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Templated Synthesis of Single-Walled Carbon Nanotube and Metal Nanoparticle Assemblies in Solution

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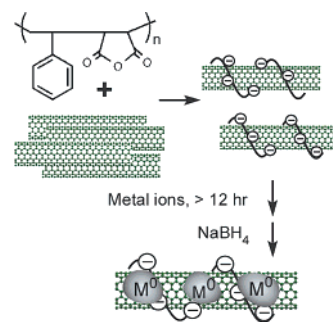
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Conjugated systems of nanomaterials may have collective properties that are drastically different than a simple combination of individual components. For example, the plasmonic coupling between metal nanoparticles (NPs) may account for the enhancement of the optical frequency electromagnetic fields at NP junctions by a factor of 10^{10} to 10^{12} as manifested in the surface-enhanced Raman spectroscopy.^{1–3} Recently, there is an increasing interest in synthesizing carbon nanotube (CNT)–metal NP composites.^{4,5} The coupling between the plasmonic modes of metal NPs and the dipole moments or plasmons of CNTs is of fundamental interest and may be utilized for light harvesting. In addition, the large surface areas and high electric conductivity make CNTs ideal supporting materials for metal NP catalysts such as Pt and Pd NPs, which have shown great promises in electrochemical cells and fuel cells.^{6–12} CNT is also a template for attaching metal NPs and NP-fused metal nanowires for hydrogen storage and for chemical and biological sensing applications.^{13–15}

Several approaches including spontaneous reduction,^{5,16} electrochemical reduction,^{17,18} substrate-enhanced electrochemical reduction,¹⁹ and NP decoration on chemically oxidized CNT side walls^{20,21} have been attempted to prepare CNT–metal NP assemblies. A challenge to this problem is the poor solubility of CNT in solutions. CNTs tend to bundle up due to strong inter-tube van der Waals interactions and hydrophobic interactions in aqueous solutions. Consequently, most reported attempts have been limited to multi-walled CNTs, large bundles of single-walled carbon nanotubes (SWNTs), or surface-attached SWNTs, and few have provided individually dispersed SWNT–metal NP assemblies for manipulation and investigation in solutions.²² Here we report a solution-phase synthesis of SWNT–metal NP assemblies that can be generally applied to common metal elements. Key to the synthesis is the poly(styrene-*alt*-maleic acid) (PSMA) surfactant,²³ which not only disperses SWNTs in solution but also acts as templates for the binding of metal ions and NPs.

As shown in Scheme 1, SWNTs are first individually dispersed in aqueous solutions in the presence of PSMA;²³ the SWNT–PSMA complexes are then incubated with metal ions for an extended period of time before the metal ions are chemically reduced and form NPs along SWNTs. In a typical experiment, 1 mg of PSMA is dissolved in 1 mL of 0.1 M NaOH solution, and ~2 mg of purified HiPCO SWNT powder (Carbon Nanotechnology Inc., Texas) is added. The mixture is then sonicated for an hour at ~5 W power and centrifuged for an hour at 15 500g. The supernatant contains individually dispersed SWNTs and free PSMA unbound to SWNTs, which is manifested by the network-like background less than 0.3 nm in height (Figure 1A). The supernatant is thus dialyzed using cellulose ester membrane with 1 million Dalton molecular weight cutoff (Spectrum Labs Inc., Rancho Dominguez, CA) to eliminate free PSMA. In order to form metal NPs, 10 μ L of 0.5 mM Pt-

Scheme 1



(terpy)Cl₂ solution is added to 100 μ L of the SWNT–PSMA solution and incubated at room temperature for more than 12 h. At last, 3 μ L of 6 mg/mL of NaBH₄ solution is added, and SWNT–metal NP assemblies are obtained in the solution.

Atomic force microscopy (AFM) and transmission electron microscopy (TEM) techniques are used to characterize the SWNT–metal NP assemblies. Figure 1 shows images of spin-cast samples on freshly cleaved mica obtained with MFP 3D AFM (Asylum Research, Santa Barbara, CA) in ambient conditions. Comparing Figure 1B and C with the SWNT–PSMA complexes in Figure 1A, it is clear that metal NPs about 3–6 nm in diameter are formed along SWNTs after the chemical reduction. The spacing between particles is about 25–100 nm. TEM micrographs show similar results (Supporting Information). Less than 10% SWNTs in the suspension (mostly <200 nm in length) show no metal particle attachment. The binding between metal NPs and the SWNT is strong enough to stand water rinsing after the complexes are deposited on the surface (Supporting Information).

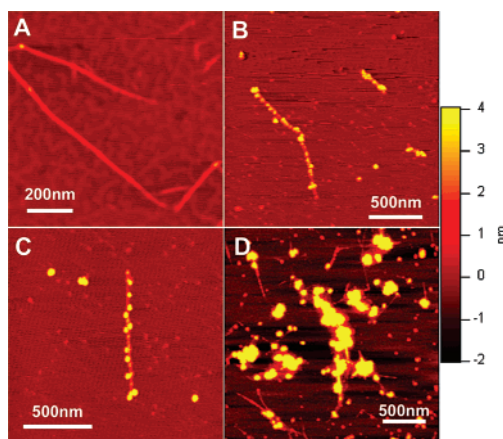


Figure 1. AFM images of (A) SWNT–PSMA complexes with free PSMA in the background; (B) SWNT–PSMA–Pd nanoparticle assemblies; (C) SWNT–PSMA–Pt nanoparticle assemblies; (D) mixture of Pd cluster and SWNT–PSMA obtained by reducing PdCl₄^{2–} without incubation. All images are on the same height scale.

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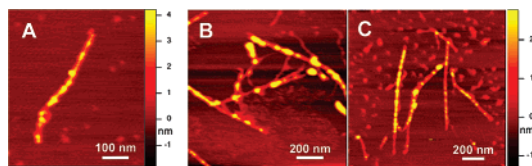


Figure 2. AFM images of SWNT–PSMA–metal nanoparticle composites: (A) Au, (B) Cu, and (C) Fe.

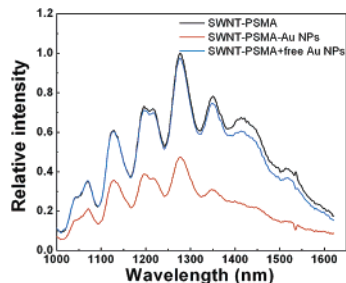


Figure 3. Fluorescent spectra excited at 785 nm, obtained on NS1 NanoSpectralyzer (Applied NanoFluorescence, LLC, Houston, TX).

A series of control experiments suggest that the binding of metal ions to the polymer surfactant template is crucial to successful preparation of SWNT–metal NP assemblies. First, reduction of metal ions by NaBH_4 in the absence of SWNT–PSMA complexes leads to large clumps of solids (Supporting Information), which suggests the presence of carbon nanotube and/or that the PSMA is essential. Choi et al. reported that the spontaneous redox reaction between SWNTs and noble metal ions could lead to the formation of metal nanoparticles.^{5,16} We test the contribution of this mechanism by mixing SWNT–PSMA complexes with $\text{Pt}(\text{terpy})^{2+}$ only and found no discernible amount of Pt nanoparticles in AFM characterization, which agrees with the observation by Quinn et al.¹⁸ The third control experiment was done by adding NaBH_4 to the SWNT–PSMA and metal ion mixture without incubation. Figure 1D shows large clusters of particles formed after this process. This indicates that the incubation of SWNT–PSMA with metal ions is critical for controlling the growth of metal nanoparticles. We reason that metal ions initially attracted to SWNT–PSMA complexes through electrostatic interactions may slowly shift the binding mode to charge-transfer interaction with SWNTs or coordination interaction with the carbonyls on PSMA over the time of incubation.^{24,25} The strong interaction between the metal ions and SWNT–PSMA reduces the ion mobility, thus limiting the metal ions available for the growth of nucleated metal NP seeds. The carbonyl groups on PSMA may also act as capping reagents for the resulting metal nanoparticles and prevent the particles from aggregating with each other.^{25,26}

The small quantity of fed metal ions is another key to this method. The molar ratio of metal ions and carboxylic acid groups on PSMA in the reaction mixture is less than 1:100. This ensures that the majority of the metal ions are bound to SWNT–PSMA complexes after incubation and prevents uncontrolled growth of metal NPs due to free ions available in solution. This method is generally applicable to other metal elements. Shown in Figure 2 are AFM images of SWNT assemblies with Au, Cu, and Fe NPs. The suspension of the complexes is stable in solution at room temperature for weeks without precipitation or aggregation.

Individually dispersed SWNTs have exciton emissions in the near infrared (NIR) region.^{27,28} We show that the SWNT emission is partially quenched in the nanoparticle complexes (Figure 3). While the interaction between SWNT excitons and metal particles needs further investigation, the partial quenching clearly indicates that metal particles are closely attached to SWNTs in the complexes

because a mixture of SWNT–PSMA suspension and free Au NP solution does not show any reduction in emission intensity.

In summary, we report a solution-phase synthesis of SWNT–metal NP assemblies that is generally applicable to common metal elements. The process utilizes polymer surfactants as SWNT dispersing reagent and then as templates for metal NP assembly. The SWNT–metal NP complexes not only have potential applications in catalysis and sensing but may also lead to novel hierarchy nanostructures such as CNT Y junctions and CNT semiconductor nanowire heterojunctions.

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Supporting Information Available: Experimental procedures for SWNT NP assemblies for Pd, Au, Cu, and Fe; TEM micrographs of SWNT–Pd and –Pt NPs; AFM images of large clusters of Pt metal when reduced in the absence of SWNT–PSMA complexes; and AFM images of complexes on substrate after rinsing in water. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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