

CONTROLLED DISPERSION OF CARBON NANOTUBES BY AMPHIPHILIC POLYELECTROLYTES

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Introduction

The field of carbon nanotube (CNT) research has exceptionally blossomed within the past decade [1]. However, all proposed applications have so far been limited by their limited insolubility in aqueous and organic solvents, as well as the diversity of tube diameters and chirality. Therefore, it is desirable to find ways to disperse CNTs in various media [2] on the one hand and separate CNTs of different diameter and chiral angle on the other hand. Noncovalent functionalization by polymer wrapping, interaction with biomolecules such as DNA or peptides and the adsorption of ionic or nonionic surfactants has emerged as the most promising tool for CNT solubilization in combination with the preservation of the intrinsic electronic and structural properties. In addition, recent reports have demonstrated the utilization of amphiphilic substances for the diameter- and/or chirality-selective separation of CNT material. Therefore, our interest has focused on the use of water-soluble amphiphilic copolymers with different chemical architecture [3] for the dispersion of single-walled carbon nanotubes (SWCNTs) in aqueous media (Fig. 1).

Significantly, very low concentrations of the copolymers, such as 0.01 wt%, cause an efficient dissolution of the SWCNTs in water accompanied by a very pronounced colloidal stability after centrifugation of the suspensions only at 12000 rpm. The individualization of SWCNTs in water in the presence of water-soluble copolymers was investigated in detail by optical absorption, dynamic scattering, and Raman spectroscopy as well as by electron microscopy.

Experimental

Chemical structure of the two copolymers used in this study is depicted in Figure 1. The C-51-2 has polydispersity of 1.5, total molecular weight 15000 gmol⁻¹ and molecular weight of the PMMA block 5800 gmol⁻¹. The C-39-3 has

polydispersity of 1.16, total molecular weight of 14600 gmol⁻¹ and molecular weight of the PMMA block 400 gmol⁻¹. When not stated otherwise, the copolymers in concentration 0.1 wt% (or alternatively 0.01 wt%) were dissolved in water with pH adjusted to a desired level. In the following experiments, pH of 1.7, 2.9, 4.2 and 10.5 were used. HiPCo tubes were added, tip ultrasonicated for 20 minutes and centrifuged at 12000 rpm for 20 minutes. For comparison water solutions of SDS at pH 10 and Triton X-100 at pH 6.5 were used instead of copolymers, but with 10x higher concentration (1 wt%).

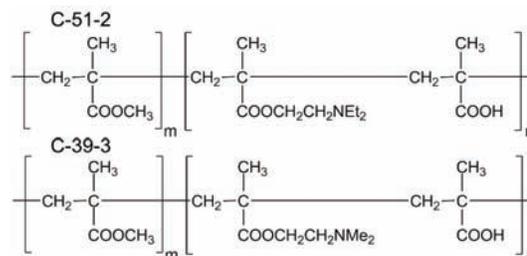


Fig. 1 Chemical structure of the amphiphilic copolymers used in this study.

Results and Discussion

The prepared SWNT-copolymer suspensions are completely stable over a period of one year without showing any sign of sedimentation or aggregation.

Figure 2 shows Raman spectra of the suspensions recorded using 785 nm excitation as measured in quartz cuvettes. For comparison, the spectra of raw SWNT in powder are shown too. The most intense peaks in the radial breathing mode (RBM) region (Fig. 2a) belong to semiconducting tubes enhanced through their E₂₂ transition. The peaks around 233 cm⁻¹ belong to S25 nanotube family. The peaks around 266 cm⁻¹ belong to the S25 family. In an isolated state, the S25 family nanotubes should be in an almost perfect resonance with the excitation wavelength (1.58 eV), because their E₂₂ transition energy varies in the range of 1.55 – 1.57 eV [4]. Their diameter varies between 0.99 and 1.10 nm. The S22 family nanotubes are slightly off-resonance with the excitation wavelength, their E₂₂ transition energies vary from 1.66 to 1.73 eV and diameters vary from 0.87 to 0.97 nm. As can be seen in Fig. 2a, the RBM intensities increase progressively for lower wavenumbers, i.e. for wider tubes belonging to the S22 family, in the spectra of the SWNT-copolymer dispersions with lowering of the pH, however, still the intensities of 233 cm⁻¹ bands (I_{RBM}(S22)) are lower than the intensities of 266 cm⁻¹ bands (I_{RBM}(S25)). The highest I_{RBM}(S22)/I_{RBM}(S25) ratio appears in the spectra of SDS- and Triton X-100-SWNT suspensions. These variations in relative intensities can be explained by the state of bundling. It is known that bundling causes red-shifting of the electronic transitions in the range of 10-30 meV [5]. Thus, in the most bundled sample, which are the raw SWNT, the S25 family nanotubes are in the best resonance with the excitation wavelength. With progressive debundling, the SWNT transition energies blue-shift and nanotubes of the S22 family appear in the best resonance.

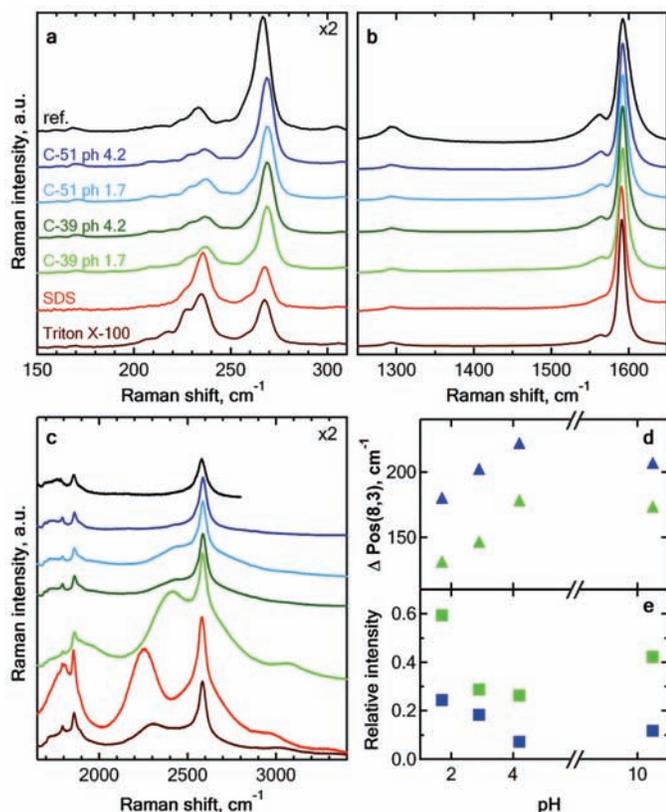


Fig. 2 Raman spectra excited with 785 nm laser of SWNT suspensions with different surfactants and copolymers at two selected pH level (a-c). Plots of (8,3) nanotube fluorescence peak position shift (d) and relative intensity (e) in Raman spectra of C-39-3 (green symbols) and C-51-2 (blue symbols) –SWNT suspension compared to SDS-SWNT suspension.

Figure 2c shows Raman spectra of the same samples in the region between 1800 and 3500 cm^{-1} . The most prominent peak in this region is the 2D band (or G') at 2600 cm^{-1} . However, other, broader bands appear in the spectra. Those bands are not of a Raman scattering origin, but they are fluorescence features of nanotubes with distinct chirality. The most intense one at 2300 cm^{-1} in the spectrum of SDS-SWNT suspension belongs to (8,3) nanotubes. As was documented in [6], the shift and intensity of these fluorescence bands in the Raman spectra may serve as another measure of dispersion quality and individualization of nanotubes. Figures 1d-e plot the variation of the (8,3) band fluorescence position (d) and its relative intensity (e) for the whole investigated pH series of C-51-2 and C-39-3 copolymers with respect to SDS suspension. It may be assumed that the smaller the shift and the higher the relative intensity of this band compared to SDS-SWNT suspension, the better the dispersion quality. Both plots reveal the same trends. Firstly, the band shift is in all cases smaller for C-39-3 suspensions compared to C-51-2 suspensions, as well as the relative intensities of this band are always higher for C-39-3 than for C-51-2 dispersions. This shows a better SWNT dispersion in suspensions produced with C-39-3 copolymer. Secondly, for both copolymers, the dispersion is

the best at the lowest pH of 1.7, then gets lower quality with increasing pH up to 4.2, but at pH of 10.5, the dispersion has approximately the same parameters as at pH 2.5.

We measured Raman spectra of selected samples also in solid state after evaporation. Even though the fluorescence bands are of a slightly lower relative intensity, they are still very pronounced, especially in the case of C-39-3/SWNT sample obtained from suspension at pH 1.7. The presence of this band in the spectra of solid samples evidences the conservation of the debundled nanotubes after evaporation. Again, the band is less intense in spectra of C-51-2/SWNT and decreases with increasing pH.

The quality of dispersion was checked also by monitoring the shifts of optical absorption bands in visible and near-infrared spectral regions. As the bands' positions correspond to transition energies of nanotubes with particular chirality, the amount of their shift again indicates the degree of bundling. We investigated the shifts of six absorption bands between 500 and 750 nm, which are the E_{22} transitions of semiconducting nanotubes with similar diameters to those in Figure 1a. The average red-shift of bands in spectra of C-39-3 suspensions at pH 1.7 compared to SDS suspensions was 3.1 nm, while the bands in C-51-2 suspensions provided an average red-shift of 4.8 nm. These shifts correspond to 7 and 15 meV, respectively.

Conclusions

Individually suspended nanotubes were prepared using block-copolymers under different conditions (pH, state of hydrolyzation) even at very low polymer concentrations (0.1-0.01wt%). Tailoring the copolymers architecture (functional groups, size of individual blocks) allows for their specific utilization in CNT-polymer composite chemistry.

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References

- [1] Dresselhaus MS, Dresselhaus G, Avouris P. Carbon nanotubes : synthesis, structure, properties, and applications. Berlin ; New York: Springer 2001.
- [2] Tasis D, Tagmatarchis N, Bianco A, Prato M. Chemistry of Carbon Nanotubes. Chemical Reviews. 2006;106(3):1105-36.
- [3] Gotzamanis G, Tsitsilianis C. Stimuli-Responsive A-b-(B-co-C) Diblock Terpolymers Bearing Polyampholyte Sequences. Macromolecular Rapid Communications. 2006;27(20):1757-63.
- [4] Weisman RB, Bachilo SM. Dependence of Optical Transition Energies on Structure for Single-Walled Carbon Nanotubes in Aqueous Suspension: An Empirical Kataura Plot. Nano Lett. 2003;3(9):1235-8.
- [5] Dresselhaus MS, Dresselhaus G, Saito R, Jorio A. Raman spectroscopy of carbon nanotubes. Phys Rep. 2005;409(2):47-99.
- [6] Moore VC, Strano MS, Haroz EH, Hauge RH, Smalley RE, Schmidt J, et al. Individually Suspended Single-Walled Carbon Nanotubes in Various Surfactants. Nano Lett. 2003;3(10):1379-82.