

The blackest black material from carbon nanotubes

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Carbon is an interesting and wonderful element not only because it forms millions of organic compounds with hydrogen, oxygen, nitrogen, sulphur and other elements, but also due to its ability to exist in different allotropic forms, which have provided a variety of nano-forms of carbon with fascinating properties. In 1985, Smalley and co-workers from Rice University, Houston, first reported the isolation of buckminsterfullerene (C_{60}), the third form of carbon¹. Several amazing discoveries followed soon after the announcement of the large-scale preparation of C_{60} by the electric arc discharge method². It was the invention of fullerene that was eventually responsible for the discovery of carbon nanotubes (CNTs). A careful examination of the carbon cathode used in the arc discharge process for preparing small carbon clusters by Sumio Iijima³ in 1991, resulted in the remarkable discovery of multi-walled CNTs and subsequent production of single-walled CNTs^{4,5}. The discovery and extensive investigations of CNTs have acquired the important status of one of the most active fields of nanoscience and nanotechnology.

Several striking characteristics of CNTs like their mechanical properties, viz. Young's modulus and tensile strength, field emission, possible storage of hydrogen in CNTs, etc. will have potential applications^{6,7}. Various applications of CNTs and functionalized CNTs are well documented⁸. Due to their superior electronic, mechanical and optical properties, CNTs find applications as new charge-transfer materials in organic photovoltaic devices which are light-weight and flexible⁹. It is, therefore, not astonishing that scientists make efforts to produce several novel materials derived from CNTs.

It is a common observation that when electromagnetic radiation strikes the surface of a body, part of the radiation energy is generally reflected, part absorbed and part transmitted⁹. This is because the ordinary materials employed are in general imperfect absorbers of radiation. However, an ideal black object absorbs perfectly, light of all wavelengths at all angles. A blackened metallic surface or carbon black comes close to an ideal

blackbody. Although carbon paints and graphite appear to be black as they absorb visible light, they are not perfectly black. They have a moderate reflection of 5–10% at the air–dielectric interface. It has been realized that a hollow sphere, blackened on the inside and with a small opening, fulfils the defined condition more satisfactorily. It is expected that any radiation that enters through the small opening is reflected repeatedly from the walls of the enclosure until all of the energy eventually becomes absorbed⁹. A Guinness world record of the lowest reflectance of $R = 0.16\text{--}0.18\%$ has been reported for NiP material¹⁰.

Thin films of aligned CNTs also exhibit interesting optical properties¹¹. In order to understand the optical properties of these arrays of CNTs, a theoretical calculation was made, which predicted low index of refraction for aligned CNT materials¹². A nanotube array may be expected

to reflect light weakly, as any radiation that enters through the small opening will be reflected repeatedly from the walls of the CNTs until all of the energy eventually becomes absorbed. These features of CNTs presumably motivated Yang *et al.*¹³ to probe whether the CNT film, containing nanotubes arranged in an ordered array, will be an ideal candidate for a perfect blackbody. They prepared a vertically aligned CNT film (VA-CNT film) by chemical vapour deposition. The VA-CNT film consists of very low density of nanotubes ($0.01\text{--}0.02\text{ g/cm}^3$) with film thickness varying from 10 to $100\text{ }\mu\text{m}$. The film deposited on a substrate can be easily peeled-off.

The scanning electron microscopy (SEM) image of the VA-CNT film (Figure 1a) shows that the film is uniform over the entire sample¹³. In Figure 1b, a side-view SEM of the same sample is shown, which reveals that the tubes are

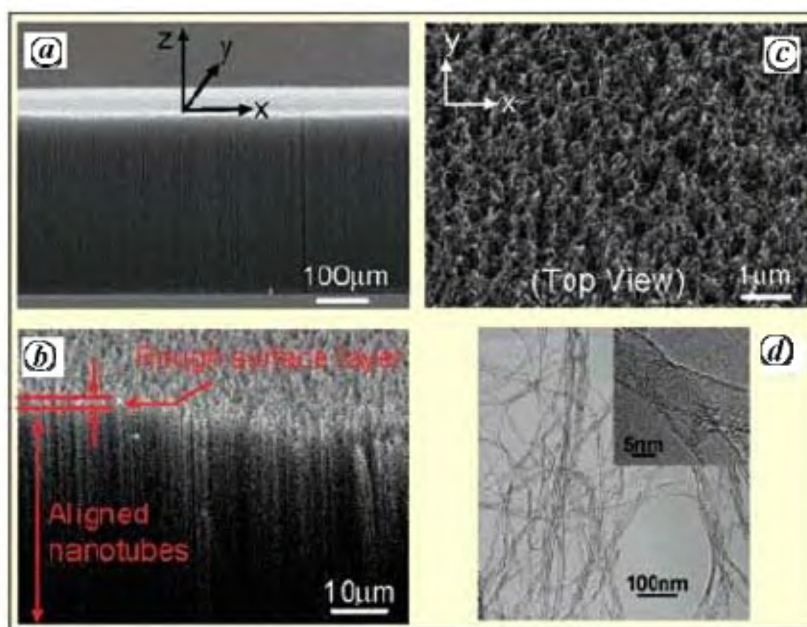


Figure 1. *a*, Scanning electron micrograph (SEM) of a VA-CNT sample. *b*, Side-view SEM image of the same sample at a higher magnification. The nanotubes are vertically aligned, forming a highly porous nanostructure. *c*, Top-view SEM image of the sample. The nanotubes are entangled with each other, forming a loosely connected random surface. The surface corrugation is of the order of 100–1000 nm. *d*, Transmission electron micrograph of the sample, indicating that most of the nanotubes are multiwalled with diameter $d \sim 10\text{ nm}$. Reprinted with permission from Yang *et al.*¹³. Copyright (2008) from American Chemical Society.



Figure 2. Photograph of a 1.4% NIST reflectance standard, a VA-CNT sample, and a piece of glassy carbon, taken under a flash light illumination. Reprinted with permission from Yang *et al.*¹³. Copyright (2008) from American Chemical Society.

straight and vertically aligned with high nanoporous structure. That the surface of the layer is corrugated has been evidenced from Figure 1c. The transmission electron microscopy image (Figure 1d) points out that the average diameter of the nanotubes is 8–10 nm. By reflectance measurements Yang *et al.*¹³ have shown that the total reflectance (R) of the film is 0.045%, which is about three times lower than that of NiP, one of the darkest materials known. In other words, the VA-CNT film is about three times darker than NiP, the Guinness-record holder. Though the VA-CNT film and glassy carbon contain only carbon, reflectance of the former is two orders of magnitude lower than that of the latter.

The qualitative degree of blackness is illustrated¹³ in Figure 2. The photograph of the National Institute of Standards and Technology (NIST)-certified standard reflectance sample is shown on the left in Figure 2 (indicated as (e)). Its certified reflectance is 1.4% at $\lambda = 450\text{--}700\text{ nm}$. The picture of glassy carbon (extreme right, Figure 2), which is considered to resemble a black glass, is not as dark as the

sample at the left. The middle photograph (Figure 2) with a value of $R = 0.045\%$ is that of the VA-CNT film, which appears to be the blackest among the three samples¹³.

According to Yang *et al.*¹³, it is the combination of the low-density array, the nanometre-size nanotubes and the random surface profile that makes the VA-CNT film the blackest object. This blackest material is expected to have applications ranging from solar energy conversion to pyroelectric detectors¹³.

However, the preparation of an ideal black material is still elusive!

1. Kroto, H. W., Heath, J. R., O'Brien, S., Curl, R. F. and Smalley, R. F., *Nature*, 1985, **318**, 162–163.
2. Kratschmer, W., Lamb, L. D., Fostiropoulos, K. and Huffman, D. R., *Nature*, 1990, **347**, 354–358.
3. Iijima, S., *Nature*, 1991, **354**, 56–58.
4. Iijima, S. and Ichihashi, T., *Nature*, 1993, **363**, 603.
5. Bethune, D. S., Kiang, C. H., de Vries, M. S., Gorman, G., Savoy, R., Vasquez, J. and Bayers, R., *Nature*, 1993, **363**, 605.

6. Poole Jr, C. P. and Owens, F. J., *Introduction to Nanotechnology*, John Wiley, New Jersey, 2003, pp. 103–132.
7. Ajayan, P. M., In *Nanostructured Materials and Nanotechnology* (ed. Nalwa, H. S.), Academic Press, San Diego, 2000, pp. 329–360.
8. Dai, L., *Carbon Nanotechnology*, Elsevier, Amsterdam, 2006.
9. Maron, S. H. and Prutton, C. F., *Principles of Physical Chemistry*, The Macmillan Company, 1967.
10. Doubleday, B., *The Darkest Man Made Substance, Guinness World Records 2004*, Dell Publishing Group, New York, 2004, p. 242.
11. de Heer, W. A. *et al.*, *Science*, 1995, **268**, 845–847.
12. Vidal, G. *et al.*, *Phys. Rev. Lett.*, 1997, **78**, 4289–4292.
13. Yang, Z.-P., Ci, L., Bur, J. A., Lin, S.-Y. and Ajayan, P. M., *Nano Lett.*, 2008, **8**, 446–451.

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