

Anion-redox nanolithia cathodes for Li-ion batteries

Zhi Zhu^{1,2}, Akihiro Kushima^{1,2}, Zongyou Yin^{1,2}, Lu Qi^{3*}, Khalil Amine⁴, Jun Lu^{4*} and Ju Li^{1,2*}

The development of lithium-air batteries is plagued by a high potential gap (>1.2 V) between charge and discharge, and poor cyclability due to the drastic phase change of O₂ (gas) and O^{x-} (condensed phase) at the cathode during battery operations. Here we report a cathode consisting of nanoscale amorphous lithia (nanolithia) confined in a cobalt oxide, enabling charge/discharge between solid Li₂O/Li₂O₂/LiO₂ without any gas evolution. The cathode has a theoretical capacity of 1,341 Ah kg⁻¹, a mass density exceeding 2.2 g cm⁻³, and a practical discharge capacity of 587 Ah kg⁻¹ at 2.55 V versus Li/Li⁺. It also displays stable cycling performance (only 1.8% loss after 130 cycles in lithium-matched full-cell tests against Li₄Ti₅O₁₂ anode), as well as a round-trip overpotential of only 0.24 V. Interestingly, the cathode is automatically protected from O₂ gas release and overcharging through the shuttling of self-generated radical species soluble in the carbonate electrolyte.

In consumer electronics, electric vehicles, and grid-scale energy storage, Li-ion batteries occupy large market shares. Most of the cathodes used in lithium ion batteries are lithium transition metal oxides, but these cathodes have a gravimetric capacity limitation because redox reactions of heavy-metal cations^{1,2} (Co, Mn, Ni, Fe, and so on) are required. In recent years, Li-air batteries^{3,4} based on the light-anion redox O₂ (gas)/O^{x-} (condensed phase) have attracted much attention. However, severe challenges remain before they can be widely used. First, most Li-air batteries have a voltage gap above 1.2 V between charge and discharge, even if catalysts are used^{5,6}. Second, few electrolytes currently available are stable enough to be used with both O₂ gas and Li_xO compounds. Third, a special and expensive membrane is required to block CO₂ and H₂O from air.

Because gas evolution and phase change between O₂ (gas) and O^{x-} (condensed phase) are required at the cathode in Li-air batteries, the nucleation and growth of such phase changes with a 10⁴-fold difference in specific volume entail a huge overpotential (η , the difference between practical and theoretical potential values) with $\eta_{\text{discharging}} > 0.1$ V in O₂ (gas) \rightarrow O^{x-} (condensed phase), and $\eta_{\text{charging}} > 1.1$ V in O^{x-} (condensed phase) \rightarrow O₂ (gas)^{5,6}. The alarmingly large η_{charging} indicates severe kinetic bottlenecks in gas-evolving solid products (for example, Li₂O and Li₂O₂) being dynamically dismantled during charging⁷. The serious overpotential loss of charge and discharge (>1.2 V; refs 5,6,8) causes severe energy efficiency and thermal management problems. Repeated phase changes with large overpotential also cause chemo-mechanical damage that limits cyclability.

Here we develop an oxygen anion-redox cathode that does not release/take O₂ (gas). We show the phase changes occur between condensed-matter phases only—that is, between Li₂O (condensed), Li₂O₂ (condensed) and LiO₂ (condensed), where the average oxygen valence state \bar{Z} changes from $\bar{Z} = -2$ (the purely ionic O²⁻ in Li₂O crystal) to \bar{Z} as small as -0.5 in covalent-ionically bonded LiO₂ solid. While LiO₂ is metastable as a bulk crystal at room temperature, it appears to be stabilized by interfacial wetting⁹ with a substrate, which has been supported by transmission electron

microscopy (TEM) with a diffraction pattern matching the *ab initio* calculated crystal structure. In surface science¹⁰ and metal-organic chemistry¹¹, it is well known that the O₂ molecule can be adsorbed as peroxide O₂²⁻ ($Z = -1$), as superoxide O₂⁻ ($Z = -0.5$), or as a mixture thereof that covers the surface. We hypothesize that a sub-10-nm porous substrate could stabilize a significant amount of LiO₂ (condensed) as an interfacial wetting layer (Fig. 1a). Since no oxygen gas evolves, we are able to fabricate an all-condensed-matter cathode for a fully sealed battery.

Nanolithia anion-redox cathode without O₂ evolution

We prepared 33 wt% Co₃O₄ as a nanoporous substrate and filled it with 67 wt% Li₂O (designated as sample NC-67, where NC stands for the nanolithia composite). The solid nanoporous skeleton is stable as the cathode cycles between Li₂O(condensed) \leftrightarrow Li₂O₂(condensed) \leftrightarrow LiO₂(condensed), providing structural integrity while the increased transport pathways and catalytic activity¹² reduce the overpotential significantly (by a factor of five, from $\eta > 1.2$ V to $\eta \approx 0.24$ V). In principle, other nanoporous skeletons may also be used for the NC. At the relatively narrow voltage range of testing (2.0–3.0 V versus Li/Li⁺), the Co ions in Co₃O₄ remains in the +2 and +3 oxidation states¹³, although there could be changes in the bonding pattern at the nanolithia/Co₃O₄ interface. The detailed configurations of the oxygen $\bar{Z} = -0.5 \leftrightarrow -2$ state in the active wetting layer need to be studied atomistically¹⁴, but this becomes practically useful only if the cathode can be cycled reversibly. By keeping oxygen above the lowest ionicity of $\bar{Z} = -0.5$, we hope to maintain it as condensed matter rather than as a gas ($Z = 0$).

The following reactions apply to the NC cathode:



The above thermodynamic voltages U_1^0 and U_2^0 are calculated from the bulk crystal formation energies^{15–17}, although nanoscale

¹Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA. ²Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA. ³College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China. ⁴Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, USA. *e-mail: qilu@pku.edu.cn; junlu@anl.gov; liju@mit.edu

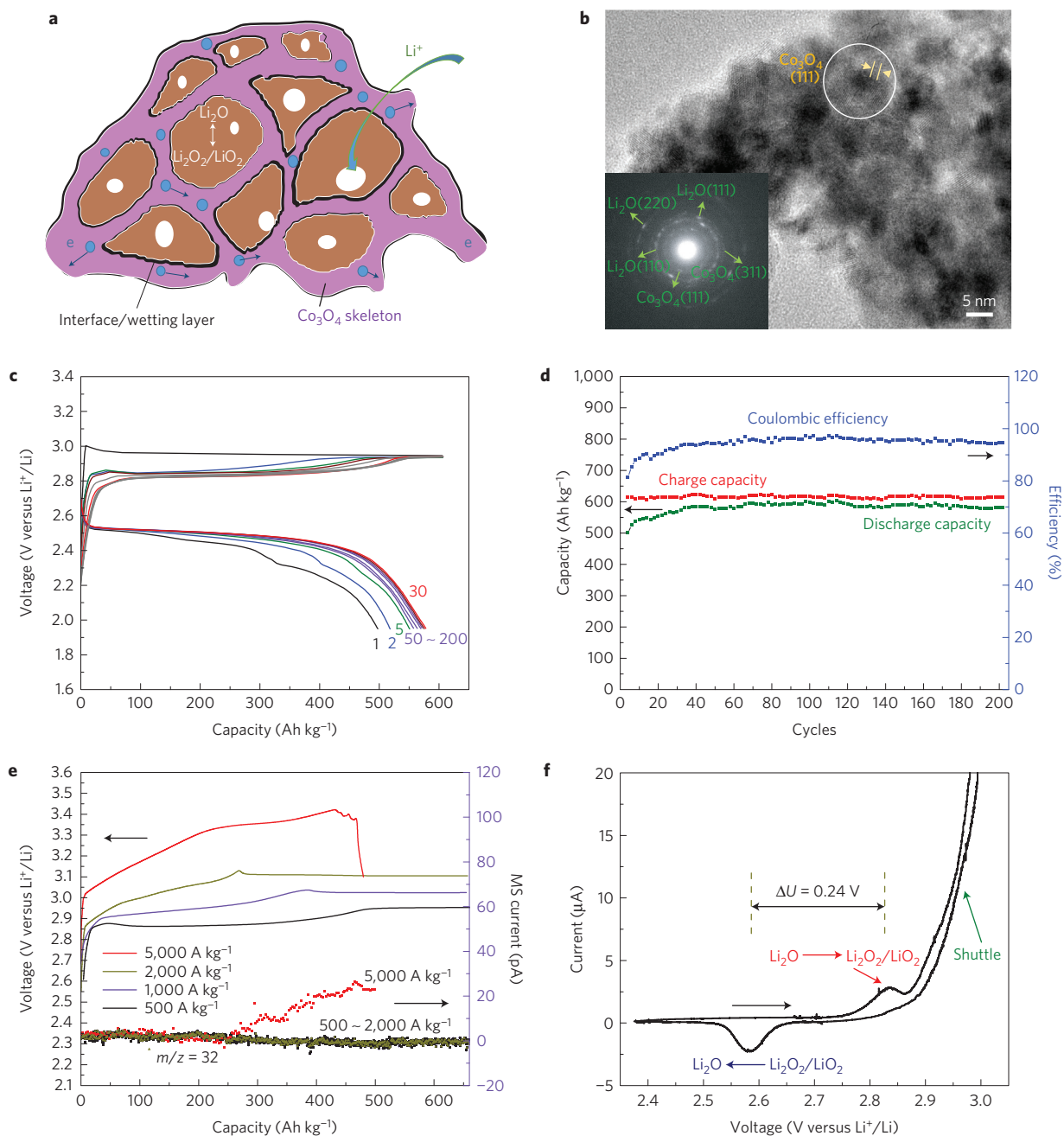


Figure 1 | The structure and electrochemical performance of nanolithia cathode. **a**, Schematic of Co_3O_4 skeleton wetted by amorphous $\text{Li}_2\text{O}/\text{Li}_2\text{O}_2/\text{LiO}_2$, the arrows indicate the diffusion paths of electrons and Li ions. **b**, Transmission electron microscopy (TEM) of the nanocomposite Li_2O and Co_3O_4 powder, the circled area is a representative structure of amorphous Li_2O confined within the Co_3O_4 skeleton. The inset is the selected-area electron diffraction pattern (SAED). **c**, Charge/discharge curves of NC-67 cathode in a coin-cell battery with Li metal anode. It was charged to 615 Ah kg^{-1} (based on Li_2O weight), then discharged to 2.0 V with constant current of 120 A kg^{-1} (based on Li_2O weight). Different cycles (1st–200th) are indicated with coloured lines. **d**, Cycling performance of charge/discharge capacity and Coulombic efficiency against Li metal anode under 120 A kg^{-1} . **e**, The charging curves (solid curves) and *in situ* differential electrochemical mass spectrometry (DEMS; dotted curves, for gas detection) at different current densities. **f**, Cyclic voltammogram of NC-67 between 2.35 and 3.0 V with a scan rate of 0.05 mV s^{-1} . The horizontal arrow indicates the scanning direction. The oxidation peak is related to the charge process from Li_2O to $\text{Li}_2\text{O}_2/\text{LiO}_2$, whereas the reduction peak is related to discharge from $\text{Li}_2\text{O}_2/\text{LiO}_2$ to Li_2O . The value of ΔU between the oxidation and reduction peaks is only 0.24 V. The high current above 2.9 V is attributed to shuttling species in electrolyte.

interfacial energy effects could shift and smear these voltages by tens of milli-electron volts. The theoretical capacity of $\text{Li}_2\text{O}/\text{LiO}_2$ is $1,341 \text{ Ah kg}^{-1}$, based on the weight of Li_2O . Although it is well known that bulk LiO_2 crystal is fairly unstable at room temperature, the LiO_2 (condensed) did form in our experiments due to the excellent catalysis and energetic stabilization by the nanoporous Co_3O_4 interfaces⁹, akin to the superoxide O_2^- ($Z = -0.5$) adsorbate

layer in surface science¹⁰ and oxygen in haemoglobin proteins¹¹. The NC cathode involves much higher capacity than the present cation-redox-based systems, even when the dead weight of Co_3O_4 is taken into account. As we will demonstrate below, lithium-matched full-cell batteries with low-cost ethylene carbonate/diethyl carbonate (EC/DEC) electrolyte can achieve gravimetric energy densities comparable to those of state-of-the-art Li–sulfur batteries¹⁸, along

with higher voltage and very stable cycling, as well as with a $5\times$ lower energy loss than the Li–air battery⁷. Okuoka *et al.*¹⁹ proposed a similar redox reaction between Li_2O and Li_2O_2 , and tested nanocomposite Li_2O with ball-milled Co_3O_4 as the cathode. Their preliminary results indicated the feasibility of using $\text{Li}_2\text{O}/\text{Li}_2\text{O}_2$ as the cathode. However, O_2 gas was inevitably generated when charging to above 190 Ah kg^{-1} around 3.2 V versus Li/Li^+ in that work. As it turns out in our work, a shuttling (some specific species dissolved in the electrolyte can carry electrons between cathode and anode through the electrolyte) mechanism²⁰ in the EC/DEC electrolyte can shunt the voltage automatically and indefinitely avoid the O_2 gas generation.

In contrast to the mechanical ball-milling approach of Okuoka *et al.*¹⁹, we achieved much more intimate contact of Li_2O with sub-10 nm Co_3O_4 by using a highly scalable chemical synthesis method followed by calcination at 300°C . Selected-area electron diffraction (SAED) in Fig. 1b and energy dispersive spectroscopy (EDS) in Supplementary Fig. 1 clearly indicate a mixture of Co_3O_4 and Li_2O , and most of the Li_2O nanoparticles are sphere-like ($\sim 5\text{ nm}$), and surrounded by a nanocrystalline Co_3O_4 skeleton. In this form, ‘solid oxygen’ in the condensed form (nanolithia) is no more than $\sim 3\text{ nm}$ away from a free surface or Co_3O_4 skeleton, and interfacial wetting effects are expected to significantly affect its electrochemical stability⁹ and kinetics^{21–23}.

The charge/discharge and cycling performance of an NC-67 cathode (mass loading $\sim 2.0\text{ mg cm}^{-2}$) opposite to a Li metal anode are shown in Fig. 1c,d and Supplementary Fig. 2. The NC-67 cathode has a discharge plateau of $\sim 2.55\text{ V}$ at a rate of 120 A kg^{-1} (based on Li_2O weight). The initial discharge capacity was 502 Ah kg^{-1} (based on Li_2O weight), then increased to 587 Ah kg^{-1} in a few cycles when charged to 615 Ah kg^{-1} . The discharge capacity loss was only 4.9% after 200 cycles. The charge plateau consists of two parts (Supplementary Fig. 2): part I, beginning at 2.80 V and gradually increasing to 2.91 V , can be due to $\text{Li}_2\text{O} \rightarrow \text{Li}_2\text{O}_2/\text{LiO}_2$, while part II, keeping nearly constant at $\sim 2.94\text{ V}$, is due to a shuttling process in the electrolyte. *In situ* differential electrochemical mass spectrometry (DEMS, Supplementary Fig. 3a) showed no O_2 or CO_2 gas generation and the voltage never exceeded 2.95 V when charged at a constant current of 120 A kg^{-1} .

DEMS was also performed under different charging currents. As shown in Fig. 1e, the voltages of both the redox and shuttle plateaus increase with higher current. When charged at 500 A kg^{-1} , $1,000\text{ A kg}^{-1}$ and $2,000\text{ A kg}^{-1}$, the shuttling produced the final shunting voltages of 2.96 V , 3.04 V and 3.14 V , respectively. The DEMS spectra indicates no O_2 generation, no matter how long the overcharging is. However, when charged at $5,000\text{ A kg}^{-1}$ ($>10\text{ C}$), the voltage continuously increases and O_2 gas evolves after the capacity reaches 250 Ah kg^{-1} , when the voltage is $\sim 3.4\text{ V}$. The shuttling thus fails to suppress the voltage increase only when the shuttling species in the liquid electrolyte cannot support an extremely high current inside the cell (for example, $5,000\text{ A kg}^{-1}$).

Transformation of the nanolithia composite cathode

X-ray photoelectron spectroscopy (XPS) plots in Supplementary Fig. 4 show that the Co ions in Co_3O_4 are electrochemically inactive in the charging process. To characterize the cathode transformation during cycling, *in situ* Raman spectroscopy was performed (Fig. 2a). On the Raman curve, a new peak at $780\sim 800\text{ cm}^{-1}$ appears when the cathode is charged to 200 Ah kg^{-1} . The peak is fairly broad, but centred at $\sim 790\text{ cm}^{-1}$, which is consistent with Li_2O_2 (ref. 24). When further charged to 400 Ah kg^{-1} , this $780\sim 800\text{ cm}^{-1}$ peak becomes higher, but remains almost unchanged when charged to $>500\text{ Ah kg}^{-1}$. A new Raman peak around $1,110\sim 1,140\text{ cm}^{-1}$ emerges at above 500 Ah kg^{-1} , becoming gradually stronger when further charged to 700 Ah kg^{-1} , and keeping stable thereafter. This peak is similar to the $1,123\text{ cm}^{-1}$ peak reported for the

O_2^- anion^{24,25} ($\bar{Z} = -0.5$). Since it is not very sharp, it is likely that some form of amorphous LiO_2 (condensed) is generated. During charge/discharge, the Raman peaks increase in height, but do not change much in position or width. When the cathode is finally discharged to 2.0 V , the intensity is very weak at $780\sim 800\text{ cm}^{-1}$ (Li_2O_2 (condensed)) and totally disappears at $1,110\sim 1,140\text{ cm}^{-1}$ (LiO_2 (condensed)). The Raman spectra of the thoroughly washed cathode at different states of charge (SOCs) still show similar peaks at $\sim 790\text{ cm}^{-1}$ and $\sim 1,130\text{ cm}^{-1}$ (Supplementary Fig. 5). This result further confirms that the peroxide and superoxide species exist in the confined amorphous solid^{21–23}, instead of only solvated in the liquid electrolyte.

As shown in Fig. 1f, there is only one pair of broad redox peaks in the cyclic voltammogram (CV) for NC-67, suggesting a nanoscale mixture of $\text{Li}_2\text{O}/\text{Li}_2\text{O}_2/\text{LiO}_2$ (condensed) with smeared transition potentials. It is known that nanoparticles, especially with sub-10-nm diameter, have a shifted thermodynamic transition (such as shifted melting point) as well as a smeared order-parameter change²⁶ that is no longer infinitely sharp, as in the first-order phase transition of an infinite crystal. The most intriguing result is that the potential gap ($\Delta U = \eta_{\text{charging}} + \eta_{\text{discharging}}$) between the oxidation (2.82 V) and reduction (2.58 V) peaks (charge/discharge) is only 0.24 V . This gap is only one-fifth of that for the Li–air battery, indicating facile redox kinetics of the nanolithia. Specifically, the oxidation peak related to the charge plateau is 2.82 V , significantly lower than that reported for the Li– O_2 battery (usually $>4.0\text{ V}$). Such a small overpotential would vastly improve the usable energy efficiency in the battery and the severe heating issue.

ΔU in cycling is mainly caused by the energy barriers involved in electron and ion transfers and phase transformations. There is a huge structural difference between gas and condensed phases; thus, any transformation of oxygen involving gas \leftrightarrow solid would entail larger ΔU ⁷ and slower kinetics, which is the case for the Li–air battery. From the present work, we conclude that condensed \leftrightarrow condensed transformations, without gas phase participation, can have lower ΔU because the atomistic environment (at least in terms of density) of oxygen does not change drastically. This is especially so with the facile kinetics at the interface with Co_3O_4 and near-surface wetting layers in this work^{21–23}.

The SAED curve in Fig. 2b after charge shows that some low-index planes of the crystalline motif (such as (002), (101), (103) and (110) of crystalline Li_2O_2 , and (110), (020), (011), (120) and (111) of crystalline LiO_2 ; ref. 27) roughly match in the charged product, even though many high-index planes do not match. The SAED result indicates that NC-67 changes to an amorphous $\text{Li}_2\text{O}/\text{Li}_2\text{O}_2/\text{LiO}_2$ mixture after charge, and this amorphization of cathode nanoparticles such as LiFePO_4 is well known²⁸. The *in situ* X-ray diffraction (XRD) result (Supplementary Fig. 6) also suggests that most of the nanolithia turn amorphous in ten cycles, similar to that of the lithium–sulfur cathode¹⁸ and lithium–aluminium anode²⁹. The amorphous \leftrightarrow amorphous transformation during cycling would also have more facile kinetics compared to crystal \leftrightarrow crystal transformations, resulting in a much lower ΔU in Fig. 1f.

We also performed ^6Li NMR on the post-dimethoxyethane (DME)-washed cathode at different SOCs (all referenced to 1 M LiCl solution). As shown in Fig. 2c, the reference Li_2O and Li_2O_2 crystals have a sharp peak at 2.90 ppm and 0.21 ppm , respectively. The discharged NC-67 cathode has a strong peak at 2.90 ppm and a tiny peak at $\sim 0.21\text{ ppm}$, indicating that the major component at this state is Li_2O , with a small amount of Li_2O_2 because of incomplete lithiation in the previous cycles. When charged to 400 Ah kg^{-1} , an obvious 0.21 ppm peak emerged, indicating that a significant amount of Li_2O_2 formed. When further charged to $>600\text{ Ah kg}^{-1}$, the peak at 0.21 ppm became higher than that at 2.90 ppm , but interestingly, another peak at -2.74 ppm appeared, regarding which we can find no report in the literature. To clarify

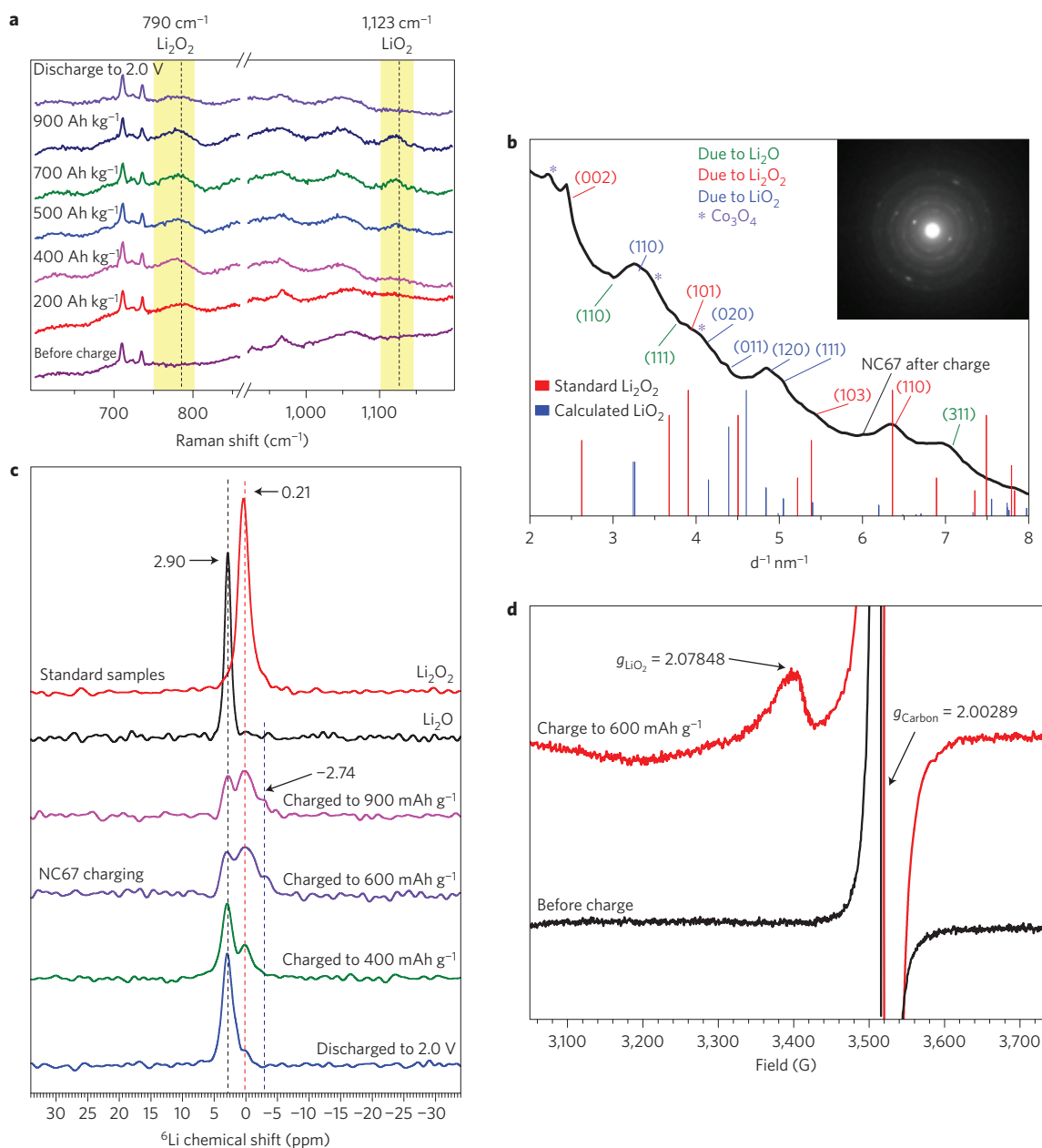


Figure 2 | The transformation of nanolithia during electrochemical cycling. **a**, *In situ* Raman at different charge/discharge states (the peaks in the yellow highlighted areas are due to Li_2O_2 and LiO_2 , respectively). **b**, *In situ* SAED pattern of the charge product at 2.95 V. The curve was obtained by digital micrograph (Gatan) from the SAED pattern in the inset. **c**, ^6Li NMR of NC-67 at different charge/discharge states after DME washing, versus standard Li_2O and Li_2O_2 crystals, all referenced to 1 M LiCl solution in room temperature. **d**, Electron spin resonance (ESR) of the NC-67 cathode before and after charge at 70 K.

what this -2.74 ppm peak signifies, we calculated the chemical shift for different Li_xO crystals using density functional theory (DFT) (Supplementary Fig. 7). The calculated chemical shift for LiO_2 is -3.1 ppm versus Li_2O_2 , or ~ -2.9 ppm versus the 1 M LiCl solution used in the experiment, matching very well with our experimental value of -2.74 ppm. Thus, our NMR measurement together with the DFT calculation firmly support the presence of LiO_2 in our deeply charged NC-67 electrode, proving the existence of an amorphous $\text{Li}_2\text{O}/\text{Li}_2\text{O}_2/\text{LiO}_2$ mixture stabilized by interfacial wetting.

Figure 2d shows the electron spin resonance (ESR) spectra for the NC-67 cathode at 70 K, before and after charge. It shows only an electron spin signal ($g = 2.00289$) from carbon before charge, indicating no other elements containing a single electron.

However, another peak with $g = 2.07848$ appears after charging. This peak is due to the single-electron spin of the superoxide (O_2^-)³. The measured g -factor is between the *ab initio* calculated values for orthorhombic bulk LiO_2 ($g = 2.085$) and molecular LiO_2 ($g = 2.045$) (ref. 3), and is closer to the former, which is consistent with the structural motif of the nanoscale amorphous LiO_2 component.

Shuttling inside electrolyte

As stated previously, an automatic shuttling mechanism protects our cathode from overcharging and oxygen gas evolution only if the charge current $\leq 2,000 \text{ A kg}^{-1}$. To test its endurance, we performed galvanostatic charging at 120 A kg^{-1} for 72 h, and the voltage never exceeded 2.95 V (Fig. 3a). Upon the first discharge, the discharge

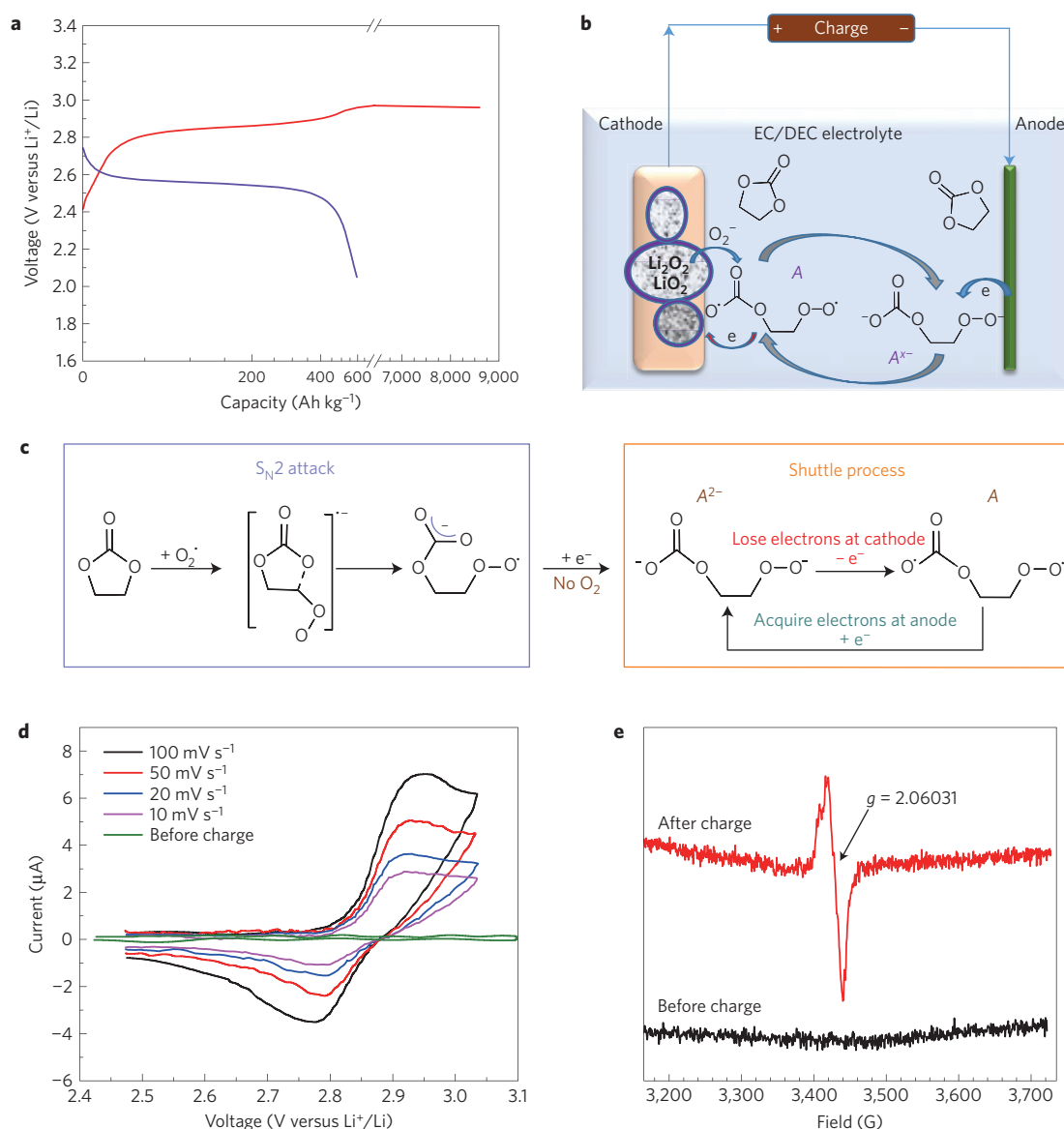


Figure 3 | Battery overcharge protection by electrolyte shuttling. **a**, Voltage profile of NC-67 cathode in three-day continuous charging to about 9,000 Ah kg⁻¹. **b, c**, Proposed reactions for the shuttling process at the end of charge. For EC in the electrolyte, the solvated O₂⁻ reacts with it, forming an intermediate radical A, the radical then diffuses to the anode and acquires electrons to become A²⁻, which diffuses back and imparts the electron; the A/A²⁻ redox cycle thus provides the shunting current through the liquid electrolyte. **d**, Cyclic voltammogram of the liquid electrolyte extracted from a battery cell before/after charging, at scanning rates from 10 to 100 mV s⁻¹ between 2.4 V and ~3.1 V in a Pt/Li/Li three-electrode system. **e**, *In situ* ESR of the isolated electrolyte extracted before/after charge, at room temperature.

capacity did not change, indicating no damage to the battery. If there had been an irreversible side reaction or oxygen release, such normal functioning after three-day overcharging would be impossible.

This shunting of potential has never been observed in the Li-air battery, and can be understood as shuttling²⁰ of soluble A/A^{x-} species, as shown in Fig. 3b,c. Because the Co₃O₄ encapsulation was not complete, some Li₂O/Li₂O₂/LiO₂ (condensed) was exposed to the liquid electrolyte, and O₂⁻ could be solvated. It is known that O₂⁻ (solvated) can attack the methylene group of carbonate solvent via the so-called S_N2 mechanism³⁰ shown in Fig. 3c. With EC as the electrolyte solvent, O₂⁻ (solvated) can be added to the methylene group, resulting in the ring opening and forming an intermediate peroxide radical A in the electrolyte³¹. A may be further oxidatively decomposed to CO₂, H₂O and Li₂CO₃ in a high O₂ (gas) partial pressure condition. However, here, because there is no O₂ gas evolution, the superoxoradicals do not decompose (Supplementary

Fig. 3b) and can diffuse to the anode and acquire electrons to become A^{x-}, which, in turn, can diffuse back to the cathode, providing the shunting current through the liquid electrolyte.

To investigate the shuttling species in isolation, we disassembled a fully charged cell and carefully collected the electrolyte by thoroughly washing the cathode foil, membrane, anode and internal cavity of the cell with EC/DEC (1:1 by volume). Then, we investigated the diluted and isolated electrolyte by CV at different scanning rates in a Pt/Li/Li three-electrode system. The CVs of both the original and the collected diluted electrolyte after charging are shown in Fig. 3d. The CV curves indicate that the fresh electrolyte has no redox peaks, consistent with the expectation that EC/DEC is electrochemically stable between 2.4 V and ~3.1 V. However, the CV of the charged electrolyte shows classical redox behaviour, with an oxidation peak of 2.91 ~ 2.95 V and a reduction peak of 2.76 ~ 2.79 V. In addition, the oxidation

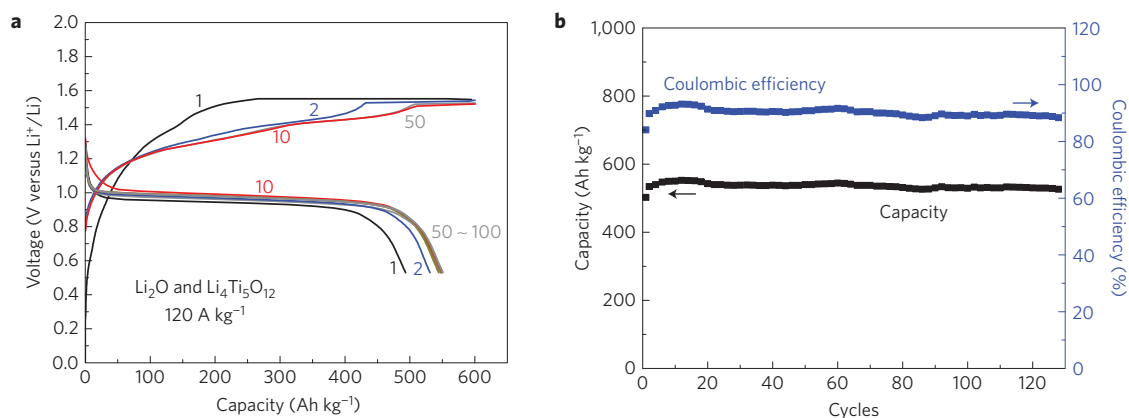


Figure 4 | Electrochemical performance of lithium-matched full-cell battery. **a,b**, Charge/discharge curves (**a**) and cycling performance (**b**) of NC-67 cathode versus $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode, whose Li capacity is only 110% that of the NC-67 cathode capacity. The coin cell was charged to 600 Ah kg^{-1} with a current of 120 A kg^{-1} based on Li_2O weight, then discharged to 0.5 V. This cell was fabricated with a Li-capacity ratio of 600:660 for NC-67 versus $\text{Li}_4\text{Ti}_5\text{O}_{12} \leftrightarrow \text{Li}_7\text{Ti}_5\text{O}_{12}$.

peak current (i_p) and the square root of the scanning rate ($v^{1/2}$) show a linear relationship ($R^2 = 0.9943$), indicating diffusion control, and further corroborating the existence of soluble redox couples in the electrolyte (Supplementary Fig. 8) that physically sustains the shuttling process.

In situ ESR was also performed to detect the shuttling species in the electrolyte at the end of charge, and the result is shown in Fig. 3e. The ESR result indicated no spin signal in the original, but an obvious radical signal at $g = 2.06031$ after charge. This g -factor is between the *ab initio* calculated values for orthorhombic bulk LiO_2 ($g = 2.085$) and molecular LiO_2 ($g = 2.045$) (ref. 3), but is closer to the latter. We thus infer that the organic superoxide radical coordinated with the solvent molecules acted as the shuttling species in the electrolyte at the end of charge, as illustrated in Fig. 3c.

Full-cell battery performance

To prove that our novel redox chemistry can drive a practical battery, we have assembled and tested a lithium-matched full cell using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as the anode, with the Li capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12} \leftrightarrow \text{Li}_7\text{Ti}_5\text{O}_{12}$ being only 110% that of the NC-67 cathode capacity (measured previously with a half-cell employing a superabundant amount of lithium metal). As shown Fig. 4a,b, although the NC-67/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ full cell had a slightly lower capacity of 549 Ah kg^{-1} at a loading of 2 mg cm^{-2} , the full-cell capacity loss was only 1.8% after 130 cycles, so the cycling performance was even more stable than that versus the Li metal anode. This lithium-matched full-cell test indicates that even if a solid-electrolyte interphase (SEI) layer formed on the cathode surface, the SEI must be very stable during cycling²⁹, despite the necessarily large volume change of nanolithia $\text{Li}_2\text{O}/\text{Li}_2\text{O}_2/\text{LiO}_2$ (all condensed).

Conclusions

We have exploited light-anion redox in a nanocomposite cathode with a sub-10-nm catalytic skeleton and amorphous nanolithia core. The gravimetric energy density is $\sim 1,500 \text{ Wh kg}^{-1}$ based on Li_2O weight, and $1,000 \text{ Wh kg}^{-1}$ based on the weight of NC-67 composite ($\text{Co}_3\text{O}_4 + \text{Li}_2\text{O}$). The mass density of our cathode paste (including binder and carbon black) exceeds 2.2 g cm^{-3} , making it also highly competitive in volumetric energy density against cathodes on the market. The NC cathode has a much reduced overpotential loss of only 0.24 V, as well as improved system-level weight and safety compared to Li-air batteries. Through the solvation and shuttling of A/A^{x-} in the electrolyte, O_2 gas generation is forestalled even if the battery is overcharged indefinitely, so this battery can work well in a completely sealed condition. Because Li_2O is in a lithiated state,

the matching anode can be air-stable C, Al (ref. 29), Si (ref. 32), and so on. Additionally, the low-cost EC/DEC-based electrolyte solvent with LiPF_6 salt works very well.

Our nanocomposite still has much room for improvement, since complete encapsulation²⁹ (instead of partial encapsulation) may lead to an even larger Co_3O_4 -lithia contact area, more efficient lithia utilization, and less O_2^- loss to the electrolyte (however, in such a scenario of complete encapsulation²⁹, to provide the shuttling, a new shuttling additive may need to be designed²⁰, at say 3.0 V versus Li/Li^+). In principle, sub-10-nm porous skeletons other than Co_3O_4 may also be adopted, such as nickel and manganese oxides. Besides a Li_2O core, one could also develop other light (and low-cost) anion-redox chemistries, for instance, redox couples involving ionic-covalent ClO_3^- , ClO^- , and so on in confined condensed-matter form without the generation of any gases (for example, Cl_2 , O_2).

Methods

Preparation of nanocomposite Li_2O and Co_3O_4 . We developed a one-pot chemical method to prepare nano-composite Li_2O and Co_3O_4 material. First, a mixture of Li_2O_2 (Sigma, 90%) and Li_2O (Aldrich, 99.5%) was added to CoCl_2 (Sigma, 99.5%) ethanol solution after ultrasonic treatment. The molar ratio of $\text{Li}_2\text{O}_2:\text{Li}_2\text{O}:\text{CoCl}_2$ is $1:n:1$, where n dictates the $\text{Li}_2\text{O}:\text{Co}_3\text{O}_4$ weight percentage in the final fully oxidized product. After stirring for 2 h at room temperature, the obtained mixture was filtered and dried at 120°C in vacuum. Then, the powder was sintered for 3 h at 300°C in O_2 to derive the final product.

Material measurements. XRD measurements were carried out by means of a Bruker D8-Advance diffractometer using $\text{Cu K}\alpha$ radiation, at 100 mA and 40 kV. The sample was scanned from 10° to 90° at a speed of 4° min^{-1} . The TEM images were taken on a JEOL JEM-2010 transmission electron microscope operating at 200 kV. The electronic valence structure of the samples was investigated through XPS. The prepared nano-composite cobalt oxide and lithia powder after the first charge and discharge were used for XPS characterization. The Raman spectra were measured using a Horiba Jobin-Yvon HR800 Raman spectrometer with a 633 nm laser. A 600 MHz Bruker NMR solid spectrometer was used to obtain ^6Li NMR with a main magnetic field of 14.1 T and a ^6Li Larmor frequency of 88.34 MHz. The rotors containing the samples were spun at a rate of $\sim 10 \text{ kHz}$ at room temperature to acquire the NMR spectra. All the chemical shifts obtained in the experiment were referenced to 1 M LiCl solution. A Bruker EMX ESR spectrometer with an ER 4199HS cavity and a Gunn diode microwave source producing X-band (9.859 GHz, $\approx 0.2 \text{ mW}$) radiation was used to detect the charged material and electrolyte. The magnetic field modulation was 100 kHz and the modulation amplitude was 1 G. The scan rates were 0.5 G s^{-1} with a time constant of 0.2 s.

***In situ* transmission electron microscopy (TEM).** A Nanofactory scanning tunnelling microscopy (STM)-TEM holder was used in the experiment. The holder is equipped with three-dimensional piezo-manipulator and biasing capability. The NC-67 cathodes were attached on a tungsten probe using conducting epoxy (Chemtronics CW2400) and mounted on one side of the holder. On the other side, we mounted another tungsten rod after scratching Li

metal to transfer a small piece of Li on the tip. The NC-67 and a piece of Li metal were brought into contact inside the TEM. By applying voltage on the working electrode versus the counter electrode (Li), Li⁺ ions diffuse through the oxide layer. To drive the Li⁺ out from NC-67, 2.95 V was applied to the working electrode with respect to the Li metal. The experiment was performed using a JEOL 2010F TEM operating at 200 kV. The SAED pattern was obtained after 30 min under 2.95 V.

Electrochemical tests. R2032 coin cells were used for the electrochemical tests in this work. Half-cells were fabricated from a cathode of 80 wt% NC-67 powder (that is, 67 wt% Li₂O, 33 wt% Co₃O₄), 15 wt% carbon black for electron conduction, and 5 wt% polyvinylidene fluoride (PVDF) binder, which was pasted on an Al current collector, at a loading of 2 mg cm⁻²; an anode of Li metal sheets; a separator of Celgard 2400 polymer; and a commercial electrolyte. For the full cell, Li₄Ti₅O₁₂ was used as the anode, with 15 wt% C65 conductor and 5 wt% PVDF. The electrolyte solution was 1 M LiPF₆ dissolved in a mixture of EC and DEC with a volume ratio of 1:1, and 2 wt% vinylene carbonate additive. A LAND CT2001A 8-channel automatic battery test system (Wuhan Lanhe Electronics) was used for charging/discharging of the cells. An electrochemical workstation (Gamry Instr, Reference 3000) was used for the CV scanning.

A self-made quantitative DEMS was used to detect and analyse the gas during the cell testing. Two glued polyether ether ketone (PEEK) capillary tubes were used to inlet and outlet gas. The cell was fabricated in a glove box where O₂ < 0.1 ppm. Then, the output tube was connected to a commercial Thermo mass spectrometer (MS). A high-purity Ar gas was used as the carrier gas with a flow rate of 3 ml min⁻¹ during the cycling process. In the constant current charge/discharge process, charge/discharge currents were 100 mA g⁻¹, and MS spectra were collected every 1 min. In the cyclic voltammetry process, the scan rate was 0.05 mV s⁻¹, and MS spectra were collected every 20 s.

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Author contributions

J.Li and Z.Z. conceived the original idea of this paper. Z.Z. performed the material synthesis and measurements, and then improved the experiments after discussions with J.Li and J.Lu. Z.Y. assisted with the Raman and XPS experiments; A.K. performed the TEM experiments and NMR calculation. Z.Z. and J.Li drafted the paper, and all authors revised it. L.Q. and K.A. provided many suggestions and guidance.

Additional information

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Competing interests

The authors declare no competing financial interests.