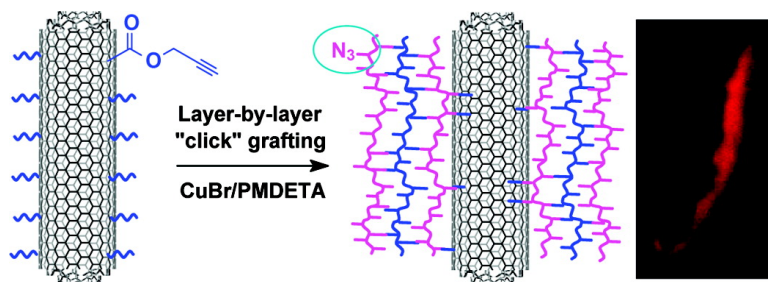


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Covalent Layer-by-Layer Functionalization of Multiwalled Carbon Nanotubes by Click Chemistry

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The covalent functionalization of multiwalled carbon nanotubes (MWNTs) by layer-by-layer (LbL) click chemistry is reported. The clickable polymers of poly(2-azidoethyl methacrylate) and poly(propargyl methacrylate) were synthesized at first by atom transfer radical polymerization (ATRP) of 2-azidoethyl methacrylate and reverse addition–fragmentation chain transfer (RAFT) polymerization of propargyl methacrylate, respectively. The two polymers were then alternately coated on alkyne-modified multiwalled carbon nanotubes using Cu(I)-catalyzed click reaction of Huisgen 1,3-dipolar cycloaddition between azides and alkynes. Thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) measurements confirm that the quantity and thickness of the clicked polymer shell on MWNTs can be well controlled by adjusting the cycles or numbers of click reaction and the polymer shell is uniform and even. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) measurements showed that there were still a great amount of residual azido groups on the surfaces of the functionalized MWNTs after clicking three layers of polymers. Furthermore, alkyne-modified rhodamine B and monoalkyne-terminated polystyrene were subsequently used to functionalize the clickable polymer grafted MWNTs, giving rise to fluorescent carbon nanotubes (CNTs) and CNT-based polystyrene brushes, respectively. It demonstrates that the residual azido groups on the surfaces of MWNTs are available for further click reaction with various functional molecules.

Introduction

Functionalization of multiwalled carbon nanotubes (MWNTs) has been of enormous interest because of the tailor-made chemical and physical properties and great potential applications of modified MWNTs especially in polymer composites.^{1–3} Various strategies to functionalize MWNTs with polymers have been explored by our group and others.^{4–16} Generally, covalent functionalization of carbon nanotubes (CNTs) is conducted via “grafting to” and “grafting from” approaches. The “grafting to” approach involves direct reaction of prepared polymers with

functional groups or reactive sites on the CNTs via esterification and amidation,¹⁷ “click” coupling,¹⁸ radical coupling,¹⁹ and anionic coupling.²⁰ The “grafting from” approach involves growth of polymer chains from CNT surfaces by means of surface-initiated polymerization (SIP) of monomers via various polymerization techniques including atom transfer radical polymerization (ATRP),²¹ nitroxide-mediated radical polymerization (NMRP),²² reversible addition–fragmentation chain-transfer (RAFT) polymerization,²³ ring-opening polymerization (ROP),²⁴ ring-opening metathesis polymerization (ROMP),²⁵ and anionic polymerization.²⁶ The “grafting to” approach has both the advantage of confirmed information of grafted polymer and disadvantages of low grafting efficiency and poor control over grafting quantity. On the contrary, the “grafting from” approach possesses the advantages of good controllability and high grafting efficiency and disadvantage of unclear molecular

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parameters of grafted polymer. On the other hand, the functional groups on the grafted polymers introduced by both approaches are only limited to several types such as hydroxyl, amino, and carboxyl, which is far from complex requirements for functionalization of CNTs. Hence, to find a novel approach that retains all the integrative advantages while overcoming the disadvantages is urgently needed. To meet the challenge, we employed layer-by-layer “click” chemistry (LbL-CC) to functionalize CNTs by alternatively grafting clickable polymeric azides and alkynes on MWNTs.

The LbL approach²⁷ is a versatile and facile technique to precisely modify surfaces of diverse substrates by circularly dipping a surface in two interactive polymer solutions alternatively. Generally, the multilayer of polymers is constructed via noncovalent electrostatic^{28–30} and hydrogen bonding^{31–33} interactions, and covalent bonding.^{34,35} In our initial work, for instance, LbL electrostatic self-assembly was conducted on polyelectrolyte-functionalized MWNTs in order to explore the application of the functionalized MWNTs.³⁶ In this work, we provide an example of a covalent LbL protocol for the controlled functionalization of MWNTs by click chemistry. Such covalent linkage offers a number of advantages, such as high stability due to the formation of a cross-linked polymer network and good control over the quantity and thickness of the polymer layers.^{37,38}

Since click chemistry was introduced by Sharpless and co-workers, a great deal of attention has been drawn due to its high efficiency and specificity in the presence of many other functional groups.^{39,40} In this regard, the Cu(I)-catalyzed azide/alkyne click reaction, a variation of the Huisgen 1,3-dipolar cycloaddition reaction between azides and alkynes, is of extreme importance and has been widely used as a versatile tool for the synthesis of functionalized carbon nanotubes,¹⁸ functional monomers,⁴¹ functional polymers,^{42,43} and so on.

The synthesis of functional materials via the combination of LbL technique and click chemistry offers a variety of superiorities. First, click reaction can be conducted in various media including water and common organic solvents (e.g., tetrahydrofuran, methanol, ethanol, *N,N*-dimethylformamide) so that both polyelectrolytes and other polymers can be used as the building materials.^{39,40} Second, the triazole linkages resulting from azides and alkynes are highly stable to hydrolysis, oxidation, or reduction.⁴⁴ Third, the residual clickable moieties after LbL cycling are available for postmodification with functional molecules,

including dyes, drugs, biomolecules, and polymers.^{45–47} Recently, the “LbL-CC” approach has been used to coat multilayers of poly(acrylic acid)³⁴ (PAA) or poly(*N*-isopropylacrylamide)³⁵ on planar substrates and fabricate click capsules.⁴⁸

Considering the versatility of the “LbL-CC” approach, it is assumed that this approach would efficiently functionalize other surfaces such as CNTs, even though the natures of CNTs are quite different from those of common surfaces such as silica. Moreover, CNTs have intrinsic excellent mechanical and physical properties, which could be applied in a wide range of fields encompassing nanocomposites to nanodevices. Thus, fabricating clickable polymer-coated CNTs would be quite interesting, since the resulting materials are not only versatile nanoplateforms that can be used to construct more complex nanostructures/nanohybrids with integrated properties by “click” chemistry but also UV-light curable composites that can be used to prepare CNT covalently reinforced high performance materials taking advantage of the UV-sensitive azido groups. We then did the exploration and achieved the successful procedure. Indeed, we find that the novel approach of LbL-CC combines the merits of both “grafting to” and “grafting from” approaches while surmounting their shortcomings and affording a versatile reactive nanoplateform of CNTs with clickable functional groups. This indicates that (1) the grafted polymer amount can be controlled by the LbL cycles, (2) the clickable polymers are prepared by controlled/living polymerizations with verified molecular weight and narrow polydispersity, and (3) the residual clickable functional groups on CNTs after polymer immobilization are still highly reactive to fulfill the function of molecular design.

Our “LbL-CC” approach to functionalize CNTs is depicted in Scheme 1. In order to get well-defined clickable polymers, we tried controlled radical polymerization (CRP) of atom transfer radical polymerization (ATRP)^{49–51} and reverse addition–fragmentation chain transfer (RAFT) polymerization.^{52,53} The first polymer containing essential azido side groups synthesized by ATRP was poly(2-azidoethyl methacrylate),⁵⁴ which was clicked on the preprepared alkyne-modified MWNTs as the first polymeric layer. Poly(propargyl methacrylate)^{55–57} synthesized by RAFT polymerization containing essential alkyne side groups was subsequently coated as the second polymeric layer via click chemistry. Once again, poly(2-azidoethyl methacrylate) was clicked on the two polymer layer grafted CNTs as the third polymeric layer. Postmodification of the functionalized CNTs with residual clickable azido groups was then verified by further click attachment using small molecules of alkyne-modified rhodamine B⁵⁸ and macromolecules of monoalkyne-terminated poly(styrene).⁵⁹

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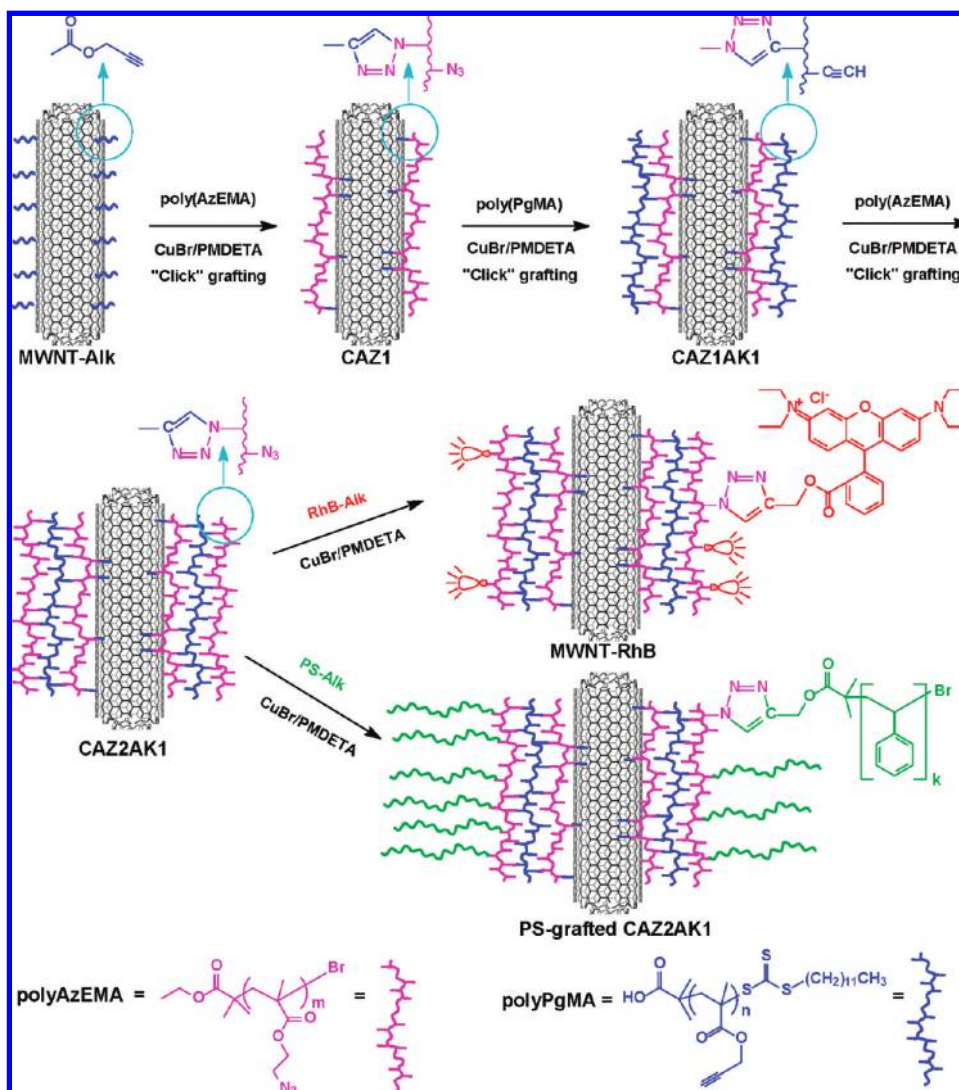
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Scheme 1. Functionalization of MWNTs by LbL-CC Approach and Further Modification of the Functionalized MWNTs with Fluorescent Dye and Polystyrene by Click Chemistry



Experimental Section

Materials. Cu(I)Br (Aldrich, 98%) was purified before use by extraction with glacial acetic acid overnight and then washed with ethanol and diethyl ether. Ethyl 2-bromoisobutyrate (99%), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), 2,2'-bipyridyl (bpy, 99%), *N,N*-(dimethylamino)pyridine (DMAP, 98%), 2-bromoisobutyrylbromide (98%), 1,3-dicyclohexylcarbodiimide (DCC, 98%), *N*-(3-dimethylamino-propyl)-*N'*-ethylcarbodiimide hydrochloride (EDC·HCl, 99%), methacrylic acid (99%), and propargyl alcohol (99%) were obtained from Alfa Aesar and used as received. Triethylamine, dichloromethane, styrene (St, Alfa Aesar, 98%), and toluene were dried over CaH₂ and distilled under reduced pressure before use. Azobisisobutyronitrile (AIBN) was recrystallized twice in methanol. Tetrahydrofuran (THF), methanol, dichloromethane (CH₂Cl₂), *N,N*-dimethylformamide (DMF), rhodamine B, 2-chloroethanol, and other organic reagents or solvents were obtained from Shanghai Reagents Company and used as received. The chain transfer agent (CTA) of *S*-1-dodecyl-*S'*-(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (DDAT)⁵⁵ for RAFT polymerization, alkyne-modified rhodamine B (RhB-Alk),⁵⁸ propargyl 2-bromoisobutyrate,⁵⁹ carboxyl-functionalized multiwalled carbon

nanotubes (MWNT-COOH, ca. 12.9 wt % -COOH groups),⁶⁰ alkyne-modified MWNTs (MWNT-Alk),⁶¹ and 2-azidoethanol⁶² were synthesized according to the published procedures.

Measurements. Molecular weights were determined by gel permeation chromatography (GPC) using a PE series 200 instrument, with polystyrene (PS) as the standard and DMF as the eluent at a flow rate of 1 mL/min. ¹H NMR spectra were obtained using a Varian Mercury Plus 400 MHz spectrometer. Fourier-transform infrared (FTIR) spectra were recorded on a PE Paragon 1000 spectrometer, and all the samples were prepared as KBr pellets. Thermal gravimetric analysis (TGA) was measured on a PE TGA-7 instrument with a heating rate of 20 °C/min in a nitrogen flow (60 mL/min). Fluorescence spectra were recorded at room temperature on a PE LS-50B fluorescence spectrometer. Fluorescence microscopy images were taken using an OLYMPUS IX71 microscope with a DIC slider at a magnification of 400 \times ($\lambda_{\text{ex}} = 520\text{--}550$ nm). X-ray photoelectron spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with Mg K α radiation ($h\nu = 1253.6$ eV). In general, the X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54°. Raman spectra were collected on a LabRam-1B Raman spectroscope

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equipped with a 632.8 nm laser source. Scanning electron microscopy (SEM) images were recorded using an LEO 1550VP field-emission microscope, and the samples were loaded onto silicon surfaces. Transmission electron microscopy (TEM) analysis was conducted on a JEOL JEL2010 field-emission electron microscope at 200 kV. Confocal fluorescence imaging was performed with a Zeiss LSM-510 laser scanning microscope. Excitation of MWNT-RhB at 543 nm was carried out with a He-Ne laser. Fluorescent decaying time was measured with an EDINBURGH INSTRUMENTS FLS920 spectrometer equipped with an nF900 Flash lamp.

Synthesis of PolyAzEMA by ATRP.⁵⁴ Typically, a mixture containing 2-azidoethyl methacrylate (AzEMA) (3.10 g, 20 mmol), CuBr (14.4 mg, 0.1 mmol), and acetone (3.1 g) was deoxygenated by bubbling with nitrogen for at least 30 min. 2,2'-Bipyridine (bpy, 31.3 mg, 0.2 mmol) was introduced under the protection of nitrogen flow. The reaction mixture was stirred for 15 min to allow the formation of the CuBr/bpy complex. The reaction mixture was heated to 50 °C, and ethyl 2-bromoisobutyrate (14.7 μ L, 0.1 mmol) was added to the mixture under a nitrogen flow. The mixture was stirred at 50 °C for 3 h, and then the Schlenk flask was removed from heat and opened to expose the catalyst to air. The mixture was diluted with THF and passed through a neutral alumina column to remove copper catalyst. The collected eluents were concentrated and precipitated into an excess of methanol. This purification cycle was repeated twice. The obtained product was dried overnight in a vacuum oven at 50 °C for 24 h to give polyAzEMA (0.95 g, $M_n = 12\,500$; $M_w/M_n = 1.37$). ¹H NMR (CDCl₃, δ , ppm): 4.32–4.26 (m, CH₃CH₂O–), 4.22–4.00 (s, –CH₂CH₂O–), 3.60–3.44 (s, –CH₂N₃), 2.17–1.83 (m, C–CH₂–C), 1.17–0.90 (m, –CH₃, –C(CH₃)₂–). IR spectrum (cm^{–1}): 2106 (N₃), 1732 (C=O).

Synthesis of PolyPgMA by RAFT Polymerization.^{55–57} A mixture of propargyl methacrylate (PgMA, 3.72 g, 30 mmol), DDAT (36.4 mg, 0.1 mmol), AIBN (3.6 mg, 0.022 mmol), and toluene (18.75 mL) was placed in a Schlenk flask and freeze–pump–thaw degassed three times. The polymerization was started by immersing the flask into an oil bath at 80 °C. After 3 h, the Schlenk flask was quenched in liquid nitrogen and exposed to the air. The reaction mixture was concentrated and precipitated into an excess of methanol. The products were collected and redissolved in methylene chloride, and the solution was reprecipitated into an excess of methanol. This purification cycle was repeated twice. The obtained product was dried overnight in a vacuum oven at 50 °C for 24 h to give polyPgMA (2.19 g, $M_n = 25\,000$; $M_w/M_n = 1.64$). ¹H NMR (CDCl₃, δ , ppm): 4.62 (s, CH₂O), 2.52 (s, C \equiv CH), 2.17–1.20 (m, C–CH₂–C of poly-PgMA, –CH₂–(CH₂)₁₀–CH₃), 1.14–0.85 (m, –CH₃ of poly-PgMA, –C(CH₃)₂–polyPgMA, –CH₂–(CH₂)₁₀–CH₃). IR spectrum (cm^{–1}): 3300, 2132 (C \equiv CH), 1734 (C=O).

Synthesis of Monoalkyne-Terminated Polystyrene (Alk-PS) by ATRP.⁵⁹ Typically, a mixture containing styrene (5.2 g, 50 mmol) and CuBr (143.5 mg, 1 mmol) was deoxygenated by bubbling with nitrogen for at least 30 min. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA, 210.9 μ L, 1 mmol) was introduced under the protection of nitrogen flow. The reaction mixture was stirred for 15 min to allow the formation of the CuBr/PMDETA complex. The reaction mixture was heated to 110 °C, and propargyl 2-bromoisobutyrate (142 mg, 1 mmol) was added to the mixture under a nitrogen flow. The mixture was stirred at 110 °C for 10 min, and then the Schlenk flask was removed from heat and opened to expose the catalyst to air. The mixture was diluted with methylene chloride and passed through a neutral alumina column to remove copper catalyst. The collected eluents were concentrated and precipitated into an excess of methanol. This purification cycle was repeated thrice. The obtained product was dried overnight in a vacuum oven at 50 °C for 24 h to give Alk-PS (2.18 g, $M_n = 2500$; $M_w/M_n = 1.32$). ¹H NMR (CDCl₃, δ , ppm): 7.32–6.31 (m, –C₆H₅O), 4.60–4.35

(d, CH₂–CH(Ph)–Br, \equiv CCH₂O–), 2.30–1.15 (m, –CH₂CH– of PS), 1.03–0.88 (s, 6H, –C(CH₃)₂–PS).

General Procedure for Layer-by-Layer Grafting on MWNTs.^{39,40} Typically, 30 mg of functionalized MWNTs was suspended in 10 mL of DMF in a 25 mL round-bottom flask. The suspension was deoxygenated by bubbling with nitrogen for at least 30 min. PolyAzEMA (300 mg, polyPgMA or polyAzEMA was added for clicking the second or the third on the corresponding polymer-coated MWNTs), CuBr (28.7 mg, 0.2 mmol), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 42.2 μ L, 0.2 mmol) were added under the protection of nitrogen flow. The mixture was stirred at room temperature for 24 h. The solid was separated from the mixture by centrifugation. The collected solid was redispersed in DMF (50 mL) and separated by centrifugation. This purification cycle was repeated thrice. After purification, the resulting solid was dried overnight in vacuum, obtaining clickable polymer-functionalized CNTs, CAZ1 (CAZ1AK1 and CAZ2AK1, respectively).

Synthesis of RhB-Alk Labeled MWNTs (MWNT-RhB).^{39,40} Typically, 3 mg of CAZ2AK1 was suspended in 10 mL of DMF in a 25 mL round-bottom flask. RhB-Alk (10 mg), CuBr (2.9 mg, 0.02 mmol), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 4.2 μ L, 0.02 mmol) were added under the protection of nitrogen flow. The mixture was stirred at room temperature for 24 h. The solid was separated from the mixture by centrifugation. The collected solid was redispersed in THF (50 mL) and separated by centrifugation. This purification cycle was repeated 10 times, until the solvent in the centrifugation tubes was colorless. After purification, the resulting solid was dried overnight in vacuum, obtaining MWNT-RhB.

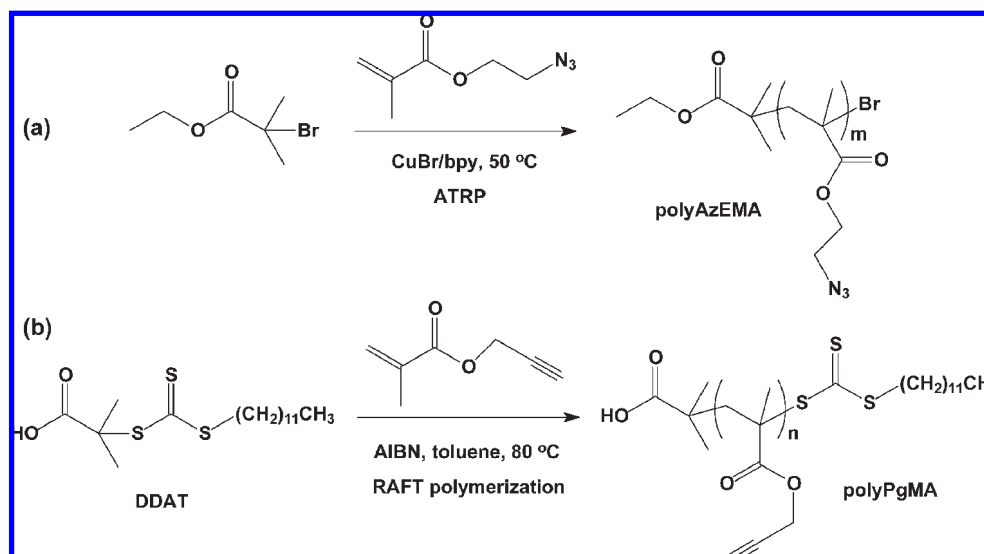
Influence of Reaction Time and Higher Temperature on the Effect of Labeling RhB-Alk on MWNTs. The as-prepared CAZ2AK1 (6 mg) was suspended in 20 mL of DMF in a 50 mL round-bottom flask. RhB-Alk (20 mg), CuBr (5.8 mg, 0.04 mmol), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 8.4 μ L, 0.04 mmol) were added into the flask under the protection of nitrogen flow. The reaction was allowed to proceed at 50 °C. After a certain time (1, 8, 24, and 48 h), a sample was taken from the reaction system using a syringe under the protection of nitrogen flow. The solid was separated from the mixture by centrifugation. The collected solid was redispersed in THF (50 mL) and separated by centrifugation. This purification cycle was repeated 10 times, until the solvent in the centrifugation tubes was colorless (no fluorescence signal of RhB-Alk was detected in the supernatant solvent). After purification, the resulting solid was dried overnight in vacuum, affording a sample of RhB-Alk labeled MWNTs.

Growing Polystyrene Brushes on Functionalized MWNTs by Click Grafting to Approach.^{39,40} A total of 30 mg of CAZ2AK1 was suspended in 10 mL of DMF in a 25 mL round-bottom flask. The suspension was deoxygenated by bubbling with nitrogen for at least 30 min. Monoalkyne-terminated polystyrene (Alk-PS, 300 mg), CuBr (28.7 mg, 0.2 mmol), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 42.2 μ L, 0.2 mmol) were added under the protection of nitrogen flow. The mixture was stirred at room temperature for 24 h. The solid was separated from the mixture by centrifugation. The collected solid was redispersed in DMF (50 mL) and separated by centrifugation. This purification cycle was repeated thrice. After purification, the resulting solid was dried overnight in vacuum, yielding CAZ2AK1-PS.

Results and Discussion

Preparation of Clickable Polymers by CRP. In order to utilize layer-by-layer click chemistry (LbL-CC) to functionalize CNTs, we prepared two kinds of novel clickable polymers of poly(2-azidoethyl methacrylate) (polyAzEMA) and poly(propargyl methacrylate) (polyPgMA) via CRP (Scheme 2). Previously,

Scheme 2. Synthesis of Poly(2-azidoethyl methacrylate) (polyAzEMA) by ATRP (a) and Poly(propargyl methacrylate) (polyPgMA) by RAFT Polymerization (b)



Matyjaszewski and co-workers polymerized 3-azidopropyl methacrylate via ATRP, and good control over molecular weight and polydispersity index (PDI) was gained.⁵⁴ Hence, we tried to synthesize well-defined poly(2-azidoethyl methacrylate) by ATRP herein. Using CuBr/bpy as catalyst and ethyl 2-bromoisobutyrate as initiator, we obtained polyAzEMA with controlled molecular weight and narrow PDI ($M_n = 12\,500$; $M_w/M_n = 1.37$) after 3 h of polymerization in acetone at 50 °C. It was reported that ATRP of propargyl methacrylate was hardly controllable ($M_w/M_n > 3.3$ at 50% monomer conversion), due to the involvement of the acetylene moiety during the radical process.⁵⁴ Therefore, we tried to prepare poly(propargyl methacrylate) by RAFT polymerization. In order to test the controllability of polymerization and large-scale availability of the polymer, we used the monomer of propargyl methacrylate directly without protection of the acetylene function employing *S*-1-dodecyl-*S'*-(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (DDAT) as the chain transfer agent (CTA).⁵⁵ No cross-linking or coupling peak was observed in GPC traces (see Figure 1C), and the resulting polyPgMA showed controlled molecular weight and relatively narrow polydispersity ($M_n = 25\,000$; $M_w/M_n = 1.64$) after 3 h of polymerization at 80 °C in toluene. This suggests that well-defined poly(propargyl methacrylate) can be prepared by RAFT polymerization of propargyl methacrylate directly, paving the way for controlled and cost-effective synthesis of polymeric alkynes. The chemical structures of the clickable polymers were confirmed by ¹H NMR and FTIR measurements (see Figure 1A, B). Figure 1A shows the ¹H NMR spectra of polyAzEMA and polyPgMA with all expected peaks. Figure 1B shows the FTIR spectra of polyAzEMA and polyPgMA. In the FTIR spectrum of polyAzEMA, the characteristic peaks of azido and carbonyl groups are observed strongly at 2106 and 1732 cm^{-1} , respectively. In the FTIR spectrum of polyPgMA, the characteristic peaks at 3300 and 2132 cm^{-1} are assigned to alkyne groups and the characteristic peak at 1734 cm^{-1} is assigned to carbonyl groups. The peaks attributed to stretching of C–H at around 2900 and 2930 cm^{-1} are observed for both samples.

Synthesis Design of Polymer-Clicked CNTs. To functionalize MWNTs using click chemistry, alkyne groups were introduced on the surfaces of MWNTs by acylation reaction. The as-prepared MWNT-COOH was suspended in thionyl chloride to

fabricate acyl chloride-functionalized MWNTs (MWNT-COCl). After thionyl chloride was removed under reduced pressure, propargyl alcohol, CHCl_3 , and anhydrous triethylamine were introduced dropwise to give alkyne-functionalized MWNTs (MWNT-Alk). The prepared clickable polymers were then alternately grafted on the MWNT-Alk using Cu(I)-catalyzed click reaction of Huisgen 1,3-dipolar cycloaddition between azides and alkynes as shown in Scheme 1. After three layers of clickable polymers were coated, a clickable nanoplateform based on the hybrids of functional polymers and MWNTs was obtained, which is quite useful for further molecular design and material synthesis. To probe the reactivity of such a nanoplateform, we synthesized a functional dye of alkyne-modified rhodamine B and a functional macromolecule of monoalkyne-terminated polystyrene and employed them to react with the click polymer grafted MWNTs. It is noteworthy that all the polymers used for click coupling can be recycled by passing through a neutral alumina column to remove copper catalyst and precipitating into an excess of methanol.

The resulting functionalized MWNTs were characterized by TGA, FTIR, Raman, XPS, SEM, and TEM measurements.

TGA Measurements. Figure 2a shows the TGA weight loss curves of pristine MWNTs and functionalized MWNTs. The weight loss of pristine MWNTs below 500 °C is less than 1%. On the contrary, the weight losses of the samples of MWNT-COOH and MWNT-Alk increase to about 12.9% and 21.5%, respectively, due to the decomposition of organic groups on the surfaces of MWNTs. Calculated from corresponding TGA weight loss data, the content of alkyne groups on the surfaces of MWNT-Alk is about 2.60 mmol per gram of MWNT-Alk. A distinct weight-loss stage below 230 °C in the TGA curves is observed for both CAZ1 and CAZ2AK1. This weight-loss stage below 230 °C is likely attributed to the decomposition of plentiful residual azido groups on the surfaces of the both samples, which is consistent with the observation of FTIR spectra given below. Significant weight losses are found for the samples of MWNTs with grafted polymer, that is, 33.5%, 49.5%, 66.8% and 83.0% for CAZ1, CAZ1AK1, CAZ2AK1 and CAZ2AK1-PS, respectively. The results are also summarized in Table 1. Figure 2b shows the relative mass increment (Inc%) as a function of grafted polymer layer. A linear correlation is found between the logarithm (to base e) of Inc% and the polymer layer for the three multisite LbL

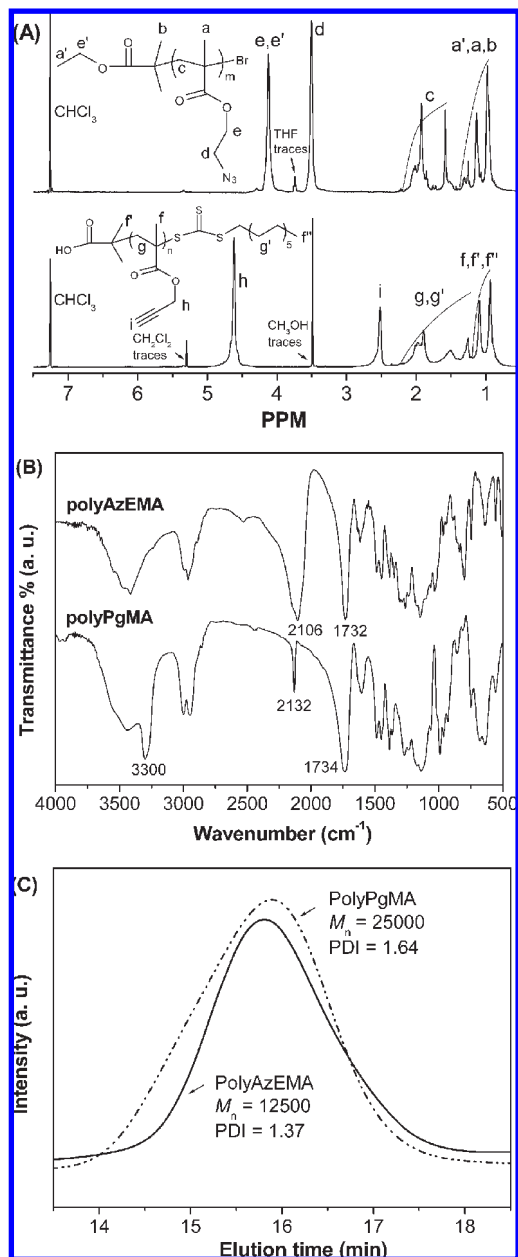


Figure 1. ¹H NMR spectra (A), FTIR spectra (B), and GPC elution curves (C) of poly(AzEMA) and poly(PgMA) used to functionalize MWNTs.

graftings, indicating that the grafted polymer content increases with the clicked layer exponentially. For the outmost layer of single site PS-grafting, the mass increment is also close to exponential compared with the inner layers, showing the high click efficiency of polymer brush growth.

The results indicate that (1) the as-prepared MWNT-Alk is highly efficient for click reaction with polyAzEMA, (2) the weight loss increases in agreement with the increasing number of polymeric layers grafted on MWNTs, so it is facile to control the quantities of polymeric coating on MWNTs by adjusting the cycles of click reaction, and (3) the weight loss of CAZ2AK1-PS is much higher than that of CAZ2AK1, demonstrating that plentiful residual azido groups on the surfaces of CAZ2AK1 are available for further modification.

FTIR, Raman, and XPS Spectra. The FTIR spectrum is quite sensitive for the click reaction due to the characteristic absorption peak of azido/alkyne groups located at ~ 2100 cm⁻¹.

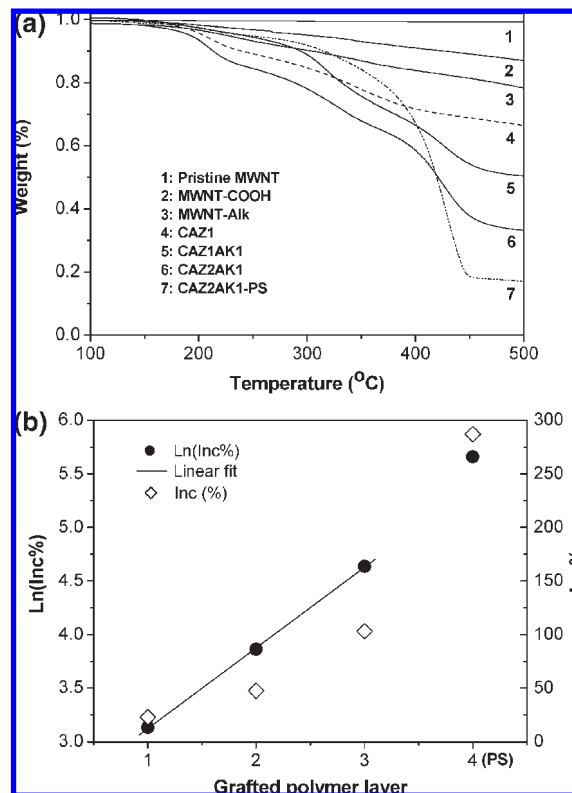


Figure 2. (a) TGA curves of the pristine MWNTs and functionalized MWNTs. (b) Logarithm of the relative increment ($\ln(\text{Inc}\%)$) and the relative mass increment ($\text{Inc}\%$) of functionalized MWNTs as a function of grafted polymer layer.

Table 1. Grafting Polymeric Layers on MWNT Surfaces via Layer-by-Layer Click Chemistry Approach

sample	substrate	polyAz EMA ^a	poly PgMA ^a	Alk- PS ^a	f_{wt}^b %	Inc % ^c	\bar{d} (nm) ^d
MWNT-Alk	MWNT-COOH	0	0		21.5		
CAZ1	MWNT-Alk	1	0		33.5	23.0	2.0 ± 0.3
CAZ1AK1	CAZ1	1	1		49.5	47.6	5.0 ± 0.5
CAZ2AK1	CAZ1AK1	2	1		66.8	103.2	7.5 ± 0.7
CAZ2AK1-PS	CAZ2AK1	2	1	1	83.0	287.0	

^aThe number of layers of corresponding polymer on MWNTs. ^bThe fraction of grafted polymer calculated from TGA results. ^cThe relative increment compared to precursor substrate with the same amount of neat CNTs. ^dThe average thickness of grafted polymer layers measured from TEM images with 8–10 nanotubes.

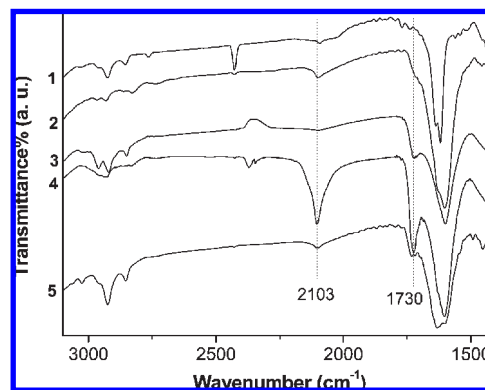


Figure 3. FTIR spectra of MWNT-Alk (1), CAZ1 (2), CAZ1AK1 (3), CAZ2AK1 (4), and CAZ2AK1-PS (5).

As shown in Figure 3, the absorption peak of the carbonyl band (C=O) at around 1730 cm^{-1} is hardly detected for MWNT-Alk, and the peak intensity increases considerably with increasing layers of polymer clicked on MWNTs for the samples of CAZ1, CAZ1AK1, and CAZ2AK1, with respect to the C=C absorption peak around 1560 cm^{-1} . The intensity of the carbonyl band is weakened for the sample of CAZ2AK1-PS owing to PS grafting. The absorption peak of alkyne groups (C≡CH) at around 2100 cm^{-1} is observed for the sample of MWNT-Alk, but the intensity of the peak is comparatively weak, with respect to the absorption peak of azido groups (N_3) at around 2103 cm^{-1} observed for the sample of CAZ1, which indicated that poly-AzEMA had been clicked on MWNT-Alk. The peak of azido or alkyne groups is hardly detected for the sample of CAZ1AK1, due to the extremely high efficiency of click reaction between azides and alkynes and the relatively weak absorption of alkyne groups. The peak of azido groups is strongly observed for the sample of CAZ2AK1, which shows that a layer of polyAzEMA has been clicked on CAZ1AK1 and there are still plenty of residual azido groups on the surface of CAZ2AK1. The peak of azido groups is also found for the sample of CAZ2AK1-PS, but the intensity greatly decreases with respect to that of CAZ2AK1, which shows that a considerable part of azido groups were consumed via click reaction. The peaks at around 2900 and 2930 cm^{-1} are observed for all five samples and the peaks can be attributed to stretching of C–H. The FTIR spectra confirmed the LbL click reactions between azides and alkynes.

Raman spectroscopy is used as a powerful tool to characterize the functionalized MWNTs, including the extent of disorder or the degree of crystallization in the functionalized MWNTs.⁶³ It is well-known that the *D*-band is related to the defects and disorder-induced modes in the curved graphene sheets, tube ends, and turbostratic structure of graphene in the MWNTs, and the *G*-band is attributed to in-plane E_{2g} zone-center mode.^{64–66} As shown in Figure 4a, the *D*- and *G*-bands of MWNTs around 1333 and 1588 cm^{-1} are clearly observed for pristine MWNTs, MWNT-COOH and MWNT-Alk. The *D*- to *G*-band intensity ratios (I_D/I_G) for MWNT-COOH and MWNT-Alk are ~ 2.18 and 2.47 , respectively, which are greater than that of pristine MWNTs (~ 1.62). By comparing the values of I_D/I_G of the three samples, we can find that the degree of disorder is increased after functionalization of MWNTs.^{64–66} The *D'*-band around 1611 cm^{-1} , attributed to the defects and disorder in MWNTs resulting from functionalization, can be barely observed for the pristine MWNTs, but it is clearly observed for MWNT-COOH and MWNT-Alk. This also indicates that the defects increase after functionalization.^{63–66} As shown in Figure 4b, for all the polymer-coated MWNTs, the *D*-, *G*- and *D'*-bands of MWNTs are also clearly observed at around 1330 , 1580 , and 1610 cm^{-1} , respectively, and the relative peak intensities are not attenuated. Even for the sample of CAZ2AK1-PS with a polymer fraction as high as 83.0%, the characteristic absorption peaks of MWNTs can still be clearly observed. Furthermore, the signals of polystyrene of CAZ2AK1-PS are not found, which is in agreement with our previous report of covalent linkage.⁶³

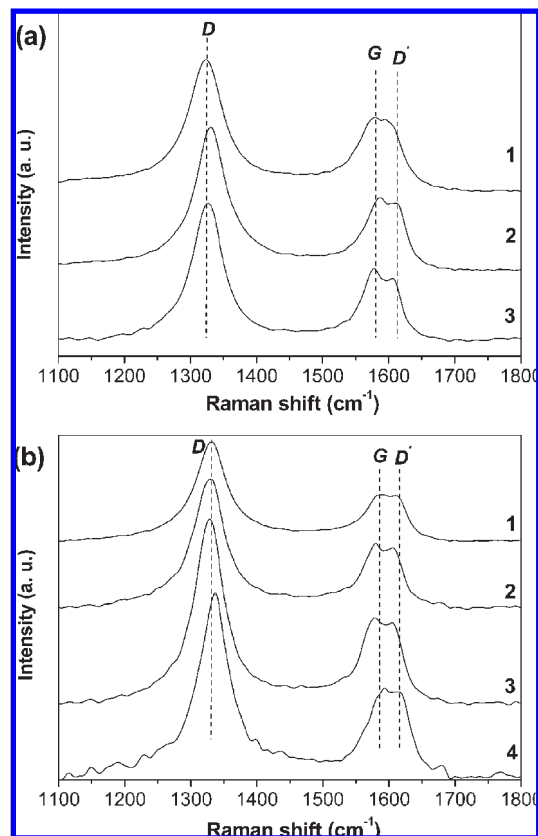


Figure 4. (a) Raman spectra of pristine MWNTs (1), MWNT-COOH (2), and MWNT-Alk (3). (b) Raman spectra of CAZ1 (1), CAZ1AK1 (2), CAZ2AK1 (3), and CAZ2AK1-PS (4).

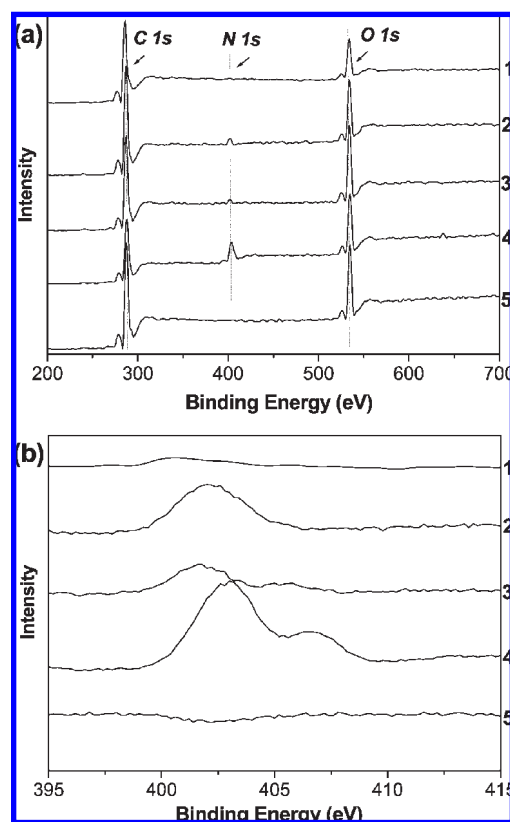


Figure 5. (a) XPS spectra of MWNT-Alk (1), CAZ1 (2), CAZ1AK1 (3), CAZ2AK1 (4), and CAZ2AK1-PS (5). (b) XPS spectra for the N (1s) region of MWNT-Alk (1), CAZ1 (2), CAZ1AK1 (3), CAZ2AK1 (4), and CAZ2AK1-PS (5).

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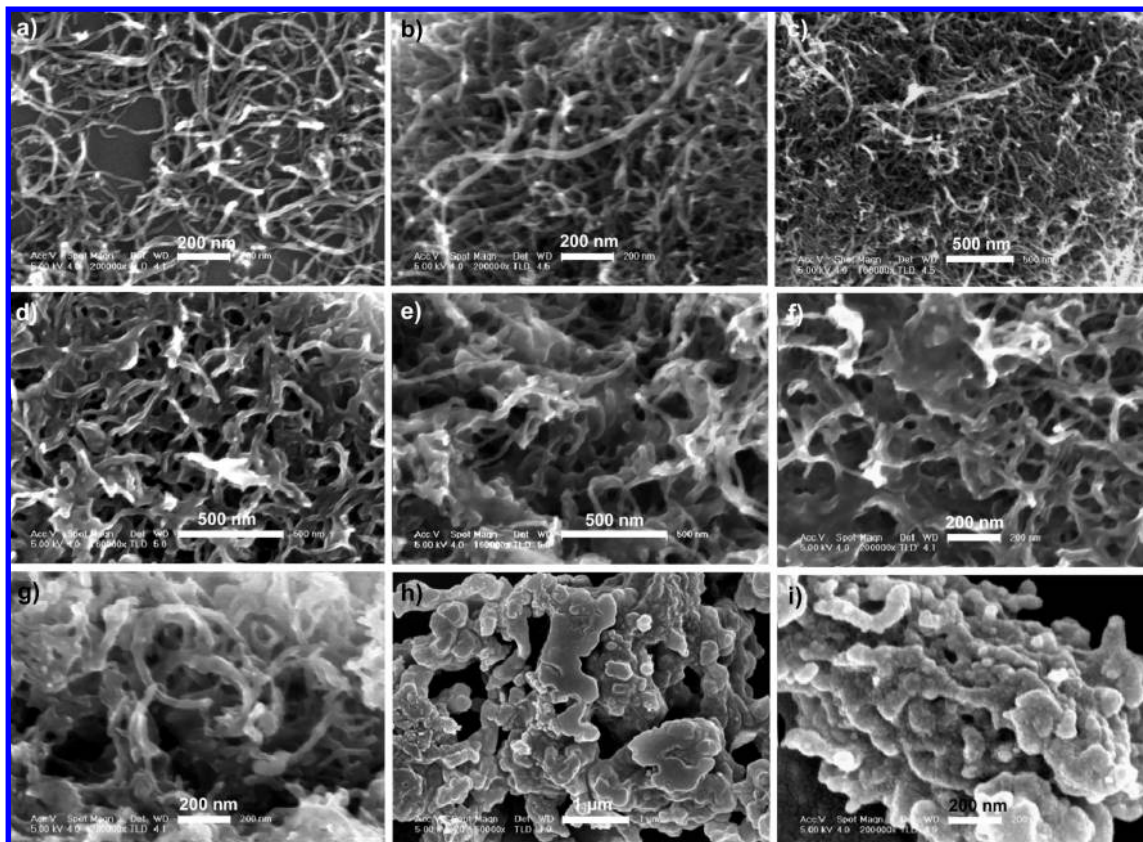


Figure 6. Representative SEM images of MWNT-Alk (a), CAZ1 (b and c), CAZ1AK1 (d and e), CAZ2AK1 (f and g), and CAZ2AK1-PS (h and i).

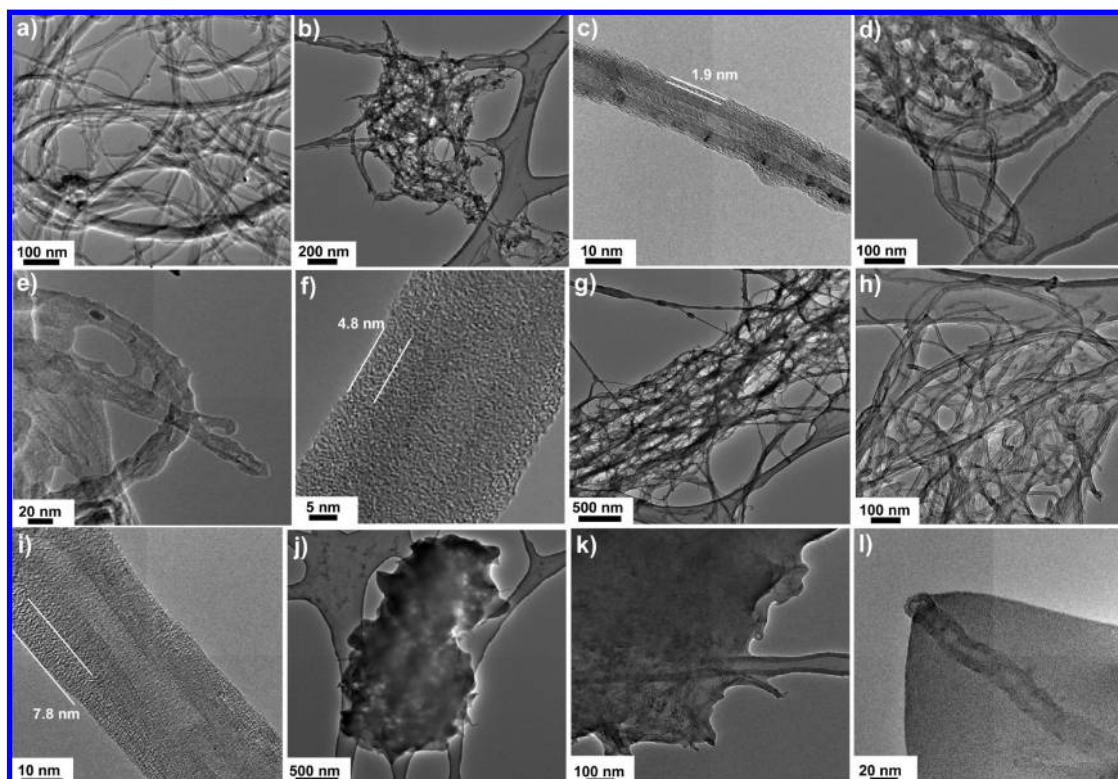


Figure 7. Representative TEM images of pristine MWNTs (a), CAZ1 (b and c), CAZ1AK1 (d–f), CAZ2AK1 (g–i), and CAZ2AK1-PS (j–l).

X-ray photoelectron spectroscopy (XPS) analysis was further employed to elucidate the surface state of functionalized MWNTs, and the results are shown in Figure 5. In Figure 5a,

two strong signals at 287.0 eV (C1s) and 535.0 eV (O1s) are observed for all the samples and a relatively weak signal is observed at 403.0 eV (N1s) only for CAZ1, CAZ1AK1, and

CAZ2AK1. The relative atomic concentrations of nitrogen of CAZ1, CAZ1AK1, and CAZ2AK1 are 2.62%, 1.82%, and 11.45%, respectively. Figure 5b shows the narrow scan spectrum of the N1s region of functionalized MWNTs. From the results, we can conclude that polyAzEMA was successfully clicked on MWNT-Alk, since the new peak of N1s appeared clearly. Since polyPgMA contains no nitrogen, the atomic concentrations of nitrogen in CAZ1AK1 decreased to 1.82%, also proving the successful click reaction between polyPgMA and the pregrafted polyAzEMA in reverse. Interestingly, the atomic concentrations of nitrogen in CAZ2AK1 increased greatly to 11.45%, showing that the third polymer layer of polyAzEMA was clicked on the second layer efficiently. Two distinct N1s peaks are observed in the narrow scan spectrum of the N1s region of CAZ2AK1, and the small peak is assigned to the relatively electron poor middle N atom of the azido group.⁶⁷ The results indicate that there are still many residual azido groups on the surface of CAZ2AK1. Because the depth sensitivity of the XPS analysis is below 10 nm and the thickness of the polymer shell of CAZ2AK1-PS (whose last layer is polystyrene) is far more than 10 nm according to the observations of TEM shown below, only peaks associated with C1s and O1s are observed, as expected.

Solubility/Dispersibility of Functionalized MWNTs. After functionalization, the resulting MWNTs showed different solubility (also see Supporting Information Figure S1). MWNT-COOH can be well dispersed in water but insoluble in weak polar or nonpolar organic solvents such as chloroform because of the hydrophilic carboxyl groups, whereas MWNT-Alk can be wettable in organic solvents and only poorly dispersible in water. The samples of CAZ1, CAZ1AK1, and CAZ2AK1 can be dispersed under ultrasonication in organic solvents such as chloroform and DMF but nonwetable in water. Moreover, the dispersibility increased with the increase of grafted polymer content or LbL cycle time: most of CAZ1 tubes aggregated again after tens of minutes when dispersed in solvent by sonication; most of CAZ1AK1 tubes could keep their good dispersibility for several hours and most of CAZ2AK1 tubes could be well dispersed in solvent for several days; CAZ2AK1-PS could keep its good dispersibility in nonpolar solvent such as CH₂Cl₂ for at least several weeks due to the high grafting of PS chains.

SEM and TEM Observations. The morphology of different samples and the click effect were evaluated by SEM measurements. Figure 6 displays the SEM images of MWNT-Alk (Figure 6a), CAZ1 (Figure 6b and c), CAZ1AK1 (Figure 6d and e), CAZ2AK1 (Figure 6f and g), and CAZ2AK1-PS (Figure 6h and i). For the sample of MWNT-Alk, the SEM image (Figure 6a) shows distinctly tubelike morphology. The surfaces of MWNT-Alk are relatively smooth and clean, which is different from those of polymer-functionalized MWNTs. For CAZ1, CAZ1AK1, and CAZ2AK1, the SEM images (Figure 6b–g) show that the spacing between MWNTs is reduced and the polymer phase becomes more continuous due to the increasing degree of polymer grafting. The polymeric layers of the three samples are even and flat. For the sample of CAZ2AK1-PS with the highest degree of polymer grafting, a compact mass is found and the polymeric layers become a continuous phase (see Figure 6h and i). The outcome of SEM observations accords well with the results obtained from TGA measurements.

The fine structure and morphology of the functionalized MWNTs were further evaluated by TEM measurements. Figure 7 shows the TEM images of pristine MWNT (Figure 7a), CAZ1

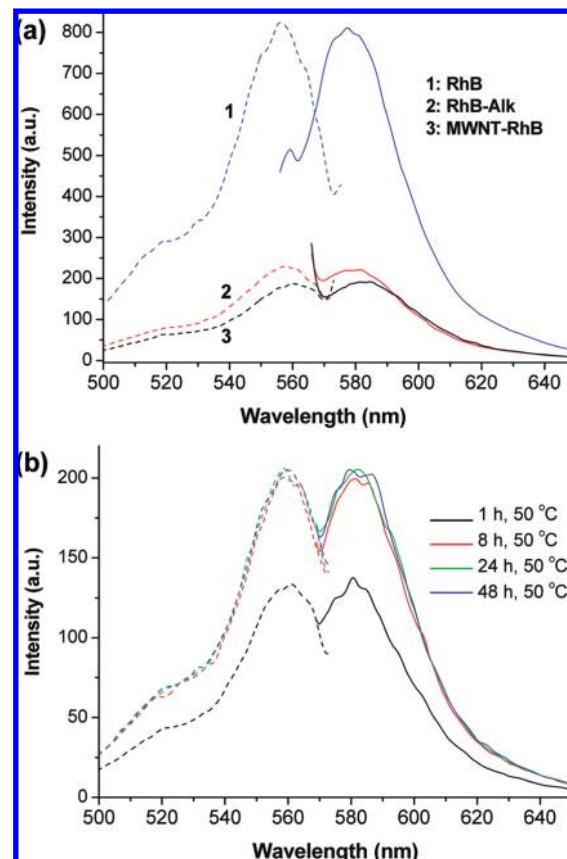


Figure 8. (a) Emission (solid line) and excitation (dashed line) fluorescence spectra of rhodamine B (RhB: $\lambda_{em} = 578$ nm and $\lambda_{ex} = 556$ nm), alkyne-modified rhodamine B (RhB-Alk: $\lambda_{em} = 580$ nm and $\lambda_{ex} = 558$ nm), and RhB-Alk labeled MWNTs (MWNT-RhB: $\lambda_{em} = 582$ nm and $\lambda_{ex} = 560$ nm) in THF solution with a concentration of ~ 0.05 , 0.02 , and 0.5 mg/mL, respectively. (b) Emission (solid line) and excitation (dashed line) fluorescence spectra of RhB-Alk labeled MWNTs prepared at 50 °C with various reaction times ($\lambda_{em} = 582$ nm and $\lambda_{ex} = 560$ nm). The sample was dispersed in THF with a concentration of 0.5 mg/mL.

(Figure 7b and c), CAZ1AK1 (Figure 7d–f), CAZ2AK1 (Figure 7g–i), and CAZ2AK1-PS (Figure 7j–l). The TEM image of pristine MWNTs shows that the surface of the sample is relatively smooth and clean (Figure 7a) and distinct from that of the polymer-functionalized MWNTs. Most of the nanotubes of the sample retain their tubular structure. For the samples of CAZ1, CAZ1AK1, and CAZ2AK1, it is found that the layers of polymer coated on the MWNTs are evenly dispersed (low magnification, Figure 7b, d, and g). A core–shell structure is observed clearly for the individual nanotubes, and the polymer shell is uniform and flat (high magnification, Figure 7c, f, and i). The thickness of the polymer shell increases considerably with increasing layers of polymer clicked on MWNTs. The average thicknesses (d , also summarized in Table 1) of the enwrapped polymer layers for CAZ1, CAZ1AK1, and CAZ2AK1 are $\sim 2.0 \pm 0.3$, $\sim 5.0 \pm 0.5$, and $\sim 7.5 \pm 0.7$ nm, respectively (see also Supporting Information Figures S2–S4). Therefore, linear correlation was found between the thickness of polymer layer and layer numbers ($R > 99.5\%$ for the linear fitting with Origin 6.0 software). The linear relationship between the thickness and LbL times is in accordance with the exponential increase in grafted polymer amounts shown in Figure 2b, since the mass increase is the function of polymer volume ($\pi R^2 \times \text{height}$ for a cylindrical structure, herein R is the radius of the cylinder) and the thickness has only linear function of the radius of an ideal

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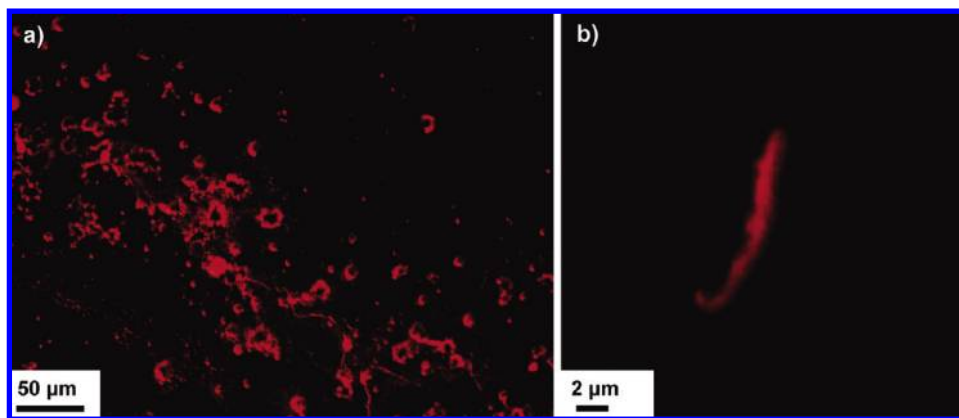


Figure 9. (a) Fluorescence microscopy image of MWNT-RhB ($\lambda_{\text{ex}} = 520\text{--}550\text{ nm}$). (b) Confocal fluorescence image of singular tube of MWNT-RhB ($\lambda_{\text{ex}} = 543\text{ nm}$); the sample was dispersed in chloroform.

cylinder. Nevertheless, the polymer thickness was calculated from limited tubes. So, these correlations may not be suitable for other cases of polymer-functionalized nanotubes. For the sample of CAZ2AK1-PS, the quantity of polymer clicked on the MWNTs is so high that the polymer shell becomes a continuous phase and only a few separate nanotubes enwrapped with polymer layers can be found (Figure 7j and k). In the higher magnification image (Figure 7l), an extremely thick shell of polymer enwrapping the tubular structure of an isolated nanotube is observed clearly.

Estimating from the SEM and TEM observations, we can conclude that (1) the thickness of the clicked polymer shell on CNTs can be well controlled by adjusting the numbers of click reaction, (2) the clicked polymer shell is uniform and even, and (3) it is facile and highly efficient to fabricate polymer-functionalized MWNTs using the layer-by-layer click chemistry approach.

Fluorescent RhB-Alk Labeled MWNTs (MWNT-RhB).

In order to prove the reactivity of the residual azido groups on the MWNTs, we conducted two experiments of macromolecular terminal click and organic dye click. The click results of macromolecular Alk-PS have been mentioned and discussed above, corroborating the high reactivity of azido groups left on MWNTs. Therefore, a highly reactive CNT-based nanoplatfrom was created after a few cycles of click reaction. This kind of nanoplatfrom is a versatile base for the fabrication of functional devices and integration of multifunction. As a model, we prepared fluorescent CNTs via dye clicking herein.

The emission and excitation properties of the resulting RhB-Alk labeled MWNTs were checked through the fluorescence spectra. Figure 8a shows the fluorescence spectra of rhodamine B (RhB), alkyne-modified rhodamine dye (RhB-Alk), and MWNT-RhB in THF. For rhodamine B, the maximum emission wavelength is 578 nm if excited at its maximum excitation wavelength of 556 nm, whereas for alkyne-modified rhodamine dye, the maximum emission and excitation wavelengths shift to 580 and 558 nm, respectively, likely due to the influence of propargyl groups. When RhB-Alk was attached to the surfaces of MWNTs, the maximum emission and excitation wavelengths were found at 582 and 560 nm, respectively, and the emission intensity became weaker. This is probably caused by the relatively small quantity of rhodamine B attached on the CNT surfaces, compared to the high density of polymer grafting. This was confirmed by FTIR spectra (figure not shown); the characteristic absorption peak of azido groups of MWNT-RhB at 2100 cm^{-1} still exists but gets smaller, which indicates that only parts of the azido groups were consumed in the click reaction. Therefore, the residual azido groups on MWNT-RhB can be further utilized to react with other functional reagents to produce multifunctional

compounds. A control experiment of mixing rhodamine B with CAZ2AK1 was also done. After purification by repeated washing with THF, no fluorescence peak was observed for the control sample if excited at 550–560 nm.

In order to check the possible reason for the low quantity of immobilized rhodamine B, we conducted the experiments of click reaction between RhB-Alk and CAZ2AK1 with different times at higher temperature ($50\text{ }^{\circ}\text{C}$). The fluorescence results are shown in Figure 8b. It was found that (1) higher temperature reaction could improve the concentration of RhB only slightly (the maximum fluorescence intensity increased from 191.4 to ~ 204) and (2) the reaction reached equilibrium at around 8 h, so the extension of reaction time from 24 to 48 h cannot lead to the considerable increase of dye content (or the conversion of alkyne/azide groups). Therefore, we think that the low concentration of rhodamine B on MWNTs after clicking is neither due to the low concentration of azido groups on the surface nor because the clicking conditions were not optimized. In our other experiments, we found that the conversion of RhB-Alk was also low if it reacted with free polymer containing azido groups (data not shown). So, the reason is likely due to the steric hindrance of rhodamine B molecule on the click reaction (e.g., the formation of a rigid 1,2,3-triazole ring is difficult). Nevertheless, more specific experiments are required to know the exact reason in the future.

Furthermore, fluorescence microscopy images were taken to demonstrate the availability of residual azides on the surfaces of CAZ2AK1 for the subsequent dye functionalization. Figure 9a shows the fluorescence microscopy image of MWNT-RhB (RhB-Alk labeled). Strong red fluorescence and wormlike morphology are clearly observed. Almost no fluorescence is observed for the sample of CAZ2AK1, as expected (see Supporting Information Figure S5). These results confirm again that the residual azido groups on the surfaces of CAZ2AK1 are available for further reaction with small functional reagents.

Confocal laser scanning microscopy was applied for further characterization of MWNT-RhB.⁶⁸ Red remarkable fluorescence was uniformly observed in the fluorescence image of MWNT-RhB (Figure 9b), suggesting alkyne-modified rhodamine dye was successfully clicked to CAZ2AK1, which has a large number of residual azido groups on the surfaces. Furthermore, a singular tube profile can be clearly observed from the red fluorescent image when the sample of MWNT-RhB was dispersed in chloroform that is a good solvent for the functionalized CNTs (see also Supporting Information Figure S6), implying that rhodamine dye

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was evenly immobilized on the tube surface and the functionalized nanotubes can be well dispersed in organic solvent of chloroform. On the other hand, the sample of MWNT-RhB cannot be dispersed in water due to the hydrophobic clickable polymers grafted on CNTs, so only entangled networks or agglomerates of CNTs can be found if water was used as the solvent (see Supporting Information Figure S7). These results further demonstrate that the red fluorescence was emitted from the nanotubes and no free dye was mixed in the sample of MWNT-RhB. In addition, fluorescent decaying time was also measured for the samples of MWNT-RhB and neat RhB-Alk (see Supporting Information Figure S8), showing that the two samples have almost the same decaying time (2.99 ns with reconvolution fit) and tendency.

Conclusions

Well-defined two clickable polymers, poly(2-azidoethyl methacrylate) and poly(propargyl methacrylate), containing essential azido or alkyne side groups were successfully synthesized by ATRP and RAFT polymerization, respectively. The two kinds of polymers were alternately clicked on the surfaces of as-prepared alkyne-modified MWNTs covalently by the layer-by-layer approach. The quantities of polymeric coating on MWNTs can be controlled by the numbers of click reaction, which was confirmed by measurements of TGA, FTIR, SEM, XPS, and TEM. The click efficiency is very high, since 49.5 and 66.8% weight losses are observed after only two and three click steps, respectively. After grafting three layers of clickable polymers on MWNTs, the presence of plenty of residual azido groups on the surfaces of the functionalized MWNTs is confirmed by FTIR and

XPS. To explore the applications of the azido-rich nanosurfaces of a reactive platform, alkyne-modified rhodamine B and mono-alkyne-terminated polystyrene were used as small functional molecules and macromolecules for postmodification of click coupling, giving rise to fluorescent CNTs and PS brush grafted CNTs, respectively. The results show that it is facile and efficient to fabricate various functionalized MWNTs by the layer-by-layer click chemistry (LbL-CC) approach and the resulting products possess plentiful clickable groups which are quite useful to further immobilize functional molecules and other expected compounds.

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Supporting Information Available: Synthesis details of AzEMA and PgMA, photographs of functionalized MWNTs placed in solvent, additional TEM images of functionalized MWNTs, fluorescence microscopy image of CAZ2AK1, more confocal fluorescence images of MWNT-RhB, and fluorescent decaying time curves of MWNT-RhB and neat RhB-Alk. This material is available free of charge via the Internet at <http://pubs.acs.org>.