



# Carbon Nanomaterials: Building Blocks in Energy Conversion Devices

by Prashant Kamat

Carbon nanotubes, fullerenes, and mesoporous carbon structures constitute a new class of carbon nanomaterials with properties that differ significantly from other forms of carbon such as graphite and diamond. The ability to custom synthesize nanotubes with attached functional groups or to assemble fullerene ( $C_{60}$  and analogues) clusters into three-dimensional (3D) arrays has opened up new avenues to design high surface area catalyst supports and materials with high photochemical and electrochemical activity. Unlike the conventional graphite phase, carbon nanostructures possess metallic or semiconductor properties that can induce catalysis by participating directly in the charge transfer process. Further, the electrochemical properties of these materials facilitate modulation of their charge transfer properties and aid in the design of catalysts for hydrogenation, sensors, and fuel cells.

Fullerenes are spherical, caged molecules with carbon atoms located at the corner of a polyhedral structure consisting of pentagons and hexagons (Fig. 1). The best known and most stable fullerene is  $C_{60}$  which is commonly referred to as buckyball or buckminster fullerene. The discovery of fullerenes by laser vaporization technique resulted in the award of the Chemistry Nobel Prize to Curl, Kroto, and Smalley in 1996.

Conventional carbon nanotubes are made of seamless cylinders of hexagonal carbon networks and are synthesized as single-wall (SWCNT) or multiwall carbon nanotubes (MWCNT) (Fig. 1). Stacked-cup carbon nanotubes (SCCNTs) consisting of truncated conical graphene layers represent a new type of nanotubes. This stacked-cup morphology provides a large degree of exposed and reactive edges in the outer and inner surfaces of the hollow tubes. Electric field alignment is a powerful technique that has been shown to orient carbon nanotubes

along a particular direction during the nanotube growth process. In addition, the carbon nanotubes can be assembled as linear bundles in suspension by applying a dc electric field. Individual nanotubes have been studied extensively for application in field emission devices.

Unique electrical and electronic properties, a wide electrochemical stability window, and high surface area have prompted many researchers to employ fullerenes and SWCNT assemblies for energy conversion devices. For example, fullerenes exhibit rich photochemistry and act as an electron shuttle in photochemical solar cells. They also play an important role in improving the performance of organic photovoltaic cells. Carbon nanotubes, in the semiconductor state, undergo charge separation when subjected to bandgap excitation. The exciton annihilation and charge separation processes have been characterized by transient absorption and emission measurements.

## Mimicking Photosynthesis

Carbon nanostructure-based donor-acceptor molecular assemblies can be engineered to mimic natural photosynthesis. Fullerene  $C_{60}$  is an excellent electron acceptor for the design of donor-bridge-acceptor molecular systems. Photoinduced charge transfer processes in fullerene-based dyads and triads have been extensively investigated by several research groups during the last decade. In these cases the excited  $C_{60}$  accepts an electron from the linked donor group to give the charge-separated state under visible light excitation. Photoinduced charge separation in these dyads has been achieved using porphyrins, phthalocyanine, ruthenium complexes, ferrocene, and anilines as electron donors.

The rate of electron transfer and charge separation efficiency is dependent on the molecular configuration, redox potential of the donor, and the medium. Clustering the fullerene-donor systems provides a unique way to stabilize electron transfer products. The stability of  $C_{60}$  anions in cluster forms opens up new ways to store and transport photochemically harnessed charge.

Novel organic solar cells have been constructed by quaternary self-organization of porphyrin and fullerenes with gold nanoparticles. The highly colored composite clusters of porphyrin gold nanoparticles and fullerenes are assembled as 3D arrays onto nanostructured  $SnO_2$  films using an electrophoretic deposition method (Fig. 2). The composite cluster electrode, when illuminated by visible light, produces photocurrent with an incident photon-to-photocurrent efficiency (IPCE) as high as 54%. This electrode exhibits a broad photocurrent response extending up to 1,000 nm.

## Fullerene and Carbon Nanotube Films on Electrodes

Fullerene clusters, SWCNTs, and SCCNTs can be deposited conveniently as thin films on optically transparent glass electrodes. The clusters of fullerenes or nanotubes suspended in a nonpolar solvent are readily driven to an electrode surface by the application of an electric field. The atomic force microscopy (AFM) and transmission electron microscopy (TEM) images of different types of carbon nanostructure films are shown in Fig. 3. These films are electrochemically active and exhibit electrocatalytic and photoelectrochemical effects.

The SWCNT films cast on optically transparent electrodes respond to visible light excitation. Figure 4 shows the IPCE of SWCNT films cast on conducting glass electrodes. The mechanism of charge

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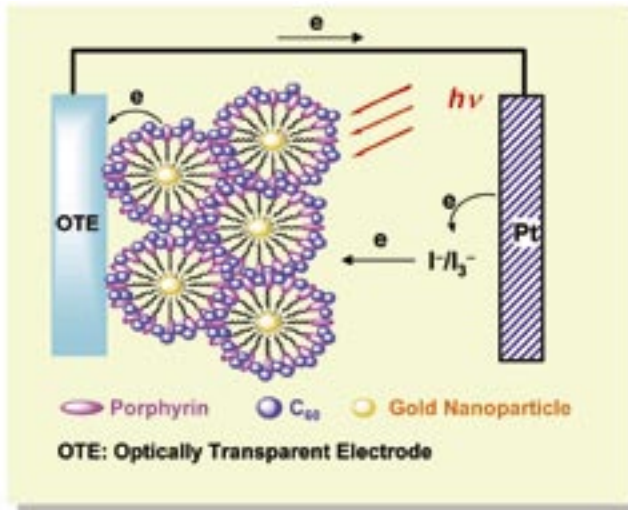
separation and photocurrent generation is also illustrated in the figure. The low photocurrent generation efficiency in these films is attributed to ultrafast recombination of photogenerated charge carriers. One way to improve charge separation is to develop composite nanostructures. Using this strategy it has been possible to enhance the photoconversion efficiency of CdS-SWCNT system. CdS particles anchored on SWCNT were able to inject electrons from its excited state thus improving the charge separation and promoting vectorial charge flow toward the collector electrode.

**Nanostructured Carbon as Catalyst Supports in Fuel Cells**

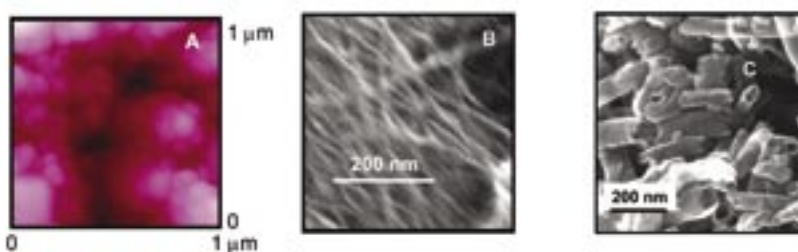
Decreasing the amount of precious metal in the electrode catalysts is a major challenge in the development of fuel cells. Such a reduction in the amount of metal catalyst in most cases can be achieved by increasing the active area of platinum that is actually utilized on an electrode surface. One way to achieve this is by using high surface area carbon supports, which generally enable higher utilization of the metal catalyst.

The electrophoretic deposition of SWCNT on a carbon fiber electrode (Toray paper) provides a simple and versatile technique to design a membrane electrode assembly (MEA) for the fuel cell. SWCNT serve as an excellent support to anchor Pt catalyst and carry out electrochemical oxidation and reduction reactions effectively similar to the existing commercial carbon black support. The effectiveness of SWCNT supported Pt and Pt-Ru catalyst has been evaluated successfully in hydrogen and direct methanol fuel cells, DMFCs (Fig. 5).

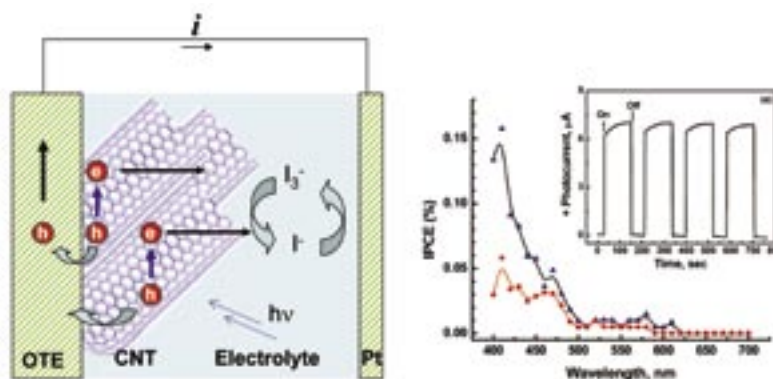
For example, Pt-Ru catalysts dispersed on SWCNTs exhibit lower onset potential for methanol oxidation. The onset potential for methanol oxidation correlates well with the maximum power density of a DMFC. Based on the evaluation of the electrochemical and fuel cell performances one can conclude that no single property of the carbon nanostructures dictates the performance of electrocatalysts in the MEA. Along with electrochemical active surface area of the MEA, the metallic character of carbon nanotubes is important in attaining higher power density in a DMFC. Nearly 30% enhancement in the power density is seen when these carbon nanotubes are used in the MEA instead of carbon black. Accelerated durability tests indicate that SWCNTs enhance the stability of the electrocatalyst during long-term use. The lower energy of CO



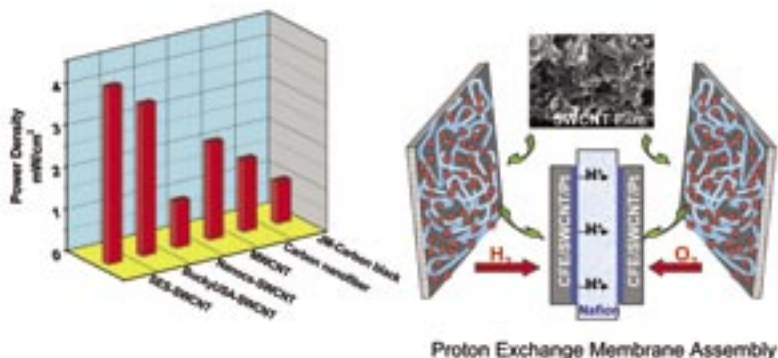
**Fig. 1.** Porphyrin- $C_{60}$ -gold electrode in a photoelectrochemical cell.



**Fig. 2.** Figure atomic force microscopy and transmission electron microscopy images of (A)  $C_{60}$  clusters; (B) single wall carbon nanotubes; and (C) stacked cup carbon nanotubes assembled on electrode surfaces.



**Fig. 3.** Harvesting light energy using carbon nanotube films. The spectral response of the electrode is shown on the right.



**Fig. 4.** Comparison of power density of passive direct methanol fuel cells with different nanostructured carbon supports.

adsorption observed with a Pt/SWCNT electrode also demonstrates the CO-tolerance of this electrocatalyst.

The rapid growth of technical interest in fullerenes and carbon nanotubes over the past decade is a result of a number of congruent factors including facile synthesis and new methods for characterization; better understanding of the electrochemical, optical, and electronic properties; and the rapid growth in computing capabilities. This trend is expected to continue into the early part of the 21st century and provide the basis for further advances in carbon nanotechnology. ■

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