

Hydrogenated SWNTs for Improved Processing

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(see Miller et al, *J. Amer. Chem. Soc.* **2008**, *130*, 2296-2303)

The continuing interest in single-wall carbon nanotubes^{1,2} (SWNTs) is based on their well-defined structure, stability, and many interesting properties linked to their small diameter and large aspect ratio.³ SWNTs usually exist as bundled structures held together by a combination of van der Waals and very weak covalent interactions.⁴ Since the most intriguing applications in nanoelectronics and structural materials require isolated SWNTs,⁵ the development of efficient methods to debundle and disperse SWNTs is highly desirable. Techniques to disperse SWNTs include physical agitation using ultrasonic waves and the addition of chemical surfactants or polymers. Ultrasonic cavitation is known to be destructive and can shorten SWNTs.^{6,7} Cavitation is also reported to induce undesired chemical reactions between SWNTs and dispersing solvents like *ortho*-dichlorobenzene.⁸ Surfactant or polymer additives coat SWNT surfaces and thus effectively reduce inter-tube attraction. They do not however penetrate deep into rigid nanotube bundles limiting their ability to disperse high concentrations of SWNTs. Chemical functionalization of SWNTs has emerged as a powerful, alternative approach to disperse SWNTs. The well studied oxidation of SWNTs using some combination of sulfuric acid, nitric acid, and occasionally hydrogen peroxide^{9,10} has been demonstrated to result in better dispersions of SWNTs in aqueous solution, consistent with the addition of polar, hydrogen bonding functional groups. This harsh treatment is known to open SWNT endcaps, shorten tube lengths, and leave carboxylic acid functional groups at dangling carbon atom sites. Other chemical functionalization strategies are reported to improve SWNT dispersion in less destructive manners. These include azomethine ylide addition,¹¹ aryl diazonium addition,¹² and fluorination.^{13,14} These chemistries largely impact the sidewalls of the SWNTs with each addition converting an sp^2 C into an sp^3 C. The addends disrupt intertube van der Waals interactions leading to enhanced dispersions.

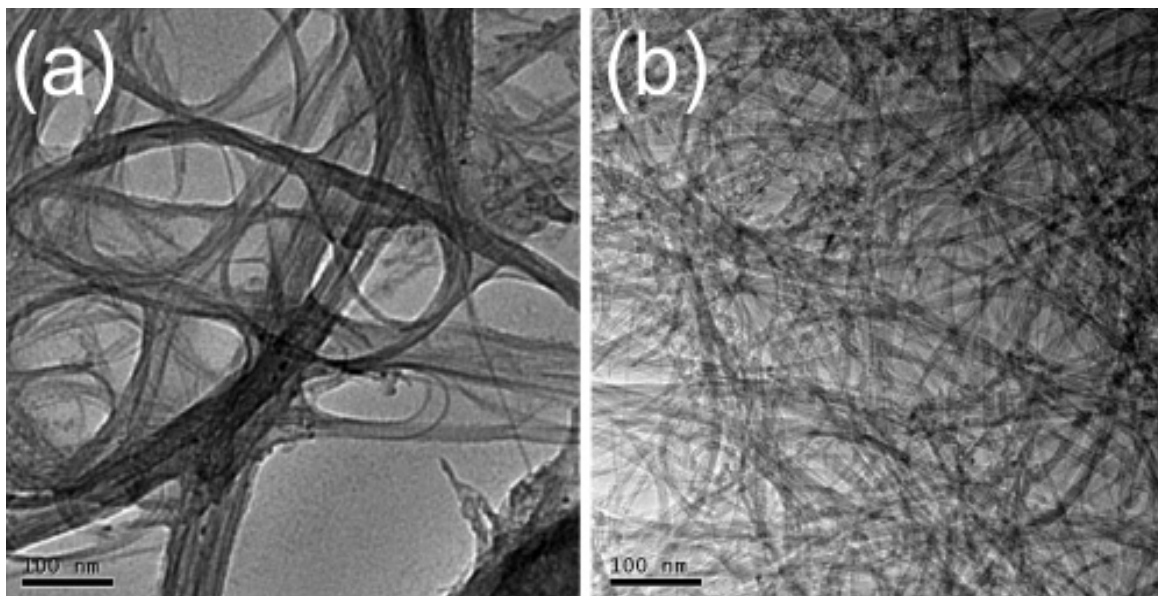


Figure 1. Transmission Electron Microscope (TEM) images of (a) bundled SWNTs before hydrogenation and (b) debundled H-SWNTs after polyamine hydrogenation.

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In this project, we studied a new chemical functionalization strategy that utilizes high boiling polyamines as hydrogenation reagent. The polyamine based hydrogenation of SWNTs is both efficient and thermally reversible. Polyamine hydrogenated SWNTs (H-SWNTs) disperse well in common organic solvents like methanol, ethanol, chloroform, and benzene. Spectroscopic evidence confirms new C-H bond formation. Electron microscopy indicates that H-SWNTs are weakened structures with significant surface modifications and reduced inter-tube attractions.

The chemistry underlying the polyamine hydrogenation process evolved from our successful polyamine hydrogenation of other nanostructured carbons, namely [60]-fullerene,¹⁵ [70]fullerene, and large fullerenes up to and including [250]fullerene.¹⁶ Previous approaches to hydrogenate SWNTs have utilized dissolving metal reductions,¹⁷ high pressure hydrogenations,^{18,19} or H-plasma procedures.^{20,21,22} We consider the polyamine hydrogenation process to be superior to other hydrogenations because it is simple, high yielding, easy to workup and scalable. Because SWNTs are less reactive than fullerenes, we have utilized relatively high reaction temperatures and elemental cobalt as catalyst. Similar conditions have also been employed to hydrogenate fullerenes.^{16,16} For both fullerenes and SWNTs, we observe only hydrogenation, and do not observe alkylation, hydroamination, or any other byproducts.

TEM images recorded before and after polyamine hydrogenation of SWNTs reveal striking differences. Before hydrogenation, the pristine SWNTs are largely bundled, as expected. After polyamine hydrogenation, the H-SWNTs appear as highly dispersed solids on the TEM grid as shown in Figure 1. These observations are corroborated by attempts to disperse SWNTs and H-SWNTs in organic solvents. After 30 s of low-power sonication in methanol, pristine SWNTs quickly fall out of solution, as illustrated in Figure 2. By contrast, H-SWNTs stay well dispersed for days. H-SWNTs also stay well dispersed for days or longer in a variety of other common organic solvents including ethanol, chloroform, and benzene.

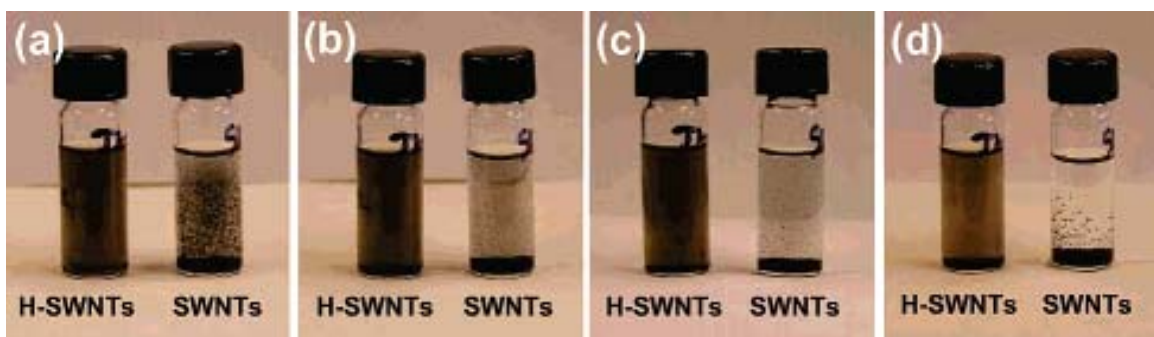


Figure 2. Visual comparison of SWNT and H-SWNT suspensions in methanol for variable times after 30 s of low-power sonication. Time since sonication is 30 s (a); 5 min (b); 1 h (c); and 48 h (d).

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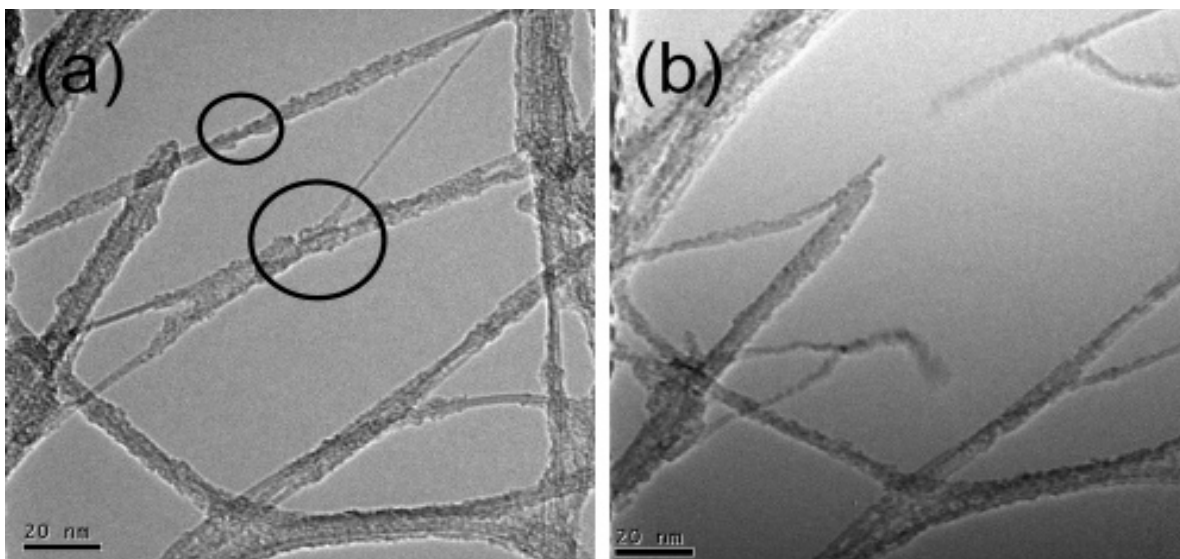


Figure 3. Time sequence of Transmission Electron Microscope images of de-bundled H-SWNTs after polyamine hydrogenation. Hydrogen-induced destabilization makes nanotubes prone to fracture, as seen by changes in the circled areas of (a).

Electron microscope images of H-SWNTs, shown in Figure 3, reveal significant surface modification as a result of polyamine hydrogenation. The hydrogenated nanotubes are weakened structures that are prone to fracture during irradiation. Thermal gravimetric analysis (TGA) under an inert gas atmosphere indicates an 8% weight loss from room temperature to 800 °C. Pekker and co-workers reported qualitatively similar TGA data for SWNTs hydrogenated using a dissolving metal reduction,²³ but they observed less than 5% weight loss up to 900 °C, indicating overall lower levels of hydrogenation. In Pekker's work, the effluent gases were analyzed by a mass spectrometer revealing the release of several molecules including hydrogen, methane, and methanol. Thus, also for our H-SWNTs, the H:C ratio cannot be determined based upon TGA analysis alone. However, given the qualitative similarities between the TGA curves, we expect at

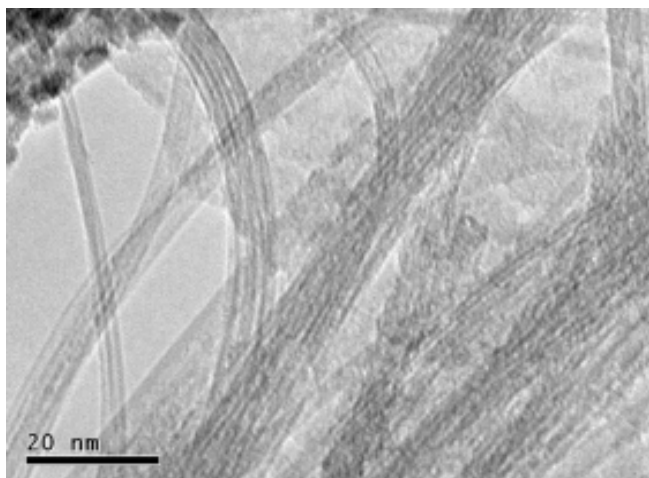


Figure 4. Transmission Electron Microscope image of the initially hydrogenated H-SWNT system of Figure 1(b) following dehydrogenation by annealing at 800 °C in a TGA furnace.

least 1 H atom for every 10 C atoms on the polyamine hydrogenated SWNTs. TEM analysis of the residual tubes after thermal annealing to 800 °C provides evidence for the reversible nature of hydrogenation. After annealing, as seen in Figure 4, the sample structure strongly resembles that of pristine SWNTs before hydrogenation.

Our Raman characterization of the H-SWNTs is consistent with the formation of functionalized SWNTs, in which sp^2 carbons are converted to sp^3 carbons. As seen in the Raman spectra depicted in Figure 5, the D band, indicative of sp^3 carbon formation along the sidewalls of the SWNT and centered at approximately 1300 cm^{-1} , grows relative

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to the graphitic G band, centered at approximately 1580 cm^{-1} , following the hydrogenation. To further characterize the nature of the bonding to SWNTs, we observed vibrational spectra of H-SWNTs using infrared spectroscopy. Our FT-IR spectra reveal $\text{C}(\text{sp}^3)\text{-H}$ stretching vibrations at 2962 cm^{-1} , 2918 cm^{-1} , and 2849 cm^{-1} as illustrated in Figure 6. Additional IR bands include a relatively intense band at 1580 cm^{-1} corresponding to $\text{C}=\text{C}$ double bond stretching. Our experimental values for $\text{C}(\text{sp}^3)\text{-H}$ stretching vibrations are in close agreement with those recorded for SWNTs hydrogenated using a H plasma²⁰ (2955 cm^{-1} , 2924 cm^{-1} , and 2854 cm^{-1}).

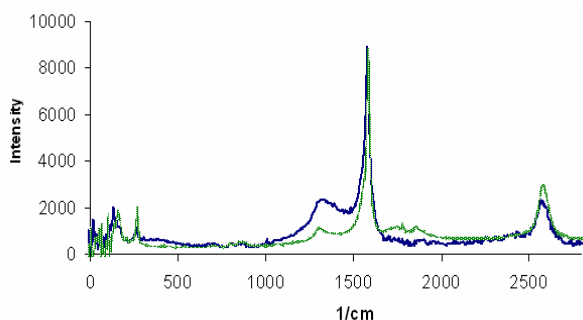


Figure 5. Raman spectra of pristine (SWNTs; dotted green line) and hydrogenated (H-SWNTs; solid blue line) single-wall carbon nanotubes.

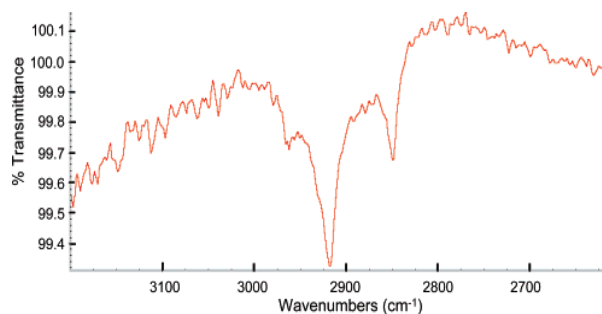


Figure 6. Infrared spectrum of hydrogenated nanotubes.

Conclusions and Future Directions. In this project, we have gained a fundamental understanding of the reversible hydrogenation of SWNTs using high boiling polyamines as hydrogenation reagents. Experimental studies show that hydrogenated SWNTs disperse well in organic solvents and exist largely as debundled tubes. These results suggest that hydrogenated SWNTs are excellent nanoelements for assembly and transfer experiments using nanotemplates developed at the Center for High-rate Nanomanufacturing. We envision that our debundled, hydrogenated SWNTs can be combined with CHN nanotemplates to align and orient single SWNTs across large wafers at high rate and with nanoscale precision.

More Information. For more information about hydrogenated carbon nanotubes, see Miller et al, *J. Amer. Chem. Soc.* **2008**, *130*, 2296-2303 or contact:

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