Microwave-Assisted Single-Step Functionalization and in Situ Derivatization of Carbon Nanotubes with Gold Nanoparticles

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Carbon nanotubes (CNTs) have remarkable properties arising from their unique electronic structure, molecular dimensions, and shape, making them attractive building blocks for creating novel electronic devices.[1] Examples include their potential use as interconnects, single electron transistors, molecular diodes, memory elements, and logic gates.[2] There is a great deal of interest in linking CNTs with other low dimensional structures such as nano-/micro-particles, proteins, and DNA, for building hybrid architectures and composites to explore and harness the novel properties arising from the nanoscale coupling for applications.[3] By combining CNT derivatization with nanostructures and organized assembly of CNTs (e.g., on planar substrates),[4a] CNT-based hybrid structures can also be conceivably used as templates to direct the hierarchical assembly of more complex architectures.[4b]

Modifying the CNT surface with desired functional groups is an important step for creating CNT-based hybrid structures and has been used to assemble CNTs and separate CNTs with different structures.[5] Examples of typical routes to functionalize CNTs include acid-based wet-chemical oxidation, esterification, diimide activation, electrochemical modification, or hydrophobic adsorption of aromatic derivatives.[6] Many of these methods typically entail multiple steps involving refluxing with strong acids combined with ultra-sonication. Such aggressive treatments can cause CNT shortening and damage due to bond fissure and high impurity concentrations due to prolonged residence times, resulting in low yields. Although electrochemical modification[6d] is mild, its utility is restricted to electrically contacted CNTs. Alternative functionalization approaches that use noninvasive and/or nonthermal excitations offer possibilities for obviating such shortcomings and are necessary to enable the maturation of simpler and more readily scalable functionalization and derivatization methods. A recent example of one such method relies on using polymer wrapping[7a] to noncovalently functionalize CNTs using macromolecules and has also been extended to uniformly decorate silica-coated Au nanoparticles onto multiwalled CNTs.[7b] In this paper, we present another alternative functionalization technique that utilizes microwave exposure of CNTs.

Microwave radiation is a well-known noninvasive and clean processing tool that has been widely used to activate or accelerate chemical reactions.[8] Typically, microwave energy decreases the kinetic barrier for reactions by altering bond vibrational and/or configuration energies of specific reactants.[9] Such activation can provide an expanded reaction range with lower temperatures and/or reduced reaction times which can obviate unwanted side reactions and products due to thermal effects and lead to accrued cost savings. Recent works have used microwaves to synthesize CNTs on a variety of supports[10a] and to join single-walled CNTs through defect generation and reconstruction.[10b] Microwaves have also been explored to assist CNT functionalization in the presence of strong oxidants (e.g., HNO_3)[10c] and enable cycloaddition to *pre-functionalized* CNTs.[10d]

Here, we describe a new eco-friendly approach of using microwaves to rapidly functionalize multiwalled CNTs with carboxyl, carbonyl, hydroxyl, and allyl termini, *without the use* of aggressive oxidants (e.g., HNO_3) or ultrasonication. We also adapt this technique to derivatize CNTs with

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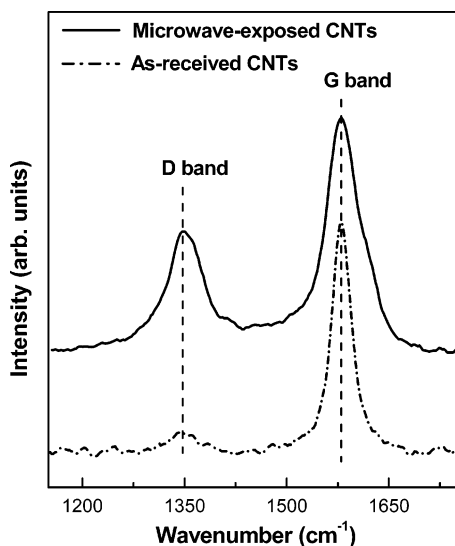
Figure 1. Raman spectra of multiwalled CNTs exposed to microwaves for 600 s as compared to as-received CNTs. The D:G ratio in the as-received CNTs is ~0.1, and in the irradiated CNTs it is ~0.52.
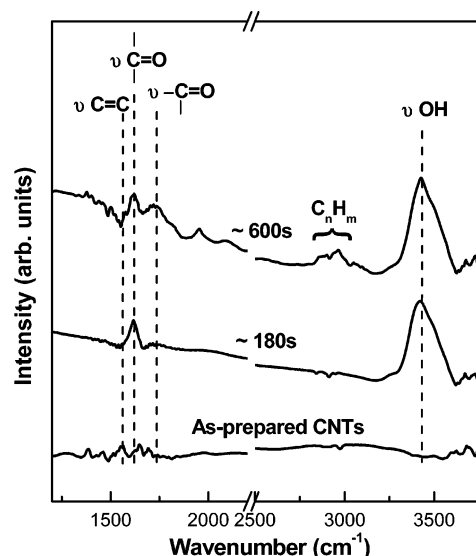

Figure 2. Fourier transform infrared spectra of CNTs exposed to microwaves (in the presence of boiling water) as compared to as-received CNTs. The microwave-exposed CNTs display signatures of allyl, carbonyl, carboxyl, and hydroxyl moieties. The exposure times to the microwaves are indicated on the respective spectra.

nanoparticles synthesized in situ by metal-ion reduction during functionalization, *all in a single processing step*. This approach offers a new way for efficiently creating hybrid nanostructures.

Multiwalled CNTs synthesized from an arc discharge[11] were dispersed in 1 mL of deionized water in a glass vial. The as-received CNTs floated on the water surface as expected, as a result of their hydrophobicity. Adding 1 mL of chloroauric acid ($HAuCl_4$) and 1 mL of ethylene glycol (both from Sigma-Aldrich) transforms the colorless suspension to a bright yellow color. No observable changes were detected in the CNTs. The vial was then closed and loaded into a domestic microwave oven (General Electric model JES738WJ) equipped with a 700 W magnetron operating at 2.45 GHz. Cyclic microwave exposures with a 20 s on time at 100% power separated by 10 s off-time intervals, for a total duration of 4500 s, were carried out to minimize solvent superheating and pressure buildup in the closed glass vial. After centrifuging, filtration and thorough washing with deionized water to remove any loosely adsorbed nanoparticles and ethylene glycol, the suspension was drop-coated onto copper grids for transmission electron microscopy (TEM) observations in a CM 12 microscope operated at 120 kV. We also microwaved drop-coated CNT films formed on quartz glass pieces from a CNT dispersion in toluene, for subsequent characterization of structural and chemical changes by Raman and infrared spectroscopies. For these experiments, a beaker containing 500 mL of water was placed alongside the samples in the microwave oven to serve as a dummy load to protect the magnetron from reflected power.

Raman spectra from KBr pellets prepared with microwave-exposed CNTs show a significantly higher D-band intensity (normalized to the G band) than that seen in as-received CNTs (see Figure 1) indicating microwave-induced defect creation, as reported previously.[10b] Additionally, we find that microwave exposure of CNTs in the presence of boiling water results in the formation of allyl, carbonyl, carboxyl,

and hydroxyl groups. This new finding is evident from the infrared spectra (Figure 2) obtained from microwave-exposed CNTs showing characteristic signatures of these moieties at 1574, 1626, 1723, and 3426 cm^{-1}, respectively. We note that the hydroxyl and carbonyl groups precede the formation of the carboxyl groups, suggesting that the —OH and —C= O moieties are formed initially, followed by the formation of —COOH moieties by progressive oxidation of the carbonyl groups upon sustained microwave exposures. This functionalization sequence is consistent with that reported for CNTs subject to mild sonication in aqueous solutions.[12] Spectra from as-received CNTs do not show any detectable signatures of these moieties. The overall tubular structure of the CNTs is largely preserved after microwave exposure, as described later. These results suggest that microwave-assisted defect generation increases the chemical reactivity of the CNTs and enables functionalization by reaction with water and oxygen, probably at the defect sites. When a similar approach is used, it is conceivable that other functional groups such as amines and thiols can be possibly generated on the CNTs by microwave exposures in controlled gaseous environments (e.g., NH_3, H_2S).

The microwave functionalization technique can be extended to realize the derivatization of the CNTs with other nanostructures, all in a single processing step. To demonstrate this concept, we synthesized and decorated Au nanoparticles by combining microwave exposure of CNTs and a microwave-assisted polyol reduction reaction of metal salts to form metal nanoparticles.[13] Microwave exposure transforms the bright colored solution of $HAuCl_4$, ethylene glycol, and deionized water with the floating CNTs, into a turbid pink solution (Figure 3). The CNTs enter the solution and settle at the vial bottom, indicative of increased hydrophilicity in the

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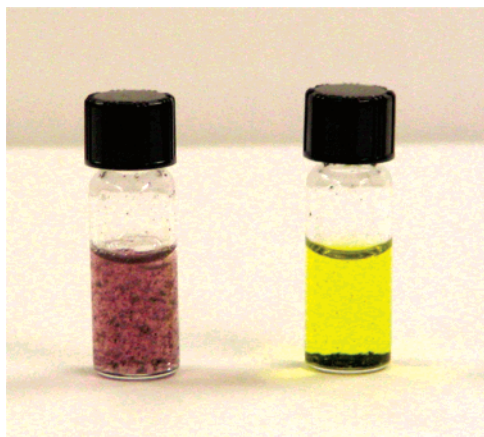
Figure 3. Vial containing CNTs derivatized with Au nanoparticles by microwave-assisted functionalization (pink color) as compared to vial containing CNTs, HAuCl$_4$, and deionized water (yellow color) after microwave exposure.

CNTs. The hydrophilicity increase is consistent with the generation of carboxyl and hydroxyl termination of CNTs indicated by the afore-described IR spectra. Microwaving similar mixtures, but without the CNTs, also produces an identical color change due to Au nanoparticle formation (see TEM results below) through HAuCl$_4$ reduction by ethylene glycol. Although HAuCl$_4$ reduction by ethylene glycol is thermodynamically favored, microwave exposure is essential to kinetically facilitate the formation of acetaldehyde, which is efficient in reducing Au(III), to form nanoparticles. Upon microwave exposure of a mixture of a CNT dispersion in deionized water and HAuCl$_4$ without ethylene glycol the CNTs sink to the vial bottom (Figure 3). But, no color changes are observed, as expected, underscoring the importance of the presence of all the reactants for CNT derivatization.

Although the CNTs shown in the image are well-dispersed, many nanotubes sink to the vial bottom, primarily due to the CNT clustering, typically of arc-discharge CNT samples, such as those used in our study. Ultrasonication is the often used solution to separate and disperse CNTs into smaller bundles and individual CNTs but can also cause functionalization and fissure. In our study, we were exclusively interested in studying the effects of microwave exposure on CNTs, without introducing adventitious functionalization and CNT fissure. Hence, we did not attempt to break up the large CNT bundles by means of stirring, shaking, or ultrasonication. A possible approach to better disperse the CNTs could be to combine mild ultrasonication prior to microwave-assisted functionalization.

TEM examination of the filtrates reveals that the functionalized CNTs are derivatized with gold nanoparticles when ethylene glycol is present (Figure 4a). A representative bright-field micrograph at a slightly higher magnification is shown in Figure 4b. The Au nanoparticles are equiaxed and decorate the CNT surfaces uniformly along its length. The nanoparticle size ranges between 3 and 10 nm, with an average of ∼6 nm and a standard deviation of ∼0.7 nm (Figure 4c). The overall tubular structure of the CNT remains intact, in contrast to rupture and tube breakage observed during functionalization by aggressive sonication and acid treatments.[14] Selected area diffraction patterns (e.g., Figure
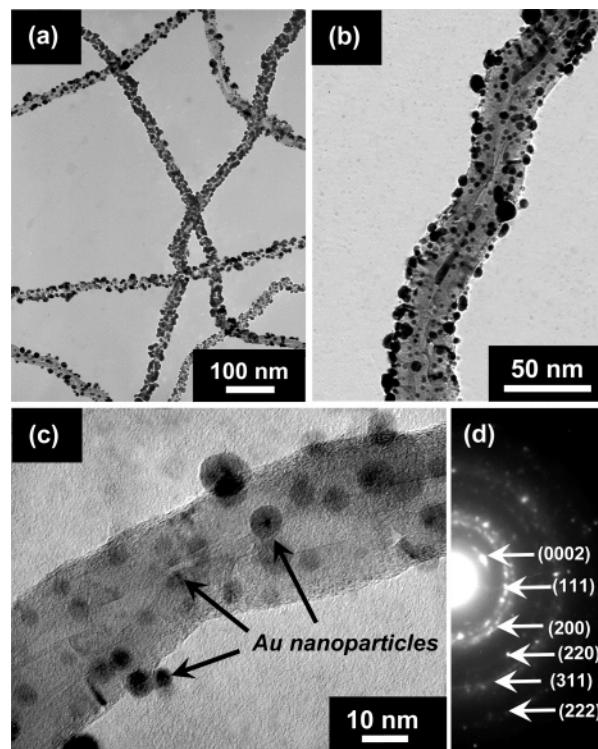

Figure 4. (a, b) Low- and (c) high-magnification bright-field TEM micrographs illustrating the decoration of multiwalled CNTs with 3−10 nm diameter Au nanoparticles. Note that the hollow of the tubes remains intact, indicating that the overall structure of the CNTs is preserved. (d) Selected area electron diffraction pattern showing diffraction spots corresponding to the (0002) basal planes of the CNTs and rings corresponding to polycrystalline fcc Au nanoparticles.

4d) reveal Bragg spots from the basal planes of the CNTs indicating that even though our functionalization method involves bond breaking, the overall CNT structure is largely preserved. The diffraction rings arise from polycrystalline face-centered cubic (fcc) Au nanoparticles.

The nanoparticles are not dislodged from the CNTs despite repeated centrifuging, washing, and rinsing during the purification process, suggesting chemical anchoring. This is supported by energy-dispersive X-ray (EDX) spectroscopy measurements (see Supporting Information) performed on samples after *repeated* washing with deionized water, which does not reveal any noticeable differences in the C Kα−Au Mα peak intensity ratio. Because we have not used any molecular coupling agents to cap the nanoparticles and the nanoparticles cannot attach strongly to CNTs via hydrophobic interactions, we deduce the presence of hydrophilic functional groups at locations where the Au nanoparticles are attached to the CNT. The uniform coverage of the nanoparticles on the CNTs indicates that the functional groups are formed throughout the length of the CNTs. We propose that the residual negative charge on the functional groups facilitates the preferred nucleation of Au nanoparticles at the functionalized locations of the CNTs by the reduction of Au(III) ions by ethylene glycol. Formation of local hot spots due to microwave-induced vibrational excitations in the vicinity of these functional groups (e.g., as reported in sonochemically

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activated Sn or Pt nanoparticle formation on CNTs)[15] could also promote preferred nucleation and growth of nanoparticles at the functionalized sites.

In summary, we have demonstrated a novel strategy of combining microwave radiation with polyol reduction of a metal salt to derivatize CNTs with Au nanoparticles in a single processing step. Exposing CNTs to microwaves results in defect creation and formation of functional groups on the CNT surface. The functional groups serve as preferred nucleation points for reducing metal ions from solution by a microwave-assisted reduction reaction, yielding CNTs that are uniformly decorated with gold nanoparticles. This simple

and convenient approach opens up a new way to scalably synthesize CNT heterostructures that could be used in developing device concepts, novel catalysts, and composites.

Supporting Information Available: A representative EDX spectrum from Au nanoparticle-decorated CNTs after purification (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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