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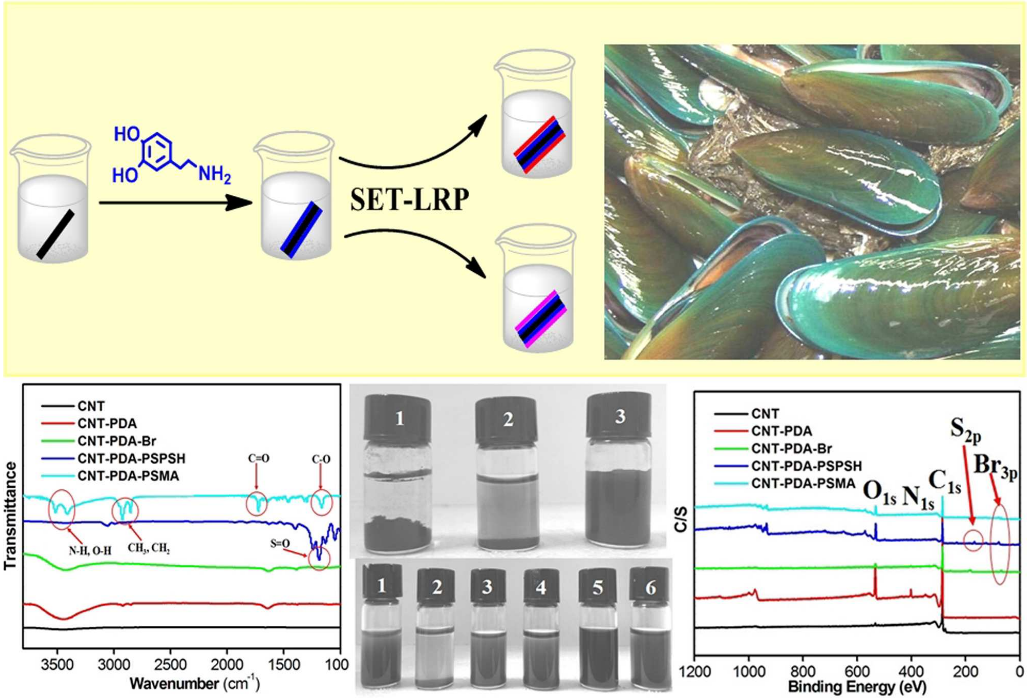

A versatile and effective strategy combination of mussel inspired chemistry and SET-LRP has been developed for preparation of hydrophilic and hydrophobic carbon nanotubes for the first time

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Full Paper

Toward the Development of Versatile Functionalized Carbon Nanotubes

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Surface modification of carbon nanotubes (CNT) with polymers is a general and effective strategy to improve the performance of CNT for applications. In this work, a facile strategy to synthesize hydrophobic and hydrophilic CNT by mussel inspired chemistry and Single-Electron Transfer Living Radical Polymerization (SET-LRP) was developed for the first time. The successful synthesis of these CNT-polymer composites was confirmed by a series of characterization techniques including transmission electron microscopy, Fourier transform infrared, thermogravimetic analysis and X-ray photoelectron spectra. These CNT exhibited obviously enhanced dispersiblity in water and different organic solvents after they were surface functionalized with hydrophilic and hydrophobic polymers. The synthetic strategy is convenient, versatile and environmentally friendly and can be extended for fabrication of many other polymer nanocomposites. Therefore, the method developed in the present work might open a new route to fabricate functional CNT-polymer composites for different applications.

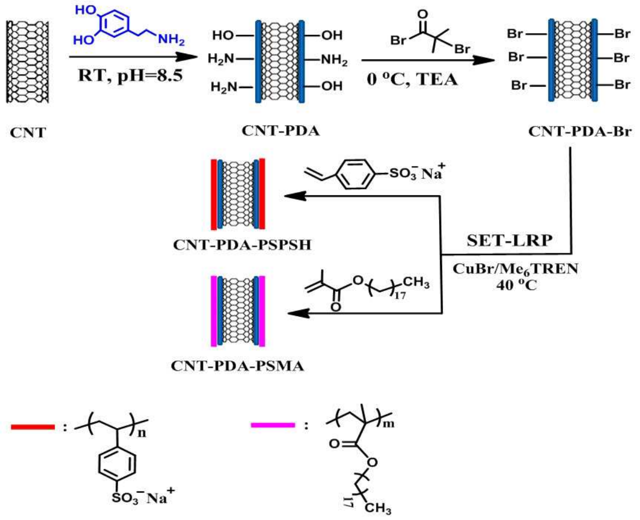
1. Introduction

Since their first discovery, carbon nanotubes (CNT), a family of one-dimensional carbon nanomaterials, have attracted considerable research interest because of their outstanding physicochemical properties and promising applications in the fields such as nanocomposite fillers, field emission displays, biomedical materials, energy storage and nano-electronics.[1, 2] For example, CNT own elastic moduli of 1 TPa and tensile strength in the region of 150 GPa.[3] The exceptional mechanical properties of CNT make them ideal reinforecements in composite materials with better stiff, strength and conductivity. However, it is still great challenge to achieve the optimal performance of these CNT-polymer nanocomposites through mixture of pristine CNT and polymers due to the poor dispersion of pristine CNT in polymer matrix and the weak interaction between CNT and polymer matrix. On the other hand, because of their high surface areas, cell membrane penetrate capability and photothermal effects, CNT have also demonstrated to be promising candidates for various biomedical applications ranged from gene/drug delivery to biosensor and photothermal treatment.[4] However, the high dispersibility of CNT in aqueous solution is a prerequisite for all the biomedical applications. It is therefore surface modification of CNT has became one of the research focus for CNT.

Over the past few decades, a number of covalent and noncovalent surface modification strategies have been developed.[5-17] Among them, surface modification of CNT via surface initiated polymerization should be the most promising strategies due to the diversity of monomers and designability of polymerization.[12, 18-26] Different living polymerization methods including atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer polymerization (RAFT), nitroxid-mediated radical polymerization (NMP) and chain transfer free radical polymerization have been reported for surface modification of CNT using a vast number of monomers.[27-35] Generally speaking, the CNT should be first oxidized using hazardous agents to introduce oxygen functional groups on the surface of CNT for immobilization of surface initiators or chain transfer agents. During this oxidation procedure, the structure of CNT will be inevitably destroyed. On the other hand, only limited density of functional groups can be introduced during the oxidation procedure due to the high chemical stability of the aromatic structure of CNT. Finally, the oxidation procedure is rather complex and hazardous agents such as concentrated sulfuric acid, nitrate acid are commonly required. Therefore, the development of novel strategy for surface modification of CNT is highly desirable.

Mussel inspired chemistry is an emerged surface modification technology, which has attracted increasing attention for different applications ranged from biological imaging and photothermal cancer treatment to energy conversion and environmental protection *etc*.[36-54] As compared other surface modification strategy, the obvious advantages of mussel inspired chemistry is the strong and universal adhesion of polydopamine (PDA) toward various materials regardless their compositions, size and shape. Apart from the special adhesion of PDA, another feature of mussel inspired chemistry is funcitonal groups can be facilely introduced onto the surface of PDA coated materials. Furthermore, the PDA coating can also provide many reactive sites, which can be further conjugated amino- or thiol-contained molecules to the surface for further applications.[55, 56] Our previous reports have demonstrated that thiol-contained small organic molecules and polymers can be used for surface modification of CNT via combination of mussel inspired chemistry and Michael addition reaction.[57, 58] These funcitonalized CNT exhibited obvious enhanced dispersibility in water and different organic medium. Given these unique features, mussel inspired chemistry is expected extreme charming for surface modification of materials via combination with surface initiated living polymerization.

Single-Electron Transfer Living Radical Polymerization (SET-LRP) is an emerged controlled living polymerization method, which has attracted increasing research interest in recent years.[59-65] The surface modification of carbon nanomaterials using SET-LRP has also demonstrated by Huang *et al*.[66-68] As compared with ATRP, SET-LRP can occur under relative low temperature, in the present of air and water but with remarkable high polymerization ratio.[69] In this contribution, a novel strategy combination of mussel inspired chemistry and SET-LRP have been reported for preparation of hydrophilic and hydrophobic polymers modified CNT for the first time. As shown in **Scheme 1**, three steps are involved in the experiment procedure: (1) the amino and hydroxyl groups were introduced onto the surface of CNT to obtain CNT-PDA by mussel inspired chemistry. (2) The SET-LRP initiator (CNT-PDA-Br) was synthesized via amidation and esterification between CNT-PDA and 2-bromo-2-methylpropionyl bromide. (3) Grafting polymerization of sodium p-styrenesulfonate hydrate (SPSH) and stearyl methacrylate (SMA) from CNT-PDA-Br was carried out by means of in situ SET-LRP method, resulting in CNT-PDA-PSPSH and CNT-PDA-PSMA. Apart from CNT, surface modification of graphene oxides, carbon nanoparticles, active black, magnetic nanoparticles, nanodiamonds, polystyrene and cellulose microfibrillated membrane, LDH microcrystals have also reported recently for the strong and universal adhesion of PDA to various materials.[70-76] The novel methodology described in this work could also be applicative for grafting polymers chains from other materials, which is of great significance to produce other polymer nanocomposites.



Scheme 1 Representative procedure for the preparation of hydrophilic and hydrophobic CNT via combination of mussel inspired chemistry and SET-LRP method.

2. Experiment

2.1 Materials

Carbon nanotubes (CNT) with diameter of 30-50 nm were purchased from sinonano (Beijing, China), dopamine hydrochloride (DA, MW:189.64 Da, >98%) were supplied from company of Sangon Biotech, Tris hydroxyl methyl aminomethan (Tris), sodium p-styrenesulfonate hydrate (SPSH, MW:206.19 Da, 90%), stearyl methacrylate (SMA, MW: 338.57 Da, 96%), ethylene diamine tetraacetic acid (EDTA, MW: 416.2, 99.0-102.0%) were obtained from Aladdin (Shanghai, China) without further purification. 2-bromo-2-methylpropionyl bromide (MW: 229.2, 98%) as the material to produce initiating groups was supplied by Heowns (Tianjin, China). The cuprous bromide (CuBr) and tris[2-(dimethylamino) ethyl] amine (Me$_6$TREN) 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 Measurements

The synthetic materials were characterized by Fourier transform infrared spectroscopy (FT-IR) using KBr pellets, The 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} using Al crucible. Samples weighting between 10 and 20 mg were heated from 30 to 600 °C in nitrogen flow (100 mL min^{-1}). Because Al crucible melts at around 620 °C, the highest temperature for TGA measurement was set at 600 °C. 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 (Eb) of the C1s peak of a carbon contaminant at 284.6 eV. The size distribution of CNT-PDA-PSPSH in water was determined using a zeta Plus apparatus (ZetaPlus, Brookhaven Instruments, Holtsville, NY) as a function of time. Each sample was ultrasonicated for 30 min prior to analysis.

2.3 Synthesis of CNT-PDA

The modified CNT coated with PDA films were prepared via mussel inspired chemistry. 100 mg pristine CNT were added to Tris buffer solution (pH = 8.5, 30 mL) and ultrasonic treatment for 10 min at 40 °C, and then the dopamine hydrochloride (100 mg) dissolved in 20 mL of Tris buffer solution was added to the forementioned solution and stirring at room temperature for 4 h. The mixed solution contained the modified CNT with PDA (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 SET-LRP initiating groups were introduced to the surface of CNT-PDA through amidation between CNT-PDA and 2-bromo-2-methylpropionyl bromide. Anhydrous CNT-PDA materials (300 mg), TEA (60 mg) and toluene (40 mL) were added to the three-nickle flask under N_2. The three-nickle 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 0-5 °C. Resulting materials were separated from toluene solution by centrifugation at 8000 rpm for 10 min. The obtained Br-containing initiating groups of materials were vigorously washed with toluene three times to remove residual reactants and dried at 50 °C for further experiment.

2.5 Preparation of CNT-PDA-PSPSH

The functional CNT with hydrophilic polymers could be prepared via SET-LRP using SPSH as monomer and Cu/Me_6TREN as catalytic system in $DMSO/CH_3CN$ solution under N_2. The mixture of CNT-PDA-Br (100 mg), SPSH (2 g, 9.7 mM), CuBr (80 mg, 0.56 mM) was removed to the polymerization bottle contained organic solution (DMSO 25 mL, CH_3CN 15 mL) and sealed under N_2. The polymerization bottles were under ultrasonic treatment for 10 min to disperse the CNT samples in organic solution. After stirring at the oil both (40 °C) for 10 min, the solution of Me_6TREN in DMSO (2 mL) was injected into the polymerization bottle using gas syringe. After reactive system kept 8 h in oil both at 40 °C. The resulting products were treated via centrifugating to eliminate the organic solution and washed with water three times, and then dried at 40 °C for 48 h. The dried CNT-PDA-PSPSH was put into the solution of EDTA (5 mol/L) to remove $Cu^{2+,}$ the pure CNT-PDA-PSPSH could be obtained for further characterization.

2.6 Synthesis of CNT-PDA-PSMA

The hydrophobic CNT-polymer composites could also be obtained through SET-LRP using SMA as monomer and CNT-PDA-Br as initiator in THF solution under N_2. The CNT-PDA-Br (100 mg), SMA (2g, 5.9 mM), CuBr (80 mg, 0.56 mM) and THF (50 mL) were put into the polymerization bottle and sealed under $N_{2.}$ The polymerization bottles were under ultrasonic treatment for 10 min to disperse uniformly the CNT samples in THF solution. After stirring for 10 min at the oil bath (40 °C) , the solution of Me_6TREN in THF (2 mL) was injected into the polymerization bottle using gas syringe. The reactive system kept 12 h in oil bath of 40 °C. Then the resulting product was treated via centrifugation to eliminate the organic solution and washed with water three times and dried at 40 °C for 48 h. The dried CNT-PDA-PSMA was treated with dialysis two days to remove Cu^{2+}, the pure CNT-PDA-PSMA could be obtained to further characterization.

3. Results and discussion

The novel strategy of combining mussel inspired chemistry and SET-LRP method was first reported to produce hydrophilic and hydrophobic polymers funcitonalized CNT in our group. As shown in **Scheme 1**, the PDA films were coated on the CNT surface via self-polymerization of DA in the alkaline solution, which introduced the functional groups (amino and hydroxyl) to the surface of CNT. These functional groups would further covalently linked with 2-bromo-2-methylpropionyl bromide to obtain Br-containing SET-LRP initiator (CNT-PDA-Br). The hydrophilic and hydrophobic polymers were directly grown from the surface of CNT via typical SET-LRP using CNT-PDA-Br as initiator and $CuBr/Me_6TREN$ as catalysis system. The CNT samples before and after modification were characterized by TEM, FT-IR, TGA and XPS.

A typical high-resolution TEM images from before and after modifying CNT samples in Fig. 1 implied that successful modification of CNT with PDA and polymers. As seen from the Fig. 1A, the diameter of pristine CNT is 30 to 50 nm, which is consistent with the information provided by distributor. The surface of pristine CNT was exceptional smooth. However, as we can seen from Fig. 1B, after modification with PDA films via mussel inspired chemistry, the surface of CNT changed to be coarse, suggesting that PDA films were attached to the CNT. Next, the perfect modification of CNT-PDA surface with hydrophilic and hydrophobic polymers by SET-LRP could be clearly observed from the Fig. 1C and D, which appeared the distinct polymer films on the CNT surface. Based on the TEM images of Fig. 1C and D, the thickness of hydrophilic and hydrophobic polymers was calculated to be 14 ± 2 and 21 ± 3 nm, respectively. Compared with previous methods, the novel strategy described in this work is rather facile, efficient and versatile. More importantly, the phenomenon of destroying CNT structure did not happen in this work. And therefore the outstanding physicochemical properties of CNT related to the structure can be preserved. It has been demonstrated that DA play a vital role in mussel inspired surface modification of nanomaterials. Following procedures may involve in surface functionalization of CNT through mussel inspired chemistry. First, DA was first adhered to the surface of CNT through interaction between catechol group of DA and CNT. And then DA was self polymerized under alkaline solution to form PDA films, which can be firmly coated on CNT due to the combination effect of catechol group and strong π-π interaction of PDA and CNT. Most importantly, the PDA films can provided a general platform for further reaction (Michael addition reaction with amino- and thiol-contained compounds, immobilization of polymerization initiator).

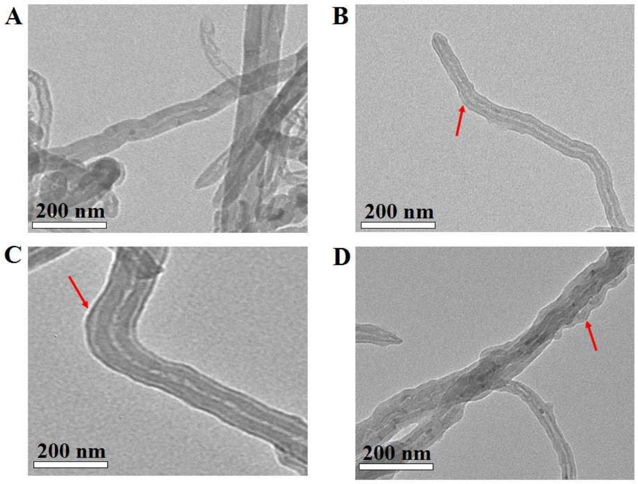


Fig 1 TEM micrographs of modified CNT with PDA and polymers, (A) pristine CNT, (B) CNT-PDA, (C) CNT-PDA-PSPSH and (D)CNT-PDA-PSMA

Except form TEM characterization, a series of other characterization techniques such as FT-IR, TGA and XPS have also been used to confirm successful modification of CNT with PDA and polymers. FT-IR spectra of the CNT samples were obtained to determine the chemical information of CNT samples. As shown in Fig. 2, no specific peaks were observed from pristine CNT. After modifying with PDA, the obvious peak located at 3470 cm^{-1} was appeared, which can be attributed to the stretching vibration of NH_2 and OH bonds. These results demonstrated that PDA films were surely coated onto the surface of CNT. However, the disappearance of peak at 3470 cm^{-1} and the appearance of peak at 1440 cm^{-1} (C-H) after reacting with 2-bromo-2-methylpropionyl bromide using CNT-PDA as substrate, confirming that Br-containing SET-LRP initiator was resoundingly prepared. Two new peaks at 2920 and 2850 cm^{-1} appeared at FT-IR spectrum of CNT-PDA-PSMA can be ascribed to the $-CH_3$ and $-CH_2$, evidencing hydrophobic polymer was grafted on CNT-PDA surface. Meanwhile, the obvious peaks at 1770 cm^{-1} and 1160 cm^{-1} assigned as the vibration of the C=O and C-O-C groups was observed in the sample of CNT-PDA-PSPSH, demonstrating the presence of the polymer (PSMA) on the CNT surface. From the FT-IR spectrum of CNT-PDA-PSPSH, the strong peaks located at 1250 cm^{-1} can be attributed to the vibration of S=O bond, indicating the hydrophilic polymers was directly grown on the surface of CNT. These FT-IR results provided direct evidence for successful modification of CNT with PDA films and polymers. Given the strong and universal adhesion of PDA to various materials, the method developed in this work might also be used for surface modification of many other materials. More importantly, various monomers can be polymerized through controlled living radical polymerization. Therefore, different polymer nanocomposites with different properties and functional components can be fabricated using the versatile method.[77-83]

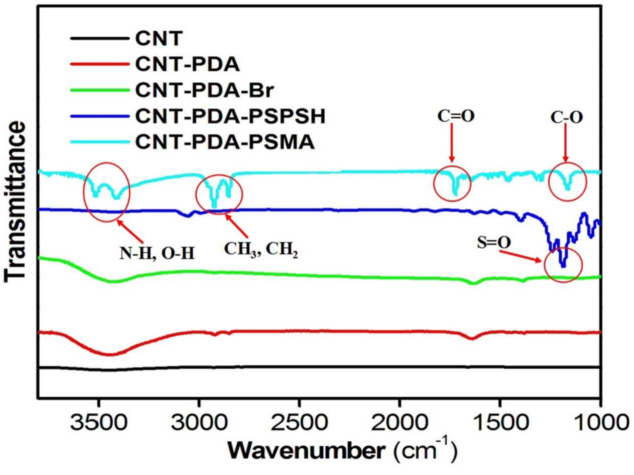


Fig 2 The FT-IR spectra of CNT smaples. As evidenced by the FT-IR spectra, a series of characteric functional groups includes NH_2, -OH, CH_3, C=O and C-O were found in the sample of CNT-PDA-PSMA. And the characteristic S=O bond was found in the sample of CNT-PDA-PSPSH. These results suggested that the hydrophobic and hydrophilic CNT were preparaed via combination of mussel inspired chemistry and SET-LRP.

Comparing with pristine CNT, the relative contents of grafted polymers on the CNT surface was determined by TGA. As shown in Fig. 3, the weight loss of pristine CNT was about 2.75% when the temperature arrived to 600 °C from 100 °C under nitrogen (the weight loss of sample before 100 °C was water), suggesting excellent thermal stability of CNT. The curve of CNT-PDA shows more weight loss (13.5%) under the same experimental conditions, which can be attributed to the loss of the PDA films, implying the PDA films were attached on the CNT through mussel inspired chemistry. From the curve of CNT-PDA-Br, the weight loss was increased to 14.7%, providing direct evidence of covalent conjugation of initiator to the CNT-PDA. Based on the TGA results, the weight percentage of initiator was calculated to be 1.2%. After hydrophilic and hydrophobic polymers were linked to the surface of CNT-PDA via SET-LRP, the weight loss of functional CNT with hydrophilic and hydrophobic polymers was increased to 34.4% and 67.7%, respectively. Through analyzing the TGA data, the grafted hydrophilic and hydrophobic polymers on the CNT surface was calculated to be 19.7% and 53.0%, respectively. Based on the TGA curves, the grafted polymers (PSPSH and PSMA) were mainly decomposed at the temperature between 300-400 °C. On the other hand, slow but continuous weight loss was also found in the samples of CNT-PDA and CNT-PDA-Br. These reulsts further confirmed that CNT can be facilely modified with hydrophilic and hydrophobic polymers successfully via combination of mussel inspired chemistry and SET-LRP.

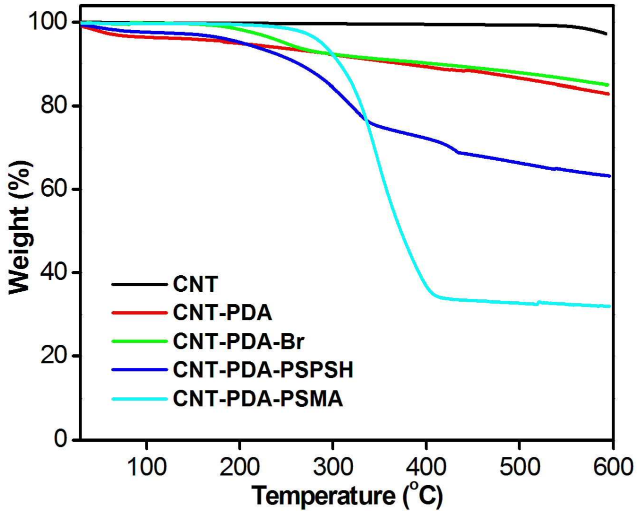


Fig 3 The TGA curves of CNT samples. The PDA and polymers immobilized on CNT were mainly decomposed at the temperature between 300-400 °C.

Fig 4 shows the DTA analysis of different CNT samples. As shown in Fig 4A, the peaks of endothermic and exothermic respectively appeared at 123.23 °C and 295.55 °C could be attributed to the thaw and crystal. On the other hand, no obvious endothermic peaks were observed in the smaple of CNT-PDA, which is consistent with the TGA results. As compared with CNT-PDA, a strong endothermic peak was observed at 568.25 and 536.67 °C in the smaples of CNT-PDA-Br and CNT-PDA-PSPSH, which may be attributed to decompose of initiator (2-bromo-2-methylpropionyl bromide) immobilized on CNT. After hydrophilic and hydrophobic polymers were grafted onto the surface of CNT, the exothermic peak appears at 324.5 °C can be ascribed to the decomposition of SO_4^{2-} (Fig 3C). It is worth noting that two endothermic peaks located between 200-300 °C and 300-404.32 °C were observed in the sample of CNT-PDA-PSMA. The first endothermic peak may be attributed to the dissociation of SMA, which was coated on CNT-PDA-PSMA via self assemble. And the second endothermic peak may be ascribed to the decompostion of PSMA, which was grafted on the CNT via SET-LRP (Fig. 3D). Take together, all of these results further confirmed the successful preparation of hydrophobic and hydrophilic CNT via the bioinspired strategy.

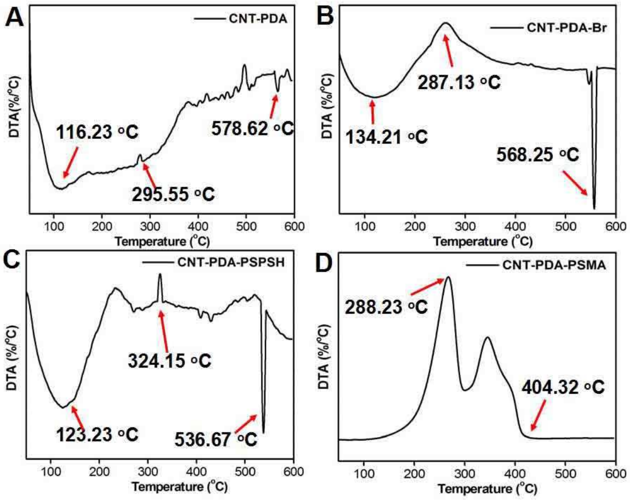


Fig. 4 DTA curves of CNT samples. (a) CNT-PDA, (b) CNT-PDA-Br, (c) CNT-PDA-PSPSH and (d) CNT-PDA-PSMA.

Fig. 5 shows the XPS analysis of CNT, CNT-PDA, CNT-PDA-Br, CNT-PDA-PSPSH and CNT-PDA-PSMA. The different elements existed in CNT samples were detected by a survey of XPS spectra ranging from 0 to 1200 eV. The existence of C, N, O, Br, S could be discovered from the XPS spectra. Compared with the pristine CNT, appearance of new element (N) in the sample of CNT-PDA demonstrated that PDA films indeed coated on the CNT surface via mussel inspired chemistry. The fact of 2-bromo-2-methylpropionyl bromide covalently immobilized on the surface of CNT-PDA could be confirmed by the discovery of a novel element (Br) in survey scan of XPS spectra. On the other hand, the signal of new element (S) was emerged in XPS spectrum of CNT-PDA-PSPSH, further indicating that SPSH polymers were directly grown on the CNT surface. More importantly, the peak intensity of O was significantly increased in polymer functionalized CNT, suggesting that hydrophilic and oilphilic polymers were linked on the surface of CNT.

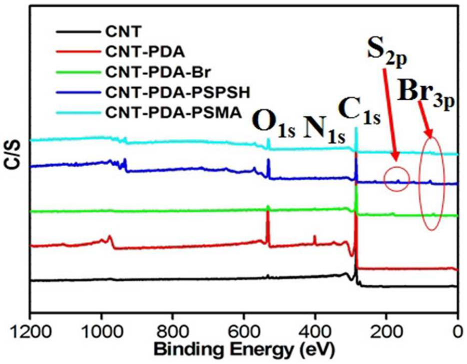


Fig 5 The XPS spectra of CNT, CNT-PDA, CNT-PDA-Br, CNT-PDA-PSPSH and CNT-PDA-PSMA. Survey scans range from 0 to 1200 eV.

The high resolution XPS spectra of CNT samples related to C1s, O1s, N1s and S2p were displayed in Fig. 6. As shown in Fig. 6A, the peak located at 168.23 eV referred to new element (S2p) were found in CNT-PDA-PSPSH, suggesting that hydrophilic polymers (PSPSH) was grew on the CNT surface. The peaks of C1s with the binding energy at 284.78 and 288.58 eV were affirmed as the sp3 and sp2 hybridised carbon atoms in the samples of modified CNT with hydrophilic and hydrophobic polymers, demonstrating that the existence of two kinds of polymers on the surface of CNT (Fig. 6B). Compared with pristine CNT, the new element peaks of modified CNT with PDA and polymers appeared between 400 to 402 eV could be attributed to the N1s (Fig. 6C), evidencing that CNT were successfully modified by PDA films via mussel inspired chemistry. However, the below detection of N element in CNT-PDA-PSMA samples could be attributed to the existence of excessive thick polymer films on the CNT surface. And the thickness of polymer films is greater than the detection thickness of instrument. After modification of CNT with hydrophilic and hydrophobic polymers by SET-LRP method, the intensity of O1s spectra was increased as compared with the XPS curve of CNT-PDA, demonstrating two kinds of polymers were perfectly grown on the surface of CNT via mussel inspired chemistry and SET-LRP (Fig. 6D).

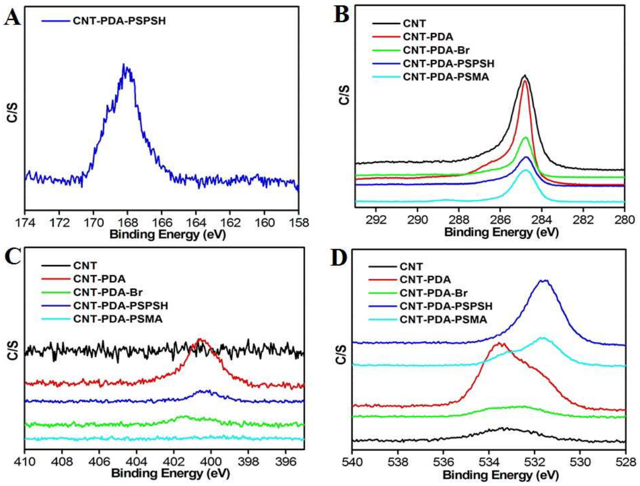


Fig 6 The high-resolution XPS spectra of CNT samples. (A) the S2p region, (B) the C1s region, (C) the N1s region and (D) the O1s region.

Based on the analysis of XPS spectra, the percentages of elements contained in CNT samples were calculated. As shown in Table 1, the major elements in pristine CNT were C (97.13%) and O (2.87%). After modification of CNT with PDA, the percentage of new element (N) (2.58%) was detected, whereas the contents of C reduced to 91.18%. Therefore, the introduction of new element (N) suggested the PDA films were covered on the CNT surface by mussel inspired chemistry. On the other hand, the novel element (Br) was detected in the CNT-PDA-Br, suggesting the successful immobilization of initiator on CNT-PDA. On the other hand, the percentage of O in the samples of CNT-PDA-PSPSH and CNT-PDA-PSMA was obviously increased, suggesting that these polymers were attached on the CNT surface via combination of mussel inspired chemistry and SET-LRP. Furthermore, the first appearance of S (content is 4.38%) in CNT-PDA-PSPSH also evidenced successful synthesis of hydrophilic CNT-polymer composites.

Table 1 Element content (%) of CNT, CNT-PDA, CNT-PDA-Br, CNT-PDA-PSPSH and CNT-PDA-PSMA

	C1s	O1s	N1s	S2p	Br3d
CNT	97.13	2.87	0	0	0
CNT-PDA	91.18	6.24	2.58	0	0
CNT-PDA-Br	83.08	7.81	4.84	0	4.27
CNT-PDA-PSPSH	69.49	23.96	2.11	4.38	0.06
CNT-PDA-PSMA	86.12	12.52	0.75	0	0.08

The effects of functional CNT with hydrophilic and hydrophobic polymers on the dispersion in water and organic solution were investigated. According to the Fig. 7, the poor dispersibility of pristine CNT in water could be observed, that was quickly precipitated in water within 5 min. After forming PDA films on the CNT surface, the water dispersibility was only sligtly enhanced because of the limited hydrophilic groups were introduced on the surface of CNT-PDA. As compared with CNT-PDA, the dispersibility of CNT-PDA-PSPSH and CNT-PDA-PSMA was significantly improved. For example, the modified CNT with PSPSH can be well dispersed in water more than 24 h, implying successful surface modification of CNT with hydrophilic polymers. On the other hand, the well dispersibility of CNT-PDA-PSMA in organic solution was also investigated in this work. As shown in Fig. S1, the pristine CNT was difficult to be dispersed in organic solution such as acetone, DMF and THF. However, after modifying with hydrophobic polymers (PSMA), the dispersibility was significantly improved. The CNT-PDA-PSMA can form a stable suspension in different organic solutions at ambient temperature for three days. These reulsts also implied that the hydrophobic polymers were perfectly grafted to the surface of CNT. Furthermore, the hydrodynamic size distribution of the hydrophilic polymers modified CNT (CNT-PDA-PSPSH) in water was also determined. As shown in Fig. S2A, the size distribution of CNT-PDA-PSPSH is 244 ± 71.7 nm with polydispersity index of 0.148. the sized distribution of CNT-PDA-PSPSH shows no significant difference at the time points of 2, 12 and 24 h (Fig. S2B-D). The size distribution measurement also suggested that CNT-PDA-PSPSH is well dispersed in aqueous solution, further implying the successful surface modification of CNT with polymers.

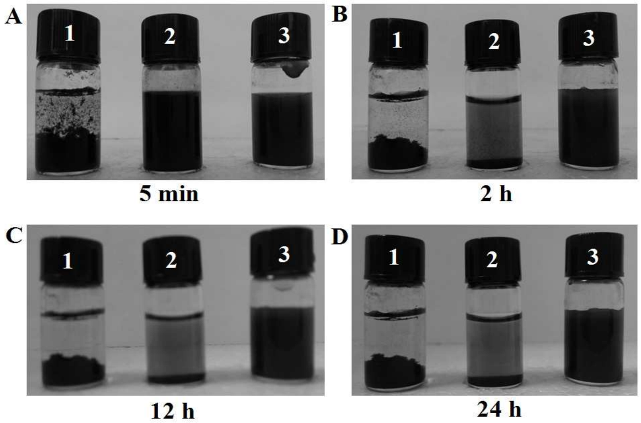


Fig. 7 Representative dispersion picture of CNT, CNT-PDA and CNT-PDA-PSPSH in water at ambient temperature at different time. (1) CNT, (2) CNT-PDA, (3) CNT-PDA-PSPSH.

Conclusion

In summary, a facile, efficient and fast strategy of functional CNT with hydrophilic and hydrophobic polymers was developed via combination of mussel inspired chemistry and SET-LRP. The functional groups such as amino and hydroxyl groups were introduced to the CNT by mussel inspired chemistry, which was followed by the facile amidation for introducing SET-LRP initiator. As compared with pristine CNT, the modified CNT with polymers by in stiu SET-LRP using CNT-PDA-Br as initiator showed increased dispersibility in water and a various of organic solvents, making them great application prospects in biomedical fields and for fabrication of nanocomposites. The novel strategy described in this work is rather simple, efficient and versatile. More importantly, many other polymers functionalized nanocomposites can also be prepared via the similar strategy because of the universal adhesive of PDA and the designability of SET-LRP. Therefore the strategy described here should be a versatile route for surface modification materials and fabrication of multifunctional nanocomposites for various applications.

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Notes

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† Electronic Supplementary Information (ESI) available: [high-resolution XPS spectra of CNT samples and dispersibility of CNT-PDA-PSMA in organic solvents were provided in supplementary information]. See DOI: 10.1039/b000000x/

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