

# Topography Mapping with Scanning Electrochemical Cell Microscopy

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mapping of both topologic and chemical properties of samples in the nanometer regime with SECCM routinely, which potentially can largely expand the field of SECCM applications.

o unveil the law of structure–activity relationship in the nanoscale is a key to understand and develop high-performance catalysts.<sup>1–3</sup> Although traditional scanning electrochemical microscopy (SECM) has been able to visualize electrochemical activity with  $\sim 10$  nm spatial resolution,<sup>4</sup> the simultaneous topography mapping usually needs to combine other technologies such as atomic force microscopy (AFM),<sup>5,6</sup> shear force-SECM,<sup>7,8</sup> and scanning ion conductance microscopy (SECM),<sup>9,10</sup> which require complex probes and thus dramatically increase the cost and difficulties. Unwin et al. developed scanning electrochemical cell microscopy (SECCM) to obtain the topographical information and electrochemical activity synchronously,<sup>11,12</sup> demonstrating remarkable advantages compared to the traditional SECM. Similar to SECM, much attention has been paid to the electrochemical activity mapping capability, while the topographical resolution is still restricted by the size and stability of the meniscus droplet.<sup>1,13-16</sup>

In SECCM measurements, the sample is used as the working electrode. An electrolyte-filled nanopipette and a Ag/AgCl or Pd-H<sub>2</sub> electrode are used as the probe and a quasi-reference counter electrode (QRCE), respectively. The topographical and electrochemical activity image acquisition is conducted through a programmed contact motion sequence between the meniscus droplet and the substrate electrode.<sup>1,17</sup> The most prominent advantage of SECCM is that it does not need to immerse the sample in solution, which completely avoids possible sample damage that could be caused by electrolyte and excludes any signal interference from the nonmeasured

area.<sup>17</sup> After more than 10 years of development, SECCM has been successfully applied to studies of two-dimensional semiconductor materials (such as  $WSe_2^{3,18,19}$  and  $MoS_2^{20-22}$ ), nanoparticles (NPs)<sup>1,23-26</sup> and nanoclusters,<sup>27</sup> carbon-based materials,<sup>28-31</sup> energy storage materials,<sup>32-34</sup> and nanofabrication.<sup>35-38</sup> Recently, SECCM was used to probe single-entity electrochemistry nanoscopically, such as iridium oxide particles,<sup>25</sup> Pt NPs<sup>24,39</sup> and Pt nanoclusters,<sup>27</sup> Au nanorods,<sup>26</sup> Au NPs<sup>1,23</sup> and Au (111) nanocrystals,<sup>16</sup> single ZIF-derived nanocomposite particles,<sup>40</sup> Sn deposited on reduced graphene oxide (rGO),<sup>41</sup> and single-crystal borondoped diamond particles.<sup>42</sup> Although some works have demonstrated the capability of electrochemical activity imaging on the scale of less than 100 nm, most of them could not record in situ topography but only correlate with other ex situ approaches, such as SEM.<sup>23,39</sup> Hill et al.<sup>3</sup> presented state-ofthe-art SECCM images that synchronously map topography and photoelectrochemical properties of p-type WSe<sub>2</sub> nanosheets with a probe ~200 to 300 nm diameter. Unwin et al. realized electrochemical and topographical images of electrodeposited Au NPs,<sup>1</sup> Au nanocrystals,<sup>16</sup> MoS<sub>2</sub>, and WS<sub>2</sub>,<sup>2</sup>

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**Figure 1.** (a) Schematic scanning procedure of SECCM; (b) TEM image of the nanopipette probe with an inner diameter of ~50 nm (inset: SEM image of the nanopipette probe (scale bar is 100 nm) with an inner diameter of ~52 nm; (c) Z-position of probe (i), applied voltage  $E_{app}$  (ii), and measured surface current  $i_{surf}$  (iii) as a function of the time during a single hop; (d) mapping of electrochemical activity of a stripe array with a linewidth of ~138 nm at  $E_{app} = -0.9 \text{ V} (2.0 \times 1.2 \ \mu\text{m}^2$ , pixel:  $30 \times 15$ ); and (e) CV curves of spot 2, spot 5, and spot 334 derived from (d).

reaching an in-plane spatial and height resolution of ~50 and ~2 nm, respectively, using a probe of ~30 nm diameter. Moreover, major improvements have been achieved for SECCM topography in recent years, including a single-barrel circuit mode and AC scanning mode,<sup>14</sup> a single-barrel nanopipette with different backpressures to increase the meniscus droplet thickness, tip perceptive capability, and imaging stability.<sup>15</sup>

In this paper, SECCM with a homemade  $\sim$ 50 nm inner diameter probe realized 65 nm line and 45 nm point resolutions simultaneously mapping both morphology and electrochemical properties of catalysts. Furthermore, precise position and repeatability tests were carried out successfully. It provides a practical scheme to realize the correlation between nanoscopic topography and catalytic activity, and potentially can be conducted routinely.

### EXPERIMENTAL SECTION

SECCM Setup. A homemade single-barrel nanopipette probe with a tip inner diameter of ~50 nm was fabricated by pulling from borosilicate glass capillaries (BF100-58-10, Harvard Apparatus) using a CO<sub>2</sub>-laser puller (P-2000, Sutter Instruments). SECCM is performed through a modified commercial AFM (Park X-10 Systems, South Korea). It consists of a nanoscale probe positioner, scanning system, and a customized single-barreled nanopipette probe as described above. In this setup (shown schematically in Figure 1), the probe was filled with 0.5 M H<sub>2</sub>SO<sub>4</sub> and mounted on the scanning head of the AFM. A Ag/AgCl wire was inserted into the nanopipette from the back end serving as a QRCE. SECCM was operated in a voltammetric "hopping" mode, where the nanopipette probe sequentially approaches the substrate electrode at a series of predefined locations following a 2D lattice. The voltammetry measurement was conducted simultaneously at each contact to establish a dynamic electrochemical mapping.

**Sample Preparation.** The details of sample fabrication are reported in the Supporting Information. The arrays with linewidths of ~65, ~109, ~138, and ~500 nm were fabricated using an electron beam lithography system (VEGA3, TESCAN, Ltd.). The Au NPs (~45 nm) were synthesized using the seed-growth method. And the fabrication of self-assembled monolayer Au NPs on the patterned substrate was carried out in a sealed glass jar with certain set ion strength and relative humidity. Then, the assembled samples were cleaned using deionized water to completely remove free ligands.

# RESULTS AND DISCUSSION

Applied key parameters and protocol of the single-channel SECCM hopping mode are outlined above. The nanopipette of ~50 nm inner diameter was fabricated successfully, as shown in Figure 1b. The Z-position, applied potential  $(E_{app})$ , and surface current  $(i_{surf})$  synchronously recorded as a function of time are shown in Figure 1c in a single "hop". For an initial probe approaching ((i) in Figure 1c),  $i_{surf}$  was used as a feedback to detect when the electrolyte meniscus of nanopipette tip start to touch the working electrode surface. When the meniscus contacts the substrate electrode, a two-electrode cell was formed and a transient  $i_{surf}$  (~7 pA) will be generated due to the reaction within the confined droplet cell. Then, the Z-approach process will be halted immediately once it reaches the threshold current, which was set as 2 pA. The  $E_{app}$ (approach voltage  $(E_a)$  was -1.2 V, herein) was chosen to be sufficient to generate a current signal large enough once the meniscus droplet physically touches the electrode for position interlock to guarantee the nanopipette itself will not crash on the sample. Then,  $E_{app}$  was switched to 0 V to stabilize the system ((ii) in Figure 1c) for a predefined holding time, followed by an electrochemical voltammetric scan (voltage ranges from 0 to -0.9 V, scan rate  $\nu$  is set to 1 V s<sup>-1</sup>,  $E_{app} - t$  is shown in Figure 1c), and HER isurf was recorded simultaneously as shown in (iii) of Figure 1c (the maximum value is



**Figure 2.** (a) SEM image of the array of nanodots with a diameter of ~500 nm; (b, c) AFM and SECCM topographical images  $(5.0 \times 5.0 \ \mu\text{m}^2, \text{pixel}: 30 \times 30, \text{ raw data shown in Figure S2}) of the array, respectively; and (d, e)$ *Z*-height derived from the AFM image and SECCM topographical image along the line marked as the white dash line in (b) and (c), respectively. (H1 is defined as the height of sample derived from the SECCM image; H2 is defined as the height of sample evaluated from the AFM image).



**Figure 3.** (a1) SEM image of the stripe array; the linewidth is ~138 nm; (a2, a3) AFM images and the corresponding *Z*-height profiles; (b1, b2) SECCM topographical images and the corresponding *Z*-height profiles at  $4.0 \times 1.2 \ \mu\text{m}^2$  scanning area and  $40 \times 12$  pixels; and (c1, c2) SECCM topographical images and the corresponding *Z*-height profile with  $2.0 \times 1.2 \ \mu\text{m}^2$  scanning area and pixels of  $30 \times 15$ . The numbers in (b2) and (c2) correspond to the scanning lines in (b1) and (c1).

 $\sim$ 2 pA and most of them are less than 1 pA, as shown in Figure 1d,e).

After it was completed, the probe was retracted and  $E_{\rm app}$  would be switched back to the value for initial approaching and ready for the next hopping and measurement cycle for the next point until it completed the mapping of the targeting area of the whole sample. Here, both approaching and voltammetric voltages were minimized to keep the stability of the droplet during the mapping process, which gave maximum current  $\sim$ 7 pA (approaching  $i_{\rm surf}$ ) and  $\sim$ 2 pA (HER  $i_{\rm surf}$ ), respectively.

An  $\sim$ 500 nm dot array and an  $\sim$ 138 nm wide stripe array were chosen to carry out the SECCM topographical test. The measuring area was chosen randomly on the sample surface to ensure the universality of the applied method. Figure 2a shows the SEM image of the dot array. As shown in Figure 2c, the SECCM topographical map of a scanning area  $(5.0 \times 5.0 \ \mu m^2)$ , pixel:  $30 \times 30$ , pixel size is 5000/30 nm) indicates a clear  $5 \times 3$ dot array. Most of the dots are imaged by three pixels, such as the one marked with the black dash circle, but some have four pixels in the *y*-direction that are attributed to multiple instances of droplet contact to the spot.<sup>23</sup> Figure 2e is the measured Z-height profile along the white dash line in Figure 2c, whose height ~38 nm is consistent with the AFM measurement (~35 nm) in Figure 2d. Moreover, the distance

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**Figure 4.** (a) Optical microscopy image of a probe location during SECCM measurement (scale bar is 40.0  $\mu$ m); (b, c) corresponding SEM images of ~109 and ~65 nm linewidth arrays, respectively (scale bar is 1.0  $\mu$ m); and (b1, b2, c1, c2) their SECCM topographical images (~109 nm: (b1) (5.0 × 1.5  $\mu$ m<sup>2</sup>, pixel: 50 × 15) and (b2) (5.0 × 2.0  $\mu$ m<sup>2</sup>, pixel: 50 × 20); ~65 nm: (c1) (5.0 × 1.5  $\mu$ m<sup>2</sup>, pixel: 50 × 15) and (c2) (5.0 × 2.0  $\mu$ m<sup>2</sup>, pixel: 50 × 20)). The scale bars of (b1), (b2), (c1), and (c2) are1.0  $\mu$ m.

between the two spots is ~1.2  $\mu$ m, which exactly matches the ones from the SEM and AFM measurements. The topographical mapping of the stripe array using SECCM is shown in Figure 3. Figure 3b1 shows the SECCM topographical map of the first scan area 4.0  $\times$  1.2  $\mu$ m<sup>2</sup> (pixel: 40  $\times$  12, pixel size is 4000/40 nm), which is close to the AFM data shown in Figure 3a2. Four clear stripes represented by two pixels each in the xdirection are observed, and their width ( $\Delta X$  defined as the width in the x-direction)  $\sim$ 200 nm coincides with the need for representing an  $\sim$ 138 nm wide line with two pixels. There are also some locations where the stripe is represented by 3 pixels, which is also due to the multiple instances as discussed above. A finer measurement  $(2.0 \times 1.2 \ \mu m^2)$ , pixel:  $30 \times 15$ , the pixel size in the x- and y-directions are 2000/30 and 1200/15 nm, respectively) including two stripes is shown in Figure 3c1. Each stripe occupies three pixels in the *x*-direction, and its  $\Delta X$ is also ~200 nm. There is also an offset displayed in Figure 3b1 (upper part of the image) and Figure 3c1 (lower part of the image).

The offset in the images could be explained as follows. It may be due to the intrinsic drawback of enlarged quantization error caused by the target imperfection, in this case, the rough edge of stripes, as shown in the SEM images (Figure 3a1). Besides, the imperfect alignment of samples relative to the probe could contribute to the measurement error in the hopping mode by a fraction of a pixel. The Z-height profiles are shown in Figure 3b2,c2, which are extracted from Figure 3b1,c1, respectively. Both the measured stripe heights are  $\sim$ 40 nm coinciding with AFM measured values ( $\sim$ 37 nm). The height discrepancy could simply be attributed to the height variation of each measured stripe, as shown in the AFM image (Figure 3a1). And more technical reasons could be due to the change of droplet meniscus of the SECCM probe during the measurement since both the droplet size and approaching speed could affect the Z-height.<sup>1,3,14</sup> The drifting of the instrument itself also should be considered.

The electrochemical activity images are shown in Figure S3, where no obvious activity difference was observed for the

surface of a uniformly deposited Au layer using electron beam evaporation. It indicates a uniform clean surface and stable scanning process, which also demonstrates the high stability of the homemade nanopipette. Furthermore, an array of "TJU-TICNN" characters made with a smaller linewidth of ~109 and ~65 nm was chosen to carry out an SECCM topographical and precise positioning test. As shown in Figure 4a, since the microscope view field is on the order of tens of micrometers, it is rather difficult to locate the probe to a precisely defined position for perfect mapping the symbols. Fortunately, the known letter-size and letter-spacing make it possible once the locations of some letters are given, as shown in Figure 4b,c. A topographic image was obtained from mapping a  $5.0 \times 1.5 \,\mu\text{m}^2$ area (pixel:  $50 \times 15$ , pixel size is 100 nm) with the probe approached a random location. The result is shown in Figure 4b1, displaying a clear letter sequence "NNTIC." The SECCM measured letter sizes and spacing are ~800 and ~400 nm, respectively. The SECCM topographical image with a scan area of 5.0  $\times$  2.0  $\mu$ m<sup>2</sup> (pixel: 50  $\times$  20, pixel size is 100 nm) is shown in Figure 4b2, indicating a better view of the whole "TJU-TICNN" symbols.

The metal line is represented by two pixels in the xdirection, corresponding to ~200 nm. And there are also some parts of lines only one pixel wide marked by the white arrows. The first character N circled by a black dash line has a clear fabrication defect, which coincides with the area marked in Figure 4b measured with the SEM (marked by the white dash arrows). The same procedure was conducted to map the arrays of "TJU-TICNN" symbols with a linewidth of ~65 nm. A clear TICNN-TJU image was obtained with linewidth represented by only one pixel ( $\sim 100$  nm), which is distinctly smaller than that in Figure 4b1,b2, as shown in Figure 4c1,c2. Similar to the above discussion, there are some positions where the line is represented by two pixels. These results evidence the ability of SECCM as a tool for nanoscale topographically mapping and precisely positioning and measuring the interested area with the developed scheme. The electrochemical activity images are shown in Figures S4 and S5. Electrochemical measurements



**Figure 5.** (a) SECCM topographical image  $(2.0 \times 2.0 \ \mu\text{m}^2)$ , pixel:  $30 \times 30$ ), corresponding to the area inside the dash-line square in (b); (b) SEM image of the Au NP self-assembled monolayer; (c, d) topographical images of the same area with different pixels, respectively ((c):  $2.0 \times 2.0 \ \mu\text{m}^2$ , pixel:  $30 \times 30$ ; (d):  $2.0 \times 2.0 \ \mu\text{m}^2$ , pixel:  $40 \times 40$ ); and (e, f) topographical and electrochemical activity images ( $E_{app} = -0.7 \text{ V}$ ) of this area, respectively ( $2.0 \times 2.0 \ \mu\text{m}^2$ , pixel:  $30 \times 30$ ). The raw data of the SECCM topographical and HER activity are shown in Figure S6.

show some enhanced currents at the top of Figure S5b, which do not correlate with the topography (Figure 4c2). It could be attributed to the possible droplet deformation or instrument disturbance during the measurement process. In summary, the activity maps were uniform and stable, which further demonstrated the stability of probe and activity imaging with SECCM.

The difficulties of topography characterization in practical studies are diverse. Recently, Tsujiguchi et al.<sup>41</sup> acquired topography and electrochemical activity of rGO-supported Sn catalysts simultaneously with a 50 nm radius probe. By comparing electron microscopy images, Baker et al.<sup>23</sup> studied the HER electrocatalytic activity and correlation to the particles morphology of Au nanocubes (~78 nm) and compared to that of Au nano-octahedra (~99 nm) using SECCM. Takahashi et al.<sup>20</sup> mapped the electrochemical properties of triangular-shaped MoS<sub>2</sub> nanosheets with a side length of ~130 nm using an ~20 nm radius nanopipette. It would be appealing to synchronously acquire topography images of the targeting system in those last two studies. To further investigate the universality of topographical measurement of this scheme, herein, an ~45 nm Au NPs selfassembled monolayer was chosen as a targeting system. The same scheme was applied as described above, and the corresponding SECCM topographical mapping is shown in Figure 5a  $(2.0 \times 2.0 \ \mu \text{m}^2)$ , pixel: 30 × 30, pixel size is 2000/30 nm). It displays a morphology that matches the one in Figure 5b marked by a dashed rectangle. The result indicates a successful SECCM topographical mapping of self-assembled NPs.

The SECCM probe is a meniscus droplet that confines the electrochemical activity measurement to the area of droplet contact, therefore achieving localized characterization and interaction with the substrate electrode.<sup>18,36</sup> The electrolyte residual and possible electrode reaction usually leaves measuring traces, 43-45 leading to an unknown change to the electrode surface, which makes it difficult to repeatedly measure the same area. However, in principle, the repeating test is feasible if there is no damage or a very minimum amount of residues. Herein, to do that, we choose 0.5 M H<sub>2</sub>SO<sub>4</sub> as the electrolyte that produces negligible damage to the Au NPs and Au film on the electrode. Besides, the surface was completely dried by exposing the sample to the purified dry nitrogen for 1 h after each mapping. And the repeated test was carried out at the same position with the same scanning size and pixel dimension. The topographical image is shown in Figure 5c (2.0  $\times$  2.0  $\mu$ m<sup>2</sup>, pixel: 30  $\times$  30, pixel size is 2000/30 nm), which displays a clear Au NPs self-assembled structure as Figure 5a with a slight deviation due to the instrument drifting. Moreover, a repeated test of this area with a finer measurement was carried out, as shown in Figure 5d ( $2.0 \times 2.0 \ \mu m^2$ , pixel:  $40 \times 40$ , pixel size is 50 nm). It also shows the same morphology of Au NPs self-assembled structure. The pixel size is 50 nm, which indirectly confirms the less than 50 nm diameter pore size of the homemade probe.

The synchronously obtained HER activity mapping is shown in Figure 5f, which indicates the higher activity of Au NPs than that of the Au substrate electrode. The inhomogeneity of the HER activity on the NP monolayer resulted from the NP random self-assembly. Although the meniscus droplet could cover more than one NPs, which surely will partially smear individual properties of each spot, it still unveils different electrochemical activities of different measuring points.<sup>1,23</sup> In this study, there were one, two, three, or four NPs in each pixel as shown in Figure 5, which displays the structure-dependent activity. The results and analysis are shown in Figures S8 and S9. The same method was used to measure a random sample area for the repeated tests. Combining the measured topographical and SEM images could precisely position and characterize the shape of the NPs. To further clarify the heterogeneity and the correlation between the topography and activity, the TEM images of the Au NPs are supplemented in Figure S7. Obvious heterogeneous activities of NPs with different sizes and shapes were observed, corresponding to different crystal facets and active sites exposed, with surface reconstruction and residual ligand desorption also affecting their activity.<sup>26</sup>

## CONCLUSIONS

In summary, a scheme of cyclic voltammetric hopping SECCM with a probe of  $\sim$ 50 nm inner diameter was applied to map arrays and realized a minimum linewidth of  $\sim$ 65 nm topographical imaging. The derived geometric dimensions from the SECCM reasonably coincide with the AFM and SEM measured ones. Synchronously mapping both the topographical and HER activity of the  $\sim$ 45 nm Au NPs self-assembled monolayer has been achieved. The selection and repeated measurements of interested areas were also carried out successfully. These results demonstrate the capability and reliability of the developed SECCM scheme for topographical mapping. This scheme provides a practical approach for exploring the nanoscale correlation of the structure and activity of materials applying SECCM.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.1c04692.

Details of sample preparation, schematic of array fabrication and the SEM images of the electrode array (Figure S1); SECCM topographical and electrochemical activity of electrode arrays (Figures S2–S5); and analysis and SECCM topographical and electrochemical activity images of self-assembled monolayer Au NPs (Figures S6–S9) (PDF)

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#### Notes

The authors declare no competing financial interest.

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