Tuning the Multifunctional Surface Chemistry of Reduced Graphene Oxide via Combined Elemental Doping and Chemical Modifications

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Supporting Information

ABSTRACT: The synthesis of graphene materials with multiple surface chemistries and functionalities is critical for further improving their properties and broadening their emerging applications. We present a simple chemical approach to obtain bulk quantities of multifunctionalized reduced graphene oxide (rGO) that combines chemical doping and functionalization using the thiol-ene click reaction. Controllable modulation of chemical multifunctionality was achieved by simultaneous nitrogen doping and gradual chemical reduction of graphene oxide (GO) using ammonia and hydrazine, followed by covalent attachment of amino-terminated thiol molecules using the thiol-ene click reaction. A series of N-doped rGO (N-rGO) precursors with different levels of oxygen groups were synthesized by adjusting the amount of reducing agent (hydrazine), followed by subsequent covalent attachment of cysteamine via the thermal thiol-ene click reaction to yield different ratios of mixed functional groups including N (pyrrolic N, graphitic N, and aminic N), S (thioether S, thiophene S, and S oxides), and O (hydroxyl O, carbonyl O, and carboxyl O) on the reduced GO surface. Detailed XPS analysis confirmed the disappearance of unstable pyridinic N in cysteamine-modified rGO and the reduction degree threshold of N-rGO for effective cysteamine modification to take place. Our study establishes a strong correlation between different reduction degrees of N-rGO with several existing oxygen functional groups and addition of new tunable functionalities including covalently attached nitrogen (amino) and sulfur (C−S, C=S, and S=O). This simple and versatile approach provides a valuable contribution for practical designing and synthesis of a broad range of functionalized graphene materials with tailorable functionalities, doping levels, and interfacial properties for potential applications such as polymer composites, supercapacitors, electrocatalysis, adsorption, and sensors.

1. INTRODUCTION

Graphene has sparked tremendous research interest over the last two decades owing to its unique 2D structure, high surface area, extraordinary electron mobility, notable mechanical strength, thermal conductivity, and structural and optical properties in a diverse range of applications across industrial sectors including composites, supercapacitors, batteries, fuel cells, inks, protective and functional coatings. Many of these applications require specific chemical functionalizations of graphene to achieve its integration with other materials, which are different in nature including polymers, organic molecules, biomolecules, metals, semiconductors, nanoparticles, or other 2D materials. Chemical functionalization of graphene powder materials is particularly needed to make stable graphene-water dispersions for improved processability to achieve better incorporation of these materials for engineering new functional and hybrid materials needed for broad applications.

Many functionalization strategies of graphene have been explored over the last two decades based on covalent or noncovalent chemical binding of organic molecules and functional groups containing oxygen (i.e., graphene oxide), nitrogen (amino), sulfur (mercapto), fluorine, or hydrogen to the carbon atoms. These methods are mostly inherited from the developments of “older” carbon nanoflavors such as fullerenes and carbon nanotubes that have paved the way for the functionalization of graphene and its derivatives today. Graphene oxide (GO), prepared from the oxidation and exfoliation of graphite in the presence of strong acids and oxidants, is one of the most popular forms of chemically (oxygen) functionalized graphene used not only as an important precursor to convert the intermediate, reduced
GO (rGO), into produce bulk graphene but also for other applications such as membranes, sensors, and composites. GO addresses some inherent disadvantages of pristine graphene such as high hydrophobicity, chemical inertness, and a lack of dispersibility in water. However, GO also has some drawbacks such as low conductivity and amorphous structure, which hinder its broader applications. Hence, a balance is required between the desirable properties of both GO and graphene to harness the benefits of both materials. Controllable reduction and chemical functionalization are considered as a rational approach in achieving these requirements is needed for many applications.

Chemical functionalization of graphene bulk materials can significantly lead to the generation of a new type of graphene-based materials, which facilitates the unprecedented properties of graphene with other compound classes. Among many explored reactions, the thiol-ene click route based on the targeted attack on the sp² carbon using thiol radicals generated by the action of either heat or light appears to be one of the most efficient and promising strategies to achieve these tasks. The assimilation of graphene with the thiol-ene click reaction has recently gained remarkable attention in advanced macro-molecular engineering and materials chemistry given the attributes that this approach is highly efficient, versatile, simple, catalyst-free, and proceeds in benign solvents under mild reaction conditions in addition to the high yield conversion.

On the other hand, elemental doping of graphene with selected elements (with N, S, B, and P) has been recognized as a desirable approach for controlling the band gap and tailoring the electrical and electron transport properties, as well as electrocatalytic performances, of graphene. This approach offers a unique way to extend the limited zero band-gap energies of graphene by the hybridization of electronic orbitals from sp² to sp³ and opening large band gaps (>4 eV), which are important for many applications. Numerous strategies were reported for individual (N) or co-doping (N and S) to insert the dual atoms simultaneously into the carbon network using gaseous, hydrothermal, and solvothermal processes with different precursors such as ammonia, thiophene, l-cysteine, hydrazine, ammonium thiocyanate, etc. These hybrid materials are used as catalysts to enhance the electrocatalytic oxygen reduction, as the anode material to improve the adsorption capability of sodium ions in sodium-ion batteries, and as metal-free cathode catalysts for the application in direct biorenewable alcohol fuel cells. However, there are still limited studies on combining these two concepts to target the heteroatom insertion in the graphene lattice with surface functionalization, which can be regarded as a highly valuable approach for engineering of a broad range of bulk graphene hybrid materials needed for many emerging applications.

The aim of this study was to demonstrate the combination of simultaneous binary-heteroatom doping and click chemistry to create bulk multifunctional graphene materials with tunable surface chemistry for more diverse electronic, sensing, catalytic, and adsorption properties and applications following our previous study, which showed promising performance for water remediation by applying multifunctional graphene composites synthesized via the thiol-ene click reaction. In this work, the controllable modulation of chemical multifunctionality is proposed by consequent elemental doping and gradual chemical reduction of GO using ammonia and hydrazine followed by covalent attachment of aminoterminated thiol molecules (cysteamine) via the thermal thiol-ene click reaction, which has not been addressed previously. Our primary focus is targeted on the fundamental understanding of the changes in the surface property to identify the chemical species (functional groups) of the thiol-ene-clicked graphene composites using reduced graphene oxide (rGO) with varied oxidation levels. The formation of the resulting derivative of nitrogen-doped and cysteamine-functionalized reduced graphene oxide (cys-N-rGO) with varying levels and configurations of oxygen, nitrogen, and sulfur atoms within the graphene framework was confirmed by a series of characterization techniques including UV−vis, Raman, XRD, TGA−DTA, FTIR, and XPS analyses. Results from this study underpin the fundamental mastery of controllable functionalization to tailor the properties of graphene and its derivatives using the combination of simultaneous binary-heteroatom doping and click chemistry, which is needed for a broad range of applications.

2. RESULTS AND DISCUSSION

2.1. Simultaneous Nitrogen Doping and Gradual Chemical Reduction of GO. In the first experiment, synthesis of N-doped reduced graphene oxide with a controllable level of oxygen functional groups was performed by simultaneous doping and chemical reduction of GO using ammonia and hydrazine (details of synthesis conditions are included in Table S1, Supporting Information). A series of characterization results including TEM, SEM, and XPS are summarized in Figure 1 and Table S2 to confirm the structural, elemental, and chemical compositions of the prepared N-doped rGO precursors. Figure 1A presents the SEM and TEM images of the typical structure of GO sheets with sizes in the nanometer range and thickness of a few graphene layers, which are used for the entire experiments. The wrinkled and fairly smooth surface of GO can be clearly observed from its SEM imaging.

Figure 1. (A) FESEM image with the inset displaying the TEM image of exfoliated GO nanosheets used for the synthesis of N-doped rGO precursors. Plots of (B) XPS survey spectra with characteristic C 1s, O 1s, and N 1s peaks; high-resolution XPS of (C) C 1s scan and (D) N 1s scan with background subtracted; (E) C/O atomic ratios, and (F) C/N atomic ratios for GO, N-GO, and N-rGO precursors (low, mild, and high).

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image, whereas the ultrathin stacked GO layers can be seen from the TEM image as incorporated in the inset of Figure 1A.

Figure 1B shows a series of survey XPS spectra recorded from GO (control), N-doped GO (N-GO), and N-doped rGO (N-rGO) with different levels of reduction (low, mild, and high) showing characteristic C 1s, O 1s, and N 1s peaks detected at ~285, ~532, and ~400 eV, respectively, indicating the presence of carbon, oxygen, and nitrogen on the surface of N-doped precursors. A series of individual high-resolution peaks showing carbon, nitrogen, and oxygen peaks for all prepared N-GO and N-rGO precursors to confirm their chemical functionalities are depicted in Figures 1C,D and S1, respectively. These spectra clearly demonstrated changes of the peak intensity as a result of the reduction in oxygen functionalities and the increased N-doping effect after treatment with ammonia and hydrazine. Normalized atomic percentages of C, O, and N calculated from the area of the survey spectra under C 1s, O 1s, and N 1s peaks, respectively, and their aspect ratios are summarized in Table S2 and Figure 1E and F, correspondingly. The XPS results showed that the highest amount of oxygen was found in control GO, with nearly 32% of oxygen detected. As expected, the atomic percentage of oxygen was slightly reduced to ~31% for N-GO and progressively to ~20% for the N-rGO precursor with the highest reduction degree as the amount of hydrazine and reduction time increased. The carbon-to-oxygen (C/O) atomic ratio determined from the XPS survey scans (Figure 1E) confirmed these changes in reduction, showing a gradual increase in the value (2.13, which is typical for GO) to 2.21 (N-GO), 2.52 (low N-rGO), 2.84 (mild N-rGO), and 3.80 (high N-rGO), which verified the gradual reduction of GO. From the literature, it is reported that upon reduction, the C/O atomic ratio can increase to 12 for highly reduced GO, depending on the type and amount of the reducing agent and the reduction conditions used. However, the primary goal in this work was having a series of rGO precursors with different levels of oxygen functional groups (C/O atomic ratio between 2 and 4), which suited the next functionalization step to attach thiol organic molecules with amino functional groups.

In addition to the decreased oxygen level, the use of hydrazine treatment with ammonia on GO provides simultaneous N-doping by the integration of nitrogen atoms into the graphene network, while ammonia can also be used to change the charge state of rGO sheets, preventing the agglomeration of graphene sheets upon reduction. The doping of N in the graphene network is confirmed from the XPS survey spectra and reflected by the progressive increase of N concentrations (Table S2) and surface-carbon-to-nitrogen (C/N) atomic ratio, as illustrated in Figure 1F. Contrary to the increasing trend of the C/O atomic ratio, the C/N atomic ratio of rGO precursors was pronouncedly decreased from the control to N-rGO of high reduction degree, implying the growing amount of N incorporated into the rGO network as the reduction degree increased. By adjusting the amount of hydrazine and reduction time progressively, the atomic percentage of O was found to decrease visibly, whereas that of N was increased simultaneously. This finding suggests that the elemental compositions of O and N on GO can be easily dictated by varying the amount of hydrazine and reduction time.

Further peak fitting analysis of the high-resolution XPS scans of C 1s, O 1s, and N 1s was carried out to determine the chemical environment and species present on the surface of GO, N-GO, and N-rGOS. To ensure that the peak fitting outcomes remain mathematically and chemically realistic, we prudently fitted and deconvoluted the high-resolution C 1s peaks into two main components (nonoxygenated and oxygenated carbon) after imposing parameter constraints as mentioned in the characterization section on their respective position and full width at half-maximum (fwhm) of the components. The nonoxygenated C components include C−C (sp3 C, ~285 eV), C==C (sp2 C, ~284.6 eV), C−N (~285.7 eV), and C−S (~285.2 eV), while the oxygenated C components consist of C−O−C (epoxide, ~287.2 eV), C−OH (hydroxyl, ~286.6 eV), C=C (carbonyl, ~288.1 eV), and HO−C==O (carboxyl, ~289.0 eV). It is noteworthy that the component assignments are conforming to the reported literature, despite that some slight shifts in terms of the position of the components were observed after the reduction treatment. The peak deconvolution studies of high-resolution C 1s spectra of GO (Figure S2A), N-GO, and N-rGO are displayed in Figure 2A−D. Control GO and N-doped GO (N-GO) showed typical characteristics of C 1s species for GO with strongly oxidized surface and oxygenated functional groups predominantly made up of epoxides (C−O−C), carboxyls (HO−C==O), carbonyls (C==O), and hydroxyls (C−OH). A higher peak intensity exhibited by C−O−C (287 eV) relative to C−C (285 eV) is an indication of an ordinary well-oxidized GO decorated with a plethora of oxygen functional groups under a harsh oxidation process. The deconvoluted C 1s spectra of other rGOS with low, mild, and high reduction degrees showed the same oxygen-containing groups, however with weaker peak intensities, clearly demonstrating a gradual reduction of oxygen groups. For low and mild N-rGOS (Figure 2B and C), the spectra show similar peaks of carbon species C−O−C (287 eV) and the C−C peak (285 eV) with the only difference that peak intensities are decreased. However, for high N-rGO, its spectrum (Figure 2D) exhibits relatively weak C−O−C (287 eV) than C−C (285 eV) peaks, revealing the formation of a highly reduced graphene structure, which is in agreement with the previous reports. In agreement with the C 1s narrow-scan analysis, the O 1s XPS plots of all of these samples characterized by their respective binding energies also indicated the formation of different oxygen-containing groups including quinone, aromatic C==O, aliphatic C−O, and aromatic C−O, which are detailed in Figures S2B (GO) and S3 (N-GO and N-rGOS). On the other hand, a very intense C==O peak (284 eV) is
observed for these materials with the product of the degree of graphene reduction, as illustrated in Figure 2D.

The high-resolution and peak deconvolution studies of N 1s spectra positioned at around 401 eV for N-GO and N-rGO are presented in Figure 2E–H. These results obviously indicate a considerable buildup of nitrogen species in all of the hydrazine-reduced graphene oxide. It could be seen that N-GO low and mild N-rGOs could be resolved into three different nitrogen-bonding configurations within the graphene lattice including pyridinic N (bonded to sp² C in a hexagonal configuration) at around 398.1−399.5 eV, pyrrolic N (bonded to sp² C in a pentagonal configuration) at 399.8−401.2 eV, and quaternary or graphitic N, which is sp³-hybridized found at 401.2−402.7 eV, as depicted in Figure 2E−H.24 According to Park et al., the peak at around 400 eV can be allotted to pyrazinic groups (non-aromatic 5-membered rings), which can be further resolved into two N 1s peaks at 398.6 and 400.5 eV representing two N atoms in different chemical environments, as illustrated in Figure 2E−H.11 Interestingly, the high N-rGOs exhibited dissimilar chemical N environments with their corresponding narrow peaks deconvoluted into pyridinic N at 399.3 eV, pyrrolic N at 400.6 eV, and N-oxides of pyridinic nitrogen at around 403 eV.25 The N-oxides detected in high N-rGO are commonly attached to nitrogen-containing dangling bonds or physisorbed species, which is concordant with the findings in the reported literature.7,33 As proposed by Stankovich et al., hydrazine is well known to feasibly ring-open epoxides and form hydrazine alcohols. Although the chemical environment of N species was not resolved in their work, the significant nitrogen incorporation in the graphene network further rendered the intriguing query on how the mechanism of deoxygenation and re-establishment of the graphene conjugated network can take place via hydrazine treatment. The mechanism of simultaneous deoxygenation and insertion of N in the graphene structure still remains an open question.31 In the work conducted by Park et al., hydrazine treatment of GO was proven to insert an aromatic nitrogen moiety in a 5-membered ring at the platelet edges of graphene, and the aromaticity of the pyrazole moiety can enhance electron conduction in the rGO due to the reduced band gap and localized electronic states of the sp² configuration of N.

They also proposed that hydrazine-reduced/substituted graphene oxide is a more precise description for GO treated by hydrazine due to the doped N in the graphene structure.12 Meanwhile, it was reported that hydrazine also resulted in nitrogen doping, evidenced by the XPS technique with about 2.86 at % nitrogen content detected as well as resolved pyridinic N, pyrrolic N, and graphitic N discovered in the graphene structure, demonstrating the excellent capacity stability and improved cyclic performance in lithium-sulfur batteries.34 Xie et al. found that graphene designed with high percentages of doped pyridinic N and pyridone N (6.8−8 at % of total nitrogen content) can be achieved by the combination of ammonia and hydrazine under hydrothermal treatment, which enhanced the capacitance and cycling performance for electrochemical applications.33 Based on the literature references and the detailed XPS analysis of high-resolution C 1s, N 1s, and O 1s in the present study, a series of N-doped rGOs with varying oxygen levels can be simply prepared using the chemical reduction approach, and the chemical structure of the obtained N-doped precursors is schematically proposed in Figure 2I and J. It should be highlighted that hydrazine exhibits dual roles as a reductant and an N-dopant for graphene oxide, which enables simultaneous N-doping and GO reduction to achieve rGO with different functionalities including several types of N groups (pyridinic, pyrrolic, and graphitic N) combined with different levels of O groups (quione, aliphatic, and aromatic O).33,34

To further verify these observations and the proposed chemical structure of the prepared precursors, XRD, UV–vis, FTIR, Raman, and DTA analyses were carried out and are presented in Figure 3. XRD patterns in Figure 3A reveal the characteristic peaks for GO (2θ = 10.78°) and N-GO (2θ = 10.76°), which were found to progressively reduce and disappear in all of the prepared N-rGOs. A new broad peak at around 2θ = 24° was observed for low-reduction-degree N-rGO, indicating the re-establishment of the conjugated rGO network, which could be attributed to the elimination of the oxygen-containing groups intercalated between the GO layers after the reduction reaction.35,36 Meanwhile, a weak peak at...
around 2θ ~ 43° was also found for high-reduction-degree N-rGO, which could be associated with the turbostratic band of the disordered carbon materials.37 The obvious peak shift observed in the XRD patterns of GO and N-rGO from approximately 11 to 24° further affirmed the presence of different reduction degrees of the N-rGOs due to varied oxygen contents and doped N that resulted after the chemical reduction treatment, as evidenced by the XPS analysis discussed previously.

The reduction degree of the N-rGO precursors was also confirmed by the UV–vis technique, and their respective UV–vis spectra are illustrated in Figure 3B, which all show a single absorption peak attributed to the π→π* transition of a C≡C bond in the aromatic carbon. The strong absorption plasmon peak recorded for the N-GO at 227 nm is found to be almost similar to that for GO at 230 nm, suggesting that oxygen groups were not significantly reduced by the ammonia treatment. On the other hand, different reduction degrees of N-rGOs exhibited significant variations in their absorption maxima, which can also be visibly recognized by the color of their dispersions (Figure S4, Supporting Information). In Figure 3B, the absorption maximum has progressively shifted to the right, moving from GO to N-rGO of high reduction degree. The red-shifted spectra to a longer wavelength indicated that there is a gradual increase in the structural features and defects formed during the doping and restoration of sp2 carbon in the graphene network.38,39 The obvious peak shift using a large amount of hydrazine for a prolonged reaction time. This finding is consistent with the previous studies, where hydrazine is effective in removing in-plane oxygen functional groups such as epoxy and hydroxyls, leaving the edge moieties such as carboxyls and carbonyls on GO.39,40 The declining peak intensity particularly for OH and C–O–C groups on rGO precursors clearly manifested that N-rGO precursors with gradual removal of oxygen groups were effectively created, in good agreement with the outcomes from the C/O atomic ratio determined using the XPS technique.

The thermal stabilities of GO, N-GO, and N-rGO samples were evaluated by both TGA and differential thermogravimetric (DTA) analyses (Figures S5 and 3D, respectively). Overall, it could be detected that all N-rGOS exhibited higher thermal stability relative to GO, which reflects the success of the reduction process of GO and the chemical reduction via the removal of attached oxygen functional groups by hydrazine. The calculated derivative mass change at ~200 °C (from 1.057 to 0.052 wt %/°C for GO control to N-rGO with the highest reduction degree) displayed in the DTA plots (Figure 3D) verified that the oxygen moieties were removed progressively by controlled chemical reduction using hydrazine. This peak can be ascribed to the decomposition of labile oxygen-containing functional groups, such as hydroxyl (–OH), epoxy [–CH (O) CH–], and carboxyl (–COOH) groups, between the layers of GO nanosheets.32 This finding demonstrates that the effective stepwise oxygen reduction degree was introduced into the N-rGO, which correlates well with the XPS elemental composition, UV–vis, FTIR, and XRD results discussed in the previous section. More details on the mass-loss events are provided in Figure S5, Supporting Information.

Finally, Raman spectra (Figure 3E) of GO, N-GO, and N-rGO with different reduction degrees were recorded to confirm the structural features and defects formed during the doping and chemical reduction processes. Two apparent peaks at approximately 1344 and 1591 cm−1 corresponding to the D and G bands, respectively, are observed, in which the D band

Figure 4. (A) Plots of XPS survey spectra with characteristic C 1s, O 1s, and N 1s peaks and high-resolution XPS of (B) C 1s scan, (C) N 1s scan, and (D) S 2p with background subtracted and their corresponding C/O, C/N, and C/S atomic ratios before and after cysteamine functionalization of N-GO and N-rGOS.
arises due to the breathing mode of aromatic rings, which requires a defect for its activation, whereas the G band can be related to the bond stretching of sp² carbon pairs in both rings and chains. The intensity ratio of the D to G bands, $I_D/I_G$ (measure for the degree of disorder), as illustrated in the inset of Figure 3E, shows that the $I_D/I_G$ ratio increases gradually from control GO to N-rGO with the highest reduction degree. The steady rise of $I_D/I_G$ values strongly reflects that defects were created in the reduced samples due to the removal of oxygen groups and doping of nitrogen atoms during the reduction of GO using hydrazine. This finding shows that the amount of defect sites present in the N-rGO precursors of different reduction degrees can be effectively controlled via the amount of hydrazine and reaction time used.

2.2. Chemical Functionalization of N-rGO via the Thermal Thiol-ene Click Reaction. In the second step, we performed further chemical functionalization on N-doped GO and N-rGO with different levels of reduction using aminoterminated thiol (cysteamine) via thiol-ene click chemistry to demonstrate the synthesis of graphene with a broad range of multifunctionalities, which includes doped nitrogen, oxygen, amino, and sulfur functional groups. A series of characterization methods were used again including XPS, XRD, FTIR, TGA–DTA, and Raman analyses to confirm the structural and chemical composition changes.

The XPS survey spectra of click-chemistry cysteamine-functionalized N-rGOs (cyst-N-rGO) are shown in Figure 4A, and the corresponding peaks of C 1s, O 1s, N 1s, and S 2p located at ~285, ~400, and ~164 eV, respectively (Figure 4B–D), clearly indicate the successful incorporation of new nitrogen and sulfur species into the rGO framework. The atomic concentrations of all the cysteamine-functionalized N-GO and N-rGOs are tabulated in Table S3, and the elemental ratios of C/O, C/N, and C/S were also calculated to determine the chemical composition of cyst-N-rGOs after the covalent attachment of cysteamine, which are depicted in Figure 4B–D. These figures and ratio numbers indicate that the C/O ratio of cyst-N-rGOs increases when compared to that of their respective N-rGO intermediates. It should be noted that the C/O atomic ratio of cyst-N-rGOs was found to be in the range of 3.50–6.17 compared to 2.21–3.80 for N-rGOs, revealing that a further reduction event had occurred with more oxygen atoms being removed in the treatment using cysteamine, indicating the role of cysteamine both as covalently attaching molecules and as an additional reducing agent in this thiol-ene click chemical reaction. Meanwhile, a substantial drop of the C/N atomic ratio is observed in cyst-N-rGOs (Figure 4C) when compared to their respective N-rGO precursors (Figure 1F) visibly indicating that cysteamine is adding more nitrogen into the graphene network by having amino groups on their ends. It is important to mention that the C atomic percentage of functionalized cyst-N-rGO increases (Table S3) when compared to that of its respective N-rGO precursors (Table S2), signifying the effective functionalization of N-rGOs and attachment of new cysteamine molecules since each cysteamine molecule has two C atoms, which enhanced the total amount of C. An interesting trend showed that cysteamine modification tends to attach more nitrogen per carbon atom on N-GO compared with N-rGO. An increasing C/S atomic ratio was observed for cyst-N-GO (2.62 at %S) and cyst-N-rGO with low (2.45 at %S) and mild (2.28 at %S) reduction levels, implying that a slightly greater amount of sulfur per carbon atom was grafted into the graphene network. Interestingly, high cyst-N-rGO with N-rGO of the highest reduction degree exhibited the lowest amount of sulfur being anchored. The significant trend found in the C/N and C/S ratios of cyst-N-GO and cyst-N-rGOs could be related to the presence of oxygen functionalities on the GO surface, which may imply the presence and the role of oxygen groups as activation agents of C=C in the thiol-ene click reaction, as also highlighted by Luong et al.6

The peak deconvolution studies of the C 1s profile for cyst-N-rGOs are displayed in Figure 5A–D. A significant decrease of the C=C signal (284 eV) was observed for all cyst-N-rGOs relative to their respective N-rGO precursors (Figure S6, Supporting Information), suggesting that C=C species were prominently involved in the functionalization using cysteamine. On the other hand, a substantial decline in the C−O−C (287 eV) peak was also noticed for cyst-N-GO and mild and low cyst-N-rGOs in contrast to their respective N-rGO precursors. The cysteamine-directed reduction events, i.e., hydrogenation and oxygen removal on these carbon species, could be greatly responsible for the diminished signals.

The dramatic decline of the C−O−C peak could be linked to the reduction process, whereas the obvious fall trend observed for the C=C bond can be associated with the thiol-ene reaction, which targeted the sp² C on the graphene network to click the −SH group on the cysteamine molecule via the thermal thiol-ene click reaction. Remarkably, the C=S species (285 eV) was detected in all the spectra of cyst-N-rGOs. The formation of C=S species in all cyst-N-rGOs can be prominently attributed to the successful anchoring of cysteamine onto the graphene oxide surface via the thermal thiol-ene click reaction. Apparently, the results showed that both the reduction and modification processes occurred simultaneously. This discovery divulges and confirms the synergistic role of cysteamine not only as an effective functionalization agent but also as a reducing agent, which was evident in our studies and has been supported in the literature.

From the N 1s deconvolution analysis, two major N 1s peak components at around 399.8−401.2 and 401.1−402.7 eV (Figure 5E−H), which could be assigned to pyrrolic and graphitic N, respectively, were detected in all of the cyst-N-rGO derivatives. Simultaneously, the binding energies positioned at around 399 and 402.7 eV were also known to be attributed to C−NH₂ and N−H bonds (N connected to a single C), respectively, which could contribute to the same peaks as found in the high-resolution N 1s spectra of all cyst-N-rGOs.24,44–46 The presence of C−NH₂ and N−H in all final products revealed that cysteamine molecules have been
of the C–S–C peak on all cys-N-rGOs clearly revealed that the cysteamine molecules are neither physically attached nor chemically bonded via amino groups but covalently bonded through the active functional group (–SH) to the rGO surface via the thermal thiol-ene click reaction, as proposed in this work. Our results also indicate that the fixed GO/cysteamine ratio used in this study is the main factor to determine the amount of S being grafted onto the surface of graphene, with the reduction degree threshold at the ratio of hydrazine/GO = 0.15 for 24 h reduction time. Moreover, owing to the lone pair of electrons possessed by sulfur, the sulfur-rich graphene composites including cys-N-GOs prepared herein can also act as an additional functional group providing an electron pair to form coordinate bonds that can be used for many applications such as the binding of the heavy metals (electron pair acceptor) for remediation of contaminants in the environment.19,53 As reported in the literature, the variation of chemical states of sulfur specifically related to the oxidized sulfur species incorporated into the carbon network plays significant roles in modulating the surface chemistry for designing high-performance capacitors.48,54 In our present study, it can be clearly observed that a combination of different S environments existing in a tunable amount was created when GO with different reduction degrees was subjected to the thiol-ene click reaction. This is an important finding and a new strategy for the design of graphene materials with properties of both graphene and GO with a specific combination of chemical elements and functionalities required for catalysis, environmental remediation, and energy storage applications.

Based on the XPS analysis of high-resolution peaks of C 1s, N 1s, and S 2p and literature data, the chemical functionalities of the obtained cys-N-rGO derivatives are identified and schematically presented in Figure 6. It could be seen that by attaching the amino-terminated thiol molecules on N-doped rGO via thiol-ene click chemistry, it is possible to create a more complex multifunctionality on graphene with additional amino and sulfur functional groups. To further confirm the presence of nitrogen, oxygen, and sulfur functional groups in the prepared cys-N-rGO derivatives, further analyses using Raman, FTIR, TGA–DTA, and XRD techniques were performed, with their results summarized in Figures 7 and S7.

The presence of functional groups in cys-N-rGos was investigated using FTIR analysis, and the results are displayed in Figure 7A. The first transmittance signal we can locate in the spectra is the –OH group stretching vibrations at ~3400 cm⁻¹ where this peak can also be found in GO, N-GO, and low and mild N-rGO precursors (Figure 3C). Among all of the cys-N-
Cysteamine was proven, with its reducing ability, to carry cysteamine to covalently attach on the reduced graphene network after cysteamine functionalization. From the FTIR analysis, it can be observed that the chemical reduction by cysteamine via the removal of the O–H group is incomplete for cys-N-GO, whereas it is complete for the rest of the cys-N-rGOs. This discovery is in good correlation with the XRD result of all cys-N-rGOs discussed in Figure S7A, Supporting Information. Furthermore for all of the cys-N-rGOs studied, the appearance of a new peak near 1435 cm\(^{-1}\) (enlarged Figure 7A), which can be attributed to C=S vibrations, was also detected.\(^{55}\) A detailed inspection of the two peaks positioned at 1384 and 1548 cm\(^{-1}\) (enlarged Figure 7A), which can be attributed to the stretching vibrations of C=N and N−H, respectively, was also identified.\(^{56−58}\) It is essential to note that all the peaks corresponding to N−H, C=N, and S−H vibrations were not detected in the FTIR spectra of their respective N-rGO precursors. Moreover, no absorption associated with the stretching vibration of the S−H group, commonly recorded between 2500 and 2600 cm\(^{-1}\) was observed, signifying the breaking of the S−H bond in cysteamine to covalently attach on the reduced graphene sheets via thiol-ene click functionalization.\(^{59,60}\) Coupled with the strong evidence from these observations, we can infer the successful grafting of the cysteamine functional groups onto the graphene framework via the thermal thiol-ene click reaction, which converted the N-GO and N-rGO precursors to cys-N-GO and cys-N-rGOs, respectively.

The TGA–DTA graphs of all cys-N-GO and cys-N-rGOs (Figures S7B and 7B) show a stepwise decreasing trend at approximately 200 °C in which this pattern is very similar to that of their respective N-rGO precursor thermograms (Figure 3D). The percentage mass loss for all cys-N-rGOs in this temperature range is significantly lower compared to that of their respective N-rGO precursors, which implies that the amount of the oxygen moiety in cys-N-rGOs is lesser compared to that in their respective N-rGO precursors. Cysteamine was proven, with its reducing ability, to carry out reduction by removing the labile oxygen functional group, which could explain this result of mass loss observed at approximately 200 °C. The thermograms of cys-N-rGOs also demonstrated a final steep mass loss starting at around 600–700 °C in which this could be linked to the pyrolysis of the more stable and labile oxygen-containing residuals attached to the skeleton of carbon atoms. It was observed that the final mass loss for most of the cys-N-rGOs (Figure 7B) produced was slightly shifted to a higher temperature compared to that of their respective N-rGO precursors (Figure 3D). This implies that higher thermal stability can be attained for the end product, cys-N-rGOs, in contrast to their respective N-rGO precursors, which can be explained by a higher reduction rate induced by additional reduction by cysteamine. The appearance of a weak shoulder at around 250 °C for all cys-N-rGOs (Figure 7B) and its absence in the thermograms of their respective N-rGO precursors (Figure 3D) further confirm that the N-rGO precursors have been successfully modified with cysteamine. This weak signal can be highly correlated to the detachment of cysteamine from cys-N-rGOs, which evidently suggests the successful incorporation of cysteamine into cys-N-rGOs sheets. This finding is also consistent with our previous study showing cysteamine can also be anchored onto graphene oxide via a one-pot modification approach.\(^{19}\)

The structural features and defects formed in the end product, cys-N-rGOs, investigated using Raman spectroscopy (Figure 7C) with two intense characteristic bands (D band at 1342 cm\(^{-1}\) and G band at 1589 cm\(^{-1}\)), were identified. The intensity ratios of the D and G bands (I\(_D\)/I\(_G\)) for all cys-N-rGOs were calculated and compared with those of their respective N-rGOs demonstrated in Figure 7D. In comparison to all N-rGO precursors, it can be seen that all cys-N-rGOs exhibit higher I\(_D\)/I\(_G\) values. This observation revealed that more defects were being created in cys-N-rGOs after the modification using cysteamine. Additionally, the amount of defect sites generated in cys-N-rGOs is highly dependent on the reduction degree of N-rGO precursors used, as manifested by the enhanced I\(_D\)/I\(_G\) ratio after cysteamine-directed modification. In short, the higher the reduction degree of the N-rGO precursor used, the more defect sites eventually created.

Figure 7. Plots of (A) FTIR, (B) DTA, and (C) Raman analyses and (D) I\(_D\)/I\(_G\) ratio for cys-N-GO and cys-N-rGOs formed from their corresponding N-GO and N-rGO precursors at different reduction levels.
in the end product, cys-N-rGOs, which is an indication of successful anchoring of cysteamine on the surface of the N-rGO precursor.

3. CONCLUSIONS

In summary, we have demonstrated a simple modification approach of graphene materials that combines chemical doping and functionalization, which is able to control their chemical composition and level of multiple functional groups with O, N, and S elements. The synthesis of a broad range of graphene precursors (N-rGO) with different functionalities was performed by simultaneous nitrogen doping and gradual chemical reduction of GO using ammonia and hydrazine, followed by covalent attachment of amino-terminated thiol molecules (cysteamine) using the thiol-ene click reaction. Controllable modulation of the chemical multifunctionality of synthesized cys-N-doped rGO (cys-N-rGO) derivatives with different levels of oxygen groups (carboxyl, hydroxyl, and carbonyl) and different ratios of mixed functional groups including N (pyrrolic N, quaternary N, and aminic N) and S (thioether S, thiophenic S, and S oxides) is confirmed by comprehensive characterization techniques including UV–vis, FTIR, Raman, XRD, TGA–DTA, and XPS analyses. Thorough XPS analysis showed the introduction of doped binary nitrogen- and sulfur-containing groups, in particular of pyrrolic N and quaternary N as well as thioether S and thiophenic S, whose level can be controlled by modulating the reduction degree of GO prior to modification using cysteamine. In addition, the XPS analysis also confirmed the disappearance of unstable pyridinic N after cysteamine modification, which unveils the protocol for the future design of N-doped graphene derivatives, in particular for oxygen reduction catalysts. This study provides mechanistic insights into the role of reduction degree of GO to be used as a synthetic platform combined with other functionalization methods such as click chemistry to create graphene materials with complex chemical multifunctionality and desirable interfacial properties such as doping level needed for a wide range of polymer composites, sensors, environmental, catalysis, and energy storage applications.

4. EXPERIMENTAL SECTION

4.1. Materials. Natural graphite rocks were obtained from a local mining site (Uley, Eyre Peninsula, South Australia, Australia), crushed into powder using a benchtop ring mill (Rocklabs), and sifted using a 25 μm sieve. Potassium permanganate (Sigma-Aldrich), 85% w/w phosphoric acid (Chem-Supply), 98% sulfuric acid (Chem-Supply), 30% hydrogen peroxide (Chem-Supply), 36% hydrochloric acid (Sigma-Aldrich), 85% w/w phosphoric acid, 64–65% hydrazine monohydrate (Sigma-Aldrich), 30% ammonia (Chem-Supply), cysteamine hydrochloride (Sigma-Aldrich), N,N-dimethylformamide (DMF, Chem-Supply), 2,2-azobis-2-methylpropionitrile (AIBN, Sigma-Aldrich), hexane (Chem-Supply), ethyl acetate (Chem-Supply), and ethanol (Chem-Supply) were used directly without prior purification.

4.2. Preparation of Graphene Oxide (GO). GO was synthesized by the oxidation of graphite according to improved Hummer’s method. Briefly, sieved graphite powder (<25 μm, 3.0 g) was added to a round-bottom flask containing KMnO₄ (180.0 g). The acid mixture (9:1 H₂SO₄/H₃PO₄) was cooled to 4 °C and slowly poured onto the graphite powder in the presence of KMnO₄ and stirred at room temperature before heating (60 °C, 16 h) to form a thick paste. The formed paste was cooled to room temperature; poured onto ice cubes in the presence of hydrogen peroxide (3 mL); washed with distilled water and 30% hydrochloric acid, followed by distilled water and ethanol. The product was centrifuged at 4200 rpm for each successive wash. The obtained GO was dispersed in ethanol and freeze-dried to give a brown product.

4.3. Preparation of N-Doped Reduced Graphene Oxide (N-rGO). A series of N-rGO samples with several reduction degrees were prepared by the reduction of GO according to reported methodology by Morimoto et al. Prepared GO (400 mg) was dispersed in distilled water (2 mg mL⁻¹) in a glass reaction flask. Hydrazine monohydrate (32, 6030, and 120 μL) was added into separate reaction flasks containing GO dispersion. The mixtures were sonicated (10 min), ammonia (80 μL) was added, and the mixtures were heated with magnetic stirring (90 °C, 2 h). N-GO was prepared as a control without hydrazine monohydrate. Subsequently, the as-formed products were cooled to room temperature, washed several times with distilled water and ethanol, and dried (40 °C, 24 h) prior to charactrizations.

4.4. Synthesis of Cysteamine-Functionalized N-GO and N-rGO (cys-N-GO and cys-N-rGO). Cysteamine-functionalized N-rGO (cys-N-rGO) was prepared as previously described in our work with some modifications. N-rGO (100 mg) was added to DMF (50 mL), sonicated (30 min) to obtain a homogeneous dispersion, and purged with N2 gas (30 min) to create an inert environment. The cysteamine reaction mixture consisting of AIBN (200 μL), cysteamine hydrochloride (200 mg), and DMF (100 mL) was sonicated (30 min) and added into the N-rGO dispersion. The dispersion was purged with N2 gas for further 30 min and transferred into a round-bottom flask, which was sealed and heated (70 °C, 12 h) in a silicon oil bath. Similarly, N-GO was treated with the cysteamine reaction mixture to produce cys-N-GO. The resulting product was cooled to room temperature and washed with a mixture of 1:1 hexane/ethyl acetate, followed by ethanol and distilled water. The product was then freeze-dried and characterized to obtain the corresponding cysteamine-functionalized derivatives.

4.5. Characterizations. Prepared GO, N-GO, N-rGO, cys-N-GO, and cys-N-rGO were characterized using several techniques including UV–visible absorbance (UV–vis), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) (Quanta 450 FEG, FEI) at an operating voltage of 10 kV and transmission electron microscopy (TEM) (Tecnai G2 Spirit) at an operating voltage of 100 kV were used to characterize the morphology of the GO. UV–vis analysis was conducted using a Shimadzu UV–vis spectrometer (UV-1601) in the range of 200–800 nm to probe the reduction degree of the samples prepared. All of the samples were diluted in ethanol prior to measurements at room temperature, with at least three independent runs of reproducible results obtained for each sample. FTIR spectroscopy (Nicolet 6700, Thermo Fisher) in the range of 500–4000 cm⁻¹ was carried out under attenuated total reflection (ATR) mode to identify the functional groups in the materials. Raman spectroscopy (LabRAM HR Evolution, Horiba Jyon Yvon Technology, Japan) with a 532 nm laser (mpc 3000) as the excitation source was used to determine the vibrational properties of the materials. All of the spectra were recorded with an integration...
time of 10 s, each on three different spots. An X-ray diffractometer (600 Miniflex, Rigaku, Japan) equipped with a Cu X-ray tube was used for analysis on GO, N-doped and cysteamine-functionalized materials to unveil the composition of the materials in the range of 2θ = 5–80° at 40 kV and 15 mA with a 10° min⁻¹ scan speed. The thermal stabilities, reduction degrees, and functionalization levels of the materials were investigated using TGA (Q500, TA Instruments) under a nitrogen atmosphere with the samples heated to 900 °C at a heating rate of 10 °C min⁻¹. The elemental compositions and chemical states of the materials were determined using XPS [AXIS Ultra DLD (Kratos, U.K.) equipped with a monochromatic Al Kα radiation source (hv = 1486.7 eV)] at 225 W, 15 kV, and 15 mA. XPS wide scans were acquired at 0.5 eV step size over 10–1100 eV at the pass energy of 160 eV, whereas the narrow scans were obtained at a 0.1 eV step size and pass energy of 20 eV. The deconvolution and fitting of peaks were performed using Casa XPS software. All of the core-level spectra involved in this work were calibrated to the primary peak (C–C/C–H peak) of the adventitious carbon at 285 eV; the relative sensitivity factor (RSF) values were set at 0.278 for C 1s, 0.668 for S 2p, 1.8 for N 1s, and 2.93 for O 1s. Meanwhile, the components in C 1s were deconvoluted by referencing to the adventitious carbon (C–C peak), with their respective fwhm confined between 1 and 1.2 eV; a constraint was also imposed on the position of the C 1s components relative to the adventitious carbon (C–C peak), and the area of the satellite peak was restricted to 0.069634 relative to the C=C peak.

■ ASSOCIATED CONTENT

2 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02642.

Synthesis conditions for N-doped and cysteamine-functionalized derivatives; high-resolution XPS O 1s scans for GO, N-GO, and N-rGOs; normalized atomic percentages of C, O, and N for GO, N-GO, and N-rGOs; high-resolution XPS deconvoluted C 1s and O 1s peaks for GO; high-resolution XPS deconvoluted C 1s and O 1s peaks for N-GO and N-rGOs; photographs of GO, N-GO, and N-rGO with varied reduction degrees dispersed in ethanol; TGA plots of GO, N-GO, and N-rGO precursors; normalized atomic percentages of C, O, and N for cysteamine-functionalized GO, N-GO, and N-rGOs plots of relative contributions of C 1s C=C and C–O–C components for N-GO, N-rGOs, cysteamine-functionalized GO, and cysteamine-functionalized rGOs; relative surface concentrations of nitrogen and sulfur species of cysteamine-functionalized GO, N-rGOs and TGA plots of cysteamine-functionalized GO and cysteamine-functionalized rGOs (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

GO, graphene oxide; N-GO, nitrogen-doped graphene oxide; N-rGO, nitrogen-doped reduced graphene oxide; cysteamine-functionalized nitrogen-doped reduced graphene oxide; H2SO4, sulfuric acid; H3PO4, phosphoric acid; H2O2, hydrogen peroxide; HCl, hydrochloric acid; C3H6N5S, cysteamine; DMF, N,N-dimethylformamide; TEM, transmission electron microscopy; SEM, scanning electron microscopy; FTIR, Fourier transform infrared spectroscopy; TGA, thermogravimetric analysis; DTA, derivative thermogravimetric analysis; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; UV, visible; UV–visible; spectroscopy; I/P, intensity ratio of D and G bands; C/O, carbon-to-oxygen atomic ratio; C/N, carbon-to-nitrogen atomic ratio; C/S, carbon-to-sulfur atomic ratio; C, carbon; O, oxygen; S, sulfur; N, nitrogen; OH, hydroxyl; CH(O)CH, epoxy; COOH, carboxyl; C≡O, carbonyl; COOR, ester; C–O–C, epoxide; C–S–C, thiocarbon; C≡S, thioketone; SO3, sulfur trioxide

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