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## Facile Functionalization of Multilayer Fullerenes (Carbon Nano-Onions) by Nitrene Chemistry and “Grafting from” Strategy

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**Abstract:** Facile functionalization of multilayer fullerenes (carbon nano-onions, CNOs) was carried out by [2 + 1] cycloaddition of nitrenes. The products were further derivatized by using the “grafting from” strategy of in situ ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP). Using one-step nitrene chemistry with high-energy reagents, such as azidoethanol and azidoethyl 2-bromo-2-methyl propanoate, in *N*-methyl-2-pyrrolidone at 160°C for 16 h, hydroxyl and bromide functionalities were introduced onto the surfaces of CNOs. These hydroxyl CNOs (CNO-OH) and bromic CNOs (CNO-Br) were extensively characterized by various techniques such as thermal gravimetric analysis (TGA), transmission

electron microscopy (TEM), Raman spectroscopy and X-ray photo electron spectroscopy (XPS). TGA measurements indicated that the surface hydroxyl and bromide group density reached 1.49 and 0.49 mmol g<sup>-1</sup>, respectively. The as-functionalized CNOs showed much better solubility in solvents than pristine CNOs. The CNO-OH were also observed to fluoresce at  $\lambda = 453$  nm in water. The CNO-OH and CNO-Br can be conveniently utilized as macroinitiators to conduct surface-initiated in-situ polymerizations.

**Keywords:** ATRP (atom transfer radical polymerization) • cycloaddition • functionalization • grafting • nano-onions

Poly( $\epsilon$ -caprolactone) (PCL, 45wt %) and polystyrene (PS, 60 wt %) were then grafted from surfaces of CNOs through the ROP of  $\epsilon$ -caprolactone with the macroinitiator CNO-OH and the ATRP of styrene with the macroinitiator CNO-Br, respectively. The structures and morphology of the resulting products were characterized by <sup>1</sup>H NMR, scanning electron microscopy (SEM), TEM, and atomic force microscopy (AFM). The polymer functionalized CNOs have good solubility/dispersibility in common organic solvents. The facile and scalable functionalization approaches can pave the way for the comprehensive investigation of chemistry of CNOs and fabrication of novel CNO-based nanomaterials and nanodevices.

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## Introduction

Since their discovery in 1991 by Iijima,<sup>[1]</sup> carbon nanotubes (CNTs) have been extensively investigated, owing to their unique structures, outstanding mechanical and physical properties, and numerous potential applications.<sup>[2]</sup> In 1992, one year after the discovery of CNTs, multilayer fullerenes (carbon nano-onions, CNOs) were discovered by Ugarte.<sup>[3]</sup> Until date, however, there have only been very limited publications exploiting the properties of these exotic nanostructural CNOs, compared to the vast amount of chemical and physical literature related to CNTs. CNOs possess unique physical and chemical properties, such as a large surface area to volume ratio, a graphitic multilayer structure/morphology, and lightness. Some potential applications have been proposed for CNOs including lubricants,<sup>[4]</sup> optical limiting materials,<sup>[5]</sup> additives for aerospace applications,<sup>[6]</sup> catalysis,<sup>[7]</sup> fuel cells,<sup>[8]</sup> gas storage,<sup>[9]</sup> and electromagnetic shielding.<sup>[10]</sup> Actually, similar to the case of CNTs, the insolubility and weak dispersibility of CNOs in water and organic solvents strongly limits their applications and hinders the study of their chemical and physical properties. To improve the solubility and to achieve surface functionalization of CNOs, two main strategies have been developed. The first involves generation and functionalization of defect sites on CNO surfaces through oxidative treatment by nitric acid and subsequent conversion into derivatives such as amides, PEGylation,<sup>[11]</sup> and organometallic structures.<sup>[12]</sup> The second method is a direct functionalization of the CNOs by using addition reactions,<sup>[13]</sup> for example, surface fluorination with elemental fluorine,<sup>[14]</sup> direct addition of a conjugated polymer,<sup>[15]</sup> direct 1,3-dipolar cycloaddition of azomethine ylides,<sup>[11]</sup> and direct [2+1] Bingel–Hirsch cyclopropanation reaction<sup>[16]</sup> on the surfaces of CNOs. However, the oxidative treatment method is usually a low yield reaction with aggressive conditions and produces many environmentally unfriendly by-products. As for the addition reactions, although the solubility of functionalized CNOs is improved the CNO surfaces still lack sufficient active functional groups for further modifications. Therefore, a cost-effective, scalable, and environmentally sustainable technology to synthesize soluble CNOs with reactive functional groups still remains unexplored.

It is known that [2+1] cycloaddition of nitrenes is one of the important addition reactions which have been successfully used to functionalize CNTs<sup>[17]</sup> and [60]fullerene (C<sub>60</sub>),<sup>[18]</sup> demonstrating its high efficiency. However, the cycloaddition of nitrenes to CNOs has never been reported. Thus important questions exist as to whether this addition reaction could be extended to functionalize CNOs and if the modified CNOs would still undergo further reactions. To answer these questions, CNOs were reacted with previously synthesized functional azides using the nitrene chemistry. The process results in soluble CNOs, which can further undergo in situ polymerizations with the immobilized functional groups, as initiating sites for polymer grafting.

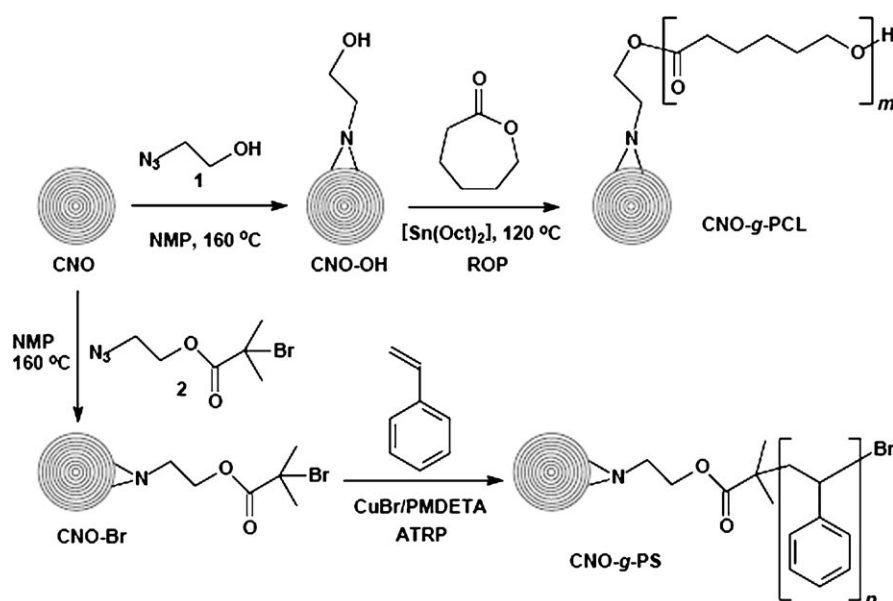
Covalent functionalization of carbon nanomaterials with polymers has been gaining considerable interest, as long

polymer chains help solubilize the nanomaterials into a wide range of solvents, even at low degree of functionalization. In addition, the individual properties of the polymer and nanomaterials can be combined to give a novel hybrid material. For the comprehensively studied CNTs, the polymer anchoring can be fulfilled by so-called “grafting to” and “grafting from” approaches. The “grafting to” technique involves bonding end-functionalized polymer to the active surface functional groups on CNTs.<sup>[19]</sup> This strategy has also been extended to functionalize CNOs recently to prepare pyridyl-functionalized CNOs (Py-CNOs), nanoporous supramolecular assemblies<sup>[12]</sup> and PEG-derivatized CNOs<sup>[11]</sup> based on the carboxylic groups on the CNO surfaces. In contrast, the “grafting from” approach is based upon the initiators previously immobilized on CNTs followed by surface-initiated polymerization of monomers, resulting in much higher grafting efficiency and control.<sup>[20]</sup> By taking advantages of controlled living-polymerization mechanisms from ionic and radical initiators, the “grafting from” approaches have been applied to covalently grow polymers from surfaces of CNTs with controllable, uniform, and designable structures. This has been achieved using atom transfer radical polymerization (ATRP),<sup>[21]</sup> reversible addition fragmentation chain transfer (RAFT) polymerization,<sup>[22]</sup> nitroxide-mediated radical polymerization (NMRP),<sup>[23]</sup> living ring-opening polymerization (ROP),<sup>[24]</sup> anionic polymerization,<sup>[25]</sup> and cationic polymerization.<sup>[26]</sup> However, functionalization of CNOs through the “grafting from” approach has not been reported so far, most likely a result of the unavailability of CNOs and the difficulty in synthesis of CNO-based macroinitiators.

Here, we report the direct addition of hydroxyl and bromide ATRP initiators to the surface of CNOs by the [2+1] cycloaddition of corresponding nitrenes. Subsequently, in situ ROP of  $\epsilon$ -caprolactone and ATRP of styrene were conducted, giving rise to biodegradable poly( $\epsilon$ -caprolactone)- and polystyrene-grafted CNOs, respectively. This successful endeavor enables us to conclude that 1) the [2+1] cycloaddition of nitrenes is a powerful method to functionalize CNOs with merits of mass-increase process and designable surface chemistry, 2) the additional functional groups on CNOs introduced by the nitrene chemistry are still highly reactive, providing a versatile nanoplatform for further modification of CNOs, and 3) the “grafting from” approach can also be used to grow polymers from the nanosurfaces of CNOs to achieve new hybrid nanomaterials.

## Results and Discussion

**Preparation of CNO-OH and CNO-Br by [2+1] cycloaddition of nitrenes:** The procedure for functionalization of CNOs by [2+1] cycloaddition of nitrenes is depicted in Scheme 1. To introduce functional groups to CNO surfaces, while simultaneously improving solubility, specific azides, 2-azidoethanol (**1**) and azidoethyl 2-bromo-2-methyl propanoate (**2**) were designed and synthesized. Similar to the [2+1] cycloaddition of nitrenes to CNTs,<sup>[17]</sup> the reaction consists of



Scheme 1. Facile functionalization of CNOs by direct [2+1] cycloaddition of nitrenes to prepare hydroxy CNOs (CNO-OH) and bromic CNOs (CNO-Br), and grafting polymer from the functional CNOs by in situ ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone and atom transfer radical polymerization (ATRP) of styrene.

the thermal decomposition of the organic azide (**1** and **2**) generating nitrenes by means of nitrogen elimination and subsequently the [2+1] cycloaddition of nitrenes to the  $\text{sp}^2$  carbon-carbon double bonds of CNOs, giving rise to hydroxy (CNO-OH) and bromic CNOs (CNO-Br), respectively. Such a protocol for functionalization of CNOs has various advantages, such as the materials required for the preparation of azides can be scalably synthesized in a relatively economical manner, guaranteeing the large-scale availability of azides and functional CNOs, also, no corrosive gas is formed as a byproduct of the reaction (the released gas is  $\text{N}_2$ ) and the solvent of NMP can be recycled easily, presenting an environmentally sustainable technology. In addition, the reactive functional groups can be introduced onto CNOs isochronously in one step, verifying the versatility of this strategy. Nevertheless, there exists the possibly explosive danger for high-energy chemicals, which obviously suggests that correct and strict operations must be followed during experiments. The details on repeated use of solvent and evaluation of this strategy to functionalize other carbon nanomaterials (e.g., CNTs) will be published elsewhere.<sup>[27]</sup>

The as-obtained products of CNO-OH and CNO-Br were analyzed by TGA (Figure 1A). The pristine CNOs show noticeable thermal stability and almost no decomposition below 600 °C. In contrast, CNO-OH and CNO-Br samples exhibit significant weight-loss during 160–450 °C, which is attributed to the decomposition of corresponding hydroxide and bromic initiator fragments on the CNO surfaces, respectively. From the TGA weight-loss data (8.8 wt% for CNO-OH and 10.2 wt% for CNO-Br), we can calculate the average density of surface groups, which is  $1.49 \text{ mmol g}^{-1}$  for CNO-OH and  $0.49 \text{ mmol g}^{-1}$  for CNO-Br, respectively. In

addition, the functionalized CNOs exhibit much better dispersibility as compared with the pristine CNOs, especially for the CNO-OH in polar solvents and water (Figure 1B, insert). UV-vis measurements showed a strong absorption for clear aqueous solutions of CNO-OH between 200–500 nm (Figure 1B). Surprisingly, we found that the CNO-OH is luminescent at 453 nm in aqueous solution (Figure 1B). The luminescence could be attributed to the trapping of excitation energy at defect sites of CNO-OH, which is phenomenologically similar to the emission observed in solubilized CNTs and carbon nanodots.<sup>[28,29]</sup>

Figure 1C shows the Raman spectra of pristine CNOs, CNO-OH, and CNO-Br. For the pristine CNOs, the  $D$  band at

$1323.9 \text{ cm}^{-1}$  is assigned to defects in the CNOs lattice including  $\text{sp}^3$ -hybridized carbon, and the  $G$  band at  $1579.6 \text{ cm}^{-1}$  originates from the vibrations of  $\text{sp}^2$ -hybridized framework.<sup>[30]</sup> Owing to the introduction of covalently bound moieties to the CNOs framework resulting in a conversion of  $\text{sp}^2$ -hybridized carbon to  $\text{sp}^3$ -hybridized carbon, the increase of the intensity ratio of  $I_D/I_G$  is an indication of increment of defects in the graphitic layers. After functionalization of CNOs by nitrenes, the  $D$  and  $G$  bands of CNO-Br are shifted to  $1320.0$  and  $1573.8 \text{ cm}^{-1}$ , respectively. The  $I_D/I_G$  ratio is 1.6 for CNOs and 1.9 for CNO-Br, indicating an increase in the number of surface defects and again confirming the successful functionalization. For CNO-OH, the  $D$  and  $G$  bands are overlapped to some extent and although the  $I_D/I_G$  ratio is difficult to calculate, the change in spectrum indicates that functionalization has occurred on the surface of pristine CNOs after [2+1] cycloaddition of nitrenes.

XPS provides direct evidence for the covalent linkage of hydroxyl and bromide onto the CNOs surfaces. The high-resolution C1s, O1s, N1s, and Br3d<sub>5</sub> XPS spectra of CNO, CNO-OH and CNO-Br are shown in Figure 2. As can be seen, the C1s XPS peak of CNOs with a binding energy of 284.6 eV is shifted significantly versus CNO-OH (284.9 eV) and CNO-Br (285.5 eV) due to the formation of  $\text{sp}^3$ -hybridized carbons on the surface of CNOs (Figure 2A). The presence of O in pristine CNOs can be explained by physically adsorbed oxygen and small amount of oxygen on the CNOs surface in the form of carboxylic groups during their production. The atomic ratio of O/C in pristine CNOs is only 0.07. However, after [2+1] cycloaddition of nitrenes onto CNOs surface, the atomic ratio of O/C is 0.21 and 0.24 for CNO-OH and CNO-Br, respectively. Moreover, the atomic ratio

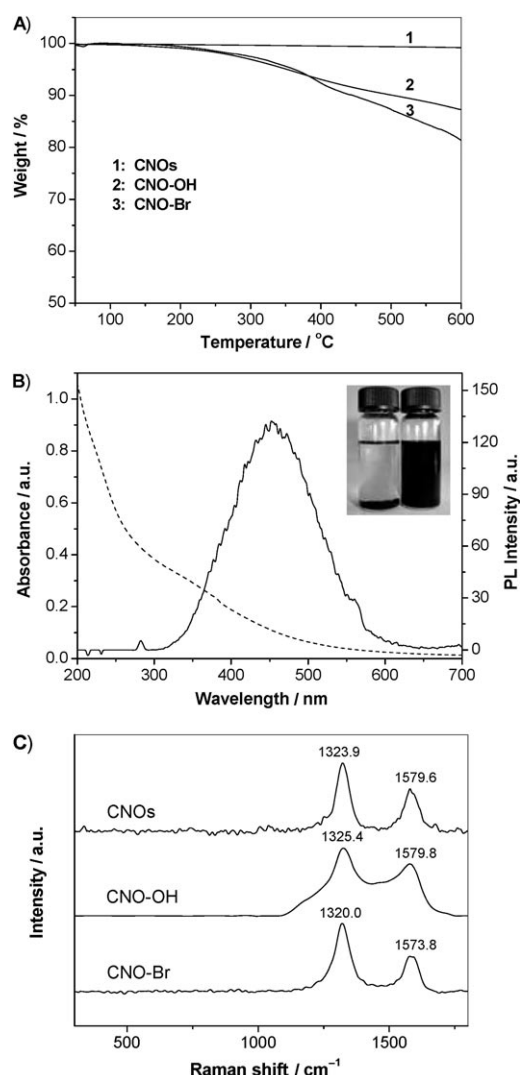


Figure 1. A) TGA weight-loss curves of pristine CNOs, CNO-OH, and CNO-Br. B) Absorbance (---) and fluorescent emission (—) spectra of CNO-OH in water. C) Raman spectra of pristine CNOs, CNO-OH, and CNO-Br. The insert of B) shows the photograph of pristine CNOs (left) and CNO-OH (right) placed in water, demonstrating the high solubility of functionalized CNOs.

of N/C for the pristine CNOs is  $\approx 0.001$ , indicating that almost no N element exists in the CNOs, while the N/C ratio increases to 0.023 for CNO-OH and 0.027 for CNO-Br, more than one order of magnitude higher than that of pristine CNOs. In addition, a distinct peak for Br3d5 at 69.4 eV can be observed for CNO-Br, confirming the presence of the Br element in the CNO-Br (Figure 2D). After ATRP of styrene, the resulting polystyrene-grafted CNOs (CNO-g-PS) still contains a little amount of Br, which again demonstrates the covalent linkage of the ATRP initiating sites and CNOs surface by [2+1] cycloaddition of nitrenes. All these results are favorable in agreement with those obtained from the TGA and Raman measurements. Combining all of the evidences, we can see that the [2+1] cycloaddition of nitrenes onto CNOs surface was successfully carried

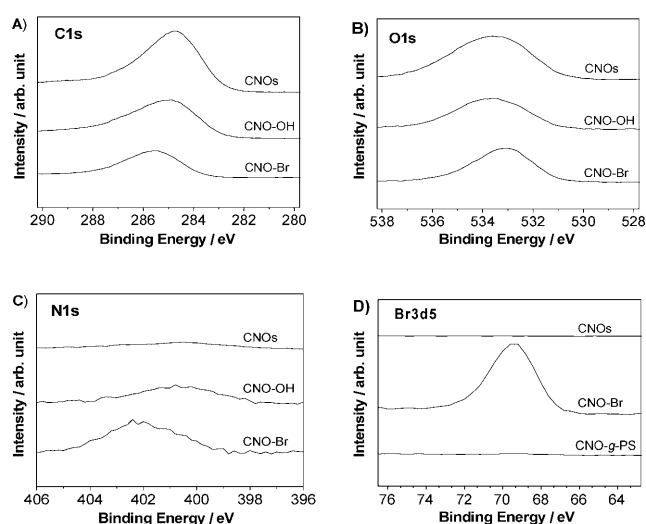


Figure 2. The XPS spectra of pristine CNOs, CNO-OH, CNO-Br, and CNO-g-PS at A) C1s, B) O1s, C) N1s, and D) Br3d5.

out and the functionalized CNOs with expected functional groups were obtained.

The TEM images of pristine CNOs, CNO-OH, and CNO-Br can be seen in Figure 3. The onion-like structures with sizes at 5–10 nm can be clearly seen from TEM image of pristine CNOs at a high magnification. As TEM cannot probe the organic functional groups on the surfaces of functionalized CNO,<sup>[11]</sup> no obvious difference can be seen between the images of pristine CNOs and organic functionalized CNOs.

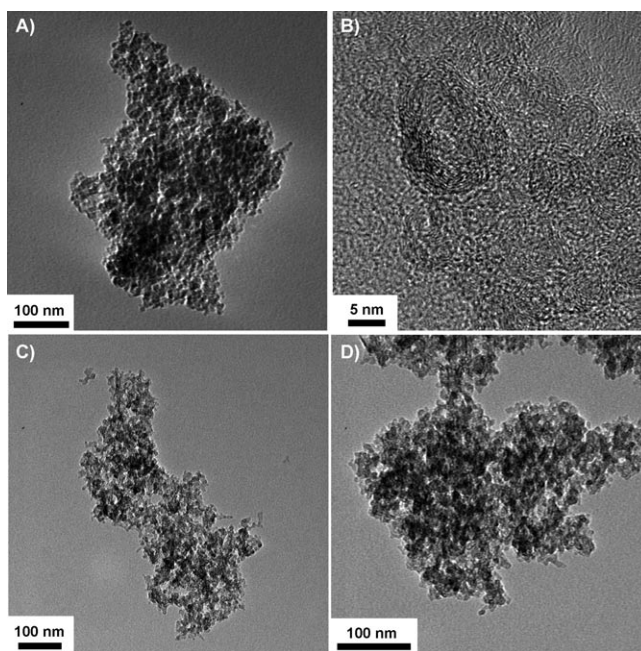


Figure 3. Representative TEM images of A,B) pristine CNOs, C) CNO-OH, and D) CNO-Br.

To further demonstrate the existence and reactivity of the expected surface functional groups immobilized on CNOs, we carried out in situ polymerizations discussed below.

**Preparation of PCL-grafted CNOs by surface-initiated ROP:** Surface-initiated ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone has been successfully performed on other surfaces such as CNTs,<sup>[24]</sup> carbon nanofibres,<sup>[31]</sup> silica, CdS,<sup>[32]</sup> and so on.<sup>[33]</sup> Herein, the hydroxyl groups of CNO-OH were also used as initiating sites for ROP of  $\epsilon$ -caprolactone, as shown in Scheme 1. The TGA curves of CNO-OH and PCL-grafted CNOs (CNO-g-PCL) can be seen in Figure 4A.

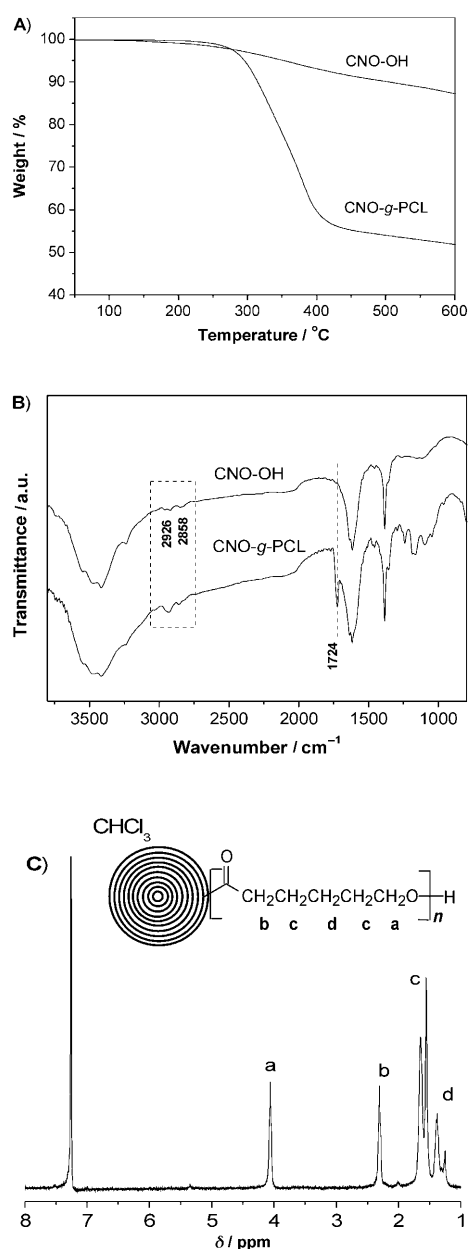


Figure 4. A) TGA weight loss curves of CNO-OH and CNO-g-PCL. B) FTIR spectra of CNO-OH and CNO-g-PCL. C) <sup>1</sup>H NMR spectrum of CNO-g-PCL in CDCl<sub>3</sub>.

The weight loss between 160–450°C for CNO-OH is 8.8%. After 24 h of polymerization, approximately 45 wt% PCL was grown from the CNO-OH surfaces. The onset of decomposition for CNO-g-PCL is  $\approx 260^\circ\text{C}$ , which is much higher than that of CNO-OH. This can be explained by the fact that PCL grafted on the CNOs have much higher decomposition temperature than the organic moieties linked to the CNOs.

The FTIR spectra of CNO-OH and CNO-g-PCL can be seen in Figure 4B. The two peaks at 2926 and 2858 cm<sup>-1</sup>, associated with sp<sup>3</sup> C–H stretching, which can be clearly observed for CNO-OH. After polymerization, the intensity of the sp<sup>3</sup> C–H stretching is increased and a carbonyl absorption peak at 1724 cm<sup>-1</sup> appears, which are in accordance with the grafted PCL structure. Since CNO-g-PCL has a good dispersibility in organic solvents, the structure of the CNO-g-PCL was further investigated by NMR spectroscopy. The hydrogen peaks of PCL units are observed clearly in the <sup>1</sup>H NMR spectrum (see Figure 4C).

In addition, we also did XRD measurements for the functionalized CNOs to probe the integrality of graphitic structures (the patterns not shown). Two peaks at  $2\theta = 24.82^\circ$  and  $43.23^\circ$  were found for the sample of CNO-g-PCL, corresponding to the (002) and (100) planes of CNOs, respectively.<sup>[14]</sup> This confirmed that the multilayer structures of CNOs were not destroyed during the polymerization.

The nanostructure and morphology of the resulting CNO-g-PCL were investigated by SEM and TEM (see Figure 5). The pristine CNOs (Figure 5A) look “blooming” and “spherulitic”, but the PCL-functionalized CNOs (Figure 5B) look more compact. Furthermore, in Figure 5B, it can be seen that CNOs are enveloped in a continuous PCL phase to form CNO-PCL composite. In the low magnification

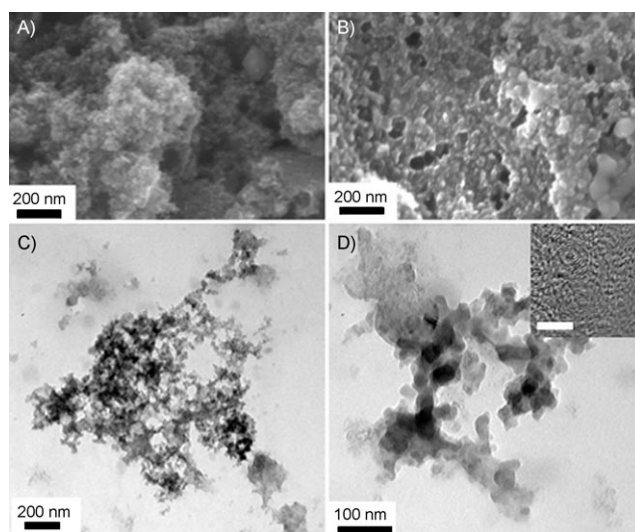


Figure 5. Representative SEM images of A) pristine CNOs and B) CNO-g-PCL; TEM images of CNO-g-PCL at C) low magnification and D) high magnification. The insert of D) shows the high-resolution TEM image (the scale bar is 5 nm), confirming the onion-like layer structure of CNO after ring-opening polymerization.

image of TEM (Figure 5C), the CNO-g-PCL shows much better dispersibility than CNOs (see Figure 3A). In the high magnification image of TEM (Figure 5D), the CNOs are enveloped by a continuous polymer phase. The retentive onion-like layer structure of CNO after grafting PCL was also clearly observed under high-resolution TEM (see Figure 5D, insert). This is in accordance with the XRD results.

#### Preparation of PS-grafted CNOs by surface-initiated ATRP

To carry out the ATRP<sup>[34]</sup> of monomer on CNOs, the ATRP initiating sites should be anchored at the outset. ATRP initiating sites have been successfully anchored to carbon black,<sup>[35]</sup> carbon spheres<sup>[36]</sup> and CNTs through multi-step reactions previously.<sup>[37]</sup> In this investigation we direct attached ATRP initiating sites to CNOs by [2+1] cycloaddition of nitrenes. Then polystyrene (PS) was grafted from the surfaces of CNOs by the surface-initiated ATRP “grafting from” approach, as shown in Scheme 1. For comparison, the pristine CNOs “initiated” ATRP of styrene (CNO-PS1) was carried out under the same condition of CNO-Br case. According to the TGA weight-loss result (Figure 6A), the PS-grafted CNOs (CNO-g-PS) decomposed in the temperature range of 400–450 °C and approximately 60% PS by mass was grown from the CNO surfaces, whereas the CNO-PS1 exhibited a much lower temperature of decomposition (start at 150 °C) and only 16% weight-loss between 150–450 °C was detected. This may be owed to the decomposition of the organic small molecules at the first stage and the PS formed

by free radical thermal polymerization at the second stage. From the TGA studies, we can conclude that the ATRP initiating sites have been successfully attached to CNO surfaces by [2+1] cycloaddition of nitrenes and still remain their reactivity. With the improved solubility, <sup>1</sup>H NMR spectroscopy may be conducted on the CNO-g-PS/CDCl<sub>3</sub> suspension and Figure 6B shows the peaks assigned to the PS grafted from CNOs.

TEM images of CNO-g-PS are shown in Figure 7A,B. Similar to the TEM images of the CNO-g-PCL (Figure 4C,D), CNOs are individually enveloped in a continuous

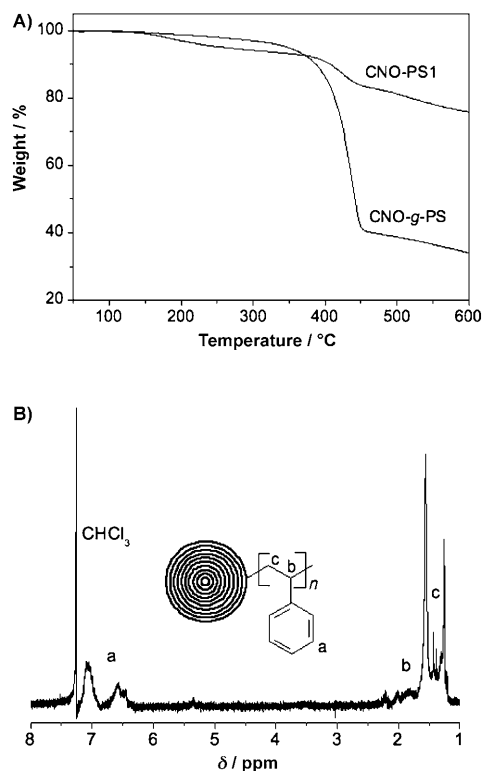


Figure 6. A) TGA weight loss curves of CNO-PS1 and CNO-g-PS. B) <sup>1</sup>H NMR spectrum of CNO-g-PS in CDCl<sub>3</sub>.

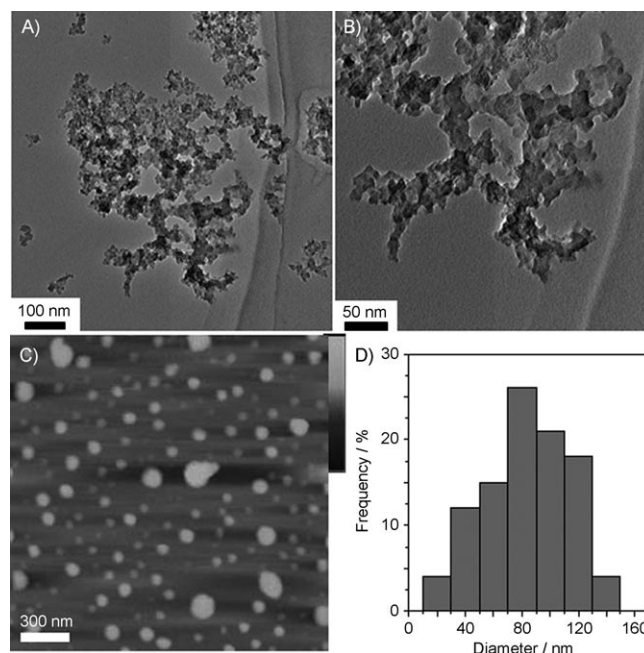


Figure 7. Representative TEM images of CNO-g-PS at A) low magnification and B) high magnification; C) AFM height image of CNO-g-PS and D) corresponding diameter frequency of the functionalized CNOs shown in C). The height calibration in C) is 50 nm.

PS phase in both images. AFM was also utilized to study the morphology of the CNO-g-PS (Figure 7C). The images reveal that the PS-grafted CNOs are well dispersed with little aggregation compared to their TEM images and, thus, their diameter can preferably be estimated from the AFM images. Their average sizes are ≈85 nm (Figure 7D), which is much larger than pristine CNOs observed from TEM images. This can be explained by grafting dense PS on CNOs surface.

## Conclusion

We have shown that functionalized-CNOs with organic functional groups can be easily achieved by direct [2+1] cycloaddition of corresponding nitrenes to CNOs. The as-prepared functionalized-CNOs have much better solubility/dispersibility in solvents than pristine CNOs. This general strat-



egy could be developed into a versatile, scalable, inexpensive, and green technology to make functionalized CNOs and other carbon nanomaterials. As can be attributed to the immobilized functional groups, growing polymers from CNO surfaces was performed for the first time through the “grafting from” approach. Accordingly, PCL- and PS-grafted CNOs were obtained by in-situ ring-opening polymerization of  $\epsilon$ -caprolactone based on the hydroxy groups and ATRP of styrene based on the ATRP-active bromic groups introduced by the nitrene chemistry, respectively. It is no doubt that the ring-opening polymerization and atom transfer radical polymerization on CNOs surface can be extended to other cyclic monomers and vinyl monomers to synthesize more CNO-based novel nanomaterials and nanodevices with tailor-made properties, even though we have only carried out several functionalization experiments, owing to the limitation of CNO raw materials at this stage. Because of the good solubility in organic solvents or in water, these functionalized-CNOs offer exciting and promising potential applications in many fields such as bio-nanotechnology.

## Experimental Section

**Materials:** The carbon nano-onions used in the present work were prepared according to the literature.<sup>[11]</sup> The 2-azidoethanol (**1**)<sup>[38]</sup> and azidoethyl 2-bromo-2-methyl propanoate (**2**)<sup>[39]</sup> were prepared in our laboratory. Stannous octoate (Aldrich,  $\text{Sn}(\text{Oct})_2$ ),  $\epsilon$ -caprolactone (Acros),  $N,N,N',N'',N'''$ -pentamethyldiethylenetriamine (Aldrich, PMDETA) were used as received. The styrene monomer was distilled before use. All other chemicals were analytical grade and used as received without further purification unless otherwise stated.

**Instrumentation:** Raman spectra were recorded by using a LabRam-1B Raman spectroscope operating at a laser wavelength of 632 nm. Thermal gravimetric analysis (TGA) was carried by using a PE TGA-7 instrument with a heating rate of  $20^\circ\text{C min}^{-1}$  in a nitrogen flow ( $20\text{ mL min}^{-1}$ ). X-ray photoelectron spectroscopy (XPS) was investigated by using a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with  $\text{MgK}\alpha$  radiation ( $h\nu = 1253.6\text{ eV}$ ), binding-energies calibration was based on C1s at 284.6 eV. Absorption and fluorescence spectra were recorded at room temperature by using a Lambda 20 UV-visible spectrometer (Perkin-Elmer) and Varian Cary Fluorescence spectrometer, respectively.  $^1\text{H NMR}$  spectra were measured by using a Varian Mercury Plus 400 MHz spectrometer using  $\text{CDCl}_3$  as the solvent. Fourier transform infrared (FTIR) spectra were recorded by using a PE Paragon 1000 spectrometer (KBr disk). X-ray powder diffraction (XRD) spectra were taken by using a Bruker AXS D8-advance X-ray diffractometer with  $\text{CuK}\alpha$  radiation. Transmission electron microscopy (TEM) studies were performed by using a JEOL JEL2010 electron microscope at 200 kV. Scanning electron microscopy (SEM) images were recorded by using FEI SIRION 200 field-emission microscope. Atomic force microscopy (AFM) was measured by using a Digital Instrument Nanoscope IIIa SPM, operating at the tapping mode.

**Synthesis of CNO-OH and CNO-Br:** In a typical experiment, 50 mg of pristine CNOs, 7 mL of  $N$ -methyl-2-pyrrolidone (NMP) and 1 mL of 2-azidoethanol (**1**) (or azidoethyl 2-bromo-2-methyl propanoate (**2**)) were placed in a dry flask. The mixture was treated with an ultrasonic bath (40 kHz) for 30 min, and then stirred at  $160^\circ\text{C}$  for 16 h. The solution was precipitated with ether. The obtained viscous solid was then dispersed in acetone and separated by centrifugation and washed with acetone. After repeated washing and centrifuging steps, the resulting solid was dried overnight in a vacuum oven at  $60^\circ\text{C}$  to obtaining 52 mg of CNO-OH (or 54 mg CNO-Br).

**Synthesis of CNO-g-PCL by ROP:** Typically, as prepared CNO-OH initiator (31 mg),  $\epsilon$ -caprolactone (1.0 g) and 0.03 wt% stannous octoate were placed in a dry flask, which was then sealed with a rubber plug. The flask was immersed in an oil bath at  $120^\circ\text{C}$  and stirred for 24 h. The mixture was dissolved in 10 mL chloroform, and subsequently centrifuged and washed with chloroform. To completely remove any ungrafted polymer, the washing and centrifuging cycle was repeated at least five times. After drying overnight under vacuum, the sample of CNO-g-PCL (42 mg) was obtained.

**Synthesis of CNO-g-PS by ATRP:** Growing polystyrene from the surfaces of carbon nano-onions was accomplished under ATRP conditions.<sup>[34]</sup> Typically, CNO-Br (35 mg) initiator, CuBr (0.010 g),  $N,N,N',N'',N'''$ -pentamethyldiethylenetriamine (PMDETA, 0.013 g) and anhydrous tetrahydrofuran (THF) were added into a flask. Then the flask was evacuated and re-filled three times with  $\text{N}_2$ , finally 1.2 g styrene was injected into the flask and the mixture was stirred at  $90^\circ\text{C}$  for 18 h. The mixture was subsequently diluted with THF and centrifuged. The resulting solid was redispersed in THF, then centrifuged and washed with THF four times. After drying overnight under vacuum, the sample of CNO-g-PS (68 mg) was obtained.

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