Dispersibility and stability improvement of unfunctionalized nanotubes in amide solvents by polymer wrapping

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Abstract

Improvement on the stability and loading of unfunctionalized single wall carbon nanotubes (SWNTs) in amide solvents is necessary to enhance the performances of SWNT-polymer composites used for optical applications (e.g., as non-linear saturable absorbers). We show that polyvinylpyrrolidone (PVP) can not only increase the stability of ultrasonically dispersed HiPco SWNTs in pure N-methyl-2-pyrrolidone (NMP), but also improve the photoluminescence emission signals from SWNTs even after 1 month of incubation. Compared to two non-ionic surfactants (Igepal DM-970 and Pluronic F-98), we find that PVP-aided SWNT dispersions in NMP can improve the SWNT loading by at least four times. Unlike surfactant-aided dispersions, the PVP-aided dispersions remain completely stable by close visual inspection even after 6 months of incubation.
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1. Introduction

Untangling the network of single wall carbon nanotube (SWNT) bundles [1] and controlling the bundle-sizes embedded in polymer matrices is critical for optimal device performance in SWNT-polymer composites for optical applications [2,3]. The most effective way to untangle SWNT bundles is through mechanical [4–13] or chemical [14–16] treatment in a liquid environment. In the first case, powerful ultrasonic treatment with dispersants is generally used to separate SWNTs by means of adsorption of dispersant molecules on SWNT sidewalls without covalent functionalization [4–13]. Covalent functionalization is necessary to prepare SWNT dispersions by chemical means [14–18]. However, disruption of the extended π network due to covalent functionalization causes changes in the absorption spectra of SWNTs in liquid dispersions [14,17], making them unsuitable for optical applications. Preparation of stable and untangled dispersion of unfunctionalized

SWNTs in different solvents is thus critical to widen the use of such composites.

Thus far, aqueous SWNT dispersions were achieved with the aid of ionic and non-ionic surfactants [4–6], water-soluble polymers [6,8] and DNA [19]. Polyvinylpyrrolidone (PVP), a linear polymer, was used to disperse [8] or stabilize [4] SWNTs in aqueous medium by a thermodynamically driven wrapping process of SWNTs by the PVP molecules [8]. Amongst the amide solvents, pure N-methyl-2-pyrrolidone (NMP) can disperse SWNTs [7] with a limit of ≈ 0.01–$0.02\,\text{g/L}$ [9,11]. We have recently shown that SWNT dispersions in pure NMP (SWNT/NMP) even at such low concentrations are thermodynamically unstable. We also reported that PVP can improve the stability of freshly prepared SWNT/NMP dispersions [12].

Here, we show that addition of PVP (molecular weight $\approx 29\,\text{kDa}$) to re-aggregated SWNT/NMP dispersions increases the photoluminescence (PL) signal intensities from the SWNTs. A SWNT/NMP dispersion is first allowed to incubate for 1 month. Decrease in the PL intensities and broadening of emission peaks indicate aggregation of SWNTs [20,21]. Addition of PVP increases

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the PL intensity, which becomes comparable to the freshly prepared dispersion. Moreover, the solutions become more stable and do not form visible aggregates unlike SWNT/NMP dispersions after 2 months of preparation. Finally, we show that PVP-aided unfunctionalized HiPco SWNT/NMP dispersions can be prepared with higher SWNT loading (≈ 0.10 g/L) compared to that of two common non-ionic (Igepal DM-970 and Pluronic F-98) surfactants. Such solution also remains remarkably stable by visual inspection even after 6 months of incubation.

2. Experimental

Dispersions of Purified HiPco [22] SWNTs (lot no. PO279; Carbon Nanotechnologies Inc.) in spectroscopic grade NMP are prepared by ultrasonic treatment (Bioruptor, Diagenode; at 270 W, 20 kHz for 1 h). These are then vacuum-filtered through binder free glass fiber filters. If used, the dispersants (surfactants or PVP) are added before the ultrasonic treatment. We divide the dispersions in three different groups. Each group consists of one or more dispersion aimed to investigate particular properties of SWNT/NMP dispersions. Table 1 lists all of them. To study the effect of stabilization in the SWNT/NMP dispersions with higher concentrations, we use 0.07 g/L as the initial SWNT concentration. This increases the SWNT loading in the filtered dispersion compared to the SWNT loading achieved if 0.03 g/L is used [12]. Note that we observe rapid aggregation of SWNTs just after the sonication process if the initial SWNT concentration exceeds 0.08 g/L. With higher SWNT loading, the shorter mean distance between the SWNTs accelerates the aggregation process. Also, we use very high initial SWNT concentration (0.28 g/L) in group B to compare the dispersion ability of the surfactants and PVP of same molar concentrations (molecular weight of Igepal DM-970 ≈ 7.2 kDa; Pluronic F-98 ≈ 13 kDa) [23]. Note that at such high concentration of SWNTs, the ultrasonicated solutions become difficult to filter because of rapid re-aggregation; which, in turn, reduces the loading of SWNTs in the

filtered dispersions. Additionally, group C contains surfactant-aided and vacuum-filtered SWNTs in D_2O (SWNT/D_2O) prepared by the same ultrasonic treatment as groups A and B. Here, sodium dodecylbenzene sulfonate (SDBS) is used. All the dispersions are sealed and stored at room temperature (21 °C). Unlike what often done in the literature [4–10,13,19], no centrifugation is used.

Absorption spectra are measured using a Perkin-Elmer Lambda 950 spectrometer with 1.3 nm steps. The background from solvent and surfactant is subtracted. Photoluminescence excitation (PLE) spectroscopy measurements are performed in a HORIBA Jobin Yvon excitation-emission spectrofluorometer (Fluorolog-3) equipped with a xenon lamp excitation source and an InGaAs detector (symphony solo) cooled by liquid nitrogen. PLE maps are measured by scanning the excitation wavelength from 500 to 800 nm with 6 nm steps and 60 s exposure for 1050–1350 nm emission range. In all the measurements, the entrance and exit slit widths are 14 nm.

3. Results and discussion

Absorption for samples A1 and C1 is presented in Fig. 1. Prominent excitonic transitions in the latter spectrum point to mostly isolated SWNTs [4,6]. Compared to previous reports on SWNT dispersions in organic solvents involving centrifugation [7,10,11,13], sharper features in the absorption spectra of sample A1 imply superior dispersion [4,20,21]. However, a considerable number of bundles are expected in sample A1 since it is not centrifuged. In addition to dielectric screening [24,25], the presence of bundles [20,21] contributes to the red shift in the absorption spectrum compared to sample C1. For example, we observe a ≈ 10 nm (≈ 24 meV) red shift at 728 nm in the absorption spectra of SWNTs in NMP (A1) compared to SWNTs in D_2O/SDBS (C1), as indicated by the dashed line in Fig. 1. Note that the average diameter of SWNT bundles in sample C1 is lower because of the efficient encapsulation of SWNTs by the SDBS micelles. SWNT concentrations in groups A and B are measured using the

Table 1
Specifications of the dispersions used in this work

Group	Sample	Initial[a] (final)[b] SWNT concentration (g/L)	Composition	Additional information
A	A1	0.07 (0.033)	SWNT/NMP	PLE map taken just after preparation
	A31	–	SWNT/NMP	PLE map taken after 31 days of incubation of A1
	A34	–	SWNT/NMP/PVP	5 g/L PVP added to A31. PLE map taken after three more days
B	B1	0.28 (0.099)	SWNT/NMP/PVP	14 g/L PVP (B1), 3.5 g/L lgepal DM-970 (B2) and 6.27 g/L Pluronic F-98 (B3) used as dispersant
	B2	0.28 (0.026)	SWNT/NMP/Igepal DM-970	
	B3	0.28 (0.015)	SWNT/NMP/Pluronic F-98	
C	C1	0.04 (–)	SWNT/D_2O/SDBS	1.4 g/L SDBS used as dispersant

[a]Estimated instrumental error is within $\pm 10\%$. Values exclude 20% catalysts and impurities present in the pristine sample [12].
[b]The final SWNT concentrations represent the average values calculated from absorption coefficients (α_λ) of SWNTs in NMP at 506, 660, 871 and 1308 nm [12].
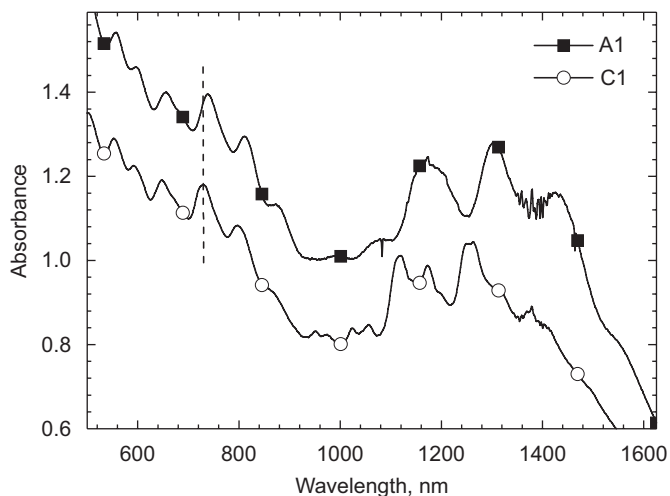
Fig. 1. Absorption spectra of SWNTs dispersed in pure NMP (A1) and in D$_2$O (C1). Background of solvent and surfactant has been subtracted from the spectra.

Beer–Lambert law. The process is detailed elsewhere [12]. Briefly, absorption coefficients (α_λ) of SWNTs in NMP at wavelength λ are determined from a series of unfiltered and ultrasonicated SWNT dispersions of known concentration. The wavelengths (λ) are chosen to match well-defined peaks in the absorption spectra of SWNTs in NMP. The α_λ determined at four different wavelengths (506, 660, 871 and 1308 nm) are then used to estimate the average SWNT concentrations in the filtered dispersions (see Table 1).

PLE can be used to determine the presence of isolated SWNTs or small bundles. Additional exciton relaxation channels exist between adjacent SWNTs in bundles [26]. Consequently, peak PL intensities vary as the bundle sizes change, conveying information on the aggregation dynamics [12,26]. We investigate the stability of samples in group A by monitoring the peak PL intensities in the 500–800 nm excitation and 1050–1350 nm emission ranges. This window covers most of the HiPco SWNT species. Fig. 2(i)–(iii) shows the PLE maps of samples A1, A31 and A34. In comparison to previously reported HiPco SWNT
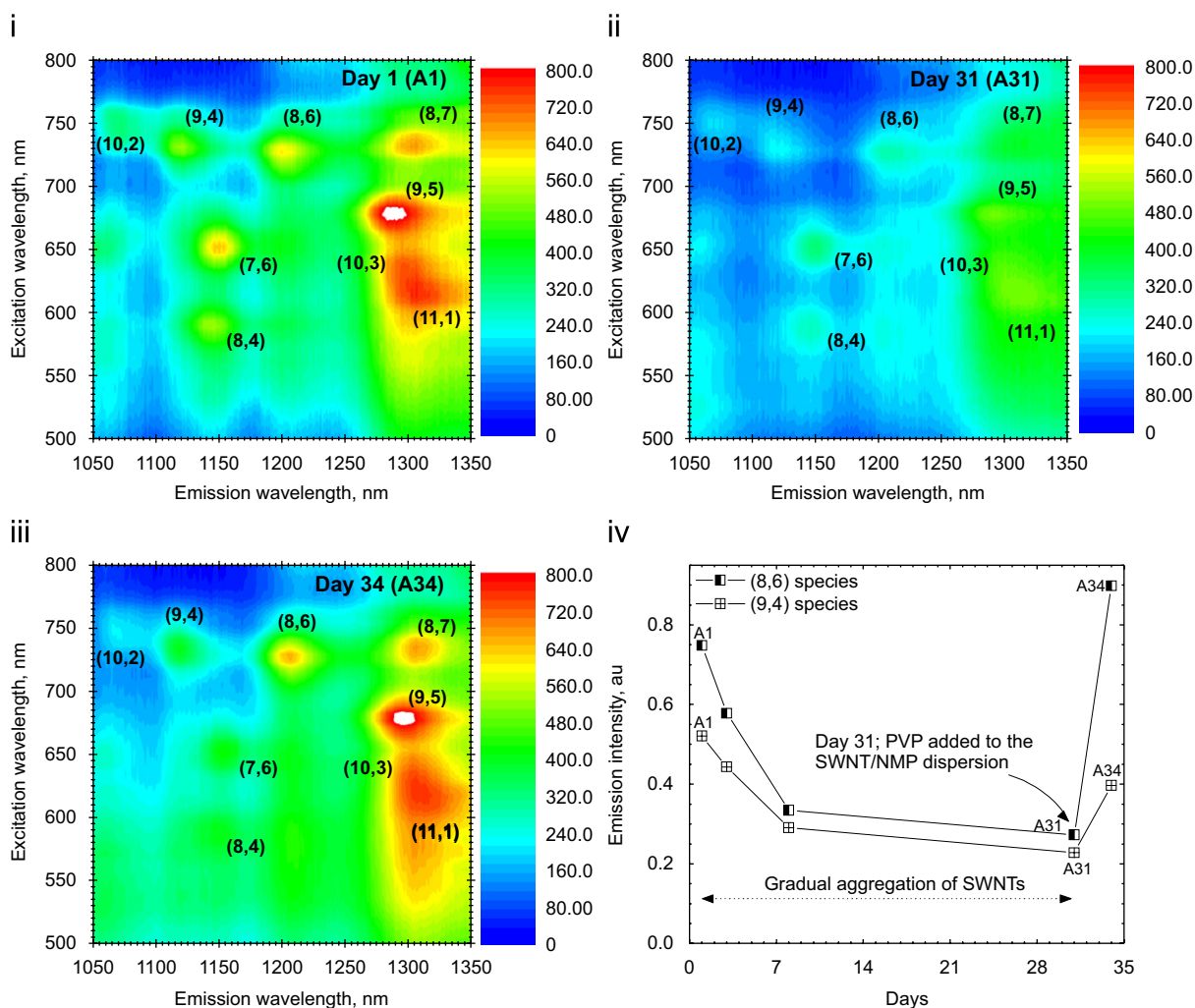

Fig. 2. PLE maps showing the effect of PVP in 'de-bundling' SWNT aggregates: (i) freshly prepared SWNT dispersion in NMP (A1); (ii) the same dispersion after 31 days of incubation (A31) with boarder and reduced PL intensities; (iii) 'de-bundling' of SWNT aggregates by PVP addition (A34); (iv) PL intensities of (8,6) and (9,4) nanotubes of group A dispersions. The three PLE maps are in the same intensity scale.

dispersions in D_2O [27], the map of D1 shows broader and red shifted emission peaks caused by dielectric screening [24,25] and by SWNT bundles [20,21]. Compared to A1, the PLE map of A31 has broadened and red shifted PL peaks with reduced PL intensities, which are both signs of formation of bigger SWNT aggregates after 31 days of incubation of A1 since the composition of A1 and A31 are same. Nevertheless, sample A31 appears aggregation-free by visual inspection. This is expected as we recently reported gradual reduction of PL intensities of SWNT/NMP dispersions of even lower SWNT concentrations (≈ 0.01 g/L) [12]. We hypothesized that similar to aqueous media [4], addition of PVP in SWNT/NMP dispersions might result in a 'competitive' adsorption process between PVP and NMP molecules with the SWNT sidewalls, even though NMP is much less polar than water [28]. Indeed, we observed improved stability of such freshly prepared dispersions by directly adding PVP [12].

Here, after 31 days of incubation, we add 5 g/L PVP to observe the effect on the re-aggregated SWNTs. Remarkably, the PLE map of sample A34 (3 days of incubation after PVP is added to sample A31) shows marked enhancement of PL signals from all the nanotube species and becomes comparable to those of map A1. We believe that the SWNT re-aggregates are 'de-bundled' by PVP molecules. Note that this process does not involve any kind of external agitation and therefore, is spontaneous. We recently reported that addition of PVP in a freshly prepared SWNT dispersion increases the PL intensity of (8,6) species by $\approx 73\%$ after 24 h [12]. Here, we observe that PVP addition to a month-old SWNT/NMP dispersion (A31) increases the PL intensity of the same species by over 300% after 72 h (A34); see Fig. 2(iv). We conclude that such large increase of PL intensity in (8,6) tubes is caused by 'de-bundling'; not because of changes in the dielectric environment. Indeed, if we assumed that changes in dielectric environment were solely responsible for PL intensity increase in Ref. [12], we would expect similar increase for (8,6) tubes from sample A31 to A34. Since this is not the case, it is reasonable to assume that 'de-bundling' of SWNT aggregates by PVP molecules plays a major role in the increase in PL intensities.

Our experimental results indicate that SWNTs prefer PVP to NMP molecules for physical adsorption without any sonication, which, in turn, helps to stabilize the SWNTs dispersed in the solution. The reason for this preference is unclear at present. The difference in change of the PL intensities for (8,6) and (9,4) species in Fig. 2(iv) implies that different nanotubes are affected differently by PVP addition. This is most likely dictated by the diameter [12]. We do not observe any family dependence. We find no evidence of 'de-bundling' or exfoliation of SWNTs when PVP and SWNT powders are simply added to pure NMP, even after 2 weeks at 80 °C, as when SWNT powders are directly added to NMP and subjected to similar treatment. Therefore, this effect is only observed on small SWNT bundles and not in much bigger entangled networks of SWNTs.

We then investigate the effect of PVP on the dispersion of SWNTs in NMP. High starting concentration of SWNTs (0.28 g/L) in NMP is used to compare the SWNT-dispersibility between PVP (B1), Igepal DM-970 (B2) and Pluronic F-98 (B3) of the same molar concentration. Absorbance spectra of the freshly prepared group B dispersions are shown in Fig. 3. PVP can 'disperse and stabilize' higher amount of SWNTs than surfactants as shown in Table 1 and approximately, over one order of magnitude more SWNTs than pure NMP [9,11]. To the best of our knowledge, this is the highest concentration of unfunctionalized SWNT dispersion reported to date when using amide solvents. Note that the SWNT concentrations in B2 and B3 can be increased marginally by using a lower starting amount of SWNTs. This minimizes rapid formation of bigger SWNT bundles just after the sonication process, facilitating the filtration, which, in turn, increases the SWNT loading. However, the stability of B2 and B3 dispersions is very poor compared to that of B1. Fig. 4 shows a photograph of group B dispersions after 10 weeks of incubation. Even though B1 has much higher SWNT loading, it remains completely stable by close visual inspection unlike B2 and B3, both of which form visible aggregations and precipitations. We find that PVP-aided dispersions remain stable for more than 6 months. Stability comparison between B2 and B3 cannot be drawn directly on a long-term basis since SWNT concentrations in these two dispersions are different. However, our results show that the surfactants used here are not suitable for the preparation of stable dispersions of unfunctionalized SWNT in NMP with high loading. PVP is the preferred choice for such instances.
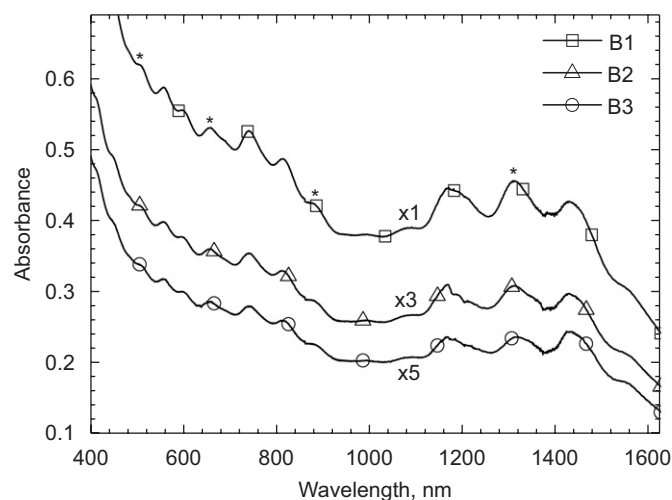

Fig. 3. Absorption spectra of SWNTs in freshly prepared B1, B2 and B3 dispersions after subtraction of solvent and surfactant background. The stars indicate the wavelengths used to estimate the SWNT loading by the Beer–Lambert law [12]. Note that, freshly prepared group B dispersions are diluted eight times during absorption measurements to minimize scattering losses due to high-SWNT concentrations.
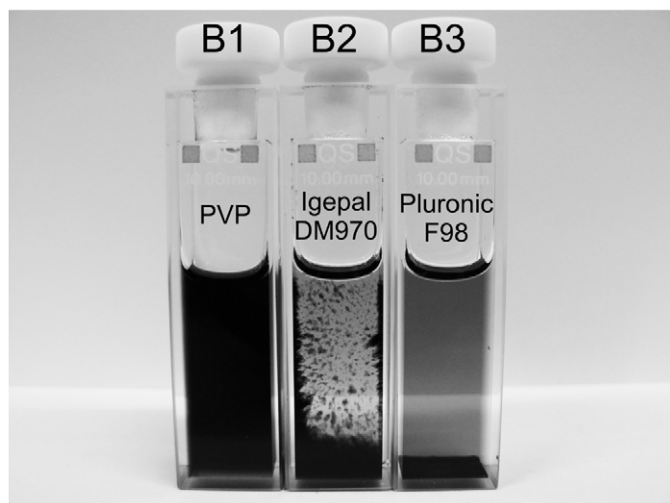
Fig. 4. Photograph of group B dispersions after 10 weeks of incubation. PVP-aided dispersion (B1) with high loading of SWNTs remains completely stable whereas both the surfactants fail to disperse high amount of SWNTs and to stabilize the dispersion (B2 and B3).

4. Conclusions

We demonstrated that re-aggregated HiPco SWNT dispersions in pure NMP can be spontaneously 'de-bundled' by adding PVP without any ultrasonic treatment. Two different non-ionic surfactants (Igepal DM-970 and Pluronic F-98) have no effect in stabilization of SWNT/NMP dispersions. We also show that it is possible to prepare PVP-aided high-concentration and stable dispersions of unfunctionalized SWNTs in NMP by adsorption of PVP molecules on SWNTs. This may provide an impetus in preparation of a variety of SWNT-polymer composites with isolated or sub-micrometer sized SWNT bundles.

Acknowledgements

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