Polymer Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Full Paper

Surface Modification of Carbon Nanotubes via Combination of Mussel Inspired Chemistry and SET-LRP

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

An efficient and facile strategy was developed for surface modification of functional carbon nanotubes (CNTs) via combination of mussel inspired chemistry and single electron transfer living radical polymerization (SET-LRP). This method involves the dopamine (DA) formation of polydopamine (PDA), which was coated on the surface of pristine CNTs via self-polymerization in alkaline solution. And then, the Br-containing initiator was covalently attached on the surface of CNTs modified with PDA. Afterward, the poly[poly(ethylene glycol) methyl ether methacrylate] (PPEGMA) was in situ growing on the surface of Br-containing CNTs via SET-LRP method. The resulting functional materials were characterized by a series of characterization techniques. It was demonstrated that PPEGMA chains were successfully conjugated to the surface of CNTs via combiantion of mussel inspired chemistry and SET-LRP. After modifying with PPEGMA, the functional CNTs remain the pristine structure, however their dispersibility was significantly improved in polar and nonpolar solution. As compared with previous methods, this strategy developed in this work is rather simple and effective. More importantly, due to the universality of mussel inspired chemistry, the novel strategy could also be used for surface modification of many other materials.

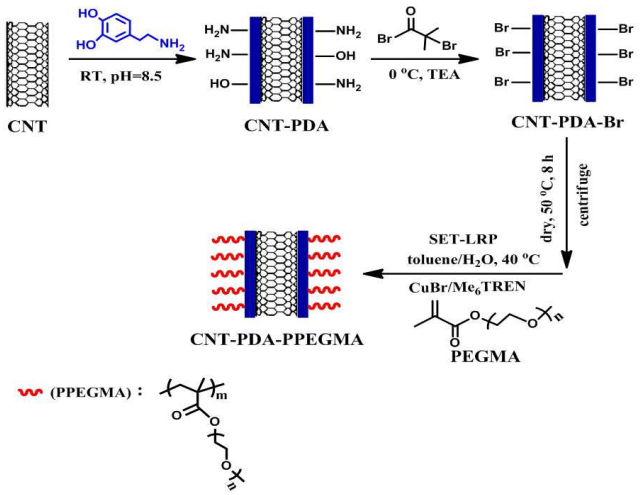
1. Introduction

Carbon nanotubes (CNTs) have led to the development of new nanotechnology because of their outstanding electronic, mechanical and thermal properties. They have been extensively explored for different applications in the fields such as nanocomposite filler, field emission displays, biomedical materials, energy storage and nano-electronics.[1-11] However, the pristine CNTs are difficult to be dispersed in all solvents due to the strong hydrophobic interaction between the individual CNTs. A number of strategies have been developed for surface modification of CNTs in order to achieve their full performance.[12-16] Among them, surface initiated polymerization has demonstrated to be efficient method for surface modification of CNTs. To date, a variety of polymers have been covalently attached on the surface of CNTs via surface initiated polymerization such as atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer polymerization (RAFT) and nitroxid-mediated radical polymerization (NMP).[17-26] Although great success of surface polymerization has been made over the past few decades, the CNTs should be first oxidized by hazardous oxidants such as concentrated sulfuric acid and nitric acid to introduce functional groups on the surface of CNTs.[27-29] These functional groups can be further reacted with polymerization initiators, which can be used for introduction a series of polymers on the CNTs via different polymerization methods. However, these polymerization strategies are based on the oxidation of CNTs, which will inevitably destroy the structure of CNTs and influence their physicochemical properties. Therefore, development of novel and efficient polymerization strategies is still of great research interest.

Mussel inspired chemistry is a simple and efficient method for the surface modification of different materials and surface regardless of their size, shape and compositions.[30] It has been demonstrated that dopamine can be self polymerized under alkaline solution and formation polydopamine (PDA) coating on a variety of surface. More importantly, the PDA coating can further reacted with amino and thiol groups through Michael addition reaction. It is therefore, a series of functional components can be further linked on the surface of materials and surfaces via mussel inspired method. Because of its simplicity, effectiveness and universality, mussel inspired chemistry has been widely explored for surface modification of materials for various applications.[31-48] For example, we have demonstrated that the PDA functionalized CNTs could be further modified with 3-mercapto-propane-sulfonate and N-dodecyl mercaptan to render them well dispersibility in water and organic solvents.[49] On the other hand, surface modification of CNTs with RAFT derived polymers has also been reported in our recent work.[50] However, to the best of our knowledge, surface modification of CNTs with polymers through combination of mussel inspired chemistry and surface initiated living radical polymerization has not been reported thus far.

Single electron transfer living radical polymerization (SET-LRP) is a high efficiency methodology for the ultrafast preparation of linear and complex topology under mild condition.[51-61] In SET-LRP, the balance was mediated by an activation process of Cu(0) and deactivation with Cu(II)X(2)/N-ligand. The Cu(0) and Cu(II)X(2) was produced by naturally disproportionate of CuX under the existence of N-ligand in organic solution. In comparison with other living radical polymerization, SET-LRP shows obviously the faster ratio of polymerization at room temperature or below, which brought us a new inspiration to efficiently grow polymers from the CNTs surface under moderate condition.[62, 63]

In this work, a novel strategy for grafting polymers from the CNTs via combination of mussel inspired chemistry and SET-LRP was described in Scheme 1. The amino and hydroxyl groups were first introduced to the surface of CNTs via mussel inspired chemistry, which could be converted to Br-containing SET-LRP initiator through amidation and esterification reaction. The synthetic Br-containing CNT-PDA (CNT-PDA-Br) can be further used for surface polymerization with poly(ethylene glycol) methyl acrylate (PEGMA) macromonomer using CuBr/Me6TREN as catalytic system via typical SET-LRP strategy. Thus obtained functional CNTs (CNT-PDA-PPEGMA) showed significantly improved dispersibility in various solvents. Furthermore, this facile and efficient method described in this work is also suitable for surface modification of other materials due to their universality of mussel inspired chemistry.



Scheme 1. Schematic representation for the synthesis of CNT-PDA-PPEGMA via combination of mussel inspired chemistry and SET-LRP strategy. PDA films were first coated on the surface of pristine CNTs via mussel inspired chemistry to obtain CNT-PDA, which contained a number of amino and hydroxyl groups. After that the initiator (2-bromo-2-methylpropionyl bromide) was further conjugated on CNT-PDA to obtain CNT-PDA-Br. Finally, the monomer (PEGMA) was further introduced on the surface of CNT-PDA-Br via SET-LRP.

2. Experiment

2.1 Materials

CNTs with diameter of 30-50 nm were purchased from sinonano (Beijing, China), dopamine hydrochloride (DA, MW:189.64 Da, >98%) was supplied from company of Sangon Biotech, Tris hydroxyl methyl aminomethan (Tris), poly(ethylene glycol) methyl ether methacrylate (PEGMA, MW:950 Da, 98%), ethylene diamine tetraacetic acid (EDTA, MW: 416.2, 99.0-102.0%) was obtained from Aladdin (Shanghai, China) without further purification. 2-bromo-2-methylpropionyl bromide (MW;229.2, 98%) as the material to produce initiator was supplied by Heowns (Tianjin, China). The cuprous bromide (CuBr) and tris[2-(dimethylamino) ethyl] amine (Me6TREN) as catalytic system were suffered by Heowns (Tianjin, China), triethylamine (TEA) was purchased from Sinopharm chemical reagent co., ltd (Shanghai, China). Other chemicals were of analytic grade and were used as received without any further purification.

2.2 Characterization

The synthetic materials were characterized by Fourier transform infrared spectroscopy (FT-IR) using KBr pellets. The Fourier transform infrared (FT-IR) spectra were supplied from Nicolet5700 (Thermo Nicolet corporation). Transmission electron microscopy (TEM) images were obtained from a Hitachi 7650B microscope operated at 80 Kv. The TEM specimens were got by putting a drop of the nanoparticle ethanol suspension on a carbon-coated copper grid. Thermal gravimetric analysis (TGA) was conducted on a TA instrument Q50 with a heating rate of 10 °C min^{-1}. Samples weighting between 10 and 20 mg were heated from 25 to 600 °C in N_2 flow (60 mL min^{-1}). N_2 as the balance gas (40 mL min^{-1}). Each sample was ultrasonicated for 30 min prior to analysis. The X-ray photoelectron spectra (XPS) were performed on a VGESCALAB 220-IXL spectrometer using an Al Kα X-ray source (1486.6 eV). The energy scale was internally calibrated by referencing to the binding energy of the C1s peak of a carbon contaminant at 284.6 eV.

2.3 Synthesis of CNT-PDA

The functional CNTs with PDA coating was prepared via mussel inspired chemistry. 100 mg of pristine CNTs were mixed with Tris buffer solution (pH = 8.5, 30 mL) and ultrasonic treament for 10 min at 40 °C, and then the dopamine hydrochloride (100 mg) dissolved in Tris buffer solution was removed to the forementioned solution and stirring at room temperature for 4 h. The mixed solution contained the CNTs with PDA coating (CNT-PDA) and Tris buffer solution was separated by centrifuging at 8000 rpm for 10 min. The obtained CNT-PDA was washed with distilled water and ethanol three times and dried at 40 °C for 12 h.

2.4 Synthesis of CNT-PDA-Br

The Br-containing initiator was introduced to the surface of CNT-PDA through amidation and esterification between PDA films and 2-bromo-2-methylpropionyl bromide. Anhydrous CNT-PDA (300 mg), TEA (60 mg) and toluene (40 mL) were added to the three-neck flask under N_2. The three-neck flask was put into ice-water bath. When the temperature was achieved to 0-5 °C in flask, the solution of 2-bromo-2-methylpropionyl bromide (30 mg) in 10 mL of toluene was added dropwise into flask. The reactive system was stirred for 4 h at 0 °C. Resulting materials were separated from toluene solution by centrifugation at 8000 rpm for 10 min. The obtained CNT-PDA-Br was vigorously washed with acetone three times to remove residual reactants and dried at 50 °C for further experiment.

2.5 PEGylation of CNTs via SET-LRP

The PPEGMA chains were directly grown from the surface of CNTs via SET-LRP strategy using CuBr/Me6TREN as catalytic/ligand system in toluene/water solution under N_2. The mixture of dried CNT-PDA-Br (100 mg), PEGMA (2 g, 2.1 mM), CuBr (80 mg, 0.56 mM), toluene (30 mL) were added to polymerization bottle and sealed under N_2. After stirring at oil bath (40 °C) for 10 min, the solution of Me6TREN in 2 mL of toluene was injected into polymerization bottle using gas tight syringe. After the reactive system maintained 2 h by immersing the polymerization bottle into an oil bath set at 40 °C, the 1 mL of water was injected into bottle to terminate reaction. The solution in reactive mixture was removed via centrifugation at 8000 rpm for 5 min. The resulting CNT-PDA-PPEGMA was washed with acetone three times and dried at 40 °C. The Cu^{2+} on the surface of CNT-PDA-PPEGMA could be eliminated using EDTA solution. The resulting CNT-PDA-PPEGMA was purified by dialysis treatment for three days with frequent refreshing of the water. The final materials were dried at 40 °C for further characterization.

3. Results and discussion

The morphology and structure of CNTs and modified CNTs was shown in Fig. 1. TEM images showed that the diameter of pristine CNTs is about 40 nm, which was well consistent with the information provided by manufacture (Fig. 1A). After surface modification of CNTs with PDA, the PDA films coated on the surface of CNTs can be clearly observed (Fig 1B), implying successful modification of CNTs with PDA. After further modified CNT-PDA with PPEGMA, the thickness of polymer films were further thicken (Fig 1D), evidencing the successfully modified CNT-PDA with PPEGMA via the surface initiated SET-LRP. Based on the TEM image in Fig. 1D, the thickness of polymer films is about 30 nm. Compared with previous methods for surface modification of CNTs. The method described in this work is rather simple and effective. More importantly, this method will not destroy the structure of CNTs. Therefore, the physicochemical properties of CNTs related to their structure can be well maintained after surface modification of CNTs with polymers.

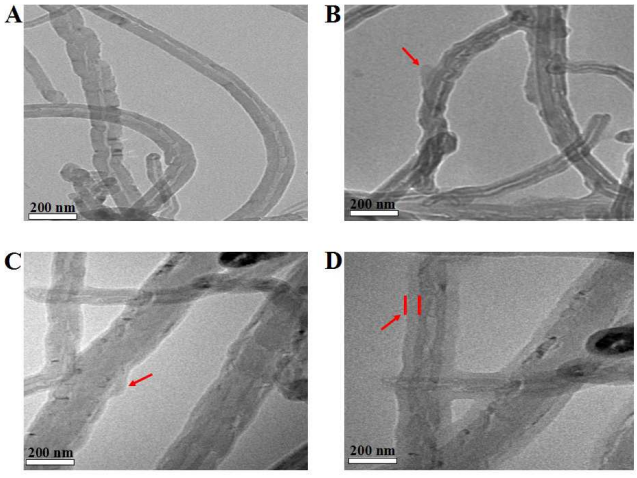


Fig. 1 Representative TEM images of (A) pristine CNTs, (B) CNT-PDA, (C) CNT-PDA-Br and (D) CNT-PDA-PPEGMA. Scale bar = 200 nm.

The PDA and polymer films coated on the surface of CNTs could be clearly observed via TEM images (Fig. 1B-D). TEM characterization given direct evidence that the CNTs were successfully functionalized by PDA and polymers via combination of mussel inspired chemistry and SET-LRP method.

Apart from TEM characterization, a series of characterization techniques such as FT-IR, XPS and TGA have also been utilized to characterize the CNT samples. As shown in Fig. 2, no specific peaks were observed in the smaple of pristine CNTs. However, a number of characteristic peaks were found after their surface was modified with PPEGMA. For example, the peak at 3450 cm^{-1} can be attributed to the stretching vibration of N-H band, which provided the evidence that PDA was successfully attached to the surface of CNTs. As compared with the spectrum of CNT-PDA, an obvious absorption peak centered at 1630 cm^{-1} was emerged in CNT-PDA-Br, which could be ascribed to C=O bond from the polymerization initiator. On the other hand, the CH- bending vibration at 1380 cm^{-1} was also found in CNT-PDA-Br. These results demonstrated that the initiator (2-bromo-2-methylpropionyl bromide) was successfully immobilized on the surface of CNT-PDA via amidation and esterification reaction. Furthermore, two peaks distributed between 3000 to 2500 cm^{-1} could be observed from sample of CNT-PDA-PPEGMA, which could be attributed to $-CH_3$ and $-CH_2$ groups belonged to PEGMA and initiator. More importantly, a series of characteristic peaks located at 1640 cm^{-1} (C=O), 1470 cm^{-1} (C-H) and 1110 cm^{-1} (C-O) were also clearly observed from samples of CNT-PDA-PPEGMA, confirming the successful grafted PPEGMA to the surface of CNTs via SET-LRP strategy. Fig. S1 shows the TGA curves of CNTs, CNT-PDA, CNT-PDA-Br and CNT-PDA-PPEGMA. The weight loss of pristine CNTs was about 2.65% when the temperature was 600 °C, indicating the excellent thermal stablility of CNTs. However, the weight loss of CNTs was significantly increased to about 13.98% after modification with PDA under the same temperature, confirming the PDA was successfully attached to the CNTs surface via mussel inspired chemistry. After CNT-PDA was further reacted with 2-bromo-2-methylpropionyl bromide in toluene solution, the weight loss of CNT-PDA-Br arrived to about 14.85%. As compared with CNT-PDA, the weight loss of CNT-PDA-Br enhanced 0.87%, which could be attributed to introduction of initiator. The TGA results also demonstrated that Br-containing initiator was indeed grafted to the surface of CNT-PDA. After further modification of CNT-PDA with PEGMA via SET-LRP strategy using CuBr/Me6TREN as catalytic system, much more weight loss was observed in the CNTs sample (CNT-PDA-PPEGMA) as compared to pure CNT-PDA. It can be seen that weight loss of CNT-PDA-PPEGMA was increased to 32.84%. Therefore, the mass percentage of polymer grafted onto the surface of CNT-PDA was calculated to be about 18%, confirming PPEGMA chains were linked on the CNTs through the combination of mussel inspired chemistry and SET-LRP.

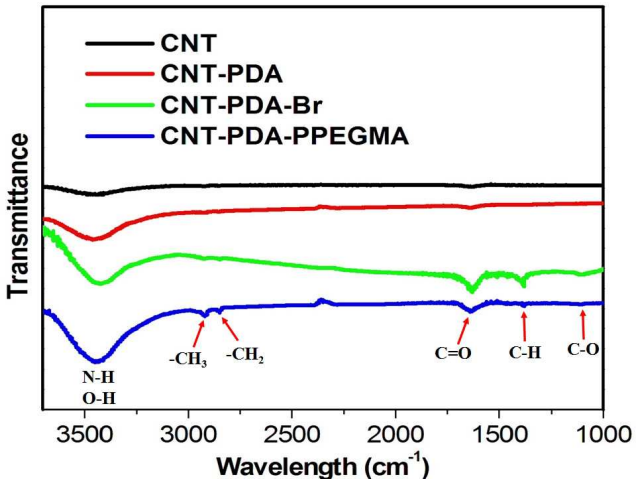


Fig. 2 FT-IR spectra of CNTs, CNT-PDA, CNT-PDA-Br and CNT-PDA-PPEGMA.

According to the XPS analysis, the different elements existed in CNT samples were detected by a survey of XPS scan ranging from 0 to 1200 eV (Fig. 3). The existence of C, N, O and Br atom was confirmed by XPS spectra. As compared with CNTs and CNT-PDA, a novel element (Br) was found in the sample of CNT-PDA-Br and CNT-PDA-PPEGMA. This results suggested that initiator was successfully immobilized on the surface of CNTs via mussel inspired chemistry. On the other hand, the peak intensity of O was significant increased, further evidencing that PDA and PPEGMA was linked on the surface of CNTs.

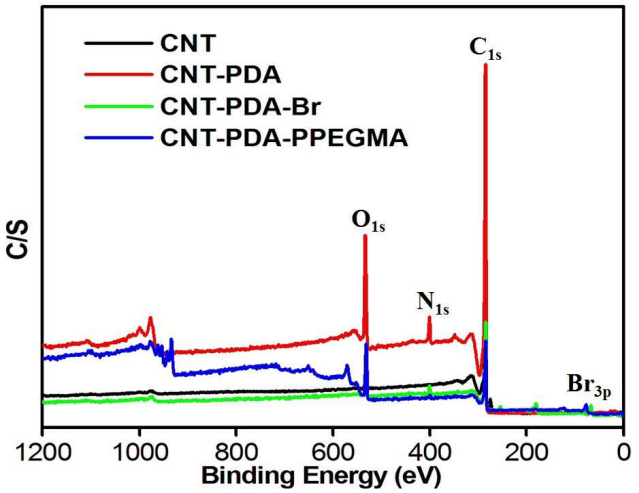


Fig. 3 The representative XPS spectra of CNT, CNT-PDA, CNT-PDA-Br and CNT-PDA-PPEGMA. (A) Survey scans the spectral region from 0 to 1200 eV.

The XPS spectra of high resolution Br3d, C1s, N1s and O1s were appeared in Fig. 4. As compared with the pristine CNTs and CNT-PDA, an obvious peak located between 66 to 70 eV was emerged in the samples of CNT-PDA-Br and CNT-PDA-PPEGMA (Fig. 4A). The emerged peak can be ascribed to the signal of Br atom. These results suggested that the initiator (2-bromo-2-methylpropionyl bromide) was conjugated on the CNT-PDA successfully. However, as compared with the sample of CNT-PDA-Br, the intensity of Br3d in the smaple of CNT-PDA-PPEGMA was obviously decreased. These results demonstrated that PEGMA was conjugated on the surface of CNT-PDA-Br through SET-LRP method. The broad peaks of four different but similar binding energy of carbon between 284 eV and 286 eV are overlapped (Fig. 4B). The broad peak located at 284.83 eV can be attributed to the sp^3-hybridised carbon atoms. The higher binding energy signal appears at 286.9 eV can be ascribed to the carbon atom band to oxygen. Furthermore, a strong peak appeared at 400.6 eV can be referred to N1s in the samples of CNT-PDA, evidencing that PDA was successfully attached to the CNTs via mussel inspired chemistry. After modification CNT-PDA with PEGMA, the intensity of N1s spectra was decreased as compared with the samples of CNT-PDA, suggesting the successful modification of CNTs with polymers (PPEGMA). Fig. 4D shows the O1s XPS spectra of CNT samples, as compared with the pristine CNT, the intensity of O1s signal was significantly enhanced in the samples of CNT-PDA, CNT-PDA-Br and CNT-PDA-PPEGMA, further indicating that CNT was successfully modified with PDA and PPEGMA through combination of mussel inspired chemistry and SET-LRP method.

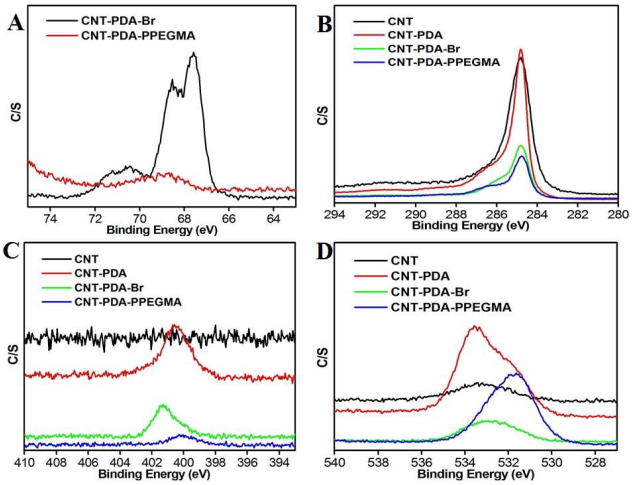


Fig. 4 The representative XPS spectra of CNT-PDA-Br and CNT-PDA-PPEGMA at the (A) Br3d region. (B) the C1s region, (C) the N1s region and (D) the O1s region.

Based on the XPS analysis, the percentages of elements in CNT samples were calculated. As listed in Table 1, the major components of pristine CNTs are C (97.13%) and O (2.87%). After modification with PDA, the percentages of C, N and O were changed to 91.18%, 2.58% and 6.24%, respectively. The appearance of new element (N) and decrease of C content demonstrated taht PDA was coated on the surface of CNTs. On the other hand, an element (Br) with percentage of 4.28% was detected in the sample of CNT-PDA-Br, suggesting that Br-containing initiator was introduced to the CNT-PDA. Accompanying with the increase of O content (from 7.81% to 23.90%) and decrease of Br content (from 4.28% to 0.43%), suggesting the successful modification of CNTs with polymers (PPEGMA).

Table 1 Element content (%) of CNT, CNT-PDA, CNT-PDA-Br and CNT-PDA-PPEGMA based on the XPS analysis

	C1s	O1s	N1s	Br3d
CNT	97.13	2.87	0	0
CNT-PDA	91.18	6.24	2.58	0
CNT-PDA-Br	83.08	7.81	4.84	4.28
CNT-PDA-PPEGMA	73.61	23.90	2.06	0.43

The dispersibility of CNT samples was also evaluated. As shown in Fig. 5A-D, the pristine CNTs was quickly deposited in water within 5 min. After modifying with PDA via mussel inspired chemistry, the water dispersibility of CNT-PDA slightly enhanced because of limited hydrophilic groups were existed on CNT-PDA. After CNTs was further modified with PPEGMA via SET-LRP, the water dispersibility of CNT-PDA-PPEGMA was significantly increased (bottle 3 in Fig. 5). The sample of CNT-PDA-PPEGMA still dispersed in water very well even the deposition time is as long as 24 h. Furthermore, apart from water, CNT-PDA-PPEGMA could also be well dispersed in a number of organic solvents such as dimethylformamide (DMF), tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO). These results further demonstrated the successful surface modification of CNTs through mussel inspired chemistry and SET-LRP.

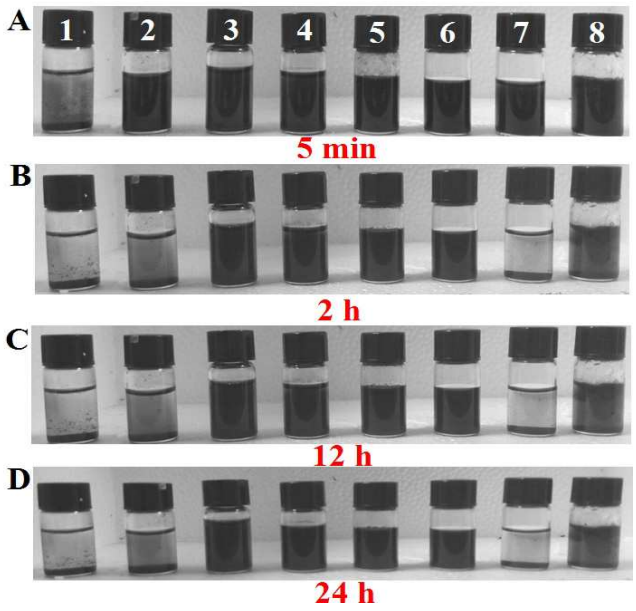


Fig. 5 Photographs of CNTs (1), CNT-PDA (2) and CNT-PDA-PPEGMA (3) in water at room temperature at different time (A) 5 min, (B) 2 h, (C) 12 h, (D) 24 h. CNT-PDA-PPEGMA was dispersed in different organic solution can be observed from (4-8) [DMSO (4), THF (5), DMF (6), CH_2Cl_2 (7), acetone (8)].

Conclusion

In summary, we developed a novel strategy for surface modification of CNTs via combination of mussel inspired chemistry and SET-LRP for the first time. These PEGylated CNT samples exhibited high dispersibility in water and organic medium, making them have great application prospects in biomedical and nanocomposites filler fields. The new method described in this work is rather simple and effective as compared with previous surface modification methods. The surface modification strategy of combination mussel inspire chemistry and SET-LRP method could quickly obtain polymer brush from the CNT surface. Due to the strong adhesion of PDA to various material regardless of their size, shape and compositions, this novel strategy could also be used to modify other important materials.

Acknowledgements

This research was supported by the National Science Foundation of China (Nos. 21134004, 21201108, 51363016, 21474057), and the National 973 Project (Nos. 2011CB935700).

Notes

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† Electronic Supplementary Information (ESI) available: [TGA analysis of CNT samples was provided in supplementary information]. See DOI: 10.1039/b000000x/

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