Photopolymerized Lipids Self-Assembly for the Solubilization of Carbon Nanotubes

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Received: February 2, 2010; Revised Manuscript Received: March 23, 2010

Because they have a great propensity to aggregation in water, solubilization of carbon nanotubes (CNTs) in aqueous media remains an important challenge. Our laboratory has reported the self-organization of synthetic lipids into hemi-micellar structures at the carbon nanotubes surface. Subsequent stabilization of these carbon nanotube/lipid assembly (CNT/LA) constructs is achieved through photopolymerization of the diyne motif of the pentacosa-10,12-diynoic lipids. Herein we investigate the scope of this coating procedure for CNT solubilization. A panel of CNTs was selected according to the method of production and the characteristics of CNTs. The study revealed that it is possible to reach a complete lipid adsorption. The TEM analyses demonstrate that lipid hemi-micellar self-assemblies can be formed around SWNTs as well as around DWNTs and MWNTs, particularly for carbon nanotubes produced by the arc-discharged method. The nanotube suspensions show a very good stability and are homogeneous for months even at a high nanotubes concentration.

I. Introduction

Since their discovery by Iijima,[1] carbon nanotubes (CNTs) have been widely studied. Carbon nanotubes are promising materials in many applications. For instance, their electrical properties,[2−4] especially their semiconducting potential, make them the component of choice for nanoelectronics. Also, their thermal and mechanical behaviors make them very attractive for applications in polymers and polymeric nanocomposites reinforcement.[5−7]

The realization of these prospects into industrial products is still hindered by many technical hurdles such as purification and separation according to their physical properties or morphologic characteristics.[8,9]

Among these drawbacks, CNTs solubilization in aqueous media remains a challenge on which several research teams are actively working. In fact, driven by hydrophobicity and π-stacking interactions carbon nanotubes have a great propensity to aggregation in water. To improve CNTs solubility, researchers have investigated their functionalization with hydrosoluble groups through formation of either covalent[10−12] or non-covalent[13,14] bonds. The first approach (covalent modification of CNTs) usually implies acid treatments to create carboxylic acids at the surface, which can then be further modified. The major weakness of this method appears to be the modification of CNTs properties, especially concerning their mechanic and electrical behavior. The second approach (wrapping CNTs with amphiphile molecules) can be performed with a wide variety of surfactants,[15−20] as well as polymers[21,22] or biomolecules,[23−25] but these associations are usually less stable.

Our laboratory has reported an alternative two-step strategy based on first the self-organization of synthetic lipids into hemi-micellar structures at the carbon nanotubes surface[26] and subsequent stabilization of these CNT/LA (carbon nanotube/lipid assembly) constructs through photopolymerization of diyne groups beard by the lipids. Further extraction of the photopolymerized lipid assemblies (PLAs) from the nanotubes affords unique nanosized objects which allowed the solubilization of hydrophobic compounds such as rylenes, fullerenes, or membrane proteins in aqueous media.[27] We observed that CNT-PLA constructs showed extremely good solubility and stability. Recent results showed that CNT-LA constructs could serve as platforms for further nano device elaboration, i.e., CNT/metal nanohybrids[28] and bionanomaterials with specific lectin affinity[29] (Figure 1). Prompted by these results, we decided to investigate in more detail the scope of our CNT-coating procedure for various types of CNTs and the solubilization properties of the resulting constructs.

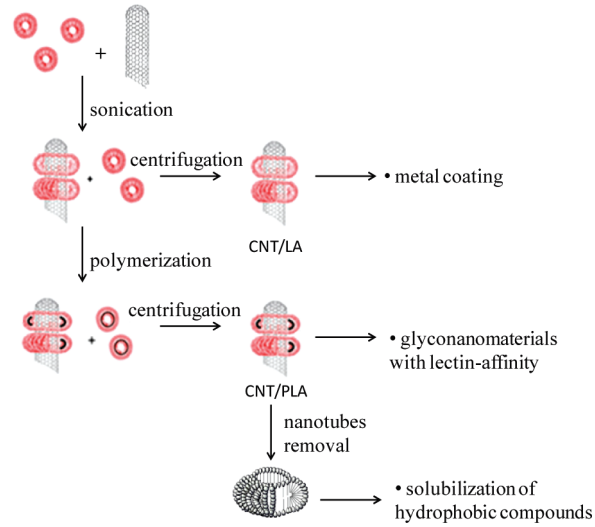

Figure 1. Formation of nanotubes coated by lipid assemblies and their further applications.

II. Experimental Methods

II.1. CNTs Used. A representative panel of eight commercial CNTs was selected, according to their method of production and their characteristics (SWNTs, DWNTs, MWNTs). Two

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10.1021/jp1010007
Published on Web 04/09/2010

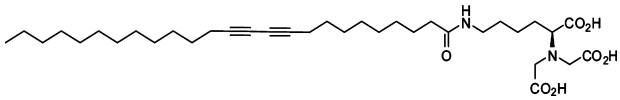

Figure 2. Chemical structure of lipid **1**.

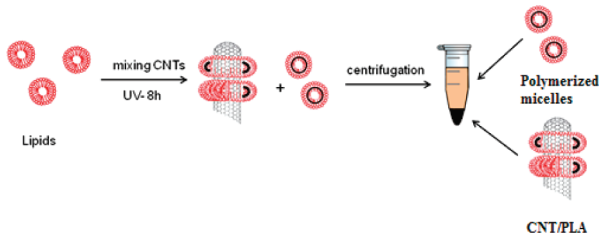

Figure 3. General process for the adsorption study: lipid and CNTs are mixed together by sonication in Tris buffer, the mixture is then polymerized under UV irradiation, and coated nanotubes are separated from the remaining micelles in solution by centrifugation. Finally, the UV−visible spectroscopy of the supernatant allows us to know by difference the lipid amount coating the CNTs.

SWNTs samples (non-purified and purified Mer) and 1 MWNTs sample (from n-Tec) were selected from the arc discharge preparation. The SWNTs Mer were purified in the laboratory by ultrasonication followed by size exclusion chromatography.[30] Also, 2 DWNTs samples (from Aldrich and Nanocyl) and 3 MWNTs samples (from Nanocyl, Sunnano and Arkema) were selected from CVD preparation. Noteworthy characteristics in terms of nanotubes diameter and impurities identification of commercially available CNTs are usually not well-defined. These impurities can be amorphous carbon and/or metal catalyst particles in various and nonsystematically specified amounts. For the present study, CNTs were used as furnished and we will consider the mass of the samples as if they were composed only of CNTs.

II.2. Lipid Used. To probe the scope and efficiency of the adsorption of lipid on the selected CNTs, we used the previously described photopolymerizable lipid **1** (Figure 2). This lipid was formed by peptidic coupling between the pentacosa-10,12-diynoic acid and an amino nitrilotriacetic acid derivative.[27]

II.3. Procedure of Suspension Carbon Nanotubes. A standardized protocol was applied starting from each CNTs source. The lipid (25 mg) was solubilized in Tris buffer (pH 8, 5 mL) by sonication in a bath (80 W during 30 min) forming spherical micelles. To the resulting solution were added carbon nanotubes (25 mg) and then the mixture was submitted to sonication (80 W during 30 min), allowing efficient dispersion. Polymerization under UV irradiation (254 nm, 48 W) stabilized the self-assemblies around nanotubes and polymerized the excess of lipid forming micelles (Figure 3). A model study on amphiphile **1** micelles in solution revealed a complete polymerization after 8 h of UV irradiation (see the Supporting Information). As a consequence, 8 h of irradiation was chosen to ensure an efficient polymerization of nanoconstructs. The separation between coated nanotubes (CNT/PLA) and remaining lipid in solution was done by centrifugation at 14250*g* for 10 min. The supernatant was removed, Tris was added, and the resulting mixture was centrifugated again for 10 min at 14250*g*. The operation was repeated twice; the final supernatant was filtered on a 0.45 μm membrane to eliminate residues of CNTs and studied by UV−vis absorption to titrate the non-adsorbed lipid in the experiment.

II.4. UV and TEM Measurements. After UV irradiation, lipids on carbon nanotubes and in solution are entirely photopolymerized. To titrate the non-adsorbed polymerized lipid in supernatant, the solution was diluted 10-fold and UV−visible

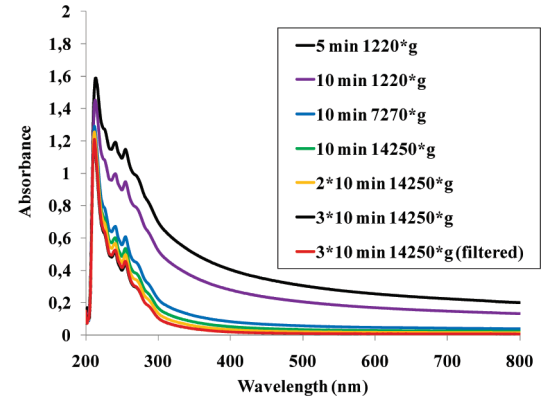

Figure 4. Influence of the centrifugation for the decantation of the CNT/LA constructs (n-Tec MWNTs in a 5 mg/mL concentration) and lipid (5 mg/mL) in Tris. UV−visible spectra of supernatants reveals the presence of CNTs in the supernatants when the centrifutation is moderate. Several cycles of centrifutation are necessary to eliminate the total amount of solubilized nanotubes and to obtain only the lipid.

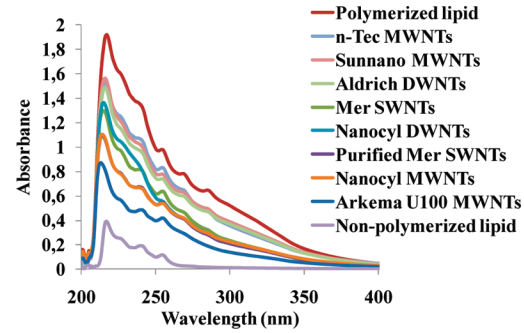

Figure 5. UV−visible spectra of lipid supernatants for the different samples of CNTs. The spectrum of polymerized lipid is used for 0% adsorption reference.

spectroscopy was realized at 285 nm, the wavelength where the photopolymerized lipid had a significant absorbance. The absorbance difference between a control sample in the absence of CNT and the supernatants produced in our assay thus indicates the amount of lipid adsorbed on nanotubes. The adsorption spectra were recorded with a Shimadzu UV-1800 spectrophotometer.

The TEM images of coated CNTs in aqueous media were taken after the removal of the lipid excess. After centrifugation, the sedimentated carbon nanotubes were separated from the aqueous solution and resuspended in a Tris buffer. A drop of sample is disposed on a carbon grid, dried, and stained with uranyl acetate. The TEM images were done with a Philips CM 120 microscope.

III. Results and Discussion

After mixing amphiphile **1** and carbon nanotubes followed by the photopolymerization, the resulting suspension seems very stable. Even after a centrifugation at 14250*g* during 10 min, some nanotubes are still suspended in solution. As shown on Figure 4, 3 cycles of centrifugation are necessary to remove completely the CNT/PLAs from the sample. Consequently, we used this protocol to execute the accurate titration of the non-adsorbed lipid. These preliminary observations of the remarkable stability of the suspension highlighted the efficiency of the coating to solubilize CNTs in an aqueous media.

According to Figure 5 and Table 1, the experiments of titration are realized with all nanotubes samples. Although the

TABLE 1: Lipid Adsorption on CNTs Calculated by Absorption Difference at 285 nm between the Initial Amount of Lipid and the Remaining Amount in the Supernatant

Mer SWNTs	purifiedMer SWNTs	Aldrich DWNTs	Nanocyl DWNTs	Nanocyl MWNTs	n-Tec MWNTs	Sunnano MWNTs	Arkema U100 MWNTs
50%	60%	28%	55%	55%	27%	24%	64%

lipid was adsorbed onto all nanotubes studied, its amount was clearly dependent on the nanotubes source. There was no evident correlation between CNT type (SWNTs, DWNTs or MWNTs) and absorbance capacity. For example, 55% of the starting lipid was adsorbed on DWNTs as well as on MWNTs, both Nanocyl samples. Also, the sample produced by CVD technique showed different behavior when purchased from different suppliers: the adsorption increased from 24% for Sunnano MWNTs to 64% for Arkema MWNTs. The purity of the nanotubes influenced the adsorption but not as much as anticipated. For raw Mer SWNTs (content in CNTs lower that 20% in weight from the supplier data), 50% of the lipid was adsorbed whereas only 60% coated the nanotubes surface of the purified Mer SWNTs, which contains more than 95% of SWNTs. Since the increase in lipid adsorption was not proportional to the nanotubes purity, partial adsorption on amorphous carbon residues probably occurred. Finally, the highest adsorption result was found to be 64% with Arkema U100 MWNTs. Thus, it seems that our process can be generally applied to a large range of nanotubes. However, strong differences in the proportion of lipid adsorbed on the various nanotubes were observed.

With these results in hand we decided to conduct a systematic study in order to analyze four representative nanotubes at various lipid/CNT ratios. The procedure described above was applied to purified Mer SWNTs, n-Tec MWNTs, Aldrich DWNTs, and Arkema U100 MWNTs. In these experiments, the starting concentration of lipid was fixed at 5 mg/mL and the amount of nanotubes varied from 0.5 to 30 mg/mL. Above this concentration in CNTs, the suspensions were too viscous to be properly studied. After polymerization and three centrifugation cycles, the supernatants containing the non-adsorbed lipids were analyzed at 285 nm. The results are expressed, as above, in percent of adsorbed lipids and are presented in Figure 6.

As expected, all samples showed the same general trend: the more nanotubes that were added, the more lipid was adsorbed. Again, Arkema U100 MWNTs displayed the highest adsorption values, and only by using these CNTs was the complete adsorption of lipids observed for a 1/4 lipid/CNTs weight ratio. Titrations by HPLC (before lipid polymerization) showed the same results (see the Supporting Information). At a 1/6 ratio, Aldrich DWNTs and purified Mer SWNTs had the similar lipid adsorption capacity. However, the SWNTs sample globally displayed higher adsorption values. The dislocation of bundles was probably promoted when the lipid was used in excess; as a consequence, for the same weight amount, SWNTs could afford a larger available surface for lipids adsorption than DWNTs or MWNTs. For n-Tec MWNTs, a maximum in the 55% of lipid adsorbed seemed to be reached for a 1/4 ratio.

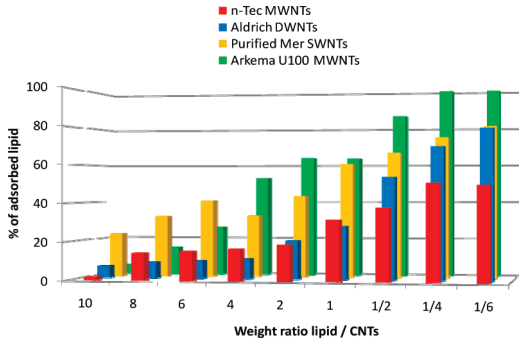

Figure 6. Lipid adsorption for different lipid/CNT ratios.

We further studied the self-assemblies of CNT/PLA by TEM. Surprisingly even though all samples appeared to be stable suspensions of CNTs in aqueous solution, we collected two distinct kinds of TEM images. In the first series, regular striations were visible at the surface of CNTs. These hemimicellar arrangements are obtained for Aldrich DWNTs (Figure 7b), n-Tec MWNTs and Arkema U100 MWNTs (Figure 7d). For purified Mer SWNTs (Figure 7a), the diameter of self-assemblies seemed larger than expected, probably because of the formation of small bundles of SWNTs. For the others (nonpurified Mer SWNTs, Nanocyl DWNTs, and MWNTs (Figure 7c), MWNTs Sunnano), these striations were not present even though some lipid was observed on CNTs. In the cases where self-assemblies were formed on nanotubes, we observed that their width varied from 10 to 12 nm for SWNTs up to 30−35 nm for some MWNTs. In contrast, the thickness of the lipid layer on the CNTs surface was fixed (8−9 nm) for all nanotubes, corresponding as expected to twice the length of one lipid. In summary, a correlation between the amount of adsorbed lipid on CNTs and the formation of self-assemblies seemed to be difficult. However, it appeared that the shape of the nanotubes and more particularly their curvature had an influence on the lipid adsorption phenomenon (random adsorption or hemimicellar arrangements). The more nanotubes that were rectilinear the more the self-assemblies were easy to visualize as was the case for n-Tec MWNTs and purified Mer SWNTs. The arc-discharge method, furnishing more rectilinear CNTs, seemed to be more appropriated for a clear and nonambiguous self-assemblies formation.

Finally we evaluated the outcome of the coating procedure in terms of stability of the resulting suspensions of CNT/PLA

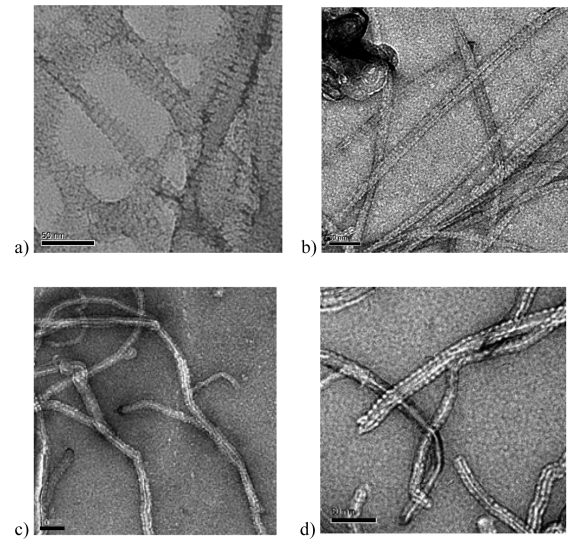

Figure 7. TEM images of coated CNTs in aqueous media after removal of the lipid excess: (a) purified Mer SWNTs, (b) Aldrich DWNTs, (c) Nanocyl MWNTs, and (d) Arkema U100 MWNTs. Scale bar = 50 nm. Samples were dried and stained with uranyl acetate.

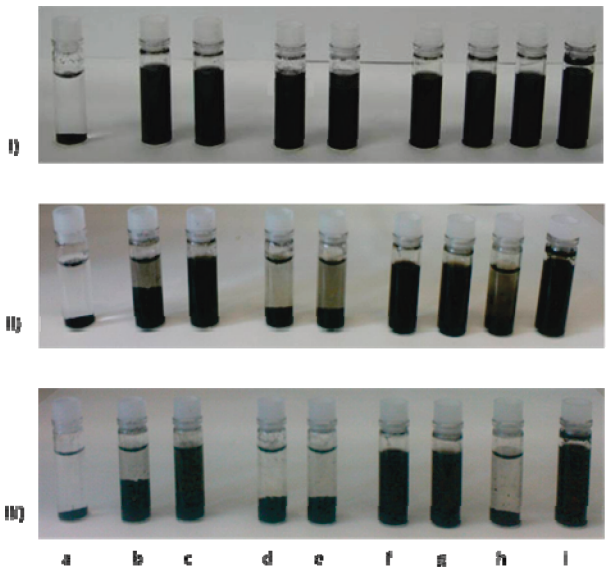

Figure 8. Pictures of the suspensions of CNT/PLAs after removal of lipid excess after (i) 1, (ii) 10, and (iii) 30 days: (a) example of CNTs (n-Tec MWNTs) without lipid **1**; (b) Mer SWNTs; (c) purified Mer SWNTs; (d) Aldrich DWNTs; (e) Nanocyl DWNTs; (f) Nanocyl MWNTs; (g) n-Tec MWNTs; (h) Sunnano MWNTs; and (i) Arkema U100 MWNTs.

TABLE 2: Conclusion on CNTs Behaviors

entry	CNTs	lipid adsorption	TEM	suspension stability
1	control	/	/	− − −
2	Mer SWNTs	+ + −	+ − −	+ + −
3	purified Mer SWNTs	+ + −	+ + +	+ + +
4	Aldrich DWNTs	+ − −	+ + +	+ + +
5	Nanocyl DWNTs	+ + −	+ − −	+ + −
6	Nanocyl MWNTs	+ + −	+ − −	+ + +
7	n-Tec MWNTs	+ − −	+ + +	+ + +
8	Sunnano MWNTs	+ − −	+ − −	+ + −
9	Arkema U100 MWNTs	+ + +	+ + −	+ + +

constructs. After removal of the lipid excess by centrifugation, coated CNTs were suspended at 5 mg/mL in Tris buffer. The sedimentation of CNTs was visually observed over a period of 3 months. After 1 day, all suspensions appeared to remain stable (Figure 8i). Noteworthy native CNTs precipitated after a few minutes, thus illustrating the huge difference between naked CNTs and coated CNTs. After 10 days (Figure 8ii) the purified Mer SWNTs gave a stable suspension whereas nonpurified Mer SWNTs precipitated, probably promoted by the large amount of impurities (samples b and c). DWNTs samples did not afford homogeneous suspensions after 10 days (samples d and e, Figure 8ii). Concerning MWNTs, only the Sunnano sample was not stable over 10 days (sample h, Figure 8ii). For all other samples, suspensions were stable. After 30 days, differences between samples were accentuated (Figure 8iii). For the CNTs samples which had led to a deposit after 10 days, the supernatants were found to be clearer after 1 month thus we can assume that the majority of nanotubes were precipitated (samples b, d, and e, Figure 8iii). The observation was the same for the Sunnano CNTs sample (sample h). For purified Mer SWNTs, Nanocyl MWNTs, n-Tec MWNTs, and Arkema U100 MWNTs, samples are still stable after 3 months.

To summarize this study and get a clear overview on all the different assays, results are summarized in Table 2. The signs + + + correspond to best results, + + − to excellent results, + − − to good results, and − − − to control experiment without lipid.

This overview shows that no obvious correlation could be drawn between the amount of adsorbed lipid on CNTs and the formation of self-assemblies as highlighted by entries 4 and 9. Moreover there is no clear relationship between the stability of the suspension and the amount of lipid adsorbed (entries 7 and 9). Thus, it seems that to some extent our process enabled us to drastically improve CNTs solubilization, albeit each nanotube being a particular case. Reaching very high solubility and stability for each specific CNTs might require fine tuning of lipid and polar head structure.

IV. Conclusion

In conclusion, and to the best of our knowledge, these results represent the first comparative study on the solubilization of different kinds of CNTs in various conditions. However, the rationalization concerning the different aspects developed in this paper is tricky and the behavior of nanotubes cannot be easily predicted in such solubilization experiments. Lipid **1** hemimicellar self-assemblies can be formed around SWNTs as well as around DWNTs and MWNTs, particularly for carbon nanotubes produced by the arc-discharged method. The study at different CNT/lipid ratios revealed that it was possible to have a complete lipid adsorption, especially at the surface of Arkema U100 MWNTs. Some of the nanotubes suspensions obtained showed a very good stability and were homogeneous for months even at a high nanotubes concentration (up to 30 mg/mL for the 1/6 ratio, i.e. 3% wt), which opens good opportunities for material reinforcement. Finally we could demonstrate that our strategy of polymerizing a lipid shell around CNTs is a general procedure that could be successfully applied to a whole range of CNTs comprising SWNTs, DWNTs, and MWNTs.

Lipid **1** permits the solubilization of CNTs in basic solution; our next challenge will be to tailor the lipid to provide CNT/PLA constructs with pH-specific solubilization properties. This study will be reported in due course.

Acknowledgment. This research was conducted with financial support from GlaxoSmithKline Les Ulis, the region of Alsace, the CNRS, and from ANR. The authors also thank Jean-Roger Desmurs for scientific discussions and for carbon nanotubes furnished.

Supporting Information Available: Photopolymerization study, lipid titration by HPLC, and TEM images of carbon nanotubes covered by photopolymerized lipid assemblies. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP1010007