

# Electroless Plating of Metals onto Carbon Nanotubes Activated by a Single-Step Activation Method

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In this work, carbon nanotubes were activated with Pd–Sn catalytic nuclei via a single-step activation approach. These activated nanotubes were used as precursors for obtaining nickel- and palladium-decorated nanotubes via electroless plating. Activation of the nanotube surfaces promoted specific deposition of metal on the catalytic tube surfaces. As a result, carbon nanotubes densely coated with metal nanoparticles were obtained with reduced metal deposition in the reaction solution.

## 1. Introduction

Since the discovery of carbon nanotubes by Iijima,<sup>1</sup> a host of applications for these nanosized graphitic tubes have been envisioned. These include their role in catalysis,<sup>2</sup> as templates for the synthesis of nanometer-sized wires,<sup>3</sup> and in the synthesis of reinforced polymer composites.<sup>4</sup> The approach toward decorated carbon nanotubes has thus far been to modify the nanotube surface by oxidation. The functional groups (carbonyl, carboxylic groups, and phenolic groups) introduced onto the surface then nucleate the deposition of metals or metal compounds onto the otherwise inert tube surface.<sup>5–6</sup> In this method, the oxidized tubes do not catalyze the redox reaction involved. Metal deposition on the tube surface occurs at the same rate as that in the reaction solution. Specific metal deposition on the nanotubes is therefore limited. We thus employed an alternative method for nanotube decoration using activated carbon nanotubes. Nanotubes coated with nickel and palladium are obtained by this approach.

Activation of the tube surface involves the introduction of catalytic seeds onto the oxidized tubes. These catalytic seeds then initiate metal deposition specifically on the nanotubes. Li et al.<sup>7</sup> studied the coating of carbon nanotubes with nickel where activation of the tubes was achieved in two steps. The first step involves the adsorption of a tin sensitizing layer and the second step introduces palladium onto the sensitizing layer.

In our work, densely coated carbon nanotubes are obtained using a single-step activation approach. Tin and palladium species are introduced onto the oxidized nanotubes by immersing the tubes in a PdCl<sub>2</sub>/SnCl<sub>2</sub> colloidal solution. A 1 M HCl accelerator is used to preferentially dissolve the protective layer, exposing a greater surface area of the catalytic Pd–Sn nuclei. When the activated and accelerated tubes are immersed in an electroless plating bath, metal deposition occurs at the catalytic sites. The deposited clusters of metal atoms then catalyze further metal deposition on the tube surface (autocatalytic process).

## 2. Experimental Section

Carbon nanotubes were synthesized by the arc-discharge method in a helium atmosphere. A voltage of 22–25 V was applied across the electrodes, and the arcing current was maintained at 120 A. Oxidized nanotubes were obtained by refluxing 0.25 g of the ground cathodic deposits in 27 mL of H<sub>2</sub>SO<sub>4</sub> (98%) and 18 mL of HNO<sub>3</sub> (70%) at 140 °C for 6 h. The sample was washed with Millipore water and then dried at 100 °C.

**2.1. Decoration via Single-Step Activation.** HCl (7.5 mL, 37%), 15 mL of Millipore water, 0.025 g of PdCl<sub>2</sub>, and 0.1 g of SnCl<sub>2</sub>·2H<sub>2</sub>O were stirred under N<sub>2</sub> gas overnight. SnCl<sub>2</sub>·2H<sub>2</sub>O (0.8 g) was then added to the above solution. The mixture was stirred for 10 min and decanted into centrifuge tubes. The excess SnCl<sub>2</sub>·2H<sub>2</sub>O and some brown precipitates were separated through centrifugation. The supernatant (clear brown solution) was used as the activating solution.

A total of 0.05 g of the oxidized carbon nanotubes was sonicated in the activating solution for 2 min, and the suspension was further stirred for 3 min. Separation of the activated tubes from the activation medium was effected through centrifugation. The activated tubes were then washed with 1 M HCl (acceleration) and Millipore water.

Nickel-decorated carbon nanotubes were obtained by stirring the activated and accelerated tubes in 50 mL of the nickel bath for 30 s. The suspension was then filtered and washed with Millipore water. The nickel electroless plating bath was composed of 30 g/L NiCl<sub>2</sub>·6H<sub>2</sub>O, 10 g/L NiSO<sub>4</sub>·6H<sub>2</sub>O, 15.5 g/L Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·1.5H<sub>2</sub>O, 100 g/L NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O, 100 g/L NH<sub>4</sub>Cl, and 2.5 g/L Pb(NO<sub>3</sub>)<sub>2</sub>, the pH was adjusted to 8.25 with NH<sub>4</sub>OH, and it had a bath temperature of 25 °C.

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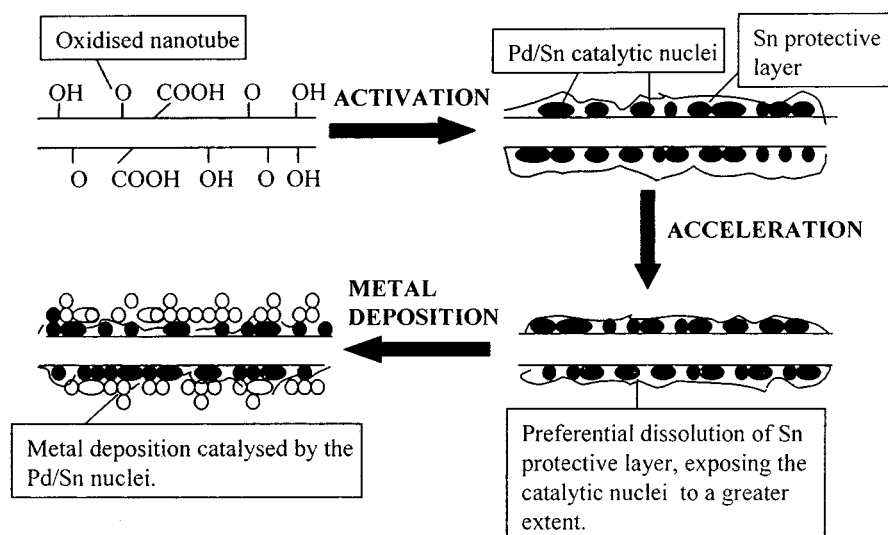
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Scheme 1



Palladium-decorated nanotubes were obtained following the same procedure, except a palladium electroless plating bath replaced the nickel bath. The palladium electroless plating bath was prepared by dissolving 0.05 g of  $\text{PdCl}_2$  in 0.1 mL of HCl and 10 mL of Millipore water. Sixteen milliliters of  $\text{NH}_4\text{OH}$  (28%) and 2.7 g of  $\text{NH}_4\text{Cl}$  were added, and the solution was left to stand for 4 h. One gram of  $\text{NaH}_2\text{PO}_2 \cdot 2\text{H}_2\text{O}$  was stirred into the solution, and the volume was made up to 100 mL with Millipore water.

The chemical processes involved in the activation, and metal deposition are schematically summarized in Scheme 1.

**2.2. Transmission Electron Microscope (TEM) Studies and Energy-Dispersive X-ray Spectroscopy (EDX).** The sample under study was sonicated in ethanol and deposited on a holey carbon nickel or copper grid. A Philips CM 200FEG transmission electron microscope was used.

### 3. Results and Discussion

Parts a and b of Figure 1 show transmission electron microscope (TEM) images of carbon nanotubes before and after activation and acceleration. As shown in Figure 1b, a large majority of the tubes are well-coated with the catalytic species. The catalytic particles are generally between 3 and 4 nm in diameter. Energy-dispersive X-ray spectroscopy (EDX) studies confirmed the presence of Pd, Sn, and O with the Pd:Sn ratio  $\sim 1:1$  (refer to the EDX spectrum in Figure 1c, a Cu holey carbon support grid was used).

Studies by Osaka et al.<sup>8</sup> on the activation and acceleration of glassy epoxy plastic boards by mixed  $\text{PdCl}_2/\text{SnCl}_2$  catalysts, suggested that large Pd–Sn colloidal particles are required for high catalytic activity. In their work, the sample covered with colloidal particles within a 40–70 nm diameter range resulted in the “best” nickel-plated film. No explanation for this observation was given. However, it is likely that large catalytic particles with their lower surface area:mass ratios, are less prone to oxidation and thus show higher catalytic activities. Work by Shu et al.<sup>10</sup> indicated that the

presence of Pd in higher oxidation states limits the autocatalytic activity of the activated substrates.

We did, however, achieve Pd and Ni deposition on the activated and accelerated nanotubes despite the nanometer size of the catalytic Pd–Sn particles. This is in line with reports by Kim et al.,<sup>11</sup> who observed copper deposition on activated amorphous substrates, where the catalytic particles were reportedly 1–2 nm in diameter and clustered into aggregates 20–30 nm across.

Figure 2a shows a carbon nanotube densely decorated with nickel electroless deposit, obtained by stirring the activated and accelerated nanotube sample in a nickel bath. Under the conditions employed, electroless plating was rapid resulting in tubes which were almost fully covered with a layer of the deposit. The thickness and density of the coating can be varied by adjusting the concentration of  $\text{H}_2\text{PO}_2^-$  reductant. An examination of the coated tubes using EDX revealed the presence of Ni and co-deposited P. Sn and Pd from the activating layer were also detected. The deposition of Pb due to the reduction of  $\text{PbNO}_3$  can be minimized by lowering the concentration of the  $\text{PbNO}_3$  stabilizer.

From the TEM micrograph in Figure 2a, the tube does appear to be covered by particles  $\sim 2$  nm in diameter. However, ordered structures were not observed for these deposited Ni clusters in high-resolution images. In the study of electroless Ni, Weil and Parker<sup>12</sup> argued that the as-deposited nickel is a metastable, supersaturated alloy consisting of P atoms trapped between the Ni atoms. The face-centered cubic (fcc) structure of Ni may be maintained within small grains. In regions where the fcc structure cannot be maintained at all, the structure is essentially amorphous.

The activated and accelerated tubes were also immersed in a Pd bath. The catalytic nuclei initiate the rapid deposition of Pd from the bath solution, resulting in densely decorated (coated) tubes as shown in Figure 2b. Palladium deposits as particles  $\sim 5$  nm in diameter.

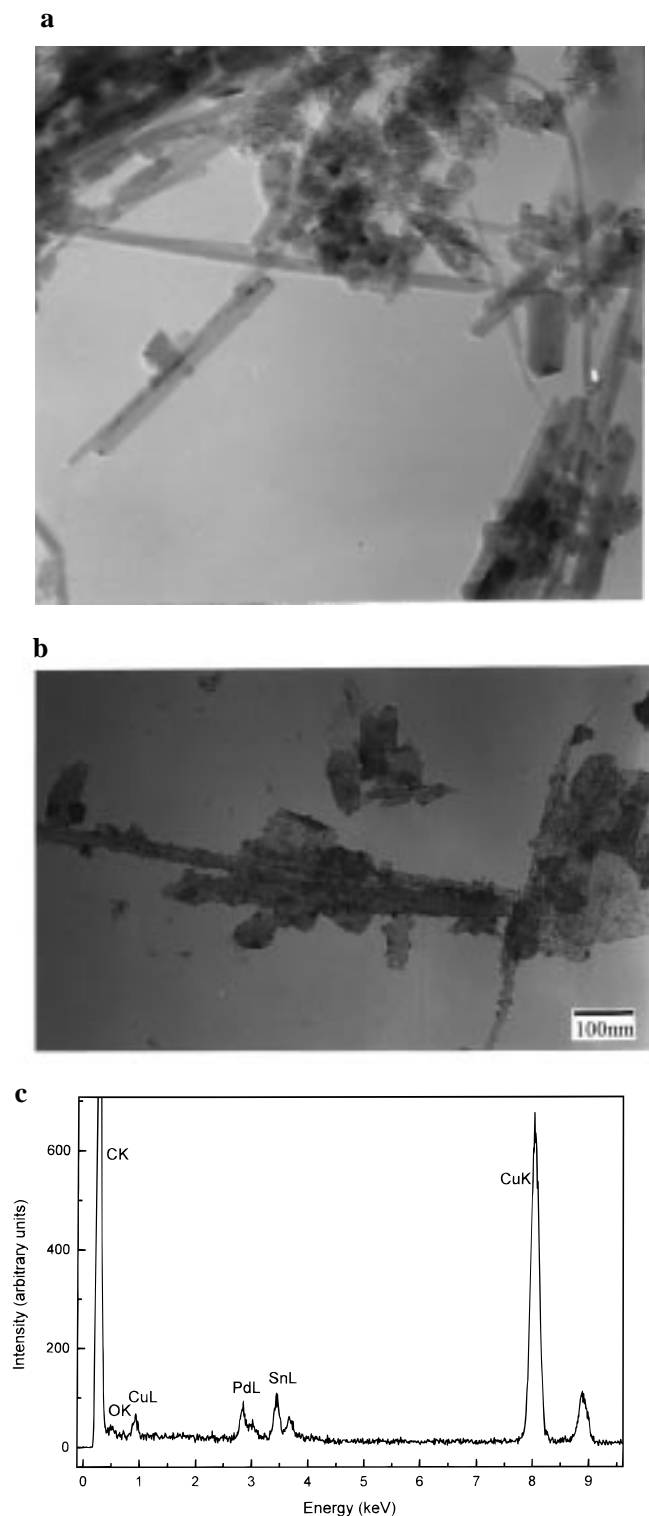
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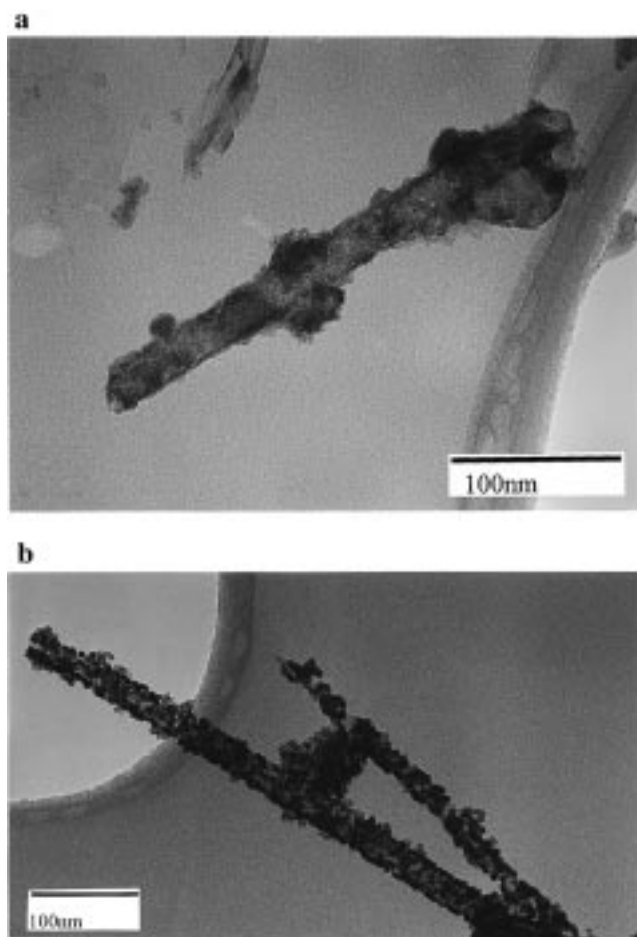
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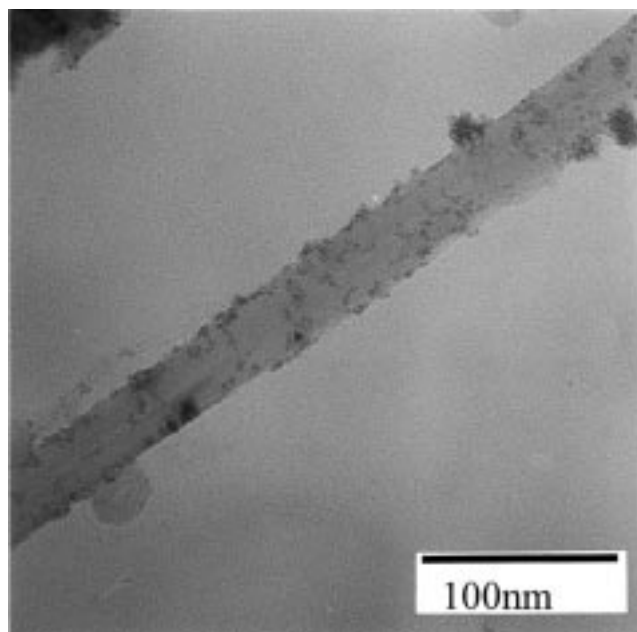


**Figure 1.** TEM micrographs of (a) untreated carbon nanotubes produced by the arc-discharge method, (b) activated and accelerated tubes, and (c) EDX spectrum of the activated and accelerated nanotubes, confirming the presence of Pd and Sn on the nanotubes. A copper holey carbon support film was used.

EDX studies confirmed the presence of Pd and Sn and a Pd:Sn atomic ratio of  $\sim 2:1$  to  $4.5:1$  was obtained. (Note that this ratio is at least 2 times greater than that obtained for the activated and accelerated tubes.) A comparison between Figures 2b and 3 clearly demonstrates that activation of the tube surface is necessary for obtaining densely decorated (coated) nanotubes.



**Figure 2.** TEM micrograph of (a) an activated and accelerated tube coated with nickel electroless deposit and (b) activated and accelerated nanotubes coated with palladium nanoparticles  $\sim 5$  nm in diameter. Copper holey carbon support films were used.



**Figure 3.** A palladium-decorated carbon nanotube obtained through palladium deposition on unactivated, oxidized nanotubes. The palladium nanoparticles do not coat the whole tube surface and are clustered at localized points along the tube.

Figure 3, showing a carbon nanotube "dotted" with palladium nanoparticles, was obtained through sonication of oxidized carbon nanotubes in  $\text{PdCl}_2/\text{HCl}$  solution followed by the addition of formaldehyde reductant.

In summary, our experimental results demonstrate the ease with which carbon nanotubes can be decorated with different metals, following single-step activation of the tube surface. Carried out under the appropriate electroless plating bath conditions, our experiments yielded densely decorated (coated) nanotubes. To the best of our knowledge, no previous research has been published on carbon nanotubes activated by the single-step procedure.

Previous published works on the metal decoration of unactivated, oxidized carbon nanotubes<sup>5,6</sup> reported tubes "dotted" with metal nanoparticles. Satishkumar's<sup>6</sup> results on Pt decoration are a notable exception. The metal-decorated tubes obtained in our research by the activation approach were generally more densely deco-

rated. For example, the Pd-coated tubes (obtained via electroless plating of tubes activated by the single step activation procedure) showed a much higher surface coverage of Pd nanoparticles than those obtained through the refluxing of oxidized nanotubes in concentrated  $\text{HNO}_3$  and  $\text{Pd}(\text{NO})_3$ .<sup>13</sup> In fact, by controlling the pH and concentrations of the constituents in the plating baths, samples containing a large number of fully coated carbon nanotubes can be obtained. These coated carbon nanotubes could be incorporated into metal matrixes to produce new composites with novel properties. Presently, the noncoated tube surface shows poor interaction with metal matrixes because most metals do not wet the tube surface. Densely decorated tubes would also be expected to show high catalytic activities.

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