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The Power of One-pot: A Hexa-component System Containing π-π stacking, Ugi reaction and RAFT polymerization for Simple Polymer-conjugation on Carbon Nanotube

Bin Yang, Yuan Zhao, Xu Ren, Xiaoyong Zhang, Changkui Fu, Yaling Zhang, Yen Wei, Lei Tao*

A hexa-component system has been successfully developed for simple polymer-conjugation on carbon nanotube. The well-known Ugi reaction has been recognized as a multicomponent click (MCC) reaction to efficiently collaborate with π-π stacking and RAFT polymerization to construct this delicate one pot system. The CNT-(co)polymer composites inherit the properties of conjugated polymers and can be well dispersed in both organic and aqueous solvents. As a simple and efficient method, this one-pot system might have potential to be a general approach to prepare carbon-based composites.

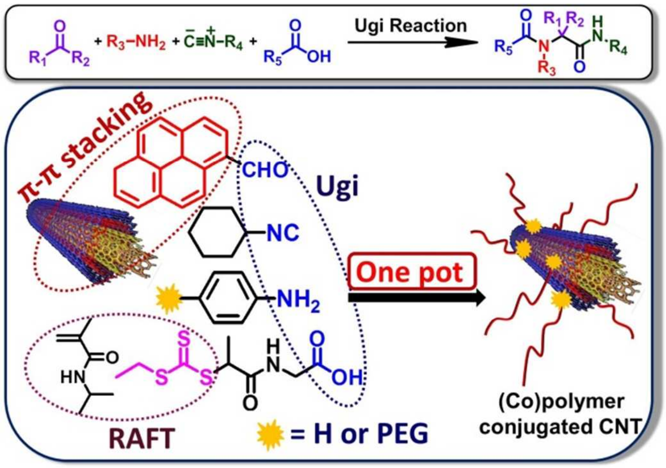
Introduction

One-pot synthetic strategy represents the pursuit of chemists to prepare sophisticated molecules through minimum synthesis and purification steps. Compared with orthodox stepwise method, the one-pot strategy is greener and more economic to save time, energy and raw materials[1, 2]. Recently, one-pot strategy has been developed as an attractive method for polymer synthesis by elaborately combining polymerization and some orthoganol organic reactions in one bottle, and various of complicated functional polymers have been thereof facilely synthesized[3-10]. For example, Haddleton and co-workers combined copper-catalyzed azide-alkyne cycloaddition (CuAAC) and atom transfer radical polymerization (ATRP) in one pot to facilely achieve glycolpolymers[11]. Perrier and co-workers developed a one-pot system including the alcohol-isocyanate reaction and reversible addition-fragmentation chain transfer (RAFT) polymerization to simply obtain end-functionalized polymers[12].

To successfully construct a one-pot reaction system, it is critical to carefully organize reactions which should be truly fast, efficient and compatible to other reaction processes, such as polymerization. Therefore, click reactions are often the first choice in most instances to fabricate one-pot systems due to their excellent reliability and selectivity. As point & shoot coupling tools, click reactions are charming to researchers outside organic area since its birth[13], and have been widely used in many hot research fields, such as material science[14, 15], life science[16], and polymer chemistry[17-22]. Meanwhile, more and more reactions have been reassessed from the perspective of click chemistry and become new members of this vibrant family[23-26]. Since the pioneer work of Meier to introduce Passerini reaction into polymer chemistry[27, 28], utilization of multicomponent reactions (MCRs) to synthesize sophisticated (co)polymers is growing as a new research trend in polymer chemistry[29-33]. During our study of MCRs, we found some highly efficient MCRs are similar as click reactions, and therefore discovered a new type of click reactions, the multicomponent click (MCC) reactions, i.e. some highly efficient and atom economic MCRs can also be considered as click reactions. Based on this concept, some famous old MCRs, such as the Biginelli reaction, the Ugi reaction, have been re-understood as MCC reactions[34-36]. Same as traditional two-component click reactions, MCC reactions are also highly efficient coupling reactions, moreover, new functional groups can be simultaneously added to the obtained compounds due to the multicomponent nature of MCC reactions. Therefore, some thorny synthetic problems, such as synthesis of multifunctional PEGylation agents for protein conjugation and preparation of middle functional copolymer and miktoarm copolymer, etc., can be simply solved by MCC reactions, demonstrating their unique superiority as the newcomers of click family[35, 37].

Encouraged by our previous research, we hope to introduce MCC reactions, Ugi reaction for example, into material science for surface modification of carbon materials to expand the application scope of these new emerging click reactions. Carbon nanotube (CNT), a cylindrical nanostructure allotrope of carbon, has been found many potential applications because of its superb mechanical and electrical properties[38-40]. However, the poor solubility of CNT in both aqueous and organic solvents hampers its real application. Although plenty of methods have been developed to solve this problem, including the conjugation of solubilizer on the CNT surface, utilization of surfactant, in-situ polymerization on CNT surface, etc.[41-48], most of those methods do suffer from tedious processes, harsh reaction conditions or unsatisfactory solubilization effect. How to efficiently disperse CNT through a simple approach is crucial for the practical application of this excellent material and still a challenge to material scientists.

Herein, we report for the first time a hexacomponent system by combining the Ugi reaction, π-π stacking (CNT-pyrene) and RAFT polymerization in one-pot to highly efficiently modify the CNT surface with polymers (**Scheme 1**). The reactions in a same reactor are compatible and collaborate well to smoothly achieve CNT-polymer complex in one shot. Moreover, middle-functional copolymer can also be simply anchored on the CNT surface to further add new function to the host CNT, indicating the speciality of Ugi reaction as a MCC reaction. All the obtained CNT-(co)polymer complexes could be stably dispersed in both organic and aqueous solvents. Meanwhile, the conjugated polymer chains on CNT surface provide new functions to the composites. Considered the simple operation, mild condition and excellent CNT surface modification, this one-pot system might have potential to be a general method to prepare carbon-based composites.



Scheme 1. (Co)polymer modification of CNT surface through one-pot strategy combining Ugi reaction, π-π stacking and RAFT polymerization.

Results and Discussion

Preparation of CNT-PNIPAAm. In the one-pot system, the six necessary components for the Ugi reaction, π-π stacking, and RAFT polymerization have to be carefully designed: a trithiocarbonate (for RAFT) containing a carboxylic group was chosen as the carboxylic source for Ugi reaction; 1-pyrenecarboxaldehyde was used for π-π stacking and as the aldehyde source of Ugi reaction; aniline and cyclohexyl isocyanide acted as the amine and the isocyanide moieties in Ugi reaction, respectively. All abovementioned compounds were mixed with 2,2'-azobis(2-methylpropionitrile) (AIBN, initiator for RAFT), N-isopropylacrylamide (NIPAAm, monomer for RAFT) and the CNT in a Schlenk tube (methanol as solvent). The Schlenk tube was sealed with a rubber septum and purged with nitrogen flow for 20 min prior to putting into a 65 °C oil bath. Before polymerization, it is clearly to see the hardly dispersed CNT at the bottom of tube (Fig. 1A), after 20 h polymerization, the CNT can be well dispersed in methanol (Fig. 1B), primarily indicating the formation of CNT-PNIPAAm complex through this simple one-pot strategy.

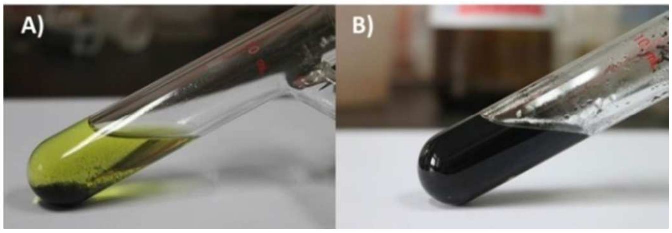


Figure 1. Photography of the reaction system before (A) and after (B) the one-pot polymerization-modification process (methanol, 65 °C, 20 h).

The CNT-PNIPAAm complex can be easily purified by washing with methanol and isolated by centrifugation (20000 rpm, 30 min, 5 times). ^{1}H NMR and Gel Permeation Chromatography (GPC) (**Fig. S1)** were used to characterize the whole system after the one-pot method. The conversion of the RAFT polymerization is about 98% according to the ^{1}H NMR spectrum. The unconjugated polymer in the solution was separated for analyses, and the M_{nGPC} is ~ 26800 with narrow PDI (1.04), indicating the RAFT polymerization process was still controlled under these one-pot conditions. Several characterizations were then taken to further analyze the CNT-PNIPAAm complex.

From the ^{1}H NMR spectrum of the purified CNT-PNIPAAm (**Fig. 2A)**, the characteristic peaks of PNIPAAm (3.86 ppm, 1.11 ppm) are clearly visible, indicating the existence of the polymer on the surface of CNT. Compared with the pristine CNT, the CNT-PNIPAAm showed new peaks at 2900 cm^{-1} (the stretching vibration bands of C-H) and 1650 cm^{-1} (the stretching vibration bands of C=O) in the FT-IR spectrum (**Fig. 2B)**, further revealing the presence of the polymer on CNT surface. The mass percentage of PNIPAAm conjugated on CNT was determined by thermal gravimetric analysis (TGA). Based on the TGA data (**Fig. 2C**), the weight loss of pristine CNT was calculated as about 5% at ~ 600 °C while the weight loss of CNT-PNIPAAm was significantly increased to 71% at ~ 600 °C, indicating the large amount of PNIPAAm (~ 66%) on the surface of CNT, further suggesting the successful modification of CNT with PNIPAAm.

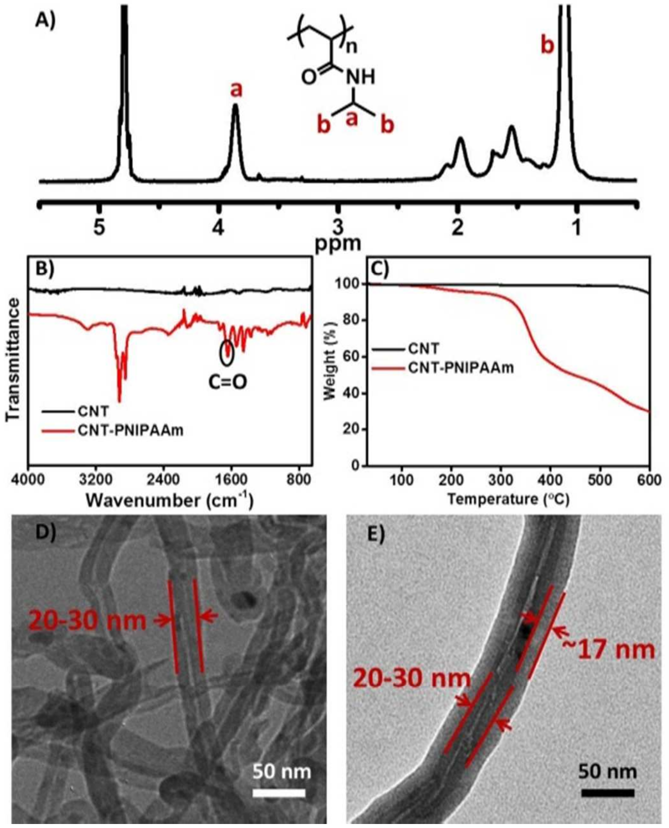


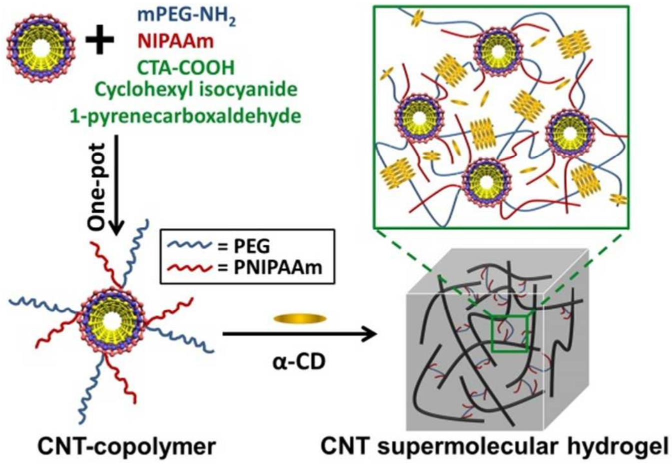
Figure 2. Characterization of CNT-PNIPAAm. ^{1}H NMR (D_2O-d_2, 400 MHz, portion) (A), FT-IR (B), and TGA (C) spectra of pristine CNT and CNT-PNIPAAm.

From the typical transmission electron microscopy (TEM) images, the diameter of the pristine CNT is measured as about 20-30 nm, consistent with the information provided by the manufacturer (**Fig. 2D**), and a thick polymer film (~ 17 nm) can be clearly observed on the CNT surface in the TEM image of CNT-PNIPAAm (**Fig. 2E**), providing direct evidence of the successful surface modification of CNT with PNIPAAm via this polymerization/modification one-pot system.

Because of the large amount of polymer on its surface, the obtained CNT-PNIPAAm can be dispersed very well in both organic and aqueous solutions. In typical laboratory solvents, such as dichloromethane, ethanol, toluene and ethyl acetate, the CNT-PNIPAAm could keep excellent dispersity for several weeks (**Fig. 3A**). The CNT-PNIPAAm should also inherit the thermosensitivity of the PNIPAAm, thus, the influence of temperature on the dispersity of CNT-PNIPAAm in aqueous solution was subsequently investigated (**Fig. 3B**). The CNT-PNIPAAm can rapidly dissolve in cold water (~ 20 °C), after heating the solution using an electric blower, the CNT-PNIPAAm was quickly precipitated due to the aggregation of PNIPAAm. When the suspension was cooled to ~ 20 °C again, CNT-PNIPAAm was observed to well re-dispersed. This reversible phase transition suggests the conjugated polymer can not only improve the solubility of CNT, but also transfer the polymer property to the composite.

Figure 3. The well dispersity of CNT-PNIPAAm in common organic solvents (A) (1: dichloromethane, 2: ethanol, 3: toluene, 4: ethyl acetate) and the influence of temperature on the water dispersity of CNT-PNIPAAm (B).

Preparation of CNT-copolymer and the CNT supermolecular hydrogel. Additionally, surface modification of CNT with miktoarm branched copolymers was also facilely fulfilled through this hexacomponent one-pot strategy to add another functional polymer to the CNT. In this case, the reaction was operated under same condition as previous described only using aniline terminated poly(ethylene glycol) methyl ether (mPEG-NH_2, M_n ~ 5150) instead of aniline as the amine source for Ugi reaction. Thus, the introduced PEG and the in situ generated PNIPAAm can be synchronously attached to the surface of CNT as a branched copolymer (**Scheme 2**). By this way, the 'grafting-from' and 'grafting-to' methods have been effectively combined together to modify CNT surface.



Scheme 2. Surface modification of CNT with branched PEG-PNIPAAm through one-pot strategy and the subsequent formation of hydrogel through supermolecular interaction between CNT-copolymers and α-CD.

From the ^{1}H NMR spectra of the purified CNT-copolymer (**Fig. 4A**), the characteristic peaks of both PEG (3.66 ppm) and PNIPAAm (3.86 ppm, 1.11 ppm) can be clearly seen.

Meanwhile, the FT-IR of the composite (**Fig. 4B**) also showed the characteristic signals of PNIPPAm (1650 cm^{-1}) and PEG (1150 cm^{-1}). Both results reveal the existence of different polymer chains on the surface of CNT. The polymer content in the CNT-copolymer complex was calculated as ~ 60% based on the TGA analysis (**Fig. S2**). From the TEM image of the CNT-copolymer (**Fig. S3**), the obvious polymer layer (~ 15 nm) can be clearly observed. All above results suggest the successful preparation of CNT-copolymer through this convenient one-pot approach.

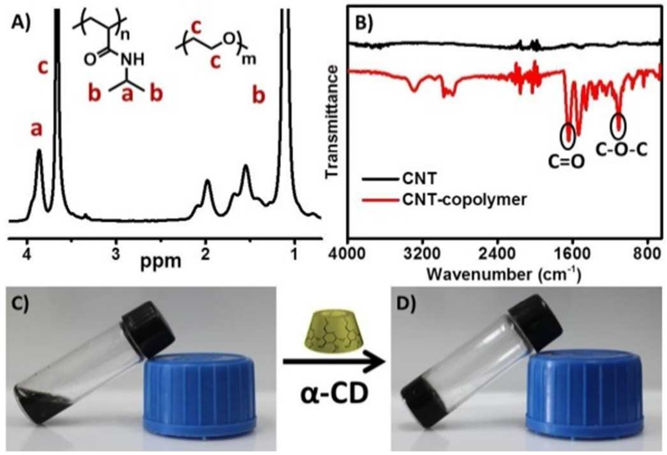


Figure 4. ^{1}H NMR spectra (D_2O-d_2, 400 MHz, portion) (A), FT-IR (B) of CNT-copolymer, and photographs of the gel process of the supramolecular hydrogel before (C) and after (D) gelation.

The introduced PEG on CNT surface can also implant its special features to the carbon material (**Scheme 2**). For instance, CNT hydrogel can be subsequently prepared through the supramolecular interaction between CNT-copolymer and α-cyclodextrin (α-CD). The CNT-copolymer was dispersed in water (**Fig. 4C**), then the saturated solution of α-CD was added. The mixture was kept under ultrasonic oscillations at 40 °C for 15 min, and then cooled down to 25 °C to generate the hydrogel (**Fig. 4D**). Two control experiments were carried out by mixing CNT-PNIPAAm with α-CD or direct using CNT-copolymer without α-CD, and no hydrogel formed in both cases (**Fig. S4 & S5**), suggesting the PEG on CNT surface is the critical gelator to create that supramolecular hydrogel.

Experimental Section

Preparation of CNT-PNIPAAm. CNT (150 mg), 1-pyrenecarboxaldehyde (30 mg, 0.13 mmol), aniline (30 mg, 0.32 mmol), 2-(2-(((ethylthio)carbonothioyl)thio)propanamido)acetic acid (40 mg, 0.15 mmol), cyclohexyl isocyanide (30 mg, 0.27 mmol), NIPAAm (1.0 g, 8.8 mmol), AIBN (13 mg, 0.08 mmol) was dissolved in 3 mL of methanol in a Schlenk tube. The tube was then sealed with a rubber septum and purged by nitrogen flow for 20 min. The tube was then put into an oil bath maintained at 65 °C for 20 h. The CNT-PNIPAAm complex can be easily purified by washing with methanol and isolated by centrifugation (20000 rpm, 30 min, 5 times). Several characterizations were then taken to further analyze the CNT-PNIPAAm complex, including ^{1}H NMR, FT-IR, TEM, and TGA.

Preparation of CNT-copolymer. CNT (150 mg), 1-pyrenecarboxaldehyde (30 mg, 0.13 mmol), mPEG-NH_2 (1.0 g, 0.19 mmol), 2-(2-(((ethylthio)carbonothioyl)thio)propanamido)acetic acid (40 mg, 0.15 mmol), cyclohexyl isocyanide (30 mg, 0.27 mmol), NIPAAm (1.0 g, 8.8 mmol), AIBN (13 mg, 0.08 mmol) was dissolved in 3 mL of methanol in a Schlenk tube. The tube was then sealed with a rubber septum and purged by nitrogen flow for 20 min. The tube was then put into an oil bath maintained at 65 °C for 20 h. The CNT-copolymer complex can be easily purified by washing with methanol and isolated by centrifugation (20000 rpm, 30 min, 5 times). Several characterizations were then taken to further analyze the CNT-copolymer complex, including ^{1}H NMR, FT-IR, TEM, and TGA.

Preparation of CNT supermolecular hydrogel. CNT-copolymer (10 mg) was dispersed in water (300 μL), and then mixed with saturated α-CD solution (300 μL). The combined solution was kept under ultrasonic oscillations at 40 °C for 15 min, and then cooled down to 25 °C to generate the supermolecular hydrogel.

Two control experiments were carried out using CNT-PNIPAAm to mix with α-CD or direct using CNT-copolymer without α-CD. No hydrogel formed in both cases.

Conclusions

In summary, one-pot strategy has been applied to efficiently synthesize polymer-conjugated CNT through a hexacomponent system containing supramolecular interaction, click reaction and polymerization. Ugi reaction has been successfully introduced into material science as a MCC reaction to collaborate with π-π stacking and RAFT polymerization, resulting in the successful one-pot system for CNT conjugation. The obtained CNT-(co)polymer composites contain plenty of polymers on the surface, and can be dispersed well in both organic and aqueous solutions. Meanwhile, the multicomponent feature of Ugi reaction makes it easy to add new function on the CNT surface, resulting in application of the CNT composites in a wider range. This new one-pot method should also be suitable for polymer modification of other nanostructural carbon materials, such as graphene and nanodiamond etc.. Currently, introducing other multicomponent click reactions into material science and using obtained CNT composites for further applications are under study.

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Notes and references

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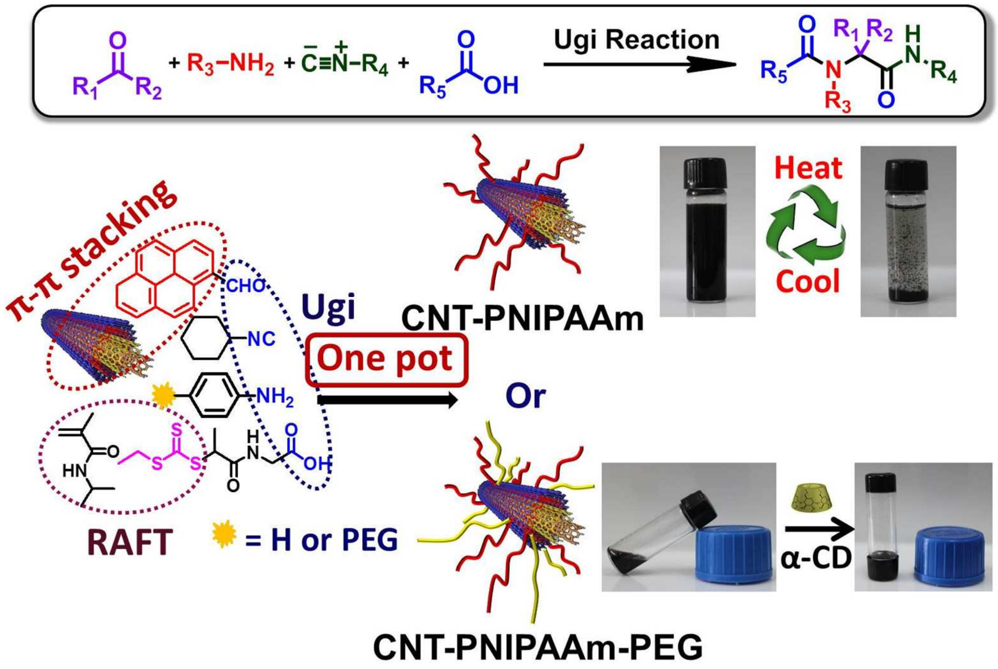
Table of Contents

The Power of One-pot: A Hexa-component System Containing π-π stacking, Ugi reaction and RAFT polymerization for Simple Polymer-conjugation on Carbon Nanotube

*Bin Yang, Yuan Zhao, Xu Ren, Xiaoyong Zhang, Changkui Fu, Yaling Zhang, Yen Wei, Lei Tao**



The well-known Ugi reaction has been recognized as a multicomponent click (MCC) reaction to efficiently collaborate with π-π stacking and RAFT polymerization to construct a delicate hexa-component one-pot system for the simple (co)polymer-modification of carbon nanotube surface.