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Thiol–Yne Click Reactions on Alkynyl–Dopamine-Modified Reduced Graphene Oxide

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Abstract: The large-scale preparation of graphene is of great importance due to its potential applications in various fields. We report herein a simple method for the simultaneous exfoliation and reduction of graphene oxide (GO) to reduced GO (rGO) by using alkynyl-terminated dopamine as the reducing agent. The reaction was performed under mild conditions to yield rGO functionalized with the dopamine derivative. The chemical reactivity of the alkynyl function was demonstrated by post-functionalization with two thiolated precursors, namely 6-(ferrocenyl)hexanethiol and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol. X-ray photoelectron spectroscopy, UV/Vis spectrophotometry, Raman spectroscopy, conductivity measurements, and cyclic voltammetry were used to characterize the resulting surfaces.

Keywords: alkynes · carbon · click chemistry · reduction · thiols

Introduction

Graphene has attracted significant research interest as a result of its remarkable electrical, thermal, and mechanical properties, which are a consequence of its two-dimensional hexagonal carbon lattice structure.[1] The top-down preparation of graphene by using graphite as a starting material is currently considered one of the most cost-effective methods for the synthesis of this two-dimensional sp^2-bonded carbon material.[2] In the first step, exfoliated graphene oxide (GO) is obtained from graphite by the use of strong acids and ultrasonication. The graphitic nature of the resulting GO nanosheets is, however, highly compromised by the presence of a large number of surface oxygen functionalities, which lead to a loss of conductivity. Reductive treatment by chemical[3] or thermal[4] methods resulted in the partial recovery of the graphitic character by removing the majority of oxygen functionalities from the GO and re-establishing to a certain extent the sp^2 network. The product is thus referred to as chemically converted graphene or reduced graphene oxide (rGO). In addition to the restoration of the sp^2 character of GO, considerable efforts are currently being directed towards the chemical modification of GO and rGO nanosheets, aiming at a better processability of graphene and fine-tuning of its electronic, optical, and electrochemical properties.[5,6] We[7–9] and others[10] have recently shown that the direct reaction of GO with dopamine or tetrathiafulvalene (TTF) allows not only the reduction of GO to rGO in an easy and environmentally friendly manner, but also results in the simultaneous modification of the rGO nanosheets with the dopamine or tetrathiafulvalene through π–π stacking interactions. The interest in rGO functionalization with dopamine derivatives has arisen from the ease with which functional groups can be introduced through its amine groups. For example, we have shown that rGO modified with dopamine bearing azide groups allows the post-functionalization with ethynylferrocene by a Cu^I-catalyzed 1,3-dipolar cycloaddition reaction.

The photochemical "click" reaction between alkynes or alkenes and thiolated molecules has attracted increasing interest in recent years because of its versatility and specificity.[11–15] It is believed that this reaction can overcome obstacles relating to the high-density deposition of ligands, the processing of large and bulky head-groups, and the direct placement of ligands possessing multiple reactive functionalities. These reactions have "click" chemistry characteristics such as high yield, regiospecificity, mild reaction conditions, and tolerance to a variety of functional groups.[13,16,17] However, in contrast to Cu^I "click" chemistry,[16] no catalyst is required as the reaction is initiated thermally or photochemically. The main difference between the thiol–ene and thiol–

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yne reactions is the possibility of anchoring two thiol molecules on to the alkyne to form a double addition product by a radical process.[11,18,19]

In this article we demonstrate that a rGO/alkynyl–dopamine nanocomposite material can be prepared by the simple reaction of GO with alkynyl–dopamine under sonication for two hours at room temperature. The interaction between the alkynyl–dopamine and rGO takes advantage of strong π–π interactions between the graphene sheets and the aromatic ring of dopamine, as shown previously.[8,10] We also develop the concept of the reaction between a thiol and the alkyne on the rGO nanocomposite. In a proof of concept experiment, 6-ferrocenylhexanethiol (HS-Fc) or 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (HS-PF) was photochemically "clicked" onto the rGO/alkynyl–dopamine derivative.

Experimental Section

Materials: Graphite powder ($<20\ \mu$), 6-ferrocenylhexanethiol (HS-Fc), 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (HS-PF), tetrahydrofuran (THF), ethanol, phosphate buffered saline (PBS), and tin-doped indium oxide coated glass (ITO; sheet resistivity 15–25 $\Omega\,\mathrm{cm}^2$) were purchased from Aldrich and used as received. NMR spectra were recorded at 25 °C, with a Bruker Avance 300 spectrometer.

Synthesis of prop-2-ynyl 5-(3,4-dihydroxyphenethylamino)-5-oxopentanoate (alkynyl-terminated dopamine): Dopamine hydrochloride (1.453 g, 9.49 mmol) was dissolved in MeOH (50 mL). Triethylamine (0.959 g, 9.49 mmol) and 2,5-dioxopyrrolidinyl prop-2-ynyl glutarate (2.31 g, 8.63 mmol, formed from 5-oxo-5-(prop-2-ynyloxy)pentanoic acid by reaction with *N*-hydroxysuccinimide) dissolved in MeOH (20 mL) were added slowly. The solution was stirred overnight at room temperature under N_2. Then the solvent was evaporated and the product dissolved in CH_2Cl_2 (100 mL). The organic layer was washed with HCl (0.5 M, 50 mL) and water (2×50 mL), and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2/CH_2Cl_2:MeOH, 10:1) to afford the alkynyl-terminated dopamine in a yield of 80% as a white solid. ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta=1.73$ (quint, $J=7.09$ Hz, 2H), 2.08 (t, $J=7.45$ Hz, 4H), 2.32 (t, $J=7.45$ Hz, 2H), 3.15 (q, $J=7.45$ Hz, 2H), 3.55 (t, $J=2.49$ Hz, 1H), 4.68 (d, $J=2.49$ Hz, 2H), 6.42 (dd, $J=7.97$ Hz, 1H), 6.56 (d, $J=2.05$ Hz, 1H), 6.62 (d, $J=7.97$ Hz, 1H), 7.86 (t, $J=5.48$ Hz, 1H), 8.66 (br s, 1H), 8.76 ppm (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=171.9$, 171.14 (C=O), 145.0, 143.4, 130.2, 119.1, 115.9, 115.4 (C=C), 78.5, 77.6 ($C\equiv C$), 51.5 (C−O), 34.7, 34.1, 32.5 (C−N and C−C=O), 20.5 ppm (C−C).

Preparation of graphene oxide (GO): Graphene oxide (GO) was synthesized from graphite powder by a modification of Hummer's method.[20] The synthesized GO (5 mg) was dispersed in water (1 mL) and exfoliated by ultrasonication for 3 h. This aqueous suspension of GO was used as a stock suspension in subsequent experiments.

Preparation of graphene/alkynyl-terminated dopamine (rGO/alkynyl–dopamine): The stock GO suspension ($5\ \mathrm{mg\,mL^{-1}}$) was diluted in water to obtain a $0.5\ \mathrm{mg\,mL^{-1}}$ solution (1:10). Alkynyl-terminated dopamine (1 mL, 10 mM) was added to the GO solution (1 mL) and the mixture was treated with ultrasound for 2 h at room temperature. The resulting black precipitate was separated from the aqueous supernatant by centrifugation at 14000 rpm for 20 min. After washing with water (three times), the resulting precipitate was dried in an oven (80 °C) and then dispersed in water by ultrasonication for 30 min.

Thiol–yne reaction on rGO/alkynyl–dopamine: rGO/alkynyl–dopamine-modified ITO electrodes were prepared by casting a solution of rGO/alkynyl–dopamine in THF (50 μL) onto previously cleaned ITO substrate and heated at 70 °C to ensure solvent evaporation. rGO/alkynyl–dopamine-modified ITO surfaces were immersed in a solution of 6-ferrocenylhexanethiol (10 mM) or 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (10 mM) or a mixture (5 mM each) in absolute ethanol under nitrogen. The interface was exposed to UV light irradiation at $\lambda=365$ nm ($P=100\%$ or $100\ \mathrm{mW\,cm^{-2}}$) for 30 min at room temperature. The resulting surface was thoroughly washed with ethanol then with water and dried under nitrogen stream.

X-ray photoelectron spectroscopy (XPS): XPS experiments were performed with a PHI 5000 VersaProbe Scanning ESCA Microprobe (ULVAC-PHI, Japan/USA) instrument at a base pressure below 5×10^{-9} mbar. Monochromatic $Al_{K\alpha}$ radiation was used and the X-ray beam, focused to a diameter of 100 μm, was scanned over a 250×250 μm surface at an operating power of 25 W (15 kV). Photoelectron survey spectra were acquired by using a hemispherical analyzer with a pass energy of 117.4 eV and an energy step of 0.4 eV. Core-level spectra were acquired with a pass energy of 23.5 eV and an energy step of 0.1 eV. All spectra were acquired with 90° between the X-ray source and analyzer, and with the use of low-energy electrons and low-energy argon ions for charge neutralization. After subtraction of the Shirley-type background, the core-level spectra were deconvoluted into their components with mixed Gaussian–Lorentzian (30:70) shape lines by using the CasaXPS software. Quantification calculations were conducted by using sensitivity factors supplied by PHI.

Cyclic voltammetry (CV): CV experiments were performed by using an Autolab 20 potentiostat (Eco Chimie, Utrecht, The Netherlands). The electrochemical cell consisted of a working electrode (ITO or modified ITO), Ag/AgCl (Bioanalytical Systems, Inc.) as the reference electrode, and platinum wire as the counter electrode. Cyclic voltammetry measurements were performed in 0.1 M PBS at a scan rate of $0.05\ \mathrm{V\,s^{-1}}$.

rGO/alkynyl–dopamine-modified ITO electrodes were prepared by casting a solution of rGO/alkynyl–dopamine in THF (50 μL) onto the ITO substrate followed by heating at 70 °C until complete evaporation of THF.

UV/Vis spectrophotometry: Absorption spectra were recorded by using a Perkin–Elmer Lambda UV/Vis 950 spectrophotometer in plastic cuvettes with an optical path of 10 mm. The wavelength range was 400–800 nm.

Raman spectroscopy: Micro-Raman spectroscopy measurements were performed on a Horiba Jobin Yvon LabRam HR Micro-Raman system combined with a 473 nm laser diode as excitation source. Visible light was focused by a 100× objective. The scattered light was collected by the same objective in backscattering configuration dispersed by a 1800 mm focal length monochromator and detected by CCD.

Conductivity measurements: Electrical conductivity was determined by the Hall effect using a HL 5500 PC system in a standard four-probe setup. The graphene sample was prepared by filtration of the dispersion through a PVDF membrane filter and then deposited in a p-doped silica wafer.

Results and Discussion

Formation of the rGO/alkynyl–dopamine nanocomposite material: Our interest in the fabrication of rGO/alkynyl–dopamine nanohybrid materials is motivated by the fact that alkynyl functional groups can be further employed for the covalent linking of thiolated molecules in a thiol–yne reaction mechanism. We have recently shown that azide-terminated dopamine can be used in a one-step reaction for the reduction of graphene and the simultaneous incorporation of azide moieties onto the graphene skeleton. The chemical reactivity of the azide function was demonstrated by post-functionalization with ethynylferrocene by the Cu^I-catalyzed 1,3-dipolar cycloaddition reaction. Although less investigat-

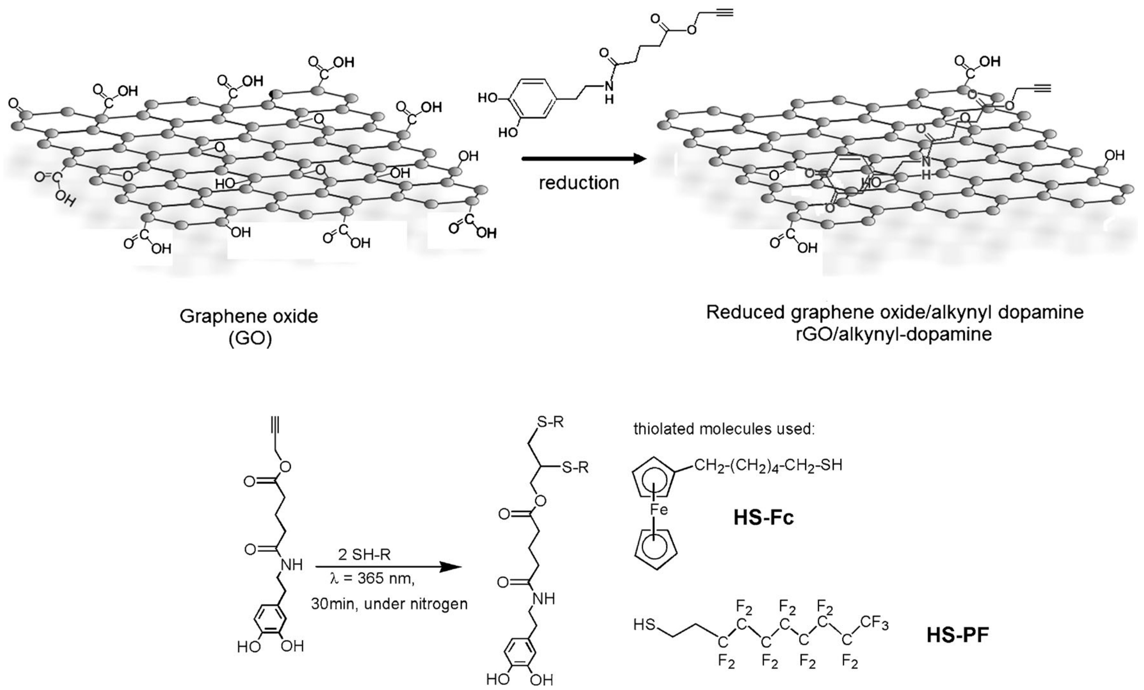

Figure 1. Top: Schematic illustration of the formation of rGO/alkynyl–dopamine nanosheets. Bottom: Reaction of the alkynyl–dopamine with thiols by the thiol–yne radical-addition mechanism.

ed than the thiol–ene reaction, thiol–yne chemistry has the advantage that the alkynyl group can react with two thiol molecules to form a double addition product.[21] Alkynyl-terminated dopamine was thus investigated for its ability to reduce GO and at the same time be incorporated into the graphene sheet. As was the case with azide-terminated dopamine, the rGO/alkynyl–dopamine nanocomposite material was readily formed by the addition of alkynyl–dopamine to GO under sonication at room temperature at neutral pH (Figure 1, top). The precipitate formed was poorly dispersed in polar solvents such as water, methanol, and ethanol, but forms stable suspensions in solvents such as DMF, DMSO, and THF with rGO/alkynyl–dopamine concentrations of up to around 0.5 $mg mL^{-1}$. The interactions between the alkynyl-terminated dopamine and graphene are most likely dominated by π-stacking between the hexagonal cells of the graphene and the aromatic ring of dopamine. However, because the alkynyl-terminated dopamine acts as reducing agent, the graphene oxide is likely to oxidize the *ortho*-quinol structure of the dopamine ligand to radical or quinone intermediates, which are likely to covalently bind to graphene or to each other.

X-ray photoelectron spectroscopy (XPS) analysis was performed on GO before and after its reaction with alkynyl-terminated dopamine to gain further information on its chemical composition. The C1s core-level XPS spectrum of GO nanosheets is displayed in Figure 2 (top, curves a) and can be deconvoluted into four components with binding energies of around 283.8, 284.7, 286.7, and 287.9 eV assigned to sp^2-hybridized carbon atoms, C−H/C−C, C−O, and C=O species, respectively. The C/O ratio of GO is 1.73, comparable to values reported in the literature.[22,23] After reaction of GO with alkynyl-terminated dopamine, XPS analysis of the resulting product indicated significant changes in the C1s core-level spectrum (Figure 2; top, curves b). The band at 283.8 eV arising from sp^2-hybridized carbon atoms became predominant, which suggests the reconstitution of the graphitic network. The bands at 285.2, 286.7, 287.9, and 289.2 can be attributed to C−H/C−C, C−O, C=O, and N−C=O/OC=O species of the dopamine derivative and of some remaining oxygen functionalities on the rGO. The C/O ratio increased to 3.6, comparable to the C/O ratio of 3.4 obtained for GO reduced with azide-functionalized dopamine.[8] The success of the incorporation of the dopamine derivative was also confirmed by the presence of 2.4 at.% nitrogen (Table 1).

The formation of rGO was also validated by UV/Vis spectrophotometry. The UV/Vis absorption spectra of GO and rGO/alkynyl–dopamine in THF are presented in Figure 2 (middle). GO dispersed in water exhibits a maximum absorption at 228 nm, attributed to the π–π* transition in the

Table 1. Atomic percentages of rGO/alkynyl–dopamine before and after reaction with thiolated ferrocene.

Interface investigated	C 1s [at.%]	O 1s [at.%]	N 1s [at.%]	Fe 2p [at.%]	S 2p (C−S) [at.%]	S2 p (S−O) [at.%]
rGO/alkynyl–dopamine	74.30	23.30	2.40	0.00	0.00	0.00
+10 mM HS-Fc	73.18	23.60	2.20	0.50	0.37	0.15
+10 mM HS-Fc upon photoirradiation	72.50	22.20	2.10	1.60	1.10	0.50

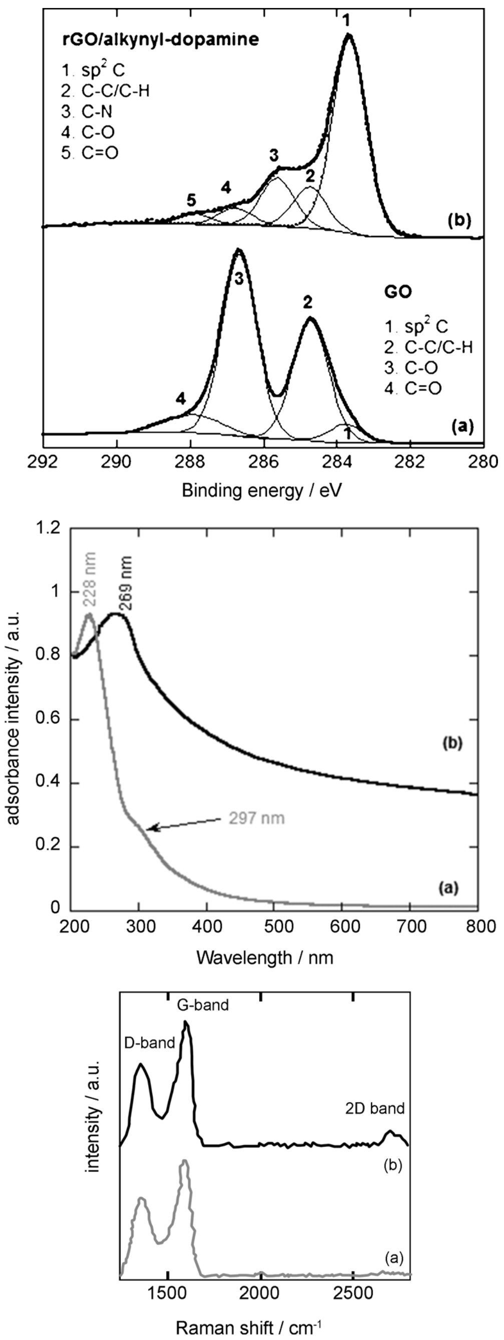

Figure 2. Top: C 1s core-level XPS spectra of GO a) before and b) after reaction with alkynyl–dopamine. Middle: UV/Vis spectra of a) GO in water and b) rGO/alkynyl–dopamine in THF. Bottom: Raman spectra of a) GO and b) rGO/alkynyl–dopamine.

C=C bonds of the aromatic skeleton, and a broad shoulder at around 297 nm due to the n–π* transition arising from the C=O bonds in the carboxylic acid functions. The spectrum of the rGO/alkynyl–dopamine nanocomposite shows a broad absorption band at 269 nm. The redshift of the band at 228 nm (GO) to 269 nm for rGO/alkynyl–dopamine is consistent with the restoration of the sp^2 structure in rGO.

Raman scattering is a useful tool for characterizing the structural properties of graphene-based materials. Figure 2 (bottom) shows the Raman spectra for GO and rGO/alkynyl–dopamine; the main features of the graphene-based materials are a D band at 1351 cm^{-1}, a G band at 1570 cm^{-1}, and a 2D band at around 2700 cm^{-1}.[24] The ratios of the intensities of the D and G bands (I_D/I_G) are 0.71 for GO and 0.67 for rGO/alkynyl–dopamine, comparable to the I_D/I_G value of 0.63 for hydrazine-reduced graphene oxide.[25]

In addition, the room-temperature conductivity of rGO/alkynyl–dopamine was measured by a standard four-probe method. The nanocomposite showed a conductivity of 0.89 S m^{-1}, which is lower than that measured for hydrazine-reduced graphene (145 S m^{-1}) by using the same technique. However, the value is comparable to that reported recently with azido-terminated tetrathiafulvalene.[7]

The amount of alkynyl–dopamine incorporated into the rGO matrix was estimated on the basis of cyclic voltammetry (CV) experiments. The rGO/alkynyl–dopamine composite material was drop-cast onto bare ITO. The drop-casting process is very reproducible and leads to homogeneous rGO/alkynyl–dopamine films of around 280 nm, comparable to rGO/azide-dopamine films (Figure 3, top).[8] Figure 3 (bottom) shows the electrochemical signature of the rGO/alkynyl–dopamine-modified ITO interface. A redox wave with $E_1^{ox} = 0.19$ V versus Ag/AgCl is observed, characteristic of dopamine oxidation in a two-electron process. The loading of alkynyl–dopamine on to the rGO surface was calcu-

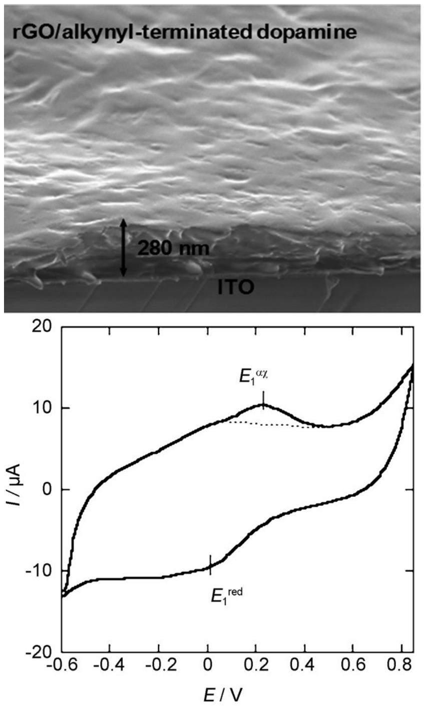

Figure 3. Top: SEM image of an ITO/graphene/alkynyl–dopamine electrode formed by drop-casting (thickness = 280 nm). Bottom: Cyclic voltammogram of an ITO electrode modified by drop-casting with rGO/alkynyl–dopamine in 0.1 M PBS (scan rate = 0.05 V s^{-1}).

lated by integrating the anodic peak area according to $\Gamma = Q_A/nFA$, in which F is the Faraday constant, n is the number of electrons exchanged ($n=2$), A is the surface area ($A = 0.12\ \mathrm{cm}^2$), and Q_A is the anodic charge transferred. A value of $\Gamma = (2.07 \pm 0.73) \times 10^{14}$ molecules cm^{-2} was obtained. This value is lower than that determined for rGO modified with TTF by a similar approach ($\Gamma = 8.9 \times 10^{14}$ molecules cm^{-2}),[9] but comparable to that obtained for unmodified dopamine ($\Gamma = (3.05 \pm 0.73) \times 10^{14}$ molecules cm^{-2}).

Thiol–yne reactions on rGO/alkynyl–dopamine-modified ITO interfaces: Because the thiol–yne reaction allows the addition of two thiolated molecules to an alkyne, it appears to be perfectly suited to obtaining high surface densities of the functional group of interest on the interface. 6-Ferrocenylhexanethiol (SH-Fc) and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol have been studied as model systems to investigate the reactivity of the reduced GO modified with alkynyl-terminated dopamine (Figure 1; bottom). The photochemical thiol–yne reactions were performed at 365 nm for 30 min under nitrogen with a light power of 100 mW cm^{-2} and the reactions were monitored by XPS. Figure 4 (top) shows the S2p core-level high-resolution XPS spectrum of rGO/alkynyl–dopamine after photochemical reaction with 6-ferrocenylhexanethiol. It can be deconvoluted into bands at 164.2 (S2p$_{3/2}$) and 165.3 eV (S2p$_{1/2}$) due to S−C bonds and contributions at higher energies, 166.9 (S2p$_{3/2}$) and 168.1 eV (S2p$_{1/2}$), due to oxidized S^{4+} in the form of S−O with a ratio of S−C/S−O of 2.2. The presence of oxidized thiols was also observed in the initial 6-ferrocenylhexanethiol solution with a S−C/S−O ratio of 2.4. This indicates that only a small fraction of 6-ferrocenylhexanethiol molecules are oxidized during the photochemical reaction and interact nonspecifically with the rGO/alkynyl-terminated dopamine nanomaterial. The atomic ratio of N/S is 1.3 (Table 1). Taking into consideration the fact that about 0.65 at % of SH-Fc is oxidized rather than reacting in the thiol–yne reaction, a ratio of N/(S−C) of 1.9 was determined, which is close to the theoretically expected ratio of N/S of 2.0 for a double addition rather than a monoaddition. The nonspecific adsorption of 6-ferrocenylhexanethiol or its oxidized counterpart onto the rGO surface was verified in a control experiment in which ITO interfaces modified with rGO/alkynyl–dopamine films were immersed in a 10 mM ethanolic solution of 6-ferrocenylhexanethiol as before for 30 min but without light irradiation. As seen from Table 1, the presence of bands due to S2s and Fe2p indicates some nonspecific adsorption onto rGO/alkynyl–dopamine interfaces most likely due to π–π stacking interactions.

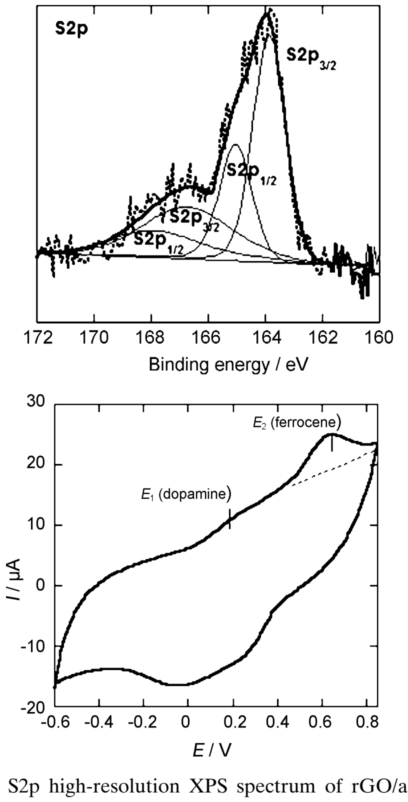

Figure 4. Top: S2p high-resolution XPS spectrum of rGO/alkynyl–dopamine after photochemical reaction ($\lambda = 365$ nm) with 10 mM 6-ferrocenylhexanethiol for 30 min at room temperature ($P = 100$ mW cm^{-2}). Bottom: CV of the ITO interface modified with rGO/alkynyl–dopamine after photochemical reaction with 10 mM 6-ferrocenylhexanethiol in 0.1 M PBS (scan rate = 0.05 V s^{-1}).

The bonded ferrocene moiety shows a redox potential at around 0.6 V versus Ag/AgCl and integration of the anodic peak area revealed a surface coverage of $\Gamma = 5.04 \times 10^{14}$ molecules cm^{-2}. This value is approximately 2.4-fold higher than that obtained for the dopamine ligand incorporated on to the rGO and suggests preferential double addition together with some nonspecific adsorption. In addition, it is much higher than that determined for rGO/dopamine-N$_3$ nanomatrices produced by using Cu^{I} click chemistry.[8]

Given the high cross-section of fluorine in XPS analysis, 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol was used as a second model compound to investigate the thiol–yne reaction. Figure 5 (top) displays the XPS survey spectrum of the rGO/alkynyl–dopamine interface after photochemical reaction for 30 min. The success of the reaction is evidenced by the presence of F1s (688 eV) and S2p (164 eV) bands in addition to C1s (284.5 eV), O1s (513 eV), and N1s (400 eV) bands. The high-resolution C1s XPS spectrum of the perfluorodecanethiol-modified rGO matrix is shown in Figure 5 (bottom). The presence of CF$_3$ and CF$_2$ groups is clearly seen by the contributions at 293.1 and 290.7 eV, respectively. The other bands arise from sp^2-hybridized carbon atoms (283.9 eV), C−C/C−H (284.5 eV), C−S/C−N/C−O (285.8 eV), and C=O (287.8 eV). The atomic ratio of N/S is 1.3, lower than the N/S = 2 expected for the double addition product, which indicates the preferential formation of the monoaddition product in this case. The formation of only the monoproduct might be due to the increase in hydrophobicity of the rGO/alkynyl–dopamine after the first addition with the water contact angle of 44° changing to 97° upon reaction with perfluorodecanethiol.

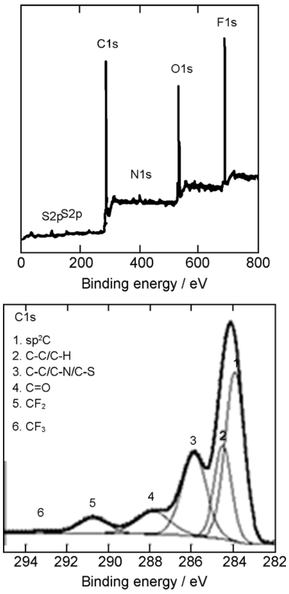

Figure 5. Top: XPS survey spectrum of rGO/alkynyl–dopamine deposited onto ITO after immersion in 10 mM 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and UV light irradiation at 365 nm for 30 min at room temperature ($P = 100\,\mathrm{mW\,cm^{-2}}$). Bottom: C1s core-level XPS spectrum after thiol–yne reaction with HS-PF.

Conclusion

This study has demonstrated that alkynyl-terminated dopamine reacts in a similar way to dopamine inducing simultaneous reduction of graphene oxide to graphene and functionalization of the rGO at room temperature under sonication. The motivation for using dopamine is that such reduced graphene oxide nanocomposites allow the postfunctionalization of rGO/alkynyl–dopamine with thiols by photochemical "click" reactions between alkynes and thiols. This approach opens up new perspectives for the covalent modification of graphene composites, which can be exploited for future applications.

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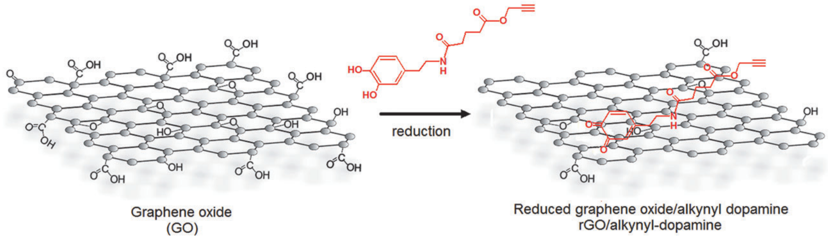

Modified graphene oxide: A simple method has been developed for the simultaneous exfoliation and reduction of graphene oxide (GO) to reduced GO (rGO) by using alkynyl-terminated dopamine as the reducing agent. The reaction was performed under mild conditions to yield rGO functionalized with the dopamine derivative (see figure). The chemical reactivity of the alkynyl function was demonstrated and the surfaces of the rGO characterized by a variety of techniques.

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