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From carbon nanobells to nickel nanotubes

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A generic strategy is proposed to prepare one dimensional (1D) metallic nanotubes by using 1D carbon nanostructures as the initial templates. Following the strategy, nickel (Ni) nanotubes are prepared by using carbon nanobells (CNBs) as the initial templates. CNBs are first prepared by microwave plasma enhanced chemical vapor deposition technique. Carbon/nickel core/shell structures are then prepared by electroplating the CNBs in a nickel-Watts electrolytic cell. In the final step, the carbon core is selectively removed by employing hydrogen plasma etching to obtain Ni nanotubes. The mechanism leading to Ni nanotubes is briefly discussed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3005592]

With the advent of various functional one-dimensional (1D) nanostructures,^{1–6} the research concerning controlled synthesis of 1D metallic nanostructures with particular size, shape, crystallinity, and structure (e.g., solid versus hollow) has become very important.^{4–6} In this context, the template-based routes have become the most common ones to prepare metallic nanostructures, especially the metallic nanowires. For instance, carbon nanotube (CNT) template-based ferromagnetic nanowires and nanotubes, more precisely CNT/metal core/shell nanostructures have been prepared.^{7–10} However, literature concerning easy removal of carbon from carbon/metal [or metal/carbon (Me/C)] core/shell structures to obtain pure metallic nanotubes (or nanowires) can hardly be found. With our quest for new nanostructures and interests in nanoscale designing,^{11–14} we herein elucidate the execution of a simple but an effective generic strategy to prepare 1D metallic nanotubes by using 1D carbon nanostructures as the initial templates; the strategy employs a combination of electroplating and etching (or combustion) processes. As an example, in this letter the preparation of pure nickel (Ni) nanotubes by using carbon nanobells¹⁵ (CNBs) as the initial templates is demonstrated. This work not only paves an easy way to prepare 1D nanostructures of electrically conductive metals such as silver and magnetic materials such as iron, but it also helps us to prepare carbon/metal core/shell structures, the intermediate structures, which by themselves may be intrinsically functional.

Figure 1(a) shows the schematic of the generic strategy to prepare 1D metallic nanotubes, in which 1D CNBs are taken as the initial templates. These structures can be first obtained by using suitable chemical vapor deposition methods. Subsequently, the Me/C core/shell nanostructures can be prepared by an electroplating process. In the final step, the carbon component can be removed by an etching process. In Fig. 1(b), a high resolution transmission electron microscope (HRTEM) image of one CNB is shown. Typical CNB structure is made up of a series of adjacent short graphite bells paralleling to each other between two compartments. Each bell is composed of several tens of graphite layers [G in Fig.

1(b)] with one end (curved) closed and the other one open resulting in numerous defects on the outer surface of the CNB all along its length (indicated with the short arrows). The idea is to use these defect sites as the nucleation centers for the Ni electrodeposition.

The experiment regarding Ni nanotubes preparation, employing the proposed strategy [Fig. 1(a)] will be discussed here. In the first step, a film composed of CNBs was grown on a silicon substrate by using microwave plasma assisted chemical vapor deposition (MWCVD) technique.¹⁵ CH₄ and N₂ gas mixture (50:1) was used. Other experimental parameters, namely, gas pressure, reaction temperature, and microwave power were maintained at 20 Torr, 550 °C, and 600 W, respectively. The growth of CNBs was carried out for 30 min (please see Ref. 16 for further details about CNBs). In the subsequent step, CNB/nickel core/shell nanostructures were prepared by an electroplating technique, wherein CNBs (film on Si) were used as cathode and a pure nickel plate was used as an anode. Ni-Watts electrolyte (pH ~ 3.8–4.2) was employed, which had a set analysis of 70 g/l Ni²⁺, 12 g/l Cl⁻, and 40 g/l H₃BO₃, balance water. During electrolytic deposition, the electrolyte was operated at a current density of about 4 A/cm² and within a temperature range from 50 to 55 °C. The electrolytic deposition time of Ni on CNBs amounted to 0.5–50 min, preferably

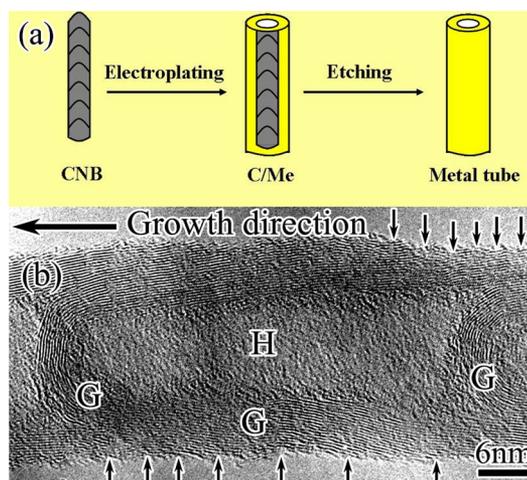


FIG. 1. (Color online) (a) The schematic to prepare metallic nanotubes and (b) HRTEM image showing the microstructure and defected outer surface of a CNB.

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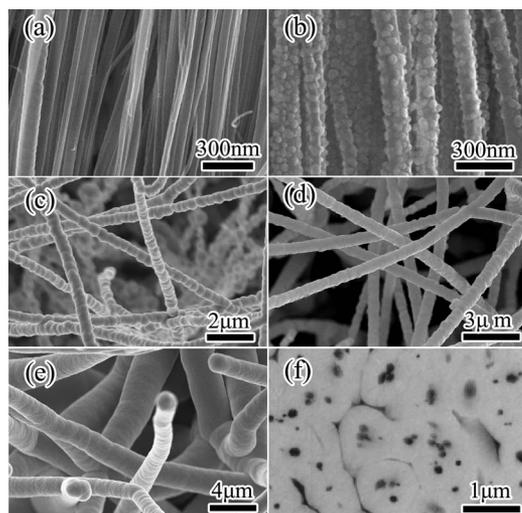


FIG. 2. The SEM images of prepared CNB/nickel core/shell structures with the electroplating times of (a) 0 s, (b) after 30 s, (c) 2 min, (d) 5 min, (e) 30 min, and (f) cross section after 50 min.

about 5 min. In the last step, in order to remove the carbon core from CNB/nickel core/shell structures, H_2 plasma etching was carried out by using MWCVD. Pure H_2 was used as the etchant gas, whose flow rate was maintained at 100 SCCM (SCCM denotes cubic centimeter per minute at STP) during the etching process, which was carried out at a gas pressure of 15 Torr. The H_2 plasma was sustained by using a microwave power of 500 W. No intentional heating of the sample was employed. The etching process was carried out for 20 min. For clarity in demonstrating the proposed strategy, the optimal experimental parameters, both in the cases of electroplating and H_2 etching have only been presented.

In this work, structural and compositional analyses of the prepared nanostructures were carried out by using scanning electron microscope (SEM), transmission electron microscope (TEM) (Hitachi H-8100) operated at 200 kV, x-ray diffraction (XRD) employing $Cu K\alpha$ radiation, and micro-Raman scattering employing 532 nm laser line.

Figure 2 shows the SEM images of the morphologies of carbon/nickel core/shell structures prepared by using different electroplating times. To understand the mechanism of nickel growth on the CNBs, different electroplating times are employed, namely, 0.5, 2, 5, 30, and 50 min with all other experimental conditions kept constant. CNBs that have not undergone any electroplating [Fig. 2(a)] exhibit a smooth surface morphology and an average diameter of 100 nm. After a deposition time of 0.5 min, it can be observed [Fig. 2(b)] that many Ni nanoparticles (~ 20 nm) are homogeneously deposited on CNB surfaces; it can also be observed that the diameters of the structures remain unchanged from those shown in Fig. 2(a). It indicates that within 30 s, Ni^{2+} ions not only impregnate at certain suitable surface sites on the CNBs but even develop into nuclei and further into nanoparticles. Figure 2(b) shows a very high nucleation density of Ni at very low deposition time indicating a great suitability of CNBs as templates for such depositions. After a deposition time of 2 min, it can be observed that each of the CNB surfaces is completely covered with Ni [Fig. 2(c)]; but the structures exhibit rough surface morphologies. These observations suggest that during the initial stage of electroplating process, the Ni^{2+} ions, are firstly deposited at the numerous

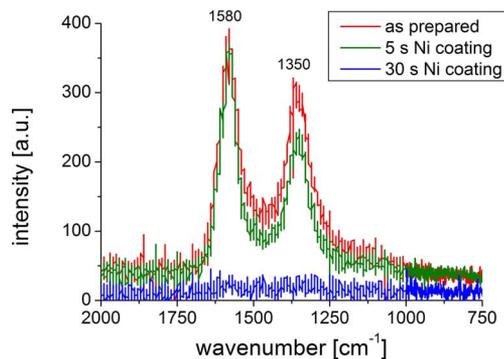


FIG. 3. (Color online) The Raman spectra of the CNBs/Ni core/shell structures with different electroplating times of 0, 5, and 30 s.

defect sites [Fig. 1(b)] on CNB surface; the defects generally facilitate low deposition energies than any other sites for the deposition of Ni ions. As a result, the Ni nanoparticles formed during initial stages of particle growth continue to grow independently with increasing time; by the end of 2 min deposition, they just coalesce and cover the entire surface of each CNB leaving a rough morphological shell. The diameter of the Ni coated CNBs (after 2 min deposition) is estimated to be about 460 nm. After a deposition time of 5 min, the diameter of CNB/Ni core/shell structures is estimated to be about 600 nm. Interestingly (as expected), here the surfaces of the nickel shells are observed to exhibit smooth morphology [Fig. 2(d)]. This indicates that Ni is continually deposited to fill in any grooves and/or empty spaces remaining after the coalescence of the growing Ni particles, finally rendering smooth surface morphology. Additionally, micro Raman scattering results show that CNB vibrational modes (D and G bands) are completely suppressed after a deposition time of 30 s indicating the complete coverage of the carbon cores. Raman spectra obtained from two different carbon/Ni core/shell structures are compared to the spectrum obtained from as-prepared CNB in Fig. 3. After 30 min of electroplating, the diameter of core/shell structures is estimated to be about $1.5 \mu m$ and the Ni shell surface maintains a smooth morphology [Fig. 2(e)]. From the estimated diameters values with the time of deposition, the average growth rate of the Ni coating can be estimated to be about 46 nm/min. When the deposition time is increased to 50 min, the individual carbon/Ni core shell structures coalesce with each other resulting in a bulk carbon/nickel composite. SEM image of the cross section of the bulk composite is shown in Fig. 2(f).

For further analysis, the carbon/nickel core/shell structures prepared with an electroplating time of 5 min are chosen. High magnification SEM and TEM images of these structures are shown in Figs. 4(a) and 4(b), respectively; here it can be observed that the CNBs are coated homogeneously except for their roots. The reasons for this observation are not yet clear and are being explored. Furthermore, XRD pattern [Fig. 4(c)] obtained from the sample under consideration shows the characteristic diffraction peaks corresponding to fcc Ni. The peaks are broad indicating nanocrystallinity of Ni.

In the final step, in order to obtain nickel nanotubes, H_2 plasma etching was employed to remove the carbon component from the carbon/nickel core/shell structures shown in Fig. 4(a). Figure 5(a) shows the low magnification SEM image of the intact Ni nanotubes. Additionally, from the SEM

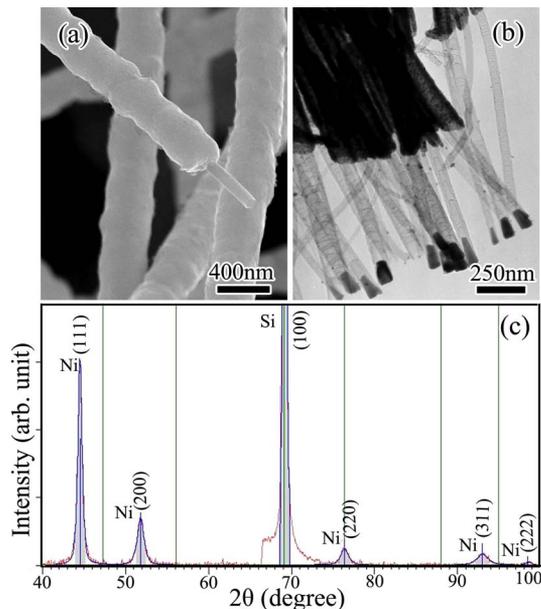


FIG. 4. (Color online) (a) SEM image of the Ni coated CNBs with the deposition time of 5 min. (b) TEM image of the Ni coated CNBs with the deposition time of 5 min. (c) The XRD pattern of the core/shell structures with the diffraction angle 2θ from 40° to 100° .

image shown in Fig. 5(b) it can be clearly observed that the carbon core has been removed completely leaving a hollow space. In other words, the Ni shell structure (a tube) remained after the etching process. The energy dispersive x-ray (EDX) analysis that was carried out along the length of the Ni nanotube shown in Fig. 5(b) confirmed the nonexistence of carbon core. The EDX analysis was carried out at 25 kV and the thickness of the Ni tube is around 40 nm. Although the exact etching mechanism is not yet understood, plausible speculations are made in the following. SEM image after etching process revealed that the individual Ni tube structures are randomly distributed on the underlying Si substrate. This observation shows that during H_2 etching, the roots of CNBs (uncoated part [Fig. 4(b)]) are etched away leading to the formation of an opening at the root end (other end being closed core/shell) of each core/shell structure. Subsequently, H^+ ions may enter into each core/shell structure from this opening and continually etch the carbon core to form gaseous hydrocarbons. However, the other end being closed, the gaseous species have to come out of the shell through the

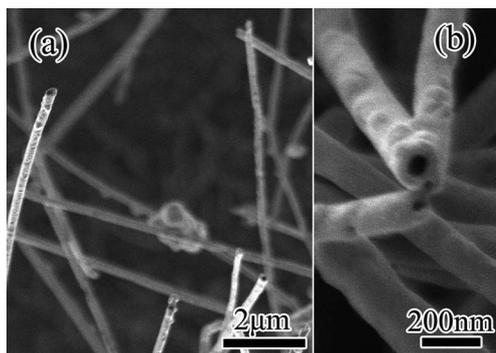


FIG. 5. (a) The SEM image of core/shell structure after H_2 plasma etching. (b) Enlarged SEM image showing the opening ends of nickel nanotubes.

only opening (H^+ entry end), a difficult possibility. On the other hand, a second and relatively easy possibility is that the H^+ ions, being very small and being abundantly available in the adopted plasma conditions, may easily diffuse through the nickel shell, reach the walls of the CNB core, and subsequently etch the core forming gaseous hydrocarbons. Since most of the carbon core is hollow [H in Fig. 1(b)], an increase in the inner pressure of the core/shell structure is expected if the etching process follows the second possibility. This increased pressure would flush away the gaseous species (produced after etching) through the opening created by etching of the uncoated roots on the CNBs. The employed concentration of H_2 ensures that the etching continuously prevails over the formation of any solid carbon clusters from the gaseous hydrocarbons. Also, it can be estimated from the very high magnification SEM image [Fig. 5(b)] that the inner diameter of the Ni nanotubes is around 100 nm, which is same as the original diameter of the initial CNB template. This observation further confirms the selective removal of carbon core by H_2 etching.

CNBs have been used as the initial templates for the preparation of 1D carbon/nickel core/shell structures. This study elucidates the execution of a generic strategy to prepare 1D metallic nanostructures by employing a combination of electroplating and MWCVD etching processes. However, a thorough investigation of the formation mechanisms of the prepared nanostructures is required and it forms the scope of our future work.

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