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Review

Functionalization of carbon nanotubes and other nanocarbons by azide chemistry

Jin Han and Chao Gao*

Following the conventional carbon allotropes of diamond and graphite, fullerene, carbon nanotubes (CNTs) and graphene as 0D, 1D and 2D graphitic macromolecules have been discovered recently in succession, declaring the unlimited potential of carbon-based nanomaterials and nanotechnology. Although CNTs exhibit significant potential applications in advanced materials and other fields due to their extraordinary mechanical strength and electrical/thermal conductivity properties, their low solubility, poor wettability and bad dispersibility in common solvents and solid matrices have limited their processing and applications. Thus, the attempt to achieve wettable/processable CNTs by functionalization has attracted increasing attention in both scientific and industrial communities. In recent years, azide chemistry has been demonstrated as a powerful means to covalently modify CNTs. It consists of two major approaches: click chemistry and nitrene chemistry, which both involve the usage of various azide compounds. The former one is based on highly reactive and stereospecifical Cu(I) catalyzed azide-alkyne cycloaddition reaction; the latter one is based on the electrophilic attack to unsaturated bonds of CNTs with nitrenes as reactive intermediates formed from thermolysis or photolysis of azides. In this mini-review paper, the azide chemistry to functionalize CNTs is highlighted and the corresponding functionalization routes to build CNT-based complex structures are also discussed. Besides, covalent functionalizations of other graphitic nanomaterials such as fullerence and graphene, via azide chemistry, are commented briefly.

Keywords: Carbon nanotubes; Functionalization; Click chemistry; Nitrene chemistry; Nanocomposites; Fullerene; Graphene

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Carbon is a common and remarkable element that not only constructs the framework of organic compounds making organism and life but also exhibits different faces with essentially different natures itself. Following the conventional carbon allotropes of diamond and graphite, fullerene, carbon nanotubes (CNTs) and graphene as 0D, 1D and 2D graphitic macromolecules have been discovered in 1985 [1], 1991 [2], and 2004 [3], respectively (see Fig. 1). As a typical kind of 1D nanomaterials, this review paper will concentrate on CNTs, especially the chemical functionalization of CNTs.

Since the first intentional report in 1991 by Iijima [2], CNTs have become the focus of nanoscience and nanotechnology because of their unique structures and unlimited potentials in a wide range of applications. CNTs can be regarded as graphitic or graphene sheets rolled up into a hollow cylinder and end-capped by a half-part of fullerene. In terms of the layer number of the rolled sheet, CNTs are classified as single-walled (SWCNTs), double-walled (DWCNTs), and multi-walled carbon nanotubes (MWCNTs). CNTs possess various marvelous attributes such as high aspect ratio, extremely high mechanical strength but ultra light, high thermal conductivity, high stability, and rich electronic properties, promising their crucial roles in many fields

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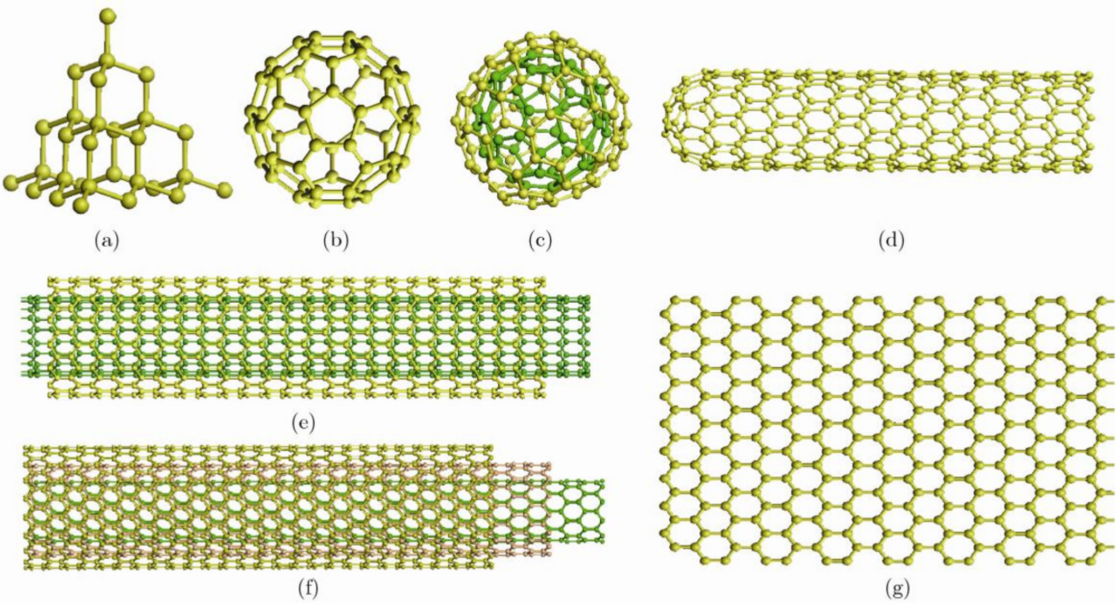


FIG. 1. Model structures of carbon: diamond (a), fullerene (b), multilayer fullerene (c), single-walled carbon nanotubes (d), double-walled carbon nanotubes (e), multi-walled carbon nanotubes (f) and graphene (g).

covering from nanocomposites to nanodevices and nanobiotechnology [4-9].

Despite such fascinating properties and significant potential applications, CNTs showed low solubility, poor wettability and bad dispersibility in common solvents and solid matrices, which pose a big challenge for their processing and applications. To meet such a challenge, chemistry approach was employed to modify the outer surface bonds of CNTs. Triggered by the pioneering work of Smalley [10] and Haddon [11], thousands of relevant papers and hundreds of patents have been published, which developed into the new research rush of chemistry of CNTs, as demonstrated by the further increasing publications (see Fig. 2). Except the dispersing and wetting of CNTs, chemical functionalization may result in other effects: (1) introduction of reactive functional groups on CNT surfaces, (2) grafting of polymer chains on CNTs, (3) fabrication of hybrid structures with integrated and tailor-made properties, (4) tuning the intrinsic properties of CNTs such as hydrophobicity, conductivity, optical property, biocompatibility, toxicity, etc., and (5) expanding the applications of CNTs.

Various chemical reactions such as hydrogenation [12], halogenation [13], esterification [14], amidation [15], cycloaddition [16], radical addition [17], nucleophilic addition [18], electrophilic addition [19], inorganic complex addition [20], ozonolysis [21], surface-initiated polymerization [22-24], and physical methods such as plasma treatment [25], π-π stacking [26] and solid-phase mechanical milling [27] have been tried to functionalize CNTs, offering alternative approaches to solubilization of CNTs with desired functionality and surface characters. These have been summarized and commented in recently published reviews. Considering the versatility and efficiency of CNT functionalization, the attention of this mini-review will be paid to azide chemistry that mainly includes azide-alkyne click chemistry and nitrene chemistry.

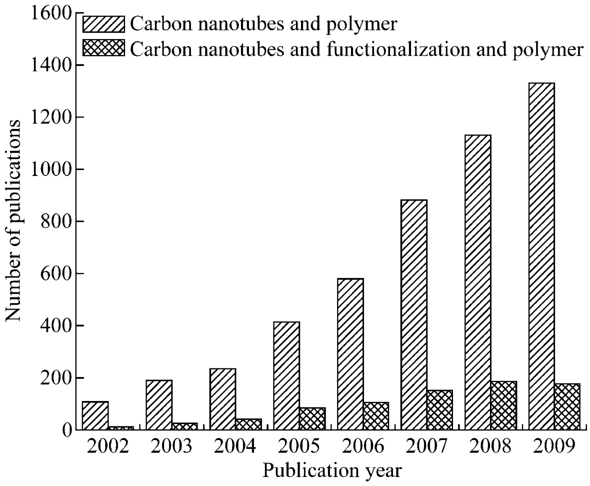
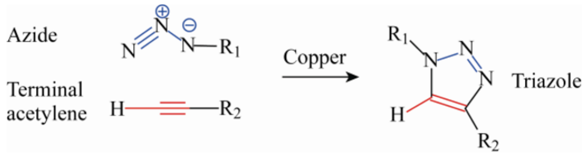


FIG. 2. Scientific publications as a function of publication year searched by the ISI web of knowledge^{SM} with "CNTs and polymer" and "CNTs and functionalization and polymer" as topics, respectively.

Functionalization of CNTs via click chemistry

The concept of azide-alkyne click chemistry

The concept of click chemistry was presented by Sharpless in 2001 [28]. The synthetic appeal of click reactions relies upon their tolerance of water and oxygen, simple reaction conditions, and high yield. In this field, the copper(I)-mediated Huisgen 1, 3-dipolar cycloaddition of organic azides and alkyne leading to 1, 2, 3-triazoles is the cream of the crops without any doubt (see Scheme 1) [29]. It has exhibited great synthetic advance in chemistry, biology, and materials science [30]. Its application in functionalization of CNTs has been proved to be very successful and is presented in the following context.

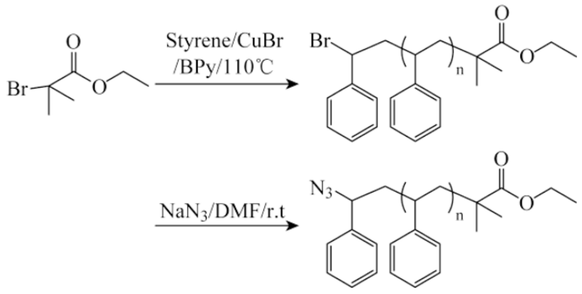


Scheme 1. Copper(I)-mediated Huisgen 1, 3-dipolar cycloaddition of azides and alkynes.

Click coupling functionalization

This type of functionalization of CNTs is typically a covalent-bond functionalization, and generally involves three main steps: (1) modification of CNTs with reactive azide or alkyne groups, (2) modification of the decorations (i.e., clickable reagents) with corresponding groups (alkyne or azide), (3) click coupling between CNTs and decorations. As far as we know, the decorations can be polymers, nanocrystals and functional organic compounds (see Table 1).

In 2005, for the first time, Adronov et al. reported the application of azide-alkyne click chemistry to functionalize CNTs with polymers [31]. The CNTs were first decorated with alkynes via Pschorr-type arylation with *p*-aminophenyl propargylether and then modified with well-defined azide-terminated polystyrene (PS) (see Scheme 2) by click coupling using several types of Cu (I) catalysts. The combination of Raman, FTIR, UV-vis, TGA, TEM and AFM measurements confirmed the click coupling. The Cu (I)/1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) catalyst system was found to be most effective for the coupling. The PS-coated CNTs had relatively high graft density of 1 polymer chain for every 200-700 carbons, and consisted of about 45% PS and exhibited good organosolubility (the highest is 233 mg/L in THF) in THF, $CHCl_3$ and CH_2Cl_2. Sulfonation of the PS-coated CNTs by acetyl sulfate made the materials water-soluble and the solubility could be adjusted by varying the degree of sulfonation [32]. Moreover, the materials possessed pH responsibility which meant the materials are soluble in water at pH between 3 and 13, otherwise, formed precipitates.



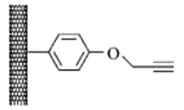
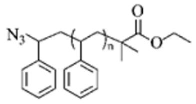
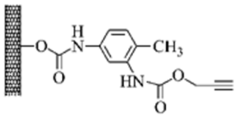
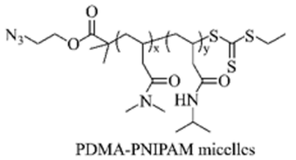
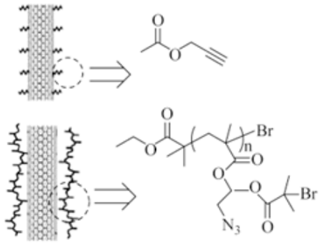
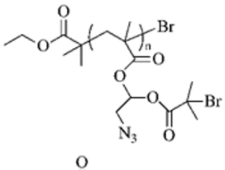
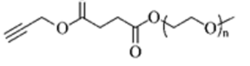
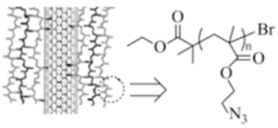
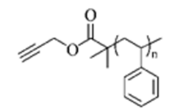
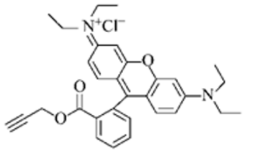
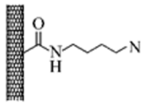
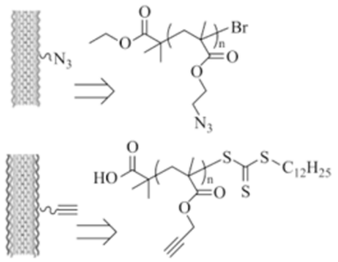
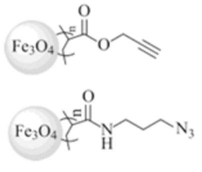
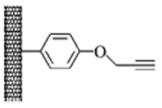
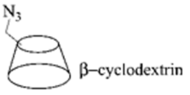
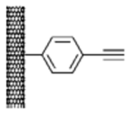
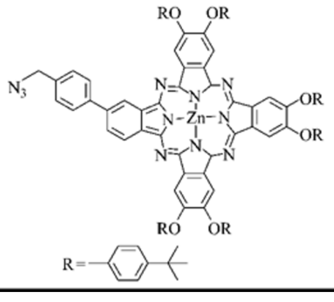
Scheme 2. Preparation of azido-terminated polystyrene via atom transfer radical polymerization (ATRP) (Reprinted with permission from ref.31. Copyright 2005. American Chemical Society).

The click coupling reaction between the alkyne-containing CNTs and azide-terminated poly (N, N-dimethylacrylamide) -*block*-poly (N-isopropylacrylamide) (PDMA-*b*-PNIPAM) diblock polymer micelles was also investigated [33]. The well-defined diblock polymer was synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization with an azide-containing chain transfer reagent. It is worthy to point out that when the micelle formed above the critical micellization temperature, the azide groups would locate at the periphery of micelles and the click coupling would be facilitated, resulting in an enhancement of grafting density.

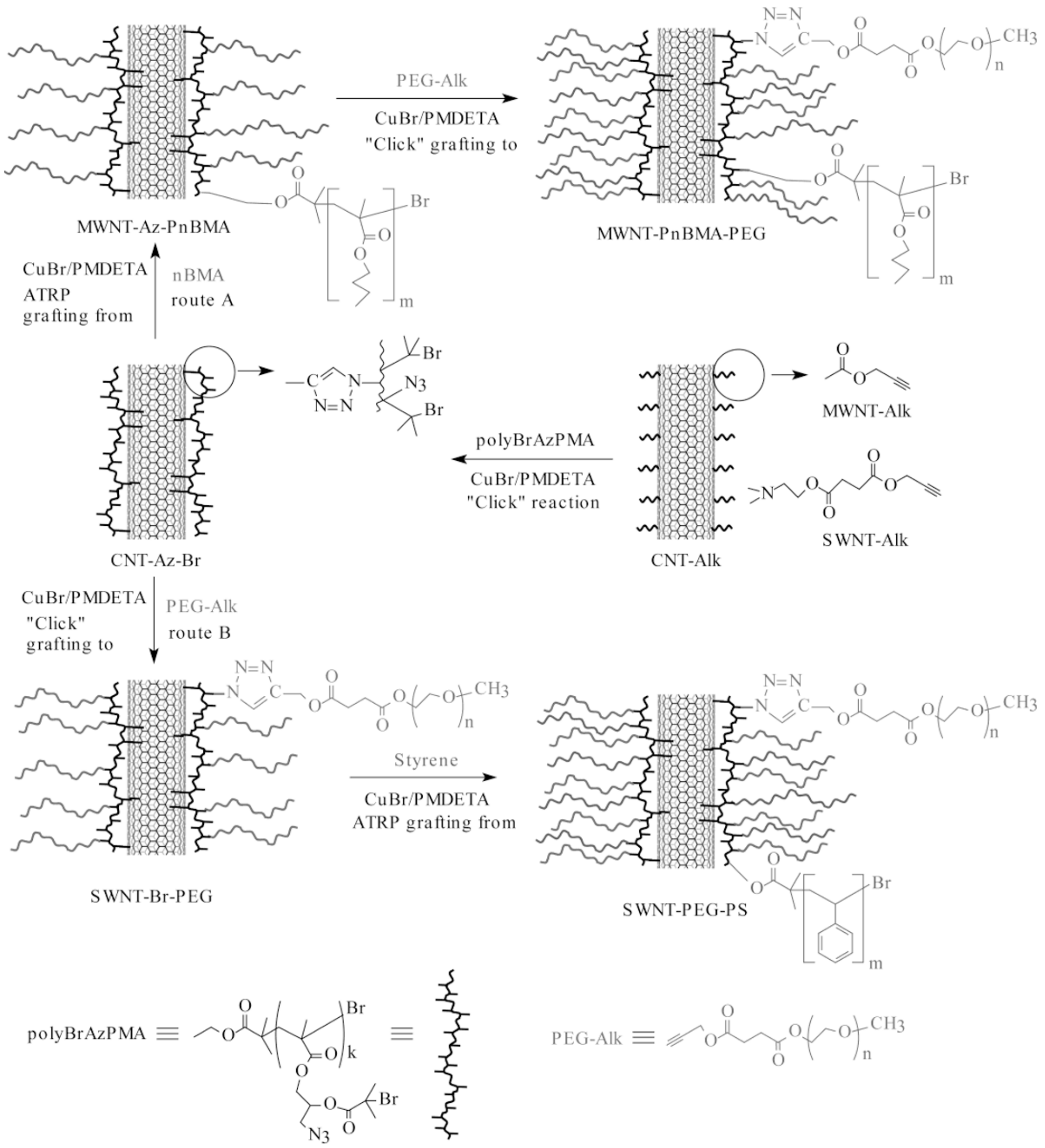
Preparation of CNTs coated with amphiphilic polymer brushes was first reported by our group by combining conventional “grafting to” and “grafting from” strategies and using a clickable macroinitiator (see Scheme 3) [34]. The clickable macroinitiator, poly (3-azido-2-(2-bromo-2-methylpropanoyloxy) propylmethacrylate) with alkyl bromo groups for initiating atom transfer radical polymerization (ATRP) and azido groups for the click reaction was first synthesized by postmodification of poly(glycidyl methacrylate) (PGMA) with sodium azide, followed by 2-bromoisobutyryl bromide. Clicking the clickable macroinitiator onto alkyne-functionalized CNTs afforded a CNT-based clickable macroinitiator. Poly (n-butyl methacrylate) (PnBMA), PS, and poly (ethylene glycol) (PEG) were subsequently grafted on CNTs via ATRP grafting from and click grafting to approaches, resulting in CNT-supported amphiphilic polymer brushes. The brushes could undergo self-assembly at the chloroform/water interface to form a special film, indicating that the brushes could form Janus structure. Such a “Gemini grafting” strategy paves the way for construction of complex structures on CNTs.

Covalent layer-by-layer (LbL) click chemistry was also introduced to functionalize CNTs (see Scheme 4) [35]. The clickable polymers of poly (2-azidoethyl methacrylate) (polyAzEMA) and poly (propargyl methacrylate) (polyPgMA) were alternately coated on alkyne-modified CNTs, forming a core-shell structure. The TEM pictures (see Fig. 3) show that the thickness of the clicked polymer shell on CNTs increases considerably with increasing layers of polymer clicked on

Table 1. Overview of click reactions on CNTs.

Clickable substrate	Clickable reagents	Catalyst/Conditions	Ref.
		CuI or $(PPh_3)_3CuBr$ /DMF/60 °C/24 h	[31]
		$CuSO_4{\cdot}5H_2O$, sodium ascorbate/ H_2O/55 °C/24 h	[33]
	 	CuBr, PMDETA/DMF/r.t./24 h	[34]
	 	CuBr, PMDETA/DMF/r.t./24 h	[35]
		$CuSO_4{\cdot}5H_2O$,sodium ascorbate/H_2O, acetonitrile/r.t.	[36]
		CuBr, PMDETA/DMF/r.t./24 h	[37]
		CuI,1,8- diazobicyclo[5.4.0]undec-7-ene (DBU) /DMF/70 °C/48 h	[38]
		$CuSO_4{\cdot}5H_2O$, sodium ascorbate/NMP/70 °C/48 h	[39]

MWCNTs and the polymer shell is uniform and even. Alkyne-modified rhodamine B was also installed on the CNTs with azide polymer layer. The confocal fluorescence image (see Fig. 4) presented a uniform red remarkable fluorescence, suggesting that there are a large number of residual azido groups on the surfaces.



Scheme 3. Synthesis of amphiphilic/Janus polymer brushes-grafted CNTs by a combination of click chemistry and ATRP approach (Reprinted with permission from ref. 34. Copyright 2008, American Chemical Society).

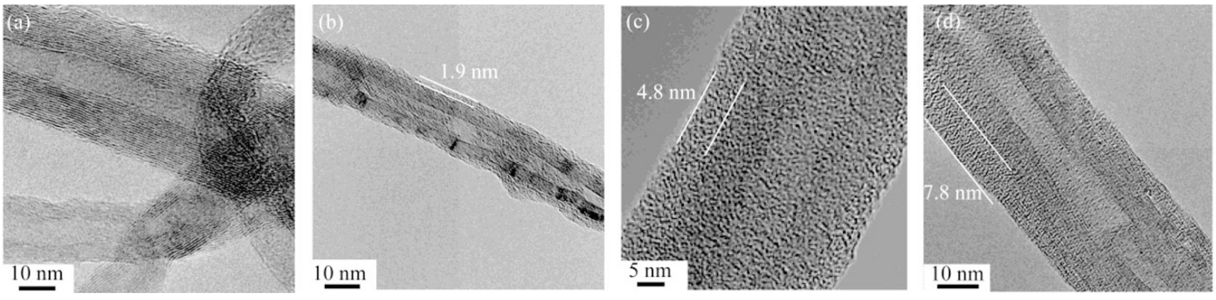
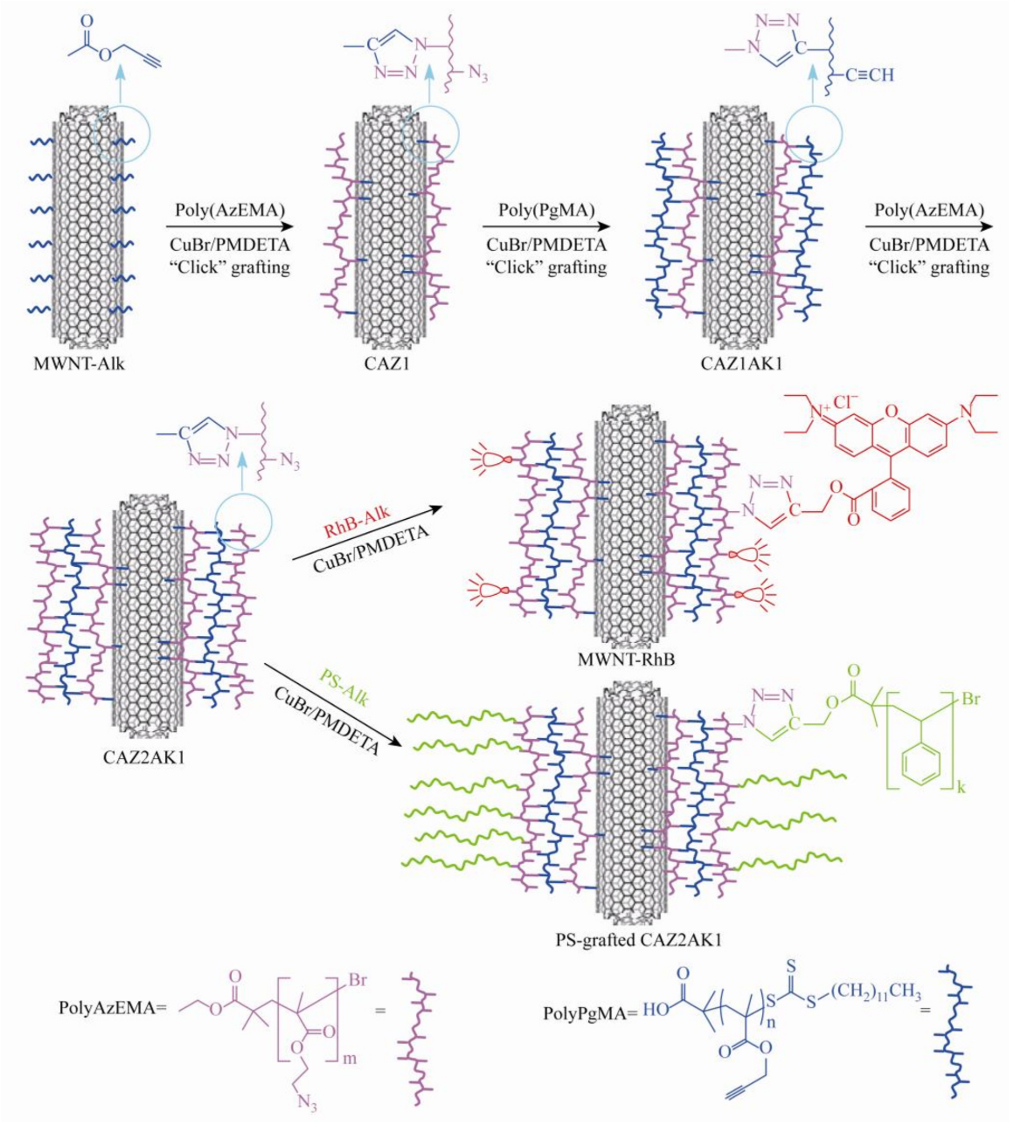


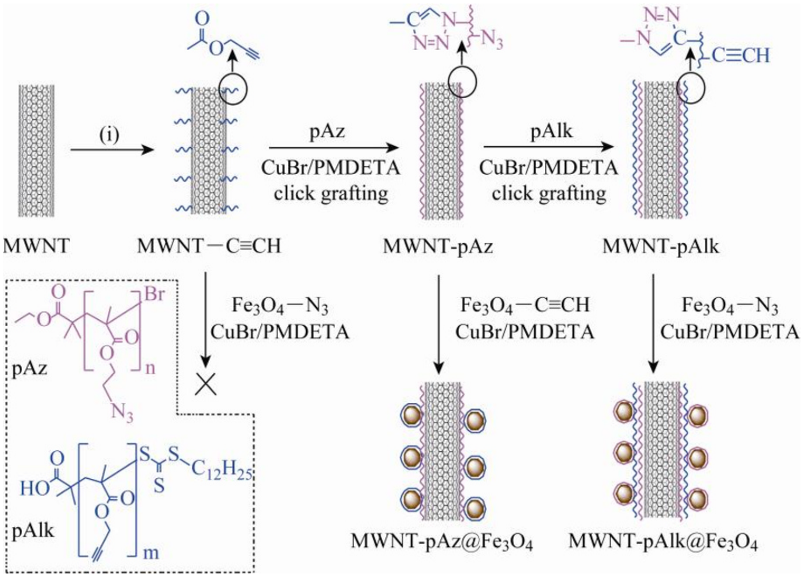
FIG. 3. Representative TEM images of pristine MWCNTs (a), CAZ1 (b), CAZ1AK1 (c) and CAZ2AK1 (d) shown in Scheme 4 (Reprinted with permission from ref. 35. Copyright 2009, American Chemical Society).

The preparation of CNT-Au nanocrystal composites was reported by Rao et al. [36]. The CNTs were first treated with concentrated HNO_3 to generate carboxyl groups on the surface, then with thionyl chloride to convert the carboxyl groups into acyl chloride, followed by reaction with 4-azidobutylamine to obtain azide-functionalized CNTs, and finally, reacted with hexynethiol-capped Au nanocrystals to afford the composites.

Gao and co-workers reported the preparation of superparamagnetic CNT-Fe_3O_4 nanohybrids (see Scheme 5) via click chemistry [37]. The direct coupling between



Scheme 4. Functionalization of MWCNTs gets through covalent LbL-click approach and further modification of the functionalized MWCNTs with fluorescent dye and polystyrene by click chemistry (Reprinted with permission from ref. 35. Copyright 2009, American Chemical Society).



Scheme 5. Preparations of CNT-Fe_3O_4 nanohybrids via click chemistry (Reprinted with permission from ref. 37. Copyright 2009, Royal Society of Chemistry).

alkyne-decorated CNTs and azide-decorated Fe_3O_4 particles failed, while the coupling reaction took place efficiently by using the CNTs coated with polymer layers. TEM images in Fig. 5 clearly showed the presence of Fe_3O_4 particles on the surfaces of

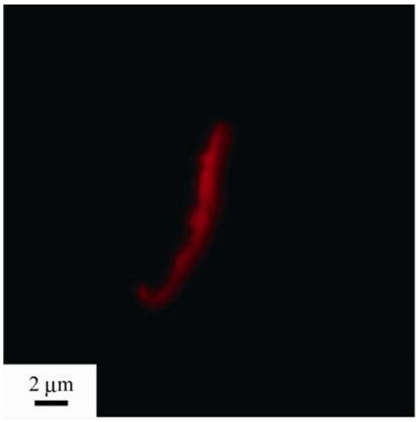


FIG. 4. Confocal fluorescence image of rhodamine B-modified CNT with azide polymer shells (Reprinted with permission from ref. 35. Copyright 2009, American Chemical Society).

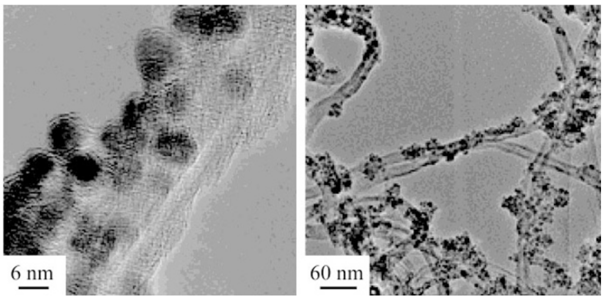


FIG. 5. TEM images of Fe_3O_4 particle-decorated CNTs via click chemistry (Reprinted with permission from ref. 37. Copyright 2009, Royal Society of Chemistry).

CNTs. This approach provides an efficient avenue to hybrid nanomaterials with tailor-made properties.

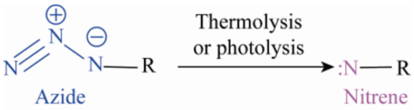
Zheng et al. anchored azide-functionalized cyclodextrins on the alkyne-functionalized CNTs following the Adronov's method to prepare a novel receptor [38]. By gradually adding the CNT receptors into the aqueous solution of quinin, the fluorescence of quinin could be gradually quenched. Campidell et al. coupled the alkyne-functionalized SWCNTs with azide-functionalized zinc-phthalocyanine (ZnPc) to afford SWCNT-ZnPc nanoconjugates [39]. By investigation on the photovoltaic properties, a photoinduced charge transfer feature was identified. Integration of the nanoconjugates into photoelectrochemical cells revealed promising photon-to-energy conversion efficiencies. The authors also tried to anchor the dendrons of zinc porphyrin (ZnP) onto the CNTs via click coupling in order to limit the disturbance on the conjugated-system of CNTs caused by covalent functionalization and studied the photophysical properties [40].

It has been demonstrated that polymers, organic functional molecules, and inorganic nanocrystals could be attached on CNTs by click chemistry, showing the versatility of click chemistry in the functionalization of CNTs.

Functionalization of CNTs via nitrene chemistry

The concept of nitrene chemistry

A nitrene (R-N :) is regarded as the nitrogen analogue of a carbene [41]. They are formed as intermediates during thermolysis or photolysis of azides with expulsion of nitrogen gas, but cannot be isolated from the reaction system due to their extremely high reactivity (see Scheme 6). The nitrogen atom has only six electrons available and is therefore considered as an electrophile. One of the well-known reactions of nitrene is cycloaddition to unsaturated bonds, affording aziridine compounds. Hence, chemists come up with the idea of functionalization of CNTs via electrophilic attack of nitrene based on the unsaturated bonds of CNT and the electrophilic nature of nitrene. The used azides and reaction conditions are summarized in Table 2.



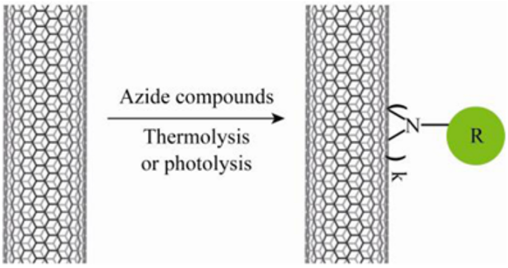
Scheme 6. Formation of nitrene intermediates from azides.

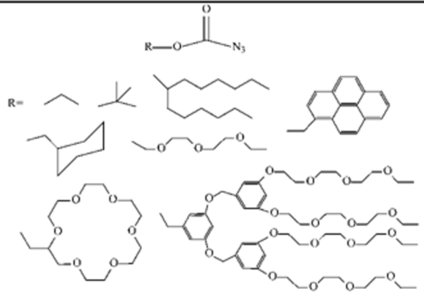
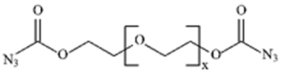
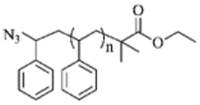
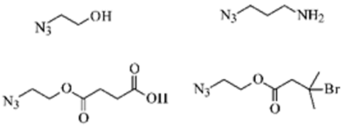
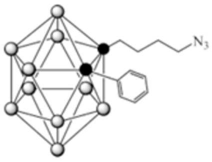
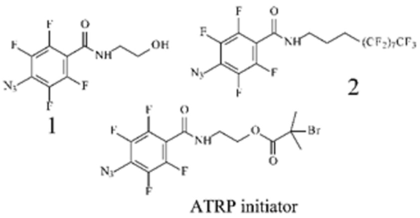
Nitrene cycloaddition functionalization of CNTs

The pioneering work for the functionalization of CNTs via nitrene chemistry was done by Holzinger et al. in 2001 [42]. Around 200-fold excess of nitrene precursor, ethyl or tert-butyl azidoformate, was added to the heated suspension of CNTs in 1, 1, 2, 2-tetrachloroethane. The reaction took place with N_2 release and after a short time the product precipitated. The precipitates were collected and washed with diethyl ether. The nitrene-functionalized CNTs could be dissolved in DMSO. In a detailed study of nitrene functionalization, a variety of nitrene precusors were employed, containing various groups, such as alkyl chains, aromatic groups, dendrimers, crown ethers, and oligoethylene glycol units [43]. When bifunctional nitrene precusors were used, cross-linked CNTs were formed which could benefit for the development of CNT-based high performance materials such as foils and fibers [44]. Ford et al. employed azido-terminated PS to directly react with CNTs at 130 °C in 1, 2-dichlorobenzene, resulting in the nanocomposites with functionalization density of 1 PS chain per 48 carbon atoms of CNTs [45].

An improved green, low cost, general and efficient one-step technology to synthesize highly dispersible functional CNTs

Table 2. Overview of nitrene cycloaddition on CNTs.



Azide reagents	Conditions	Ref.
	1,2-dichlorobenzene/130 °C/60 h	[42,43]
	1,1,2,2-tetrachloroethane/160 °C	[44]
	1,2-dichlorobenzene/130 °C/60 h	[45]
	N-methyl-2-pyrrolidinone/160 °C/18 h	[46]
	1,2-dichloro-benzene/reflux/1 week	[49]
 1 2 ATRP initiator	UV exposure/5 min	[50]

from pristine CNTs was developed by our group recently [46]. Scalable synthesis of functional azides up to hundreds of grams with various reactive groups (i.e., -OH, -NH$_2$, -COOH and –Br) was achieved at first. The azides were anchored onto the convex surfaces of CNTs via nitrene addition under a relatively mild condition in one-step without significant damage to CNTs. The typical TEM images in Fig. 6 show that MWCNTs modified with hydroxyl groups (MWCNT-OH) exhibit much better dispersibility than pristine MWCNTs, and the networks of CNTs were exfoliated as many individual nanotubes and some nanotubes were cut to shorter ones through ultrasonication and functionalization. All of the samples show no obvious surface damage or corrosion after the one-step functionalization and the smooth curve surfaces remain intact. Such a fine effect is essentially different from that of aforementioned nitric acid oxidation method which may lead to serious surface eroding or even degraded completely. The degree of functionalization could be easily controlled by varying the feed ratio of the azide compounds to CNTs. A series of reactions, such as surface polymerizations, amidation and reduction of metal ions were preformed on the functional CNTs, affording CNT-polymer and CNT-Pt nanohybrids (see Scheme 7). These reactions also

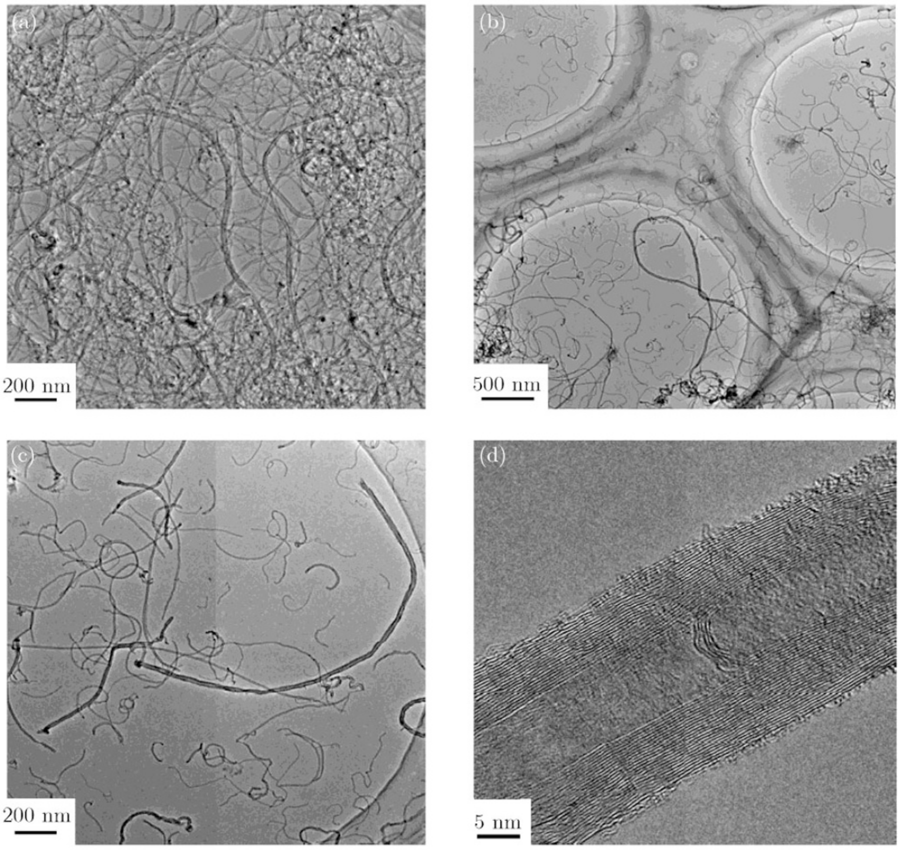
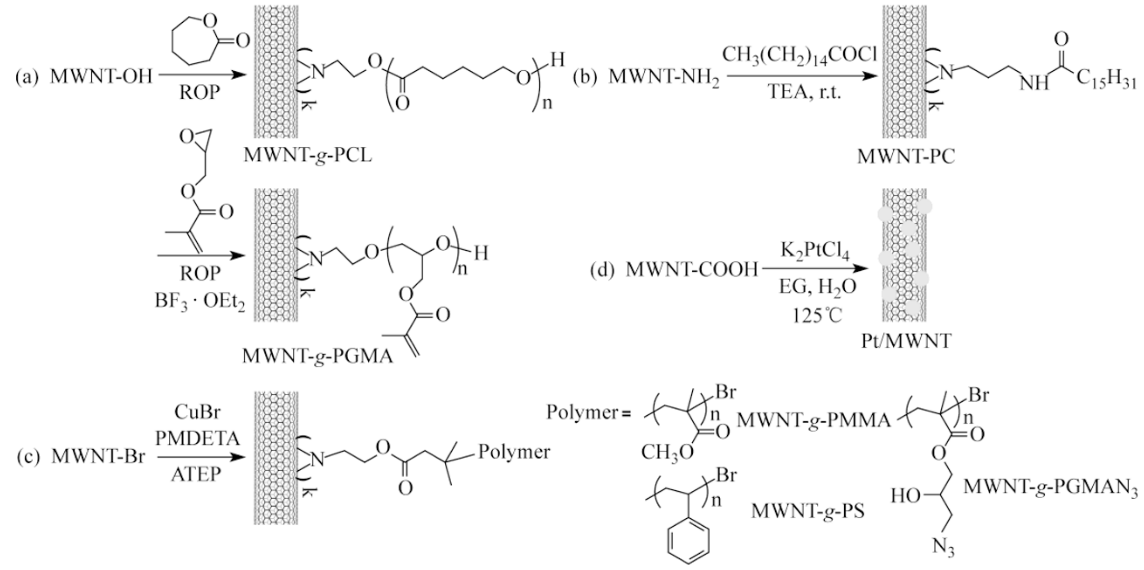


FIG. 6. Representative TEM images of pristine MWCNTs (a) and MWCNT-OH (b-d). Other functionalized MWCNTs showed similar TEM images to the MWCNT-OH (Reprinted with permission from ref. 46. Copyright 2009, American Chemical Society).



Scheme 7. Further chemical reactions on nitrene-functionalized CNTs (Reprinted with permission from ref. 46. Copyright 2009, American Chemical Society).

confirmed the reactivity of immobilized functional groups, laying the foundation for further material-design. Besides, biocompatible hyperbranched polyglycerol (HPG) was grafted from the surfaces of hydroxyl group-decorated CNTs by in situ anionic ring-opening polymerization of glycidol [47]. Fluorescent molecules of rhodamine 6B were attached to the HPG-coated CNTs by esterification to generate fluorescent CNTs. Alternatively, biomolecules such as peptides could be attached to CNTs for the purpose of targeted drug-delivery [48].

Zhu et al. prepared water-soluble carborane cage-functionalized CNTs [49]. The azide-modified C_2B_{10} cage were anchored on the CNTs via nitrene cycloaddition. By refluxing the ethanolic solution of C_2B_{10} cage-functionalized CNTs with sodium hydroxide, both the C_2B_{10} cages and the aziridine rings were transformed, affording water-soluble CNTs with nido-C_2B_9 cages and ethoxide groups on the side walls. The composites were investigated with tissue distribution experiments and found to preferentially distribute in tumor cells than in blood and other organs, suggesting that they are potential candidates as effective boron delivery nanovehicles for boron neutron capture therapy in cancer treatment. Frechet et al. prepared CNT-based forests from silicon substrates and functionalized them with perfluoroarylazides via nitrene cycloaddition by UV exposure through a photomask to create functional patterns (see Table 2) [50]. Immobilization of ATRP intiators on the forest and the following surface polymerization of N-isopropylacrylamide afforded the forest surface with PNIPAM polymer patterns. An interesting synthetic mimic to the back of the Stenocara beetle of the Namib desert, a stable micropatterned superhydrophilic-superhydrophobic surface, was also prepared in two steps: (1). blanket modification with molecule **1** to generate superhydrophilic surfaces; (2). reaction with molecule **2** by UV exposure through a photomask to reverse the superhydrophilic nature of the exposed region to the superhydrophobic nature and keep the unexposed region without change.

Therefore, linear and dendritic polymers, inorganic molecules, and organic functional molecules can be bonded to CNTs via nitrene chemistry, displaying the high efficiency of nitrene chemistry in the preparation of functional CNTs. The greatest advantage of nitrene chemistry over click chemistry lies in that pristine CNTs can be directly used as materials for nitrene coupling whereas pre-modification of CNTs is generally needed for click chemistry functionalization.

Functionalization of fullerene and graphene via azide chemistry

Except CNTs, functionalizations of fullerene and graphene have also attracted increasing attention for both scientists and engineers. Functionalization of the two allotropes of CNTs via azide chemistry has been demonstrated as a powerful way to form new functional materials and similarly, it falls into two sections: click chemistry and nitrene chemistry.

Functionalization of fullerene via click chemistry

Functionalization of fullerene via click chemistry was carried out in recent years. Generally, azide or alkyne groups have to be first installed on the fullerenes, and then other functional molecules are introduced via click coupling. For instance, Nierengarten et al. reported the introduction of azide groups via Bingel reaction to prepare a T_h-symmetrical C-60 hexakis-adduct and the modification of the adduction with various alkyne-containing compounds (see Scheme 8) [51]. Giordani et al. anchored 4-(trimethylsilylethynyl)aniline onto multilayer fullerenes via Pschorr-type arylation and coupled them with the azide-decorated zinc porphyrin after eliminating the trimethylsilyl group using tetra-n-butylammonium fluoride (see Scheme 9) [52].

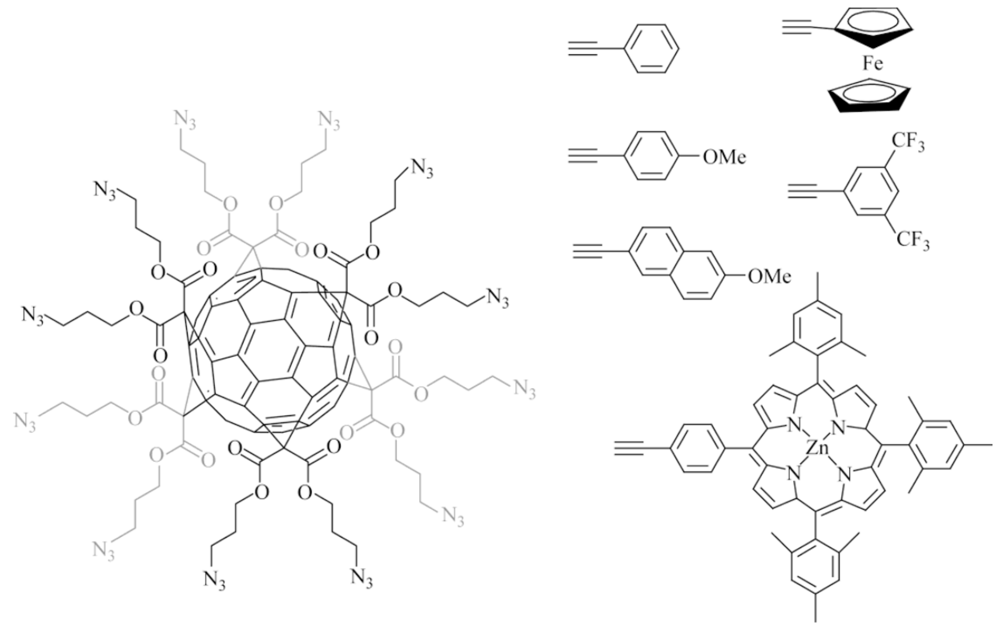
Functionalization of fullerene via nitrene chemistry

The research on modification of fullerene via nitrene chemistry was initiated in 1993. Prato et al. refluxed an equimolar solution of C-60 and (trimethylsilyl)-ethoxylmethyl azide in chlorobenzene to prepare functional C-60 (see Scheme 10(a)) [53]. This type of modification via nitrene cycloaddition has a great advantage that mainly monoaddition occurs and thus there is relatively little crosslinking which is often brought by the multifunctional nature of C-60 [54]. In the following years, various functional molecules were incorporated onto C-60 in this way, such as oligosaccharides and metal-oligopyridine complexes, and photo-induced cycloaddition method was also developed. In 1994, Hawker reported the synthesis of C-60 pendent PS via nitrene addition, which initiated the research on preparation of C-60-polymer naoncomposites via nitrene chemistry (see Scheme 10(b)) [55]. C-60 was then combined with many kinds of polymers, such as polyether [56], poly (acrylic acid) [57], poly (p-phenylene vinylene) [58], polyferrocenylsilane [59] and so on. Preparations of the polymer composites with various structures, like star [56], palmtree [60], miktoarm [61], and end-cap [56,57], were reported.

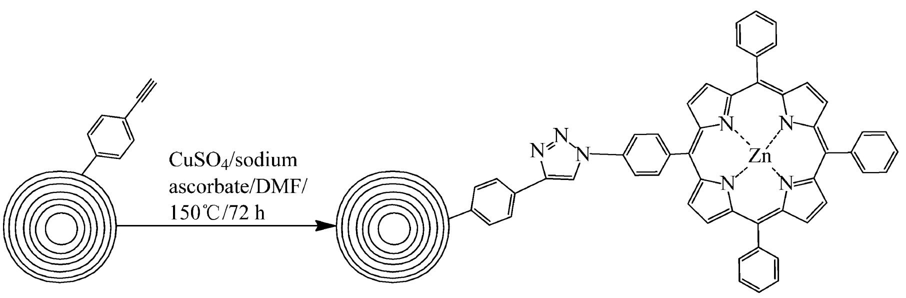
Recently, our group developed a facile technology to synthesize functional multilayer fullerenes (alternative name, carbon nano-onions, CNOs) in large-scale (see Scheme 11) [62]. In situ ring-opening polymerization (ROP) of ε-caprolactone and ATRP of styrene were successfully carried out with CNO-OH and CNO-Br as initiators, respectively.

Preliminary functionalization of graphene via azide chemistry

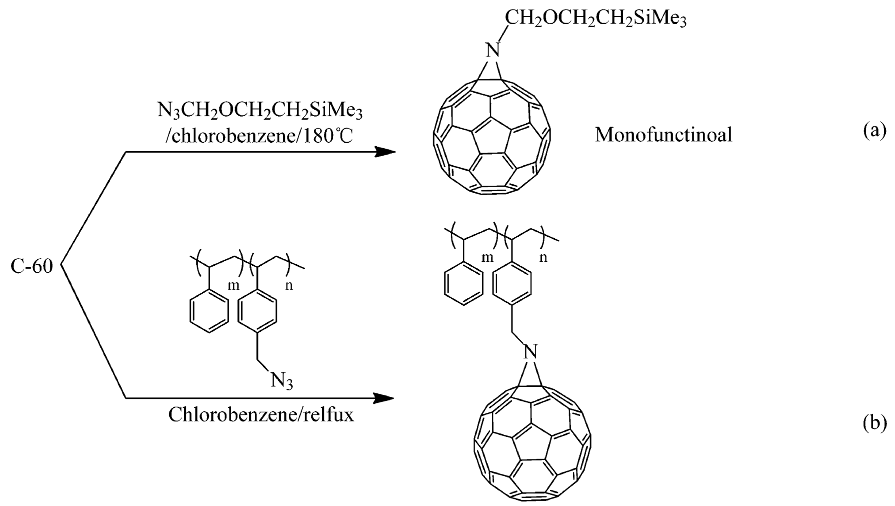
Graphene, as an emerging 2D nanomaterial, is very attractive due to its unique attributes [63,64]. Researches on its functionalization via azide chemistry have been explored recently. For example, Choi et al. modified graphene with azidotrimethylsilane via nitrene addition [65]. Our group developed a general approach to functionalize graphene nanosheets by nitrene chemistry from oxidized grapheme (see Fig. 7). Desired functional groups (e.g., -OH, -NH_2, -COOH, -Br, etc.), alkyl chains, and polymers could be covalently and stably linked on graphene sheets. Significantly, the nitrene



Scheme 8. Modification of C-60 via click chemistry. Reprinted with permission from ref. 51. Copyright 2008, Royal Society of Chemistry.



Scheme 9. Modification of multilayer fullerenes via click chemistry (Reprinted with permission from ref. 52. Copyright 2010, American Chemical Society).

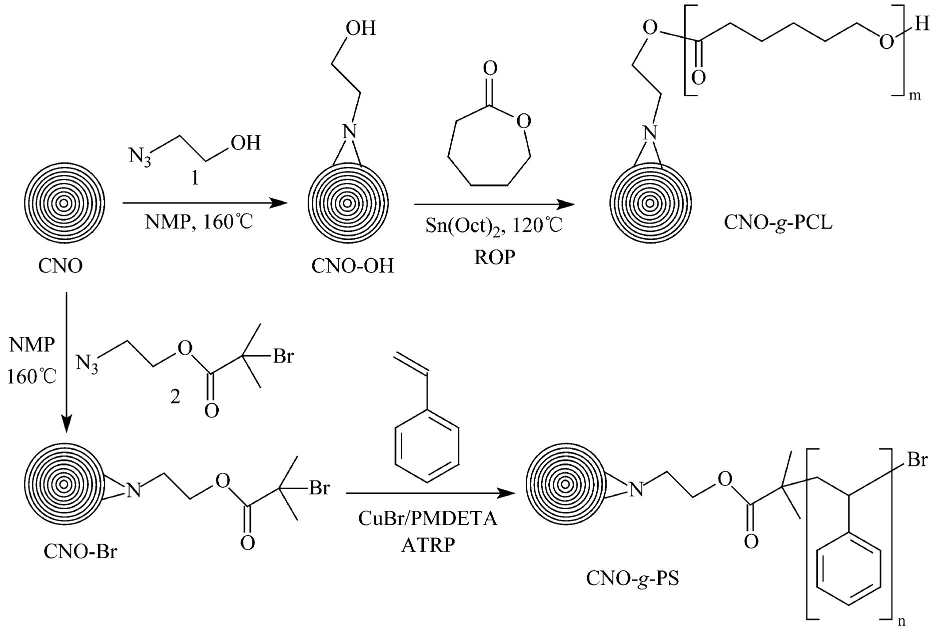


Scheme 10. Modification of fullerene via nitrene chemistry [53, 55].

-functionalized graphene sheets are still individually dispersed and highly conductive, opening the door for fabrication of multifunctional high-performance composites [66]. Our group also explored the functionalization of oxidized graphene nanosheets (OGNs) by click chemistry, allowing that various amino acids and polymers, such as PEG and PS, can be attached to OGNs [67]. Now the chemistry of graphene and OGNs is calling chemists for more devotion to exploit this new mine.

Conclusions and outlook

Azide chemistry, including click chemisty and nitrene chemistry, has been demonstrated as a highly efficient, modular



Scheme 11. Facile functionalization of CNOs by direct nitrene cycloaddition to prepare hydroxyl CNOs (CNO-OH) and bromic CNOs (CNO-Br), and grafting polymer from the functional CNOs by in situ ring-opening polymerization (ROP) of ε-caprolactone and ATRP of styrene (Reprinted with permission from ref. 62. Copyright 2009, Wiley).

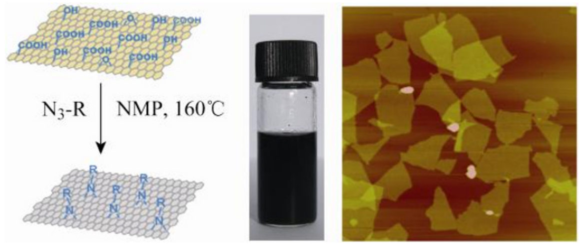


FIG. 7. Functionalization of graphene via nitrene chemistry under mild condition: scheme of functionalization reaction of graphene via nitrene chemistry (left), homogeneous and stable solution of functionalized graphene in chloroform (center) and AFM image of functionalized graphene (right) [66].

approach to functionalize carbon nanomaterials. The one-step nitrene chemistry methodology has pushed the experimental functionalization towards large-scale production. The strategies, such as "grafting to", "grafting from", their combination and layer-by-layer coating, are all available for preparing complex sturctures. Azide chemistry provides unlimited resources for the advance of these carbon-based nanomaterials, which probably initiates the revolution of new materials, energy and techniques.

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