

Crystallization: A commercial block copolymer poly(ethylene glycol)-*block*-poly(methacrylic acid) (PEG-*b*-PMAA, PEG = 3000 g mol⁻¹, PMAA = 700 g mol⁻¹) was obtained from T. Goldschmidt AG, Essen, Germany. The carboxylic acid groups of this copolymer were partially phosphonated (21 %) to give a copolymer with carboxylated and phosphonated groups, PEG-*b*-PMAA-PO₃H₂. The crystallization of BaCrO₄ in the presence of the polymer was carried out in a 5 mL glass bottle. The polymer concentration was kept at 1 g L⁻¹. In a typical synthesis, 0.12 mL 0.05 M BaCl₂ (Sigma Aldrich, 99 %) was added to 3 mL of polymer solution (1 g L⁻¹) under vigorous stirring at room temperature, resulting in a final BaCrO₄ concentration of 2 mM. After 3 min, 0.12 mL 0.05 M Na₂CrO₄ (Sigma Aldrich, 99 %) solution was added to the mixture. Then 20 μL of the PSS/PAH capsule solution (0.5 vol.-%) was injected into the solution under stirring for 3 min. The pH value was kept at 5.5. Then the solution was left static for up to two to five days before the precipitates were collected for characterization. The precipitates were left to stand in their mother solutions for at least 24 h to ensure complete equilibration. All precipitates were carefully washed repeatedly with distilled water and then stirred gently before placing one drop of the solution onto copper TEM grids or SEM stubs. In some cases, the solution that contained precipitate was sonicated for 3 min to ensure good dispersion of the particles.

Characterization: Dry powder samples were used for the measurements of X-ray powder diffraction (XRD) using a PDS 120 (Nonius GmbH, Solingen) with Cu Kα radiation. The characterization was done by using scanning electron microscopy (SEM) with a DSM 940 A (Carl Zeiss, Jena) microscope, by transmission electron microscopy (TEM) with a Zeiss EM 912 Omega microscope, and high-resolution transmission electron microscopy (HRTEM) and electron diffraction with a Philips CM 12 microscope operating at 120 kV (equipped with an EDAX 9800 analyzer). The ζ-potential of the initial solution was measured using a Malvern Zetasizer 4 by taking the average of five measurements at the stationary level. All measurements were performed in air-equilibrated water (~pH 5.5). The computer modeling of the cell structure and the crystal face cleavage of BaCrO₄ were done with Cerius² software (Accelrys).

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Polyaniline Nanotubes Doped with Sulfonated Carbon Nanotubes Made Via a Self-Assembly Process**

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The investigation of materials with nanotubular structure is of great importance from both scientific and technological points of view due to their unique properties and promising potential applications in nanodevices. Carbon nanotubes (CNTs), for example, have been investigated for use in a wide range of devices, including nanoelectronic and biomedical devices.^[1] Recent reports on the mass production of CNTs^[2] and their soluble derivatives^[3] have promoted a great deal of interest in developing multifunctional carbon nanotube composites with other materials. In this context, carbon nanotubes have been used to impart electrical properties to non-conducting materials (e.g., polymers) for electronic applications.^[4]

On the other hand, conducting polymers (CPs) have also been investigated for similar applications.^[5] The combination of CNTs and CPs has been demonstrated to lead to composite materials possessing the properties of each of the constituent components with a synergistic effect.^[6] Examples include highly efficient photovoltaic cells based on the composite materials of CNTs with poly(*p*-phenylene vinylene)^[7] or poly(3-octylthiophene),^[8] conjugated polymer/carbon nanotube composite LEDs with low current densities and good thermal stabilities,^[9] and aligned carbon nanotube/conducting polymer coaxial nanowires of high surface and interface areas.^[10]

Although conducting polymers synthesized by a conventional chemical or electrochemical method often show granular, spherical, or fibrous morphology,^[11] the template-synthesis method has been used to produce conducting polymer nanotubes and nanofibers.^[12] The template method involves the use of a nanoporous template with each pore acting as a tiny reaction vessel to generate polymer nanotubes/nanofibers of uniform diameter and length, which makes them attractive for various applications. In this regard, some aligned CP nanotube/nanofiber arrays have been shown to exhibit field emission properties of importance for flat panel displays.^[13]

One of our group (M. Wan) has recently developed a self-assembly method to synthesize conducting polymer micro/nanotubes in the presence of appropriate organic dopants but, unlike the template method, without an external template.^[14]

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For example, polyaniline (PANI) nanotubes were prepared via an in situ polymerization of aniline on a self-assembled supramolecular template consisting of the monomers and dopants.^[15] In particular, we have used sulfonated fullerene ($C_{60}(OSO_3H)_6$) as the protonic acid dopant for the preparation of PANI nanotubes.^[16]

In this communication, we report, for the first time, the use of sulfonated multiwalled carbon nanotubes (designated as MWNT-(OSO_3H)_n) as the self-assembled “template” for the formation of PANI nanostructures. We prepared not only PANI-coated MWNT-(OSO_3H)_n but also PANI nanotubes doped with MWNT-(OSO_3H)_n (designated as PANI-c-MWNT-(OSO_3H)_n and PANI-d-MWNT-(OSO_3H)_n, respectively). Mechanisms governing the formation of the PANI nanostructures, their morphologies, and electrical properties are also discussed.

Figure 1 shows the scanning and transmission electron microscopy (SEM and TEM) images and electron diffraction patterns for MWNT-(OSO_3H)_n, PANI-c-MWNT-(OSO_3H)_n,

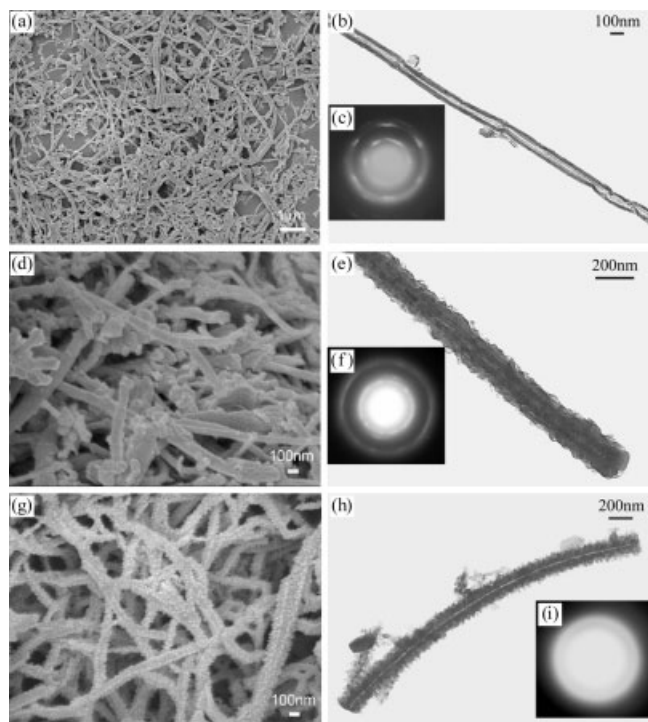


Fig. 1. SEM images (a,d,g), TEM images (b,e,h), and electron diffraction patterns (c,f,i) of: a–c) MWNT-(OSO_3H)_n; d–f) PANI-c-MWNT-(OSO_3H)_n; g–i) PANI-d-MWNT-(OSO_3H)_n nanotubes.

and PANI-d-MWNT-(OSO_3H)_n. As one can see in Figure 1, the MWNT-(OSO_3H)_n sample contains almost pure nanotubes of diameters in the range of tens to hundreds of nanometers (Fig. 1a); the hollow core is clearly evident in the TEM image (Fig. 1b). The corresponding electron diffraction pattern (Fig. 1c) reveals a crystalline structure.

The morphologic structure of the resulting PANI-MWNT-(OSO_3H)_n composites was found to change with the weight ratio of aniline to MWNT-(OSO_3H)_n. When the aniline to

MWNT-(OSO_3H)_n ratio is less than or equal to 1 (e.g., 1:2 or 1:1), the polymerization of aniline occurs dominantly on the surface of MWNT-(OSO_3H)_n, resulting in the formation of PANI-coated MWNT-(OSO_3H)_n (i.e., PANI-c-MWNT-(OSO_3H)_n, see Figs. 1d and 1e for aniline/MWNT-(OSO_3H)_n = 1:1). Figure 1e clearly shows a layer of uniformly coated PANI film (ca. 10 nm thick) on the MWNT-(OSO_3H)_n nanotube surface. The coaxial structure of the resulting PANI-c-MWNT-(OSO_3H)_n nanotubes is also confirmed by the corresponding electron diffraction pattern given in Figure 1f, which shows diffraction rings characteristic of the PANI “shell” and diffraction spots arising from the MWNT-(OSO_3H)_n “core”.

When the ratio of aniline to MWNT-(OSO_3H)_n became equal to or greater than 2:1 (e.g., 2:1, 4:1, and 8:1), the PANI-d-MWNT-(OSO_3H)_n nanotubes formed via a self-assembly process with an outer diameter in the range of 100–200 nm and inner diameters from several nanometers down to even zero (nanofibers) (see Figs. 1g and 1h for aniline/MWNT-(OSO_3H)_n = 8:1). Compared with PANI-c-MWNT-(OSO_3H)_n, the surface of the PANI-d-MWNT-(OSO_3H)_n nanotubes is very rough, as revealed by SEM and TEM examinations (Figs. 1g and 1h). Furthermore, the electron diffraction pattern of PANI-d-MWNT-(OSO_3H)_n given in Figure 1i indicates an amorphous structure.

The formation of PANI-coated MWNT-(OSO_3H)_n is believed to arise from the polymerization of aniline on the MWNT-(OSO_3H)_n nanotube surface with the MWNT-(OSO_3H)_n acting as the in-situ dopant, whereas the formation mechanism for PANI-d-MWNT-(OSO_3H)_n deserves some discussion. Our previous investigation has demonstrated that PANI nanotubes can be obtained by the self-assembly method with organic sulfonic acids, such as β -naphthalene sulfonic acid (β -NSA), as a dopant.^[15] This is because micelles formed by β -NSA and/or anilinium salt act as a tubular supramolecular template for the formation of the PANI nanotubes,^[15] which is much like the use of surfactant micelles as a template for the formation of mesoporous materials.^[17] In the aniline/MWNT-(OSO_3H)_n system, however, the H₂O-dispersed MWNT-(OSO_3H)_n might not only act as the supramolecular template through micellization with anilinium cations,^[18] which in turn are generated by H⁺ transfer from the $-OSO_3H$ groups, but also play the role of the dopant of PANI. The doped PANI or its oligomer is actually a sort of cationic polyelectrolyte with a very rigid backbone structure, which has the tendency to form self-assembled nanotube-like micelles induced by the “anionic-type” MWNT-(OSO_3H)_n^[19] in the process of polymerization, leading to the formation of PANI-d-MWNT-(OSO_3H)_n nanotubes.

The molecular structures of the MWNT-(OSO_3H)_n, PANI-c-MWNT-(OSO_3H)_n, and PANI-d-MWNT-(OSO_3H)_n nanotubes were characterized by Raman spectroscopy (Fig. 2). Two strong peaks at 1582 and 1335 cm⁻¹ were observed for MWNT-(OSO_3H)_n, attributable to stretching of the D mode and G mode.^[20] In the corresponding Raman spectra for PANI-c-MWNT-(OSO_3H)_n and PANI-d-MWNT-(OSO_3H)_n prepared at aniline/MWNT-(OSO_3H)_n = 1:1 and 8:1, respec-

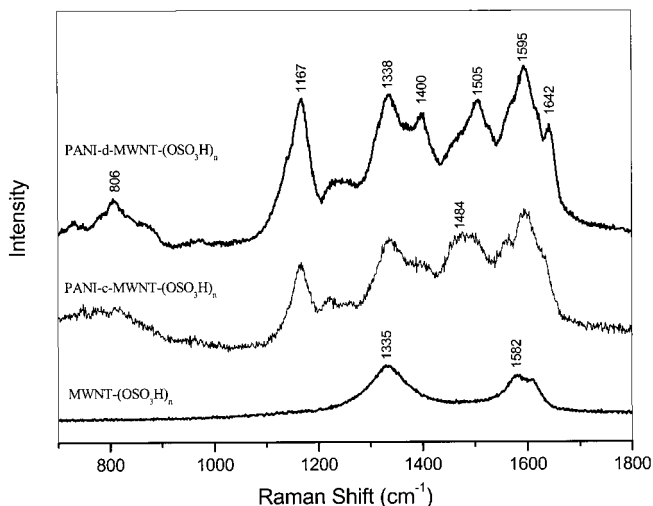


Fig. 2. Raman spectra of MWNT-(OSO₃H)_n, PANI-c-MWNT-(OSO₃H)_n, and PANI-d-MWNT-(OSO₃H)_n nanotubes.

tively, C–H bending of the quinoid/benzenoid ring at 1167 cm⁻¹, C–N⁺ stretching at 1338 cm⁻¹, and C–C stretching of the benzenoid ring at 1595 cm⁻¹ were observed, indicating the presence of the doped PANI structures.^[21] The Raman spectrum of PANI-d-MWNT-(OSO₃H)_n nanotubes differs from that of PANI-c-MWNT-(OSO₃H)_n nanotubes in that the peak intensities at 806 cm⁻¹ (deformation of the benzenoid ring), 1400 cm⁻¹ (electronic absorption of free charge carriers), 1505 cm⁻¹ (N–H bending), and 1642 cm⁻¹ (C–C stretching of the benzenoid ring) are stronger for the former than for the latter, while the peak at 1484 cm⁻¹ (C=N stretching) was weaker for the PANI-d-MWNT-(OSO₃H)_n nanotubes. The above differences in the Raman spectra might result from the different conformations and structures of PANI in the two samples.^[21] This is also supported by the UV-vis-NIR absorption spectra presented below.

As shown in Figure 3, no absorption peak was observed for MWNT-(OSO₃H)_n over 300–1400 nm. Both PANI-c-MWNT-

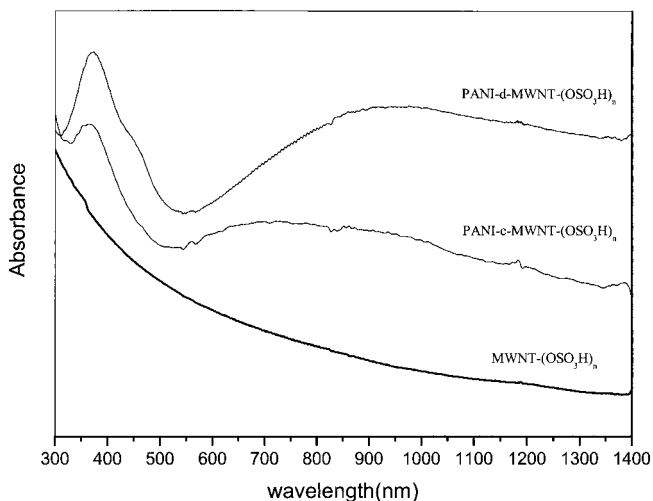


Fig. 3. UV-vis-NIR spectra of MWNT-(OSO₃H)_n, PANI-c-MWNT-(OSO₃H)_n, and PANI-d-MWNT-(OSO₃H)_n nanotubes.

(OSO₃H)_n and PANI-d-MWNT-(OSO₃H)_n nanotubes dispersed in alcohol, however, show a π - π^* transition of the benzenoid ring of PANI at 370 nm, along with a free carrier tail extending into the near-infrared region (>1000 nm), indicating a doped state for the PANI chains.^[22] Moreover, the PANI-d-MWNT-(OSO₃H)_n nanotubes gave two peaks (ca. 450 nm and 880 nm) characteristic of localized polarons,^[22] whereas the localized polaron peak for PANI-c-MWNT-(OSO₃H)_n shifted to 720 nm and its free carrier tail became much weaker. Therefore, the optical absorption results, together with the Raman spectra, indicate that PANI chains in both PANI-c-MWNT-(OSO₃H)_n and PANI-d-MWNT-(OSO₃H)_n nanotubes are in the doped state, but with different chain conformation. The PANI chains in the PANI-d-MWNT-(OSO₃H)_n sample have apparently assumed a more extended conformation due to its nanotubular structure.

Accordingly, the standard Van Der Pauwe DC four-probe method^[23] was used to measure the conductivities of the resulting PANI-c-MWNT-(OSO₃H)_n and PANI-d-MWNT-(OSO₃H)_n nanotubes. The room-temperature conductivities of PANI-d-MWNT-(OSO₃H)_n and PANI-c-MWNT-(OSO₃H)_n are 1.4×10^{-2} S/cm and 2.2×10^{-2} S/cm, respectively. The relatively low conductivities for both of them are due to the low doping level in both cases. X-ray photoelectron spectroscopy (XPS) results revealed that the doping level (calculated by N⁺/N ratio) of PANI-c-MWNT-(OSO₃H)_n and PANI-d-MWNT-(OSO₃H)_n nanotubes are 0.24 and 0.19, respectively. The temperature dependence of conductivity for both samples exhibits a typical semiconductor behavior. A one-dimensional variable range hopping (1D-VRH) model ($\ln \sigma(T) \propto T^{-1/2}$ relationship) provides the best fit to the data of PANI-d-MWNT-(OSO₃H)_n nanotubes (Fig. 4),^[24] while the corresponding data for PANI-c-MWNT-(OSO₃H)_n show a small deviation from the 1D-VRH mode, as is found for polypyrrole-coated CNTs.^[6a] The hopping barrier (T_0 value) deduced from the slope of $\ln \sigma(T) \propto T^{-1/2}$ lines is about 2.7×10^4 K for PANI-d-MWNT-(OSO₃H)_n nanotubes, which is

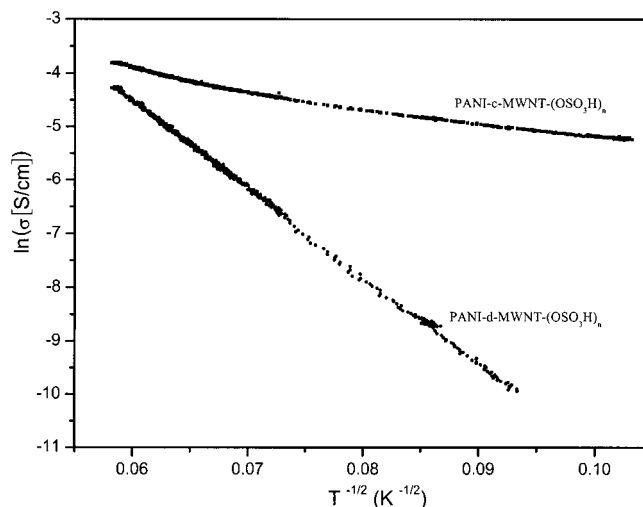


Fig. 4. Temperature dependence of the conductivity of PANI-c-MWNT-(OSO₃H)_n and PANI-d-MWNT-(OSO₃H)_n nanotubes.

much higher than that of PANI-c-MWNT-(OSO₃H)_n (1.0 × 10³ K). In view of the molecular structure, room-temperature conductivity, and doping level, the above measured higher hopping barrier of PANI-d-MWNT-(OSO₃H)_n than that of PANI-c-MWNT-(OSO₃H)_n nanotubes may indicate that carbon nanotubes rather than PANI play a more important role in regulating the electrical properties at low temperature.

In summary, we have synthesized PANI nanotubes doped with MWNT-(OSO₃H)_n through a self-assembly method in the presence of MWNT-(OSO₃H)_n as the protonic acid dopant. The morphology of the resulting PANI doped by MWNT-(OSO₃H)_n can be controlled by the aniline to MWNT-(OSO₃H)_n ratio. Only PANI-coated MWNT-(OSO₃H)_n [i.e., PANI-c-MWNT-(OSO₃H)_n] was observed when the ratio aniline/MWNT-(OSO₃H)_n ≤ 1. When the ratio aniline/MWNT-(OSO₃H)_n ≥ 2, a secondary, supramolecular-type MWNT-(OSO₃H)_n-doped PANI nanotube [i.e., PANI-d-MWNT-(OSO₃H)_n] formed. The formation of PANI-c-MWNT-(OSO₃H)_n arises from the polymerization of aniline on the surface of MWNT-(OSO₃H)_n nanotubes with the MWNT-(OSO₃H)_n acting as the dopant, while PANI-d-MWNT-(OSO₃H)_n is derived from a self-assembly process induced by the interaction between MWNT-(OSO₃H)_n and PANI.

Experimental

Preparation of Sulfonated Carbon Nanotubes [MWNT-(OSO₃H)_n]: Multi-walled carbon nanotubes (MWNTs) were synthesized by pyrolysis of iron(II) phthalocyanine [25] under Ar/H₂ and were purified in 3 N nitric acid according to the reported method [26]. The acid-oxidized MWNTs were then used to produce the hydrogensulfated MWNTs [designated as MWNT-(OSO₃H)_n] by directly sulfating the acid-oxidized MWNTs of multi-hydroxyl groups in the presence of concentrated sulfuric acid, as is the case for the preparation of hydrogensulfated fullerene from polyhydroxylated fullerene [22a].

Reactions leading to the hydrogen-sulfated MWNTs were followed by Fourier transform infrared (FTIR), XPS, and SEM while the -OSO₃H content in the resulting MWNT-(OSO₃H)_n was estimated by determining the pH value of an aqueous MWNT-(OSO₃H)_n solution of a predetermined concentration and crosschecked by XPS measurements. SEM images showed that the tubular structure of the carbon nanotubes was largely retained, although some of them were shortened.

Based on the XPS data, the content of functional groups in the acid-oxidized carbon nanotubes was estimated to be about 6.7 at.-% hydroxyl groups and 3.3 at.-% carbonyl groups. Among the 6.7 at.-% -OH groups, about 64.5% of them were converted into -OSO₃H groups after reacting with fuming sulfuric acid. The corresponding results from the solution pH titration showed a similar magnitude but slightly lower values, indicating the more surface-sensitive nature of the XPS technique.

Synthesis of PANI Doped by MWNT-(OSO₃H)_n: Different weight ratios of aniline (18 μL) and MWNT-(OSO₃H)_n were dissolved in deionized water (2 mL) by ultrasonication. Ammonium peroxide sulfate ((NH₄)₂S₂O₈, APS, 46 mg) was added to the above mixture under ultrasonication. The reaction then proceeded in the stationary state for 12 h at 0–5 °C (in an ice bath). Finally, the precipitate was separated by centrifugation and washed with deionized water, methanol, and ethyl ether consecutively prior to drying under a dynamic vacuum for 24 h at room temperature.

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Controlling Dielectric and Optical Properties of Ordered Mesoporous Organosilicate Films**

By A. Ruud Balkenende,* Femke K. de Theije, and J. C. Koen Kriege

Surfactant-templated mesoporous thin films with ordered, nanometer-sized pores offer a high degree of uniformity that is of interest in diverse application areas like membranes, (bio)molecular sensors, shape-selective catalysis, and low-k dielectrics. The properties of the internal surface area often are adapted by inclusion of (pendant) organic groups. Here we report on the single-step formation of mesoporous hybrid

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