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Mechanistic Study for Facile Electrochemical Patterning of Surfaces with Metal Oxides

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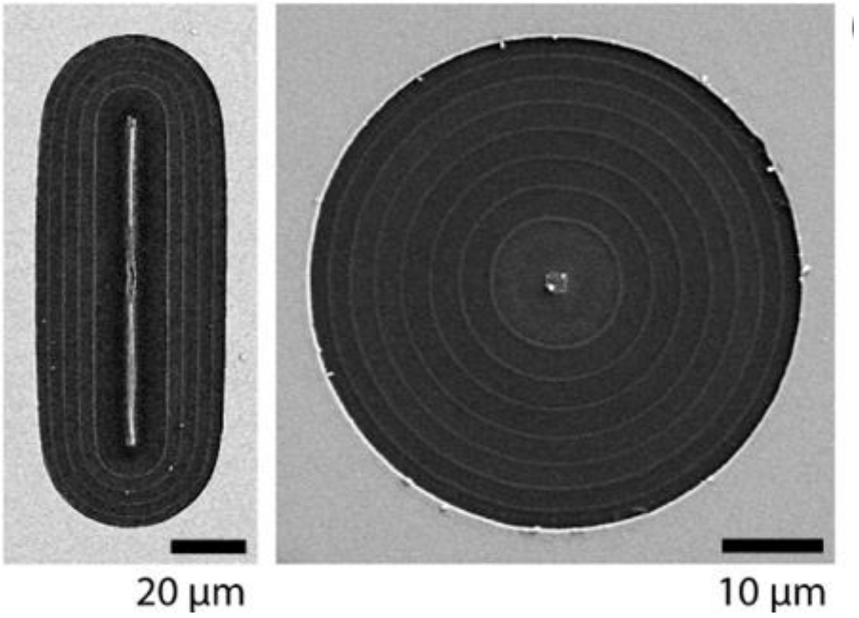
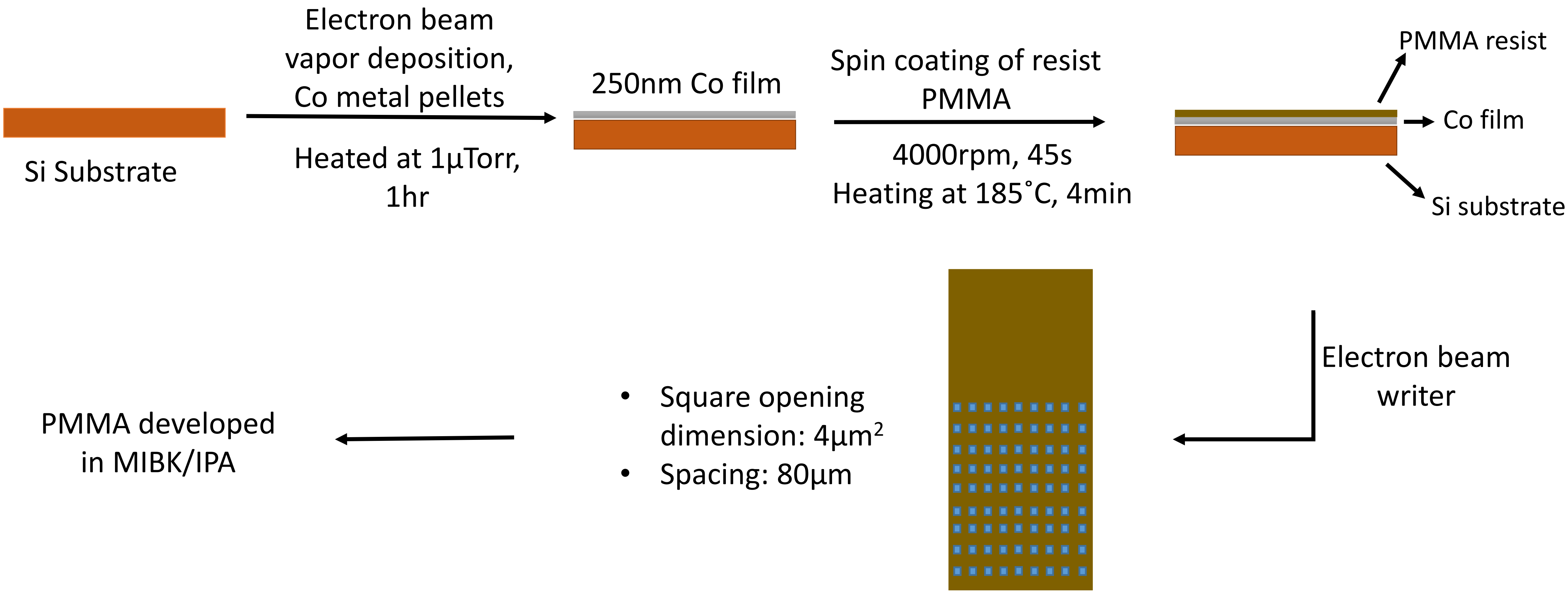
RIPPLE (reactive interface patterning promoted by lithographic electrochemistry)

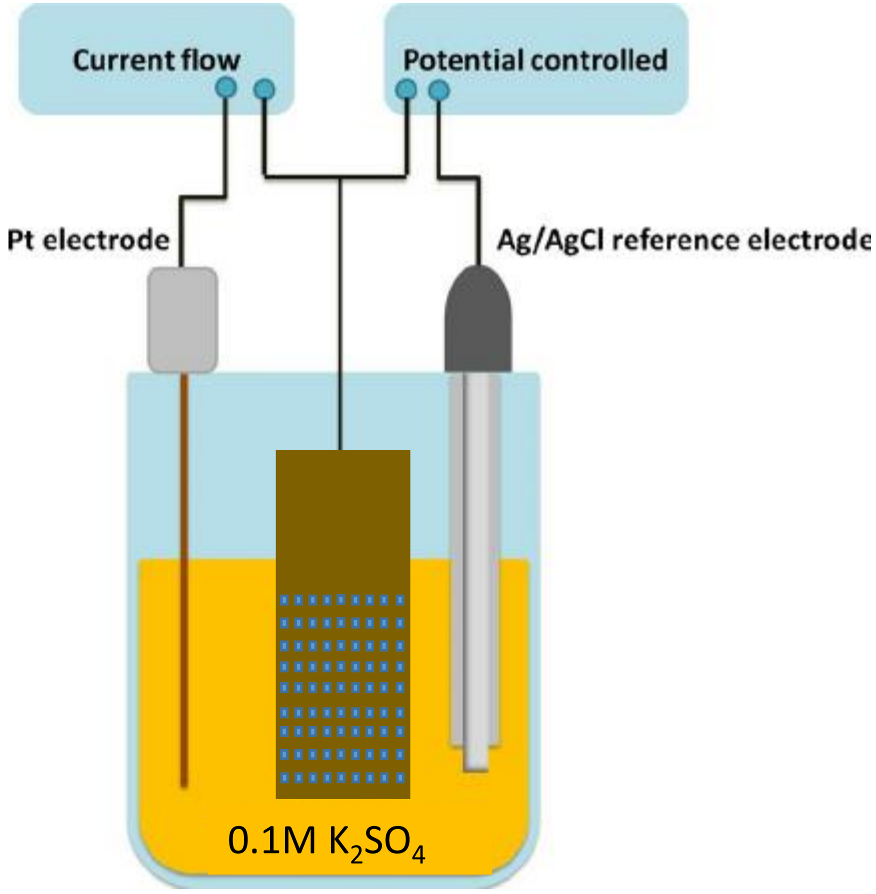
- Formation and propagation of periodically spaced submicron structures over large areas.
- Etching and patterning of an inorganic material when it is subjected to applied cyclic potentials in the presence of electrolyte.
- The patterns can be tuned over micrometer and submicrometer length scales.

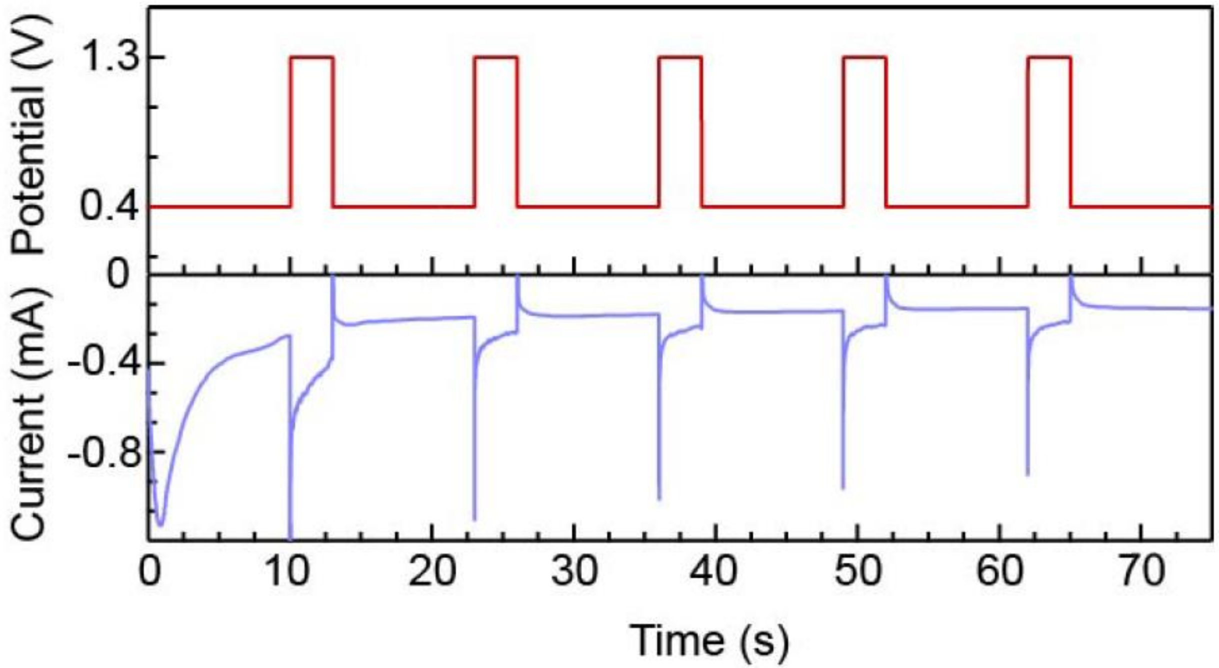


Fabrication of working electrode

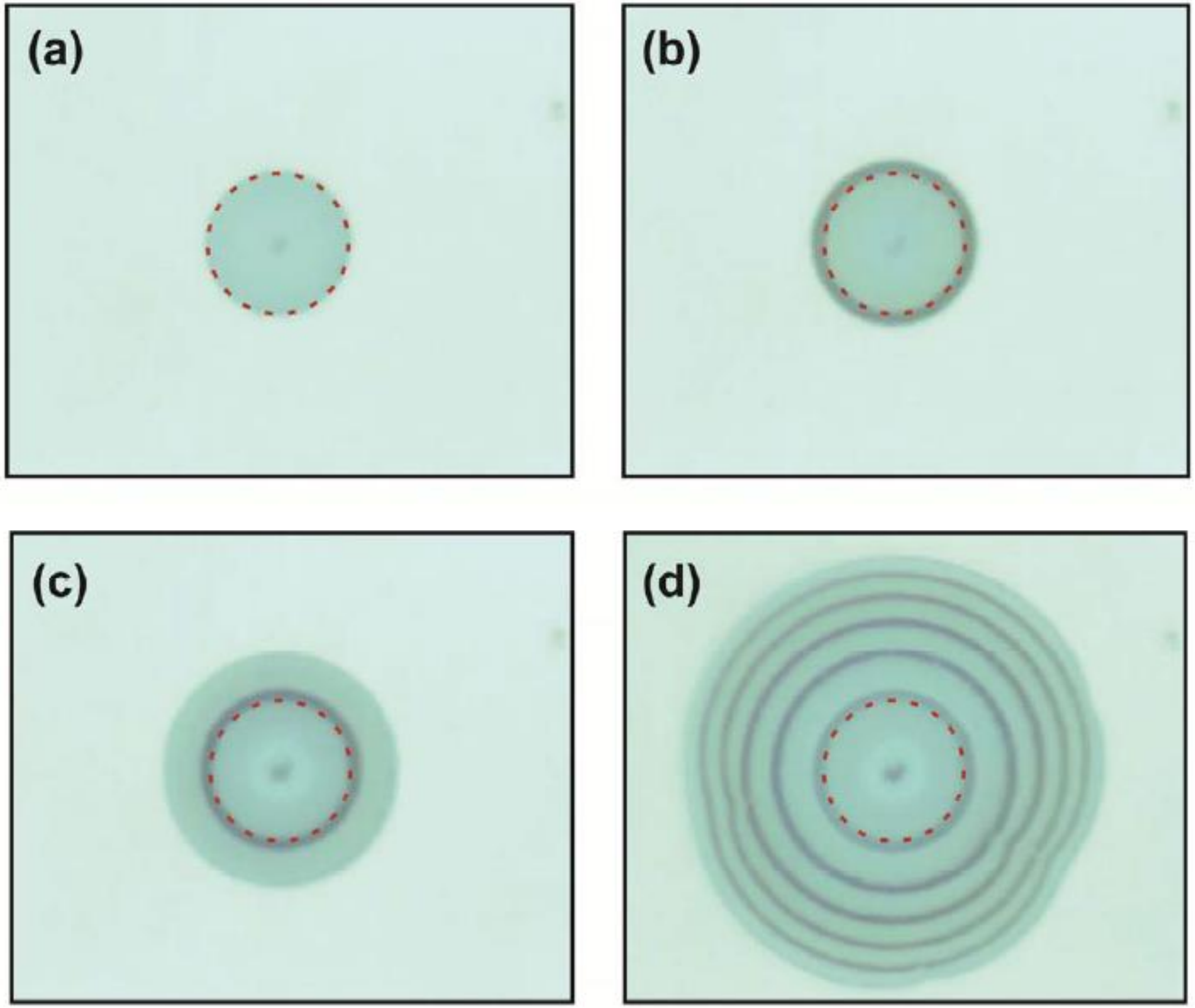


Electrochemical experiments





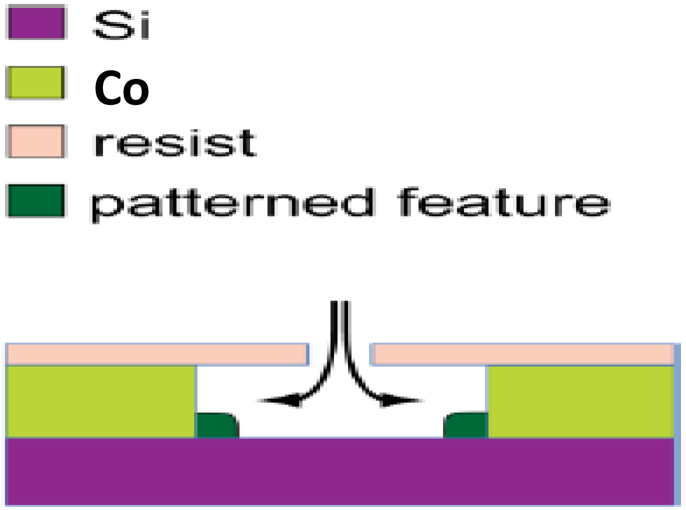
(*top*) Potential–time view
(*bottom*) corresponding current-time view of a binary-potential step method for patterning cobalt in 0.1 M K_2SO_4.



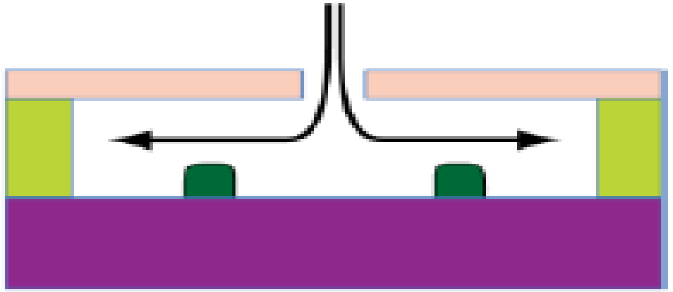
Evolution of the same pattern generated by alternating between 0.4 V (10 s) and 1.3 V (3 s) ten times
(a)After 10 s, (b) 13 s (c) 23 s, and (d) the final pattern (75 s).
Red dashed-circle corresponds to the etch front after applying 0.4 V for 10 s.

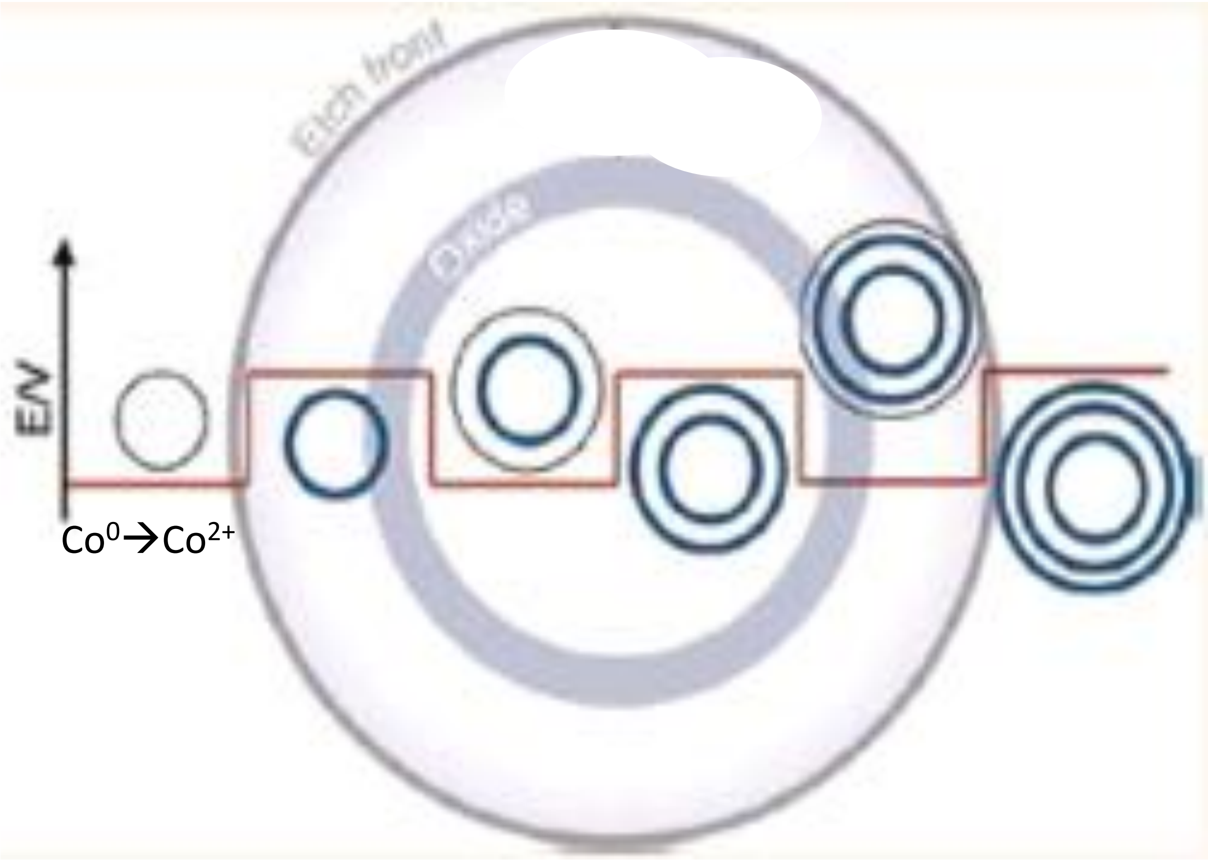
Sample imaged at 63× magnification using water immersion objective.

RIPPLE model

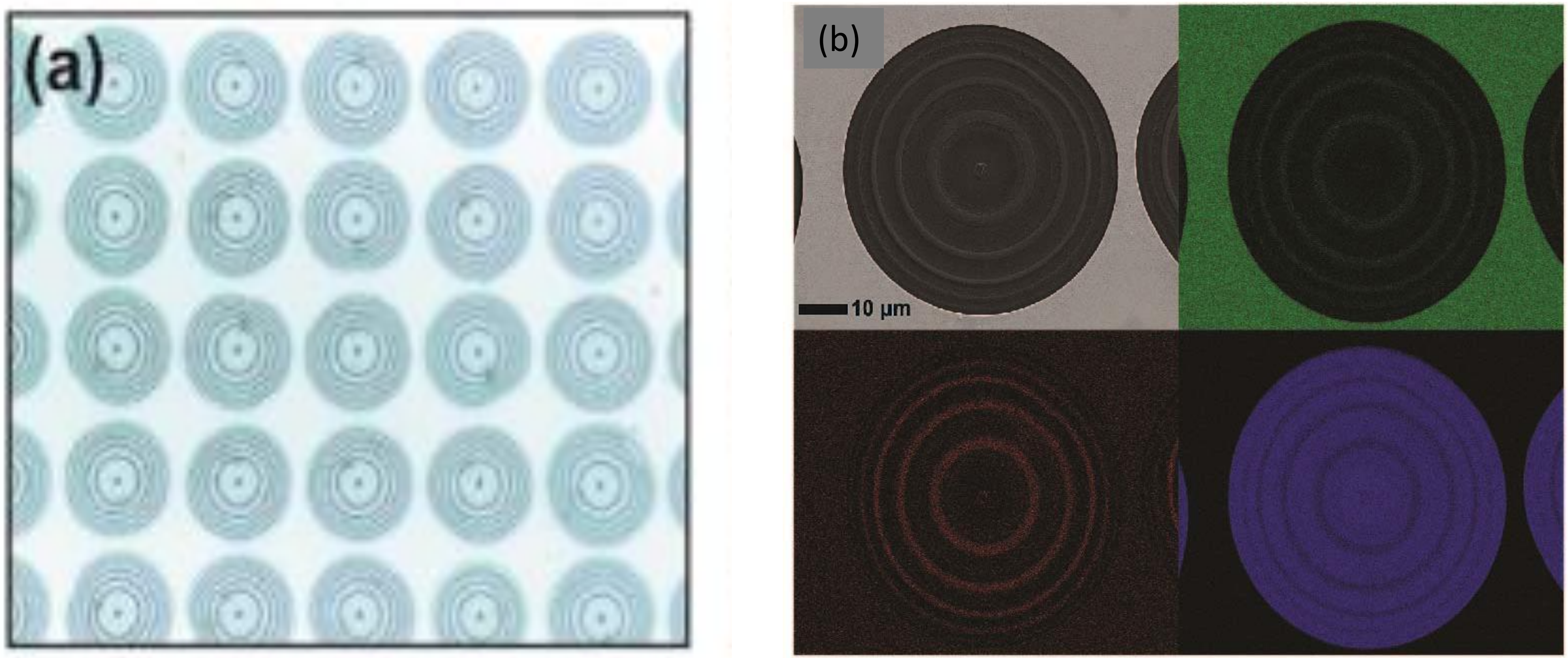


Cross section of working electrode



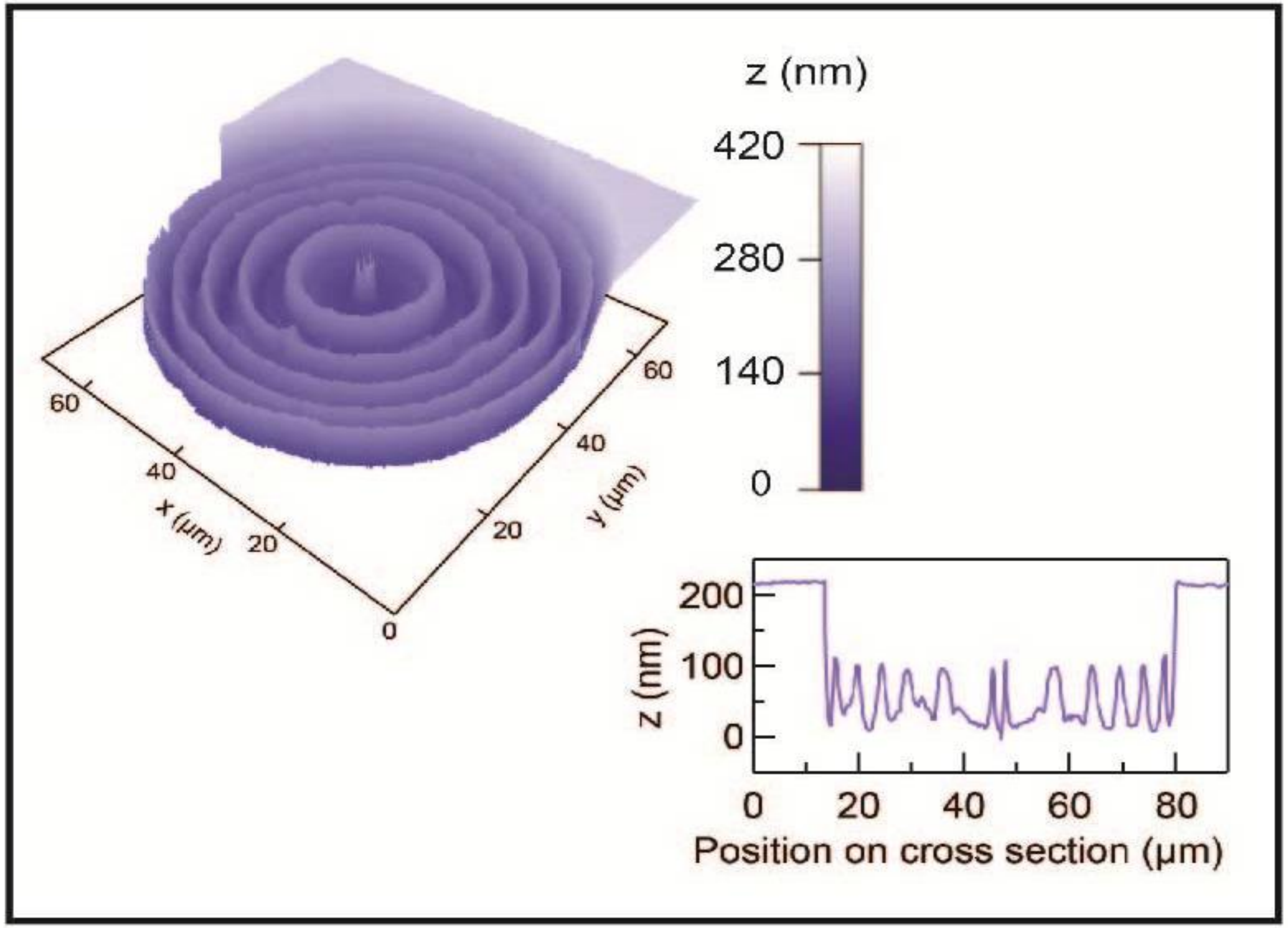


Co thin film (green) is exposed at defined sites through a resist layer (beige).
Lateral etching (at 0.4V) of Co proceeds underneath the resist layer.



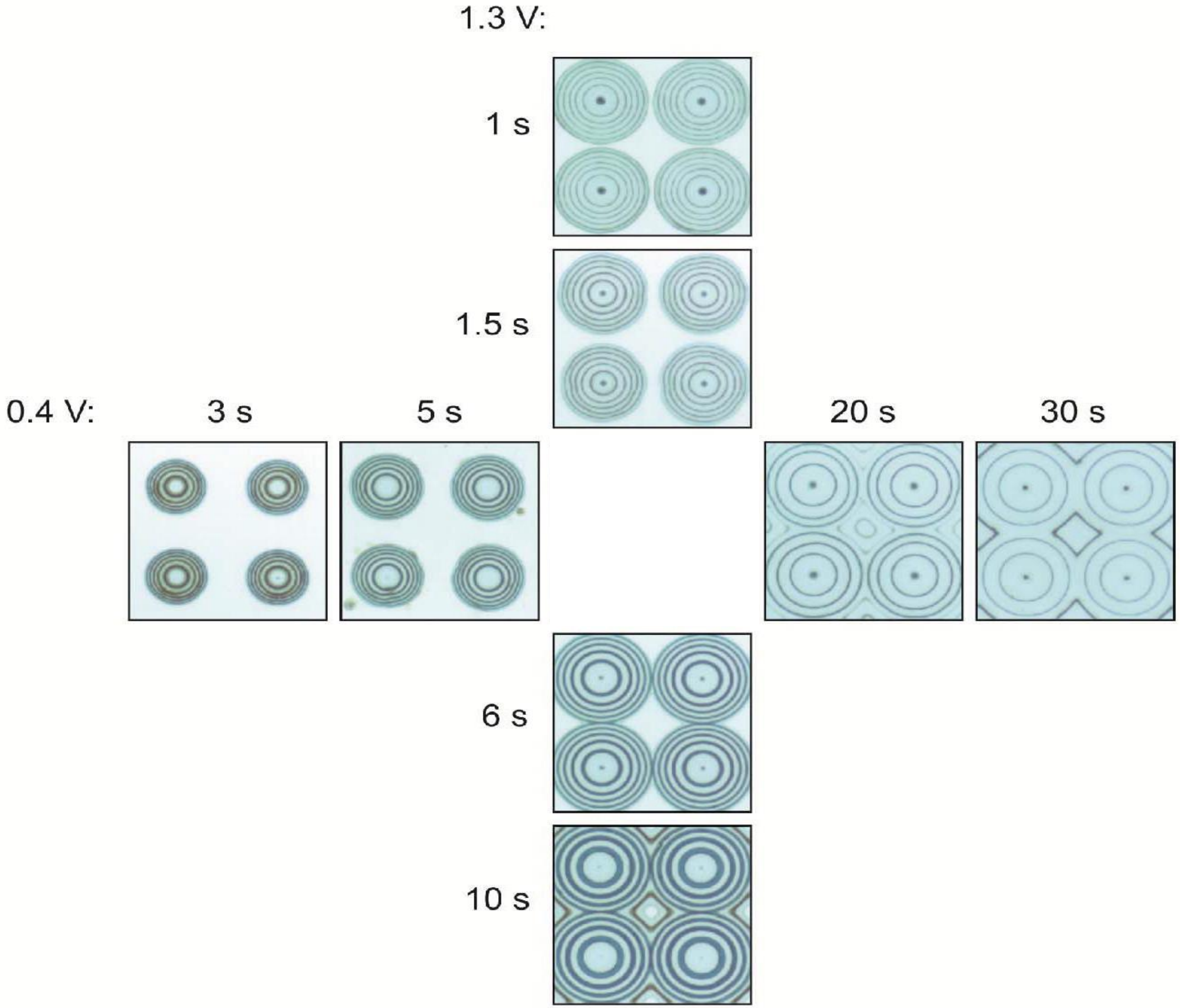
Patterns formed by alternating between 0.4 V (10 s) and 1.3 V (3 s) 10 times in 0.1 M K_2SO_4.
(a) Optical microscope images at 50× magnification.
(b) SEM image (top left) and EDS elemental maps of cobalt (green), oxygen (red), and silicon (blue).

AFM height profile



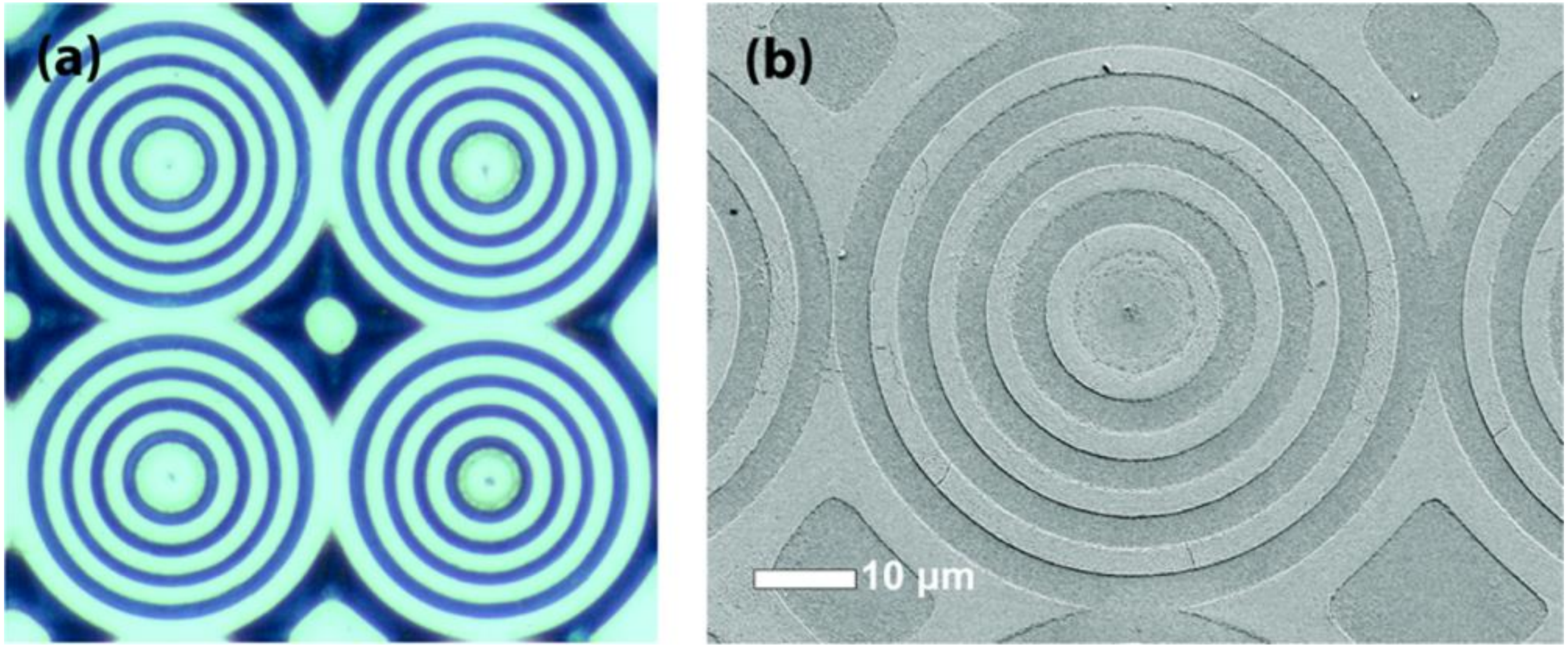
AFM map with height-profile of a diametric cross section (inset on right). Ridges are 1.4μm wide and 130 nm tall

Dependence of pattern geometry on potential duration

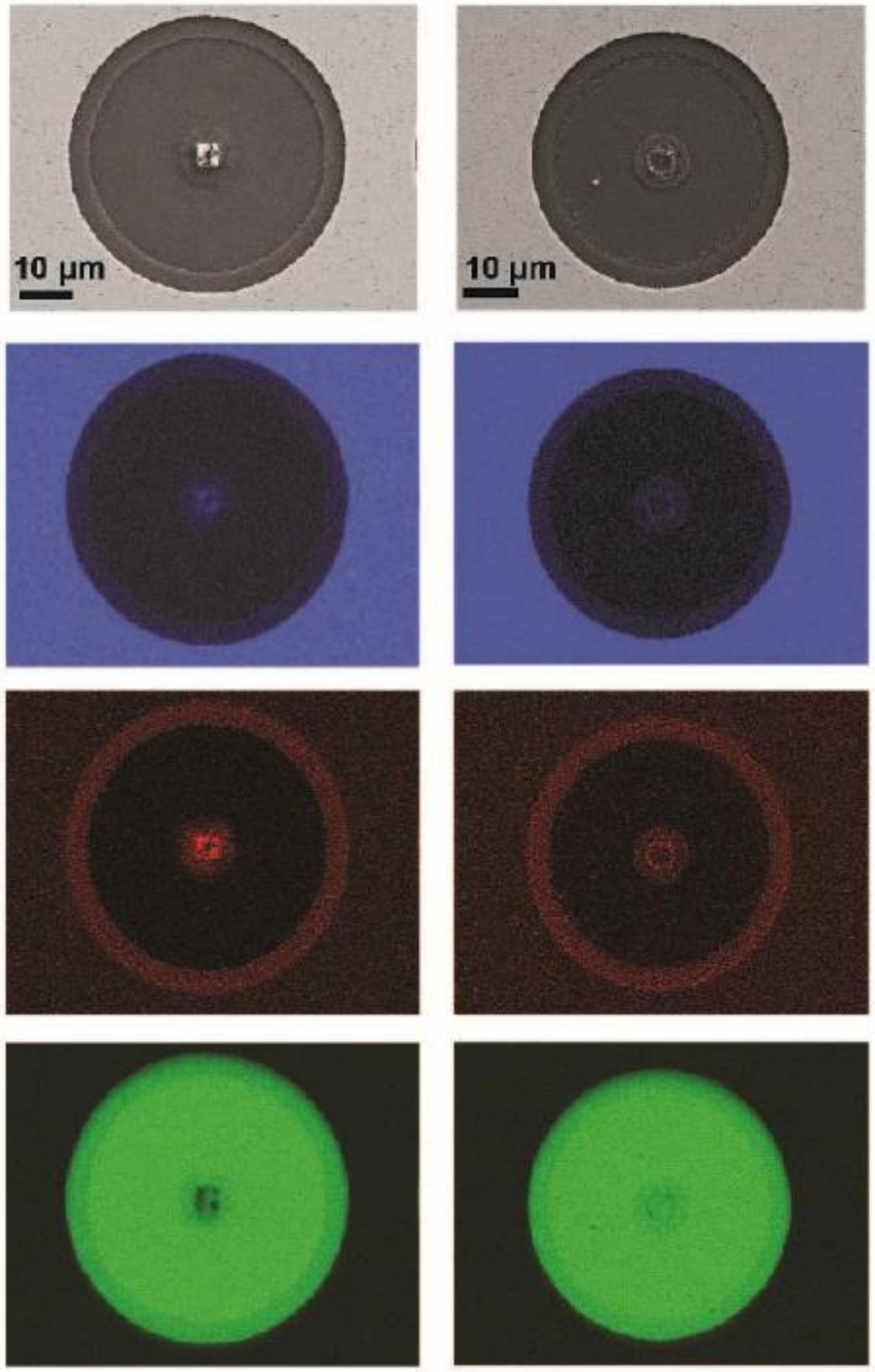


- Five applications of the two-potential sequence, 0.4 V and 1.3 V, followed by one application of 0.4 V.
- To determine the effect of the duration of 0.4 V, 1.3 V was held for 3 s for each application and 0.4 V was held for the specified time indicated over each image (*horizontal row*).
- Similarly, 0.4 V was held at 10 s each application and 1.3 V was held for the time identified at the left of each image (*vertical column*).
- Samples imaged at 50× magnification.

Uniform ring spacing



Patterns with conserved radial dimensions (3.0 µm width and 3.8 µm spacing) formed by sequentially increasing potential step durations (binary potential steps held for 5, 7, 9, 12, and 15s) in 0.1 M K2SO4. Images from (a) optical microscope with 50× objective and (b) SEM



Oxide formation pathway

Applying 0.4 V over 30 s, followed by 1.3 V over 20 s successively (left column) and

After a 30 min delay (right column).

SEM images (grey) and EDS maps for cobalt (blue), oxygen (red), and silicon (green).

Conclusion

- The mechanism of pattern formation by RIPPLE establishes that the ring position depends on the distance of cobalt ion diffusion into bulk electrolyte, with the kinetics limited by the diffusion of Co^{2+} from the etching front to the opening.
- The sequence and duration of electrochemical steps allows precise control of submicrometer structures & pattern geometry.
- The high throughput, facile, and large area patterning of submicron inorganic structures by RIPPLE could enable new and emerging opportunities in energy conversion, storage, catalysis and sensing.

Thank you!