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Stable and Responsive Fluorescent Carbon Nanotube Silica Gels

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ABSTRACT

Here we report a general route to prepare silica nanocomposite gels doped with fluorescent single walled carbon nanotubes (SWNT). We show that tetramethylorthosilicate (TMOS) vapors can be used to gel an aqueous suspension of surfactant-wrapped SWNT while maintaining fluorescence from the semiconducting nanotubes. The vapor phase silica process is performed at room temperature and is simple, reproducible, relatively quick, and requires no dilution of SWNT dispersions. However, exposure of aqueous SWNT suspensions to TMOS vapors resulted in an acidification of the suspension prior to gelation that caused a decrease in the emission signal from sodium dodecylsulfate (SDS) wrapped SWNT. We also show that although the SWNT are encapsulated in silica the emission signal from the encapsulated SWNT may be attenuated by exposing the nanocomposites to small aromatic molecules known to mitigate SWNT emission. These results demonstrate a new route for the preparation of highly luminescent SWNT/silica composite materials that are potentially useful for future sensing applications.

INTRODUCTION

Single walled carbon nanotubes (SWNT) possess unique mechanical, electrical and luminescence properties due to their nanoscale structure based on a cylindrical sheet of graphene. (*1-3*) As such, carbon nanotubes show a promising future in the fields of sensing, optics, nanotechnology, electronics, and materials science. Recently, we have been particularly focused on exploiting the near-infrared (NIR) emission signal arising from isolated semiconducting SWNT for sensing applications.(*4, 5*) Isolation of SWNT can be readily accomplished by suspending SWNT in aqueous solution *via* addition of surfactants.(*6, 7*) In order to fully harness the unique NIR properties of SWNT, there is a need to develop nanocomposites that readily incorporate isolated nanotubes. Silica is an ideal material for encapsulation of fluorescent SWNT, as it is generally inert, optically transparent, and permeable.(*5*) Here we used a vapor diffusion method to prepare silica nanocomposites containing fluorescent SDS-wrapped SWNT. The SWNT/silica nanocomposites prepared in this way retain over 50% of the initial emission signal intensity observed from SWNT prior to encapsulation. In addition, the SWNT luminescence signal was shown to be sensitive to the addition of small aromatic compounds, which demonstrates the possibility of future sensing applications with these materials.

EXPERIMENTAL

SWNT were synthesized by high-pressure decomposition of carbon monoxide (HiPco).(*6, 8*) The SWNT dispersion was prepared at 1 wt% sodium dodecylsulfate (SDS) in D_2O using standard suspension procedures.(*7*) A SWNT aqueous dispersion (~1 ml) was placed in a Petri dish along with a Teflon-coated cap containing TMOS (0.5 ml, Aldrich, 99 %) in a closed container for at least 1-2 hours at room temperature. After the desired exposure time, the SWNT suspension was aged at room temperature to form a gel. Fluorescence and FT-IR spectroscopy techniques were used to characterize the resulting gels. An aromatic molecule, 4-amino-1,1-azobenzene-3,4-disulphonic acid (AB, Aldrich; 1 M (aq)) was used to probe the sensitivity of SWNT emission in both the aqueous suspension and silica gel samples.

RESULTS AND DISCUSSION

Synthesis of gels

A schematic of the chemical vapor deposition process used to prepare SWNT/silica nanocomposites is shown in Fig. 1A. Open containers of tetramethylorthosilicate (TMOS) and an aqueous dispersion of SDS-wrapped SWNT were placed inside a larger vessel that was sealed in air and kept at room temperature.(*9*) Due to the volatile nature of TMOS at room temperature, the precursor quickly fills the atmosphere in the sealed vessel. When the vapors reach the aqueous solution/air interface they hydrolyze to form silicilic acid and methanol according to equation 1.

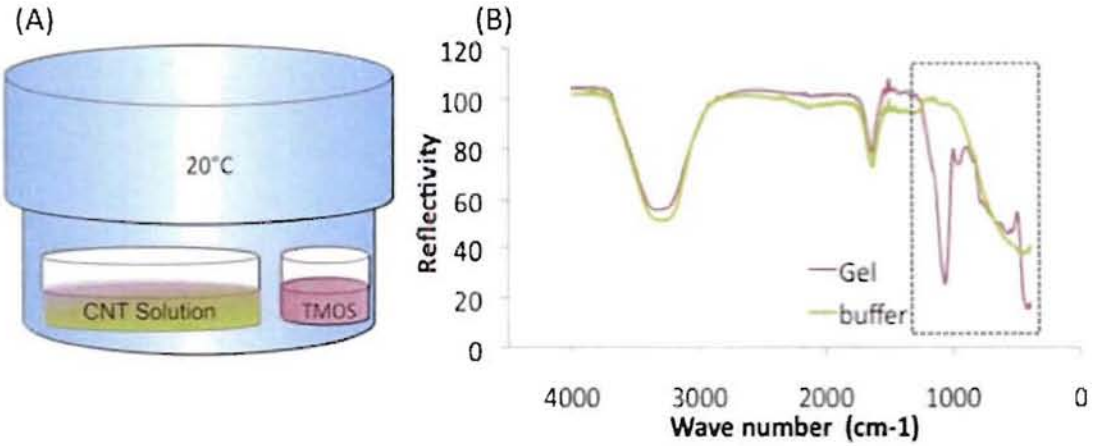

Figure 1. (**A**) Schematic of the vapor transfer process used to prepare SDS/SWNT/silica gel nanocomposites. (**B**) FT-IR spectra of 10 mM sodium phosphate buffer (i) before exposure (green) and (ii) after exposure (pink) to TMOS.

Further condensation leads to formation of Si-O-Si linkages resulting in a homogeneous silica gel (equation 2).

$$Si(OCH_3)_4 + 4H_2O \rightarrow Si(OH)_4 + 4CH_3OH \quad (1)$$

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \quad (2)$$

The slow rate of transfer of TMOS precursor molecules into the SWNT aqueous suspension leads to minimal methanol presence in the aqueous solution at any given time. This is advantageous because methanol can disrupt the SDS/SWNT assembly leading to aggregation of SWNT and loss of emission. To demonstrate the lack of methanol in the as prepared gels, an FT-IR spectrum of an aqueous solution before and after exposure to TMOS vapor is shown in Fig. 1B. Notice that there are no significant features around 2900 cm^{-1} where one would expect C-H modes to be present due to methanol or incomplete condensation of TMOS. In addition, both spectra have a broad absorption band between 4000 and 3000 cm^{-1} that corresponds to the fundamental stretching vibrations of different types of hydroxyl groups (H-OH and Si-OH in our case). The spectrum taken after exposure to TMOS vapors also shows new bands at 1062, 964, 810 and 445 cm^{-1} (highlighted by the box in Fig. 1B). Bands at similar wave numbers in the spectra of crystalline and amorphous SiO_2 have been assigned to characteristic vibrations of Si-O-Si bridges cross-linking the silicate network.

Fluorescence from SWNT Nanocomposites

Near-infrared emission observed from SDS-wrapped SWNT in solution and upon encapsulation in a silica gel is shown in Fig. 2.

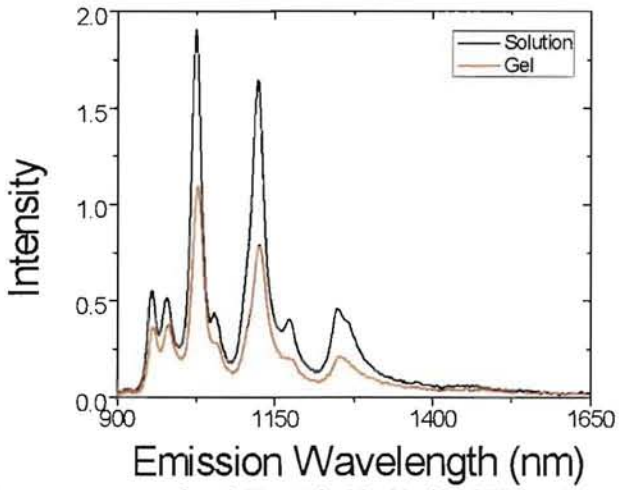

Figure 2. (A) SDS/SWNT aqueous suspension (pH = 7 in black), (B) Silica gel prepared from a suspension of SDS/SWNT (pH ~ 5.5 after exposure to TMOS vapor in red). Fluorescence spectra collected using an excitation wavelength of 640 nm.

Each emission peak is due to a different chirality of SWNT. Notice that all of the emission features observed from the SWNT dispersions were maintained in the SWNT/silica gels, although there was an overall decrease in fluorescence intensity upon encapsulation. In particular, the larger diameter tubes that emit at longer wavelengths decreased to a much greater extent. These changes in emission behavior are consistent with previous results observed upon acidification of surfactant-wrapped SWNT aqueous dispersions.(*10*) In fact, a significant drop in pH was measured by a pH meter before and after exposure to TMOS vapor. The initial SWNT suspension had a pH of ~7, while after exposure to TMOS the pH dropped to 5.5. Interactions

between protons in solution and SWNT are known to quench the photoluminescence signal from SWNT.(*8*)

Bleaching of SWNT emission by Aromatic Molecules

The SDS-wrapped SWNT in solution and encapsulated in silica were exposed to small azobenzene-type (AB) molecules that have previously been shown to bleach the SWNT photoluminescence signal in suspension and silica.(*5, 11*) Fluorescence spectra were recorded before and after 4 hrs of AB exposure. This time was sufficient for complete diffusion of AB into the silica gels containing SWNT, and also to achieve an emission steady state. As seen in Fig. 3, the SDS/SWNT suspension and SWNT/silica gels respond similarly with virtually complete bleaching upon addition of AB. These results suggest that the encapsulation of the SWNT in silica does not inhibit the accessibility of small molecules to the surface of the nanotubes.

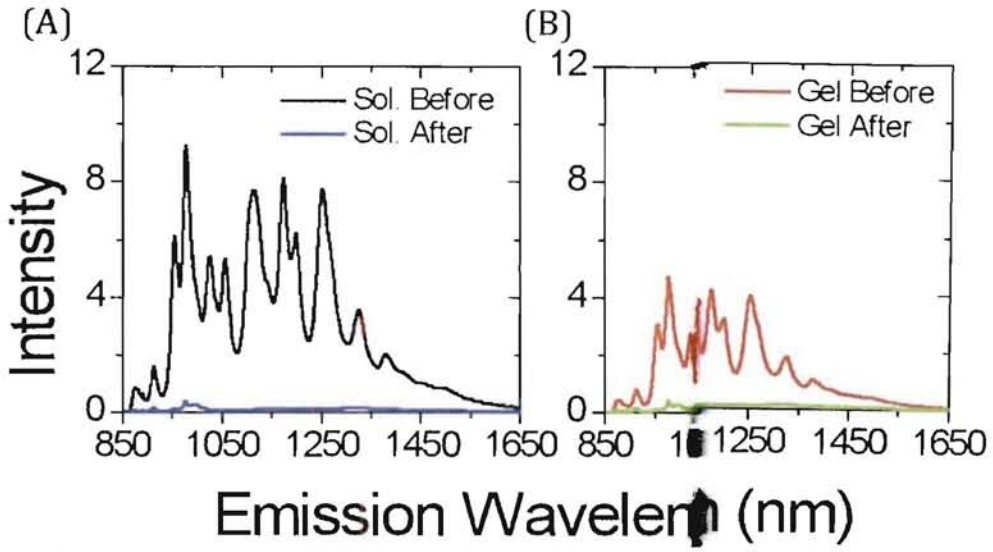

Figure 3. Fluorescence spectra for SWNT in solution and silica gels upon exposure to azobenzene-type molecules. (**A**) SDS/SWNT (suspension) before (black) and after AB exposure, 4 hrs (blue). (**B**) SDS/SWNT encapsulated in silica before (red) and after AB exposure, 4 hrs (green). Fluorescence spectra collected using an excitation wavelength of 785 nm.

CONCLUSIONS

We have successfully shown the immobilization of surfactant-wrapped SWNT in silica gels using a vapor phase process. The photoluminescence intensity from encapsulated SWNT was maintained after formation of the silica gel. We also showed that emission from SWNT encapsulated in silica may still be mitigated by exposure to small aromatic molecules. These results demonstrate a new route for the preparation of highly luminescent SWNT/silica composite materials potentially useful for future sensing applications.

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