Donnet, G. Nansè and P. Fioux, *Carbon*, 1995, **33**, 63.
- Comprehensive Organometallic Chemistry*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1982, vol. 1.