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Supporting Information

Dynamic Broadband Plasmonic Absorber enabled by Electrochemical Lithium Metal Batteries

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1. Fabrication Process

1.1 Preparation of substrate with Au nanoparticles

The substrate material is one of the key factors affecting the morphology of lithium particles because different deposited substrates have different nucleation overpotential with lithium metal. The smaller the overpotential is, the more easily lithium is deposited on this substrate. Au is a material with zero lithium nucleation overpotential, so lithium deposition does not need to overcome the energy barrier, and it is suitable as a selective deposition site for lithium. To achieve high absorption of the substrate in the visible band in this study, it is necessary that the initial Au structure has low absorption to visible light, that is, high reflectivity. Importantly, the optical properties of the Au structure, which are closely related to their shape, size, and other factors, are determined by the thickness of the Au film, annealing temperature, and annealing method. The following is a specific description of the exploration:

(1) Thickness of Au film: A small ion sputtering instrument model SD-900 used to sputter Au film has the advantages of low cost, convenience, simplicity, and easy operation. The thickness of the Au film is controlled by the sputtering time and current. Generally, the longer the time, the thicker the Au film; The larger the current, the larger the particles, and the thicker the Au film. In this experiment, the time of sputtering Au was controlled at 30 s to explore the morphology of Au particles under different currents of 15 mA, 25 mA, and 50 mA.

(2) Annealing temperature: The effects of different annealing temperatures on the morphology of Au particles were compared. The Au sample sputtered was placed in a tube furnace and annealed in an Ar atmosphere. The temperature is 200 ℃, 400 ℃ and 800 ℃ respectively. The sputtering time is 30 s, the current is 15 mA, the annealing method is rapid annealing, and the holding time is 10 minutes.

(3) Annealing method: Conventional annealing in tube furnaces and rapid annealing outside furnaces are adopted. The sample with the sputtering time of 30 s and the current of 15 mA was placed in a tube furnace (Ar atmosphere), and the annealing temperature was 400 ℃ for 10 minutes. Then it was quickly taken out and annealed in air. The same set of samples was held under the same conditions for 10 minutes and then slowly cooled and annealed in an Ar atmosphere.

1.2 Morphology characterization and analysis of Au nanoparticles substrate

The samples under different preparation conditions were characterized by scanning electron microscopy (SEM). As shown in Figure S1, Figures S1 a-f correspond to samples A-F respectively. The Au plating current of samples A, B, and C was 15 mA, and the annealing conditions were 200 ℃ for 10 min, 400 ℃, 10 min; and 600 ℃ for 10 min, respectively. Samples of D and E were rapidly annealed at 400 ℃ for 10 min, and Au plating currents were 25 mA and 35 mA, respectively. Sample F was annealed at 400 ℃ and the Au plating current was 15 mA.

It can be seen from Figure S1 that the larger the plating current, the larger the gold particles. And with the increasing of the annealing temperature and annealing cooling rate, the boundary between particles is clearer. By comparing Figure S1 a-c, the higher the annealing temperature is, the more spherical the shape of the particles is and the larger distance is between the particles under the same current and annealing method because the surface tension between particles gets strengthened under higher temperatures. At 600 ℃, the sample has a non-granular dendrite morphology, which is because the tension between the gold films becomes more obvious with the increase in temperature. With the gradual increase of the current, the gold size gradually becomes larger with more Au nanoparticles under the same annealing conditions and annealing temperatures in samples A, D, and E. What's more, the slow annealing method is more likely to form a ball and the particle size is distributed between 8 nm and 13 nm, which is consistent with the previous simulation (Figure S4).

In conclusion, the sample F morphology obtained by Au sputtering with 10 mA current, 10 min annealing at 400 ℃, and slow cooling is in agreement with the simulation.

1.3 Fabrication chart of negative electrode of the planar battery

The negative electrode of the battery is prepared on a quartz glass sheet. The 25 mm × 13 mm × 1 mm quartz glass sheet was first cleaned with ethanol and deionized water and then cleaned by oxygen plasma cleaner for 10 min to get a clean quartz substrate. Then, one side of the quartz sheet is glued with polyimide tape and placed in the magnetron sputtering coater. The conductive substrate sample of the metal W film with a thickness of about 120 nm is obtained by plating at a power of 50 W for one hour. The conductive W substrate was put into the gold sputtering instrument and sprayed for 30 s between 0 mA and 10 mA currents to get the W substrate decorated with Au sputtering. After that, a tube furnace was used to hold the battery for 10 minutes at 400 ℃, and the negative electrode of the battery was obtained after conventional cooling. The preparation flow chart is shown in Figure S2.

1.4 Spectrogram and morphology of the suitable substrate

The image of sample F composed of random Au particles is shown by SEM in Figure S3. We test the in situ reflectance and it reaches up to 90%.

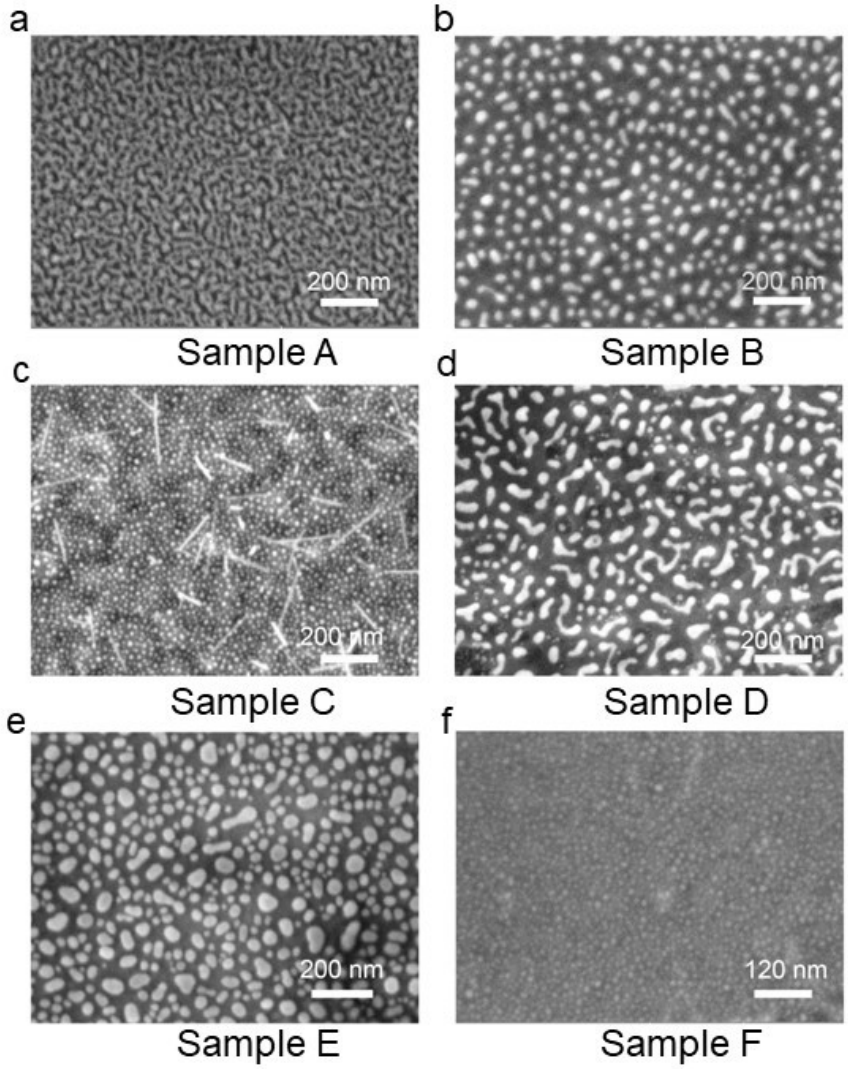

Figure S1 | SEM images of Au nanoparticles prepared under different conditions. (a) Current at 15 mA and temperature at 200 ℃ for rapid annealing. (b) Current at 15 mA and temperature at 400 ℃ for rapid annealing. (c) Current at 15 mA and temperature at 600 ℃ for rapid annealing. (d) Current at 25 mA and temperature at 400 ℃ for rapid annealing. (e) Current at 35 mA and temperature at 400 ℃ for rapid annealing. (f) Current at 15 mA and temperature at 400 ℃ for conventional annealing.

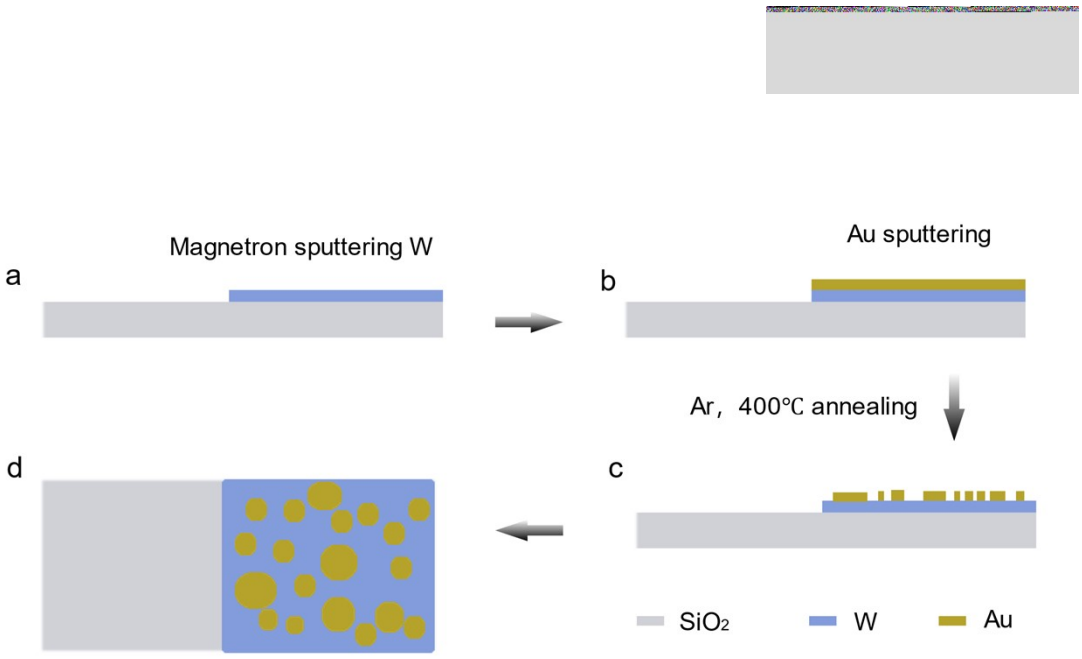

Figure S2 | Fabrication chart of a planar battery. (a) Magnetic sputtering a layer of W. (b) sputtering Au film. (c) thermal annealing. (d) Top view of the planar battery.

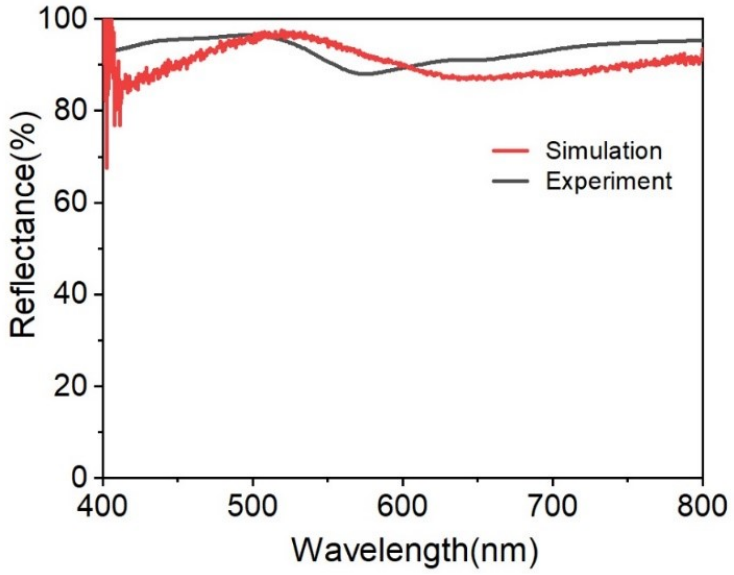

Figure S3 | Comparison between experimental and simulated reflectance of Au substrate.

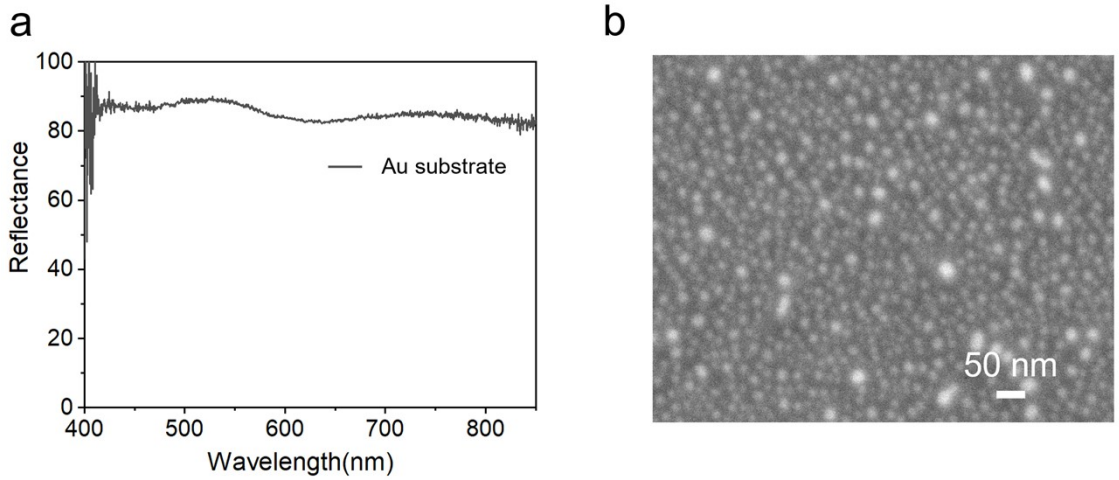

Figure S4 | Reflectance and morphology of Au substrate. (a) original reflection spectrum. (b) SEM image of original Au substrate.

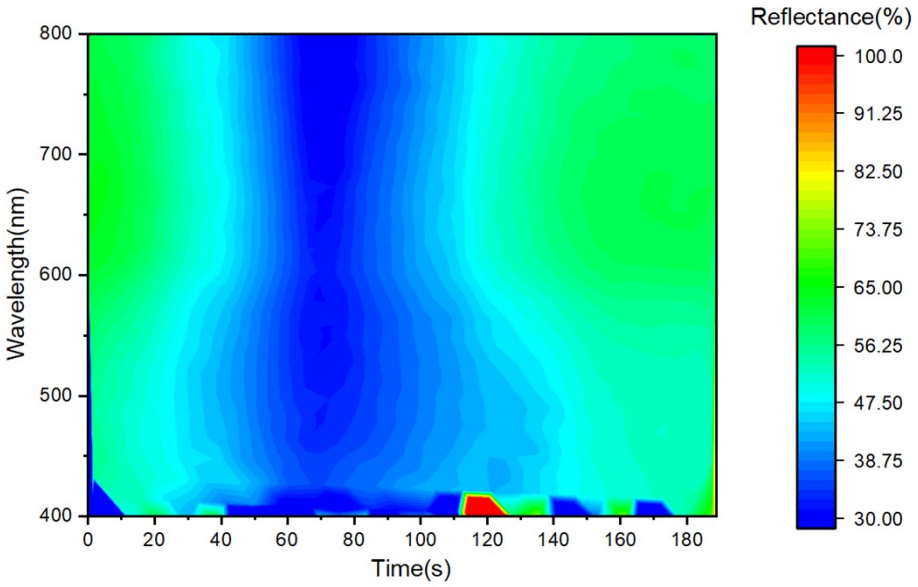

Figure S5 | Continuous reflectance distribution diagram of the absorber of random Li NPs over the 6th cycle. It is shown that the reflectance of the full cycle with the increasing time during charging and discharging.

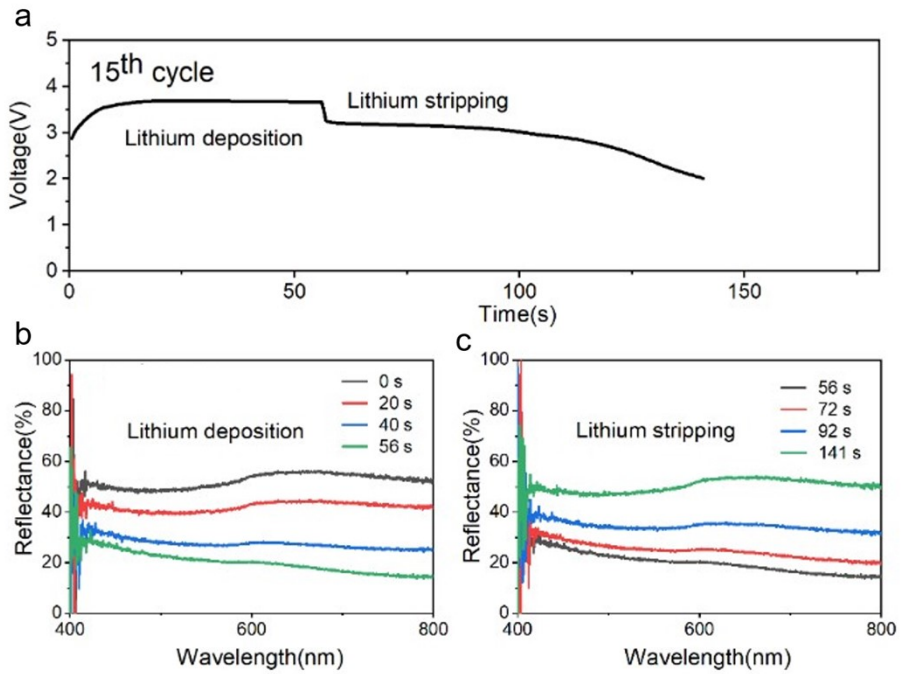

Figure S6 | In situ reflectance characterization of the 15th cycle. (a) Battery voltage during lithium deposition and stripping process. (b) In situ reflectance curve during lithium deposition at 50 μA. (c) In situ reflectance curve during lithium stripping at 25 μA.

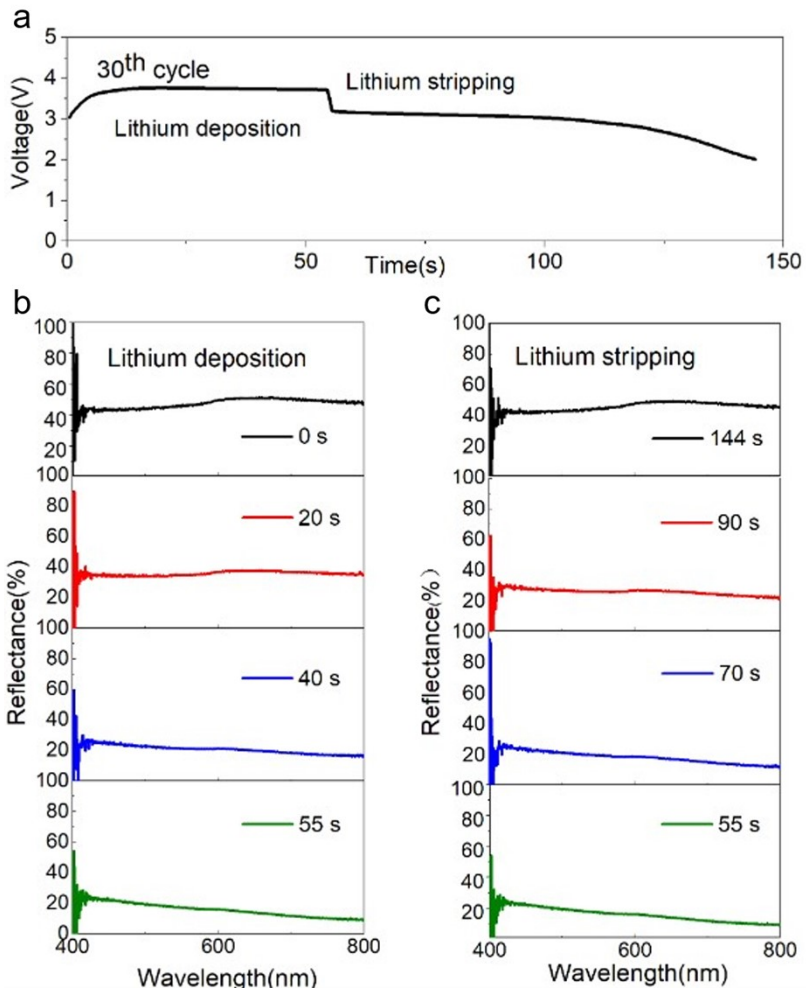

Figure S7 | In-situ reflectance characterization of the 30th cycle. (a) Battery voltage during lithium deposition and stripping process. (b) In situ reflectance curve during lithium deposition at 50 μA. (c) In situ reflectance curve during lithium stripping at 25 μA. The reaction area of the battery is about 0.4 cm^2, so the current density is 0.125 mA/cm^2 at charging and 0.0625 mA/cm^2 at discharging.