Modular preparation of novel graphene-based functional architectures using two steps organic reactions: towards high performance energy storage

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Abstract: Graphene-based materials have recently attracted a great attention due to their extraordinary physical and chemical properties, which make them attractive candidates for many technological applications in sensing, opto-electronics, catalysis and energy storage. Their chemical functionalization is key in order to tune properties. Here a novel two steps synthesis approach enabling high degree of covalent functionalization of graphene oxide (GO) is devised, thereby making it possible the facile attachment of various robust functional molecules. Such a process relies initially on the grafting of an ethylenediamine linker followed by a second step consisting in the condensation reaction between aldehyde and amine groups to form imine bonds. As testbeds two kinds of graphene-based functional systems, i.e. porphyrin modified GO and ferrocene modified GO, are prepared. Such hybrid systems are characterized by various spectroscopic and microscopic techniques. The degree of functionalization is quantified as the attachment of one porphyrin or ferrocene unit each 34 or 77 carbon atoms of the GO scaffold, respectively, which is much higher than values obtained upon using various established chemical approaches to functionalize GO, such as condensation, cycloaddition or coupling reactions. For the first time, the reduced form of ferrocene modified GO was employed as electrode materials in supercapacitors, showing a specific capacitance of 127 F g⁻¹ at a current density of 1 A g⁻¹, with capacitance retention of $\approx$ 93% after 5000 cycles at the same current density, demonstrating a great potential in high performance energy storage devices.

Introduction

Graphene and related compounds have attracted an increasingly greater attention during the past decade due to their extraordinary mechanical, electrical and thermal properties which rendered them key components for various technological applications in opto-electronics, sensing as well as energy conversion and storage.^[1-23] Graphene can be produced by various top-down and bottom-up methods, including mechanical exfoliation, chemical vapor deposition (CVD), liquid-phase exfoliation and reduction of graphene oxide (GO), etc.^[1, 24]

processing cumbersome,^[25] yielding worse performances in practical applications. Because of these reasons, a great effort has been paid to the development of facile, reliable and low-cost synthetic routes towards the preparation of highly dispersible and processable graphene derivatives.^[10, 26]

The properties of graphene can be engineered via chemical functionalization.^[27] The latter can offer major improvements and tuning of fundamental interfacial characteristics such as dispersibility, wettability and processability of graphene. On the same time, it can also impart new optical, electronic, magnetic, catalytic, or electrochemical properties to the material through the introduction of additional functional units.^[28, 29] Graphene can be functionalized at the covalent or non-covalent level.^[9, 26, 30] On the one hand, non-covalent functionalization can largely preserve the intrinsic properties of graphene but it suffers from limited stability.^[27, 31] On the other hand, covalent functionalization of graphene yields more stable and robust systems. It is fair to note that although a great attention has been paid during the last five years on the covalent functionalization of pristine graphene; despite several chemical strategies has been used (e.g. cycloadditions,^[32] diazonium salts,^[33] nucleophilic addition,^[34] and click chemistry,^[33] etc.), the achieved degree of functionalization is often rather modest and long reaction times are normally required.^[35]

Graphene oxide (GO), the oxidized version of graphene, possess a unique chemical structure: it exposes on its basal plane and at its edges various oxygen containing functional groups including epoxy, carboxylic and hydroxyl.^[36] Such functionalities does not only render GO dispersible in various solvents, but also represent highly reactive sites for the functionalization of the 2D scaffold using non-covalent and covalent approaches. Hence, GO represents the ideal platform for building graphene-based multifunctional hybrid systems. For example, GO can be functionalized with specific moieties through condensation reactions between the carboxylic groups on GO with -NH₂-OH groups of the foreign molecules.^[37-41] However, due to the limited amount of carboxylic groups on GO, the functionalization degree is often low (with one functional unit attached each hundreds of carbon atoms of GO scaffold).^[40] Therefore, the development of novel facile, effective, not aggressive, and robust functionalization strategies in a modular manner is highly desired to generate advanced graphene derivatives with a much higher degree of functionalization, together with specific properties and certain functions for various applications. To the best of our knowledge, the use of α,ω alkanediamine modified GO as a precursor followed by a second step of aldehyde-amine condensation reaction yielding imine as a route to prepare graphene-based functional materials via a two-steps organic reactions route has not been reported, which renders it possible to attach various robust molecules onto GO. Herein, two kinds of graphene-based functional systems, consisting of GO functionalized with either porphyrin or

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A major and common obstacle in handling graphene-based materials is their low dispersibility due to its tendency to undergo aggregation in common solvents. As a result, the strong π - π interactions between the individual sheets renders the material's

ferrocene, have been prepared via a two-steps organic reaction combining nucleophilic addition and imine chemistry.^[42] An in-depth characterization of the two hybrid systems has been carried out by means of various spectroscopic and microscopic techniques. The application of reduced ferrocene modified GO in high-performance supercapacitors was also demonstrated.

Results and Discussion

GO covalently functionalized with either porphyrin or ferrocene was prepared by means of a two-steps reaction portrayed in Scheme 1. In the first step ethylenediamine was reacted with GO; this involves the ring opening reaction of epoxy units on GO by reacting with the -NH_2 group of ethylenediamine, and also Schiff-base chemistry between the ketone groups on GO and the -NH_2 group of ethylenediamine. The short backbone of the ethylenediamine was chosen to avoid occurrence of back-folding, i.e., to have the two amino groups of an individual molecule covalently binding the same GO sheet. Furthermore, compared with aromatic diamines, ethylenediamine possesses a higher reactivity (more nucleophilic) towards the oxygen functional groups (epoxyl, carbonyl) on GO, moreover it does not undergo polymerization in the presence of GO.

In the second step Schiff-base chemistry of the -NH_2 group on ethylenediamine modified GO reacting with porphyrin-CHO/ferrocene-CHO takes place. In order to prove the covalent attachment of porphyrin/ferrocene to GO, control experiments were carried out by reacting ethylenediamine modified GO with porphyrin/ferrocene not exposing a -CHO sidegroup.

Scheme 1. Scheme of preparation of functionalized graphene derivatives using a two step reaction approach. In the first step, the addition of ethylenediamine to GO yields both ring opening reaction of epoxy groups on GO by reacting with the -NH_2 group of ethylenediamine, and also Schiff-base chemistry between the ketone groups on GO and the -NH_2 group of ethylenediamine. In the second step, the -NH_2 group on ethylenediamine modified GO was further reacted with porphyrin-CHO or ferrocene-CHO to obtain porphyrin/ferrocene modified GO. Control experiments were performed by reacting ethylenediamine modified GO with porphyrin/ferrocene without a -CHO group.

2.1. Ethylenediamine modified GO

In the first step, GO (40 mg) was reacted with ethylenediamine molecules (500 mg) in a mixture of ethanol/water (1:1 in vol., 80 ml) at room temperature for 24 h. The solid was washed with a copious amount of DMF and ethanol in order to remove the unbound ethylenediamine molecules completely (see the

experimental section for further details). The as-obtained ethylenediamine modified GO was characterized by several spectroscopic techniques. The chemical functionalization of GO with ethylenediamine was firstly proved by Fourier-transform infrared spectroscopy (FTIR) measurement (Figure 1a). The FTIR spectrum of the pristine GO displays features at 1731, 1620, 1223 and 1047 cm^{-1} which can be ascribed to C=O , C=C , C-OH and C-O-C (epoxy) stretching, respectively.^[40] The feature at 1409 cm^{-1} can be attributed to CO-H bending (deformation vibration). After reacting GO with ethylenediamine molecules, the band associated to the epoxy groups of GO at $\approx 1047\text{ cm}^{-1}$ disappears, whereas a new band at 1033 cm^{-1} emerges which can be attributed to the formation of C-N bond. Moreover, the signal coming from the carbonyl groups of GO largely reduces, most likely because of the formation of imines through the condensation reaction between carbonyl and free amine moieties.^[43] The new band emerging at 1635 cm^{-1} is due to the overlap of C=N and C=C bonds. The formation of the C-N band together with a much weaker carbonyl band, both clearly indicate the successful covalent functionalization of GO by ethylenediamine molecules. Figure 1b shows the UV/Vis absorption spectra of both GO and ethylenediamine modified GO in water. The pristine GO exhibits an absorption peak at ca. $\lambda = 230\text{ nm}$ (due to the $\pi\text{-}\pi^*$ transition of C=C), with an additional shoulder peak at $\approx 304\text{ nm}$, which can be ascribed to the $\text{n-}\pi^*$ transition of the C=O moiety.^[44] Conversely, in the ethylenediamine modified GO, the absorption peak is red-shifted to $\lambda = 234\text{ nm}$. Such a shift provides evidence for the occurrence of some chemical reduction during the reaction, i.e., the electronic conjugation in GO is to a certain extent restored.^[45] Raman spectroscopy has been widely employed for the characterization of graphitic materials. The Raman spectrum of GO powders (Fig. 1c) shows a disorder band (D band) and an in-plane vibration of sp^2 carbon lattice (G band) at ≈ 1345 and 1598 cm^{-1} , respectively, with an $\text{I}_\text{D}/\text{I}_\text{G}$ ratio of ≈ 0.8 .^[40] The comparison of the Raman spectrum of pristine with the one of the ethylenediamine functionalized GO, revealed that the latter displays an increased D/G ratio (≈ 0.9), in line with the chemical reduction of GO during the ethylenediamine grafting evidenced by the red-shift of the UV absorption peak at $\approx 230\text{ nm}$. X-ray Diffraction (XRD) was also conducted for both pristine GO and ethylenediamine modified GO in powder form. A sharp peak at $\approx 11.6^\circ$ is observed for GO (Figure 1d), indicating an interlayer spacing of 0.76 nm attributed to the (002) reflection of the stacked GO sheets, similar to the values reported previously.^[43, 46] On the other hand, the ethylenediamine modified GO does not display any obvious peak, providing evidence for its more amorphous/disordered structure.

Figure 1. (a) FTIR, (b) UV/Vis, (c) Raman, and (d) XRD characterization of GO and ethylenediamine modified GO.

X-ray Photoelectron Spectroscopy (XPS) offers insight into the surface elemental compositions and chemical bonding configurations. Figure 3 displays the N1s XPS spectra of both GO and ethylenediamine modified GO. Pristine GO exhibits mostly noisy N1s spectrum, indicating a negligible nitrogen content (Figure 2a). In contrast, the N1s spectrum of ethylenediamine modified GO displays an increase of the nitrogen content, up to 5.2%, being higher than the case of GO reacting with benzidines under the same reaction conditions ($\approx 3.1\%$),^[43] also higher than triethylene glycol amine modified GO ($\approx 1.9\%$).^[47] Furthermore, two peaks can be deconvoluted in the N1s spectrum (Figure 2b): the former at ≈ 399 eV can be assigned to C-N, and the latter one at ≈ 401 eV can be attributed to the formation of imine bonds.^[43] From the content of nitrogen and carbon in the XPS spectra (Table S1) it was possible to estimate the degree of functionalization, being ca. one ethylenediamine moiety each 12 carbon atoms of the GO scaffold, thus being over two times higher than the case of GO reacting with benzidines under the same reaction conditions ($\approx$ each 30 carbon atoms of the GO scaffold),^[43] and also higher than triethylene glycol amine modified GO ($\approx$ each 31 carbon atoms of the GO scaffold).^[47] The high degree of functionalization of the ethylenediamine modified GO during the first step reaction renders the possibility of attaching more functional molecules in the following second step reaction.

Figure 2. XPS N1s spectra of (a) pristine GO, and (b) ethylenediamine modified GO.

The thermal stability of both GO and ethylenediamine modified GO was studied by Thermal Gravimetric Analysis (TGA). Figure S1 reveals that GO displays a weight loss of $\approx 13\%$ at $T < 100$ °C due to the desorption of water residues, a weight loss of $\approx 25\%$ at T ranging between 150 and 200 °C, which can be attributed to the release of labile oxygen functional groups, and a final residual mass of $\approx 37\%$ at 800 °C. In contrast, ethylenediamine modified GO displays a weight loss of $\approx 10\%$ at $T < 100$ °C, a further weight loss of $\approx 16\%$ between 150 and 200 °C, with an overall residual mass of $\approx 43\%$ at $T = 800$ °C. Therefore, ethylenediamine-GO hybrids exhibits a greater thermal stability than pristine GO.

Figure 3. Topographical AFM images recorded in intermittent contact mode and measured thickness of (a) pristine GO, and (b) ethylenediamine modified GO. The increase in the thickness of ethylenediamine modified GO indicates the successful functionalization of GO.

The morphology of isolated flakes of both GO and ethylenediamine modified GO was explored by Atomic Force Microscopy (AFM) imaging in intermittent contact mode. Figure 3a reveals that GO possesses a thickness of $\approx 0.8 \pm 0.1$ nm due to the presence of oxygen functional groups, suggesting its single-layer nature.^[40, 43] For ethylenediamine modified GO, the measured thickness is $\approx 1.2 \pm 0.1$ nm (Figure 3b), thus displaying average increase of 0.4 nm which can be attributed to the chemical attachment of ethylenediamine moiety onto GO. A similar increase in the height profile has been also observed in both chemically modified GO and other chemically functionalized graphene systems.^[48-50] The morphology of ethylenediamine modified GO was further studied by both TEM (Figure S2b) and SEM (Figure S3). TEM study indicates very thin flake structures of ethylenediamine modified GO. SEM measurement of ethylenediamine modified GO in the solid state shows some flake features. The presence of nitrogen element was also confirmed by EDX mapping (Figure S3). Overall, the successful modification of GO with ethylenediamine represented an essential prerequisite: such a hybrid system was used as intermediate for the functionalization of GO with specific functional moieties. Towards this end, as prototypical functional units we have focussed our attention on porphyrin and ferrocene.

Porphyrin is a common photoactive molecule which has been widely used in catalysis, sensing, biomedical, energy and optical related applications.^[51-55] Conversely, ferrocene is a well-known redox-active molecule, which has been shown to represent a suitable building block for applications in sensing, and electrochemically switchable devices and memories, etc.^[56, 57]

2.2. Porphyrin modified GO

Chemical modification of graphene with porphyrin can generate interesting donor/acceptor hybrid systems for energy conversion and storage, and optoelectronic devices.^[58, 59]

In the second step of the reaction, ethylenediamine modified GO (20 mg) was further reacted with porphyrin-CHO (30 mg) in ethanol (40 ml) at 80 °C for 24 h, using Schiff-base chemistry (see the experimental section for details). To further prove the covalent grafting of porphyrin onto GO to form the hybrid system, a control experiment was conducted by reacting ethylenediamine modified GO (20 mg) with porphyrin (30 mg) not exposing a -CHO group (control 1) in ethanol (40 ml). For both porphyrin modified graphene and the control 1, a copious amount of DMF and ethanol was employed to wash the solid sample until no obvious absorption peaks of porphyrin were observed in the supernatant (monitored by UV/Vis absorption), indicating the physisorbed porphyrin molecules were successfully removed in both cases.

Figure 4. Spectroscopic characterization of porphyrin modified GO. (a) UV/Vis absorption spectra of porphyrin-CHO, porphyrin modified GO and control 1. (b) FTIR spectra of porphyrin-CHO, porphyrin modified GO. The spectrum of ethylenediamine modified GO was displayed for comparison. (c) N1s XPS spectra of porphyrin modified GO.

Figure 4a displays the UV/Vis absorption spectra of porphyrin-CHO, porphyrin modified GO and control 1 in ethanol. Porphyrin-CHO exhibits a typical Soret band at 415 nm, with additional Q bands at longer wavelengths. Porphyrin modified GO possesses a broad peak at 425 nm, assigned to the absorption of porphyrin in the hybrid material. Due to the strong light scattering of graphene, the Q bands in the hybrid system are hardly observed. Conversely, in the control 1, neither the

Soret band nor Q bands can be observed in the absorption spectrum, thereby providing strong evidence that porphyrin molecules are indeed covalently attached onto GO in the GO-porphyrin hybrid system. Moreover, the shift of the Soret band in the hybrid system relative to the one of porphyrin-CHO indicates the existence of some electronic interactions between graphene and porphyrin. The presence of porphyrin in the hybrid system was further characterized by FTIR (Figure 4b). Compared with ethylenediamine modified GO, the porphyrin-GO hybrid shows some additional features between 1000 and 1500 cm^{-1} (for example at 1153, 1207, 1446 cm^{-1}), coming from the porphyrin molecules. The XPS N1s spectra of porphyrin modified GO can be also deconvoluted to two peaks at ≈ 399 (C-N) and 401 eV (C=N), respectively (Figure 4c).^[43] It should be noted that the relative ratio of the two peaks in the hybrid material changes to 2.7:1 when compared to the case of ethylenediamine modified GO (3.7:1), due to the formation of new C=N bonds between GO and porphyrin during the second step reaction. Based on the XPS measurement (Table S1), the degree of functionalization for porphyrin modified GO was calculated as one porphyrin unit each 34 carbon atoms of the GO scaffold. This value is much higher than the porphyrin modified reduced GO using a Suzuki coupling reaction,^[60] and porphyrin modified liquid phase exfoliated graphene via cycloaddition reactions,^[59] which exhibited one porphyrin unit each ≈ 400 and 240 carbon atoms, respectively.

Figure 5. Fluorescence emission and fluorescence lifetime measurement of porphyrin-CHO and porphyrin modified GO. (a) UV/Vis absorption spectra of porphyrin-CHO and porphyrin modified GO. The absorbance of the Soret band was kept the same for the two samples, before subjected to fluorescence measurement. (b) Fluorescence emission measurement of porphyrin-CHO and porphyrin modified GO. The absorbance of porphyrin was maintained the same, as shown in Figure 5a. Fluorescence lifetime measurement of (c) porphyrin-CHO, and (d) porphyrin modified GO.

The mutual electronic interaction between graphene and porphyrin in the excited state was further studied by fluorescence spectroscopy. Before the fluorescence measurement, the absorbance of the Soret band in the porphyrin-CHO was

maintained the same as porphyrin modified GO (Figure 5a). When excited with a wavelength of 405 nm, the free porphyrin-CHO shows two intense fluorescence peaks at 606 and 653 nm (Figure 5b). In contrast, the porphyrin-GO hybrid displays an obvious reduction in the intensity of fluorescence (Figure 5b). The same trend was also observed for the fluorescence quantum yield, amounting to 5% and 0.2% for porphyrin-CHO and porphyrin modified GO, respectively (Table S2). Fluorescence lifetime measurements were also performed for both porphyrin-CHO and porphyrin modified GO. The fluorescence lifetime for porphyrin-CHO amounts to 1.93 ns (Figure 5c), while it largely reduces to ≈ 0.21 ns for porphyrin modified GO (Figure 5d). Fluorescence emission, quantum yield and fluorescence lifetime measurement, all together indicate that there is a strong electronic cross-talk between GO and porphyrin in the hybrid system.

The morphology of porphyrin-GO hybrid was also investigated by TEM (Figure S2c) and SEM (Figure S4). As in the case of GO and ethylenediamine modified GO, for porphyrin modified GO, TEM measurement again shows very thin flake features (Figure S2c). SEM measurement displays the morphology of porphyrin modified GO in the solid state form, with some flake like structures visible. EDX mapping proves the presence of nitrogen in the hybrid system (Figure S4). When compared with GO and ethylenediamine modified GO, the porphyrin modified GO exhibits a higher thermal stability. The hybrid material shows a weight loss of $\approx 7\%$ at $T < 100^\circ\text{C}$, a weight loss of $\approx 10\%$ at T ranging between 110 and 225°C , followed by a further weight loss of $\approx 20\%$ until $T \approx 550^\circ\text{C}$, with an overall residual mass of $\approx 57\%$ at $T = 800^\circ\text{C}$ (Figure S1).

2.3. Ferrocene modified GO

Hybrid system consisting of graphene and ferrocene can combine the double electric double-layer capacitance from the former and pseudo-capacitance from the latter. Therefore, ferrocene modified GO can be potentially used as electrode materials for energy storage.

In order to demonstrate the wide applicability of the proposed reaction scheme, ferrocene was also chemically attached onto ethylenediamine modified GO using the same chemical approach. Briefly, ethylenediamine modified GO (20 mg) was reacted with ferrocene-CHO (80 mg) in ethanol (40 ml) at 80°C for 24 h. Importantly, a control experiment was also performed by reacting ethylenediamine modified GO (20 mg) with ferrocene not exposing a $-\text{CHO}$ group (control 2) in ethanol (40 ml). For both ferrocene modified GO and the control 2, a copious amount of DMF and ethanol were employed to wash the solid sample until no obvious absorption peaks of ferrocene can be observed in the supernatant (monitored by UV/Vis absorption), indicating the physisorbed ferrocene molecules were successfully removed in both cases. The UV-vis spectra in Figure 6a show that ferrocenecarboxaldehyde exhibits absorption peaks at 269, 340 and 462 nm . A small shoulder peak at $\approx 380\text{ nm}$ is observed in ferrocene modified GO, which is attributed to the absorption of the ferrocene moiety. In contrast, the control 2 sample, obtained by combining ethylenediamine modified GO with ferrocene not exposing an aldehyde group, does not exhibit such a spectral feature. The presence of ferrocene in the hybrid system is further confirmed by cyclic voltammetry (CV) measurement (Figure 6b). Ferrocenecarboxaldehyde (Ferrocene-CHO) displays the typical two redox peaks of ferrocene, at 0.65 and 0.73 V , respectively. For ferrocene modified GO, the CV curve shows two broaden redox peaks at ≈ 0.54 and 0.62 V , respectively, attributing to the ferrocene molecules. The broadening and shift of the two peaks in the hybrid material might be due to the interaction between ferrocene and graphene. Again, the control 2 does not exhibit any features of ferrocene in its CV curve. Furthermore, the XPS analysis reveals the presence of the $\text{Fe}2\text{p}$ signals ($\text{Fe}2\text{p}_{1/2}$ and $\text{Fe}2\text{p}_{3/2}$) in ferrocene modified GO while such a signal has not been observed in the control 2 (Figure 6c). By and large, UV/Vis, CV and XPS analysis indicates that ferrocene is indeed covalently attached onto graphene in the hybrid GO-ferrocene system. The morphology of ferrocene modified GO was also studied by TEM (Figure S2d) and SEM (Figure S5). Similar to GO and ethylenediamine modified GO, TEM measurement performed on ferrocene modified GO again shows very thin flake features (Figure S2d). SEM measurement reveals that the morphology of ferrocene modified GO in the solid state consists of flake like structures. EDX mapping of the hybrid material further confirms the presence of N and Fe elements (Figure S5). It is worth to mention that, compared with GO, ethylenediamine modified GO and porphyrin/ferrocene modified GO did not display obvious change in their morphology during the wet chemical functionalization process (Figure S2).

The XPS $\text{N}1\text{s}$ spectrum of ferrocene-GO hybrid can also be deconvoluted to two peaks: the peak at $\approx 399\text{ eV}$ is assigned to N-C, while the other one at about 401 eV can be attributed to imine bonds (Figure 6d).^[43] Based on the content of carbon and iron in the hybrid material, the degree of functionalization was estimated being one ferrocene moiety each 77 carbon atoms of the GO platform. The degree of functionalization varies when different reagents are used in the second-step reaction, depending on their reactivity.

Figure 6. (a) FTIR, (b) UV/Vis, (c) Raman, and (d) XPS characterization of GO and ethylenediamine modified GO.

The presence of ferrocene in ferrocene modified GO was further confirmed by FTIR (Figure 7a). Compared with ethylenediamine modified GO, the ferrocene modified GO exhibits some additional bands in the range of 1500 and 650 cm^{-1} (for example at 1157, 1373, 1435 cm^{-1}), which are also observed in the starting material of ferrocene-CHO, thus indicating that it can be ascribed to the ferrocene moiety. Raman measurement was also conducted for ferrocene modified GO (Figure 7b). When compared with the one of ethylenediamine modified GO (0.9), ferrocene modified GO displays an increased D/G ratio (1.04), indicating the occurrence of a chemical reduction during the reaction. Such a result is also in agreement with the TGA measurement (Figure S1). Similar to porphyrin modified GO, the ferrocene modified GO also features a greater thermal stability compared to ethylenediamine modified GO and pristine GO. The hybrid material shows a weight loss of $\approx 5\%$ at $T < 100^\circ\text{C}$, a second stage weight loss of $\approx 10\%$ at T ranging between 110 and 225°C , followed by a further weight loss of $\approx 15\%$ until $T \approx 460^\circ\text{C}$, with an overall residual mass of $\approx 64\%$ at $T = 800^\circ\text{C}$ (Figure S1).

Figure 7. Characterization of ferrocene modified GO. (a) FTIR spectra of ferrocene-CHO, ethylenediamine modified GO (for comparison) and ferrocene modified GO. (b) Raman spectra of ethylenediamine modified GO (for comparison) and ferrocene modified GO.

Standard four-point probe measurements revealed that the ferrocene modified GO possess an electrical conductivity of $\approx 0.4 \text{ S m}^{-1}$, which is at least four orders of magnitude higher than the one of pristine GO (10^{-8} – 10^{-5} S m^{-1}).^[61] Such a conductivity is however not sufficient for the direct use of ferrocene modified GO as electrode materials in high performance supercapacitors. The hybrid was therefore chemically reduced with hydrazine, yielding an increased electrical conductivity up to 146 S m^{-1} . Such reduced ferrocene modified GO hybrid was directly exploited as electrode materials for supercapacitors. For comparison, the control 2 sample was also chemically treated with hydrazine (with an electrical conductivity of 201 S m^{-1}) and further used as electrode materials for supercapacitors.

Figure 8. Supercapacitor performance of reduced ferrocene modified GO using a two-electrode configuration. (a) Galvanostatic charge/discharge curves at a current density of 1 A g^{-1} . (b) Nyquist plots. (c) Zoom-in view at high frequency range of Nyquist plots. (d) Cycle stability of Galvanostatic charge-discharge at a current density of 1 A g^{-1} over 5000 cycles.

Currently, it is highly recommended and desired to use two-electrode system for supercapacitors measurement, as it reflects the true performance of devices.^[23] The performance of the supercapacitor based on reduced ferrocene modified GO electrodes was determined in a two-electrode configuration in 6 M KOH. Figure 8a depicts the galvanostatic charge/discharge curve of reduced ferrocene modified GO at a current density of 1 A g^{-1} between 0 and 1 V, in which the specific capacitance was calculated as $\approx 127 \text{ F g}^{-1}$. The value is higher than the previous examples of graphene/polyaniline^[62] ($\approx 100 \text{ F g}^{-1}$) and graphene/polypyrrole^[63] ($\approx 95 \text{ F g}^{-1}$) at the same current density also performed under a two-electrode condition. Furthermore, the reduced control 2 sample only shows a specific capacitance of 96 F g^{-1} (Figure S7). Obviously, the surface chemistry of GO plays an important role in determining the electrochemical performance of the electrode materials for supercapacitors. In the case of reduced ferrocene modified GO, the introduction of ferrocene units can contribute to the pseudo-capacitance of the device, thereby leading to an outperformed electrochemical capability compared with the reduced control 2 sample.

Electrochemical impedance spectroscopy (EIS) is widely used to measure the response of an electrochemical cell to a low amplitude perturbation as a function of frequency. EIS was conducted for reduced ferrocene modified GO from 0.01 to 100 kHz, as plotted in the Nyquist plot (Figure 8b). At lower frequencies, the impedance spectrum is a straight line showing a slope of 45° , which is related to a diffusion control process. At higher frequencies closed to 100 kHz (Figure 8c), by reading the real axis value of intercept on the X-axis, the solution resistance of the electrolyte amounts to $0.92\ \Omega$. The other intercept point of the semicircle on the X-axis is equal to the sum of solution resistance (R_s , also referred as uncompensated solution resistance) and charge transfer resistance (also named as polarization resistance, R_{ct}). The diameter of the semicircle stands for charge transfer resistance, which is $\approx 0.49\ \Omega$. The low ohmic solution resistance and charge transfer resistance are beneficial to the final electrochemical performance of supercapacitors. Long term cycle stability is also required for practical applications of supercapacitors, and was performed via Galvanostatic charge–discharge cycles at a current density of $1\ \text{A g}^{-1}$. After 5000 cycles, $\approx 93\%$ of the initial specific capacitance was retained (Figure 8d), providing unambiguous evidence for its long-term stability and reversibility as working electrode materials in supercapacitors.

The high specific capacitance of reduced ferrocene modified GO could be due to the synergistic effect of graphene and ferrocene. The redox process of ferrocene, and also the possible charge transfer process between ferrocene and graphene, both can contribute to the enhanced electrochemical performance compared with the reduced control 2 sample.

Conclusions

In summary, we have devised a novel modular approach to produce covalent GO-based functional hybrid systems. Our synthetic strategy consists in the reaction of ethylenediamine with GO, followed by the use of Schiff-base chemistry to tether aldehyde exposing functional molecules towards this scaffold. As model systems, two prototypical functional moieties such as the photoactive porphyrins and redox active ferrocenes possessing reactive $-\text{CHO}$ groups were chosen. The multiscale properties of the hybrid materials were explored by UV/Vis, XPS, FTIR, TGA, Raman and FL spectroscopy, QYs/lifetime, CV, XRD, AFM, TEM and SEM/EDX. The degree of functionalization can be up to each 34 and 77 carbon atoms possessing one porphyrin/ferrocene unit for porphyrin/ferrocene modified GO, respectively, which is much higher than similar systems using established chemical approaches. For the first time, the reduced form of ferrocene modified GO was employed as electrode materials in supercapacitors, showing a specific capacitance of $127\ \text{F g}^{-1}$ at a current density of $1\ \text{A g}^{-1}$, combined with excellent cycle stability over 5000 cycles. Our novel synthetic approach is simple, and of general applicability for attaching functional moieties to GO, thus largely broadening graphene based systems. This study will also help to better understand the structure (surface chemistry) and (electrochemical) property

relationship. It can be expected that, due to the large amount of functional units available, whose properties can be combined with the unique features of graphene using our approach to fabricate novel graphene based multifunctional hybrids for specific applications in solar cells, catalysis, energy conversion and storage.

Experimental Section

Characterization: UV/Vis spectra were performed on a JASCO V-670 UV/Vis Spectrometer. Fourier Transform Infrared Spectroscopy (FTIR) were recorded using a Thermo Scientific Nicolet 6700 FTIR Spectrometer equipped with a Smart Orbit accessory. Transmission electron microscopy (TEM) measurement was carried out using a Philips CM120 (120 kV). Scanning electron microscope (SEM) was performed on an FEI Quanta 250 FEG instrument. Atomic force microscopy (AFM) was conducted on a Veeco Dimension 3100 operating on a Nanoscope IV control unit. Raman spectra were recorded on a Renishaw setup (excitation at 532 nm). Thermal gravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA851e system under N_2 atmosphere. Wide-angle X-ray scattering (WAXS) was conducted on a SAXSess X-Ray Scattering instrument (Anton Paar GmbH, Austria). X-ray photoelectron spectrometer (XPS) measurement was performed on a Thermo Scientific K-Alpha instrument. Fluorescence measurement was recorded on a Cary Eclipse Fluorescence Spectrophotometer. Fluorescence lifetime was measured using time-correlated single photon counting (TCSPC) module (PicoQuant PicoHarp 300). Quantum yield was determined using 5,10,15,20-Tetraphenylporphyrin (TPP) in ethanol as a standard/reference. Electrochemical measurements were conducted using a PGSTAT204 instrument (Autolab). The electrodes for supercapacitor measurement were fabricated by mixing reduced ferrocene modified GO with carbon black and PTFE.

Materials: Graphene oxide (Graphenea, $4\ \text{mg ml}^{-1}$ in water), ethylenediamine ($\geq 99\%$, Sigma-Aldrich), ferrocenecarboxaldehyde (98% , Sigma-Aldrich), and ferrocene (98% , Sigma-Aldrich) were used as received without any further purification. Porphyrin-CHO (TPP-CHO) and TPP were synthesized according to literature procedures.^[64]

Ethylenediamine modified GO: GO ($40\ \text{mg}$) in water ($40\ \text{mL}$) and ethylenediamine ($500\ \text{mg}$) in ethanol ($40\ \text{mL}$) were physically mixed, and the reaction mixture was reacted at room temperature for 24 h. Then the reaction mixture was centrifuged and washed with a large amount of DMF and ethanol to completely remove the unreacted ethylenediamine molecules. Finally, the sediment was further dried to obtain the desired product.

Porphyrin/ferrocene modified GO hybrid systems: ethylenediamine modified GO ($20\ \text{mg}$) and TPP-CHO ($30\ \text{mg}$)/ferrocenecarboxaldehyde ($80\ \text{mg}$) were reacted in ethanol ($40\ \text{mL}$) at 80°C for 24 h. Then the reaction mixture was centrifuged and washed with a large amount of DMF and ethanol to completely remove the unreacted TPP-CHO/ferrocenecarboxaldehyde until no obvious absorption peaks of porphyrin/ferrocene were observed for the supernatant (monitored by UV/Vis absorption). Finally, the sediment was further dried to obtain the desired product.

Control samples: in order to prove the covalent linkage between porphyrin/ferrocene and GO in porphyrin/ferrocene modified GO, control experiments were also performed. Ethylenediamine modified GO ($20\ \text{mg}$) and TPP ($30\ \text{mg}$)/ferrocene ($80\ \text{mg}$) were reacted in ethanol ($40\ \text{mL}$) at 80°C

°C for 24 h. The workup procedure was the same as the above hybrid systems. The obtained sample using TPP and ferrocene was named as control 1 and control 2, respectively.

Chemical reduction of ferrocene modified GO/control 2: Ferrocene modified GO or control 2 sample was reacted with hydrazine at 80 °C for 24 h. The obtained solid sample was dried in vacuum and employed directly as the electrode material for supercapacitor measurement.

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Keywords: Graphene oxide • functionalization • nucleophilic addition • imine chemistry • supercapacitors

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