Supporting Information

Photo-assisted electrochemical micro-patterning of gold film

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1. Conversion from BF intensity to electrochemical current of single pattern of Au film

In this work, electrochemical current, i.e., the rate of Au film etching, of single pattern of Au film taken shape was calculated from its BF intensity (transparency ratio) by using the expression below (Equation S1).[1-2] In this equation, i is the electrochemical current, k is the conversion factor, and the I_{BF} is the BF transparency ratio as a function of time (t). The conversion factor, k, describes the corresponding number of the electrons (atoms) would be transferred from the change of transparency ratio (%) of the single Au film pattern during the unit time (s). Three steps needed to obtain the conversion factor k are as follow.

$$i = k\frac{dI_{BF}}{dt} \qquad \text{(Equation S1)}$$

Firstly, calculate the volume of the Au film patterns from the change of BF intensity. As the Au film etching, there existed less and less Au atoms to prevent the detection light beam to enter the camera. A linear dependence of optical transmission ratio (T(%) = 1.16E-05*V(nm^3)) on the volume of holes was observed in our system. The optical transparency ratio was calculated by comparing the BF intensity of region of interest (ROI) before (I_0) and after (I_t) experiment (T(%) = ($I_t - I_0$)/ I_0*100) and the ROI is the region of 16*16 pixels (80 nm per pixel) that including the entire single Au film pattern (Figure S1a). The volume of Au hole, which was calculated by the formula for calculating the volume of a cylinder ($V=\pi\times(d/2)^2\times h$). The diameter (d) of the cylinder (i.e., Au holes) was measured by the SEM (Figure S1b) and the height (h) was provided by AFM ((Figure S1c).

Secondly, calculate the electrons needed to transfer (atoms needed to dissolve) with the corresponding Au film patterning for the certain volume. Au crystal structure is face-centered cubic, i.e., there are four Au atoms in one unit cell, and the volume of the Au unit cell is 0.013 nm^3. In the Au film photoelectrochemical etching process, there was one electron for each one Au atom to participate in the etching process. The quantitative model between the the volume and the number of electrons transferred is N_{ele} = 1*(4/0.013)*V (nm^3).

Finally, the photo-assisted electrochemical etching current was gained by first-order differential of the number of electrons transferred with time. So far, we have achieved the conversion from dynamic BF intensity to etching current of the 50 nm Au film.

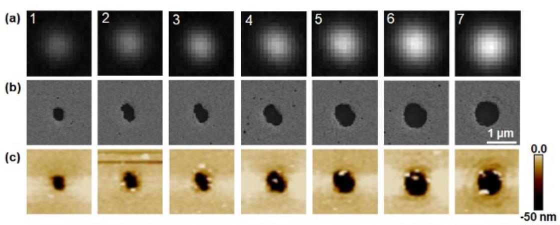

Figure S1. The transparency ratio of Au holes linearly increases with volume. A series of holes with different sizes were fabricated and characterized with BF (a), SEM (b) and AFM (c) images.

2. Linearly dependence of optical current on the illumination laser power

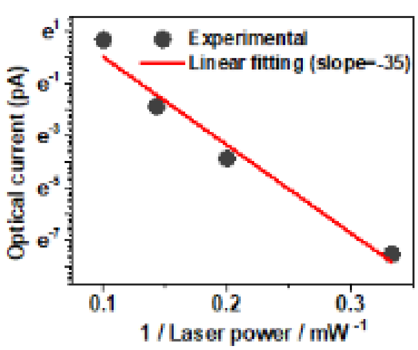

Figure S2. Linearly dependence of optical current (etching rate) on the reciprocal of laser power (surface temperature of Au film illuminated by 405 nm laser).

3. OCP measurement on Au film electrode with different size

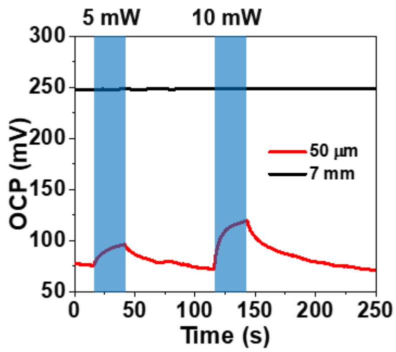

Figure S3. The OCP of the system increased 20 mV upon the illumination of 5 mW laser beam on a 50-μm electrode, while no obvious change in OCP can be detected when repeating the same experiment on a 7-mm electrode.

4. Photo-assisted electrochemical micro-patterning of Cr film

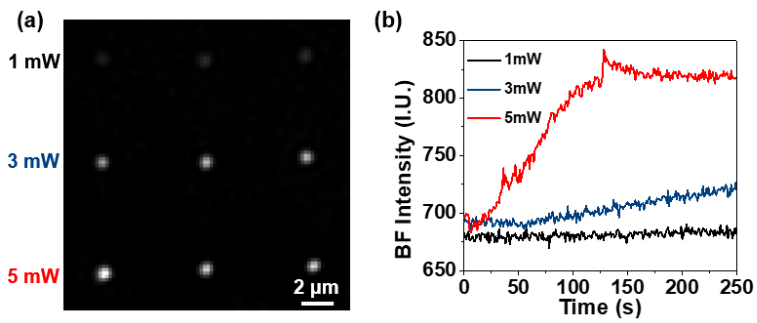

Figure S4. Photoelectrochemical etching of pure Cr film under different laser power. (a) BF image of Cr holes etched with different laser power. (b) Time-dependent BF Intensity of the hole formed under illuminated with different 405 nm laser power. The results indicated that Cr was more reactive than Au in our system, and it would not affect the etching of gold.

5. Photo-assisted electrochemical etching performance on gold films with different thickness

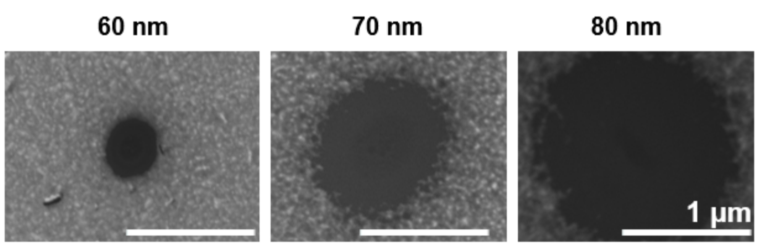

Figure S5. Holes were obtained in gold film with different thickness under same reaction condition. The laser power is 10 mW and bias voltage is 100 mV and the reaction time is 50 s. Under the same conditions, it was found that smaller holes were obtained in thinner gold film.

6. Photo-assisted electrochemical etching performance with the different concentration of dissolved oxygen in the solution

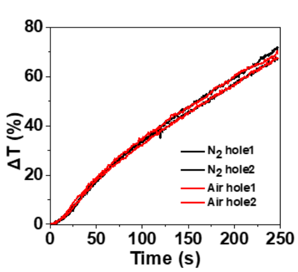

Figure S6. Holes were obtained in different concentration of dissolved oxygen in the solution (0.5 M Na_2S and 0.5 M Na_2SO_3). The results indicated that the etching kinetics is independent with the concentration of dissolved oxygen in the solution.

REFERENCES

1. Chakri, S.; Patel, A. N.; Frateur, I.; Kanoufi, F.; Sutter, E. M. M.; Tran, T. T. M.; Tribollet, B.; Vivier, V. Imaging of a Thin Oxide Film Formation from the Combination of Surface Reflectivity and Electrochemical Methods. Anal. Chem. 2017, 89, 5303-5310.

2. Jiang, D.; Jiang, Y.; Li, Z.; Liu, T.; Wo, X.; Fang, Y.; Tao, N.; Wang, W.; Chen, H. Y. Optical Imaging of Phase Transition and Li-Ion Diffusion Kinetics of Single LiCoO2 Nanoparticles During Electro-chemical Cycling. J. Am. Chem. Soc. 2017, 139, 186-192.