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► **To cite this version:**

Kevin Jaouen, Olivier Henrotte, Stéphane Campidelli, Bruno Joussetme, Vincent Derycke, et al.. Localized electrochemistry for the investigation and the modification of 2D materials. Applied Materials Today, 2017, 8, pp.116 - 124. 10.1016/j.apmt.2017.05.001 . cea-01546754

HAL Id: cea-01546754

<https://cea.hal.science/cea-01546754>

Submitted on 26 Jun 2017

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Localized electrochemistry for the investigation and the modification of 2D materials

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Abstract

In this review, we present the state of the art regarding the interplay between two emerging fields, namely localized electrochemistry and 2D materials. Electrochemistry involves oxidations and reductions taking place at an electrode immersed in a solution. When the substrate is composed of 2D materials or layered materials, electrochemistry can be used to investigate or modify these layers. It is thus an essential link between 2D materials and their applications, in particular those related to sustainable energy conversion and storage. In addition, the properties of 2D materials often differ along their edges, at defect sites or upon folding and stacking. Most interesting properties (such as catalytic activity, conductivity, chemical reactivity, etc.) drastically depend on such inhomogeneity or imperfections, which can be purposely induced (by functionalization or nanostructuring) or not (intrinsic defects resulting from the material synthesis or consequences of the material handling and deposition processes). These key aspects are suitably investigated using local electrochemical strategies, which allow both the analysis and the local modification of 2D materials. This article reviews the most significant results of this rapidly growing field.

Introduction

2D materials are foreseen as key building blocks in an increasing number of applications ranging from electronics to energy storage and conversion devices. Since Novoselov et al. isolated single-layer graphene by simple mechanical exfoliation in 2004¹ the fabrication of 2D materials has made very rapid progresses, and the community has now access to a wide variety of 2D materials with many different properties. They can be derived from graphene (graphene oxide, few layer graphene, etc)² or contain transition metal dichalcogenides.³ However, while 2D materials already lead to performance improvement in several examples⁴ (electrocatalysis,⁵ optoelectronics,⁶ etc), the understanding of the precise origin of such improvement remains challenging. In fact the integration of new materials into functional devices critically relies on our ability to both understand and modify their intrinsic properties. In this regard, the study of the interface of two systems (e.g. 2D materials and ionic solutions) to investigate electron transfer implying oxidation-reduction reactions known as “electrochemistry” appears particularly appealing to analyze new 2D layers and improve their functionality. It must be noticed that in devices, global performances are the result of many contributions coming from different elements present in the functional layer. In fact, the inherent heterogeneity (edges, folds, defects, stacks...) of the deposited 2D materials is both a chance –as the particular properties of the modified surface are often due to such heterogeneities– and a challenge –as their analysis or modification require local investigations.

There are two main strategies to explore the electrochemical properties of 2D materials and relate them to local information. The first one consists in performing standard electrochemistry on substrates having variable and identified amounts (or percentage) of specific features under investigation (edges, planes, stacks, etc). This requires complementary experiments using conventional characterization tools (Atomic Force Microscopy (AFM), Scanning Electron Microscopy, (SEM)...). An alternative and particularly powerful approach relies on electrochemical scanning probe techniques. In this case, an electrode (such as a functional AFM cantilever, a microelectrode or a pipette, see below) is used as local probe and moved over the substrates to provide an electrochemical map of the substrate. Depending on the scanning conditions different information can be obtained. In this review, we start by presenting the different local probe techniques that can be used to perform localized electrochemical investigations of 2D materials. Then, we present the studies in which localized electrochemistry experiments are used to evaluate some key properties of 2D materials. Finally, in a last part, we focus on contributions related to material modifications (electrochemical functionalization, etching...), which allow modulation of the properties in a spatially controlled manner.

1. Local probe techniques

To combine electrochemistry and micrometric or submicrometric investigations, the most common strategy is to use a small probe and displace it in the vicinity of the materials. Depending on the type of probe, different techniques are considered.

The most common technique to perform local electrochemistry uses a microdisk electrode, i.e. a metallic wire surrounded by an insulator as schematically illustrated in figure 1a. In this case, the local probe technique is named “Scanning Electrochemical Microscopy” abbreviated as SECM.⁷ Introduced in 1989, the technique combines a standard electrochemistry set up (three-electrode system) with motors and positioning systems to move the probe which can be micro- to nano-sized. The probe is usually the working electrode in the electrochemical set up, which means that both the current and the potential are accessible experimentally. The size of the probe determines the spatial resolution of the study that ranges typically from 10 μm to 1 μm . With a bipotentiostat, it is possible to monitor the electric potentials of both the substrate and the tip. The SECM configuration offers a large variety of electrochemical characterizations through the change of the experimental sequences such as the probe and substrate potentials, or the electrolyte content.⁸ Electrochemical measurements can also be combined with Atomic Force Microscopy in a combined AFM-SECM approach (Fig. 1b) to get simultaneously topological and electrochemical information.⁹ This permits the deconvolution of the two contributions and a more precise evaluation of the electrochemical activity. Another technique derived from SECM known as Scanning ElectroChemical Cell Microscopy (SECCM) consists of a dual-channel pipette with a Quasi-Counter-Reference Electrode (QCRE) in each channel with a fixed potential bias between both (Fig. 1c).¹⁰ Only the probe is filled with solution so that only the area of interest is analyzed. When the solution is confined with a micropipette, the technique is called “microdroplet cell” (Fig. 1d) and micrometric spatial resolution can be achieved.¹¹

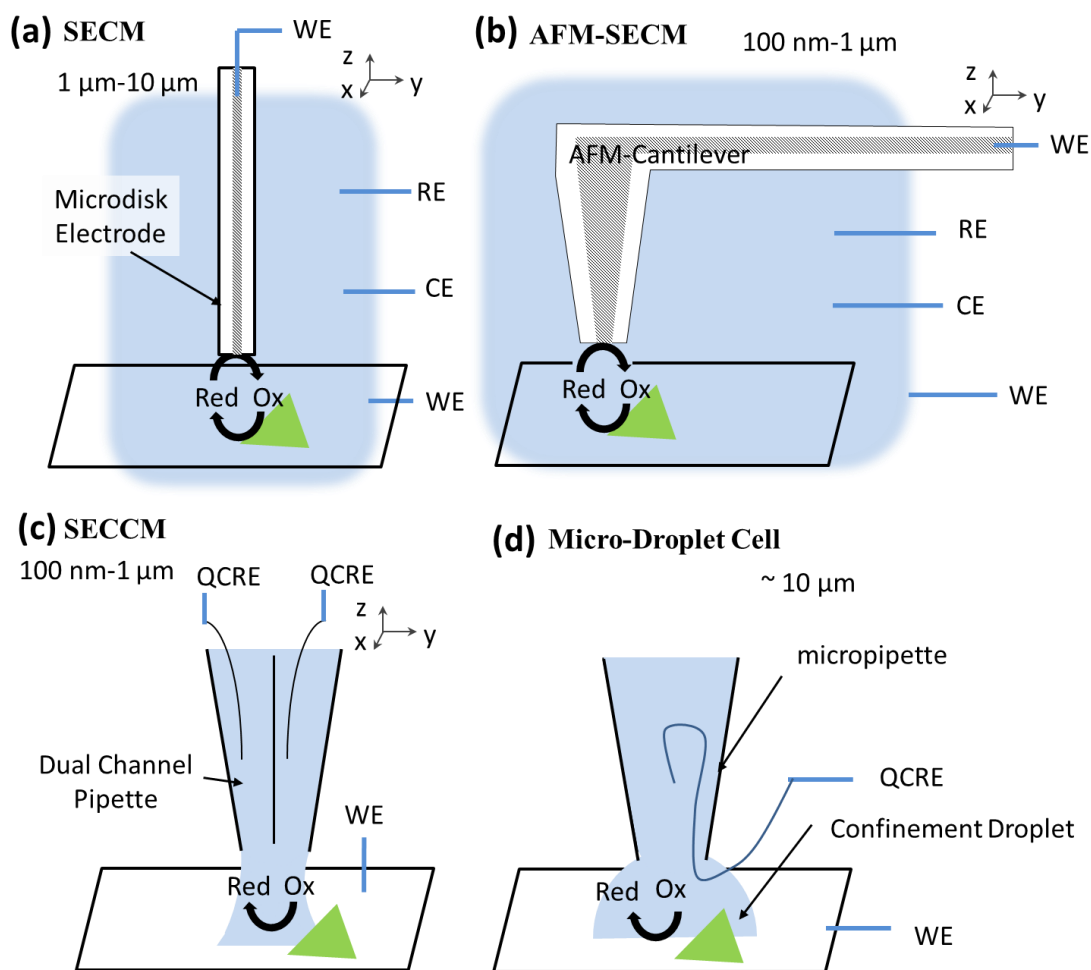


Figure 1. Presentation of the different probe techniques to perform localized electrochemistry (a) SECM, (b) AFM-SECM, (c) SECCM, (d) Microdroplet cell. WE: Working Electrode, CE: Counter Electrode, RE: Reference Electrode, QCRE: Quasi Counter Reference Electrode. The green triangle represents a piece of 2D material under study.

2. Characterization of electronic transfers

Most of the time, the source of the measured probe signal is unambiguously identified thanks to concordant non-electrochemical images, generally obtained by SEM, AFM or spectroscopy (see examples below). In the following part, different investigations of 2D materials are reviewed. In a first section, the investigations dealing with simple electron transfers between the layer and a redox mediator present in the electrolyte solution, such as ferrocene, are presented. The charge transfer kinetic associated to these simple processes informs on the ability of the 2D layer to exchange electrons with its environment. In a second section, the studies of more complex reactions (involving multistep mechanisms and absorbed species) are reviewed. Finally, the investigations of the transport of species (electrons, absorbed species, etc.) within or on top of the layer(s) are presented.

2.1. Redox mediator charge transfers

First, local electrochemistry is used to investigate how simple charge transfers occur at surfaces covered with layered materials, with a special focus on graphene. In this

configuration, the probe is used as an electrode to extract or bring electrons to these materials, through the solution that contains a redox mediator such as typically $\text{Fe}(\text{CN})_6^{3-}$ or Ferrocene. Local electrochemistry is perfectly suitable to investigate the impact of defects and edges on electronic transfers. In fact, such investigation of layered materials follows extensive studies on bulk materials exhibiting crystalline surfaces.¹² In particular, highly oriented pyrolytic graphite (HOPG) has been extensively investigated.^{12c} Using standard electrochemistry^{12b, 13} or local probes¹⁴ structural defects (see figure 2) are identified as more efficient locations for electron exchanges between the solution and the surface. The effective activity of graphite basal plane is also the subject of intense debates.¹⁵ SECCM shows that basal planes can effectively exchange electrons with a solution,¹⁶ even when $\text{Fe}(\text{CN})_6^{3-}$ is used as redox mediator, which is well known to have a low charge transfer kinetic.

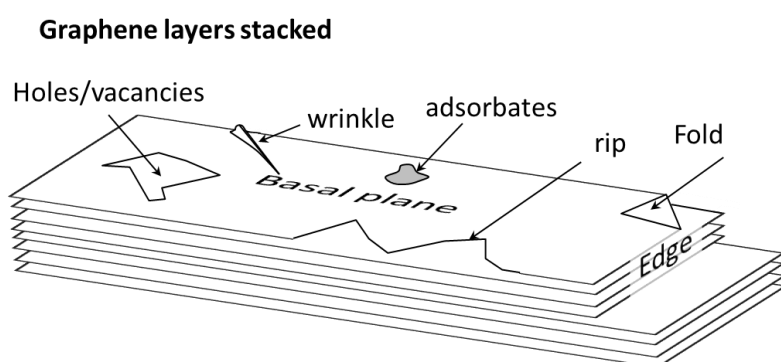


Figure 2. Schematic view of the graphite surface and examples of local sites with potentially different electrochemical activity

How these conclusions are transferable from HOPG to 2D materials is also investigated. This is done either with local probes^{9c, 17} or surface templating.¹⁸ It is concluded that charge transfer is more favorable on graphene than on HOPG: both the defects^{17b, 18a, b} and the basal plane^{18c} have a higher activity on graphene than on HOPG. Different redox mediators are considered, and small kinetic constants for $\text{Fe}(\text{CN})_6^{3-}$ and higher constants for ferrocene are observed.¹⁹ These observations are in line with the previously mentioned studies dealing with HOPG. The importance of folding effects at graphene edges is also investigated by electrochemistry. It shows that the charge transfer is about 35 times faster at open-edged than at folded-edges.²⁰ The number of layers also impacts the charge transfer constants: conversely to what can be expected from the difference between bulk materials and monolayers, with graphene^{11, 21} or MoS_2 ²² the general trend is to observe an enhanced charge transfer upon increasing the number of layers, as illustrated in figure 3. Quantitative studies show that the charge transfer kinetics (with $\text{Fe}(\text{CN})_6^{3-}$ and IrCl_6^{2-}) on graphene approximately double when going from 1 to 2 layers.²³ With 2D materials, the surface underneath the layer impacts the transfer kinetics, for example by trapping charges in the vicinity of the 2D materials, thereby screening part of the applied potential.²⁴ Gold subsurface also enhances the charge transfer by a factor of about 5 due to electronic coupling between the layer and the gold.²⁵ The high sensitivity of the charge transfer to the sublayer and to the redox mediator is similarly observed on graphene oxide (GO) and on reduced graphene oxide (r-GO).²⁶

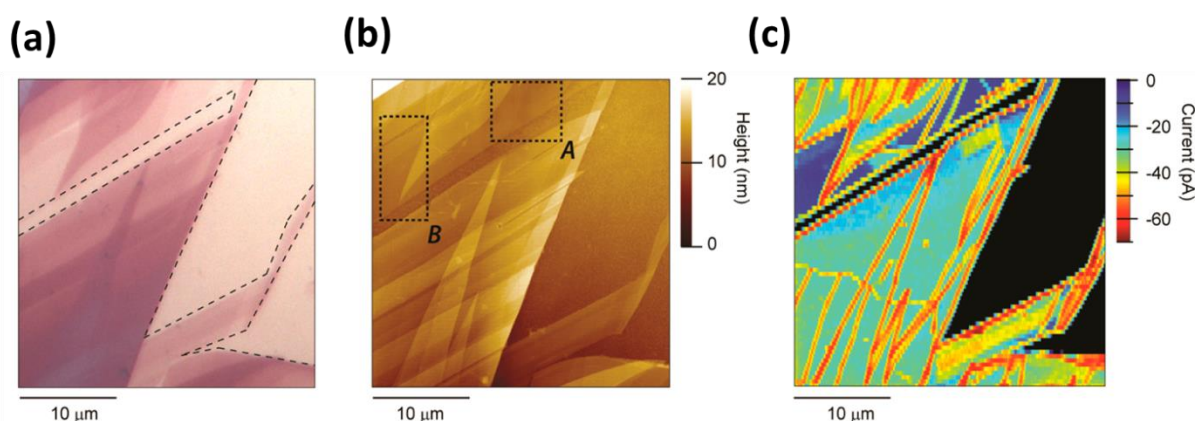


Figure 3. Microscopy of exfoliated graphene on a Si/SiO₂ substrate. (a) Optical microscopy image (dashed lines define the boundaries between the graphene sample and the substrate), (b) AFM topographical image, and (c) SECCM map for the reduction of Ru(NH₃)₆³⁺. Reprinted with permission from ^{21b}. The areas identified as dotted rectangles in figure b have lower SECCM response in figure c.

2.2. Electrocatalysis

The growing role of layered materials in energy storage and conversion devices^{5b} makes the understanding of their electrocatalytic properties of paramount importance. This is notably the case for the Oxygen Reduction Reaction (ORR) and Hydrogen Evolution Reaction (HER) encountered in fuel cells and electrolyzers.^{5a} Only few studies of ORR catalysis on 2D materials are presently available. With a microdroplet cell, ORR on HOPG is observed as being more efficient on edges than on basal planes²⁷ similarly as for simpler charge transfers. ORR performances of MoSe₂ and r-GO hybrid nanostructures are evaluated with SECM, providing direct evidence of the synergy between both components.²⁸

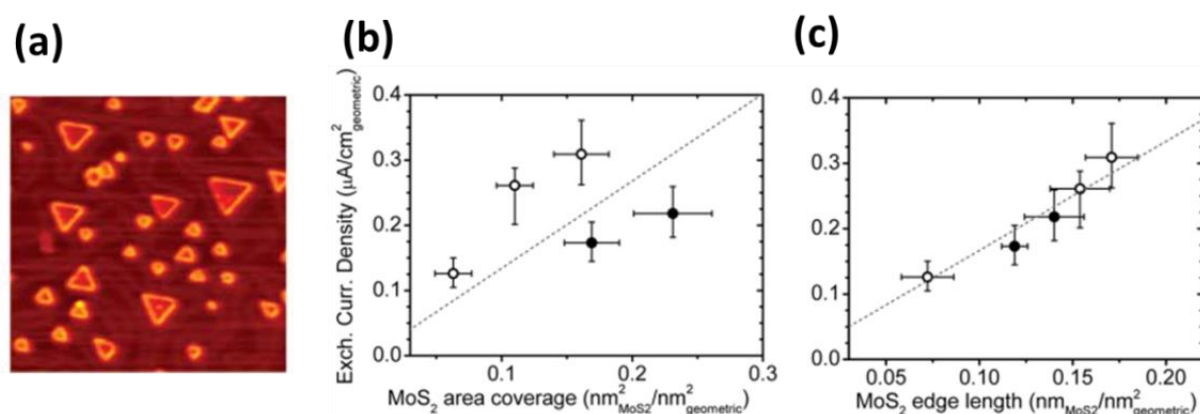


Figure 4. (a) Illustrative STM image (47 nm x 47nm) of MoS₂ on Au(111). Exchange current density regarding H₂ evolution versus MoS₂ area coverage (b) and MoS₂ edge length (c). A strong linear correlation is only observed in the latter case. Open and filled circles correspond to different annealing temperatures of the samples (400 and 550°C respectively). Reprinted with permission from ²⁹.

HER is very much investigated on MoS₂.³⁰ The enhanced activity of edges is observed with substrates covered by MoS₂ flakes having different sizes, which generate different edge contents on the samples (figure 4).²⁹ The enhanced activity of edges is also observed on macroscopic MoS₂ crystals having basal or edge exposed planes.^{12b} Studied with SECM, sulfur vacancies within the plane are found to enhance the kinetic constants by a factor of 4 if the structure is strained,³¹ while the surface coverage of adsorbed H₂ at the surface increases when decreasing the substrate potential.³²

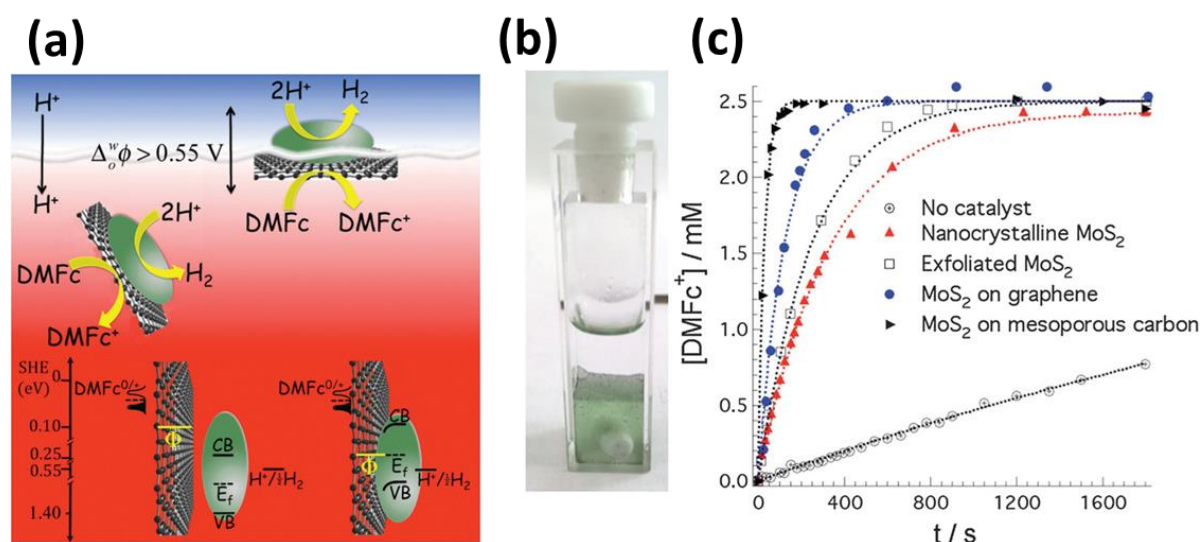


Figure 5. Investigation of 2D materials using the interface between 2 immiscible electrolyte solutions. (a) Scheme of the process for HER assessment, (b) The UV-vis cell used to follow the reaction, (c) Experimental results showing that MoS₂ on mesoporous carbon has the highest activity. Reprinted with permission from ³³.

At the border of the scope of this review dealing with localized electrochemistry, it is worth mentioning that the electrocatalytic activity of MoS₂ toward HER can also be investigated by trapping 2D layers at the interface between 2 immiscible electrolyte solutions, as presented in figure 5. The activity toward HER is studied by biphasic reactions monitored by UV/Vis spectroscopy. The presence of MoS₂ edges and the strong electronic coupling between the MoS₂ and the support leads to enhanced performances.³³ Surprisingly few studies perform localized electrochemistry to investigate the photocatalytic activity of 2D materials. Scanning photocurrent microscopy³⁴, which uses a laser beam focused on the surface (figure 6a) and evaluates the generated current at the substrate to map the quantum yield of a sample with micrometric lateral resolution. With this technique, the photoproduction of H₂ by Pt nanoparticles deposited on WSe₂ layers is observed to be very heterogeneous along the crystal (figure 6b-c).³⁵ Such strategy perfectly matches the ongoing increasing complexity of the photocatalytic systems. A rapid growth of the utilization of scanning photocurrent microscopy can thus be anticipated in the next years.

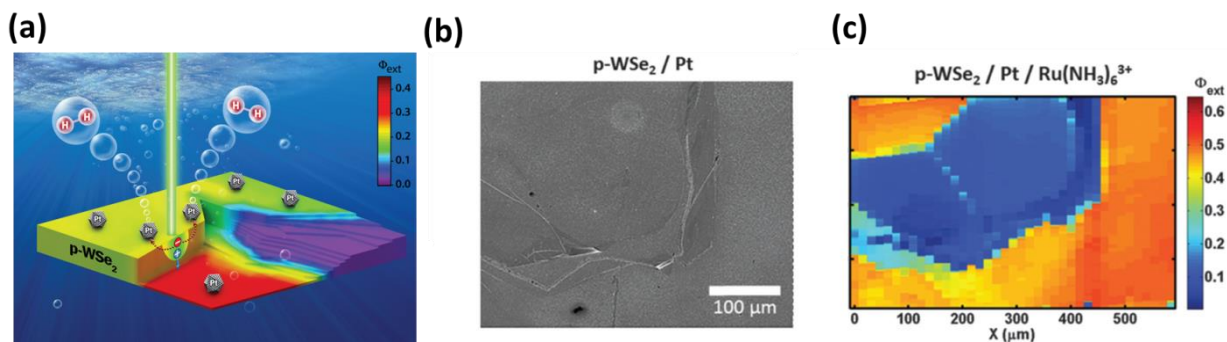


Figure 6. (a) Principle of Scanning photocurrent microscopy applied to the investigation of Pt-WSe₂. Example of combined SEM (b) and quantum yield map (c) obtained in the presence of Ru(NH₃)₆³⁺. Reprinted with permission from ³⁵.

2.3. Electrons, ions and molecules transport on surfaces

In sections 2.1 and 2.2, the mentioned studies are related to charge transfers occurring perpendicularly to the layers, from the material to the electrolyte. Local measurements also

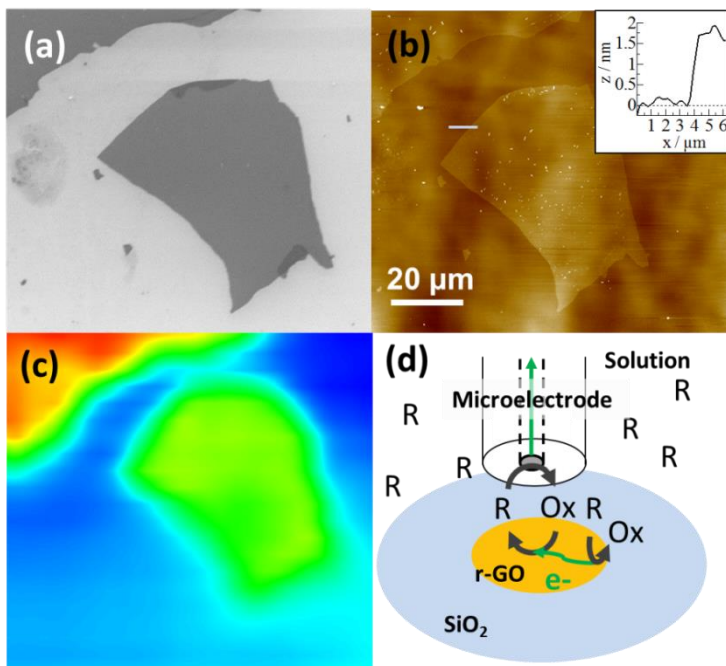


Figure 7. Micrographs of the same r-GO flake deposited on Si/SiO₂ wafer. (a) SEM image, (b) AFM image and (c) SECM image obtained using Ferrocene as redox mediator. (d) Scheme presenting the different steps involved in the feedback loop between the probe and the microelectrode during SECM measurements. Reprinted with permission from ⁶⁰.

permit to investigate the transport of molecules, ions or electrons parallel to the surface. **Electronic transport** on r-GO flakes is investigated with SECM, as illustrated in figure 7. The measurement provides information on the local conductivity of the substrate via a feedback loop between the probe and the flake (figure 7d). Both the intrinsic conductivity³⁶ (measured on individual flakes) and the contact resistance³⁷ between r-GO flakes (evaluated on perfectly identified flake-flake junctions within small aggregates) can be quantified. The measurements show that when the

GO flakes are reduced with hydroiodic acid (HI),³⁸ the contact resistance is 5 times larger than the flake resistance. The macroscopic resistance of r-GO thin films is thus mostly governed by contacts between flakes.

Concerning the **transport of molecules**, surface diffusion on graphene of a tripodal cobalt complex was investigated with SECM.³⁹ The technique permits to observe the evolution of a spot of molecules deposited on the layer, by measuring its hindering effect on the charge transfer between the graphene and the solution. By surface diffusion, the surface concentration decreases and the exchange of electrons between the graphene and the solution is reactivated. With this strategy, the diffusion is measured to be slower on graphene than in solution, but faster than in solids. Concerning the **transport of ions**, the Li⁺ intercalation within few layer graphene was investigated. Electrochemistry coupled to Raman spectroscopy⁴⁰ shows the increase of strain upon intercalation when decreasing the number of layers. SECM (using a Hg-capped microelectrode, see⁴¹ for more details) on purposely templated substrates concludes that Li ions move into graphene interlayers more efficiently through the edge planes.⁴² Li intercalation within MoS₂ was followed with Raman spectroscopy and in situ optical observations.⁴³ The study shows how the optical transmission and the electronic conductivity of the layers are impacted by the intercalation process.

To conclude on this part, many of the technical difficulties associated to localized electrochemical analysis of 2D materials have now been overcome, and many protocols to investigate a precise process on a given layer are now available. The observed features depend on the observation scale: as an illustration, nanometric artifacts do not have an observable signature if micrometric probes are used. This is for example the case in figure 7, where AFM and SEM show flake folding that is not observed with SECM performed with a 10 μm diameter microelectrode. The next step is now to use the methods on series of 2D materials in order to improve the understanding of these systems. This is particularly the case in electrocatalysis, where the diversity of situations, the sensitivity of the processes to defects and the complexity of the mechanisms perfectly match the versatility of localized electrochemistry. Besides, it can be noticed that some 2D materials exist under different phases (1T and 2H for MoS₂).⁴⁴ These have very different electronic and optic properties, and this could be advantageously studied by localized electrochemistry. At the present moment, we do not have knowledge of such studies.

3. Material modification

Localized electrochemistry is also used to modify locally 2D materials with a spatial resolution mainly limited by the probe size. This is a highly versatile alternative to template-based strategies such as photolithography. Probe-induced surface modification is very popular for other materials than 2-dimensional ones.⁴⁵ Regarding the modification of 2D materials, as detailed in the following, the existing works mainly deal with graphene or graphene derivatives such as GO, so that many routes for the modification of other 2D materials are not explored yet.

3.1. Localized oxidation of 2D materials

The scientific community has been working on the probe-induced modification of graphene since 2008.⁴⁶ Most of the studies use a well-known technique, Local Anodic Oxidation (LAO), which was introduced in 1989 for creating holes on graphite surface with an STM.⁴⁷ The electrochemical nature of the process was identified soon after, as illustrated in figure 8a.⁴⁸

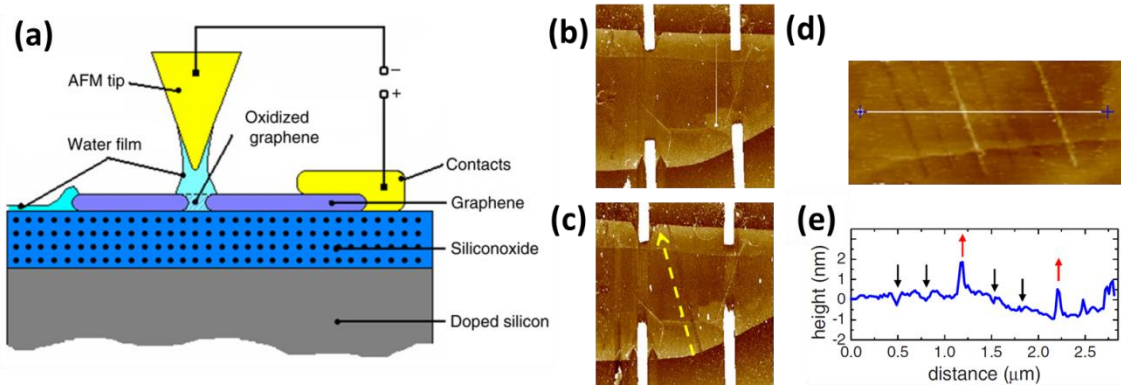


Figure 8. (a) Principle of local anodic oxidation (LAO) on graphene with an AFM. Reprinted with permission from^{46a}. (b-c) AFM images of a graphene flake before (b) and after (c) LAO. The cut follows the yellow dashed arrow. (d-e) AFM (d) and height profile (e) showing that trenches or bumps can be created on graphene by LAO. Reprinted with permission from^{46b}.

With graphene, most studies employ conductive AFM (C-AFM) both in contact or tapping mode. Different degrees of modifications of graphene can be achieved by oxidation leading to either GO formation or surface etching.⁴⁶ As illustrated in Figure 8(c-d), etching leads to trenches while oxidation leads to bumps.^{46b} At high voltage, low scanning speed favors etching.⁴⁹ By optimizing the LAO conditions graphene nano-constrictions as small as 10 nm can be fabricated.⁵⁰ It should be noted that only two localized oxidation studies of other materials were reported, both using an AFM tip as patterning probe. The first one describes the patterning of semiconducting TaS₂ layers leading to the formation of insulating Ta₂O₅ regions⁵¹ while the second one describes the patterning of semiconducting MoS₂ layers leading to the formation of insulating MoO_xS_y regions.⁵²

3.2. Localized reduction of 2D Materials

Compared to oxidation, local reduction of 2D materials is hardly studied. Similarly as for oxidation with LAO, C-AFM can be used. Most of the time, the goal is to locally reduce GO to restore some electrical conductivity.⁵³ One study notably shows that the localized reduction of GO can be used to pattern the channel of ambipolar field-effect transistors.⁵⁴ Soon after it was found that humidity and the number of layers have an important impact on the spatial resolution of this reduction process, and that generation and transport of protons limit the reaction kinetics.⁵⁵ Unlike oxidation, other methods than STM and AFM can be used to locally reduce 2D materials. By combining photolithography, electrochemical reduction and wet etching techniques, r-GO microarrays were fabricated,⁵⁶ as shown in figure 9.

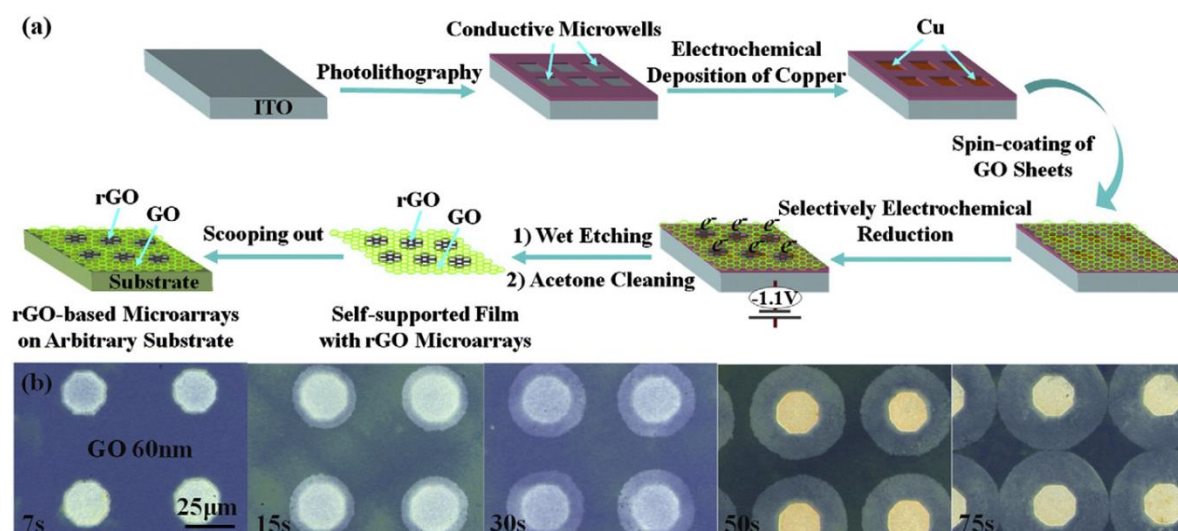


Figure 9. Process combining micropatterning and electrochemistry to reduce locally GO. (a) Overview of the process (b) Laser microscopy images showing the pattern size obtained for different electrochemical reductions durations. Reprinted with permission from ⁵⁶.

Microelectrodes in a SECM configuration are also used to locally reduce GO by electrogenerated naphthalene radical anions, as shown in figure 10.⁵⁷ Both the chemical composition of the layer and the electrical conductivity are modified during the process, as shown in figure 10b and 10c, respectively.⁵⁷

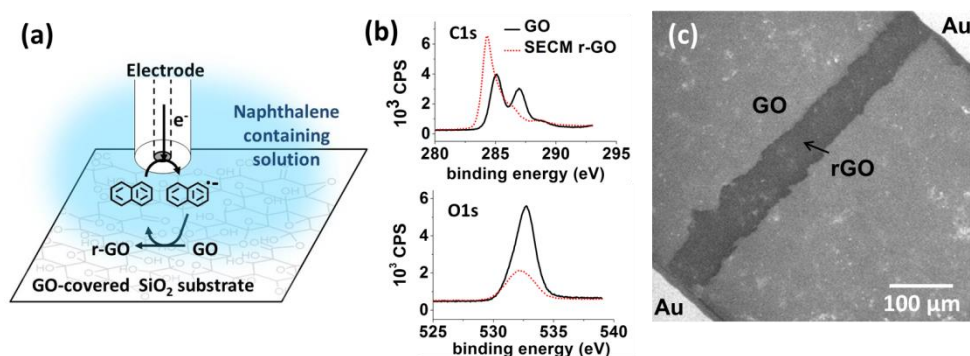


Figure 10. Localized reduction of GO with naphthalene radical anions generated by a negatively polarized microelectrode. (a) Scheme of the procedure (b) XPS data (C1s and O1s core levels) on GO and after SECM-induced reduction in r-GO. (c) SEM image of an r-GO line (within a GO thin film) connected to gold electrodes. Reprinted with permission from ⁵⁷.

3.3. Functionalization of 2D materials

Local electrochemistry is also used to perform more complex transformations. After reduction of GO, the increased conductivity of the r-GO motifs can be used to perform localized diazonium electrografting.⁵⁷ Diazonium functionalization is a well-known reaction on sp^2 carbon materials⁵⁸ that was also performed on HOPG with SECCM.⁵⁹ Local carboxylation of multilayered graphene is demonstrated with an SECM, as shown in figure 11.⁶⁰ It demonstrates that the degree of modification can be controlled by the electrolysis duration.

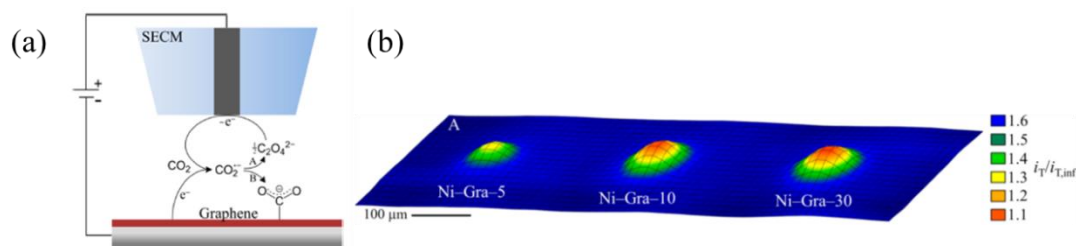


Figure 11. CO_2 functionalization of graphene with SECM. (a) Scheme presenting the strategy. (b) SECM image obtained after reduction, showing a decrease in the ability of the functionalized zones to exchange charges with the solution, due to the presence of the CO_2 moieties. Reprinted with permission from ⁶⁰.

Another approach uses 2D layers placed at the interface between two immiscible liquids, as already presented in figure 4, to perform electrodeposition of an inorganic compound selectively at one side of the 2D material.⁶¹ Alternatively, the 2D layers can be deposited on a sacrificial substrate that undergoes oxidation upon electrodeposition.⁶² These strategies lead to Janus types of 2D materials having promising electrocatalytic activities toward HER.

To conclude on this part, literature shows that the diversity of surface modifications with conventional electrochemistry can in most cases be transferred into local modifications. The main challenges of this field are to improve the spatial resolution and to generate more complex patterns while limiting the modification time. Surface modification can also be an interesting support for surface reactivity analysis as for example in reference ^{15c}, where the adsorption on HOPG of an anthraquinone derivative is used to show that edges do not present an enhanced electrochemical activity.

Conclusion

Utilization of local electrochemistry for analysis, patterning or functionalization of 2D materials is a rapidly growing field. At the present stage, most of the reported studies focus on graphene or analogues such as graphene oxide and reduced graphene oxide, and the most typical characterization concerns the evaluation of the kinetic constant associated to simple charge transfers. From this basis, much needs to be done in order to better understand 2D materials thanks to localized electrochemistry. This is particularly the case as the relatively recent utilization of other 2D materials than graphene gives unprecedented access to original properties, which opens new research directions and generates new needs in terms of characterization, understanding and modification. As an illustration, the photochemical properties of dichalcogenides are particularly promising in photocatalysis, but several fundamental studies regarding the underlying processes are still missing. These would combine local electrochemistry with spectroscopy and other microscopy techniques. Besides, it should be noted that only a very limited number of studies combine local electrochemistry experiments with numerical simulations. Such combination could drastically increase the outcomes by enabling a quantitative interpretation of the measurements. In any case, localized electrochemistry has the potentiality to cover many needs for analysis and modification of 2D materials and thus to provide information and solutions of particular relevance for future devices and applications.

Acknowledgments

This work was supported by a public grant overseen by the French National Research Agency (ANR) as part of the “Investissements d’Avenir” program (Labex NanoSaclay, reference: ANR-10-LABX-0035).

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