

Insights into behavior on the nanoscale

Scanning Electrochemical Cell Microscopy enables the analysis of electrochemical surface activity at nanometer level.

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Heterogeneous catalysts play an important role in the development of new technologies for the energy transition. These consist of thin metal oxide layers coating solid substrates with large surface areas. Scanning probe microscopy methods provide insights into various surface parameters. Scanning Electrochemical Cell Microscopy (SECCM) has proven to be particularly effective and offers a window into the nanoscale behavior of photocatalytic materials.

Electrochemistry is one of the key disciplines where near-future developments might fundamentally shape our daily life. One example of such applications is modern lithium ion batteries that already power a large bandwidth of devices, ranging from pocket-sized gadgets like mobile phones to large-scale applications like electric cars. As we face an increasing demand of faster and larger energy storage, novel systems such as fuel cells and supercapacitors, and innovative approaches like power-to-gas or power-to-hydrogen are gaining traction. With it, the need for cutting-edge catalysts becomes paramount.

Heterogeneous catalysts, composed of thin, catalytically active metal oxide layers coating solid substrates with large surface areas, play a pivotal role in such systems [1]. Their effectiveness hinges on factors like surface acidity, chemical composition, and overall shape [2, 3]. To unravel the intricacies of such catalysts and design novel systems, understanding the interplay between

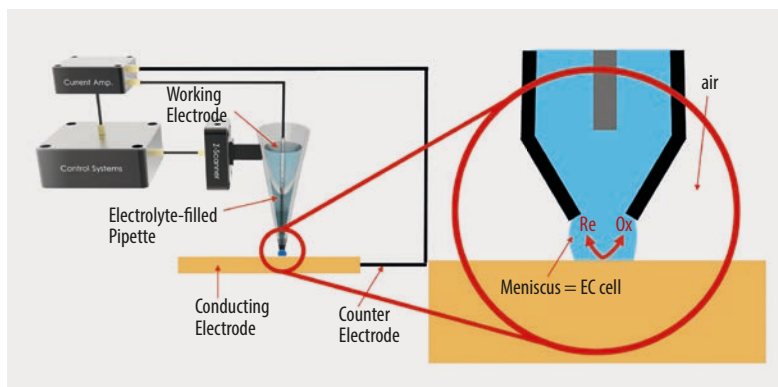


Fig. 1 In the SECCM setup implemented in a Park Systems NX10, a micropipette is filled with an electrolyte and equipped with a working electrode. When brought in close proximity to a target sample surface, a droplet at the aperture of the pipette forms a meniscus that serves as a small electrochemical cell. Electrochemical reactions can be triggered and monitored by applying an electric bias and measuring the current flow. After measuring the EC characteristics in one specific location, the pipette is lifted by a few tens of microns, moved to the next location of interest and approached again in a “hopping motion” along a grid pattern.

structure, physical properties, and local catalytic activity becomes imperative.

Scanning Probe Microscopy (SPM) is the collective name of an ensemble of techniques offering nanometer-scale insights into surface parameters such as roughness, conductivity, adhesion, and surface potential [4, 5]. In particular, Scanning Electrochemical Cell Microscopy (SECCM) emerged as a powerful tool for electrochemical characterization. Pioneered by E. Daviddi and P. R. Unwin, it employs a pipette with a nanometer-sized aperture filled with electrolyte and equipped with an electrode (Fig. 1) [6].

When approached to the surface of interest by a few tens of nanometers, a liquid droplet hanging at the aperture of the pipette forms a meniscus with the surface. This meniscus represents an electrochemi-

cal cell with nanoscale dimensions and allows for the application of a bias between the sample and the pipette electrode. Such bias induces electrochemical reactions that can be monitored by measuring the current flow.

The diameter of the resulting electrochemical cell mainly depends on the pipette aperture diameter but also varies depending on electrolyte viscosity, surface tension, and surface wettability [7]. The aperture can be precisely controlled using a special pipette puller and ranges from 100 to 500 nanometers although quartz pipettes can have aperture diameters below 50 nm. Using piezo scanners, the pipette can be precisely positioned with respect to the sample by means of nanometer size movements. Typically, an AgCl coated silver wire is used as a quasi-reference electro-

de, but other approaches consist of palladium wires with intercalated hydrogen ions that can be utilized for measurements in harsh conditions, such as solutions containing perchlorate ions or potassium hydroxide [6].

Park Systems developed a commercially available add-on that allows for an easy integration of pipette-based SPM techniques such as SECCM into their versatile atomic force microscopes. In the following we present a few examples where this technique has been implemented on Park Systems NX series tools.

Films under the microscope

One example for the utility of such measurements is titanium oxide (TiO_2), a well-studied photocatalyst [9, 10] whose properties are deeply influenced by the presence and relative position of oxygen vacancies within its crystal lattice. While those within the bulk act as n-doping centers, creating energy states near the conduction band, surface oxygen vacancies create electron traps and serve as local catalytic centers [11–13].

Recent studies have demonstrated the effectiveness of simple UV-ozone treatment in reducing the concentration of surface oxygen vacancies [8]. This reduction not only decreases the trap density but also enhances vertical conductivity through the TiO_2 thin film.

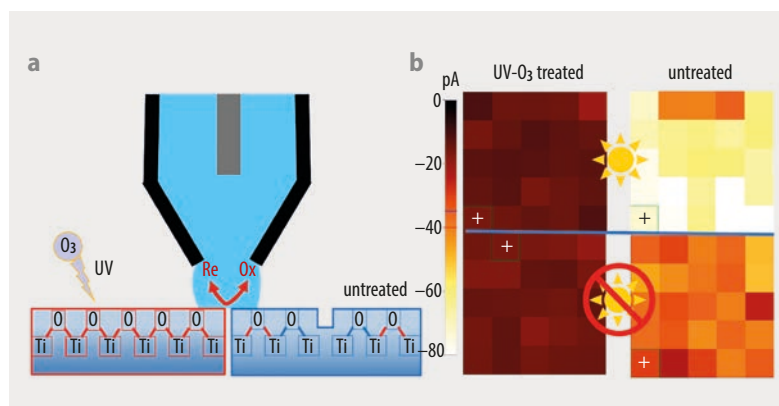


Fig. 2 One of the TiO_2 films on a FTO substrate (a) has been annealed at 500 °C while the other was also subjected to UV-ozone treatment which has removed surface oxygen vacancies [8]. The four SECCM images (b) show the treated and untreated surfaces, with lighting (top images) and without (bottom images). The maximum current of IV-curves measured on a 5 × 5 grid with a pixel size of approximately $1 \mu\text{m}^2$ is displayed.

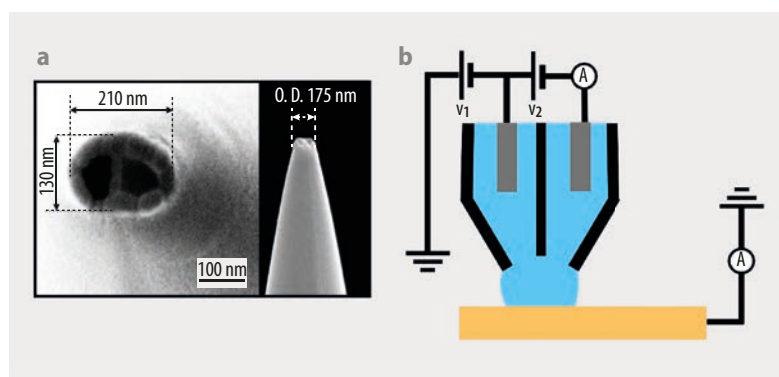
However, due to their catalytic activity, such a reduced trap density should also cause a reduced catalytic activity. **Fig. 2** shows two 100 nm thick TiO_2 films on fluorine-doped tin oxide (FTO) substrates that were prepared via spin-coating and subsequently annealed at 500 °C for 30 minutes. Afterwards, one sample underwent 30 minutes of UV-ozone treatment, while the other remained untreated.

To investigate the local catalytic water-splitting properties, SECCM was conducted with a Park Systems NX10 utilizing a standard phosphate buffer electrolyte solution. A series of 25 individual current-voltage (IV) curves was recorded on a 5×5 grid, with applied biases

sweeping between +1.5 and –1.5 V. The samples were illuminated or kept dark during the measurements (**Fig. 2b**).

Under illumination, the defect-rich pristine TiO_2 surface exhibited an average maximum current of 70 pA, which is more than three times higher than the defect-poor treated surface. Since the photocatalytic activity of these oxygen vacancies depends on the absorption of blue light, the Faraday current decreased significantly in the defect-rich sample under dark conditions. In contrast, the latter showed constantly low Faraday current values regardless of the lighting conditions.

Fig. 3 The SEM image (a) shows a double barrel used for SECCM measurements. A DC bias voltage between a pipette electrode and the sample (V_1) helps to measure the local Faraday current (b). Additional AC bias is applied between the two pipette electrodes (V_2) to detect the meniscus formation on the surface.



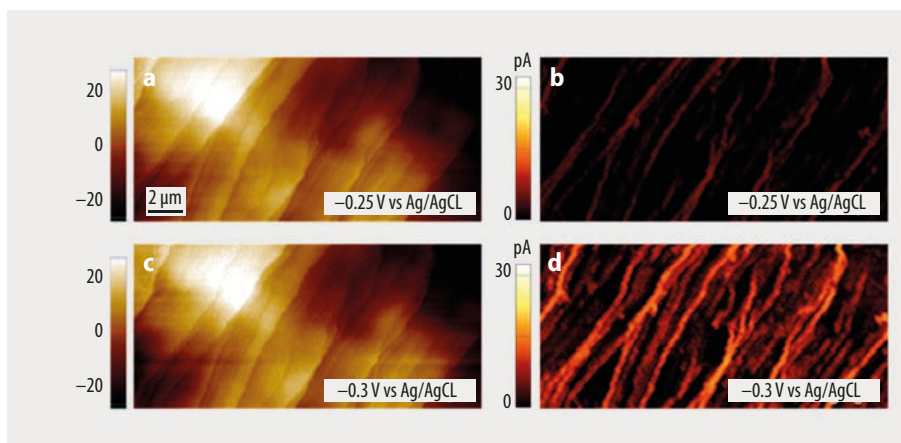


Fig. 4 The images show the topography (a and c) as well as the local Faraday current (b and d) of an HOPG surface at different applied biases using a double barrel SECCM.

The lack of reference

Despite the value of such insights, traditional single-barrel setups face inherent limitations due to the absence of a reference electrode, which may lead to multiple issues: possibly changing electrochemical potentials, inconsistency of measurements and no independent signal to map both the Faraday current and respective topography. To address this challenge, one solution has been the introduction of double barrel pipettes. Each barrel houses an AgCl/Ag quasi reference electrode, between which an AC bias is applied. This setup allows for the detection of the meniscus formation through changes in AC current. Simultaneously, a DC potential can be applied to monitor the Faraday current, enabling the detection of electrochemical reactions. This approach has been successfully applied in recent studies, including the investigation of facet-dependent electrocatalytic activity of gold nanoparticles [14].

In another example (**Fig. 4**) a dual-barrel configuration was used to simultaneously record topography and local Faraday current on highly oriented pyrolytic graphite (HOPG) with a Park Systems NX12 [15]. HOPG served as a model for 2D materials, which have garnered attention for their potential applications in water splitting and batteries

[16]. Here, a $\text{Ru}(\text{NH}_3)_6^{2+} / \text{Ru}(\text{NH}_3)_6^{3+}$ redox couple was used to map the Faraday response at different applied biases. Increased bias revealed enhanced electroactivity at step edges and the basal plane, with step edges displaying intensified intensity corresponding to the number of graphene layers.

In conclusion, the application of SECCM offers valuable insights into the nanoscale behavior of photocatalytic or charge selective materials, paving the way for enhanced efficiency and tailored design in various applications, including water splitting and energy storage. The adoption of double barrel pipettes represents a significant advancement in SECCM methodology, enhancing its capabilities for correlating topography with electrochemical activity at the nanoscale.

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