supplementary information

Electrolyte Concentration Modulates the Surface Structure Evolution of Au(111) Cathodes

Yue Feng,[‡ab] Yu-Qi Wang,[‡*a] Jiaju Fu,[a] Zi-Cong Wang,[ab] Dong Wang, [*ab] and Li-Jun Wan [*ab]

[a] CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, CAS Research/Education Center for Excellence in Molecular Sciences, Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

[‡] These authors contributed equally.

* Corresponding author. E-mail: wyqchem@iccas.ac.cn (Y. Q. W.); wangd@iccas.ac.cn (D. W.); wanlijun@iccas.ac.cn (L. J. W.)

Results and discussion

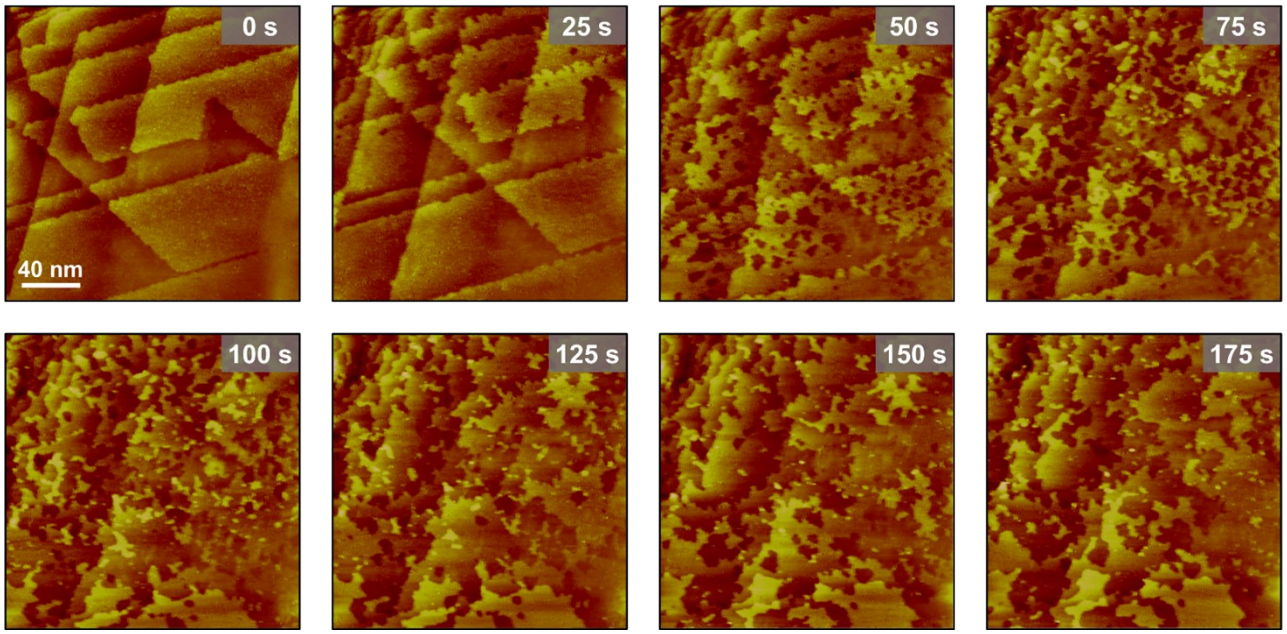

Fig. S1. EC-STM images of Au(111) in CO_2-saturated 1 M $CsHCO_3$ electrolyte after the potential step from 0 V to -0.1 V.

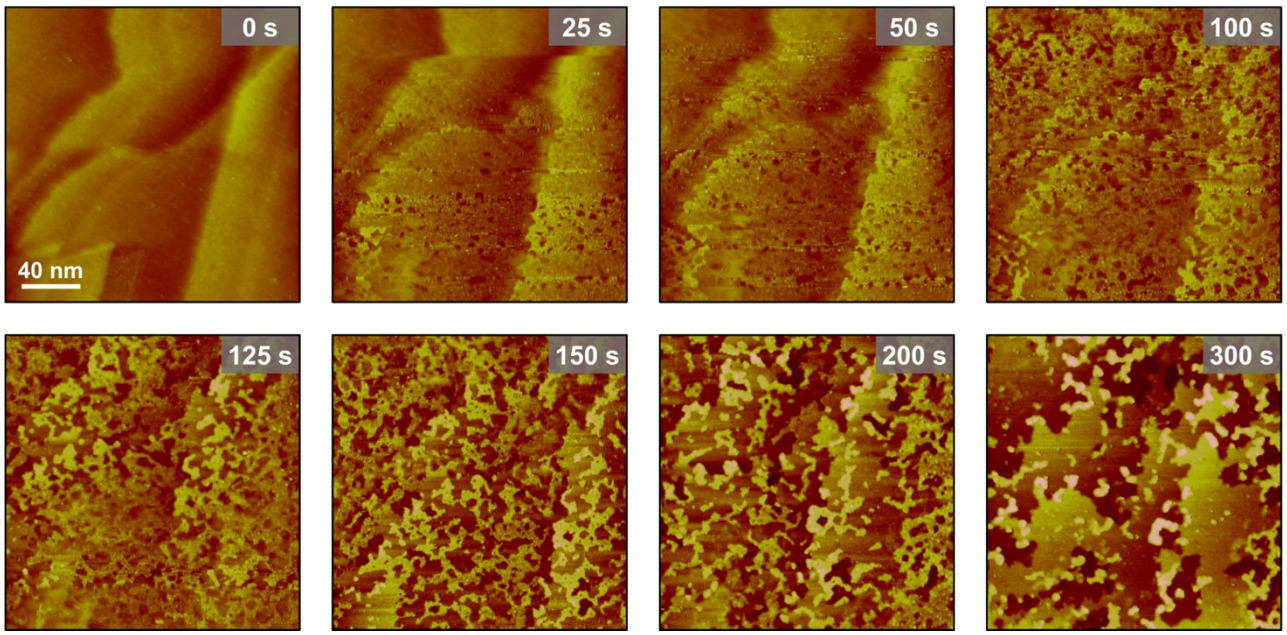

Fig. S2. EC-STM images of Au(111) in CO_2-saturated 1 M $RbHCO_3$ electrolyte after the potential step from 0 V to -0.1 V.

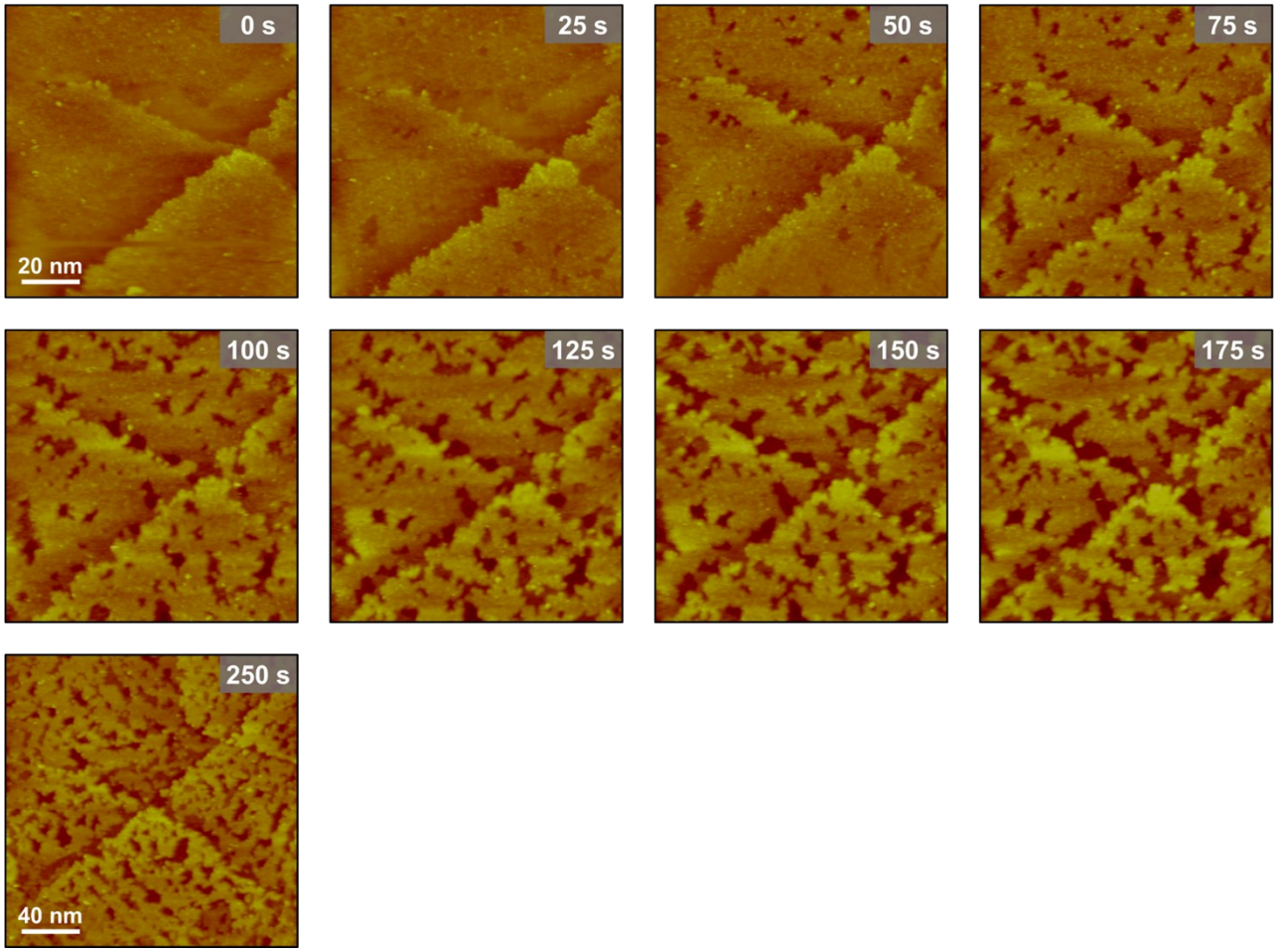

Fig. S3. EC-STM images of Au(111) in CO_2-saturated 1 M $KHCO_3$ electrolyte after the potential step from 0 V to -0.1 V.

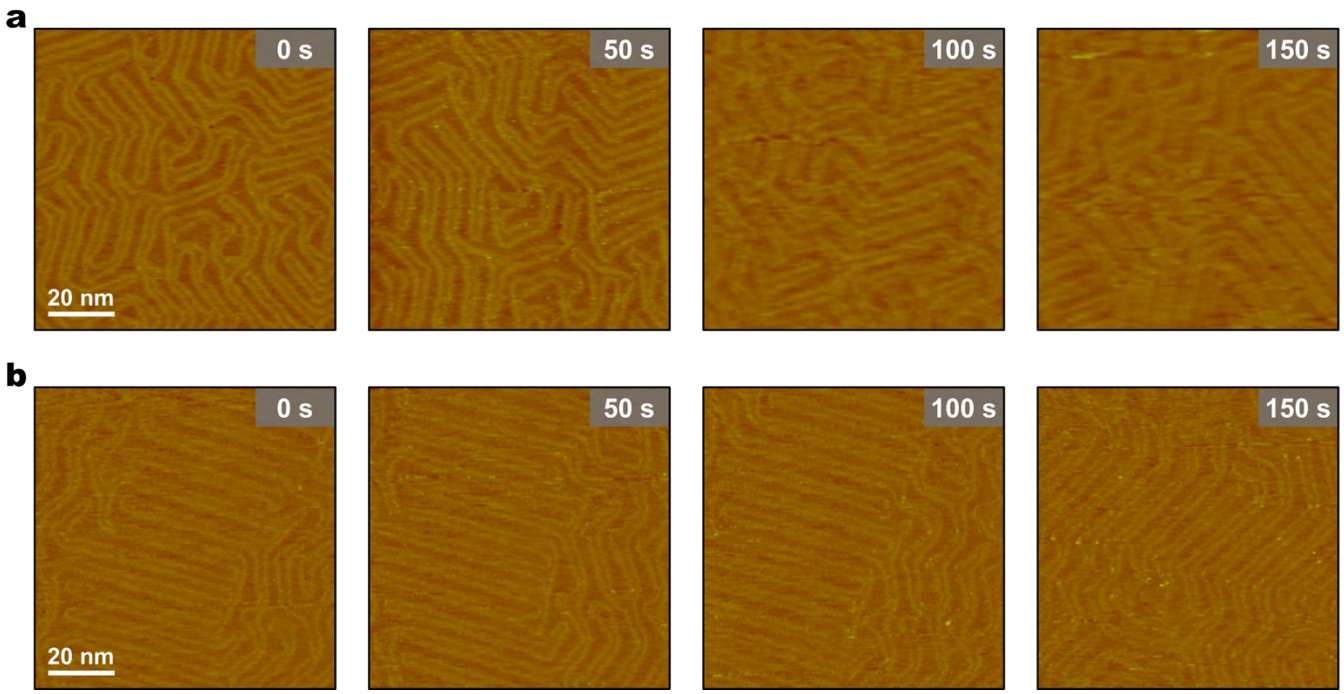

Fig. S4. EC-STM images of Au(111) in CO_2-saturated 1 M (a) $NaHCO_3$ and (b) $LiHCO_3$ electrolytes after the potential step from 0 V to -0.1 V.

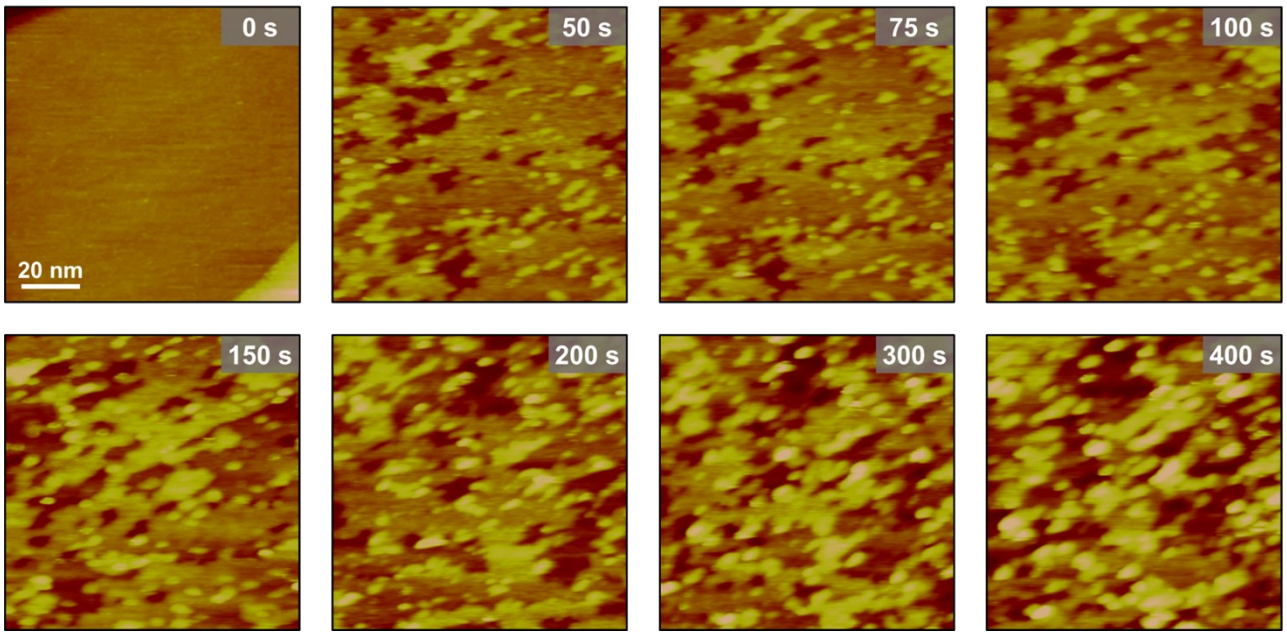

Fig. S5. EC-STM images of Au(111) in CO_2-saturated 0.5 M $CsHCO_3$ electrolyte after the potential step from -0.1 V to -0.2 V.

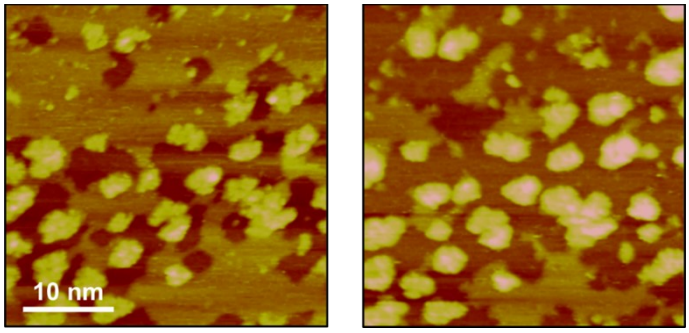

Fig. S6. In situ EC-STM images of Au(111) in CO_2-saturated 0.5 M $CsHCO_3$ electrolyte at -0.2 V showing the release and clustering of surface Au atoms.

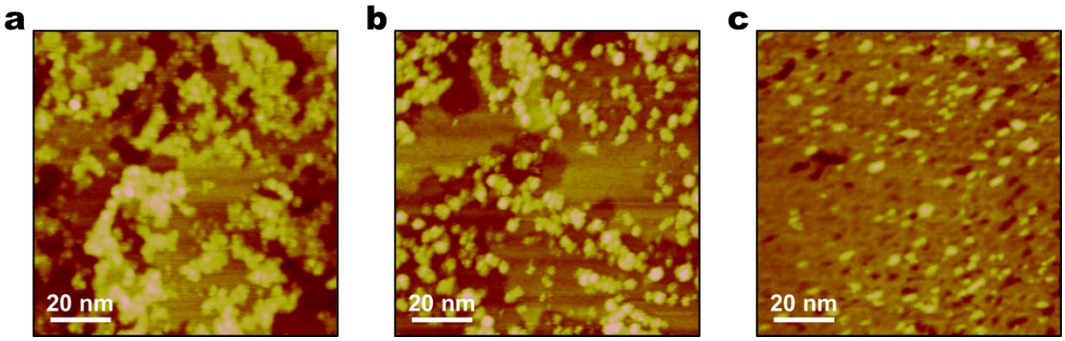

Fig. S7. EC-STM images of Au(111) in CO_2-saturated 0.5 M (a) $CsHCO_3$, (a) $RbHCO_3$, and (a) $KHCO_3$ electrolytes after the potential step from -0.1 V to -0.2 V for 200 s.

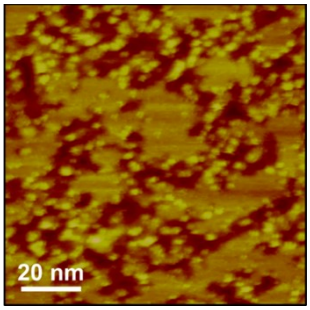

Fig. S8. EC-STM image of Au(111) in CO_2-saturated 0.4 M $CsHCO_3$ electrolyte after the potential step from -0.1 V to -0.2 V for 200 s.

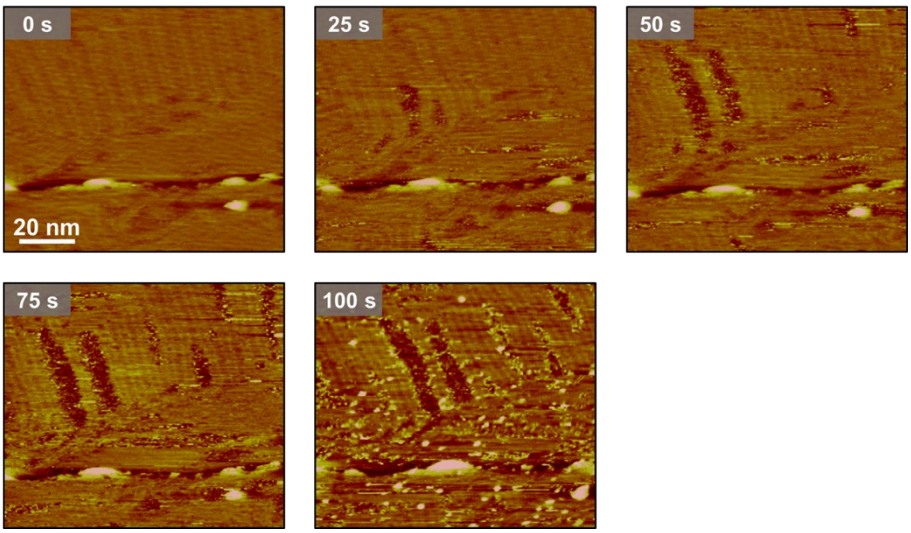

Fig. S9. EC-STM images of Au(111) in CO_2-saturated 0.3 M $CsHCO_3$ electrolyte after the potential step from -0.1 V to -0.2 V.

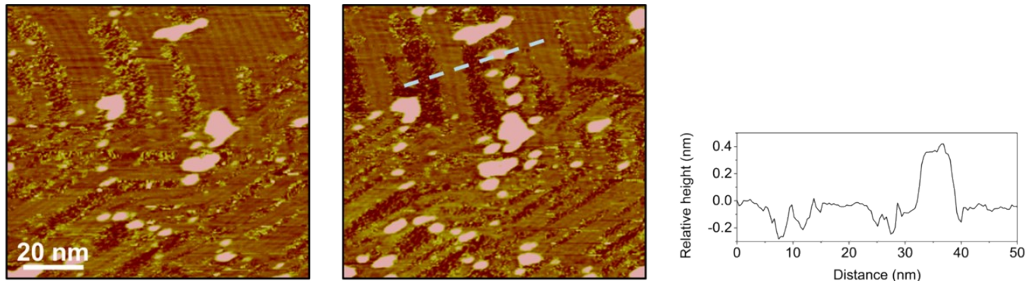

Fig. S10. In situ EC-STM images of Au(111) in CO_2-saturated 0.3 M $CsHCO_3$ electrolyte at -0.2 V showing the release and clustering of surface Au atoms. Cross-section corresponding to the dashed line.

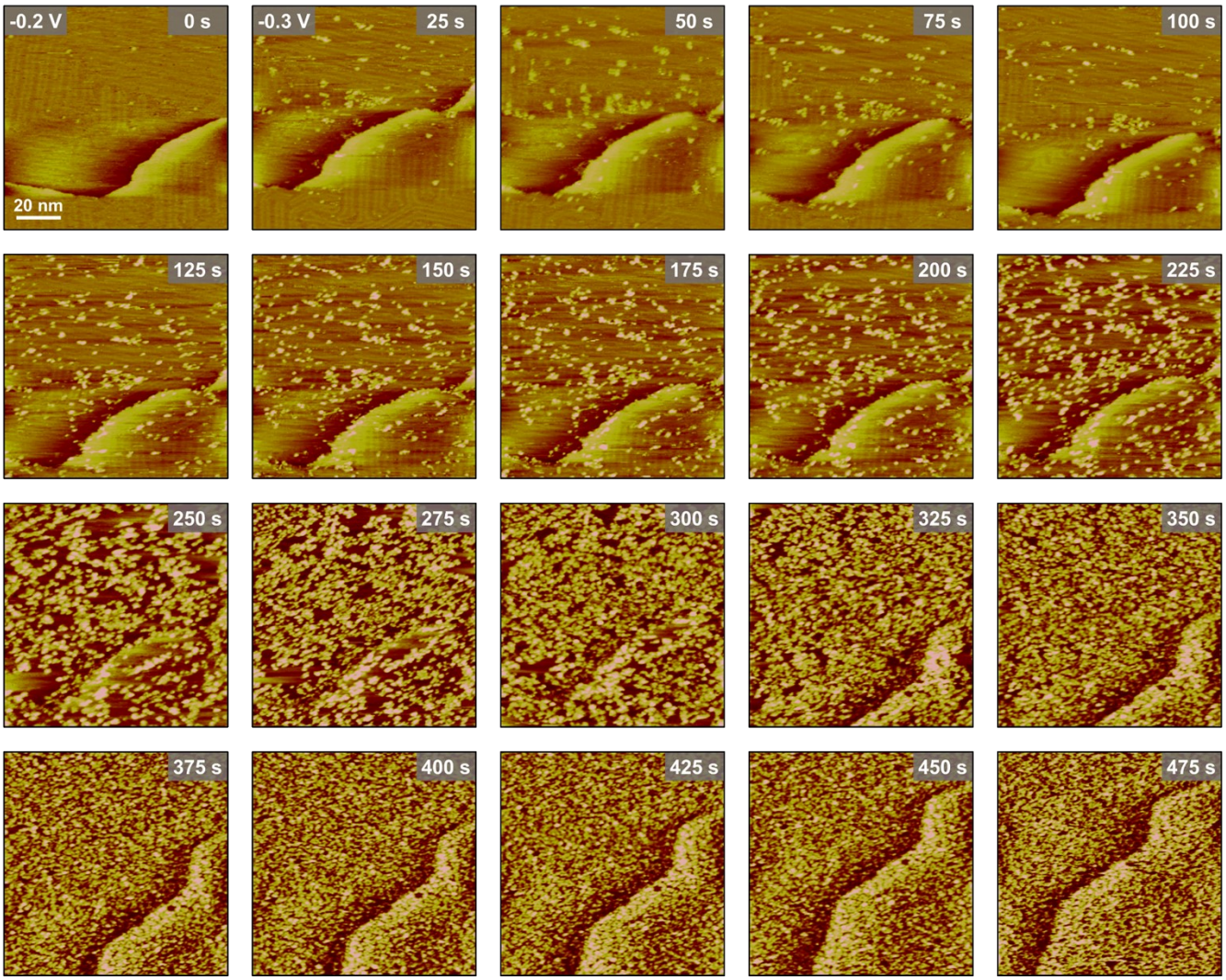

Fig. S11. EC-STM images of Au(111) in CO_2-saturated 0.2 M $CsHCO_3$ electrolyte after the potential step from -0.2 V to -0.3 V.

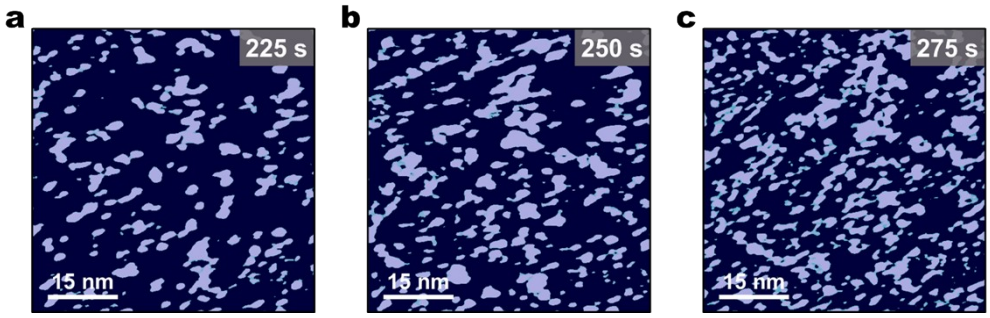

Fig. S12. Particle analysis of Au(111) surface roughened in CO_2-saturated 0.2 M $CsHCO_3$ electrolyte. EC-STM images of the roughened Au(111) surface are shown in Fig. S11. (a-c) Processed EC-STM images by particle analysis (Digital Instruments, Inc.) showing the unroughened Au(111) region (dark blue) and surface Au clusters (pale blue).

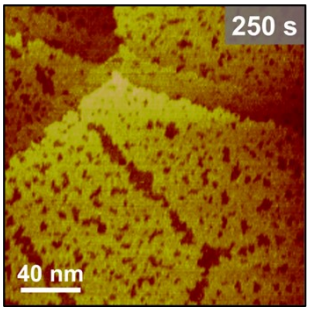

Fig. S13. EC-STM image of Au(111) in Ar-purged 1 M $KHCO_3$ electrolyte at 250 s after the potential step from 0 V to -0.1 V.

Here, the influence of CO_2 on the structure evolution of Au(111) under cathodic polarization is investigated. It has been reported that the surface morphology of Au(111) in CO_2-saturated and Ar-purged 0.1 M $CsHCO_3$ electrolytes is nearly identical at −0.4 V,[1] indicating that the role of CO_2 in Au(111) surface restructuring is neglectable in dilute electrolytes. For concentrated electrolytes, as shown in Fig. S13, the morphology of Au(111) in Ar-purged 1 M $KHCO_3$ at −0.1 V is similar to that obtained in CO_2-saturated 1 M $KHCO_3$ at the same potential (Fig. S3). These results suggest that the contribution of CO_2 to the cathodic structure evolution of Au(111) is minor, which can be attributed to the weak interaction between CO_2 and Au.

Moreover, the influence of HCO_3^- was evaluated under different electrolyte concentrations. In 0.1 M electrolytes, Au(111) exhibits similar surface morphologies in Ar-purged $CsHCO_3$ and $CsClO_4$ at −0.4 V, indicating that HCO_3^- has a negligible effect on Au(111) surface restructuring.[1] In 1 M electrolytes at −0.1 V, the Au(111) surface remains atomically flat in $LiHCO_3$ (Fig. S4), whereas severe corrosion is observed in $CsHCO_3$ (Fig. 1), demonstrating that surface restructuring in concentrated electrolytes is primarily driven by AM^+ rather than HCO_3^-. Moreover, it has been reported that HCO_3^- interacts weakly with Au under cathodic potentials, with a physisorption free energy of 22 kJ mol^{-1} at 0 V,[2] which further supports the conclusion that HCO_3^- plays a minimal role in driving surface structure evolution.

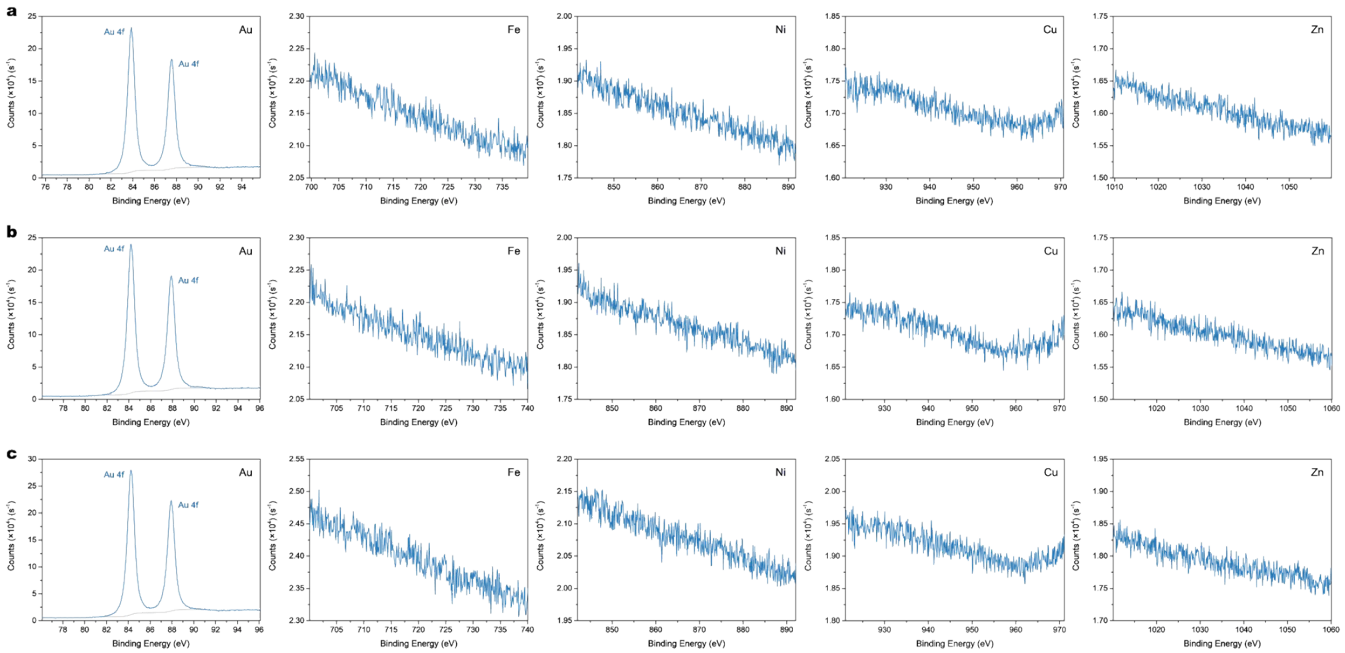

Fig. S14. XPS of Au(111) surfaces after roughened in CO_2-saturated (a) 1 M $CsHCO_3$ electrolyte at -0.1 V, (b) 0.5 M $CsHCO_3$ electrolyte at -0.2 V, and (c) 0.2 M $CsHCO_3$ electrolyte at -0.3 V for 15 min.

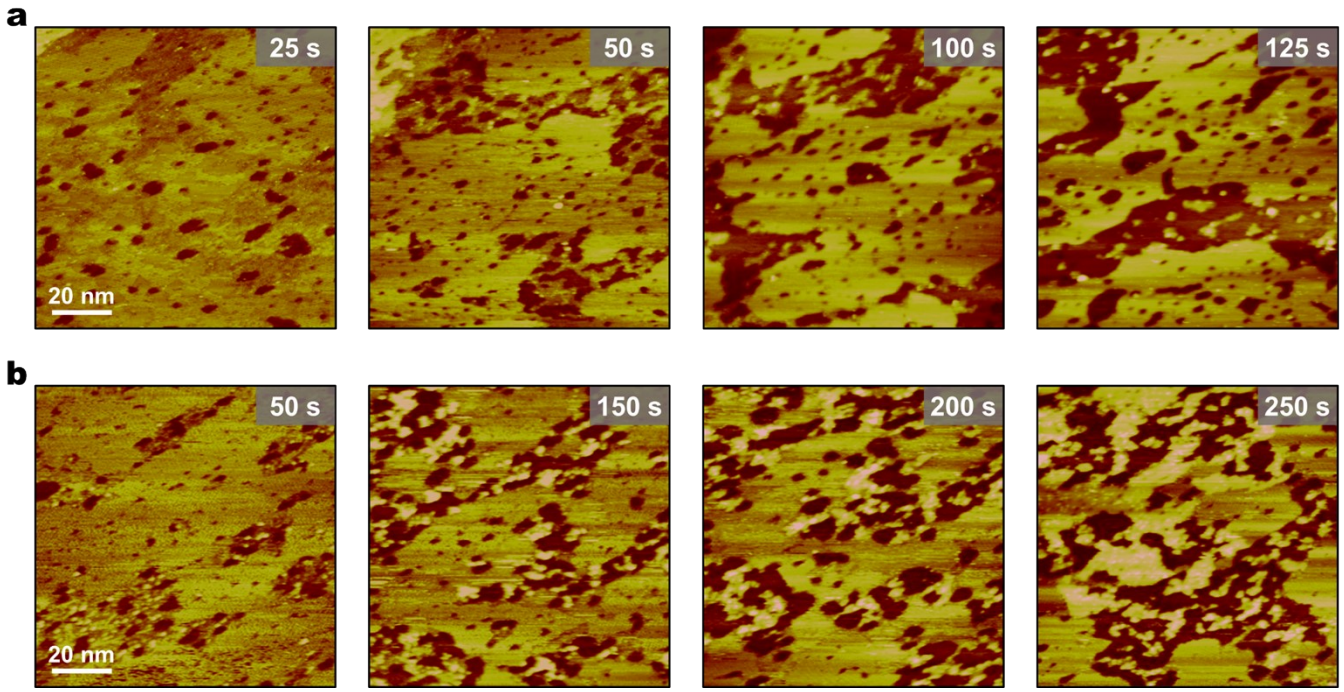

Fig. S15. EC-STM images of Au(111) in CO_2-saturated 0.1 M $CsHCO_3$ electrolyte containing 10 mM PA after the potential step from -0.1 V to -0.2 V.

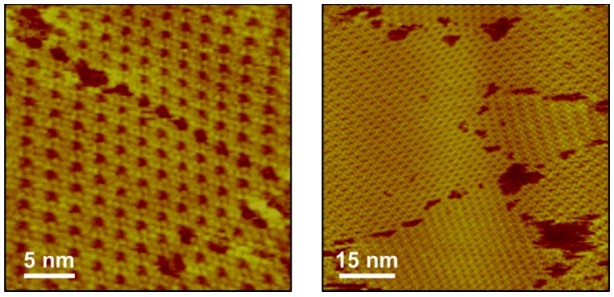

Fig. S16. EC-STM images of Au(111) in CO_2-saturated 0.1 M $NaHCO_3$ electrolyte containing 10 mM PA after the potential step from -0.1 V to -0.2 V.

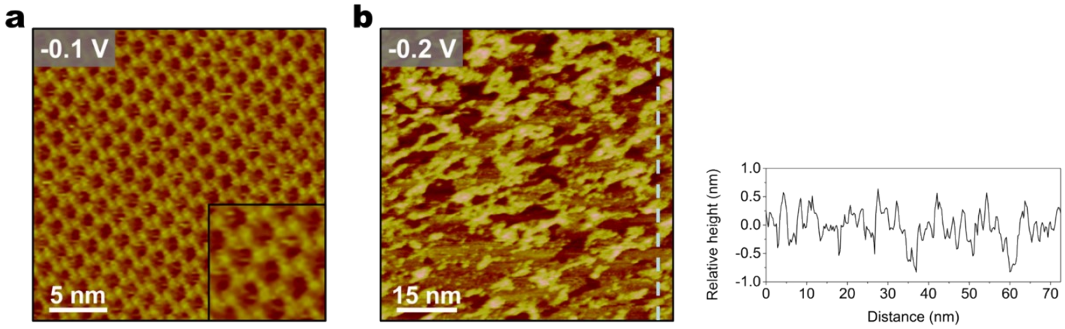

Fig. S17. EC-STM images of Au(111) in CO_2-saturated 0.1 M $CsHCO_3$ electrolyte containing 10 mM TMA at (a) -0.1 V and (b) -0.2 V. Cross-section corresponding to the dashed line.

In CO_2-saturated 0.1 M $CsHCO_3$ electrolyte containing 10 mM TMA, a well-ordered self-assembled monolayer of TMA is formed on the Au(111) surface at -0.1 V. Each bright spot represents a TMA molecule.

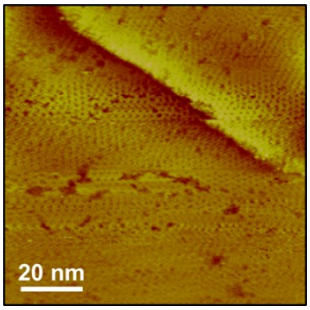

Fig. S18. EC-STM image of Au(111) in CO_2-saturated 0.1 M $CsHCO_3$ electrolyte containing 10 mM OPA at -0.2 V.

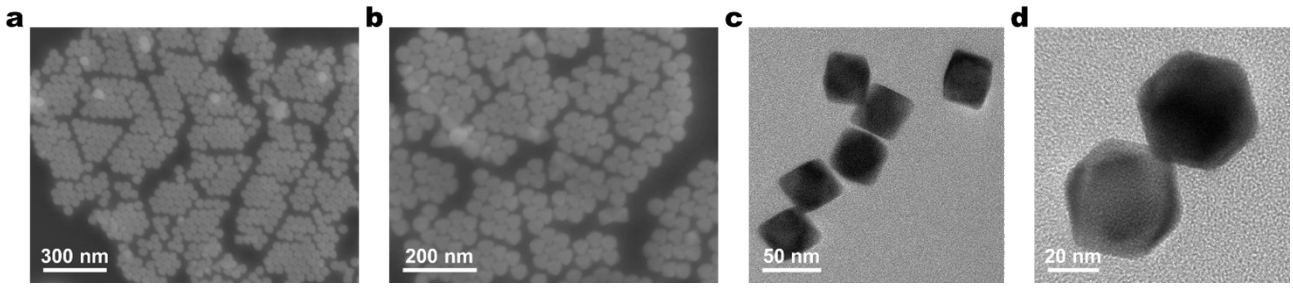

Fig. S19. Au NPs characterized by (a and b) transmission electron microscopy (TEM) and (c and d) scanning electron microscopy (SEM).

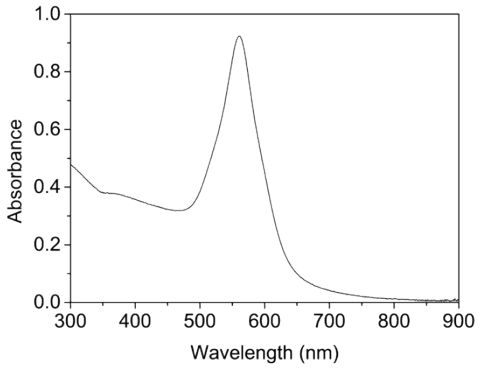

Fig. S20. Au NPs characterized by UV-Vis spectroscopy.

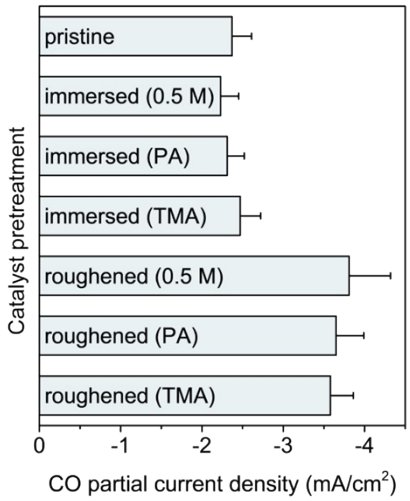

Fig. S21. CO partial current density of pristine and pretreated Au NPs electrodes measured at −0.8 V in CO_2-saturated 0.1 M $CsHCO_3$ electrolyte. The pretreated Au NPs electrodes are immersed or roughened (at -0.8 V) in 0.5 M $CsHCO_3$ electrolyte, 0.1 M $CsHCO_3$ electrolyte (containing 10 mM PA), and 0.1 M $CsHCO_3$ electrolyte (containing 10 mM TMA).

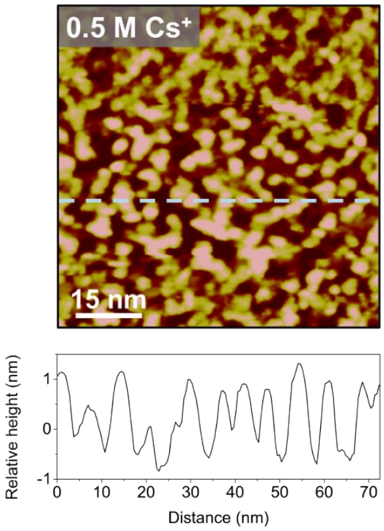

Fig. S22. EC-STM image of Au(111) in CO_2-saturated 0.5 M $CsHCO_3$ electrolytes at -0.8 V.

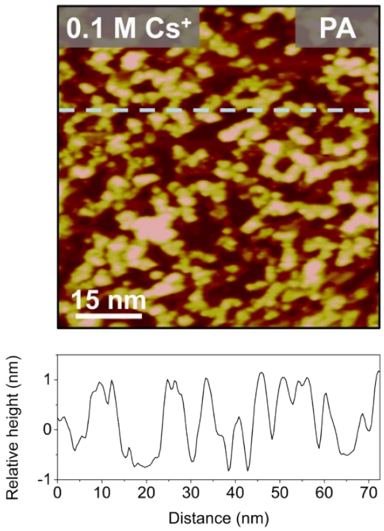

Fig. S23. EC-STM image of Au(111) in CO_2-saturated 0.1 M $CsHCO_3$ electrolytes containing 10 mM PA at -0.8 V.

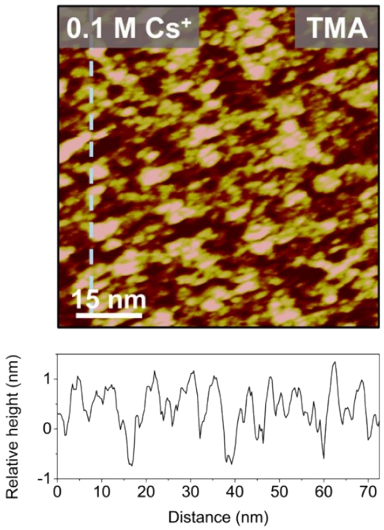

Fig. S24. EC-STM image of Au(111) in CO_2-saturated 0.1 M $CsHCO_3$ electrolytes containing 10 mM TMA at -0.8 V.

References

1 Y.-Q. Wang, J. Fu, Y. Feng, K. Zhao, L. Wang, J.-Y. Cai, X. Wang, T. Chen, F. Yang, J.-S. Hu, B. Xu, D. Wang and L.-J. Wan, *J. Am. Chem. Soc.*, 2024, **146**, 27713–27724.

2 J. M. Yoo, J. Ingenmey, M. Salanne and M. R. Lukatskaya, *J. Am. Chem. Soc.*, 2024, **146**, 31768–31777.