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ChemComm
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Novel iron-decorated carbon nanorods from fullerene soot

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Received (in Cambridge, UK) 1st December 2003, Accepted 13th January 2004
First published as an Advance Article on the web 10th February 2004

A novel form of nano-sized carbon rods decorated with monodispersed iron particles in a size range of 30–50 nm on their surface is successfully synthesized by arcing discharge of composite electrodes made from iron particles and fullerene soot; this will be of potential as catalyst for hydrogenation reactions.

Since the discovery of carbon nanotubes (CNTs) in 1991,[1] a number of novel one-dimensional nanostructured carbon materials have been reported, including nanocones,[2] conical crystallite,[3] nanoscrolls,[4] tubular graphite cones[5] and nanopipettes,[6] depending on the techniques and the carbon precursors used. Here, we report that a novel form of nanostructured carbon, or carbon nanorods, can be prepared in large quantity from carbon electrodes made of a mixture of fullerene soot and iron particles by arc discharge method, of which the surface is decorated by nanosized iron particles. The fullerene soot, a by-product of CNTs production by arc discharge, is normally regarded as waste, has a yield of *ca.* 40–60wt%, depending on the arcing conditions and the type of the CNTs produced. Unfortunately, so far few efforts have been made to effectively make use of the soot. It has been shown that various forms of carbon materials such as carbon fibers and CNTs are very good catalyst supports due to their high surface area and chemical inertness, particularly in strong basic and acid environments.[7–8] In this field, the challenging task is how to prepare good carbon-supported catalysts with high performance for some specific reactions. This work aims to make full use of fullerene soot, a kind of waste carbon material, to directly prepare carbon supported and nano-sized iron catalysts that might be of great potential in catalytic hydrogenation reactions.

For the preparation of iron-decorated carbon nanorods, an electrode made of iron particles and fullerene soot was used as the anode in arcing discharge experiments. The fullerene soot used was a by-product obtained by arcing graphite electrodes for production of multi-walled CNTs. The soot-derived anodes were made according to the following procedure. The soot without any pre-treatment was first fully dried at 110 °C for 3 h before use; then, was finely mixed with binder (coal tar) and iron powder with a size of *ca.*120 μm. The weight ratios of the binder and iron powder to the soot were 30% and 5%, respectively. The mixed paste was subsequently pressed at *ca.* 10–20 MPa to form rods that were put into an electric furnace and carbonized in argon to make electrodes. Finally, iron-doped carbon composite anodes with a diameter of *ca.* 9 mm were obtained. For all of the arcing experiments, the cathode was made by a high purity graphite rod, which was not consumed during the arcing process. The arc-discharge experiments were carried out in helium at a pressure of 0.065 MPa and with a direct current of 40–50 A and a voltage of 50–70 V. The arcing time normally lasted about 15–20 min. After arc discharge, a large quantity of web-like or film-like materials were collected from the reactor wall, and examined by scanning electron microscopy (SEM, JSM-5600LV), transmission electron microscopy (TEM, JEM-2000EX), XPS (VG ESCALB MK-2) and XRD, and at the same time, were also tested as catalyst for benzene hydrogenation.

Typical SEM images of the as-obtained film-like carbons are shown in Fig. 1, from which it can be seen that the as-obtained products are uniform thread-like bundles or look like spun cotton sliver after drafting, and are quite similar to the bundles of single-walled CNTs.[9] The high magnification SEM image, as shown in Fig. 1b, reveals that the thread-like bundles actually consist of numerous short rod-like carbons with diameters ranging from several tens to a hundred nanometers.

The as-obtained film-like carbon deposits were further examined by TEM, which confirms that all the rod-like carbons are coated with nanosized iron particles in a relatively uniform way, as can be seen in Fig. 2. Fig. 2a shows a typical image of Fe-decorated nanorods, of which the lengths vary from several hundred nanometers up to several tens of micrometers with diameters in the

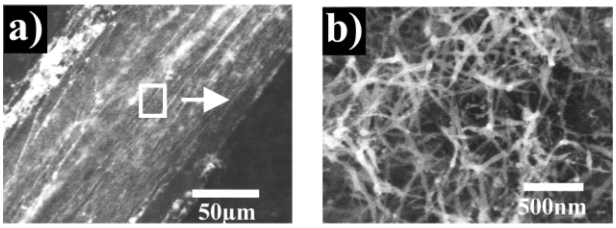

Fig. 1 SEM images of iron-decorated carbon nanorods; (a) a low magnification SEM image, showing the as-obtained products are uniform thread-like bundles, (b) a magnified SEM image of the section marked by a square in (a), showing the thread-like bundles are actually made of short rod-like carbons with diverse morphology.

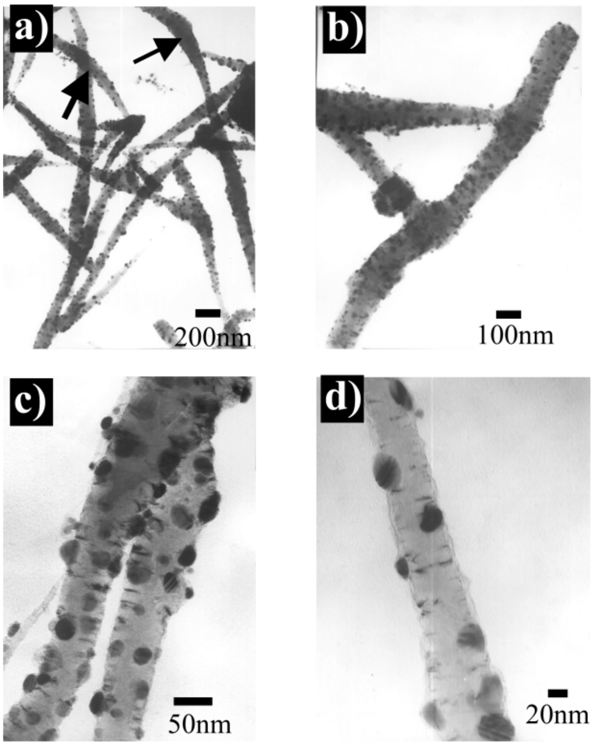

Fig. 2 TEM images of Fe-decorated nanorods; (a) many nanorods with numerous nanosized metals on their surface, (b) three nanorods joined together form an interesting triangle, (c) and (d) high magnification images showing that the deposited iron particles are quite uniform with a size of 30–50 nm.

DOI: 10.1039/b315552h

range 60–150 nm. It can be seen clearly that numerous well-dispersed, spherical iron particles are anchored onto the surface of these carbon rods, which is very similar to the metal-covered CNTs reported in the literature.[10] In addition, it is interesting to note that some rods are thick in the middle and gradually become thinner towards the ends, as indicated by arrows in Fig. 2a, and some nanorods join together and form a triangle structure as shown in Fig. 2b. Figs. 2c,d are magnified TEM images of iron-decorated nanorods, showing the average diameters of the deposited iron particles to be in the range of 30–50 nm. Further detailed TEM examinations reveal that some particles seem to be partly embedded in the carbon, as can be seen in Fig. 2d, implying that the interaction between metal particles and carbon nanorods is quite strong, which would be advantageous for eliminating or reducing the catalyst leaching when the carbon-supported metal catalysts are used in liquid phase catalytic reactions. The samples were also characterized by XPS: the typical XPS Fe (2p) spectrum (Fig. 3) shows three main peaks that can be assigned to Fe^0 at 707.4 eV and 720.6 eV and Fe^{3+} at 711.2 eV. This implies that the iron-decorated carbon nanorods are Fe^0-rich. The Fe^{3+} component detected might be formed due to the exposure of the samples to air. The XPS analysis also reveals that the content of iron on the surface of carbon nanorods is *ca*. 1.34%, which is further confirmed by the electron probe analysis (EPMA-1600).

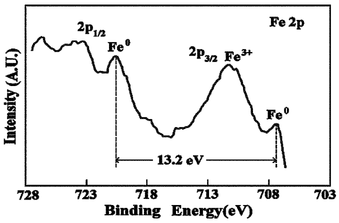

Fig. 3 XPS Fe (2p) spectrum of iron nanoparticles decorated on the surface of carbon nanorods, showing the presence of Fe^0 and Fe^{3+}.

X-ray diffraction (XRD) studies were also conducted and the typical XRD pattern is shown in Fig. 4, in which the diffraction peaks corresponding to the iron nanoparticles and the graphite can be clearly seen. From the (002) graphite reflection at *ca.* 27°, the spacing between adjacent graphite layers is estimated to be 0.3401 nm. Another peak at 43.2° can be attributed to those γ-Fe particles with fcc structure, which means that most of the iron particles are in ordinary metallic phase.

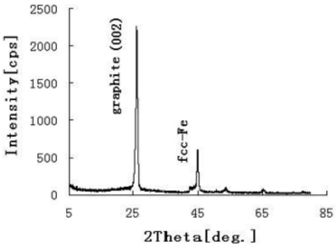

Fig. 4 XRD pattern of iron-decorated carbon nanorods.

An attempt was also made to understand the formation mechanism of these iron-decorated carbon nanorods, for this purpose the arcing process was monitored by *in-situ* optical emission spectrum (OES). The spectra recorded covers a region of 300–600 nm in which the OES lines corresponding to Fe and carbon species in the reaction system were scanned. The OES results show the presence of Fe in a wavelength range of 400–450 nm and C_2 species. The presence of C_2 dimers is evidenced by three typical OES peaks at 554.0 nm, 558.3 nm and 563.5 nm, as shown in Fig. 5, indicating that the C_2 species has played an important role in the formation of carbon nanorods. It is well known that one of the formation paths of fullerenes and CNTs is the C_2 addition scheme.[11] The OES results discussed above lead one to believe that the formation of the iron-decorated carbon nanorods may follow a scheme that is similar to the formation mechanism of fullerenes and CNTs.

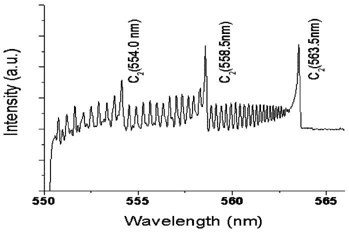

Fig. 5 The optical emission spectra of arc plasma during the preparation process of carbon nanorodes, showing the presence of C_2 dimers.

It would be easy for one to envision that for carbon nanorods decorated with nanosized iron particles, one of the application potentials is use as catalyst in chemical reactions. This has been demonstrated by the hydrogenation of benzene to cyclohexane. For the hydrogenation runs, benzene was added into and mixed with D.I. water in a volume ratio of 1 to 10, and the mixture, together with 50 mg of the iron-decorated carbon nanorods, was put into an autoclave with a volume of 250 ml. The hydrogenation of benzene was conducted under constant stirring at 140 °C in H_2 with an initial pressure of 5.0 MPa, and the products were analysed by GC-MS (HP 6890GC/ 5973MSD). It was found that benzene had been converted to cyclohexane, and under the conditions adopted, the conversion could reach 100% in 60 min, implying that the iron nanoparticles supported on carbon nanorods are quite active for benzene hydrogenation. It should be noted that for blank experiments with CNTs and fullerene soot as catalysts that were conducted under the same conditions, no hydrogenation of benzene was observed. These preliminary but encouraging results lead one to believe that the Fe-decorated carbon nanorods might be of potential as active catalysts for hydrogenations similar to the benzene hydrogenation.

In summary, we have demonstrated that novel Fe-decorated nanorods can be produced by arcing composite electrodes made from fullerene soot that is a by-product of fullerenes and CNTs. On the basis of OES analysis, it is believed that C_2 dimers may function as a precursor in the formation process of these novel carbon nanorods. This work will lead to a new and simple approach for making carbon-supported metals that may have great potential as catalysts.

This work was partly supported by the National Science Foundation of China (No. 29976006, 20376011), the Natural Science Foundation of Liaoning Province (No. 9810300701, 2001101003) and the Ministry of Education of China.

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