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In situ synthesis of carbon nanotubes decorated with palladium nanoparticles using arc-discharge in solution method

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A unique, simple, inexpensive, and one-step synthesis route to produce carbon nanotubes (CNTs) decorated with palladium nanoparticles using a simplified dc arc-discharge in solution is reported. Zero-loss energy filtered transmission electron microscopy and scanning transmission electron microscopy confirm the presence of 3 nm palladium nanoparticles. Such palladium nanoparticles form during the reduction of palladium tetra-chloro-square-planar complex. The deconvoluted x-ray photoelectron spectroscopy envelope shows the presence of palladium on the decorated CNTs. The energy dispersive spectroscopy suggests no functionalization of atomic chlorine to the sidewall of the CNTs. The presence of dislodged graphene sheets with wavy morphology supports the formation of CNTs through the “scroll mechanism.” © 2004 American Institute of Physics.
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I. INTRODUCTION

While pristine carbon nanotubes (CNTs) have unique properties to serve as hydrogen storage materials, and for optoelectronic and catalysis applications,^{1–5} CNTs combined with selective elements and compounds exhibit enhanced desirable properties to serve as nanoscale chemical reactors for aforementioned applications.^{4,6–12} Palladium nanoparticles on CNTs have received considerable attention for a variety of such potential applications. Ye, Lin, and Wai⁶ reported the deposition of 5–10 nm sized palladium nanoparticles on multiwalled CNTs (MWCNTs) by hydrogen reduction of Pd(II)- β -diketone precursors in the presence of supercritical carbon dioxide. The system showed⁶ promising catalytic properties towards hydrogenation of olefins in carbon dioxide and electro-reduction of oxygen in fuel cell application. CNTs can also act as field-effect transistors by coupling with metals. However, the presence of a Schottky barrier at the metal-CNT junction is a serious problem.^{13,14} In order to circumvent such problem, Javey and co-workers¹⁵ have recently fabricated a high-performance ballistic nanotube field-effect transistor using a palladium-single wall carbon nanotube (SWCNT) junction that reduces the Schottky barrier to a great extent. Hydrogen storage in CNTs has been a subject of intense research.^{1,2,16–21} Earlier reports¹⁷ suggest that to power electric vehicles effectively, the storage potential of CNTs must exceed 8 wt % of hydrogen. However, recent studies^{18,19} confirm that hydrogen uptake in CNTs is limited to 2 wt %. CNTs decorated Pd-nanoparticles exhibit fascinat-

ing and desirable properties for nanoscale storage as palladium has very high affinity towards hydrogen.^{22,23}

Generally, the decoration of CNTs with nanoparticles is accomplished as a postprocessing step^{6–11} which involves deposition of nanoparticles on nanotubes by various means. Such additional steps of nanotube decoration are not only inefficient but also increase the overall production cost. A technique, which simultaneously decorates the nanotube during its synthesis, is inherently devoid of such disadvantages. Besides a few preliminary investigations^{24–28} on arc-discharge in liquid phase on synthesis of carbonaceous materials, detailed studies on the *in situ* decoration of nanoparticles supported CNTs have not been attempted so far. Hsin and co-workers²⁶ attempted to produce metal-filled CNTs using arc discharge in a cobalt sulfate solution, which resulted in the formation of CNTs filled with not only metallic cobalt but also cobalt sulfide particles. The encapsulated particles were mostly rod-shaped. Moreover, the mechanism of the encapsulation of such particles was not clear from such attempts.²⁶

The aim of the present work is to develop a simple and inexpensive *in situ* synthesis method for the production of CNTs decorated with *in situ* synthesized Pd nanoparticles. The present study also focuses on the mechanistic aspects of the formation of metallic particles and the nanotubes. The synthesized CNTs decorated with palladium nanoparticles have been characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS) for their size, morphology, chemical constituent, and chemical state, respectively.

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FIG. 1. Schematic diagram of the especially designed cell for arc-discharge in solution; (a) double-wall glass; (b) steel plates; tubes for precursor solution (c) in and (d) out; cooled water (e) in and (f) out.

II. EXPERIMENTAL

A. Setup

CNTs decorated with palladium nanoparticles have been synthesized using a custom designed experimental setup. It has four main components: a cell, a dc power supply system, a filtering unit, and a chilling loop. Figure 1 shows the schematic diagram of the cell with a height of 20 cm that consists of a double-walled glass with 2 cm thickness for flowing of cold water at 7 °C to facilitate cooling. The inner diameter of the cylindrical cell is 10 cm. The cell has two inlets and two outlets. One pair of inlet and outlet is connected to the volume between the double walls for cooling of the cell with a flow of chilled water. The other pair is directly connected to the interior for filling in and filtering out the decorated nanotubes from the cell. Two stainless steel plates are placed on the two open ends of the cylindrical cell. The stainless steel plates are used to connect the anode and the cathode electrodes.

B. Method of synthesis

A palladium chloride solution of 2.087 mM concentration was prepared by dissolving 99.999% pure palladium chloride, obtained from Sigma Aldrich in deionized water. The resistance of the deionized water used in the present investigation was greater than 10 M Ω . In order to ensure complete dissolution of the palladium chloride, hydrochloric acid was added to reach 0.1 M concentration in the solution. The synthesis of CNTs was carried out in a reactor containing the palladium chloride solution. Two graphite electrodes with a diameter of 6.15 mm, acting as a cathode and an anode, were immersed in the palladium chloride solution inside the reactor. The anode and the cathode materials were obtained from Alfa Aesar with 99.9995% purity. A direct current power supply (model: Dual Mig 131/2 by Chicago Electric) was connected to the graphite electrodes. The electrodes were brought in contact to strike an arc and separated immediately to a distance of ≈ 1 mm to sustain the arc inside the solution. The synthesis was carried out at an open circuit potential of 28 V with an optimized direct current of 75 A. CNTs decorated with palladium nanoparticles were collected from the solution for their characterization.

To study the consumption of the electrode during the arc-discharge in the solution, the weight and the length of the electrodes were monitored throughout the experiment. The

FIG. 2. (a) Weight change of cathode and anode electrodes with time during arc-discharge in solution. (b) Overall weight change of anode and cathode with time during arc-discharge in solution.

initial weights of the two electrodes were recorded after keeping the electrode inside the furnace at 150 °C for 1 h. The weight differences were measured every 2 min after drying off the electrode in the furnace for 30 min at 150 °C. The evaporation rate of the solution has also been followed by measuring the volume of the solution every 2 min after cooling down to room temperature.

C. Characterization

High-resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM) studies were carried out, using a FEI Tecnai F30 at 300 kV, to investigate the size and structure of the CNTs and the palladium nanoparticles. Selected area electron diffraction (SAED) pattern of the Pd nanoparticles was also collected. For elemental analysis an energy dispersive spectroscopy (EDS) system attached to the TEM was used.

The chemical state of the Pd nanoparticles was investigated using XPS on a Perkin-Elmer PHI 5400 system at a pressure of $\approx 10^{-9}$ Torr. Nonmonochromatic Mg- K_{α} x-radiation with energy 1253.6 eV at a power of 350 W was used for the analysis. To achieve the maximum resolution, both survey and individual high-resolution XPS spectra were recorded with pass energies of 44.75 and 35.95 eV, respectively. The spectrometer was calibrated using a metallic gold standard (Au4f7/2=84.0 $\pm$ 0.1 eV). Any charging shift produced by the specimens were removed by using a binding energy scale referenced²⁹ to that of C(1s) of the adventitious carbon line at 284.6 eV.

FIG. 3. (a) SEM micrograph of a graphite rod before the experiment. After 10 min of arc-discharge (b) SEM micrograph of the anode, (c) SEM micrograph of the cathode; images of graphite rods (d) before, and (e) after the experiment.

The CNTs and the morphologies of the electrodes were characterized using a JEOL T-300 SEM system with the accelerating voltage of 10 and 5 kV, respectively.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) represent the weight change of each electrode and that of their cumulative in every 2 min, respectively. The weight change relationship in the present system can be mathematically expressed with the following equation:

$$\Delta W = k \times t, \quad (1)$$

where, t is time in minutes and ΔW is the weight change in g cm^{-2} during arc-discharge in solution, and k is the normalized kinetic parameter in $\text{g cm}^{-2} \text{min}^{-1}$. The experimental values of k in Eq. (1) for cathode and anode are 0.52 and $-2.73 \text{ g cm}^{-2} \text{min}^{-1}$, respectively. The k value of combine anode and cathode electrodes is $-2.17 \text{ g cm}^{-2} \text{min}^{-1}$. The cathode gains weight with time whereas the anode loses weight with time during the arc discharge. The overall weight of the electrodes decreases with time. A portion of the excessive heat produced in the solution during arcing help evaporating the solution. The evaporation rate of the water during arc-discharge in solution in the present system was found to be $3.2 \text{ cm}^3 \text{min}^{-1}$. The temperature at the site of the region of the arc is expected to be greater than 3500°C . Hence, the plasma region produced by the arc adjacent to the electrodes is enveloped by a solution-vapor interface. There

FIG. 4. SEM image of CNTs taken from the tip of the cathode.

FIG. 5. HRTEM image of a nanotube shows the inner and outer diameters; the inset micrograph reveals the distance between two concentric walls.

is a substantial thermal gradient across the plasma region. The temperature at the anode edge is more than 3500°C , while it is 100°C at the solution-vapor interface. Assuming the temperature at the center of the arc being 3727°C , a rough estimation²⁷ of the gradient yields 1209 K mm^{-1} . The loss of weight of the electrodes is due to the formation of carbon dioxide, carbon monoxide, CNTs, and other carbonaceous materials including dislodged graphene sheets, carbon onions, amorphous carbon, and carbon rods. Such carbonaceous materials were formed inside the plasma region at various temperature zones.²⁷

Figure 3(a) shows the surface of an electrode prior to the experiment. Figures 3(b) and 3(c) show the anode and the cathode electrodes after arc-discharge in solution, respectively. The structure of the anode surface has significantly changed after the arc-discharge. The morphology of the cathode surface is also uneven due to the deposition of the carbonaceous materials. Figures 3(d) and 3(e) represent overall picture of the electrodes before and after the experiment, respectively. SEM investigation of the cathode materials reveals a deposition of CNTs. Such hillocks of deposited CNTs are presented in Fig. 4. The inner and outer diameters of a CNT as shown in the HRTEM micrograph of Fig. 5 are 3 and 10 nm, respectively. The inset picture of Fig. 5 shows that the distance between the two concentric walls is 0.359 nm. Such distance of the interwall spacing supports the literature data.³⁰ Franklin³¹ reported an interlayer spacing in graphite to be 0.37 nm. A TEM bright-field image of a CNT decorated with palladium nanoparticles is shown in Fig. 6. The diameter of the CNT is $\approx 15 \text{ nm}$. The spherical darker regions in Fig. 6 correspond to the palladium nanoparticles of $\approx 3 \text{ nm}$ in diameter. A few of them are marked in Fig. 6. EDS

FIG. 6. Bright-field image; marked black spots are palladium nanoparticles decorated around a CNT.

FIG. 7. EDS Spectrum of CNT decorated with Pd collected from TEM.

spectra were collected along the longitudinal axis of the CNT to characterize the palladium nanoparticles (see Fig. 7). The EDS spectrum reveals the presence of the carbon and the palladium. A copper grid was used in the TEM study; hence a Cu peak is also observed in the spectrum. It is worth mentioning that the EDS spectrum does not show any chlorine peak which suggests that chlorine was not present either as palladium chloride inside the nanotubes or as atomic chlorine attached to the sidewall. Sidewall functionalization of CNTs with fluorine using HF vapor at greater than 600 °C has been reported,³² however, till date there has been no study reported on the functionalization of chlorine atoms.

A zero-loss energy filtered image of palladium nanoparticles decorated CNT is shown in Fig. 8(a). A dense agglomeration of palladium nanoparticles in the center of the projected CNT can be observed in Fig. 8(a). To confirm further, a carbon map and a palladium map have been collected using the Gatan imaging filter on the same portion of the nanotube. Such palladium and carbon maps of the CNT are shown in Figs. 8(b) and 8(c), respectively. Figure 8(b) shows that the bulged area of the CNT is caused by the deposition of several palladium nanoparticles. The palladium map also reveals that the CNT is decorated with palladium nanoparticles, however, the micrograph [Fig. 8(b)] does not clearly show that all nanoparticles are outside the CNT. HRTEM is used to investigate the actual position of the palladium nanoparticles. A CNT with nicely decorated and well-separated palladium nanoparticles is shown in Fig. 9(a). HRTEM micrograph shows the lattice fringes of both the CNT and the palladium nanoparticles. The same CNT has also been investigated with a STEM using a high-angle annular dark field detector for

FIG. 8. (a) Zero-loss energy filtered TEM image; energy-loss maps of (b) palladium, and (c) carbon.

FIG. 9. (a) HRTEM image with black spots (b) STEM image of the same nanotube reveals the palladium nanoparticles (white spots) decorated around the nanotube (c) HRTEM image showing the lattice fringes of the CNT.

z-contrast imaging [see Fig. 9(b)]. Because of the high atomic weight, palladium nanoparticles in Fig. 8(a) appear as bright spots. HRTEM micrograph in Fig. 9(c) shows the lattice fringes of the CNT.

In order to investigate the crystal structure of the palladium nanoparticles, selected-area diffraction patterns (SAED) were collected in the TEM mode. Figure 10 shows a Fourier-filtered SAED pattern with nine distinct Debye-Scherrer rings compatible with a face-centered-cubic crystal structure of the palladium particles. XPS is used to confirm the chemical state of the palladium nanoparticles. The deconvoluted XPS spectrum with the Pd(3*d*) envelope is shown in Fig. 11, revealing the presence of Pd(3*d*_{5/2}) and Pd(3*d*_{3/2}) peaks at binding energy values of 335.6 and 340.9 eV, respectively. Such binding energies are similar to those reported for palladium in the literature.³³ The presence of a small amount of palladium oxide has also been observed in the XPS envelope as shown in Fig. 11.

IV. MECHANISM OF FORMATION OF PALLADIUM NANOPARTICLES

Palladium nanoparticles have been synthesized from a mixture of 2.087 mM of palladium chloride and of 0.1M hydrochloric acid. In a hydrochloric acid medium, PdCl₂ transforms³⁴ into [PdCl₄]²⁻, a palladium tetra-chloro-square planar complex, as shown in Eq. (2). The reduction of such

FIG. 10. Fourier filtered diffraction pattern of palladium nanoparticles on CNT.

FIG. 11. XPS Pd(3d) envelope taken from the CNTs decorated with Pd nanoparticles.

complex to metallic palladium (Pd^0) shown in Eq. (3) is the subsequent step during arc-discharge in solution.

During the arc-discharge in solution, a simultaneous formation of CNT and the reduction of $[\text{PdCl}_4]^{2-}$ to Pd nanoparticles as well as their *in situ* decoration of CNTs is possibly taking place. Although the exact mechanism for the reduction of palladium chloride into nanoparticles of metallic Pd is not clear, the following possibilities may be considered.

- (1) Reduction of palladium ions into atomic palladium in the solution might take place with the help of reducing gases such as carbon monoxide and hydrogen. Such reducing gases are expected to form near the electrodes during the arc-discharge process,

The formation of such reducing gases due to the reaction of carbon with water vapor during arc-discharge in solution was reported by others.²⁶

- (2) The temperature at the site of the arc is expected²⁷ to be greater than 3500 °C. Hence, the plasma region produced by the arc adjacent to the electrodes is enveloped by a solution-vapor interface. There is a substantial thermal gradient across the plasma region. The decomposition temperature of the palladium chloride^{35,36} is 738 °C at ambient atmospheric pressure. Thermal decomposition process possibly leads to the formation of atomic palladium and chlorine gas near the electrodes which is the probable reason for the absence of the chlorine peak in the EDS spectrum (Fig. 7). Thermally dissociated palladium nanoparticles may subsequently decorate the CNTs.
- (3) The plasma region near the electrodes formed during the arc-discharge is an excellent source of electrons.³⁷ The palladium ions situated near the solution-vapor interface can be reduced to palladium atoms accepting electrons from such electron pool.
- (4) The formation of atomic Pd through an electrochemical process under the applied bias³³ is another possibility.

FIG. 12. TEM micrograph of dislodged graphene sheets showing the wavy morphology.

V. MECHANISM OF FORMATION OF CNTS

The CNT specimens were extensively studied using TEM to unravel the mechanism of the formation of CNTs during the arc-discharge in solution. The formation of CNTs by rolling of graphitic carbon sheets from the anode material during the arc-discharge was suggested.^{38–40} Recent attempt from this laboratory on arc-discharge in solution revealed that the formation of some of the nanotubes remained incomplete.⁴⁰ It was observed that the original graphene sheets were partially rolled up leaving behind some tub-shaped portions. The presence of such tub-shaped portions suggests that the CNTs were formed by rolling of graphitic layers from the anode materials.⁴⁰ In the present study, the HRTEM micrograph in Fig. 12 also shows a dislodged graphene sheets with a wavy surface morphology. Theoretical calculations⁴¹ predict that a tubular structure is energetically more favorable than a flat graphene sheet. The observation of curved or wavy nongraphitic carbon³¹ in the present investigation supports the scroll mechanism³⁸ for the formation of CNTs. Ebbesen and Ajayan⁴² attempted to find such wavy graphene sheet as an evidence to establish this formation mechanism. However, they could not observe the presence of any such graphene sheet in their study.

A careful examination of more CNT specimens that were synthesized using arc-discharge in solution revealed the for-

FIG. 13. (a) A TEM micrograph revealing inner walls capped in a periodic manner, the number of walls is same for both sides of the nanotube. (b) Unequal number of walls. (c) CNT with the same numbers of walls on both sides.

mation of multiwalled CNTs. Figure 13(a) shows a HRTEM micrograph of such a nanotube with nested cylindrical graphitic layers. A few layers are closed inside the nanotube by caps before final closure of the nanotube. Inner walls of CNTs in Fig. 13(a) have no access to carbon from outside for capping. It is likely that the inner walls closed before closing of the outer layer. Once a cap is formed on the tip of an inner cylindrical layer, the layer cannot grow further. Iijima *et al.*⁴³ showed such capped CNT that was formed by transformation of the cone to cylindrical structure with the incorporation of a defect that induces a negative curvature at the tip of the CNT. To establish the mechanism of formation of CNTs, extensive TEM investigations were carried out in the present study, however, no open-ended CNTs could be observed. The formation of a cap on the CNTs and the absence of the open-ended CNTs hint that a mechanism other than the scroll mechanism might be responsible for CNT formation. Interestingly, Fig. 13(b) shows different numbers of walls on the two sides of a nanotube with a final closure by a single cap. Figure 13(b) also reveals the presence of incomplete and bent layers at the inner concentric wall, as marked with an arrow. Such defects could initiate an inner cap with time. The scroll mechanism can form a convoluted multiwalled CNT which could eventually transform to a concentric multiwalled CNT by the process of rearrangement of carbon atoms as suggested by Yasuda *et al.*⁴⁴ Figure 13(c) shows the same numbers of walls in the two sides of a CNT which may support the scroll mechanism. The formation of a cap on the CNT was possibly from the systematic deposition of atomic carbon produced during the arc-discharge process. The presence of large numbers of CNTs on the surface of the cathode electrode, as presented in Figs. 3(e) and 4, indicates deposition of CNTs. Inside the plasma zone during the arc-discharge in solution, positively charged carbon ions migrate to the cathode surface under the applied bias and might help sustaining the growth of the CNTs.

VI. CONCLUSIONS

In situ synthesis of Pd-nanoparticles-decorated CNTs using arc-discharge in solution process has been successfully carried out for possible hydrogen storage and other catalytic applications. The present study opens up not only a simple and an inexpensive route to synthesize CNTs, but also provides a possibility of large-scale production of clean CNTs without any use of vacuum systems. High-resolution transmission electron microscopy and scanning transmission electron microscopy images confirm the presence of palladium nanoparticles 3 nm in diameter. Such palladium nanoparticles are found to form during reduction of palladium tetrachloro-square planar complexes. The deconvoluted XPS envelope shows the presence of metallic palladium. Energy dispersive spectroscopy suggests no functionalization of atomic chlorine to the sidewall of the CNTs. HRTEM results revealing the presence of capped CNTs indicate a possibility of another mechanism of formation other than the scroll mechanism. However, the presence of dislodged graphene sheets with wavy morphology strongly supports the formation of CNTs through the "scroll mechanism."

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