

## Conference paper

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# Watching atoms at work during reactions

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**Abstract:** The development of new technologies for the current energy and environmental challenges requires the acquisition of a very fundamental knowledge about the structure and activity of catalytic materials at the nanometric scale. As a consequence, *in situ* and *operando* methodologies are blossoming, but only a fraction of them really aims at a local vision that would allow watching atoms at work during reactions. In this short report, we want to outline the merits of a new technique based on scanning tunnelling microscopy (Current-roughness electrochemical scanning tunneling microscopy, cr-EC-STM) which can visualize electrocatalytic reactions down at the single atom level. Results of two case studies in the field of hydrogen evolution reaction (HER) are briefly summarized, witnessing the capability of cr-EC-STM to provide critical information about the structure and catalytic performance of the active sites with atomic resolution.

**Keywords:** Avogadro Colloquia 2022; electrocatalysis; hydrogen; *operando* and *in situ*; scanning probe microscopies; scanning tunneling microscopy (STM).

## Introduction

Catalysis is probably the most pervasive and impacting principle of Chemistry [1]. It allows to carry out thermodynamically favored, but kinetically disadvantaged, reactions in acceptable times. Furthermore, in the presence of an external energy input (*e.g.* photo and electrocatalysis), even thermodynamically unfavorable reactions become feasible.

Chemical catalysis can be divided into three large chapters: *enzymatic* catalysis, fundamental for the chemistry of life, *homogeneous* and *heterogeneous* catalysis [2]. Homogeneous catalysis has the advantage of a high selectivity and efficiency and plays an increasingly important role in fine chemical synthesis and pharmaceuticals, while heterogenous catalysis plays a fundamental role in the chemical industry (about 85% of all catalytic processes at an industrial level are heterogeneous) [3]. Scheme 1 reported below illustrates some of the strategic sectors where heterogeneous catalysis plays a fundamental role.

The fundamental ingredient of heterogeneous catalysis is the presence of the surface of a solid bearing catalytic sites, which is the “stage” where the chemical actors (the reactants) represent the *drama* of the transformation, through the facilitated reactive path of the catalyst, which eventually leads to the product formation. The presence of the catalyst allows interactions among the actors, which otherwise would be impossible; in chemical terms, this translates into the formation of an activated complex that, after breaking the interactions with the catalyst surface, gives the free final product (desorption).

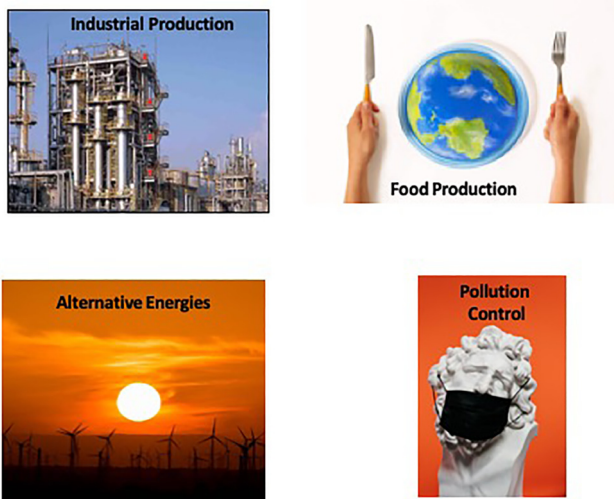
However, it must be immediately clear that the “stage” can be very broad and inhomogeneous: in scientific terms this means that usually the catalytic sites are numerous and differentiated from each other. Only the most reactive ones will lead to final products, which therefore are often mixed with secondary products. This is the

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**Scheme 1:** Some examples of sectors where heterogeneous catalysis has a decisive impact.

reason for the poor selectivity of heterogeneous catalysis. On the other hand, high selectivity is a relevant goal because it avoids troublesome separations of the desired products from unwanted species and provides better final conversions (turn-over frequency, TOF).

An accurate correlation between an atomically well-defined site and its catalytic activity is a challenging task because standard characterization techniques provide only area-averaged information, so connecting specific figures of merit to a single type of microscopic unit is not trivial, given that various structural and morphological features can be co-present on the same “real” catalyst. Thanks to the progress made by the analytical methods of Surface Science, in the last two decades scientists have tried to get the process of optimizing catalysts out of excessive empiricism [4] and trial & error methods (see Nobel Prize for Chemistry to Prof. Gerhard Ertl in 2007 [5]).

A possible solution to an immediate understanding of catalytic processes, would be to observe the atoms at work during the reaction that takes place on the surfaces of a catalyst and this would allow a knowledge-based approach to catalyst optimization, identifying the most efficient catalytic sites and maximizing their presence.

### ***In situ* and *operando* methods**

With the beginning of the new millennium, two “old” Latin words have overwhelmingly attracted the attention of people working in the field of catalyst characterization: *in situ* and *operando* [6]. We speak of *in situ* investigations when the evaluation of the catalyst is made under controlled pressure, atmosphere and temperature conditions, like those encountered during catalysis, but without this automatically implying any temporal evolution. Conversely, we speak of *operando* when the *in situ* investigations monitor the temporal evolution of the catalytic system and catalytic performances as the reactions take place. These concepts can be applied to a variety of advanced characterization techniques (microscopic, spectroscopic and diffractometric, see Table 1).

Among the characterization techniques, those based on probe microscopy (scanning tunneling microscopy, STM, and Atomic Force Microscopy, AFM) are unique because they can directly see the atoms/molecules in real time, thus they apply as the most suitable methodology for *in situ/operando* in the field of heterogeneous catalysis. In fact, the probe is capable of monitoring locally (with atomic resolution) and in real time the dynamic phenomena that occur on the catalyst. Transmission electron microscopy, TEM could also obtain similar information, but stringent experimental requirements and procedural complications make this task much more complex.

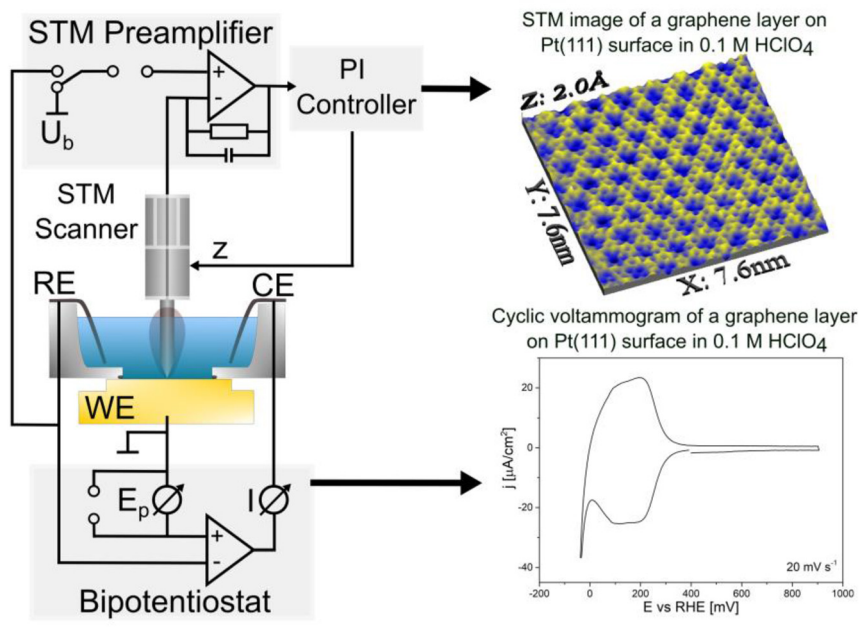
**Table 1:** Advanced *in situ* and *operando* characterization techniques.

| <i>In situ</i>                                 | <i>In situ and operando</i>  | Features   |
|--|--|--|
| Microscopic techniques                         | Scanning tunneling microscopy (STM)                                    | Real-time atomic resolution by directly imaging atoms              |
|  | Atomic Force Microscopy (EC-AFM)                                       |  |
|  | Scanning electrochemical microscopy (SECM)                             | Sub-micrometer resolution  |
| Scanning electron microscopy (SEM)             |  | Sub-micrometer resolution  |
| Spectroscopic and diffractometric techniques   | Transmission electron microscopy (TEM)                                 | Atomic resolution <i>in situ</i> ; <i>operando</i> nm resolution   |
|  | X-ray absorption near edge structure (XANES)                           | Electronic state, bulk geometry included, coordination environment |
|  | Extended X-ray absorption fine structure (EXAFS)                       |  |
|  | Raman  | Vibrational mode of investigated material                          |
|  | Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS)             | Elemental analysis, chemical shift and oxidation state             |
| Fourier-transform infrared spectroscopy (FTIR) | Vibration mode exhibited by probe molecules adsorbed on surface sites. |  |
| Synchrotron powder X-ray diffraction (XRD)     | Crystal structure (only periodic structures)                           |  |

## Electrochemical scanning tunneling microscopy (EC-STM) and hydrogen evolution sites

One of the great advantages of STM is that, even if originally developed in ultra-high vacuum conditions, the tunneling phenomenon can occur also when molecules/atoms present in the environment are positioned between the tip of the probe and the investigated surface. This ensures the possibility of studying catalytic processes in the presence of gas or in a liquid environment opening the way to *operando* studies of electrochemical (EC) processes by EC-STM with atomic resolution. Recently, significant progress has been made in the study by EC-STM of processes occurring on the surface of an electrode using an instrumental set-up where the electrode surface is the working electrode in contact with the electrolyte (see Fig. 1).

The cornerstone of this technique is that the electron tunneling barrier sensed by the tip under a constant bias is statistically perturbed by the dynamical phenomena occurring on the surface as for example an electrocatalytic reaction, which entails the constant formation and/or elimination of charged species. The crucial point that makes possible the study of reactions on the electrode is consequent to the demonstration that a distinct noise in tunneling current can be clearly measured on the catalytic sites where such dynamic phenomena are in progress (noise-EC-STM, n-EC-STM) [7]. In other words, monitoring the noise in the tunneling current it is possible to see the progressive ignition of the different electrocatalytic sites as the potential applied to the electrode varies. In the last few years, we have developed an advanced version of n-EC-STM called Current-roughness-EC-STM (cr-EC-STM) [8]. This method introduces quantitative and reliable methods for determining the aforementioned noise. The mathematical treatment of the noise can provide new quantitative descriptors, which can be related to standard electrocatalytic figures of merits (*e.g.*, macroscopic onset potential, Tafel slope, and TOF), but with sub-nanometric spatial resolution. This new method was able to determine at the atomic level the nature, the relative abundance and the specific activity of the sites where the electrocatalytic processes take place.



**Fig. 1:** A simplified schematic illustration of the bipotentiostatic four-electrode electrochemical scanning tunneling microscopy (EC-STM) configuration. On the right, an example of STM image obtained with such a device and the corresponding cyclic voltammogram.

The main upshot of the cr-EC-STM method is related to the possibility to express the information conveyed by the noise affecting the tunneling current into a single scalar quantity. In this way it is possible to associate a single numerical value with each tested electrodic potential, allowing to include the information of a full potentiodynamic scan in a simple bi-dimensional graph. Taking the cue from the parameter used to define the roughness of a surface (*i.e.*, the root mean square of local corrugation with respect to reference value), we proposed that the effect of any dynamical process that perturbs the tunneling junction can be quantified by a new parameter ( $l_0$ ), as reported in the following Equation:

$$I_0 = \sqrt{\frac{\sum_{i,j} [I(x_i, y_j) - I_{SET}]^2}{N}}$$

where  $I(x_i, y_j)$  are tunneling current values at the point of  $(x_i, y_j)$  coordinates and  $I_{SET}$  is the current in the feedback loop. We define the value  $l_0$  as the raw tunneling current: it describes the local deviation of the recorded tunneling current from the set value that is a value independent from the statistical distribution of current values, and is the same for a given STM image.

Then, we developed a local descriptor  $L$ , which is obtained from the normalization of  $l_0$  for a series of spurious factors such as tunneling parameters, size of the investigated area, the local electronic corrugation etc. The  $L$  parameter describes the changes of the tunneling current due to the reaction environment during the potentiodynamic scan, and can be used to obtain a set of curves  $L(x, y)$  vs. the EC potential ( $E$ ) for each catalytic site (or any point of interest,  $(x_0, y_0)$  in the EC-STM image). Interestingly, the  $L(E)$  vs.  $E$  plot typically exhibits a sigmoidal profile. These current roughness plots provide quantitative parameters such as the noise amplitude ( $\Delta L$ , the height of the  $L$  step), the local onset potential ( $E_{on}$ ), which can be used to compare the relative activity of different sites and even to determine the reaction mechanism (*i.e.*, local Tafel slope). Readers interested in the mathematical details of the developed method are directed to ref. [8]. In this contribution we will only focus on the discussion of the most interesting results obtained in some case studies in the field of hydrogen evolution reaction (HER).

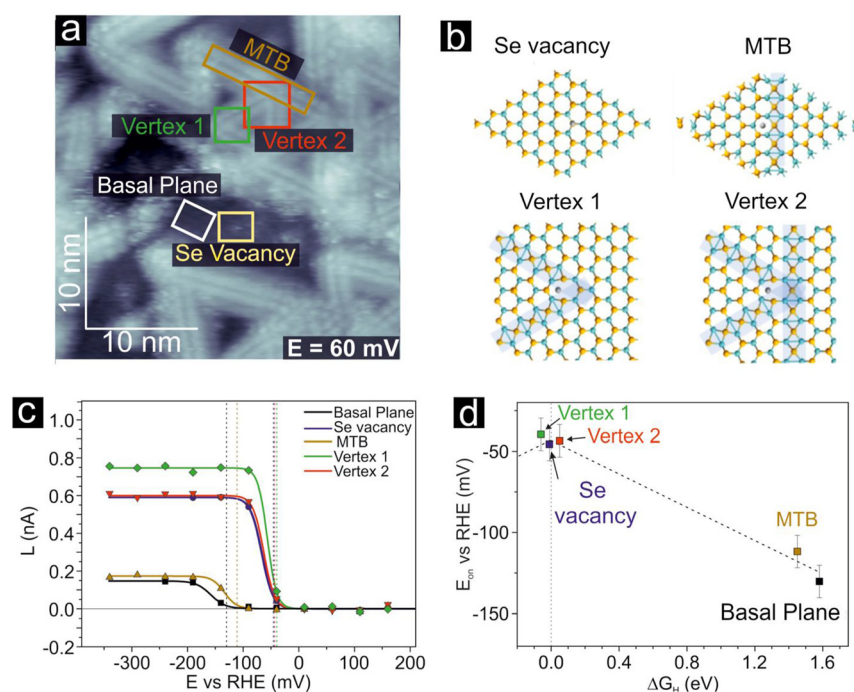
## Some case studies

### Electroactivity of point defects

Grain boundaries (GBs) are 3D extended defects in polycrystalline materials. When it comes to 2D materials, GBs turn to be line defects. Along such line defects, which usually are unfavorable for the conduction, optical, magnetic properties of 2D systems, varied and complex chemistry can be at play, therefore GBs represent a potential source of electrocatalytic sites. Recently, we investigated an original strategy for improving the HER activity of transition metal dichalcogenides (TMDs) by exploiting a particular type of line defects referred to as mirror twin boundaries (MTBs), *i.e.*, the boundary separating two grains rotated by 180°. The presence of MTBs implies undercoordinated atoms that bring innovative electronic properties, while spectroscopic investigations suggested that atoms in MTBs have metallic properties [9].

A MoSe<sub>2</sub> monolayer grown on a bilayer of graphene (Gr) supported on a 6HSiC(0001) single crystal (MoSe<sub>2</sub>/Gr/SiC) exhibits a high density of MTBs (Fig. 2a). Exploiting such a system, we could investigate by n-EC-STM the electrocatalytic activity of atoms located both on linear MTBs or at the intersections of MTBs (Fig. 2b). In Fig. 2c we report the different  $L(E)$  curves measured for the Se atom of the unperturbed basal plane standard, the Se atoms on the MTB line, the vertex 1 and 2 Se atoms and for a Se vacancy on the basal plane: the onset potential of the HER ( $E_{\text{on}}$ ) of the MTB and vertex sites show a lower overpotential of 20 and 90 mV, respectively, compared to the  $E_{\text{on}}$  of the basal plane (−130 mV vs. RHE), so that the macroscopic electrocatalytic behavior of the MoSe<sub>2</sub>/Gr/SiC at the early onset of HER can be associated with these sites. On the other hand, a similar  $E_{\text{on}}$  of the Se vacancy in the basal plane can be anticipated from the relative  $L(E)$  curve, but such isolated Se-vacancies, far from the MTBs, are very uncommon defects on the catalyst surface, so the Se-vacancies have a negligible effect on the catalytic activity for this specific system.

Noteworthy, the sequence of reactivity experimentally observed by n-EC-STM perfectly agrees with the linear trend of  $\Delta G_H$  obtained by Density Functional Theory (DFT) simulations as shown in Fig. 2d. Thus, the robustness of the cr-EC-STM procedure results to be validated.

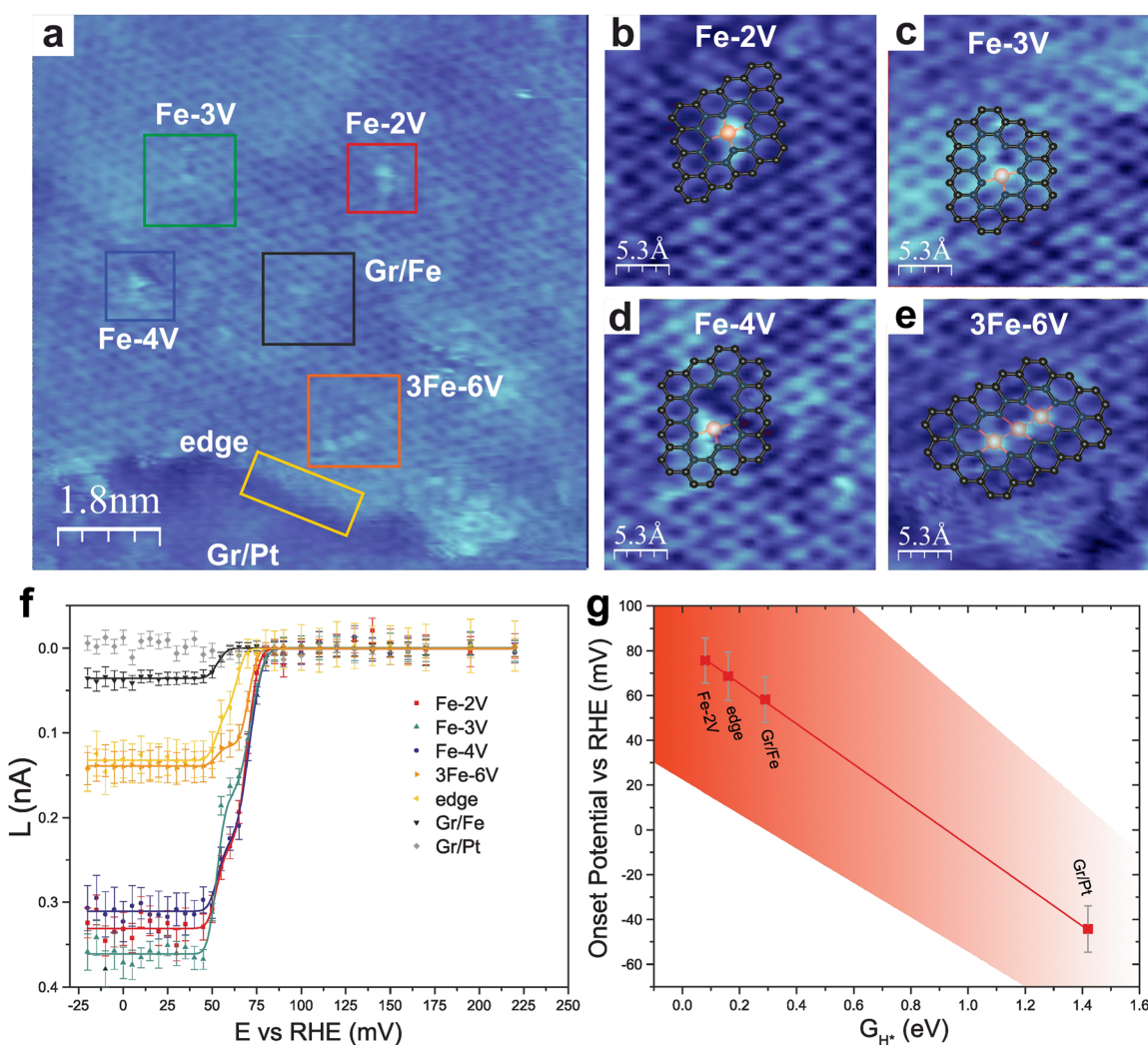


**Fig. 2:** EC-STM image of MoSe<sub>2</sub> layer recorded at an electrode potential of 60 mV vs. RHE,  $I_T = 1.84$  nA,  $U_B = 89$  mV. (b) Atomic structures of a MoSe<sub>2</sub> monolayer on pristine MTB and two different vertices. (c) Fit of the current roughness  $L$  as a function the EC potential for different structural features highlighted in rectangles in panel (a). (d) Plot of onset potential vs. Gibbs free energy for HER showing a linear relationship (from ref [9]).

## Electroactivity of single metal atom catalysts

Nowadays, the term single-atom catalyst (SAC) is a real hot entry in catalysis: it can imply both adsorption (adatoms) or incorporation of single atoms on the exposed surface of a catalyst [10]. The main advantage of SACs is the so-called “atom economy”, which allows to use even catalysts based on expensive and rare elements (critical raw materials), given the extremely small amount required in applications. A very distinctive feature of the most recent studies on SACs is the accurate description at atomic level of both the single-atom and the support with a particular attention to the single-atom coordination. All these aspects are crucial to describe the rather innovative chemistry of SACs.

In a recent paper, we studied the HER activity of single Fe atoms that can be trapped inside carbon vacancies in Gr [11]. They can be prepared by growing first a Gr layer on the Pt(111) surface and then depositing an ultrathin film of Fe. After a gentle annealing the Fe diffuses under the Gr at the interface with Pt, but during this process some Fe atoms remain trapped in the Gr layer, producing Fe SACs stuck into double or multiple carbon vacancies: Fig. 3a–e) report their EC-STM images, where some of these SACs can be recognized in carbon vacancy pockets of



**Fig. 3:** EC-STM topographic images of the Gr/Fe(1.8 ml)/Pt(111) surface recorded at  $E = 195$  mV vs. RHE: STM image showing the different structural units investigated (a), Fe-2V (b), Fe-3V (c), Fe-4V (d), 3Fe-6V (e). Tunnelling parameters:  $I_t = 1.50$  nA,  $U_b = -16$  mV. (f) Normalized current roughness  $L$  as a function of  $E$  extracted from the areas outlined by the rectangular boxes in (a). (g) Plot of onset potential versus Gibbs free energy of adsorption ( $\Delta G_{H^*}$ ) showing a linear relationship (from ref. [11]).

different dimensions (indicated as nV in Fig. 3). In addition, among others, also three Fe atoms captured on a 6V pocket have been discerned (3Fe-6V in Fig. 3e). The noise analysis was applied to ascertain the chemical activity of such different structural features, including also the perfect Gr layer covering either the Fe film or the Pt surface as benchmarks. From the relative  $L(E)$  plots (Fig. 3f), some interesting information can be deduced: the Gr layer on the Pt surface strongly decreases the catalytic activity, while its presence on the Fe layer has an opposite effect and indeed the Gr covered Fe film is almost as active as bare Pt, the most active pure element on the periodic table in the HER in acid conditions. However, the most intriguing results are the extremely high activity observed for the Fe SACs, which exhibit the lowest  $E_{\text{on}}$  values. These experimental results are confirmed by DFT calculations which tell us that Fe SACs trapped within carbon vacancies show almost zero Gibbs free energy of adsorption of hydrogen.

## Conclusions and perspectives

To face the current energy scenario is mandatory to develop new technologies and materials for EC applications. The scientific community is taking a lot of efforts to investigate new catalysts: almost every element of the periodic table in its pure form or combined with (many) others has been deeply investigated. Moreover, the burgeoning fields of high throughput synthesis and machine learning make possible an ever-growing production of new materials. In this complex scenario cr-EC-STM can play a significant role because is the only technique that allows characterizing the structural properties of catalytic sites and, at the same time, evaluating their chemical activity, on a very local scale. These unique features make possible the evaluation of relative activities and the amount of multiple catalytic sites, providing very precise structure-activity relationships in electrocatalysis. Therefore, cr-EC-STM has the potential to accelerate the development and optimization of new catalytic materials offering a rational design, leading the way in the big technological challenges of tomorrow.

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