Supporting Information

Simultaneous Power Generation and CO_2 Valorization by Aqueous Al-CO_2 Batteries Using Nanostructured Bi_2S_3 as the Cathode Electrocatalyst

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Experimental section

Preparation of Bi_2S_3 nanoplatelets: Bi_2S_3 NPs were prepared via a facile solvothermal method. In brief, 75 mg of bismuth acetate ($Bi(CH_3COO)_3$, 99.99%, J&K Chemical) was firstly dissolved in 30 mL of ethylene glycol (99 %, J&K Chemical) contained in a 50 mL three-necked flask with the assistance of >30 min bath sonication. The solution was purged with N_2 and gradually heated to 200 ℃. At this temperature, 25 mg of solid thiourea (99.0 %, Aladdin) was rapidly added to the reaction solution. It was further reacted at 200 ℃ for another 5 min. After cooling down to room temperature, the solid product was collected by centrifugation, sequentially washed with ethanol and water, and finally lyophilized.

Material characterizations: SEM imaging was performed on a Zeiss G500 scanning electron microscope. TEM imaging was conducted on a FEI Tecnai F20 transmission electron microscope at an accelerate voltage of 200 kV. XRD pattern was collected on a PANalytical X-ray diffractometer using Cu Kα radiation. XPS analysis was carried out on an SSI S-Probe X-ray photoelectron spectrometer.

Electrochemical CO_2RR measurements: The catalyst ink was first prepared by dispersing 1 mg of Bi_2S_3 NPs and 0.5 mg of Ketjen black in 250 μL of ethanol, 30 μL of water and 10 μL of 5 wt% Nafion solution under the assistance of ultra-sonication for >30 min. It was then uniformly drop-cast onto a Teflon-treated carbon fiber paper (AvCarb P75T from Fuelcellstore) to achieve a catalyst loading of 1 mg cm^{-2}. Electrochemical CO_2RR was carried out in a custom-built flow cell reactor as described in our previous publication (*Nat. Commun.* **2019**, *10*, 2807) using Bi_2S_3-loaded GDL as the working electrode, Ag/AgCl as the reference electrode and an Ir-coated Ti plate as the counter electrode. The volume of cathodic and anodic compartments was ~ 6.5 cm^3 each. They were separated by an anion exchange membrane (Sustainion from Dioxide Materials). The electrolyte was 1 M KOH solution. During CO_2RR measurements, CO_2 gas was continuously fed to the backside of the working electrode

at 70 sccm. The catholyte was circulated at 5 sccm driven by a peristaltic pump. Polarization curves were collected at a scan rate of 10 mV s^{-1} at 90% iR compensation. All potential readings were measured against Ag/AgCl and converted to RHE. The amount of formate in the catholyte was quantified using an ion chromatograph (IC, Dionex ICS-600) as described in our previous publication (*Nat. Commun.* **2018**, *9*, 1320).

Aqueous Al-CO_2 batteries: To assemble aqueous Al-CO_2 batteries, Bi_2S_3-loaded GDL was paired with either a commercial Al foil (40 × 40 mm^2, 0.2 mm thick, 99.999%) or a piece of Al sheet cut from used Al beverage cans in the same flow-cell configuration. The electrolyte was 1 M KOH and was forced to circulate at 10 sccm throughout the cathodic and anodic compartments. Discharging curves were collected at a scan rate of 10 mV s^{-1}. Chronoamperometric tests were conducted at different discharge voltages. The amount of produced formate in the catholyte was determined by the ion chromatograph.

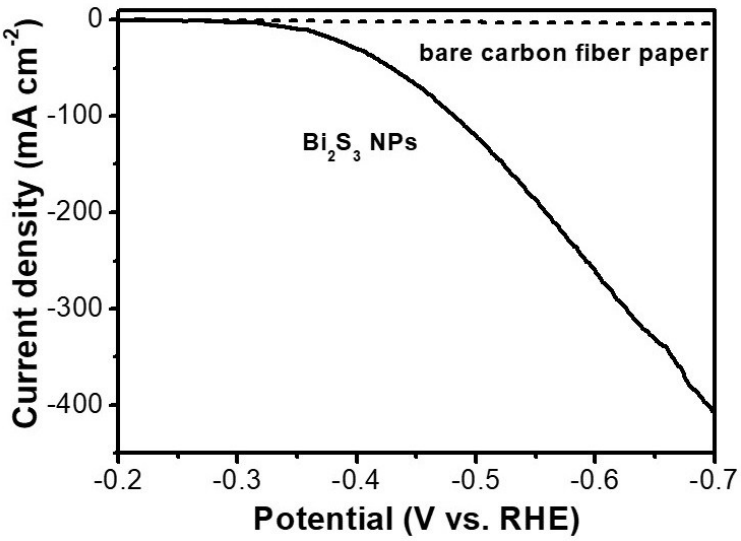

Figure S1. Polarization curves of bare carbon fiber paper and Bi_2S_3-loaded carbon fiber paper electrodes under CO_2 in 1 M KOH using a three-electrode flow-cell configuration.

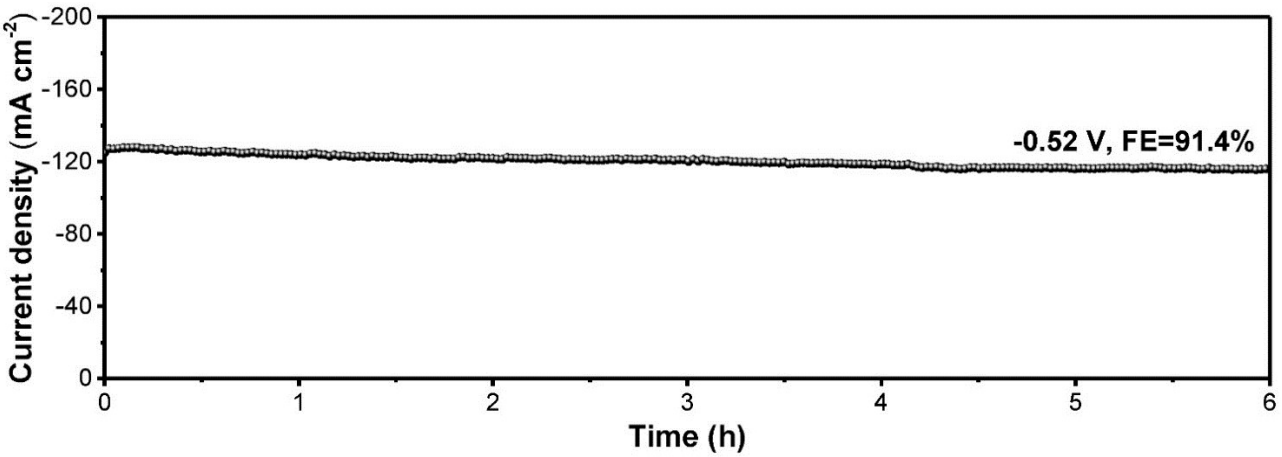

Figure S2. Chronoamperometric response of Bi_2S_3 NPs at -0.52 V versus RHE under CO_2 in 1 M KOH using a three-electrode flow-cell configuration.