Site-Selective Bipolar Electrodeposition of Gold Clusters on Graphene Oxide Microsheets at a 3D Air|Liquid Interface

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An innovative wireless approach is proposed for asymmetric site-selective deposition of gold clusters on graphene oxide microsheets by performing bipolar electrochemistry at the 3D air|liquid interface present in an assembly of bubbles constituting a foam. Exfoliated graphene oxide (EGO) microsheets are introduced into a bipolar electrochemical cell, which is filled with the foam composed of a nonionic surfactant, water, and a gold metal precursor. The EGO microparticles are located exclusively at the air|liquid interface, providing a unique 2D reaction space for bipolar electrodeposition, deployed in the 3D volume of the reactor. The application of an external electric field on such a medium enables a focalization of the polarization potential gradient and simultaneously restricts the mobility of the EGO particles, leading to their preferential in-plane orientation with respect to the electric field lines, greatly facilitating their successful site selective modification with gold clusters.

1. Introduction

Graphene, a 2D layered carbon-material has attracted numerous research activities over the past decades and enabled significant progresses in nanotechnology due to its unique physico-chemical properties.[1–4] Important efforts have been made to develop strategies for the production of large amounts of graphene. High quality single or few layers graphene can be successfully prepared by chemical vapor deposition (CVD), but only in rather small quantities.[5] Alternatively, graphene oxide can be prepared using chemical exfoliation starting from natural graphite.[6–8] In order to avoid hazardous chemical approaches, electrochemical exfoliation has also been proposed as another practical route. It proved to be rather tunable by changing key electrochemical parameters such as the composition of the electrolyte.[9–11] Highly conductive exfoliated graphene oxide (EGO) can be obtained with high yield by applying moderate DC current to simple graphitic carbon, employed as working electrode immersed in an electrolyte solution. Subsequently, numerous studies have been dedicated to the modification of the EGO surface in order to improve the reactivity, solubility, and electronic structure, which could expand the range of potential applications of graphene-based materials.[12] Additionally, the functionalization of graphene and other carbon materials such as carbon beads, fibers and nanotubes with metal clusters can improve their activity, e.g., as catalysts.[13–16] Electrochemical deposition leads in general very easily to metal layers on carbon objects with tunable shape, size, and position.[17] However, for 2D materials this is less straightforward due to the fact that they need to be fixed on an electrode surface in order to be electrochemically wired.[18] Consequently, multiple steps are required to pretreat and prepare a given substrate.[19] Also, the direct electric contact mostly leads to a homogeneous deposition over the entire electrode surface. Therefore, it is difficult to only partially cover 2D objects with metal or selectively deposit patches at a precise position.[20–22] One way around this drawback of classic electrodeposition is based on the use of bipolar electrochemistry (BPE), which has been proven as an efficient way for contactless electrochemical modification, allowing a good spatial control of the deposition.[20–22] BPE is based on the polarization of a conducting or semiconducting object (called a bipolar electrode) immersed in solution while an external electric field is applied across the electrolyte by two feeder electrodes.[23–27] Due to this polarization, an
interfacial difference of potential ($\Delta V$) is generated between the two extremities of the conductive object. The value of this $\Delta V$ depends directly on the length of the object and the applied electric field. If $\Delta V$ is large enough, opposite redox reactions can occur at the two extremities of the bipolar object. An oxidation will occur on one side (referred as anodic pole), whereas a reduction simultaneously proceeds at the opposite side (referred as cathodic pole). Thus, this technique is somehow an electrochemically-induced break of symmetry that enables an asymmetric surface modification or the synthesis of Janus particles, with a wide range of applications from sensing and catalysis to photochemistry and electronic devices. For carbon and graphite particles, metal clusters such as Pd, Au, or Cu were successfully deposited at opposite peripheries by changing the direction of the electric field in a BPE cell.

However, during the deposition, random changes in the orientation of the bipolar electrode should be avoided because they are detrimental for site-selective deposition. Therefore, the bipolar objects need to be either fixed on an insulating support or immobilized in a gel to ensure site-selective electrodeposition. Alternatively, selective gold cluster deposition on one end of carbon nanotubes (CNTs) was achieved using BPE performed in a capillary electrophoresis setup. In this case, the orientation of CNTs can be maintained during the electrodeposition event due to their anisotropy. Bidimensional microscale graphene has also been prepared by positioning graphene at a biphasic organic/water interface provided by two immiscible electrolyte solutions.

For example, Pd and water interface provided by microscale graphene has also been prepared by positioning particles, with a wide range of applications from sensing and catalysis to photochemistry and electronic devices. Changing the direction of the electric field in a BPE cell.

The electrochemical deposition of Au particles selectively on only one extremity of the microobjects.

2. Results and Discussion

EGO sheets were successfully synthesized via electrochemical exfoliation with an average lateral flake size of 28 (± 8) µm measured by scanning electron microscopy (SEM) (Figure S1c, Supporting Information). Some unexfoliated graphite clusters are also observed (brighter particles in Figure S1a in the Supporting Information), but most of the particles are bare EGO sheets (Figure S1b, Supporting Information). The atomic force microscopy image shown in Figure S2a (Supporting Information) evidences multi-layer graphene oxide with an average thickness of ≈8 nm, attributed to a stack of 6–7 layers, since the thickness of a graphene monolayer ranges from 1.0 to 1.2 nm. (Figure S2b, Supporting Information). Additionally, Raman spectra (Figure S3, Supporting Information) also confirm the presence of multiple layers of graphene (number of layers > 5) as deduced from the features of the 2D peak (at 2691 cm$^{-1}$) compared to the pristine graphite rod. The defects attributed to oxygenated functionalities and sp$^2$-hybridized carbon atoms on the EGO surface are determined by a high intensity ratio of D (at 1346 cm$^{-1}$) and G (at 1583 cm$^{-1}$) bands, respectively. These oxygen induced defects typically appear in normal graphene oxide. The presence of this functionality in the graphic planes can distort its sp$^2$ network, causing a poor conductivity. However, the D’ band (at ≈2929 cm$^{-1}$) induced by a lattice disorder on the EGO, is hardly distinguishable. Furthermore, the relative ratio between 2D and G peak intensity is larger than that of conventional graphene oxide or chemically-reduced graphene. This indicates a partial recovering of sp$^2$ C=C bonds and leads to more efficient hole mobility.

Therefore, the EGO produced by this method shows a promising sp$^2$ C=C backbone structure and opens the opportunity for further electro-induced modification by using BPE.

The electrochemical reduction of HAuCl$_4$ (AuCl$_4^-$ + 3e$^-$ → Au) has a standard potential $E^0$ of +0.99 V versus NHE. On the other hand, water oxidation (2H$_2$O → O$_2$ + 4e$^-$ + 4H$^+$) takes place at $E^0 = +1.23$ V versus NHE. Based on these two half-reactions, the minimum polarization potential difference that is necessary to modify the EGO particles is 0.24 V. In the experimental setup (Figure 1a), the reaction compartment (middle cuvette) is combined with two chambers filled with supporting electrolyte that connect both electrode compartments. The two ends of the reaction compartment are sealed with a Nafion film to avoid a mechanical perturbation of the reaction space by bubble evolution occurring at the feeder electrodes during BPE, and to confine the foam in a well-defined volume. The distance between the two feeder electrodes is fixed at 3 cm and the typical applied potential difference is 0.6 kV. This means that the polarization potential across an individual EGO particle is estimated to be ≈0.5 V, which is roughly twice the required minimum voltage, deduced from the standard potentials (see the Supporting Information for details of the calculation). The EGO/C$_{16}$E$_8$/HAuCl$_4$ mixture was injected into the reaction compartment and converted into foam by purging N$_2$ before the BPE experiment (see Figure S4a in the Supporting Information). The formation of foam and the typical bubble diameter...
was observed by bright field optical microscopy (Figure 1b). The bubbles are organized as an ensemble of compact and uniform empty spheres, stabilized by the C16E8 surfactant, each bubble being surrounded by six other bubbles in a horizontal plane according to a hexagonal packing. The bubbles have a diameter ranging from 150 to 280 µm, thus they are much bigger than the typical size of the EGO flakes, which allows accommodating easily several EGO particles around one bubble. As can be seen from the high-resolution bright field microscope image displayed in Figure 1c, the EGO particles are located at the bubble periphery. This indicates that they readily adsorb at the bubble interface due to a stabilization by the surfactant. Individual EGO sheets are confined at the interface between bubbles, as illustrated in Figure S4b in the Supporting Information. This affinity is a key parameter to limit the motion of the EGO sheets during BPE. Their presence in the foam might also influence the drainage rate along the bubble wall and thus lead to a stabilization of the foam.[39] By removing the remaining solution after foaming, most of the polarization potential is expected to drop along the bubble surface when the driving voltage (E) is applied across the reaction space (see Figure 1d). Typically, the local electric field lines will perfectly follow the curvature of a bubble, resulting in a focalization of the electric field. The direct and most important consequence is that automatically the main plane of all EGO flakes is perfectly aligned with the electric field, in contrast to other bulk BPE experiments where orientation is much more difficult to control. This ensures a maximum polarization and a better overall yield of modified particles.

After the solutions of EGO-C16E8 and HAuCl4 were mixed and foamed, 0.6 kV was applied immediately to the feeder electrodes (Figure 2). The gas evolution occurs on both feeder electrodes, originating from the reduction and oxidation of water, respectively. The initial current measured during BPE is around 4.5 mA (see Figure S5 in the Supporting Information). This current gradually decreases while the electrochemical reactions proceed and stabilizes around 2 mA after the first 60 s. The drop of the overall current is directly caused by Joule heating. When the electric field is applied, charge carriers...
generate thermal motion, and this heating ultimately causes a gradual destabilization of the foam structure at the macroscopic level. An additional effect leading to a first drop in current can be also ascribed to the gas formation at the feeder electrodes which might partially block the electrode surfaces. Observing more closely the reaction compartment (zoom in Figure 2) reveals that the foam slowly starts reorganizing after the first 60 s, explaining the concomitant change in current. This phenomenon gets amplified with time, causing bubble coalescence, which becomes clearly visible after 180 s and continues until the end of the BPE run (i.e., 300 s). However, the majority of the foam remains, which is confirmed by the steady current recording from 60 to 300 s (Figure S5, Supporting Information). We were able to tune the experimental conditions in such a way that the characteristic time, necessary to achieve the metal deposition, is compatible with the time scale of the appearance of the Joule effect. In other words, the Joule effect does not prevent from carrying out successfully the modification experiments.

After collecting and washing the samples by centrifugation, a few drops of the Au/EGO suspension are dried on a copper tape at 70 °C. Figure 3 gathers representative SEM images and the corresponding energy-dispersive X-ray spectroscopy (EDX) maps of the products as a function of reaction time. A control experiment without applying the electric field revealed only bare EGOs particles (Figure 3a). Already after 30 s, small gold clusters can be detected (Figure 3b). When the reaction is prolonged to 150 s, several gold clusters with a larger size are clearly observed, but, most importantly, only at one extremity of the EGO sheets (Figure 3c). At 300 s, EGO particles are decorated with much larger Au deposits (Figure 3d,e). In summary, a longer deposition time also leads to a more pronounced Au cluster formation in terms of size and/or number of clusters deposited at the EGO periphery. However, making a direct correlation is not straightforward, as the final morphology of the gold clusters also depends on the size of the individual graphene oxide sheets that are modified. For the same voltage difference, applied between the feeder electrodes, graphene oxide sheets with a smaller dimension will experience a lower polarization potential difference, and thus the deposited metal clusters will have a different size and morphology. Also, the microscopic structure of the nucleation site (flat, edge, kink site, sharp tip, etc.) where the metal deposition starts will have an impact on the final morphology of the metal. Extending the reaction time for a given voltage corresponds actually indirectly to a control of the deposition charge density, even though the overall current is dominated by the ionic bypass current and not by the faradaic current going through the graphene sheets. Under these conditions and based on over a hundred of individual particles observed by SEM, it was estimated that more than 60% of EGO flakes were selectively modified by Au at only one extremity. It is quite likely that the flakes, which at the end of the bipolar experiment are not modified, correspond to the fraction of graphene with a too high degree of oxidation, thus becoming eventually an insulator or at least a very bad conductor.
In order to optimize the experimental conditions, the effect of the applied potential was also studied. The SEM and corresponding EDX images of Au/EGO synthesized with 0.1, 0.3, 0.4, and 0.6 kV are gathered in Figure S6 in the Supporting Information. When applying 0.1 kV the generated polarization potential difference (0.09V) is not enough compared to the thermodynamic threshold of 0.24 V, thus leading to unmodified EGO (Figure S6a, Supporting Information). Both, 0.3 and 0.4 kV allow the deposition of Au particles at the EGO periphery (Figure S6b,c, Supporting Information, respectively). The yield and particle size can be further increased when applying 0.6 kV (Figure S6d, Supporting Information). Therefore, in the range of potentials tested, 0.6 kV gave the best results.

In this work, we assume that the dimensionality of the reaction space plays a key role for controlling the degree of freedom of EGO particles, by confining them at the interface between the bubbles constituting the foam. In order to confirm this hypothesis, we carried out a control experiment in the same setup and with the same applied potential, but without generating foam. We used the same volume of EGO-C_{16}E_8-HAuCl_4 solution (see Figure S7a in the Supporting Information) and in that case the initial current reaches 16 mA (Figure S7d, Supporting Information), leading to a very fast heat generation inside the reaction compartment due to the Joule effect. The temperature of the solution gradually increases during the first 60 s (Figure S7b, Supporting Information) before the solution completely evaporates within 240 s (Figure S7c, Supporting Information). Simultaneously, the overall current decreases with time and finally reaches zero.

Under these conditions, metal deposition occurs randomly and Figure 4a,e shows the resulting modified EGO sheets, with Au clusters located everywhere on the EGO basal plane. This delocalized Au deposition indicates that the microsheets are constantly changing orientation while the electric field is applied. It confirms that the foam induces a restriction of EGO orientation and mobility, which is crucial to achieve a clean site-selective modification. In strong contrast to this, when the reaction compartment is filled with C_{16}E_8 foam, not only the initial current is much lower, but most of the Au clusters are exclusively deposited at one extremity of the EGO periphery (Figure 4b–d). However, the size and morphology of these Au clusters can vary. Different shapes and sizes of Au deposits can be found, from small single clusters (Figure 4f) to multiple clusters (Figure 4g), or eventually bigger Au particles like the one displayed in Figure 4h. The intrinsic properties of the individual EGO flakes, such as their conductivity due to the specific degree of oxidation, possible defects, and the geometry (size and shape) are responsible for these variations.

Fluorescence measurements can also be carried out since the Au metal particles can be selectively labeled by fluorescent dyes. Fluorescent molecules with a cyanate functionality, such as rhodamine B isothiocyanate (RhBITC) and fluorescein...
isothiocyanate (FITC) are widely used for the functionalization of gold nanoparticles because they can directly bind to the Au surface under mild conditions. Therefore, these dyes were used to further prove the successful modification of EGO sheets with Au. Figure 5a,b shows bright-field images of modified EGO particles labeled with RhBITC and FITC, respectively. After removing the dye molecules that are not specifically attached to either the gold clusters or the graphene plane by centrifugation, the corresponding fluorescent images of the samples were recorded (Figure 5c,d). The labeled Au/EGO particles exhibit strongly fluorescing spots, localized on their surface. It is noteworthy that these images are presented without post-treatment. When performing an artificial color-enhancement (Figure 5e,f), bright spots can be clearly distinguished at one side of the graphene boundary, whereas bare EGO does not show any significant fluorescence (results not represented).

3. Conclusion

To conclude, we demonstrate that site-selective deposition of Au on EGO sheets can be achieved by using BPE in combination with a 3D air|liquid interface, provided by a foam generated with the help of C_{16}E_{8} surfactant. This foam constitutes a unique network to accommodate EGO microflakes by adsorption at the interface, thus drastically limiting the degree of mobility of these bipolar electrodes. An additional positive effect is the confinement of the electric field lines in the walls of the bubbles, guaranteeing a favorable parallel orientation of the basal plane of the EGO sheets with respect to the imposed potential gradient. The morphology of the Au clusters and the yield of the modification can be tuned by changing the reaction time. However, the exact size and morphology of the clusters also depends on several other parameters, such as the globally applied driving force, as well as the size and the morphology of the individual graphene oxide sheets, as this has an impact on the nucleation of the metal growth. However, the most crucial feature of these hybrid objects is not so much the exact shape of the Au clusters, but their anisotropic deposition. These results show for the first time the added value of using a foam as an interfacial reaction space for constraining the mobility and orientation of carbon microparticles during BPE experiments. In the absence of foam, the corresponding bulk solution experiments result in uncontrolled electrodeposition due to the freely rotating EGO flakes. The proof-of-principle experiments clearly demonstrate the advantages of using bipolar electrochemistry in combination with a 2D interface as a reaction space provided by the foam. The present proof-of-principle experiments, carried out with EGO and gold salt, might be generalized to other 2D materials and different metal precursors in order to generate a large variety of asymmetric hybrid micro-materials. Such anisotropic metal/carbon microobjects can have a variety of potential applications, ranging from catalysis and photochemistry to sensing, energy conversion, and self-propulsion.

4. Experimental Section

Electroosmosis of Graphene Oxide: The exfoliation of graphite was carried out by an electrochemical process in an inorganic electrolyte in order to minimize the degree of oxidation of the exfoliated graphene oxide (EGO) as described by Sharif et al.[11] It is known that the oxygenated functionalities are able to alter the sp² hybridization of the graphene planes, causing a lower electronic delocalization, which is detrimental for conductivity.[16] Introducing (NH₄)₂HPO₄ in the system
The end of both tubes was closed by a Nafion membrane to separate the reaction compartment from the feeder electrode compartments. The foam was generated by gradually passing N₂ through the solution with a 50 µm (φ) syringe. Subsequently, the fraction of the initial solution which was not transformed into foam (typically ~40 µl) was removed from the experimental setup (see Figure S4a in the Supporting Information). Then, 3 mL of supporting electrolyte (0.4 × 10⁻³ M KCl) was filled into both electrode compartments and 9 × 20 mm² graphite plates were used as feeder electrodes. The BPE setup was connected to a DC power supply (Heinzinger PNC 10000 ~200 pos) and the applied potential was varied from 0.1 to 0.6 kV for 5 min for bipolar electrodeposition of Au on EGO. Finally, modified EGO was separated by centrifugation at 1000 rpm for 10 min. The Au/EGO precipitate was then washed several times with water and redispersed in 0.1 mL water for future use. Approximately, 20 µL of Au/EGO was dropped on a Cu grid and dried at 70 °C prior to SEM imaging. SEM images and EDX data were collected with a Tescan Vega 3 microscope from Bruker. Additionally, a portion of Au/EGO was labeled by a fluorescent dye such as rhodamine B isothiocyanate (RhBITC, Aldrich) and fluorescein isothiocyanate (FITC, Aldrich), by adding 5 µL Au/EGO suspension to 10 µL 0.05 × 10⁻³ M of the fluorescent dyes dissolved in ethanol. Afterwards, the suspension was left overnight, and the excess dye was removed by centrifugation and washed twice by ethanol prior to optical microscopy characterization. Bright field and fluorescence images were collected with a Leica DMi8 inverted microscope equipped with a CCD camera.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the French Ministry of Research, CNRS and Bordeaux INP. The authors also thank the Development and Promotion of Science Technology Talents Project (DPST) and Kasetsart University Research Development Institute (KURDI) for a scholarship. The work has also been funded by the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (grant agreement n° 741251, ERC Advanced grant ELECTRA). The authors also acknowledge the facilities and grant from the program of the Research Network NANOTEC (RNN).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

bipolar electrochemistry, foam, graphene oxide, hybrid materials, surface functionalization

Received: February 8, 2022
Revised: April 15, 2022
Published online: June 24, 2022

Figure 5. a,b) Bright-field images, c,d) original fluorescence images, and e,f) color enhanced images of as prepared samples. Images (a), (c), and (e) show a large EGO particle with two Au clusters labeled with RhBITC. Images (b), (d), and (f) show two small EGO particles with Au clusters labeled with FITC.

suppresses the oxidation of hydroxyl groups during the exfoliation process via the formation of a phosphate intermediate. Bipolar Electrodeposition of Au on EGO: Prior to preparing the foam, the EGO suspension, and an aqueous solution of octaethylene glycol monohexadecyl ether (Sigma, ≥98% (GC), C₁₆E₈), used as a foam constituent, were mixed, and stirred for 12 h. Then the EGO-C₁₆E₈ solution was combined with HAuCl₄ stock solution. The final mixture is composed of 0.0067 mg mL⁻¹ EGO, 0.1 × 10⁻⁶ M HAuCl₄ and 20 mg mL⁻¹ C₁₆E₈. Then, 100 µL of the solution was poured into the bipolar electrochemical cell. The cell was built with a central cuvette (4 mm × 10 mm × 45 mm), which is connected with two other 10 × 10 mm² cuvettes by glass tubes (φ = 4 mm) as shown in Figure 1a.
