

Contents lists available at ScienceDirect

Sensors and Actuators: B. Chemical



journal homepage: www.elsevier.com/locate/snb

A simple approach for effectively improving the resolution of scanning electrochemical cell microscopy

ng

Gen Liu^{a, d}, Hao Li^a, Yuchen Xu^a, Kaimin Zhang^a, Luzhen Hao^a, Xue Yu^a, Yanqing Ma^{a,b,c,*}, Lei Ma^{a,b,*}

^a Tianjin International Center for Nanoparticles and Nanosystems, Tianjin University, 300072, PR China

^b Tianjin Key Laboratory of Low-dimensional Electronic Materials and Advanced Instrumentation, Tianjin 300072, PR China

^c School of Precision Instrument and Opto-electronics Engineering, Tianjin University, Tianjin 300072, PR China

^d College of Physics and Electronic Engineering, Taishan University, Taian, Shandong 271000, PR China

ARTICLE INFO

Keywords: High-resolution Scanning electrochemical cell microscopy Oil coating Gold nanoplate

ABSTRACT

The high-resolution scanning electrochemical cell microscopy (SECCM) is a powerful tool that can directly explore the structure-property correlation of materials at nanometer scale. However, so far, the attainable maximum resolution is still restricted by the diameter of the droplet probe. Here, we report a simple and effective approach that can highly reduce the effective size of a nanopipette probe in SECCM. The effective working size was reduced to tens of nanometers by using the conventional droplet probe with an opening size of \sim 129 nm through one-step oil coating. Furthermore, both the topographical and electrochemical activity of the Au nanoplate were simultaneously recorded successfully at the pixel size of sub-10 nm in the x-axis direction, meaning the potential to achieve a sub-10 nm resolution. Finally, the modified probe displays excellent applicability with acidic, neutral and alkaline electrolytes. The method retains the advantages of the droplet probe and breaks the limitation of its opening size on the SECCM imaging resolution, opening a broad avenue for both further rapid commercialization and broad applications of SECCM.

1. Introduction

Scanning electrochemical cell microscopy (SECCM) is designed to record the topography and electrochemical activity of materials simultaneously which is able to reveal the structure-property correlation in microscopic scale [1–3]. Since it was invented in 2010 [1], it has been widely applied to study nanoparticles [4–11], single-crystalline and polycrystalline materials [2,3,12–14], carbon-based materials [15–17], nanofabrication [18,19], energy storage materials[20,21], semiconductor [22–25], and corrosion science [26–28]. However, the high-resolution imaging acquisition is still largely restricted by the following three factors (1) the size of opening, (2) poor stability and (3) the existence of electrolyte residues on the samples [29–31].

In SECCM measurements, an electrolyte-filled nanopipette with an embedded reference electrode is used as probe [32]. A meniscus droplet formed at the opening of the SECCM tip, whose size is approximately equal to the diameter of the nanopipette [31]. The height and electrochemical activity information of a series of predefined points is recorded through the hopping motion of probes with the droplet contacting with

the surface of targeting system at those points which is the so-called hopping mode [32]. It requires that the hoping span, which is reflected as pixel size of the image, must be larger than the probe diameter in order to avoid the overlap of adjacent pixels and eliminate the effect of residual electrolyte [31,32]. Thus, the early research mainly focused on continuous minimizing the size of nanopipette opening [32,33]. Unwin et al. realized electrochemical and topographical images of Au NPs[32], Au nanocrystals [33], MoS₂ and WS₂[34], reaching an in-plane spatial and height resolution of \sim 50 and \sim 2 nm, respectively, using a probe of with the opening about ~30 nm diameter. Takahashi et al. [35] mapped the electrochemical properties of triangular MoS₂ nanosheets with a side length of \sim 130 nm through a \sim 20 nm radius nanopipette. Our group [36] recorded the topographical and electrochemical activity images of ~45 nm self-assembled Au nanoparticles monolayer, realizing a ~65 nm resolution using a ~50 nm diameter probe. However, to further improving its resolution is greatly limited by the available minimum size of nanopipette opening. Apparently, shrinking the spatial span between adjacent pixels in hopping mode is a key to achieve the high-resolution. Recently, Jin et al. [37] established an all-solid SECCM

https://doi.org/10.1016/j.snb.2024.135603

Received 30 November 2023; Received in revised form 26 February 2024; Accepted 3 March 2024 Available online 12 March 2024 0925-4005/© 2024 Elsevier B.V. All rights reserved.

^{*} Corresponding authors at: Tianjin International Center for Nanoparticles and Nanosystems, Tianjin University, 300072, PR China. *E-mail addresses:* mayanqing@tju.edu.cn (Y. Ma), lei.ma@tju.edu.cn (L. Ma).

using polyacrylamide as a solid electrolyte. The morphology and electrochemical activity of the graphene are recorded using the all-solid probe with the outer diameter of ~ 20 nm, reaching the lateral and vertical spatial resolutions down to ~ 10 nm and nearly no residue left on the scanned area. However, the probe fabrication is a rather complicated process with sophisticated facilities and requiring much know-how and experiences.

In this paper, we report a simple but effective approach that can eliminate the restriction of the pixel-overlap in hopping mode due to the minimum size of the nanopipette opening through modifying the droplet probe. This method takes full advantage of the non-miscibility of oil to water. In 2020, Shkirskiy et al. [38] first reported the oil-immersion SECCM. Then, Li et al. [39] reported an oil-immersed scanning micropipette contact method in the same year. Subsequently, the oil-immersion SECCM has been used in some important studies and provides an improvement in spatial resolution, except the sample is covered in an oil rather than the tip [40–42]. Here, the feasibility of this method was demonstrated by the successful simultaneous recording of the high-resolution topographical and electrochemical images of the standard array electrode and gold nanoplates. Furthermore, the modified probe was successfully applied in acidic, neutral and alkaline electrolyte systems.

2. Methods

2.1. The fabrication of modified probe

The home-made single-barrel nanopipette probe with a tip inner diameter of ~ 129 nm (Fig. S1) was fabricated by pulling from borosilicate glass capillaries (BF100–58–10, Harvard Apparatus, U.S.A.) using a CO₂-laser puller (P-2000, Sutter Instruments, U.S.A.). The singlebarrel nanopipette probe was mounted on the scanning head of the SECCM (based on the atomic force microscopy (AFM), Park NX-10 Systems, South Korea) to prepare the modified one. The oil-coating procedure is completed by approaching the tip to the surface of the pump oil / simethicone with approaching speed less than 1.0 μ m s⁻¹ to avoid the tip breakage until contact (Fig. 1(a, b)). There are clearly visible shadows in the microscope view of AFM platform when the tip contacts the oil surface, as the white arrow shown in the inset in Fig. 1b. The approaching process will be stopped right after the contact occurs. Then the probe is slowly lifted after holding for $\sim 10-15$ s (Fig. 1c), and a thin oil film would cover the end of the nanopipette, as shown in Fig. 1e0. After exposure in air for about 15 min to avoid the excessive oil, then, it is ready for electrolyte filling and to carry out the SECCM measurement. The oil is hard to get back over to the pipette due to the surface tension, which was further demonstrated by the scanning ion conductivity results (Fig. S2). Moreover, due to the surface tension between the electrolyte and oil film, the actual diameter of exposed electrolyte meniscus (Fig. 1(e1, e2)) can be much smaller than the unmodified ones (Fig. 1d1). Fig. 1e3 shows the sectional view of the modified probe, however, there is no direct evidence indicating that the oil film can completely cover the droplet probe (Fig. 1(e1, e2)).

2.2. SECCM measurement

SECCM is performed through a modified commercial AFM, more setup details have been reported previously [36]. The fabrication of SECCM samples were described in the supporting information. The electrochemical measurement details in the SECCM experiments include:1) **'TJU-TICNN' electrode array**, the sample bias was set to 1.0 V ~ 1.2 V, scan rate: 1.0 V/s (PBS buffer solution), 0 V ~ -1.2 V, scan rate: 1.0 V/s (0.5 M H₂SO₄); 2) **Au nanoplate**, the sample bias was set to 1.7 V ~ 1.9 V, scan rate: 1.0 V/s (PBS buffer solution), -0.9 V ~ -1.2 V, scan rate: 1.0 V/s (0.5 M H₂SO₄); and 1.5 V ~2.0 V, scan rate: 1.0 V/s (1.0 M NaOH); 3) **Cr/Au electrode by evaporation coating**, the sample bias was set to -0.2 V ~ 0.5 V / 0.6 V, scan rate: 0.5 V/s



Fig. 1. (a-c) The schematic diagram of the probe modifying process, (a) unmodified, (b) modifying/contacting, (c) modified; (the insets correspond to the optical microscopy images of the probe tip, b shows obvious shadow when contacting which is marked as the white arrow); (d) the schematic diagram of the unmodified nanopipette (d0) and the probe droplet after filling electrolyte (d1), d2 is the sectional view of the probe with droplet; (e) the schematic diagram of the modified nanopipette (e0) and the probe droplet after filling electrolyte (e1, e2) after coating, e1 and e2 represents the part and almost complete oil-covered droplet, respectively; e3 is the sectional view of the modified probe with droplet.

 $(5 \text{ mM Fe}(CN)_6^{3-} \text{ in } 1.0 \text{ M KCl}); 4)$ **NiO sample**, the sample bias was set to 1.7 V ~ 2.2 V, scan rate: 1.0 V/s (PBS buffer solution). The scan size and pixels of each SECCM measurement have been described in the caption of the Figure.

3. Results and discussion

3.1. The SECCM measurements of 'TICNN-TJU' array electrode

Herein, the pump oil and PBS buffer solution (pH = 7.28 \pm 0.02) were used as coating oil and electrolyte, respectively. The nanopipette has an ending opening of a diameter of ~129 nm (Fig. S1). To demonstrate its high-resolution imaging capability, the 'TICNN-TJU' array electrode with the linewidth of $\sim 120 \text{ nm}$ (the inset in Fig. 2a) was chosen as model sample. The sample surface is evaporated Au film (sheet resistance is \sim 3–4 Ω) as described in detail in supporting information. Fig. 2a shows a 'ICN-TJU' letters with the scan size of 3.0×3.0 μ m² (pixels: 20 × 20). The linewidth of the letter occupied ~2–3 pixels which is \sim 300–450 nm which is much wider than the actual size due to the large nanopipette diameter. Fig. 2b is a measurement of an area of $2.0 \times 1.5 \ \mu\text{m}^2$ (pixels: 100×20). It yields a pixel size of 20 nm in the xaxis direction. It yields a pixel size of 20 nm in the x-axis direction which indicates a successful measurement of adjacent pixels in hopping mode with negligible influences of point overlapping. To further demonstrate its capability in x, y-plane, the pixel size was set to 30 nm (scan size: 1.5 \times 1.5 μ m², 50 \times 50) to measure the single letter 'J'. As displayed in Fig. 2c, a well discerned letter 'J' with linewidth \sim 300 nm (\sim 10 pixels) in x-axis direction was imaged. It reached a minimum imaging pixel size of 20 nm which demonstrates a successful overlapping test of adjacent pixels in hopping mode using the modified probes. The overlap of pixels means the possible influence of electrolyte residual to the measured results of their neighbor points^{3,17}. It typically shows a gradually current increase along the scanning direction due to the continuously increased contact area caused by the electrolyte residual caused by the pixels overlapping (Fig. S3). Here, the electrochemical activity images (Fig. 2 (d, e, f)) recorded simultaneously display no obvious change, meaning the residues have little effect on the continuous scanning. This further demonstrates the feasibility and stability of the modified probes.

To further study the residues, the contact angle measurements were performed. The results (Fig. S4, S5, S6) indicate that initially the oil modifiers and water show similar contact angles, but the former decrease much rapidly. The contact angle of pump oil and simethicone on the surface of Au film decreases from ~ 94° to ~40° and ~ 102° to ~55° within 1.0 s, respectively, while that of the PBS buffer solution keep it at ~ 93°. Each single 'hop' is 0.5 s including 0.1 s for stabilizing the probe and 0.4 s for electrochemical data acquisition. The contact angle measurements suggest that there are more wetting of the electrode surface using oil. However, the residues only have little effect on the continuous scanning based on the SECCM measurements (Fig. 2).

To further elaborate the little oil residues, a step of pre-hopping could be performed. Fig. S7 shows the schematic diagram of optimizing the distance of probe approaching to the sample surface. Initially approaching the probe to the sample surface to evaluate the optimized distance so that the top of exposed solution contacts the sample surface (case 1 in Fig. S7) but not the coating oil layer, if it does that when we approach same spot second time it will give the nearly identical signal otherwise it will acquire much less or almost no signal. The reason is that due to the good wettability of oil to the sample surface, once the oil contact to the surface it will swiftly spread and cover the spot to form an insulating layer who will avoid the solvent contact the sample therefore no electrochemical reaction initiates (case 2 in Fig. S7). Neither preconditioning nor pre-hopping of the pipette are needed before starting the imaging process based on our experimental experience. The SECCM imaging process could be performed directly after filling the electrolyte. The status of the modified probe has few differences compared to that of the unmodified one in the optical image. Once the oil-coating has a negative impact on the droplet probe, it would result in a changed optical image. Thus, the status of the probe could be monitored by the



Fig. 2. (a-c) the SECCM topographical images of the 'TICNN-TJU' array electrode measured with the probe modified by pump oil (the electrolyte is PBS buffer solution, $pH = 7.28 \pm 0.02$) with different scan size; a, $3.0 \times 3.0 \ \mu\text{m}^2$ (pixels: 20×20); b, $2.0 \times 1.5 \ \mu\text{m}^2$ (pixels: 100×20); c, $1.5 \times 1.5 \ \mu\text{m}^2$ (pixels: 50×50); (d-f) the simultaneously recorded electrochemical activity images (at 1.1 V) of a, b and c, respectively; (the inset in a is the SEM image of the sample, the scale bar is 2.0 \ \mu\text{m}).

optical microscope, as shown in Fig. 1. The test could be carried out if the probe status is normal in the optical image.

3.2. The SECCM measurements of Au nanoplates

Subsequently, gold nanoplates were selected to further demonstrate its application. The Au nanoplate was dispersed on the patterned indium tin oxide glass (ITO, sheet resistance is \sim 7–9 Ω) as described in detail in supporting information. The hexagonal Au nanoplate (Fig. 3a) with the side length of \sim 0.83–1.16 µm was measured within the scan area of 5.0 \times 5.0 μ m² (pixels: 10 \times 10) to define its precise location. The brighter area in Fig. 3b corresponds to the Au nanoplate which is further confirmed by the electrochemical activity image (inset in Fig. 3b). A finer SECCM imaging test was carried out referring to the predefined location. The pixels were set to 128×20 (scan size: $4.0 \times 4.0 \ \mu\text{m}^2$) to meet the requirement of commercial application. Both the topography and electrochemical activity images in Fig. 3(d, e), display a clear hexagonal structure with the measured side length of \sim 1.16 µm, \sim 0.84 µm and $\sim 1.16 \,\mu\text{m}$, which are almost identical with the value of $\sim 1.16 \,\mu\text{m}$, \sim 0.83 µm and \sim 1.16 µm measured in Fig. 3a. Furthermore, Fig. 3f is the Z-height curve along the red arrow pointed direction in Fig. 3d, whose height of \sim 53 nm is consistent with the AFM measurement (\sim 53 nm) in Fig. 3c. It corresponds to a pixel size of $4000 / 128 \sim 31.3$ nm. To further confirm its repeatability and achievable maximum resolution, more nanoplates have been measured.

15.6 nm (scan size: $2.0 \times 2.0 \ \mu\text{m}^2$, pixels: 128×40) and $1000/128 \sim$ 7.8 nm (scan size: $1.0 \times 0.8 \ \mu\text{m}^2$, pixels: 128×8). Both the topography in Fig. 4 g, and i show clear Au nanoplate structure, which are further confirmed by the simultaneously obtained activity image (Fig. 4(h, j)). All the SECCM topographies in Fig. 4(c, e, g, i) clearly and precisely reflect both the structure and size of the nanoplate, and accurately correspond to the high active area in the measured electrochemical activity image (Fig. 4(d, f, h, j)). These results demonstrate a successful SECCM imaging with the pixel size of sub-10 nm using a physical opening of probe more than 100 nm. Then, an even smaller pixel size was achieved in line scanning. There, the $y = 0.5 \ \mu m$ was selected as the scanning line as shown in Fig. 4c, a series of scans are performed with the pixel sizes start from 400 nm (4.0 $\mu m,$ pixels: 10 \times 1) and down to 6 nm (3.0 μm , pixels: 500 \times 1). As demonstrated in Fig. 4 l, the measured Z-height profiles suggest a height of ~43 nm of gold nanoplate which is very close to the measured height of ~42 nm using AFM (Fig. 4k). The electrochemical activity information recorded simultaneously in Fig. 4 m also displays a relative higher activity on the nanoplate. Furthermore, a one-to-one correspondence between the Zheight and the relevant activity are built. It also indicates that the influence of electrolyte residual to the Z-height measurement is negligible.

The increased current in Fig. 4(d, f, h, j, m) could result from the pixel overlapping or the surface changes caused by the multiple tests in the same area. In theory, the current should gradually increase along the scanning direction if there are the pixels overlapping due to the continuously increase contact area caused by the residual (Fig. S3). However, the current in Fig. 4(f, h, j, m) does not show this trend. Both the oil and electrolyte residues could affect the repeatable measurement. As discussed previously, if there are the coating oil layer residue, it will acquire much less or almost no signal at the same spot since the good wettability of oil to the sample surface (Fig. S(4, 5, 6)) which will blockade electrochemical reaction as statements and shown in Fig. S7. Here, the successful repeatable tests further demonstrate few oil residues. Thus, the results prove the advantages of this method and the potential feasibility of repeatable imaging.



Fig. 3. (a) The AFM image of the Au nanoplate; (b) the SECCM topographical images of the nanoplate with different scan size of $5.0 \times 5.0 \ \mu\text{m}^2$ (pixels: 10×10), the inset is the electrochemical activity image at 1.9 V, the scale bar is $1.0 \ \mu\text{m}$; (c) the Z-height curves derived from (a); (d) and (e) the SECCM topographical and electrochemical activity (at 1.9 V) images of it with the scan size of $4.0 \times 4.0 \ \mu\text{m}^2$ (pixels: 128×20), respectively; (f) the Z-height curves derived from (d).



Fig. 4. (a) and (b) The AFM and SEM image of the Au nanoplate, respectively; (c), (e), (g) and (i) the SECCM topographical images of the nanoplate with different scan size (c, $4.0 \times 4.0 \ \mu\text{m}^2$, pixels: 10×10 ; e, $4.0 \times 4.0 \ \mu\text{m}^2$, pixels: 128×20 ; g, $2.0 \times 2.0 \ \mu\text{m}^2$, pixels: 128×40 ; and i, $1.0 \times 0.8 \ \mu\text{m}^2$, pixels: 128×8); (d), (f), (h) and (j) the corresponding SECCM electrochemical activity (at 1.9 V) images of (c), (e), (g) and (i), respectively, (the measurement from c to j is continuous, with only the time to change the parameters in test interval); (k) the Z-height profile that derived from (a); (l) and (m) the Z-height and activity (at 1.9 V) profiles recorded simultaneously in linear scanning with different pixel size in the x-axis direction, $400 \ \text{nm}$, $4.0 \ \mu\text{m}$, pixels: 20×1), $100 \ \text{nm}$ ($4.0 \ \mu\text{m}$, pixels: 320×1), $200 \ \text{nm}$ ($4.0 \ \mu\text{m}$, pixels: 20×1), $100 \ \text{nm}$ ($4.0 \ \mu\text{m}$, pixels: 320×1), $8 \ \text{nm}$ ($4.0 \ \mu\text{m}$, pixels: 500×1), and $6 \ \text{nm}$ ($3.0 \ \mu\text{m}$, pixels: 500×1) (the Z-height and current data were offset by $0.07 \ \text{and} 0.15$ in sequence when plotted, respectively).

Then, the exposed droplet probe after modifying was further studied by selecting the Fe (CN)₆³⁻ as the redox species to carry out the SECCM measurements. Both sides of the pulled pipette were selected as the unmodified and modified (modified by the pump oil) probe. The pixel size was set to 1.0 μ m (5.0 \times 5.0 μ m², pixels: 5 \times 5) to separate the adjacent pixel to observe the change of electrochemical activity. The results are shown in Fig. 5 and Fig. S9.

The Fig. 5(a, b) shows large weakening of measured current when using the modified probe comparing to the unmodified one, again which signals dramatically dimmish of the exposed solvent droplet as we expected. The CV curves (Figs. 5e, 5 f) extracted from Figs. 5a, 5b (marked as white Arabic numerals 1, 2, 3, 4, 5) indicate the redox peak disappeared in Fig. 5 f, exhibiting a limiting current of \sim 3.0 pA at -0.2 V (the value is \sim 9.0 pA measured by the unmodified probe). The well resolved redox peak could be attributed to the high activity of the evaporated Au surface. It again verified the reduction of the exposed electrolyte droplet size through oil modification on the pipette tip. Similarly, the pixel size was set to 20 nm ($0.8 \times 0.2 \,\mu\text{m}^2$, pixels: 40×10) and 10 nm (0.4 \times 0.2 μm^2 , pixels: 40 \times 10) to further define its size and imaging stability. The current magnitude in Fig. 5(c, d) is similar to that in Fig. 5b. The CV curves in Fig. 5(g, h) further demonstrated it. The CV curves measured at the pixel size of 10 nm (Fig. 5 h) are similar to that of the pixel size of 1.0 µm (Fig. 5 f). Furthermore, the CV curves of adjacent pixels show few changes, as shown in Fig. 5(g, h), indicating a potential achievable high-resolution. However, to get a perfect high-resolution (especially the sub-10 nm resolution) SECCM image in the Fe $(CN)_6^3$ and Cr/Au electrode system is still challenging. Fig. 5(c, d) display the activity differences on the Cr/Au electrode surface, which could attribute to the higher resolution detected subtle surface differences. The analytical expressions for diffusion limited-current at a hemispherical

electrode and a SECCM are $i_{lim}^{hemi} = 2\pi RnFD_{Ox}C_{b,Ox}$ and $i_{lim}^{SECCM} = i_{lim}^{hemi}(1 - \cos(\gamma) \ (i_{lim}^{x}$ is the diffusion limited-current, R is the appropriate-radius hemispherical electrode(here R $\approx r_d$), here the reactant (Ox) is Fe(CN)_6^3. *F* is the Faraday's constant (*F* = 96485 C/mol), *n* is the number of electrons transferred, D_{Ox} is its diffusion coefficient, $C_{b,Ox}$ is the bulk concentration of Ox, γ is the nanopipette half angle (~3°, Fig. S1)), respectively[43]. These calculations yield a pipet radius ~15 nm, which is larger than the reached imaging pixel size. It could result from the unknown change of *h* and θ caused by the oil coating (the inset in Fig. 5 f) leading to the calculated radius require further correction³⁸. Thus, the precise exposed droplet size of the modified probe would be further studied in the future work.

To further demonstrate the universality of this method, the modified probe was performed in 0.5 M H_2SO_4 and 1.0 M NaOH electrolyte systems, respectively. High-resolution topography and electrochemical activity imaging of the Au nanoplates were recorded simultaneously, as shown in Fig. 6(a, b, c) and Fig. S10, suggesting the successful applications in both acidic and alkaline environments. The modified probe was further used to record the high-resolution topography and electrochemical activity imaging of NiO particle successfully, as shown in Fig. S12. Furthermore, the high resolution SECCM imaging test was also successfully run using the probe modified by the simethicone, as shown in Fig. 6(d, e, f). The successfully recorded high-resolution SECCM images, further demonstrate the excellent universality of the method.

4. Conclusions

In summary, the SECCM probe modified through a simple step of tipoil coating was developed, which successfully realized the highresolution SECCM imaging. It breaks the restriction that the reachable



Fig. 5. (a) and (b) the SECCM electrochemical activity (at -0.2 V) images of the Cr/Au electrode measured by the unmodified and modified (modified by the pump oil) probe, respectively, (the electrolyte is 5 mM Fe(CN)₆³⁻ in 1 M KCl, the scan size is $5.0 \times 5.0 \ \mu\text{m}^2$, pixels: 5×5 , the unmodified and modified probe are the both sides of the pulled pipette.); (c) and (d) the SECCM electrochemical activity (at -0.2 V) images of the Cr/Au electrode measured by the modified probe used in b with different scan size (c, $0.8 \times 0.2 \ \mu\text{m}^2$, pixels: 40×10 ; d, $0.4 \times 0.2 \ \mu\text{m}^2$, pixels: 40×10 ; (e), (f), (g) and (h) the cyclic voltammetry (CV) curves extracted from (a), (b), (c) and (d) (marked as black Arabic numerals 1, 2, 3, 4, 5), respectively, the insets in (e) and (f) correspond to the geometry of a two-dimensional cylindrically symmetric conical SECCM pipet tip (e: unmodified, f: modified) with meniscus in contact with a substrate electrode (γ is the nanopipette half angle, θ is the contact angle of the meniscus, *h* is the height of the meniscus, *r_p* is the radius of the nanopipette, *r_d* is the contact radius of the meniscus.).



Fig. 6. (a) and (d) the SEM images of different Au nanoplates; (b) and (c) the SECCM topographical and electrochemical activity (at -1.2 V) imaging of the Au nanoplate in (a) measured with the probe modified by pump oil, respectively, (electrolyte: 0.5 M H₂SO₄, scan size: $4.0 \times 3.0 \ \mu\text{m}^2$, pixels: 128×10); (e) and (f) the SECCM topographical and electrochemical activity (at 1.9 V) imaging of the Au nanoplate in (d) measured with the probe modified by simethicone, respectively, (electrolyte: PBS buffer solution, pH = 7.28 ± 0.02 , scan size: $3.0 \times 3.0 \ \mu\text{m}^2$, pixels: 128×10 , the raw data is shown in Fig. S11).

maximum resolution or the minimum distinguishable pixel is larger than the diameter of nanopipette opening in hopping mode. High-resolution topographical and electrochemical activity imaging of the 'TICNN-TJU' array electrode and the Au nanoplate were recorded simultaneously with the minimum pixel size of sub-10 nm by using the modified nanopipette with a diameter of ~129 nm. Moreover, the SECCM measurements using the redox species of $Fe(CN)_6^3$ -further demonstrate no pixel overlapping at the pixel size of 10 nm. Using both the probes modified by pump oil and simethicone succeed in obtaining the high-resolution imaging measurement and applicable to neutral, acidic and

alkaline electrolyte systems. This method achieves high-resolution SECCM images using a large size probe, greatly improves the imaging resolution just applying a simple trick which potentially can largely facile and broaden the applications of SECCM.

CRediT authorship contribution statement

Gen Liu: Investigation, Data acquisition, Writing - original draft. Hao Li: Data acquisition, review and editing. Yuchen Xu: Sample preparation, reviewing and editing. Kaimin Zhang: Data curation, reviewing and editing. Luzhen Hao: Data curation, reviewing and editing. Xue Yu: Sample preparation, Investigation. Yanqing Ma: Methodology, Writing - review & editing, Supervision. Lei Ma: Conceived and supervised the whole project, Methodology, Conceptualization, Funding acquisition, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This work was financially supported by the National Key R&D Program of China (No. 2020YFC2004602) and the Natural Science Foundation of Shandong Province (No. ZR2023QB226).

Supporting information

More detailed contents include the schematics of array fabrication and the SEM images of the nanopipette (Fig. S1), the voltage-scanning ion conductivity curves (Fig. S2), the SECCM topographical and electrochemical activity imaging of the 'TICNN-TJU' array electrode, the Cr/ Au electrode, the Au nanoplate and NiO particle (Fig. S3, S9, S10, S11, S12), the contact angle results (Fig. S4, S5, S6), the schematic diagram of optimizing the distance of probe approaching (Fig. S7), the SEM images (Fig. S8), the AFM images of the Cr/Au electrode (Fig. S13).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2024.135603.

References

- N. Ebejer, M. Schnippering, A.W. Colburn, M.A. Edwards, P.R. Unwin, Localized high resolution electrochemistry and multifunctional imaging: scanning electrochemical cell microscopy, Anal Chem. 82 (2010) 9141–9145.
- [2] S.X. Guo, C.L. Bentley, M. Kang, A.M. Bond, P.R. Unwin, J. Zhang, Advanced spatiotemporal voltammetric techniques for kinetic analysis and active site determination in the electrochemical reduction of CO₂, Acc. Chem. Res. 55 (2022) 241–251.
- [3] J.T. Mefford, A.R. Akbashev, M. Kang, C.L. Bentley, W.E. Gent, H.D. Deng, W. C. Chueh, et al., Correlative operando microscopy of oxygen evolution electrocatalysts, Nature 593 (2021) 67–73.
- [4] M. Li, K.H. Ye, W. Qiu, Y. Wang, H. Ren, Heterogeneity between and within single hematite nanorods as electrocatalysts for oxygen evolution reaction, J. Am. Chem. Soc. 144 (2022) 5247–5252.
- [5] S. Jeong, M.H. Choi, G.S. Jagdale, Y. Zhong, N.P. Siepser, Y. Wang, X. Ye, et al., Unraveling the structural sensitivity of CO2 electroreduction at facet-defined nanocrystals via correlative single-entity and macroelectrode measurements, J. Am. Chem. Soc. 144 (2022) 12673–12680.
- [6] T. Tsujiguchi, Y. Kawabe, S. Jeong, T. Ohto, S. Kukunuri, H. Kuramochi, Y. Ito, et al., Acceleration of electrochemical CO2 reduction to formate at the Sn/reduced graphene oxide interface, ACS Catal. 11 (2021) 3310–3318.

- [7] E.B. Tetteh, T. Löffler, T. Tarnev, T. Quast, P. Wilde, H.B. Aiyappa, W. Schuhmann, et al., Calibrating SECCM measurements by means of a nanoelectrode ruler. The intrinsic oxygen reduction activity of PtNi catalyst nanoparticles, Nano Res. 15 (2021) 1564–1569.
- [8] X. Lu, M. Li, Y. Peng, X. Xi, M. Li, Q. Chen, A. Dong, Direct probing of the oxygen evolution reaction at single NiFe2O4 nanocrystal superparticles with tunable structures, J. Am. Chem. Soc. 143 (2021) 16925–16929.
- [9] G.S. Jagdale, M.H. Choi, N.P. Siepser, S. Jeong, Y. Wang, R.X. Skalla, L.A. Baker, et al., Electrospray deposition for single nanoparticle studies, Anal. Methods 13 (2021) 4105–4113.
- [10] R. Gao, M.A. Edwards, Y. Qiu, K. Barman, H.S. White, Visualization of hydrogen evolution at individual platinum nanoparticles at a buried interface, J. Am. Chem. Soc. 142 (2020) 8890–8896.
- [11] M. Choi, N.P. Siepser, S. Jeong, Y. Wang, G. Jagdale, X. Ye, L.A. Baker, Probing single-particle electrocatalytic activity at facet-controlled gold nanocrystals, Nano Lett. 20 (2020) 1233–1239.
- [12] O.J. Wahab, M. Kang, E. Daviddi, M. Walker, P.R. Unwin, Screening surface structure-electrochemical activity relationships of copper electrodes under Co2 electroreduction conditions, ACS Catal. 12 (2022) 6578–6588.
- [13] M. Li, Y. Wang, B. Blount, E. Gordon, J.A. Munoz-Castaneda, Z. Ye, H. Ren, Stochastic local breakdown of oxide film on Ni from identical-location imaging: one single site at a time, Nano Lett. 22 (2022) 6313–6319.
- [14] T. Ando, K. Asai, J. Macpherson, Y. Einaga, T. Fukuma, Y. Takahashi, Nanoscale Reactivity mapping of a single-crystal boron-doped diamond particle, Anal. Chem. 93 (2021) 5831–5838.
- [15] C.L. Bentley, M. Kang, S. Bukola, S.E. Creager, P.R. Unwin, High-resolution ion-flux imaging of proton transport through graphene nafion membranes, ACS Nano 16 (2022) 5233–5245.
- [16] R. Jin, L. Cheng, H. Lu, J. Zhuang, D. Jiang, H.-Y. Chen, High spatial resolution electrochemical microscopic observation of enhanced charging under bias at active sites of N-rGO, ACS Appl. Energy Mater. 4 (2021) 3502–3507.
- [17] P.R. Unwin, A.G. Güell, G. Zhang, Nanoscale electrochemistry of sp2 carbon materials: from graphite and graphene to carbon nanotubes, Acc. Chem. Res 49 (2016) 2041–2048.
- [18] E. Oswald, A.L. Gaus, J. Kund, M. Kullmer, J. Romer, S. Weizenegger, C. Kranz, et al., Cobaloxime complex salts: synthesis, patterning on carbon nanomembranes and heterogeneous hydrogen evolution studies, Chemistry 27 (2021) 16896–16903.
- [19] C.L. Bentley, M. Kang, P.R. Unwin, Scanning electrochemical cell microscopy (SECCM) in aprotic solvents: practical considerations and applications, Anal. Chem. 92 (2020) 11673–11680.
- [20] T. Yamamoto, T. Ando, Y. Kawabe, T. Fukuma, H. Enomoto, Y. Nishijima, Y. Takahashi, et al., Characterization of the depth of discharge-dependent charge transfer resistance of a single LiFePO4 particle, Anal. Chem. 93 (2021) 14448–14453.
- [21] Y. Takahashi, T. Yamashita, D. Takamatsu, A. Kumatani, T. Fukuma, Nanoscale kinetic imaging of lithium ion secondary battery materials using scanning electrochemical cell microscopy, Chem. Commun. 56 (2020) 9324–9327.
- [22] M.V. Makarova, F. Amano, S. Nomura, C. Tateishi, T. Fukuma, Y. Takahashi, Y. E. Korchev, Direct electrochemical visualization of the orthogonal charge separation in anatase nanotube photoanodes for water splitting, ACS Catal. 12 (2022) 1201–1208.
- [23] J.W. Hill, C.M. Hill, Directly visualizing carrier transport and recombination at individual defects within 2D semiconductors, Chem. Sci. 12 (2021) 5102–5112.
- [24] J.W. Hill, C.M. Hill, Directly mapping photoelectrochemical behavior within individual transition metal dichalcogenide nanosheets, Nano Lett. 19 (2019) 5710–5716.
- [25] C.L. Tolbert, C.M. Hill, Electrochemically probing exciton transport in monolayers of two-dimensional semiconductors, Faraday Discuss. 233 (2022) 163–174.
- [26] Y. Wang, M. Li, E. Gordon, Z. Ye, H. Ren, Nanoscale colocalized electrochemical and structural mapping of metal dissolution reaction, Anal. Chem. 94 (2022) 9058–9064.
- [27] L.C. Yule, V. Shkirskiy, J. Aarons, G. West, B.A. Shollock, C.L. Bentley, P.R. Unwin, Nanoscale electrochemical visualization of grain-dependent anodic iron dissolution from low carbon steel, Electrochim. Acta 332 (2020) 1–12, 135267.
- [28] S. Liu, M. Shi, Y. Zhou, R. Li, Z. Xie, D. Hu, et al., Hu, G.,Scanning electrochemical cell microscopy: a powerful method to study the intergranular corrosions of archaeological silver artifacts, J. Comput. Cult. Herit. 46 (2020) 176–183.
- [29] E. Daviddi, L.F. Gaudin, C.L. Bentley, Scanning electrochemical cell microscopy: High-resolution structure-property studies of mono- and polycrystalline electrode materials, Curr. Opin. Electrochem 34 (2022) 101006.
- [30] J. Zhuang, Z.W. Wang, Q.Q. Zheng, X.B. Liao, Scanning electrochemical cell microscopy stable imaging method with a backpressure at the back of its nanopipet, IEEE Sens. J. 21 (2021) 5240–5248.
- [31] D. Valavanis, P. Ciocci, G.N. Meloni, P. Morris, J.F. Lemineur, I.J. McPherson, P. R. Unwin, et al., Hybrid scanning electrochemical cell microscopy-interference reflection microscopy (SECCM-IRM): tracking phase formation on surfaces in small volumes, Faraday Discuss. 233 (2022) 122–148.
- [32] C.L. Bentley, M. Kang, P.R. Unwin, Nanoscale structure dynamics within electrocatalytic materials, J. Am. Chem. Soc. 139 (2017) 16813–16821.
- [33] C.L. Bentley, P.R. Unwin, Nanoscale electrochemical movies and synchronous topographical mapping of electrocatalytic materials, Faraday Discuss. 210 (2018) 365–379.
- [34] B. Tao, P.R. Unwin, C.L. Bentley, Nanoscale variations in the electrocatalytic activity of layered transition-metal dichalcogenides, J. Phys. Chem. C. 124 (2019) 789–798.

G. Liu et al.

- [35] Y. Takahashi, Y. Kobayashi, Z. Wang, Y. Ito, M. Ota, H. Ida, T. Matsue, et al., Highresolution electrochemical mapping of the hydrogen evolution reaction on transition-metal dichalcogenide nanosheets, Angew. Chem. Int. Ed. 59 (2020) 3601–3608.
- [36] G. Liu, L. Hao, H. Li, K. Zhang, X. Yu, D. Li, L. Ma, et al., Topography mapping with
- scanning electrochemical cell microscopy, Anal. Chem. 94 (2022) 5248–5254.
 [37] R. Jin, H.-y Lu, L. Cheng, J. Zhuang, D. Jiang, H.-Y. Chen, Highly spatial imaging of electrochemical activity on the wrinkles of graphene using all-solid scanning electrochemical cell microscopy, Fundam. Res. 2 (2022) 193–197.
- [38] V. Shkirskiy, L.C. Yule, E. Daviddi, C.L. Bentley, J. Aarons, G. West, P.R. Unwin, Nanoscale scanning electrochemical cell microscopy and correlative surface structural analysis to map anodic and cathodic reactions on polycrystalline Zn in acid media, J. Electrochem. Soc. 167 (2020) 041507.
- [39] Y. Li, A. Morel, D. Gallant, J. Mauzeroll, Oil-immersed scanning micropipette contact method enabling long-term corrosion mapping, Anal. Chem. 92 (2020) 12415–12422.
- [40] E. Daviddi, V. Shkirskiy, P.M. Kirkman, M.P. Robin, C.L. Bentley, P.R. Unwin, Nanoscale electrochemistry in a copper/aqueous/oil three-phase system: surface structure–activity-corrosion potential relationships.Chem, Sci 12 (2021) 3055–3069.
- [41] E. Daviddi, V. Shkirskiy, P.M. Kirkman, M.P. Robin, C.L. Bentley, P.R. Unwin, Screening the surface structure-dependent action of a benzotriazole derivative on copper electrochemistry in a triple-phase nanoscale environment, J. Phys. Chem. C., Nanomater. Interfaces 126 (2022) 14897–14907.
- [42] M. Kang, C.L. Bentley, J.T. Mefford, W.C. Chueh, P.R. Unwin, Multiscale analysis of electrocatalytic particle activities: linking nanoscale measurements and ensemble behavior, ACS Nano 17 (2023) 21493–21505.
- [43] K.L. Anderson, M.A. Edwards, Evaluating analytical expressions for scanning electrochemical cell microscopy (SECCM), Anal. Chem. 95 (2023) 8258–8266.

Gen Liu received his Ph.D degree from Tianjin International Center for Nanoparticles and Nanosystems in Tianjin University. Presently, he is a lecturer in Taishan University. His research interest is to study micro-catalytic process by using SECCM techniques.

Hao Li received his B.S. degree from Yanshan University in 2013. He is currently pursuing his master's degree in Tianjin International Center for Nanoparticles and Nanosystems of

Tianjin University. His research is mainly focus on scanning electrochemical cell microscopy (SECCM) technique and its application on catalysis study.

Yuchen Xu received his B.S. degree from Tianjin University in 2021. He is currently pursuing his Master's degree in Tianjin International Center for Nanoparticles and Nanosystems of Tianjin University. His current research interest is studying catalytic mechanism of Transition Metal Dichalcogenides.

Kaimin Zhang received her B.S. degree from North China University of Water Resources and Electric Power in 2016. She is currently pursuing her Ph.D. degree in Tianjin International Center for Nanoparticles and Nanosystems, Tianjin university. Her current research interest is developing new materials and relevant fabrication methods for quantum chips.

Luzhen Hao received her B.S. degree from Hebei Normal University in 2019. She is currently pursuing her Ph.D degree in Tianjin International Center for Nanoparticles and Nanosystems, Tianjin University. Her current research interest is on graphene-gallium nitride composite electronics devices.

Xue Yu received her Ph.D from Tianjin International Center for Nanoparticles and Nanosystems in Tianjin University in 2023. Then she is a lecturer in Xinjiang University. Her current research interest is catalysts design, synthesis and characterizations.

Yanqing Ma received her Ph.D. in physical chemistry from Lanzhou Institute of Chemical Physics, CAS in 2009. She joined the International Center for Nanoparticles and Nanosystems in Tianjin University in 2017. Her research focuses on developing twodimensional catalyst and graphene based energy storage devices and sensors.

Lei Ma received his Ph.D in 2009. In 2015, he joined the faculty to Tianjin University as a full Professor and built Tianjin International Center for Nanaparticles and Nanosystems. His current research focuses on the cluster physics, graphene electronics, chemistry, low dimensional condensed matter and their applications on energy materials and devices.