Localized Reduction of Graphene Oxide by Electrogenerated Naphthalene Radical Anions and Subsequent Diazonium Electrografting

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S *Supporting Information*

ABSTRACT: Herein, we describe a new localized functionalization method of graphene oxide (GO) deposited on a silicon oxide surface. The functionalization starts with the reduction of GO by electrogenerated naphthalene radical anions. The source of reducers is a microelectrode moving close to the substrate in a typical scanning electrochemical microscopy (SECM) configuration. Then, the recovery of electronic conductivity upon reduction enables the selective electrochemical functionalization of the patterns. The illustrative example is the electrografting of reduced-GO with a diazonium salt bearing a protonated amino group that can further immobilize gold nanoparticles by simple immersion. This study opens new routes for the construction of multifunctional patterned surfaces.

Graphene and graphene analogues such as GO or reduced-GO (r-GO) are attracting increasing attention from the scientific community. These materials have outstanding properties, so many potential applications in the fields of electronics, sensors, catalysis, and energy storage are being considered.[1]

GO combines several advantages such as availability in large quantity, low cost, and easy processability.[1c,2] However, contrary to graphene, GO is electronically insulating and has to be reduced into a conductive material.[3] Presently the most effective and widespread chemical reduction procedures consist in the exposition of the substrate to hydrogen iodide (HI)[4] or hydrazine.[3a] Developing localized reduction or functionalization procedures is an important field of research, as this approach would open the way to several applications in electronics or sensing.[2a] In the literature, localized reduction procedures have been proposed with physical reduction methods, either with a femtosecond laser[5] for micrometric modifications or using an AFM probe to locally heat the substrate.[6]

Scanning electrochemical microscopy (SECM) is an electroanalytical technique that involves the displacement of a microelectrode close to the studied surface. It is more and more commonly used for the local characterization of interfaces both at the nano- and micrometric scales.[7] Yet SECM and derived (like scanning electrochemical cell microscopy) methods are also useful techniques for local surface

modifications,[8] all the more as fast lithographic protocols have been developed.[9] To the best of our knowledge, SECM has never been used to modify a GO covered substrate, despite the fact that chemical reduction by SECM holds great potential for (i) the electrochemical activation of the reaction without contact and (ii) the local and fast modification of GO films at different scales by adjusting the SECM parameters (electrode diameter, displacement speed, etc).

The present work introduces a SECM-based local functionalization of thin (2−3 nm) GO films, made following a recently developed transfer technique.[10] The whole procedure involves two independent steps: a localized reduction followed by a selective electrografting. The reduction process, adapted for the first time to GO, is based on the electrogeneration of naphthalene radical anions by the SECM microelectrode placed in the vicinity of the substrate. The possibility to localize the reduction at different length scales is confirmed by the use of different electrode sizes. The localized reduction is associated with the formation of conductive r-GO patterns that can be further electrografted. This is illustrated by the grafting of a diazonium derivative bearing an ammonium group. This function is able to immobilize negatively charged gold nanoparticles through electrostatic interactions. The study highlights the potential of SECM as a tool for versatile surface functionalizations and opens the way to new modifications of GO at various scales.

For the local reduction of GO, we adopted a strategy similar to the one used to pattern substrates covered with fluorinated polymers[8e,11] or perfluoroalkylsilanes monolayers.[12] The principle of the experiment is presented in Figure 1a. The GO-covered substrate was immersed in a solution containing naphthalene. The electrode was then positioned in its vicinity and biased at a highly reductive potential (−2.6 V vs SCE). The reduction of naphthalene ($E° = −2.44$ V vs SCE)[11] at the electrode generated radical anions that diffused from the microelectrode to the surface and reduced the GO thin layer. Naphthalene was chosen among several polyaromatic organic compounds for its highly negative reduction potential, which makes the generated radical anion very reactive.[11]
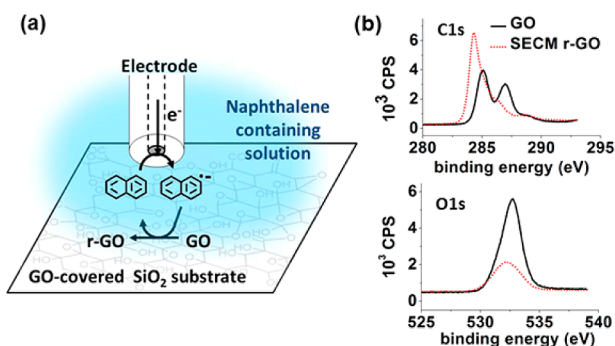
Figure 1. (a) Schematic view of the GO reduction procedure using electrogenerated radical anions. (b) Impact of the reduction on the C1s and O1s XPS signatures.

The r-GO material was analyzed by conventional surface characterization techniques, namely, XPS and four-probe resistivity measurements. For this purpose, conditions adapted to the reduction of large areas were first chosen: an electrode of 125 μm in radius (r_{tip}) was fixed at 100 μm above the GO-covered substrate. The electrode was then negatively polarized during 5 min, leading to a modified area of about 2 mm^2. This experiment was repeated several times (the tip was moved between each reduction step) in order to obtain a modified area of about 1 cm^2. As in this part of the study the GO-covered substrate was a transparent slide of quartz, the modification could be visualized through a decrease of the transparency of the reduced zone, in accordance with literature.[13] Four-probe measurements showed that the surface resistivity of the modified area dropped from an unmeasurable value (i.e., in the TΩ/sq range) to about 800 kΩ/sq. Such a resistivity is about 10 times higher than that obtained with the optimized chemical reduction (exposition to HI during 1 h) applied to a similar GO-covered substrate (60 kOhm/sq). The XPS analysis is presented in Figure 1b. The Figure displays the C1s and O1s spectra of a modified and an unmodified area on the same substrate. First, in GO, the carbon signal appears at high binding energy, corresponding to oxidized functions such as epoxy, hydroxyl, carbonyl or carboxyl. The sp^2 contribution (near 284 eV) is indeed almost inexistent. Conversely, the apparition of a dominant peak at a binding energy of 284.2 eV after exposition to the electrogenerated naphthalene radical anions proves that the treatment partially restored aromatic carbons within the GO structure. Furthermore the O1s signal shows that the modification is associated to a clear decrease of the amount of oxygen. These XPS results are in accordance with the literature on GO- and r-GO-covered substrates.[14] Quantitatively the O/C ratio corrected from the contribution of the underlying SiO$_2$ contribution goes from about 35% for GO to 8.5% after reduction (see calculation details in the Supporting Information). This proves that exposition to radical naphthalene anions unambiguously leads to the local formation of r-GO areas. During the reduction, the breaking of the C–O bonds proceeds probably similarly as for a direct electro-chemical reduction of GO,[13] but with the naphthalene radical anion as the electron supplier.

A very powerful advantage of the proposed reduction procedure is the possibility to tune the size and geometry of the reduced zone. Several experimental parameters impact the spatial distribution of the modification as previously discussed on self-assembled monolayers.[15] Here, we present the effect of the electrode size and displacement speed on the size of the

r-GO patterns. For this purpose, the increase in electronic conductivity expected from the reduction of GO was evaluated at a local scale. The same experimental setup was used, with the microelectrode serving as a local probe of the conductivity.[16] Briefly, the measurement of the current associated to a redox mediator such as ferrocene provides information on the local conductivity of the substrate via a feedback loop between the probe and the substrate. Figure 2a,b display SECM images
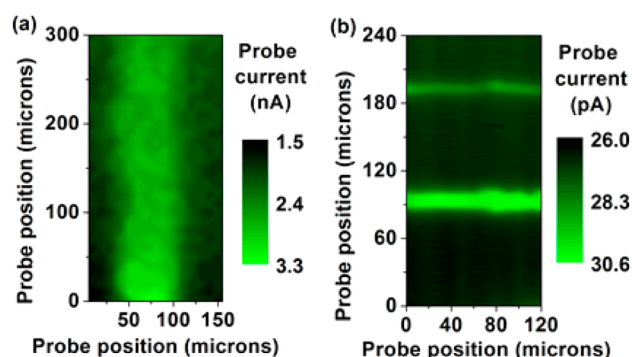

Figure 2. SECM images of a r-GO with [Fc] = 1 mM. (a) r_{tip} = 5 μm, $d_{tip-substrate}$ = 10 μm, displacement speed during reduction 1000 μm/s, and [Naphthalene] = 80 mM. (b) r_{tip} = 500 nm, $d_{tip-substrate}$ = 3 μm, displacement speed during reduction 400 μm/s (top) and 100 μm/s (bottom). [Naphthalene] = 25 mM.

obtained after reduction with a moving microelectrode (Figure 2a, electrode radius: 5 μm) or submicrometric electrode (Figure 2b, electrode radius: 500 nm). The width of the resulting conducting lines is about 50 μm for the 5 μm electrode (Figure 2a), and 8 ± 3 and 18 ± 5 μm, depending on the displacement speed (respectively 400 and 100 μm/s) for the 500 nm electrode (Figure 2b). First this shows that small microelectrodes improve the spatial resolution of the modification, provided that the decrease of the electrode size is accordingly accompanied by a decrease of the electrode–substrate distance. Second, Figure 2b demonstrates that a higher scanning rate permits to narrow the width of the reduced lines. Very high displacement speeds are thus desirable, all the more as they decrease the processing duration. In summary the results presented in Figure 2 illustrate the versatility of the proposed procedure for the tuning of the spatial distribution of the reduction. In addition, a lower naphthalene concentration can be used to further decrease the spatial extension of the modifications. This paves the way for nanometer-scale reduction of GO.

In a final step, we show that the local increase in conductivity, associated to the modification of GO into r-GO, permits a selective diazonium electrografting. The electro-grafting of a diazonium derivative is a well-established procedure enabling the introduction of a wide variety of chemical functions, with a covalent binding to the grafted surface.[17] For this purpose, a r-GO line generated according to the procedure described above was first connected with a gold electrode using mask evaporation. The result is displayed in the SEM image presented in Figure 3a. The measurement of the current–voltage relationship between two consecutive gold electrodes lead to a resistance of about 1 MΩ/sq, more than 5 orders of magnitude lower than the resistivity of unmodified GO. The localized electrografting of the diazonium derivative was then performed using the connected r-GO line as working
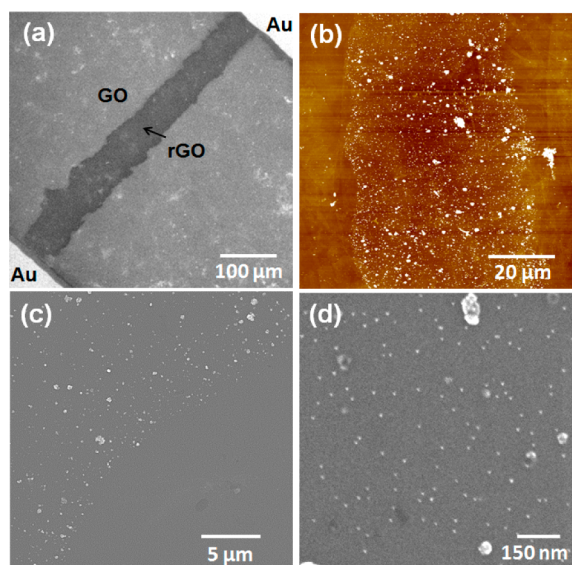
Figure 3. (a) SEM image (0.5 kV) of a reduced line between two gold connection lines obtained after a displacement at 50 μm/s with a microelectrode having a radius of 5 μm, placed at about 10 μm from the substrate. [Naphthalene] = 50 mM. AFM image (b) and SEM at 30 kV images (c,d) obtained after electrografting of 4-amino-ethylbenzenediazonium and exposition to a 5 nm gold nanoparticles suspension. AFM scale: 0−200 nm in thickness.

electrode. Negative potential sweeps were applied to a gold electrode connected to the r-GO line. An electron was thus transferred from the r-GO to the diazonium, generating an aryl radical that covalently bounded to the r-GO, as already observed on other carbon substrates.[17a] In order to confirm the local grafting, a diazonium bearing a protonated aliphatic amine (namely, the acidic form of the 4-aminoethylbenzenediazonium) was first electrografted. Then the electrofunctionalized substrate was dipped during 1 h into a suspension of citrate-coated 5 nm gold nanoparticles to immobilize detectable elements on the substrate via electrostatic interactions.[18] Figure 3b−d show an AFM image (Figure 3b) and SEM images (Figure 3c,d) of the electrografted r-GO line after immersion in the gold nanoparticles suspension.

The AFM image (Figure 3b) clearly shows the presence of topological features in the r-GO stripe. Agglomerates are observable, fixed by an underlying layer that cannot be distinguished from the intrinsic topology of the GO layer. The grafted layer is thus very thin, maximally a few nm thick. Figure 3c, obtained at the frontier between the reduced and the nonreduced areas presents a clear demarcation. Figure 3d shows that the modified zone is regularly covered by individual nano-objects with a density of about 200 elements/μm^2 (nonmodified areas display very limited parasitic deposition with a density <10 elements/μm^2). The elements are not densely packed, but distributed homogeneously over the entire functionalized area. It is worth noting that only the r-GO directly connected to the gold electrode displayed the features observed in Figure 3b−d.

In summary this work presents a localized reduction procedure of GO-covered substrates, based on the electro-generation of naphthalene radical anions at a SECM electrode. The created r-GO lines are 5 orders of magnitude more conducting than GO. A diazonium derivative can be further selectively electrografted on one r-GO line, as demonstrated by

the fixation of ammonium functions that immobilized negatively charged gold nanoparticles by simple immersion. The fact that the nonmodified zones are insulating leads to patterns that can be independently addressed. The GO-covered SiO$_2$ substrate with SECM-generated r-GO patterns can thus be considered as a versatile functional platform.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and XPS analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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