Green and Highly Efficient Functionalization of Carbon Nanotubes by Combination of 1,3-Dipolar Cycloaddition and Curtius Rearrangement Reactions

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Introduction

The discovery of carbon nanotubes (CNT) and the prospect of developing novel carbon-based nanomaterials have sparked worldwide interest among researchers due to its unique structures and remarkable mechanical, thermal and electrical properties. Among many different applications of CNT, polymer nanocomposites have been extensively investigated in the past decade. The key challenges for preparation of high-performance polymer nanocomposites are homogeneous dispersion, good compatibilization, and stabilization of CNT in the matrices. An effective approach for these requirements involves an integration of chemically modified carbon nanotubes containing different functional groups into a polymer matrix, which not only serves to facilitate dispersion, but also can modify interfacial properties. The global trend of seeking for environmentally friendly green techniques in chemical modification of CNT has rapidly and inevitably expanded. In this paper, green chemical functionalization of carbon nanotubes containing isocyanate groups via Curtius rearrangement is studied, which has not been explored as far as we know. Based on the wealth chemistry of isocyanate groups, the functionalized carbon nanotubes containing isocyanate groups can thus extend nanotube chemistry greatly, and may be promising to prepare for example, polymer/carbon nanotube composites and coatings. The Curtius rearrangement is an environmentally friendly and green reaction among multitudinous rearrangement reactions, which can react quite easily and almost does not have pollution. In addition, an important utilitarian feature of this reaction is that a diverse assortment of carboxylic acids can be converted into their corresponding acyl azides, which can conveniently undergo thermal rearrangement to isocyanates in one pot. Therefore, the application of the Curtius rearrangement reaction in CNT chemistry would be intriguing and promising.

Polyamide 6 (PA6) is an important commodity polymer that exhibits excellent chemical stability and mechanical strength properties. CNT/PA6 hybrids have attracted much attention due to the possibility of obtaining new nanocomposites with remarkable mechanical properties and better biocompatibility. General approaches to prepare such nanocomposites are melt compounding and ring-opening polymerization from the CNT surfaces. Nevertheless, the high viscosity of the polymer suppresses the free movement of the CNT in the matrix during mixing, which therefore often gives rise to inhomogeneous dispersion and the low loading level of the nanotubes. In the case of ring-opening polymerization, PA6-grafted CNT could usually penetrate and become a part of the matrix and thus bridge the connection of the CNT and the matrix. When properly executed, the resulting materials can produce homogeneously blended composites in which phase separation is precluded by chemistry. Sun and co-workers reported the functionalization of oxidized single-walled carbon nanotube (SWCNT) with PA6 by using the grafting-from strategy in a two-step process. Unfortunately, the oxidative process under harsh conditions utilizing strong acids such as concentrated sulfuric or nitric acid in which carboxylic acid...
moieties are created on nanotubes simultaneously cuts the CNT into small pieces, which decreases the aspect ratio of the nanotubes. However, aspect ratio must be large to maximize the load transfer to the nanotubes, which is crucial to optimize composite strength and stiffness. Therefore, the acid treatment, the most utilized method to modify CNT to date, has failed to fully realize the enormous potential of carbon nanotubes, which in fact has deteriorated the performance of the materials prepared.

To avoid cutting CNT during modification, it was also found that isocyanate functionalized multiwalled carbon nanotubes (MWCNT), prepared by directly reacting the commercial hydroxyl functionalized MWCNT with excess toluene 2,4-diisocyanate (TDI), can be used as initiator precursor to conduct anionic ring-opening polymerization of ε-caprolactam. However, it is well known that the toxicity of TDI causes environmental problems, thus greatly limits its usage and becomes a major obstacle for further development. Therefore, there is an urgent need to develop a green and environmental-friendly approach to functionalize CNT and at the same time to maintain their remarkable properties such as high aspect ratios. Herein, we present a new method of CNT functionalization by combination of 1,3-dipolar cycloaddition of azomethine ylides and Curtius rearrangement of azides as an isocyanate free process for this need.

**Experimental**

**General procedures and materials**

Pristine SWCNT was purchased from the Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences, and used without further purification. The diameter of SWCNT is about 1–2 nm. ε-Caprolactam, trimellitic anhydride, N-methylglycine, 3,4-dihydroxybenzadehyde and sodium were purchased from Shanghai Chemical Reagents Company. ε-Caprolactam was recrystallized from acetone and the crystals were dried in vacuo at 40 °C for 2 d before use. Both NMP and DMF were dried with CaH₂ and redistilled before use. Diphenylphosphorazidate (DPPA) was purchased from Aldrich and stored at 4 °C.

**Synthetic procedures**

**SWCNT-f-OH** Microwave irradiations were carried out in a CEM Discover reactor of America. Exclusively vitreous vessels with a volume of 10 mL or 100 mL are equipped for the system to provide security during reaction demanding high temperature and pressure. 20 mg pristine SWNT was suspended in CH₂Cl₂ (5 mL) with 0.66 mmol 3,4-dihydroxybenzadehyde (91 mg) and N-methylglycine (62 mg, 0.70 mmol) in a microwave quartz vessel. After sonication for 5 min, the solvent was evaporated under reduced pressure. The vessel was closed, and the mixture was irradiated for 1 h at different power and temperatures. The detailed procedures followed a reference literature. After microwave irradiation, the crude sample was collected when the temperature was naturally cooled to lower than 50 °C and was then dispersed in 75 mL of CH₂Cl₂ and sonicated for 5 min. The solution was filtered on a Millipore membrane (PTFE, 0.2 μm), and the collected black solid sample was washed with 75 mL of methanol and with 75 mL of CH₂Cl₂ (sonicated and filtered). After being dried in vacuo at 40 °C for 24 h, SWNT-f-OH sample was obtained.

**SWCNT-f-ArCOOH** SWCNT-f-OH (20 mg, 0.29 mmol OH) and trimellitic anhydride (80 mg, 0.42 mmol) were stirred overnight at room temperature in DMF (30 mL). The resulting product was isolated by centrifugation and washed with acetone.

**SWCNT-f-caprolactam** 30 mg of SWCNT-f-ArCOOH sample was mixed with DPPA (0.6 mL, 27.6 mmol) and Et₃N (1.0 mL, 7.36 mmol), and the mixture was stirred in 40 mL of dried NMP at room temperature for 12 h. Then 2 g of ε-caprolactam (17.6 mmol) was added and the temperature was raised up to 110 °C and stirring was continued for 20 h. The product was isolated by filtration using 0.22 μm PVDF membrane. The solid sample from the filtration was extracted with chloroform for 6 h in a Soxhlet extractor to remove any residual ε-caprolactam. Upon drying in vacuo at room temperature, the dark powdery ε-caprolactam-functionalized SWCNT (SWCNT-f-caprolactam) sample was obtained.

**SWCNT-g-PA6** SWCNT-f-caprolactam (50 mg) was mixed with ε-caprolactam (5 g, 44 mmol), and sodium (30 mg, 1.3 mmol) was added to the mixture as initiator. The polymerization was carried out at 170 °C under nitrogen protection for 24 h. The reaction mixture was dissolved in formic acid (10 mL), precipitated into water (50 mL), and filtered (using 0.22 μm PTFE membrane). The resulting solid sample was washed successively (25 mL each) with formic acid, water, and formic acid again to remove sodium salts and those polymers not attached to the nanotubes (until no such polymers were found in the filtrate). The collected solid was redispersed in formic acid (10 mL), sonicated for 5 min, centrifuged and filtered to retain the dark supernatant. Finally, formic acid was evaporated from the solution and the PA6-functionalized SWCNT (SWCNT-g-PA6) solid sample thus obtained was dried overnight.

**Characterization**

FTIR spectra over the range of 400–4000 cm⁻¹ were recorded on a Nicolet Magna 550 spectrometer using KBr pellets. Raman spectra over the range of 1000–2400 cm⁻¹ were measured on a Dilor Labram-1B Raman spectrometer using He-Ne laser at 632.8 nm. TGA measurements were carried out using a Perkin-Elmer Pyris-1 series thermal analysis system under nitrogen at a heating rate of 20 °C/min. For the TEM observation, a small amount of the functionalized SWNT
was suspended in DMF and a drop of the suspension was placed on a copper grid. After being air-dried, the sample was investigated by Phillips CM300 FEG TEM at accelerating voltage of 300 kV. Solubility measurements were carried out by dispersing the samples into formic acid by means of an ultrasonic generator.

Results and discussion

As shown in Scheme 1, pristine SWCNT was initially functionalized by 1,3-dipolar cycloaddition using N-methylglycine and 3,4-dihydroxybenzaldehyde in solvent-free conditions under microwave irradiation. Normally, although 1,3-dipolar cycloaddition of azomethine ylides can readily occur on CNT, a severe limitation to this process is long reaction time necessary to make the reaction efficient (5 d) for the conventional thermal conditions. Microwave irradiation, as a noninvasive and cleaning processing tool, has been used to efficiently activate or accelerate this type of reaction. Very recently, Prato et al. have also reported that a solvent-free technique with the aid of microwave irradiation produces the functionalized nanotubes just in 1 h, paving the way to large-scale functionalization.

Raman spectrum has been prevalently applied for providing qualitative information on the status of sidewall functionalization of CNT. Raman spectra of pristine SWCNT and the resulting hydroxyl-functionalized SWCNT (SWCNT-f-OH) are shown in Figure 1. The
The FTIR spectrum of SWCNT-f-OH sample [Figure 2(a)] shows the C—H stretching features at 2928 and 2862 cm\(^{-1}\) that do not appear in the spectrum of pristine SWCNT [Figure 2(b)]. The large IR bands observed at ca. 3422 and 1627 cm\(^{-1}\) are attributed to the asymmetrical stretching and scissoring vibrations, respectively, due to presence of trace water in the KBr pellet used.\(^{11}\)

TGA was employed in order to determine the degree of the functionalization onto the tube surface (Figure 3). The pristine SWCNT and SWCNT-f-OH present weight loss of about 5\% and 24\% at 800 °C, respectively. This roughly corresponds to the presence of one functional hydroxyl-terminated group per 68 carbon atoms.

After transformation of SWCNT-f-ArCOOH into the corresponding azide using diphenylphosphoryl azide (DPPA), thermal decomposition of carbonyl azide groups \textit{in-situ} generated the corresponding isocyanates via Curtius rearrangement, which were then reacted with \(\varepsilon\)-caprolactam to form acyl caprolactam initiator (SWCNT-f-caprolactam) in a one-pot-process without the need of intermediate purification. It is worthy of being mentioned that, although 4-NCO is more reactive than 2-NCO in the intermediate (\textit{i.e.} aromatic isocyanates functionalized CNT, SWCNT-f-ArNCO) towards...
the hydroxyl groups, it is almost undifferentiated for the reaction between NCO and NH. Therefore, the urea groups (NHCON) in the SWCNT-f-caprolactam are attributed to the reaction of both 4-NCO and 2-NCO with NH in ε-caprolactam.

It is expected that PA6 chains can grow or graft from the sidewalls of SWCNT, and the grafted PA6 can act as in situ compatibilizers, which not only results in uniform dispersion of SWCNT in the matrix but also solves the compatibility and viscosity matching problems during the fabrication of polymer composites. All polymerizations were performed at 170 °C, thus yielding polymer-functionalized nanotubes as depicted in Scheme 1. As expected, the TGA data clearly suggested that polymer (PA6) chains have been covalently grafted onto the surface of SWCNT (Figure 5).

**Figure 5** Thermogravimetric analysis data for (a) pristine SWCNT, (b) SWCNT-f-ArCOOH, (c) SWCNT-f-caprolactam and (d) SWCNT-g-PA6.

TGA curves of pristine SWCNT, SWCNT-f-ArCOOH, SWCNT-f-caprolactam and SWCNT-g-PA6 in nitrogen at a heating rate of 20 °C/min are shown in Figure 5. The weight loss of pristine SWCNT below 600 °C is less than 3%. However, there is an obvious weight loss stage between 150 and 600 °C for SWCNT-f-ArCOOH (19%), SWCNT-f-caprolactam (24%) and SWCNT-g-PA6 (40%) due to the organic attachment. It was noteworthy that the adsorbed PA6 has been efficiently removed from the products by filtration and washing, as mentioned in the experimental procedures. The parallel experiments, in which the pristine SWCNT was mixed with free PA6 in formic acid followed by efficient filtration and washing, proved that the quantity of the adsorbed PA6 was lower than 5 wt%.

The morphologies of the SWCNT and SWCNT-g-PA6 were further investigated by TEM as shown in Figure 6. The tube surface of pristine SWCNT was relatively smooth and clean (Figure 6A), while in case of SWCNT-g-PA6, the coarser surface could be obviously observed (Figure 6B), indicating that SWCNT was coated by a layer of polymer chains because of the chemical linkage.

**Figure 6** TEM images of pristine SWCNT (A) and PA6 functionalized SWCNT (B).

It was also found that with the present grafted strategy, the SWCNT-g-PA6 obtained could be easily dispersed in highly polar solvents such as formic acid without agglomeration. The dispersion of pristine SWCNT and SWCNT-g-PA6 samples in formic acid was presented (Figure 7). The resulting clear, dark-brown solution of SWCNT-g-PA6 remained stable for a period of at least 6 month, while the solution of pristine SWNT started to flocculate and precipitate within 5 min after sonication upon standing. This solubility of the functionalized nanotube sample in some organic solvents may prove valuable to the homogeneous dispersion of SWCNT in PA6 or other matrices for fabricating high-performance polymer nanocomposites.

**Figure 7** Photographs of pristine SWCNT (A) and SWCNT-g-PA6 (B) in formic acid.

**Conclusions**

In summary, we herein describe a novel synthetic strategy to graft PA6 onto the surface of SWCNT by anionic ring-opening polymerization, in which a green
and highly efficient functionalization of carbon nanotubes was used for the first time by combining 1,3-dipolar cycloaddition and Curtius rearrangement reactions. This is a relatively convenient but still reasonably controllable method to chemically modify carbon nanotubes with commodity polymers. Obviously, our protocol offers several advantages over the reported methods: (1) it does not require acid treatment and sacrifice the high aspect ratios of CNT, which is beneficial for the nanotubes reinforced polymer composites; (2) the toxic reagent and polluting substances such as thionyl chloride, TDI, may be avoided in view of environmental protection. It is possible that the reactive nanotube-bound isocyanate species via Curtius reaction based on isocyanate chemistry as well as on isocyanate free processes could react with other functionalized small molecules or polymers and then would expand the horizons of carbon nanotube chemistry. Further studies are required to develop optimal processing techniques to gear Curtius rearrangement for the wider applications.

References
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