The excessive emission of CO$_2$ and the energy crisis are two major issues facing humanity. Thus, the electrochemical reduction of CO$_2$ and its utilization in metal–CO$_2$ batteries have attracted wide attention because the batteries can simultaneously accelerate CO$_2$ fixation/utilization and energy storage/release. Here, rechargeable Al–CO$_2$ batteries are proposed and realized, which use chemically stable Al as the anode. The batteries display small discharge/charge voltage gaps down to 0.091 V and high energy efficiencies up to 87.7%, indicating an efficient battery performance. Their chemical reaction mechanism to produce the performance is revealed to be $4\text{Al} + 9\text{CO}_2 \leftrightarrow 2\text{Al}_2(\text{CO}_3)_3 + 3\text{C}$, by which CO$_2$ is reversibly utilized. These batteries are envisaged to effectively and safely serve as a potential CO$_2$ fixation/utilization strategy with stable Al.

Rechargeable Al–CO$_2$ Batteries for Reversible Utilization of CO$_2$

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The utilization and fixation of CO$_2$ by metal–CO$_2$ batteries are emerging as a “killing two birds with one stone” strategy, which is economic and promising for handling the challenges of the increasing energy crisis and greenhouse gas CO$_2$ emission.\textsuperscript{[1–4]} The initial success was obtained from Li–CO$_2$ batteries in 2014, which adopted Li metal anode and carbon cathode for the CO$_2$ capture and energy storage.\textsuperscript{[5]} Immediately, many efforts have been expanded on developing new cathode materials,\textsuperscript{[5–9]} stable electrolyte systems,\textsuperscript{[10,11]} and Na anodes for metal–CO$_2$ batteries.\textsuperscript{[12,13]} These works are pioneering and inspiring breakthroughs. However, both Li and Na are highly active metals that are easy to react with ambient air or structural metals used for the storage or transportation of the batteries. Therefore, it is urgent to find chemically stable metals for serving as anodes toward the safe applications of metal–CO$_2$ batteries. Very recently, Sadat and Archer developed an O$_2$-assisted Al–CO$_2$ electrochemical cell for CO$_2$ capture/conversion and electric power generation.\textsuperscript{[14]} All of the above researches inspire us to develop rechargeable Al–CO$_2$ batteries. Al possesses not only a much lower chemical reactivity and thus a much higher safety than Li and Na but also a high theoretical specific capacity (2978 mAh g$^{-1}$), comparable to those of Li and Na (3860 and 1165 mAh g$^{-1}$).\textsuperscript{[15]} Moreover, the theoretical capacity of a rechargeable Al–CO$_2$ battery is 638 mAh g$^{-1}$, also comparable to the capacities of rechargeable Li–CO$_2$, Na–CO$_2$, and Li-ion batteries (Figure S1, Supporting Information), which have been widely studied.\textsuperscript{[16,17]}

Herein, we propose and realize rechargeable Al–CO$_2$ batteries with Al foils as anodes, ionic liquid electrolytes, and Pd-coated nanoporous gold (NPG@Pd) pieces as catalyst cathodes. Pure CO$_2$ is adopted as the active material in the cathodes. The prototype batteries display small gaps down to 0.091 V between discharge and charge plateaus at the current density of 333 mA g$^{-1}$ and thus energy efficiencies (EEs) up to 87.7%, which are both comparable to those of reported Li/Na–CO$_2$ batteries. We have characterized the NPG@Pd cathodes and the discharge products and then revealed the battery reaction mechanism to be $4\text{Al} + 9\text{CO}_2 \leftrightarrow 2\text{Al}_2(\text{CO}_3)_3 + 3\text{C}$. In the reaction, Al$_2$(CO$_3$)$_3$ and C form from CO$_2$ during discharging and decompose upon charging, which is a reversible utilization of CO$_2$. This work provides a fundamental and technological progress toward high-efficient, high-safety, green and rechargeable energy devices for exploiting and fixing CO$_2$.

A proposed Al–CO$_2$ battery consists of an Al-foil anode, an ionic liquid electrolyte and an NPG@Pd cathode (see its schematic image in Figure S2, Supporting Information). The ionic liquid electrolyte can be made by mixing ultradry AlCl$_3$ and 1-ethyl-3-methylimidazolium chloride with a mole ratio of 1.3.\textsuperscript{[14]} In this battery, the CO$_2$ reduction is the battery reaction taking place at the solid–liquid–gas three-phase interfaces on
the cathode surface (see more details in Figure S2, Supporting Information). Thus, the cathode should have high activity to catalyze the CO₂ reduction, high electronic conductivity to transfer electrons, and high porosity to promote the gas/electrolyte permeation and storage of discharge products, but maintain inert to the electrolyte. These requirements might be met by NPG@Pd electrodes, because it is reported that Pd has high activity for catalyzing the CO₂ reduction, and NPG has high electronic conductivity and high porosity, although they have not been employed in metal–CO₂ batteries so far. Specifically, our previous result has measured the specific surface area of NPG, given it to be 30–90 m² g⁻¹ and found the values to be comparable to that of Au nanoparticles, indicating a large porosity.

The as-prepared NPG@Pd cathodes have been characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning TEM (STEM), high-angle annular dark field (HAADF) imaging of aberration-corrected STEM, and energy dispersive X-ray spectroscopy (EDS). The results are shown in Figure 1, which indicates that NPG@Pd pieces have bicontinuous nanoporous structures with clean surfaces, their average pore size and ligament width are around 25 nm, and their Au ligaments are covered by epitaxial Pd coatings, similar to our previous NPG@Pd@Pt samples. Further, the existence of Pd coatings is confirmed by cyclic voltammograms (Figure S3, Supporting Information), which exhibit palladium oxide formation/reduction peaks for NPG@Pd. The electrochemically active surface area (ECSA) of NPG@Pd was measured using the Brummer’s method to be 33.5 cm² cm⁻², much larger than that of NPG without Pd (5.2 cm² cm⁻²), suggesting a sufficient electrode/electrolyte/gas three-phase interface for the battery reactions, efficient electrolyte permeation and ionic/electronic transportation. This ECSA comparison is in agreement with reported results. Besides, the large porosity of NPG@Pd also provides sufficient spaces for uptaking solid discharge products.

Figure 1. Morphology and structure of the as-prepared NPG@Pd cathodes. a,b) Low- and high-magnification SEM images of NPG@Pd. c) Low-magnification HAADF-STEM image and d) its corresponding EDS elemental mapping result of NPG@Pd. e) High-resolution HAADF-STEM image and f–h) its corresponding EDS elemental mapping results of NPG@Pd. In (d) and (f)–(h), Au and Pd are shown in green and red, respectively.

The rechargeable Al–CO₂ batteries were assembled in the form of coin-type cells, and their electrochemical performances were characterized by sealing them in pure-CO₂-filled glass containers (see more details in the Experimental Section). In this work, all applied current density and achieved specific capacity values were normalized to the mass of NPG@Pd cathodes. Figure 2a shows the discharge–charge curves of two Al–CO₂ batteries with NPG@Pd or NPG as cathodes at the current density of 333 mA g⁻¹ by controlling the discharge/charge time at 10 h, which is similar to the reported (see more details and full discharge curves in Figure S4, Supporting Information). The discharge terminal voltage of the NPG Al–CO₂ battery is 0.420 V, while the one of the NPG@Pd Al–CO₂ battery is as high as 0.627 V, revealing that the NPG@Pd cathode led to a smaller overpotential and thus had a higher efficient electrochemical CO₂-reduction catalytic activity for the CO₂ reduction. This finding is in agreement with reported results about the efficient electrochemical CO₂-reduction catalytic activity of Pd-containing materials. Further, the charging process of the NPG@Pd Al–CO₂ battery finished at 0.735 V, in contrast to the 0.830 V value of the NPG Al–CO₂ battery, indicating that the NPG electrode possesses a lower catalytic activity than NPG@Pd for the CO₂ formation from discharge products in the batteries. This suggests that Pd has a higher activity to catalyze the oxidation of carbon than Au. By the above performances, the recharge/charge voltage gap of the NPG@Pd Al–CO₂ battery is only 0.091 V, giving an EE of 87.7%. The two values are both better than those of the NPG Al–CO₂ battery (0.342 V and 60.3%). It is worth noting that the voltage gaps and EEs of Li–CO₂, Na–CO₂, and Al–air batteries are reported to be 0.7–2.2 V and 55–79%, 0.6–2.3 V and 57–81%, and 0.2–1.9 V and 20–64%, respectively. Because a small voltage gap and thus a high EE imply a low energy loss, the NPG@Pd Al–CO₂ battery possesses an efficient battery performance. Besides, Figure 2a shows that the initial discharge voltages of
the two Al–CO₂ batteries are 0.73 V (NPG) and 0.76 V (NPG@Pd), also reflecting the different catalytic activities of their cathode catalysts (see more details in the caption of Figure S4, Supporting Information). In addition, we have measured the initial discharge and charge curves of the batteries in pure Ar and found that the electrolyte decomposition did not contribute to the capacity of the NPG@Pd Al–CO₂ batteries, and that the capacity of the NPG Al–CO₂ batteries might be affected by the electrolyte decomposition (see details in Figure S5, Supporting Information).

The reaction processes of rechargeable Li–CO₂ and Na–CO₂ batteries are 4Li/Na + 3 CO₂ ↔ 2Li₂/Na₂CO₃ + C[6] Thus, we speculate that the rechargeable Al–CO₂ batteries should follow the equation of 4Al + 9CO₂ ↔ 2Al₂(CO₃)₃ + 3C (see its schematic image in Figure S6, Supporting Information). To verify this mechanism, the discharge products were characterized by confocal micro-Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy and electron energy-loss spectroscopy (EELS). In the Raman spectrum of an NPG@Pd cathode taken from a discharged battery.
Figure 3. Cyclability of rechargeable Al–CO2 batteries. a) Successive discharge/charge cycles of two Al–CO2 batteries with NPG@Pd or NPG at 333 mA g\(^{-1}\), in which the test time for each discharge/charge process was 1 h (see Figure S10, Supporting Information, for the cycling result when 10 h was used). b) Detailed illustration of the 1st, 2nd, 5th, 10th, 20th, and 30th discharge/charge cycles of the Al–CO2 battery with an NPG@Pd cathode in (a). See Figure S11 in the Supporting Information for the NPG cathode and Figures S12–S14 in the Supporting Information for more details.

(Figure 2b), the peaks at 1081 and 1180 cm\(^{-1}\) can be assigned to CO\(_2^2^-\) in Al\(_2\)(CO\(_3\))\(_3\), while the other characteristic peaks at 1333 cm\(^{-1}\) (D band) and 1573 cm\(^{-1}\) (G band) are corresponding to carbon products.\([10,27–32]\) Figure 2c indicates that the C1s peak in XPS of a discharged NPG@Pd cathode can be deconvoluted into three sub-peaks. The sub-peak at 284.6 eV can be assigned to C–C from the C products, while the sub-peaks at 286.1 and 288.8 eV are associated with the C=O and O–C=O in Al\(_2\)(CO\(_3\))\(_3\).\([31,14]\) As displayed in Figure 2d, the FTIR spectrum of a discharged NPG@Pd cathode shows clearly vibration bands at around 857 and 1436 cm\(^{-1}\). These bands belong to CO\(_2^2^-\).\([6]\)

After charging, the FTIR vibration band at 857 cm\(^{-1}\) disappeared, and those at around 1436 cm\(^{-1}\) weakened obviously (Figure 2d), revealing the decomposition of most of the Al\(_2\)(CO\(_3\))\(_3\) products during charging. Figure 2b shows that the Raman signals of C and Al\(_2\)(CO\(_3\))\(_3\) were obviously higher than noise before charging and then became almost buried by noise after charging. The C 1s and the Al 2p XPS peaks of C correspond to clean. These results further verify the reversible battery reaction to be 4Al + 9CO\(_2\) ⇔ 2Al\(_2\)(CO\(_3\))\(_3\) + 3C, indicating the reversible utilization of CO\(_2\) in the rechargeable Al–CO\(_2\) batteries. It is worth noting that this reaction mechanism is very similar to that of Li–CO\(_2\) batteries with pure CO\(_2\), 4Li + 3CO\(_2\) ⇔ 2Li\(_2\)CO\(_3\) + C.\([5,31,32,36]\)

The battery cyclability was tested by performing discharge/charge cycles at a constant current density of 333 mA g\(^{-1}\) with a limited time of 1 h for each discharge/charge process (see more details in Figure S10, Supporting Information) and the results are given in Figure 3. Figure 3a shows that the charge voltages of the Al–CO\(_2\) battery with an NPG@Pd cathode were always lower than those of the latter, and the discharge/charge voltage gaps of the former were always smaller than those of the latter (see more details in Figures S11–S14, Supporting Information). These comparisons indicate the highly efficient performances of the NPG@Pd cathode. Figure 3b illustrates that both the discharge and charge curves of the NPG@Pd Al–CO\(_2\) battery have flat plateaus, indicating a stable performance. Figure 3 and Figures S12 and S14 in the Supporting Information also outline that the charge terminal voltage of the NPG@Pd battery rose slightly from the initial value of 0.74 to 0.78 V at the 30th cycle, and the discharge terminal voltage decreased from 0.72 to 0.57 V. The former increase is rather small, indicative of the performance stability, but the latter decrease is larger than the former, which might result from possible partial coverage of NPG@Pd surfaces by undecomposed discharge products (Figure 2g). In addition, when the test time for each discharge/charge was 10 h, the cyclability of the Al–CO\(_2\) batteries with NPG@Pd and NPG became worse (Figure S10, Supporting Information), suggesting that further improving the cathode catalysts or electrolytes may be required.
In summary, rechargeable Al–CO$_2$ batteries were first proposed and realized with Al foil anodes, ionic liquid electrolytes, and NPG@Pd cathodes. Their battery reaction mechanism follows $4\text{Al} + 9\text{CO}_2 \leftrightarrow 2\text{Al}_2(\text{CO}_3)_3 + 3\text{C}$ and contains the reversible utilization of CO$_2$. They exhibited high reversibility, small discharge/charge voltage gaps down to 0.091 V, and high EEs up to 87.7%.

The batteries were also realized with NPG cathodes, indicating the generalizability of the Al–CO$_2$ battery concept, although the NPG Al–CO$_2$ batteries showed worse performances than those with NPG@Pd. These results provide an incentive and promising approach for the safe and green fixation/utilization of CO$_2$ and the development of next-generation safe energy storage/release systems.

**Experimental Section**

**Materials Preparation**: NPG leaf samples were prepared by dealloying commercial 12-carat gold leaves in concentrated HNO$_3$ at 30 °C for 0.5 h. The deposition of Pd on NPG was carried out by reducing PdCl$_2$ with the hydrazine hydrate vapor at 30 °C for 0.5 h. After that, the as-prepared NPG@Pd and NPG samples were washed by deionized water for several times. Then, the NPG@Pd and NPG samples were dried at 110 °C under vacuum for 10 h.

**Materials Characterization**: SEM images were taken by FEI Verios 460L. EELS, STEM, and EDS mapping images were collected using FEI Talos F200X and FEI Titan Cubed Themis G2 300 equipped with a probe corrector. The Raman spectra were collected on a Horiba Scientific (excitation wavelength, 532 nm). The surface properties of the NPG@Pd cathodes were analyzed by means of an X-ray photoelectron spectrometer (ESCALAB 250Xi, ThermoFisher Scientific) with monochromatized Al K$_x$ X-rays as the excitation source and C 1s (284.60 eV) as the reference line. The FTIR spectra were recorded on a PerkinElmer Frontier Mid-IR FTIR infrared spectroscopy in the range of 1550–800 cm$^{-1}$. A Hiden quadrupole MS (HPR-20 QICPlus/QIC-20) with leak inlets was used for gas analysis.

**Battery Assembly**: Each battery was assembled in the form of a 2032 coin-type cell with a pure Al foil as the anode, an NPG@Pd or NPG piece as the cathode, and glass fiber (Whatman GF/A) as the separator. One side of each coin cell has seven holes as “CO$_2$-breath” channels. All cells were assembled in an Ar-filled glove box with less than 0.1 ppm of both oxygen and moisture. The used electrolyte was a freshly prepared solution of ionic liquid electrolyte, which was made by mixing aluminum chloride ([EMIm][Cl], Aldrich) with a mole ratio of 1:1.

**Electrochemical Measurements**: Each battery was put into a glass container, into which pure CO$_2$ was piped. Galvanostatic discharge/charge cycling was tested with the potential window range from 0.3 to 2.0 V on an Arbin Battery Testing System. After cycling, each battery was carefully disassembled in a glove box to retrieve its electrodes. The electrodes were subsequently rinsed in glycol dimethyl ether to remove residual electrolyte and then were dried at room temperature.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

Al–CO$_2$ batteries, cathode design, CO$_2$ fixation/utilization, nanoporous gold@Pd, rechargeable

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