

Direct Production of Carbon Nanotubes/Metal Nanoparticles Hybrids from a Redox Reaction between Metal Ions and Reduced Carbon Nanotubes

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ABSTRACT A method to decorate single-walled and multiwalled carbon nanotubes (CNTs) with metal nanoparticles (NPs) based on the formation of a CNT polyelectrolyte is reported. Such a method does not rely on CNT surface functionalization or the use of surfactants. It has been tested for gold (Au) and palladium (Pd). The resulting hybrids present metal NPs highly dispersed along the tube walls and with small size dispersion. The average diameters of the Au and Pd NPs were ~ 5 and ~ 3 nm, respectively. This method paves the way for large-scale decoration of CNTs with metal NPs.

KEYWORDS: carbon nanotubes • metal nanoparticles • decorating • composite

Carbon nanotubes (CNTs) have remarkable electronic properties, large surface area, and good thermal and chemical stability (1, 2). These characteristics make CNTs very promising in their use as supports for catalytic nanoparticles (NPs) in several chemical processes (3, 4). Because pristine CNTs exhibit inert surfaces and poor dispersion in several solvents due to strong van der Waals interactions, many efforts to attach metal NPs directly on the surface of pristine CNTs have been unsuccessful, usually giving rise to large metallic agglomerates (5). As a result, the majority of the approaches for NP attachment developed so far rely on the creation of defects at the tube surface, mainly acid groups, which can act as nucleation centers. However, such a modification inherently leads to the disruption of electronic and mechanical properties of pristine materials, limiting their possible applications (6, 7).

Penicaud et al. reported that single-walled CNTs (SWCNTs) can form a "polyelectrolyte salt" when reduced by alkali metals in aprotic solvents (8). This process is mediated by naphthalene, which acts as a carrier of electrons between the alkali metal and the nanotubes (8, 9). As a result, a solution of highly charged SWCNTs (up to one excess negative charge for every 10 C atoms) and alkali-cation counterions is obtained. The SWCNT salt can be easily dissolved in a wide range of solvents without the need for sonification, addition of surfactants, or functionalization (8). Other studies have shown that negatively charged SWCNTs exhibit strong nu-

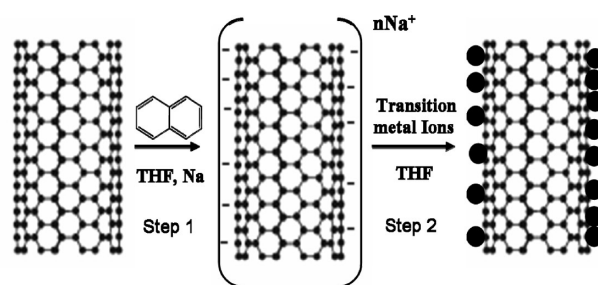


FIGURE 1. Reaction scheme.

cleophilic character and high reduction potential (9–12). There has been an indication that multiwalled CNTs (MWNTs) also can be electrically charged by chemical reduction (13, 14). In addition, it is well-known that sodium naphthalenide solutions in aprotic solvents can be efficiently used in metal NP synthesis because these compounds are strong reducing agents (15, 16).

In this work, we demonstrate a one-pot method in which the electrons accumulated in a CNT polyelectrolyte are used to promote the localized reduction of metal ions, resulting in the decoration of the CNT by metal NPs. This process is very straightforward and does not require either the use of surfactants or any previous surface functionalization of the CNTs. In Figure 1, we present a reaction scheme for the process. First, CNTs are reduced by metallic Na in an aprotic organic solvent, resulting in a solution of exfoliated negatively charged CNTs. This step is based on the method proposed by Penicaud et al. (8). The CNT reduction is promoted by the presence of naphthalene molecules, which mediate the charge transfer between the Na atoms and the CNTs (9). In a second step, metal cations are added to the solution and are immediately reduced upon contact with the CNTs, because of excess electrons, forming particles along the CNT surface. This process has been tested successfully

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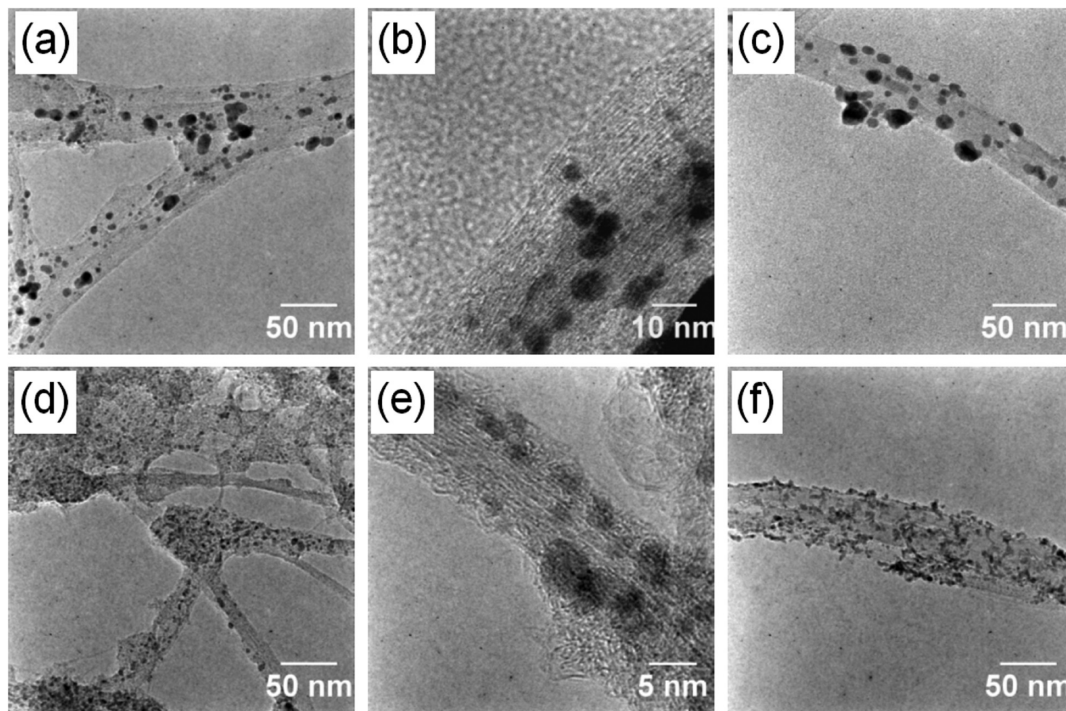


FIGURE 2. TEM images of CNTs decorated with (a and b) Au/SWNTs, (c) Au/MWNTs, (d and e) Pd/SWNTs, and (f) Pd/MWNTs.

for Au and Pd, suggesting that it can be universally applied to any metal.

The analysis of the produced materials by energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) confirms the presence of the desired metals (either Au or Pd) in the decorated CNTs (see Figures S4–S6 in the Supporting Information) and indicates that the metal cations were reduced in the CNT solution because peaks corresponding to the metallic Au (or Pd) phases were identifiable in the XRD patterns. The EDS spectra also registered the presence of small amounts of Fe in the MWNT samples. The Fe was used as a catalyst in the chemical vapor deposition of the MWNT and was not completely removed by the mild purification process employed. Also, importantly, there is no

evidence of Na in the EDS spectra, implying that any residual metal is completely removed in the washing step.

The morphology of the produced materials was investigated by transmission electron microscopy (TEM). Figure 2 presents the TEM images of (a and b) Au/SWNT, (c and d) Pd/SWNT, (e) Au/MWNT, and (f) Pd/MWNT. These images demonstrate that, for all hybrids, the CNTs were uniformly coated by the metal particles. For both metals, no significant differences in the size and morphology are observed between the NPs covering the two types of CNTs. In the SWNT samples, it is observed that the NPs are spread along thin bundles of tubes instead of along individual tubes, indicating that the SWNTs were not completely exfoliated in the first step of the reaction. On the other hand, significant differences can be readily observed between the Au/CNT and Pd/CNT samples. The Pd NPs are smaller, have lower size dispersion, and are more densely distributed along the CNTs. Statistical analysis of several TEM images (Figure 3) reveals that the Pd NPs have an average diameter of 3 nm for both SWNT and MWNT hybrids whereas the Au NPs have average diameters of 5 and 7 nm for the SWNT and MWNT hybrids, respectively. A similar difference in the NP diameter was observed by Zhang et al. for a SWNT decorated by metal evaporation (17). This difference is attributed to the differences in interaction between the metal and CNT and can be described by classical nucleation theory (17). Because Pd has a larger interaction with C surfaces than Au, a higher nucleation density of Pd NPs is expected (and thus a lower NP diameter, as observed in Figure 2).

The uniform dispersion of the metal NPs on the surface of the CNT observed in the TEM images indicates that there is a high density of nucleation sites for metal deposition at the CNT surfaces. If one considers that excess electrons

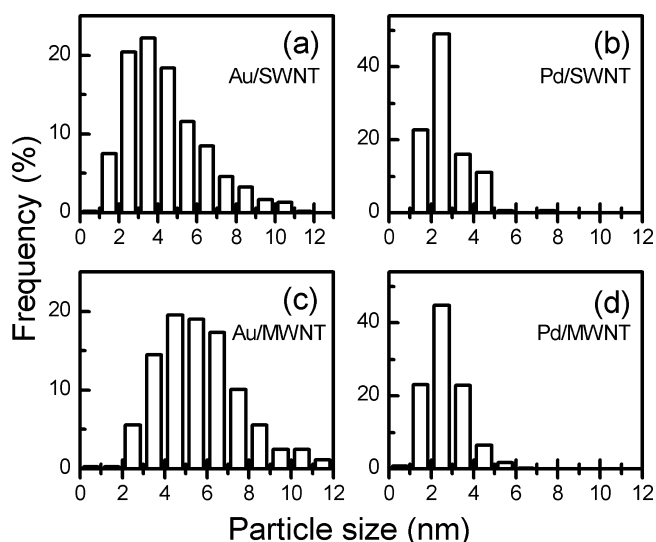


FIGURE 3. Size distribution for metal NPs on CNT surfaces (a) Au/SWNT, (b) Pd/SWNT, (c) Au/MWNT, and (d) Pd/MWNT.

accumulated in a pristine tube become highly delocalized, it is expected that the metal ion reduction and subsequent NP formation may occur at any position along the tube outer surface. As a result, a high dispersion of the NPs along the CNT surface and small NP sizes can be achieved.

It is important to note that the SWNT reduction process described in step 1 (see Figure 1) includes cyclic reduction/oxidation reactions of the naphthalene molecules (10). As a result, after the end of the SWNT reduction, naphthalene is also reduced by the excess Na forming sodium naphthalenide complexes. Therefore, in step 2, the reduction of metal ions by sodium naphthalenide may also occur in parallel (15). In fact, we have observed that the ratio between the concentration of sodium naphthalenide and CNTs in the solution is a key parameter that regulates the metal NP formation. Small concentrations of sodium naphthalenide result in high dispersions of metal NPs without significant aggregation and a high anchoring efficiency (i.e., almost all metal ions introduced in the solution become effectively attached to the CNT surfaces). However, above a threshold naphthalene concentration, the reduction of metal ions by sodium naphthalenide becomes dominant, resulting in the formation of free metal NPs in the solution and poor NP dispersion on the CNT surfaces. A systematic study of these effects is being carried out and will be the subject of a longer article.

In summary, we have demonstrated that Au and Pd metal NPs can be successfully anchored to the surfaces of MWNT and SWNT by using a simple one-pot method without the need of any surfactants or previous CNT surface functionalization. This method results in high dispersions of metal clusters on the CNT surfaces. We believe that this process can potentially be scalable to large quantities and be applied to a wide range of metals.

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Note Added after ASAP Publication. This paper was released ASAP on September 21, 2009, with incorrect artwork for Figures 2 and 3. The correct version was posted on October 2, 2009.

Supporting Information Available: More details of the sample preparation and characterization including results from SEM, Raman spectroscopy, EDS, and XRD. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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