

PEGYLATED SINGLE-WALLED CARBON NANOTUBES WITH GELABLE BLOCK COPOLYMERS*

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Abstract Functional amphiphilic block copolymer poly(ethylene glycol)-*block*-poly[(3-(triethoxysilyl)propyl methacrylate)-*co*-(1-pyrene-methyl) methacrylate], PEG₁₁₃-*b*-P(TEPM₂₆-*co*-PyMMA₄), was synthesized *via* atom transfer radical polymerization (ATRP) initiated by monomethoxy capped poly(ethylene glycol) bromoisobutyrate. This polymer exhibited strong ability to disperse and exfoliate single-walled carbon nanotubes (SWNTs) in different solvents due to the adhesion of pyrene units to surface of SWNTs. In aqueous solution, the PTEPM segments that were located on the nanotube surfaces with the pyrene units could be gelated and, as a result, the silica oxide networks with PEG coronas were formed on the surface of nanotubes, which ensured the composites with a good dispersibility and stability. Furthermore, functional silane coupling agents, 3-mercaptopropyltrimethoxysilane and 3-aminopropyltriethoxysilane, were introduced during dispersion of SWNTs using the block copolymers. They were co-gelated with PTEPM segments, and the —SH and —NH₂ functionalities were introduced into the silica oxide coats respectively.

Keywords: Amphiphilic block copolymer; Functionality; PEGylated; Single-walled carbon nanotubes.

INTRODUCTION

Nanomaterials have attracted much attention in the biological and biomedical applications recently, where single-walled carbon nanotubes (SWNTs)^[1], Au nanoparticles^[2] and magnetic nanoparticles^[3] have been investigated in the diagnosis and therapy. Due to their very thin diameter and the large aspect ratio, it was reported that SWNTs may be up-taken by cells easily, indicating that SWNTs may be used as multi-functional carriers for drug delivery, therapy and diagnosis^[4–6]. To achieve such purpose, carbon nanotubes should be endowed with solubility, biocompatibility, and functional groups by modification, such as grafting polymers to their surfaces^[7]. Though covalent modification is a common way to disperse and functionalize the SWNTs, the defects of SWNTs may be produced during modification process which is tedious for application purpose^[5, 8]. Moreover, preserving the intrinsic physical properties of SWNTs is very important for biomedical imaging and therapy^[9–11]. Thus noncovalent functionalization of SWNTs by surfactants or amphiphilic polymers *via* hydrophobic or π - π interaction has attracted much attentions^[12]. However, the detachment of weakly adsorbed molecules may result in instability, which becomes the disadvantage of this approach.

PEG is a very important polymer for improving pharmacological performance of drugs and biomaterials due to its high water solubility and lack of toxicity and immunogenicity. Incorporation of PEG chains on the surface of SWNTs is a common method to improve the solubility and biocompatibility of SWNT conjugates^[13].

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Dai *et al.* have found that PEG can improve the blood circulation time of SWNTs dramatically, which is critical to the application of SWNT for imaging and drug delivery^[14, 15]. However, the surfactants being coated along the SWNT surface may become unstable in serum due to de-adsorption of the coating molecules^[16]. Moreover, in order to endow the functions of targeting, imaging and therapy, the functionalization of SWNT surface is needed, which becomes a challenge for noncovalent modification approach. Recently, Wang *et al.* have reported a novel approach to bind polymers onto the surfaces of SWNTs firmly by crosslinking the adsorbed block copolymers^[17]. The pristine SWNTs were dispersed into solution with the aid of poly(ethylene glycol)-*b*-poly(acrylic acid)-*b*-polystyrene triblock copolymers, and then the poly(acrylic acid) layers were crosslinked by diamine chemicals. By this approach, carbon nanotubes were caged inside a shell of crosslinked triblock copolymers. However, this approach is difficult to conduct and further induce functionalities. Therefore, it is important to develop a facile method to fix PEG polymers on the nanotubes without destroying the SWNT surfaces and, at the same time, to incorporate functional groups.

This group has reported that the block copolymers bearing alkoxyisilyl groups, like PEG-*b*-poly(3-(triethoxysilyl)propyl methacrylate) (PEG-*b*-PTEPM), may self-assemble in an aqueous solution to give spherical micelles and vesicles^[18, 19]. It is noteworthy that these nanoparticles can be stabilized by inducing gelation reaction inside the aggregates and, therefore, the morphologies of the nanoparticles were stabilized by crosslinked silica networks. Moreover, these particles can be easily functionalized by co-assembly and gelation approach, namely, small molecular silanes bearing functionalities may be incorporated into the microdomains of alkoxyisilyl blocks and then be co-gelated with the block copolymers^[20]. So, it is possible to provide a stable coating along the surface of SWNTs by physical adsorption and further to introduce functionalities.

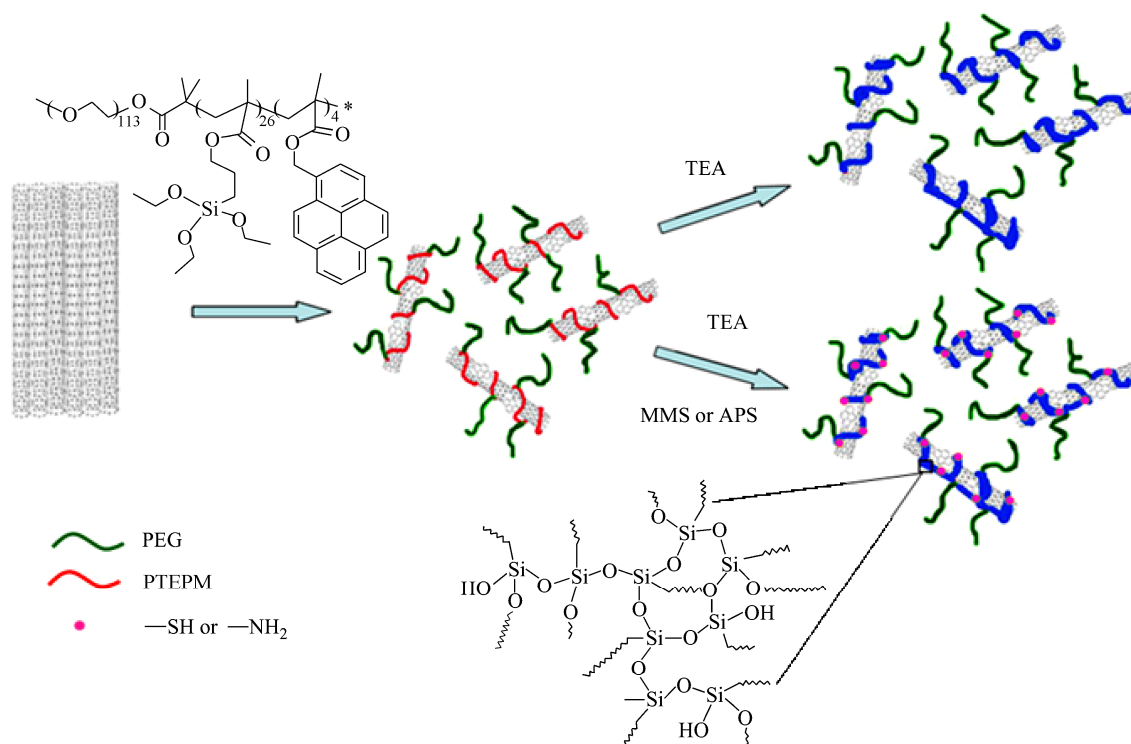


Fig. 1 Schematic presentation to modify and functionalize SWNTs using PEG-*b*-P(TEPM-*co*-PyMMA)

Herein, amphiphilic block copolymer PEG-*b*-P(TEPM-*co*-PyMMA) bearing pyrene methacrylate (PyMMA) was designed and synthesized for dispersing and functionalizing SWNTs as shown in Fig. 1. The pyrene units supply anchoring sites for π - π interaction to the surface of SWNTs, the TEPM units function as sol-

gelable groups to form a thin crosslinked layers on the surface and the PEG segments play a role to endow the water solubility and the potential pharmacological functions. The novel functional block copolymers could disperse the SWNTs efficiently in different solvents. By inducing gelation of PTEPM segments, the SWNTs were wrapped with crosslinked polymer layers but without covalent linkages, which ensure the conjugates with a good stability and dispersibility. Furthermore, functional silane-coupling agents were introduced to react with the PTEPM segments and to provide the conjugates with functional groups^[20]. This method provides a facile way to fabricate PEG coated SWNT conjugates with multiple functions.

EXPERIMENTAL

Materials

3-(Trimethoxysilyl)propyl methacrylate (> 95%, Wuhan University Silicone New Material Co.) was used as received. 3-(Triethoxysilyl)propyl methacrylate (TEPM) was synthesized according to a literature from 3-(trimethoxysilyl)propyl methacrylate^[21]. (1-Pyrene-methyl)-methacrylate (PyMMA) was synthesized from 1-pyrenemethanol and methacryloyl chloride as described in literature^[22]. Pristine SWNTs (Timesnano, prepared by chemical vapor deposition method, 90 wt%, 1–2 nm in diameter and several micrometers in length) were used without further purification. Monomethoxy capped poly(ethylene glycol)s (PEG-OH) with molecular weight 5000 was purchased from Aldrich and used as received. Macromolecular initiator (PEG-Br) was synthesized by PEG₁₁₃-OH and 2-bromoisobutyl bromide as reported previously^[23]. *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) was purchased from Aldrich. Triethylamine (TEA, > 99%, Aldrich) was dried over KOH before use. 3-Mercaptopropyltrimethoxysilane (MMS, 95%) and 3-aminopropyltriethoxysilane (APS, 95%) were purchased and distilled before use. 5-[(4,6-Dichlorotriazin-2-yl) amino] fluorescein hydrochloride (DTAF·2HCl, > 90%, Sigma) was used as received. All other chemical reagents were used directly without further purification.

Synthesis of PEG-*b*-P(TEPM-*co*-PyMMA) Copolymer

PEG-Br (500 mg, 0.1 mmol), TEPM (1.45 g, 5 mmol), PyMMA (300 mg, 1 mmol), CuBr (14 mg, 0.1 mmol) and degassed THF (5 mL) were charged into a 10 mL of Schlenk flask equipped with a magnetic stirring bar. After being degassed by three freeze-pump-thaw cycles, the mixture was stirred at room temperature for 10 min, and then PMDETA (20 μ L, 0.1 mmol) was added *via* a nitrogen-purged syringe. The flask was immersed in an oil bath thermostat at 60°C. After 12 h, the polymerization reaction was terminated and the reaction mixture was diluted with THF. Copper catalyst was removed by passing through a basic alumina column. The resulting solution was concentrated by a rotary evaporator, and the product was precipitated in hexane at –78°C three times. Finally, a waxy solid product was obtained after drying under vacuum at 30°C for 24 h. Size exclusion chromatography (SEC) provided the number-average molecular weights and the polydispersity index. The polymerization degrees of the TEPM and PyMMA were determined by ¹H-NMR spectroscopy.

Modification of SWNTs with Block Copolymer

10 mg of raw SWNTs and 20 mg of PEG₁₁₃-*b*-P(TEPM₂₆-*co*-PyMMA₄) were charged into a flask with 20 mL of ethanol, and the mixture was sonicated for 30 min, followed by centrifugation at 10000 r/min for 10 min, yielding a suspension of SWNTs with polymer coating. The precipitate was collected and dried under vacuum for 24 h; then the amounts of SWNTs and polymer were determined by thermogravimetric analysis (TGA) to estimate the amount of SWNTs in the solution^[24]. The excessive copolymer was removed by filtrating through a polycarbonate membrane (0.22 μ m of pore size) and washing with ethanol. Then the polymer functionalized SWNTs were re-dispersed in ethanol (0.1 mg/mL).

Gelation of the Polymer Modified SWNTs

2 mL of the as-prepared SWNTs solution of ethanol was charged into a flask, and then 8 mL of water was added dropwise under vigorous stirring. During this process, some precipitates formed and were removed by centrifugation. Then a drop of TEA was subsequently added to the mixture to induce the hydrolysis and

polycondensation of silane units within the composites. After 48 h, the sample was filtrated and washed with ethanol to remove TEA. The composite could disperse in different solvents, including water, acetone, ethanol and THF *etc.*

Functionalization of SWNTs by Silane Coupling Agents

3 μL of the silane-coupling agent, MMS or APS, was mixed with 2 mL of the as-prepared SWNTs solution in ethanol, and then 8 mL of water was added dropwise under vigorous stirring. After removing of the precipitates that formed during the addition of water, a drop of TEA was added to the mixture. After two days, the sample was filtrated and washed extensively with ethanol to remove TEA. The purified functional SWNTs were re-dispersed in ethanol and kept for further use.

Loading Au Nanoparticles onto the Polymer Functionalized SWNTs

Method A: preparation of SWNTs loaded with pre-prepared Au NPs

Au NPs were prepared according to the standard sodium citrate reduction method^[25] and the mean diameter measured by TEM was about 18 nm. 2 mL of the prepared Au NPs (0.01 wt%) solution was added to 3 mL of the sulphhydryl-functionalized SWNTs solution and stirred for 24 h, and then a drop of mixture was taken for TEM analysis.

Method B: in situ formation of Au NPs onto amine-functionalized SWNTs

The composite produced by the co-self-assembly of polymer modified SWNTs and APS was employed to load Au NPs *in situ*. 2 mL of HAuCl_4 aqueous solution (0.01 wt%) was added to 3 mL of the functional SWNTs solution directly and stirred for 48 h at room temperature. A drop of the sample was dripped onto copper grids to observe the morphology.

Labeling of the Composites by Fluorescent Dyes

To check the reactivity of the functional group on the surface of nanotubes, fluorescent molecule DTAF $\cdot 2\text{HCl}$ was chosen to react with amine-functionalized SWNTs under basic condition. 1 mL of DTAF $\cdot 2\text{HCl}$ ethanol solution (10 mg/mL) was added to 2 mL of the dispersion of amine-functionalized SWNTs, then 1 mL of NaOH (2 mol/L) aqueous solution was added and the mixture was kept stirring for 2 days at ambient temperature. Finally, the mixture was repeatedly sonicated, filtrated and washed with a great deal of ethanol to remove unreacted DTAF.

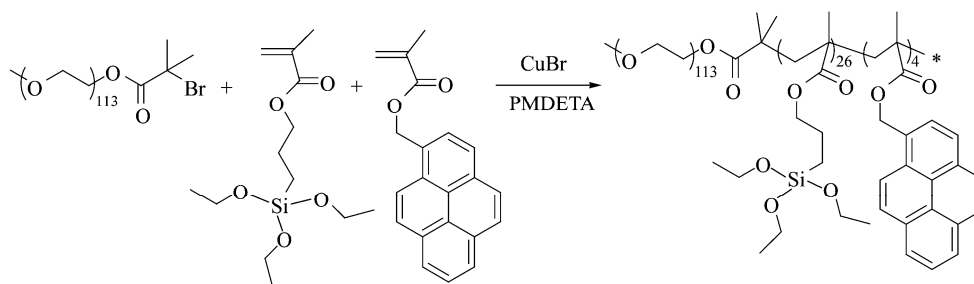
Characterization Instruments

^1H -NMR spectra were recorded on a Bruker DMX400 spectrometer with CDCl_3 as solvent at room temperature. Molecular weights and molecular weight distributions of block copolymers were determined by SEC using a Waters 515 pump and a Waters 2414 differential refractive index detector. The eluent was THF at a flow rate of 1 mL/min at 35°C. Polystyrene standards were used for the calibration. The UV/Vis spectra were acquired on a Shimadzu UV-1601PC spectrophotometer. The amount of SWNTs in the precipitate was determined using a NETZSCH4 instrument for TGA at a 50 mL/min flowing rate of nitrogen atmosphere. The temperature was increased from room temperature to 700°C at a rate of 10 K/min. TEM observations were conducted on a Hitachi H-800 instrument operated at an accelerating voltage of 100 kV. The sample was prepared by dropping the solution of modified SWNTs or composites onto copper grids coated with Formvar and carbon film. High-resolution TEM images were acquired on a JEOL 2200FS field emission transmission electron microscope at the accelerating voltage being 200 kV. Fourier-transform infrared (FTIR) spectra were recorded by a deuterate triglycine sulfate (DTGS) detector on a Bruker EQUINOX 55 spectrometer and processed by the Bruker OPUS program. Samples were prepared by milling with potassium bromide (KBr) to form a very fine powder and then compressed into a thin pellet. Confocal fluorescence microscopy (CFM) images were acquired on a Zeiss LMS 510 laser scanning confocal microscope. The 488 nm line from a mercury laser was used for excitation, and fluorescence emission was detected using a 505 nm band-pass filter.

RESULTS AND DISCUSSION

Synthesis and Characterization of PEG-*b*-P(TEPM-*co*-PyMMA) Copolymer

As shown in Scheme 1, the copolymerization of TEPM and PyMMA was carried out by ATRP with an isobromobutyryl modified PEG as the initiator. SEC analysis of the product indicated the M_n to be 9800 and the polydispersity to be 1.24 relatively to the polystyrene standards. As assigned in the $^1\text{H-NMR}$ spectrum (Fig. 2), the characteristic proton resonances from different components of block copolymers could be found. By a comparison of the integration area of the methylene proton b of the PEG segment to that of the aromatic proton l from pyrene and the methylene proton h from TEPM, the polymer molecular weight was determined to be 13700 and the ratio of TEPM:PyMMA to be 26:4.



Scheme 1 Synthesis route of PEG-*b*-P(TEPM-*co*-PyMMA) block copolymer by ATRP

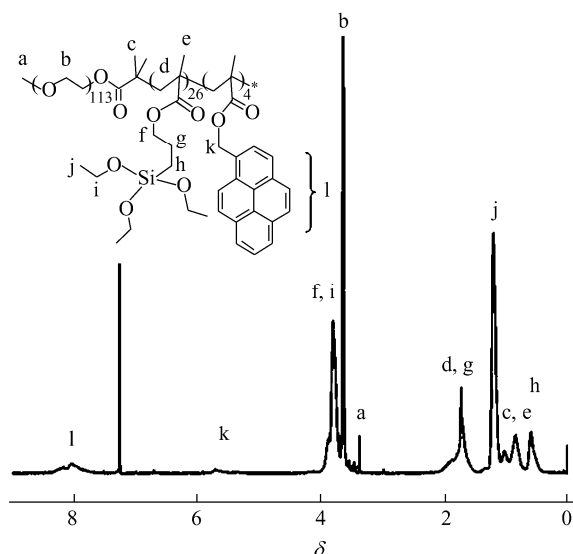


Fig. 2 The $^1\text{H-NMR}$ spectrum of block copolymer prepared through ATRP method

Dispersing SWNTs with Block Copolymers

It is known that the copolymers containing pyrene segments may effectively disperse and exfoliate SWNTs due to the strong π - π interaction between pyrene units with side wall of nanotubes^[26–29]. Herein, the block copolymer PEG₁₁₃-*b*-P(TEPM₂₆-*co*-PyMMA₄) also showed well interaction with SWNTs in solvents including chloroform, THF, acetone, ethanol *etc.* Ethanol was chosen to prepare the SWNT suspension with aid of the block copolymers. After sonication, the suspension was supercentrifuged for 10 min at 10000 r/min to separate the undispersed SWNT bundles and impurities, and the precipitates were collected, dried and weighed. The amount of SWNTs in the precipitates was determined by TGA. Then the exact amount of SWNTs in the solution was determined based on the amounts of feed and precipitates. After filtering and washing with ethanol to remove

the unattached polymers, the modified SWNTs were re-dispersed in ethanol for use. As shown in Fig. 3, the exfoliated individual or thin bundles of SWNTs were clearly observed from the TEM image. This solution of SWNTs was kept for several months without visible changes.

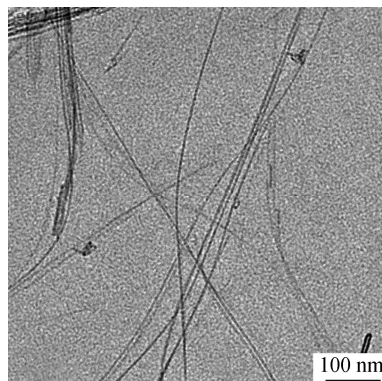


Fig. 3 TEM image of the dispersion of SWNTs in ethanol by PEG₁₁₃-*b*-P(TEPM₂₆-*co*-PyMMA₄) block copolymer

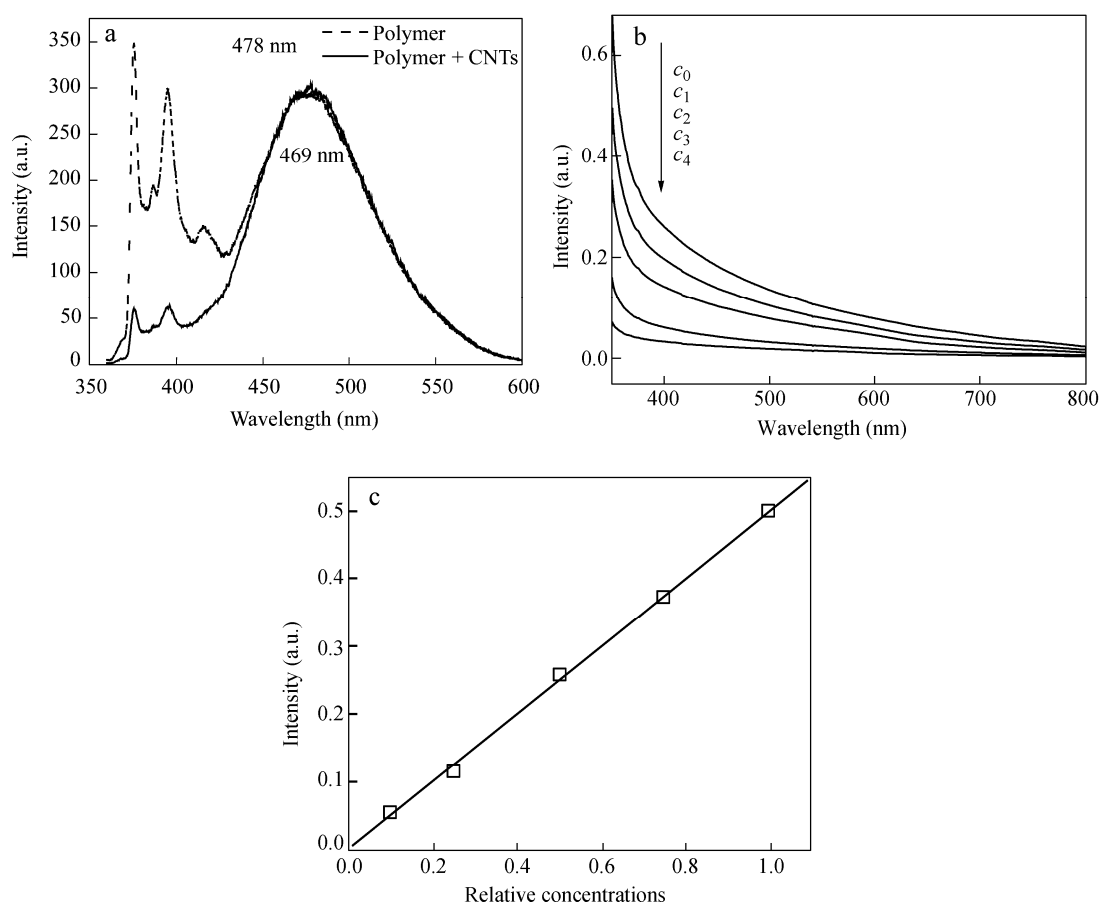


Fig. 4 (a) Fluorescence emission ($\lambda_{\text{ex}} = 340$ nm) spectra of free polymers and composites in ethanol; (b) UV/Vis absorption spectra of polymer coated SWNTs in ethanol solutions of different relative concentration ($c_0 = 0.1$ mg/mL; c_1 : $3/4c_0$; c_2 : $1/2c_0$; c_3 : $1/4c_0$; c_4 : $1/10c_0$); (c) The Lambert-Beer's plot for the absorption at 400 nm

The intimate interaction between pyrene and the SWNT surface was confirmed by quenching of pyrene fluorescence relative to free copolymer in ethanol (Fig. 4a, peaks at 375 and 395 nm). Meanwhile, the pyrene segments formed dimers in solution because ethanol is not a good solvent for pyrene as indicated by the peak at *ca.* 470 nm^[30]. To confirm the homogenous dispersion of the block copolymer modified SWNTs in solutions, UV/Vis absorption spectra of the SWNTs dispersion in ethanol at different concentrations were measured as shown in Fig. 4(b). The intensity versus concentration followed a linear relation (Fig. 4c), *i.e.* following Lambert-Beer's law^[31].

Since PTEPM is soluble in ethanol, driving force to disperse SWNTs in ethanol is based upon the interaction of pyrene units and nanotube surface. However, water is a poor solvent of PTEPM and, therefore, addition of water could induce the self-assembly of amphiphilic block copolymers along the surfaces of SWNTs, where the hydrophilic PEG should extend to the solution. After gelation of the PTEPM segments, owing to the tethered PEG corona, the surface modified SWNTs still formed homogenous suspension in different solvents. As shown in Fig. 5(a), macroscopically homogeneous solutions were obtained by dispersing the modified SWNTs in THF, ethanol, and water. TEM image (Fig. 5b) showed that single tubes or bundles of SWNT were well-dispersed and some tubes adhered to each other that might be due to the gelation between different nanotubes. High-resolution TEM image (Fig. 5c) of the same sample clearly indicated the surface of nanotubes was adhered with a layer of polymers (as the arrows pointed in Fig. 5c).

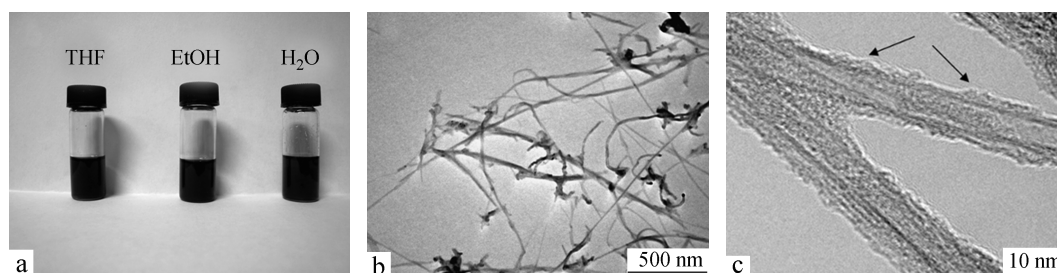


Fig. 5 (a) Photograph of the SWNTs coated with gelated block copolymers dispersed in THF, ethanol and water, (b) TEM image and (c) high-resolution TEM image of the SWNT composites

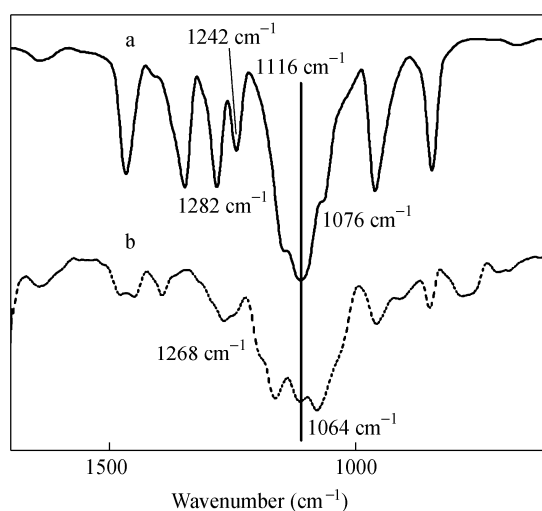


Fig. 6 FTIR spectra of the block copolymer coated SWNTs (a) before and (b) after gelation

To check the reaction of PTEPM, FTIR spectra before and after the gelation of the polymer modified SWNTs were compared (Fig. 6). It was clearly observed that after gelation all peaks were broadened, indicating

the occurrence of gelation reaction. The asymmetric absorption peaks of Si—O—C at 1064 cm^{-1} was changed to that of Si—O—Si at 1076 cm^{-1} due to the reaction. The absorption peak at 1116 cm^{-1} was assigned to the stretching vibration of C—O bond, where the decline of intensity compared to nearby peaks was caused by the loss of ethoxy group of the polymer. The C—O stretching at 1242 and 1282 cm^{-1} from the esters of PyMMA and TEPM became a broad peak (1268 cm^{-1}), which was due to the gelation.

Functionalization of Dispersed SWNTs by Introducing Functional Silanes

Previously we have found that the silane coupling agents MMS can be incorporated into the PTEPM domains of PEG-*b*-PTEPM self-assemblies in aqueous solution^[20]. Co-gelation may fuse MMS units and PTEPM segments into a whole network and, as a result, the —SH groups of MMS units were introduced into the gelated nanoparticles. This is a facile approach to functionalize the nanomaterials modified with PTEPM. Herein, MMS and APS were added into the ethanol dispersion of the SWNTs respectively. When water was introduced, hydrophobic MMS or APS could be enriched into the hydrophobic layers of PTEPM segments on the surfaces of nanotubes. By inducing gelation, MMS or APS could be *co*-gelated with PTEPM segments to form the silica oxide network, and the functional groups of silanes were introduced into the block copolymer wrapped SWNTs.

As shown by TEM images in Figs. 7(a) and 7(b), after being functionalized with sulphhydryl and amine respectively, the modified SWNT exhibited a well dispersibility in solutions. To check the sulphhydryl and amine groups on the surface of nanotubes, Au nanoparticles were introduced to the solution because both the sulphhydryl and amine have strong interaction with Au NPs. For the case of MMS modified system, Au NPs were preformed and added into the nanotube dispersion. It clearly indicated that the Au nanoparticles were organized along the nanotubes, demonstrating the presence of sulphhydryl functionalities on the SWNTs (Fig. 7c). For the case of APS modification, aqueous solution of HAuCl₄ was added directly and Au NPs were formed by self-reduction by the amine groups^[32] and the formation of the Au nanoparticles on the surface of nanotubes was observed (Fig. 7d). These results indicated the existence of the functionalities introduced through adding functional silanes during gelating fixation of block copolymers.

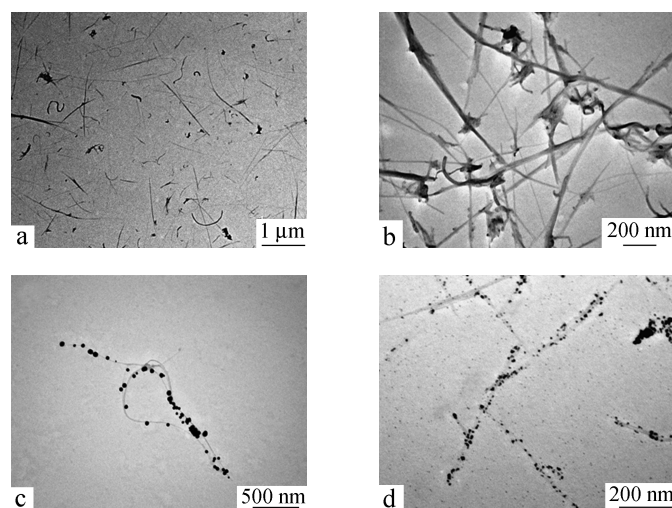


Fig. 7 TEM images of SWNTs functionalized with (a) sulphhydryls and (b) amines by introducing MMS and APS, respectively, and images of functionalized SWNTs loaded with Au nanoparticles by (c) MMS and (d) APS, respectively

Fluorescence labeling is an important method in bioimaging, herein, fluorescent molecule DTAF was chosen to react with the amine-functionalized SWNTs to explore the further application of the PEGylated SWNTs. The dichloro-s-triazinyl ring of DTAF is highly reactive toward nucleophiles, especially amines, under basic conditions^[33]. The DTAF modified sample dispersed in ethanol, free DTAF and the amine-functionalized

SWNTs were measured with UV/Vis spectroscopy and the spectra were collected in Fig. 8(a). Line c exhibited a typical absorption peak of DTAF, demonstrating that the fluorescent molecules were conjugated with SWNTs. The DTAF functionalized SWNTs were still well dispersed in solution as observed by TEM (Fig. 8b). Moreover, a drop of the DTAF labeled SWNTs solution was dropped onto a glass slide, and then the sample was observed after drying by CFM to reveal the fluorescence labeling directly. As shown in Fig. 8(c), SWNTs successfully labeled with DTAF were confirmed by the fluorescence signal, and the bright areas of micron was attributed to the aggregation of SWNTs formed during the drying process, which represented the fluorescence labeling of SWNTs.

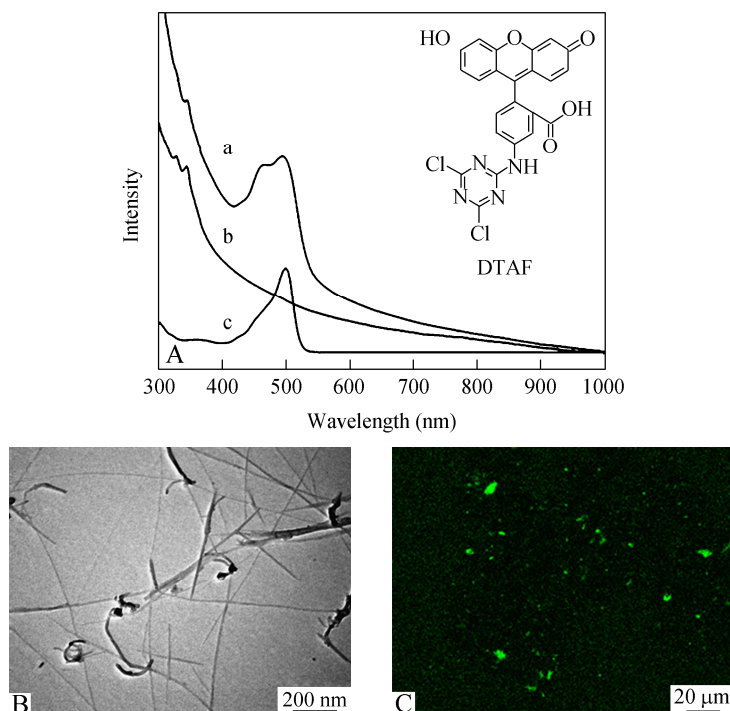


Fig. 8 (A) UV/Vis spectra of (a) DTAF solution, (b) amine functionalized SWNTs and (c) DTAF functionalized SWNTs, (B) TEM image of the DTAF functionalized SWNTs and (C) CFM image of the DTAF functionalized SWNTs

CONCLUSIONS

Functional block copolymer PEG₁₁₃-*b*-P(TEPM₂₆-*co*-PyMMA₄) was synthesized, and it has exhibited multiple properties to functionalize the SWNTs facilely. It may disperse and exfoliate the SWNTs in different solvent due to adhesion of the pyrene units to the surface of SWNTs. In aqueous solution, the block copolymers that self-assembled along the nanotubes can be gelated to form a silica oxide layer to cage the SWNTs firmly. Moreover, by addition of MMS or APS during gelation, the SWNTs can be functionalized facilely with —SH and —NH₂ respectively, which can be used to capture Au NPs and couple fluorescent dyes. Therefore, this research has supplied a useful polymer that can versatily modify and functionalize carbon nanotubes as well as other carbon nanomaterials like graphenes. It is noteworthy that no chemical linkage exists between the nanotubes and copolymers which is very important for keeping the properties of pristine carbon nanomaterials. Due to the tethered PEG coronas from the PEG-*b*-P(TEPM-*co*-PyMMA) block copolymers, the PEGylated carbon nanomaterials can be applied for evaluating their properties for potential biomedicine application.

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