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Dispersion of multi-walled carbon nanotubes in an aqueous medium by water-dispersible conjugated polymer nanoparticles†

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Vertically aligned multi-walled carbon nanotubes (MWCNTs) synthesized by the alcohol catalytic CVD (ACCVD) technique are dispersed in water with the aid of water-dispersible conjugated polymer nanoparticles (CPNs). The interactions between CPNs and CNTs are studied with spectroscopy (UV-Vis, fluorescence and Raman) and electron microscopy techniques are used to confirm attachment of CPNs to the CNT sidewalls.

Carbon nanotubes (CNTs) are highly versatile materials with interesting mechanical and electrical properties and having wide application in the optoelectronics (*e.g.* LED and photovoltaic) and biomedical areas.[1] However, the most important problem associated with CNTs is the solubility due to bundling caused by van der Waals interactions of carbon nanotube walls. Thus, it is important to solubilise carbon nanotubes using appropriate methods in order to expand their application areas.

Solubilisation can be realized by functionalization of the surface of the carbon nanotubes *via* covalent attachment of the suitable functional groups or by non-covalent interactions between the CNT surface and proper dispersants.[2] Among many non-covalent solubilisation approaches, the use of conjugated polymers as dispersants is getting increasing attention because while this approach helps keep the good electrical and mechanical properties of CNTs untouched, unique electrical and optical properties can be created in CNTs *via* conjugated polymers (CPs).[3] Thus, through functionalization a new composite material with controllable properties can be synthesized which can potentially find applications in many important areas such as LED, photovoltaic and biomedical applications.[1]

Depending on the conjugated polymer used as dispersant agent, the resultant CP/CNT composite system can be made dispersible in organic solvents or in water. While conjugated polymers are not very efficient in solubilising CNTs in water, even incremental advances in this regard may be considered a significant step towards enabling widespread usage of CNTs, especially in biomedical applications, if good water solubility can be achieved through CP/CNT composite systems.

To this end, we designed a new strategy to achieve good water dispersibility of carbon nanotubes and obtain CP/CNT composite materials. In this approach, first a hydrophobic and non-wat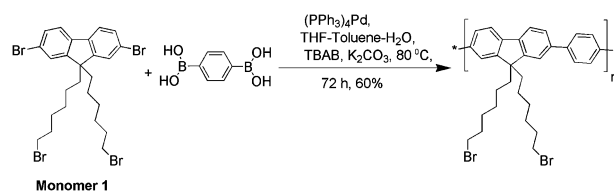er soluble conjugated polymer was converted into water dispersible nanoparticles and then the dispersion of carbon nanotubes in water with the aid of these conjugated polymer nanoparticles (CPNs) was achieved. The sizes of the CPNs were determined by dynamic light scattering (DLS) measurements and confirmed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). During TEM analysis of CPN/CNT interaction energy-dispersive X-ray spectroscopy (EDX) was also used to confirm the presence of bromine in the polymer nanoparticles. Further characterisation to provide clues regarding the interaction between CPNs and CNTs was done by spectroscopic techniques (UV-Vis, fluorescence and Raman).

Poly[9,9-bis-(6′-bromohexylfluorene-2,7-diyl)-*co*-(benzene-1,4-diyl)] (PFB-B) is synthesised by the Suzuki coupling reaction of monomer 1[4] and phenylenediboronic acid following the reaction in Scheme 1.

PFB-B is characterized by spectroscopic methods (^{1}H-NMR, UV-Vis, and fluorescence) and its molecular weight is determined by gel permeation chromatography (GPC). Its number average molecular weight is calculated as 1.4×10^4 Da with polydispersity index of 2.3.

We prepared conjugated polymer nanoparticles in two different sizes using the re-precipitation method.[5] This method involves the dissolution of the polymer in a good solvent (*e.g.* THF) and injecting the polymer solution in a poor solvent (*e.g.* water) for the polymer and subsequent rapid stirring of the dispersion *via* ultrasonication. After the removal of the good solvent, nearly spherical nanoparticles are obtained. The size of the nanoparticles can be tuned by varying the concentration of the polymer and the volume of the poor solvent used. The average sizes of the nanoparticles were determined first by DLS as ∼70 nm and ∼40 nm average sizes as shown in Fig. 1.

After the synthesis and characterization of nanoparticles, we set out to investigate their interactions with CNTs. For this purpose we used vertically aligned multi-walled CNTs[6] grown in our laboratory using the ACCVD technique. The reason for using vertically aligned CNTs was that because of the growth technique utilized the CNTs produced have a very tight diameter and length distribution.[7] The CNTs synthesized using this technique have a very tight diameter

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† Electronic supplementary information (ESI) available: Experimental details, SEM image of pristine CNTs dispersion in water, TEM image of CPNs and EDX spectra of CPNs. See DOI: 10.1039/c0cc00510j
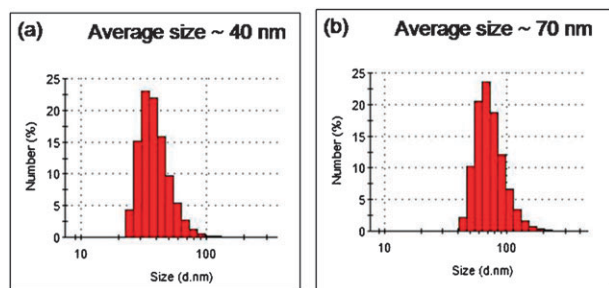

Scheme 1 Synthesis of poly[9,9-bis-(6′-bromohexylfluorene-2,7-diyl)-*alt co*-(benzene-1,4-diyl)] (PFB-B).

Fig. 1 Histograms for 40 nm (a) and 70 nm (b) CPNs measured by DLS.

and length distribution, and also don't require further purification.[7] Vertically aligned CNTs grown on Si (100) substrates (10 × 10 mm with a CNT density of $1 \times 10^{10}/\text{cm}^2$) were then immersed in a vial with CPN–water dispersion. The contents of the vial were sonicated for about an hour. As a control, CNTs were also sonicated in a vial only with water.

As shown in Fig. 2a, upon introduction of CNTs the colour of the CPN–water dispersion in the vial turns greyish indicating good dispersion. Good dispersion can be achieved with a minimum mass ratio of 0.2 for CPN to CNT demonstrating that CPN is a remarkably efficient dispersant for CNTs in water. The highest CNT concentration of stable dispersions is found to be around 0.25 mg mL^{-1} using 0.2 : 1 polymer to CNT mass ratio. Although some precipitation can occur after 12 h, dispersions could be restored after a few minutes of sonication. We also noticed that CPNs with average size of 40 nm are better dispersants than the CPNs with larger average size; while we are further exploring this aspect, our initial findings indicate an interplay between CNT radius and CPN size.

The interaction between CPNs and CNTs was first investigated by UV-Vis and fluorescence spectroscopies. Fig. 3a shows the UV-Vis spectra of 40 and 70 nm-sized CPNs in the presence and absence of CNTs in water. Absorption spectra did not indicate a significant change suggesting that the electronic structure of the nanoparticles was not altered upon complexation with CNTs. CPNs in water exhibit a strong fluorescence emission at 421 nm. After dispersing the CNTs using 40 and 70 nm-sized CPN–water dispersions, some quenching in the fluorescent emission of the dispersions was observed; 25% and 10%, respectively. This is probably due to energy transfer (Fig. 3b) which seems to be more efficient with smaller CPNs (40 nm) than the larger CPNs (70 nm) suggesting the interaction between 40 nm-sized CPNs and CNTs to be relatively stronger.
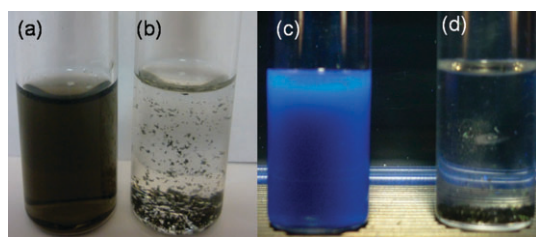

Fig. 2 Images of CPN (40 nm-sized)–CNT with 0.2 : 1 CPN to CNT mass ratio (a, c) and CNT–water dispersion (b, d) under ambient (a, b) and UV-light irradiation (c, d).
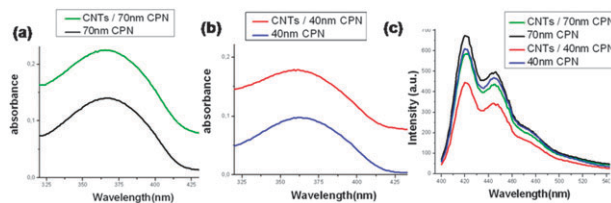

Fig. 3 The UV-Vis absorption (a, b) and emission spectra (c) of 40 and 70 nm-sized CPNs in water and CPN–CNT dispersions.

Raman spectroscopy was also used to examine the interaction between CNTs and CPNs. The first-order Raman spectra from pristine CNTs dispersed in water and CPN–CNT mixtures are given in Fig. 4 and related numerical data are provided in Table 1. The CNTs dispersed in water show all of the expected first-order structures, namely D, G, and D′ bands. The origins for the first-order bands in CNT Raman spectra have been reviewed in detail recently.[8] The intensity ratio of the G band versus the D band, I_G/I_D can provide important clues regarding the defectiveness of CNTs, as the intensity of the D band is generally considered to be directly proportional to the defect density in the hexagonal carbon network of CNTs.[9] In our study, we found that CPN–CNT mixtures indicated markedly lower I_G/I_D ratios than CNTs dispersed in water, as shown in Table 1. A similar behaviour has been reported by Patole et al.[10] for polystyrene attached CNTs where saturation of the dangling bonds in the hexagonal network has been offered as an explanation. Lower D band intensities and the disappearance of the D′ band for CPN–CNT mixtures as shown in Fig. 4 also suggest that the CPN/CNT interaction induced changes in the CNTs surface. We have also observed a small shift of the G band to higher frequency for CPN–CNT mixtures, which is also consistent with the interaction of polymer with CNT surface.

We have investigated the interaction between CPNs and CNTs using electron microscopy techniques, as well. SEM images in Fig. 5a and b clearly show CPN covered CNTs for both sizes of CPN–CNT dispersions. These images also show that the majority of CNTs are de-bundled, while SEM images from CNTs dispersed in water show bundled CNT layers (See ESI, Fig. S3). Furthermore, the dispersion of CNTs and
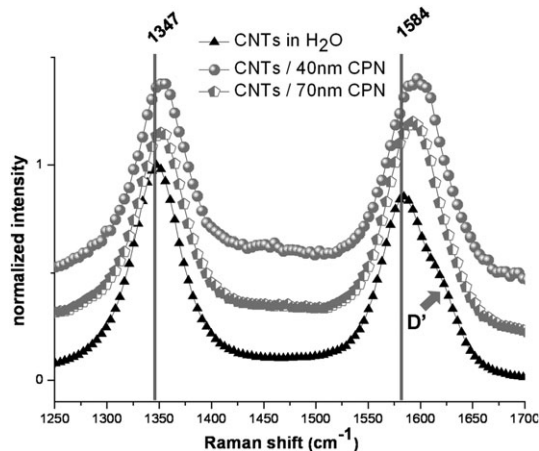

Fig. 4 The first-order Raman spectra from pristine CNTs dispersed in water and CPN–water dispersions.

Table 1 Numerical data regarding Raman spectra analysis

	D peak position/cm^{-1}	G peak position/cm^{-1}	Δ(G–D)/cm^{-1}	I_G/I_D
A	1347	1584	237	0.7
B	1352	1593	241	0.8
C	1356	1597	241	1.0

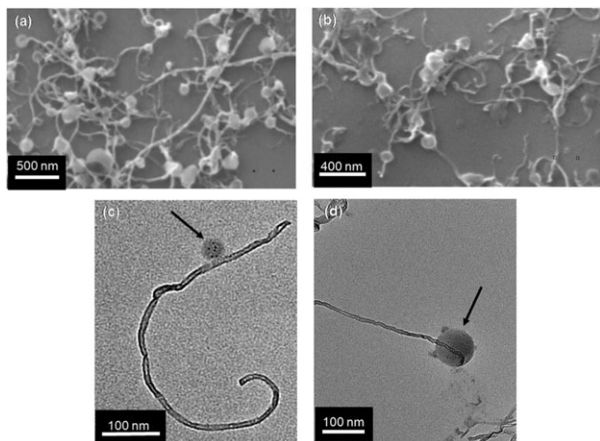A: Pristine CNT in water; B: CNTs/70 nm CPNs; C: CNTs/40 nm CPNs.

Fig. 5 40 nm (a) and 70 nm (b) CPNs attached to CNTs imaged by SEM; 40 nm (c) and 70 nm (d) CPNs by TEM.

the attachment of CPNs on nanotube surfaces were examined by TEM, as shown in Fig. 5c and d. EDX analysis clearly revealing the presence of bromine in nanoparticles attached on CNTs confirms CNT–CPN interaction (See ESI, Fig. S4). Overall, our data suggest an adequately strong and stable molecular interaction between the CPNs and CNT walls, most likely π–π stacking interactions between the polymer aromatic backbones and carbon nanotube side-walls as well as due to the hydrophobic effect. We are continuing our efforts to provide more detail regarding this interaction using techniques such as advanced electron microscopy and first principles density functional theory calculations.[11]

In conclusion, we demonstrated that CNTs can be debundled and then dispersed in aqueous media in the presence of non-ionic conjugated polymer nanoparticles. Data gathered from spectroscopic and microscopic techniques evidently confirm the interaction of CPNs with CNTs. The optical properties of CPNs are not significantly altered upon complex formation indicating further that the interactions between CPNs and CNTs are non-covalent interactions. This feature can be advantageous for many applications such as light emitting diodes, bioimaging and biosensing.[12]

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6 From this point on in the text, CNT abbreviation is used to denote multi-walled CNT.

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