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Paper

One-pot polymer modification of carbon nanotubes through mercaptoacetic acid locking imine reaction and π-π stacking

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ABSTRACT: By 'grafting to' strategy, polymers (poly(ethylene glycol), poly(methyl methacrylate)) have been facilely linked on carbon nanotube (CNT) surface through simultaneous π-π stacking and mercaptoacetic acid locking imine (MALI) reaction to achieve the CNT-polymer complex. The targeted polymers could be effectively anchored on CNT surface under mild condition (room temperature, catalyst 10 free), and the therefore obtained CNT-polymer complex can be well dispersed in regular used organic or aqueous solvents, suggesting this simple method an efficient approach to prepare CNT-polymer nanocomposite.

INTRODUCTION

Carbon nanotube (CNT) is a promising carbon material because 15 of its attractive structural, mechanical and electronic properties[1-12], but the poor solubility in normal used solvents greatly constrict its utilization realm. Anchoring polymers onto CNT surface to generate nanocomposites is the prevalent method to effectively improve the solubility of CNTs in common used organic or 20 aqueous solvents, the 'grafting from' (growing polymer chains from CNT surface) and 'grafting to' (linking synthesized polymer chains on CNT surface) strategies have therefore been appealed[13-22]. In spite of more polymer content in the CNT-polymer composite, the 'grafting from' approach is limited in the available 25 polymerization methods and the lack of regularity of attached polymers. With the development of modern coupling reactions, well-prepared polymers can also be efficiently attached on CNT surface through the 'grafting to' approach to achieve polymer-CNT nanocomposites, leading to more and more attention on that 30 straightforward strategy[23, 24]. Recently, we reassessed the highly efficient multicomponent reactions as click reactions[25-27], and combined the tricomponent Biginelli, tetracomponent Ugi reactions with π-π interaction to simply prepared CNT-polymer nanocomposites by one-pot fashion[28, 29]. However, the Biginelli 35 reaction still need heating and catalyst (Lewis acids) for successful implementation, leaving improvement space for greener strategies[30-34]. In current research, another tricomponent reaction, mecaptoacetic acid locking imine (MALI) reaction[35-37] was used to combine the supramolecular interaction (π-π stacking) 40 to prepare CNT-polymer complex through 'grafting to' approach. MALI reaction has also been valued as a tri-component click reaction which is consisted of easy available aldehyde, amine and α-sulfydryl carbonyl compound. MALI reaction possesses similar features of traditional click reactions, such as modularity, high 45 efficiency and atom economy, and can effectively process under room temperature without external added catalyst. Therefore, the MALI reaction was chosen to combined with π-π stacking to

construct a one-pot reaction system to facilely achieve polymer-CNT complex (**Scheme 1**).
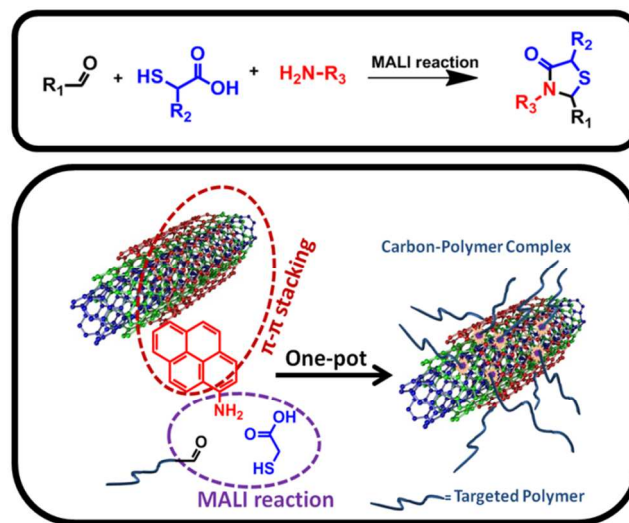
50 **Scheme 1**.One-pot surface modification of MWCNT through the MALI reaction and π-π stacking.

In this paper, aldehyde terminated synthetic polymers, i.e. methoxypolyethylene glycol (mPEG) and 55 poly(methylmethacrylate) (PMMA) have been utilized as the target polymers to accomplish surface modification of multi-wall (MWCNT) by the combination of MALI reaction and π-π stacking[38-44]. 1-Aminopyrene acts as the bridge to stack on MWCNT while take part in the MALI reaction as the necessary 60 amine source. Aldehyde terminated polymers could be thus linked to the surface of MWCNT. Various characteristic detections have been employed to prove the achievement of MWCNT-polymer composite. The MWCNT-polymer complexes embodied properties of linking polymers, and the solubility of 65 MWCNT has been dramatically enhanced, leading to well

dispersion of those polymer modified MWCNT in regular organic or aqueous solvents.

Considered the general interaction between pyrene and carbon-based nanomaterials, including CNTs, graphene and nanodiamond etc., this simple and straightforward one-pot strategy containing supramolecular recognition and click reaction might have potential as a general method to modify carbon-based nanomaterials and expand their application realms.

MATERIALS

Methoxypolyethylene glycol (mPEG, Mn ~ 5000, Aldrich), N, N'-dicyclohexylcarbodiimide (DCC, Aladdin, ≥ 99.0%), 4-dimethylamiopryidine (DMAP, Aladdin, 99%), 4-formylbenzoic acid (Aladdin, ≥ 99.0%), 1-aminopyrene (Aladdin, ≥ 99.0%), mercaptoacetic acid (Aladin, ≥ 99.0%), acetic acid (J&K Chemical, 99.8%) and methyl methacrylate (MMA, J&K Chemical, 99%) were used as purchased. 2, 2`-Azoisobutyronitrile (AIBN, J&K Chemical, 99%) was recrystalized twice from acetone before using. (4-Cyano-4-(((ethylthio)carbonothioyl)thio) pentanoic acid[45, 46] and 4-((6-hydroxyhexyl)oxy) benzaldehyde were synthesized as previous literatures[47-49].

EXPERIMENT

Synthesis of aldehyde terminated mPEG

Water in mPEG (M_n ~ 5000) was removed through azeotrope with toluene. 4-Formylbenzoic acid (0.18 g, 1.2 mmol) was dissolved into tetrahydrofuran (0.5 mL) priority while dehydrated mPEG (5.0 g, 1.0 mmol) was dissolved into dichloromethane (4.5 mL). The two solutions were mixed together, then, DCC (0.41 g, 2.0 mmol) and DMAP (12 mg, 0.1 mmol) were added into the system under nitrogen atmosphere. The reaction was conducted for 4 h at 25 °C, and the aldehyde terminated mPEG can be obtained through precipitation in ethyl ether as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$, δ/ppm): 10.07 (s, 1H, CHO), 8.18 (d, $J = 7.4$ Hz, 2H, CHOCC$\underline{H}$CHCCOO), 7.92 (d, $J = 7.4$ Hz, 2H, CHOCCHC$\underline{H}$CCOO), 4.47 (s, 2H, CH$_2$OCO), 3.80-3.30 (m, 464H, OC$\underline{H_2}$C$\underline{H_2}$O), 3.38 (s, 3H, CH$_3$O).

Synthesis of chain transfer agent (CTA) for Raft polymerization

4-Cyano-4-(((ethylthio)carbonothioyl)thio) pentanoic acid (3.0 g, 11.41 mmol) and 4-((6-hydroxyhexyl)oxy) benzaldehyde (3.8 g, 17.10 mmol) were dissolved into dichloromethane (5.0 mL), then DCC (4.7 g, 22.81 mmol) and DMAP (0.14 g, 1.14 mmol) were added under nitrogen atmosphere. The system was maintained for 4 h at 25 °C. Targeted CTA as a yellow oil (4.89 g, yield: 91.8%) could be obtained through chromatographic column using petroleum ether/ethyl acetate (3/1) as the eluant.
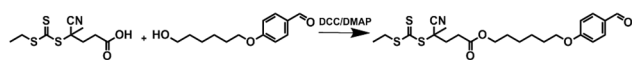
^{1}H NMR (400 MHz, CDCl$_3$, δ/ppm): 9.84 (s, 1H, CHO), 7.80 (d, $J = 7.4$ Hz, 2H, CHOCC$\underline{H}$CHCOCH$_2$), 6.96 (d, $J = 7.4$ Hz, 2H, CHOCCHC$\underline{H}$COCH$_2$), 4.21-3.93 (m, 4H, C$\underline{H_2}$OCO, OC$\underline{H_2}$CH$_2$), 3.32(m, 2H, CH$_3$C$\underline{H_2}$), 2.64-2.30 (m, 4H, CC$\underline{H_2}$C$\underline{H_2}$CO), 1.90-1.40 (m, 11H, C(CN)C$\underline{H_3}$, OCH$_2$(C$\underline{H_2}$)$_4$CH$_2$O), 1.31 (t, 3H, CH$_2$C$\underline{H_3}$).

^{13}C NMR (100 MHz, CDCl$_3$, δ/ppm): 216.84, 190.91, 171.61, 164.22, 132.09, 129.87, 119.08, 114.81, 68.24, 65.09, 53.55, 46.44, 33.97, 31.45, 29.88, 29.02, 28.54, 25.75, 24.95, 12.84.

IR (v/cm^{-1}): 2932, 2858, 2738, 2117, 1732, 1688, 1599, 1576, 1509, 1451, 1426, 1394, 1311, 1254, 1215, 1182, 1175, 1110, 1075, 1031, 859, 831, 801, 734, 702

ESI-MS: observed (expected): 467.13 (468.13) [M+H$^+$]

Synthesis of aldehyde terminated PMMA

MMA (3.00 g, 30.0 mmol), AIBN (10 mg, 0.06 mmol) and CTA (140 mg, 0.3 mmol) were mixed into toluene (5.0 mL) in a dry Schlenk tube. The system was degassed through three freeze-pump-thaw cycles and then maintained for 10 h at 70 °C. The polymer could be purified through precipitation from THF to cold methanol three times. Then the obtained PMMA was kept under vacuum at 60 °C until constant weight.
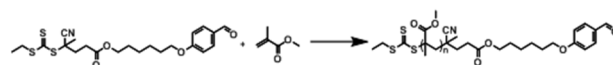
^{1}H NMR (400 MHz, CDCl$_3$, δ/ppm): 9.85 (s, 1H, CHO), 7.80 (d, $J = 8.1$ Hz, 2H, CHOCC$\underline{H}$CHCOCH$_2$), 6.96 (d, $J = 8.1$ Hz, 2H, CHOCCHC$\underline{H}$COCH$_2$), 4.12-3.95 (m, 4H, C$\underline{H_2}$OCO, OC$\underline{H_2}$CH$_2$), 3.72-3.45 (s, 305H, OCH$_3$), 3.20 (m, 2H, CH$_3$C$\underline{H_2}$), 2.46 (t, 2H, CC$\underline{H_2}$CH$_2$CO), 2.10-1.58 (s, 202H, CCH$_2$C), 1.05-0.65 (s, 303H, CCH$_3$).

GPC analysis revealed the polydispersity index (PDI ~ 1.13) and the molecular weight (M_{nGPC}~ 9500) of the obtained PMMA. From the NMR spectrum, by comparison between the peak of chain-end aldehyde group (9.85 ppm) and the peak of ester methyl group (3.75-3.45 ppm), the molecular weight of the obtained polymer was calculated as M_{nNMR}~ 10500, consistent with the GPC result.

Synthesis of MWCNT-polymer composite

Before we prepared the MWCNT-polymer composite, the model reaction has been carried out to prove that the MALI reaction could proceed smoothly without CNT. From the ^{1}H NMR spectrum of the crude taken directly from the reaction system, the aldehyde peak (~ 10.08 ppm) was almost disappeared in 4 h while a specific MALI product peak (~ 6.75 ppm) could be clearly observed (**Fig. 1S**). Then, MWCNT (50 mg), aldehyde terminated mPEG (472 mg, 0.09 mmol) and 1-aminopyrene (20 mg, 0.09 mmol) were dissolved into acetic acid (1.10 mL) at 25 °C for 1 h. The mercaptoacetic acid (42 mg, 0.45 mmol) was added into the mixture and the system was kept at 25 °C for 5 h. The MWCNT-mPEG could be separated from mixture by centrifugation (8,000 rpm, 30 min), then washed with acetone (50 mL) for 3 times to removed unreacted polymer and other impurities. MWCNT-mPEG was collected and kept in vacuum oven at 60 °C until constant weight.

The MWCNT-PMMA was prepared through same procedure.

RESULTS AND DISCUSSION

Grafting mPEG on surface of MWCNT through the collaboration of π-π stacking and MALI reaction

From the ^{1}H NMR spectrum, the chain end decoration rate of the mPEG could be calculated through comparison between peak at 10.07 ppm (aldehyde group) and peak at 3.38 ppm (methyl group), 98% terminated hydroxyl group of mPEG has been successfully transformed into target aldehyde group (**Fig. 1A**). The GPC traces of the polymers before and after modification are almost same (**Fig. 2S**), suggesting the negligible influence of the DCC coupling reaction on the polymer main chain.

Several characteristic detections were taken to analyze purified MWCNT-mPEG complex. From fourier transform infrared spectroscopy (FT-IR), MWCNT-mPEG composite possessed feature absorption peak of mPEG (C-O-C, 1120 cm^{-1}), in contrast, origin MWCNT has no signal response at all (**Fig. 1B**). Meanwhile, from the Raman spectrum, for MWCNT-mPEG, ratio of integrated peak value at 1350 cm^{-1} and at 1580 cm^{-1} was 92.8% while the ratio is 85.1% for origin MWCNT (**Fig. 3S**). Both results preliminarily suggested the existent mPEG on MWCNT surface. Thermogravimetric analysis (TGA) data indicated that MWCNT-mPEG composite has apparent weight loss (~ 30%) at 500 °C which should be attributed to surface anchored mPEG, while origin MWCNT has almost no weight loss at the same temperature (**Fig. 1C**). The transmission electron microscope (TEM) showed visual existing polymer of the MWCNT-mPEG composite, polymer layer (~ 10 nm) could be clearly observed to smoothly blanket on the MWCNT surface (**Fig. 1E**) while the origin MWCNT (**Fig. 1D**) was flatness. All these data suggested the successful modification of MWCNT with mPEG through the combination of MALI reaction and π-π stacking.
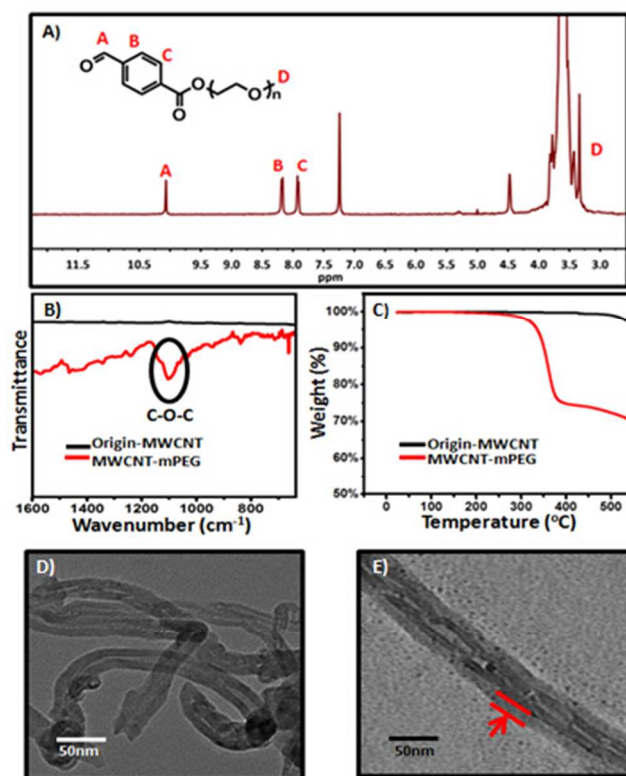
Figure 1. ^{1}H NMR spectrum of aldehyde terminated mPEG (CDCl$_3$, 400 MHz) (A). Characterization of MWCNT-mPEG: FT-IR (B), TGA (C). TEM images of origin MWCNT (D) and MWCNT-mPEG (E).

The dispersibility of obtained MWCNT-mPEG was studied using water and dichloromethane as the typical aqueous and organic solvents, respectively (**Fig. 2**). The origin mPEG was found to quickly subsided onto the bottom of bottles, while the MWCNT-mPEG composite can form stable solution in both solvents. Actually, the MWCNT-mPEG can dissolve quite well and the homogeneous solution can keep for several days without occurrence of precipitation, suggesting the excellent solubilization of the attached polymer on the MWCNT surface.
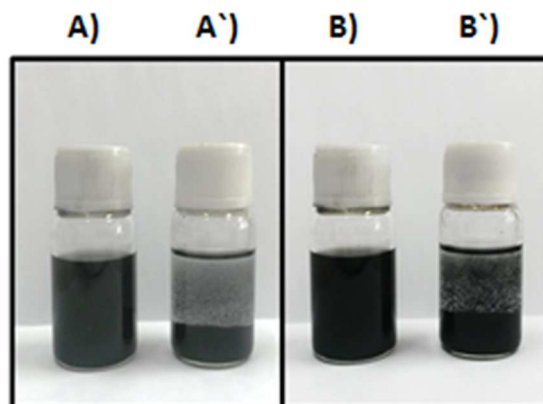
Figure 2. Solubility comparison between MWCNT-mPEG and origin MWCNT in water (A and A`) and dichloromethane (B and B`).

Grafting PMMA on surface of MWCNT through the collaboration of π-π stacking and MALI reaction

Aldehyde terminated PMMA was prepared as the typical

synthetic polymer through RAFT process. Several analyses were taken to confirm the polymer structure. From the ^{1}H NMR spectrum, characteristic peak at 9.85 ppm (aldehyde group at the chain end) and 3.75-3.45 ppm (ester methyl group in the main chain) could be clearly observed, indicating successfully obtained aldehyde terminated PMMA (**Fig. 3A**). By comparing the integral ratio of the aldehyde and ester methyl peaks, the molecular weight of the polymer was calculated as ~10500. The GPC analysis showed the polymer has narrow PDI (~1.13) while molecular weight is 9500 (**Fig. 3B**).

After the one pot modification, the MWCNT-PMMA composite was collected for further characterization. Information from FT-IR clearly showed the typical absorption signal of carbonyl group (C=O, 1690 cm^{-1}) in the MWCNT-PMMA complex, suggesting the existing PMMA on modified MWCNT surface (**Fig. 3C**). TGA data revealed approximately 20% of PMMA in the MWCNT-PMMA composite (**Fig. 3D**). TEM gave intuitive illustration that the surface of MWCNT has been encompassed by polymer with around 8-12 nm thickness (**Fig. 3E**). From the Raman spectrum, for MWCNT-PMMA, ratio of integrated peak value at 1350 cm^{-1} and at 1580 cm^{-1} has increased from 85.1% to 95.6% (**Fig. 4S**). All above data confirmed successful realization of polymer modification on the surface of MWCNT.
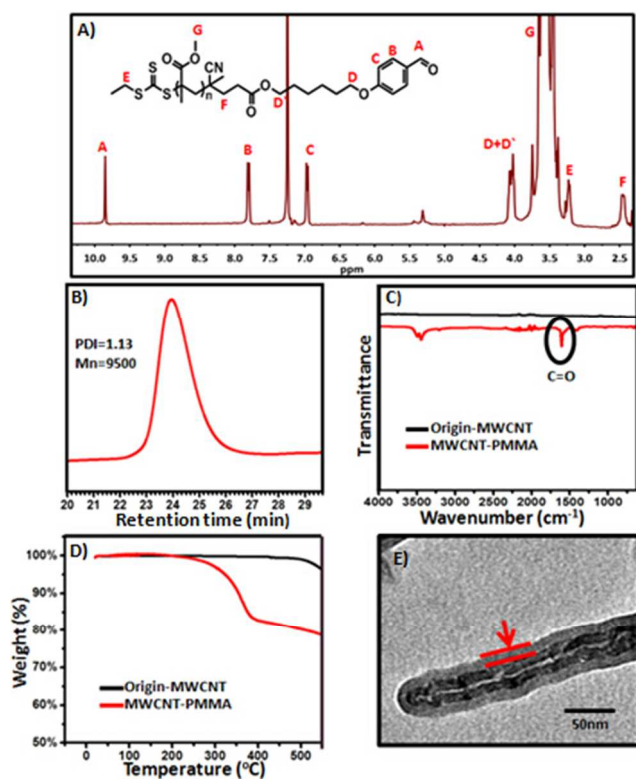

Figure 3. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) (A) and GPC trace (B) of aldehyde terminated PMMA. Characterization of MWCNT-PMMA: FT-IR (C), TGA (D), TEM images (E) of the MWCNT-PMMA complex.

Dispersibility of MWCNT-PMMA in organic solvents has also been tested. Obvious solubility difference for MWCNT-PMMA and origin MWCNT could be easily observed in toluene, acetone and tetrahydrofuran. The MWCNT-PMMA composite could be smoothly dispersed into above mentioned solvents and keep stable for several days. In contrast, origin-MWCNT has been found to promptly precipitate to the bottom of bottles (**Fig. 4**), confirming the obviously enhanced dispersibility of the MWCNT by the surface-anchored polymer.
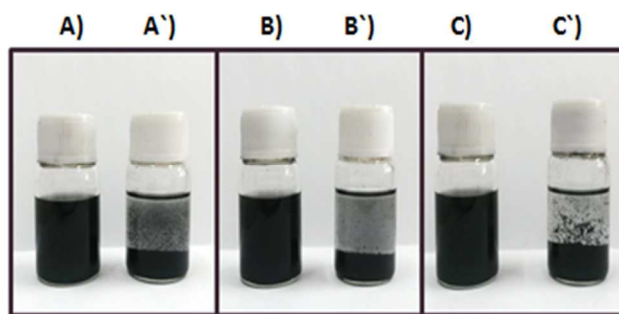

Figure 4. Solubility comparison between MWCNT-PMMA and origin MWCNT in toluene (A and A`), acetone (B and B`) and tetrahydrofuran (C and C`).

Conclusions

A facile one-pot system has been successfully constructed by the combination of MALI reaction and π-π stacking to effectively achieve MWCNT-polymer composites. Well defined polymers could be simply and efficiently linked on surface of MWCNT through 'grafting to' strategy. Polymer properties, such as the molecular weight and stereoscopic structure of polymer, and the interaction between polymer and reaction solvent might directly interfere the quantity of anchored polymer on MWCNT surface. In current research, a little more mPEG (~ 30%) was found to link on MWCNT surface than PMMA (~ 20%). We also did some work to evaluate effect of grafted density on final solubility. For example, different mPEG including mPEG-450, mPEG-1900 and mPEG-5000 were all used for the decoration of carbon nanotubes surface and the grafted polymer contents were similar (~ 15%-20%) through TGA data (unpresented data), indicating the higher molecular weight polymer leads to lower grafting density. However, MWCNT-mPEG(450) could not dissolve well in targeted solvents and quickly precipitated on the bottom of tube. The obvious solubility improvement of CNT with mPEG-1900 has been observed, the composite can well dispersed in solvents and trace sediment has be found after two weeks. The MWCNT-mPEG(5000) can dissolve so well in sovents that no precipitation has been found even after one month. Actually, the MWCNT-mPEG(5000) can only be obtained through a long time high-speed centrifugal approach (8000 rpm, 10 min for three times), illustrating the that molecule weight of polymer plays more important role than the polymer grafting density on the final solubility of the nanocomposite. MWCNT inherited the feature of anchored polymer, and its poor solubility has been dramatically improved in organic or aqueous solvents. The solubility of mPEG-MWCNT in methanol and PMMA-MWCNT in toluene has been evaluated as 1%-10%, thus, the MWCNT-polymer could be classified as soluble substance. This one-pot method might have potential application in surface modification for various carbon-base materials, such as graphene, graphene oxide, nanodiamond etc. Currently, exploring and expanding other multicomponent reaction into MWCNT surface modification are under study.

ASSOCIATED CONTENT

Supporting information

The Raman spectra of the pristine and polymer-modified MWCNTs. The GPC spectra before and after modification for mPEG. The instrumental analysis list.

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