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Short Communication

A high-energy-density and long-cycling-lifespan Mars battery

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In 2004, Mars Science Laboratory (MSL) of National Aeronautics and Space Administration (NASA) landed two rovers, Courage and Opportunity, to unveil the mysteries of Mars. In 2021, China became the second country to successfully land Zhurong rover on the surface of Mars by Tianwen 1 probe, achieving the goal of 90 Martian days. ExoMars-2022 was planned by the European Space Agency and the Russian Federal Space Agency. Mars exploration has become a battleground for economic and technological competition among major powers. The rover is an important piece of technical equipment for near-Mars exploration, of which the energy supply system guarantees multimode fine exploration [1,2]. Currently, driving Mars rovers and other exploration equipment on Mars mainly rely on two types of electric power: One is portable Li-ion batteries (LIBs), and another is large-scale solar panels and nuclear batteries [3]. The necessary rechargeable LIBs have been applied in almost all Mars rovers and even the first Mars helicopters, which are used in combination with nuclear batteries (e.g., Perseverance and Curiosity) or solar panels (e.g., Zhurong). However, due to a very limited energy density of ~350 Wh kg^{-1}, LIBs reduce the fault tolerance of aerospace missions and increase mission launch cost [4]. Therefore, a higher-energy-density and longer-stable-cycling battery system is called to enhance payload and science capabilities in space missions.

Li-CO_2 batteries are a next-generation energy storage system capable of an ultrahigh theoretical specific energy of up to 1876 Wh kg^{-1}, widely considered to apply to Mars exploration [5]. However, the performance and reaction mechanism of pure CO_2 in Li-gas batteries cannot fundamentally substitute for the Mars atmosphere. The Mars atmosphere includes not only carbon dioxide (CO_2, 95.32%) but also other trace gases, such as nitrogen (N_2, 2.7%), argon (Ar, 1.6%), oxygen (O_2, 0.13%), carbon monoxide (CO, 0.08%), and possibly water (H_2O) [6]. Trace amounts of active O_2 and CO from inexhaustible atmosphere source have been identified to alter the reaction mechanisms. NASA reported that they recently were focused about the effect of multi-component gases on the performance of Li-CO_2 batteries. Zhang's group [7] used the rotating ring-disk electrode (RRDE) and ^{13}C nuclear magnetic resonance (NMR) spectra technique to reveal the positive activation effect of O_2 for CO_2 reduction reaction (CO_2RR). Our group [8] recently found that a small amount of O_2 (1%) can promote the operating voltage of Li-CO_2 batteries by ~60%. Li's group [9] demonstrated that the CO in CO_2 can reduce the product crystallinity and the charging potential. Therefore, the actual operation of the Li-Mars gas battery is very complicated, and the investigation of transforming Li-CO_2 to a Li-Mars gas battery is necessary, similar to the transformation of Li-O_2 to Li-air battery.

Mars is a day and night planet with a diurnal temperature span of around 60 °C, and night temperature can be below subzero. To avoid cryogenic freezing of LIBs, the mature temperature control technologies, such as phase change materials and heaters, have been deployed on Mars rovers [10,11]. In addition, Mars rover can be put into a hibernation protocol that does not work to avoid periods of extreme temperature. The diurnal temperature fluctuations of 60 °C remain unresolved and severely impact Mars battery performance. To be more specific, a low operating temperature usually causes poor reaction interfaces and slow reaction kinetics, ultimately leading to a low capacity and cycling life. Therefore, it is important to investigate the wide-temperature electrochemical performances of Li-Mars gas batteries in the Mars energy system for practical applications.

In this short communication, a proof-of-concept of Mars battery is provided and its potential in the Mars environment for exploration is assessed. As a special energy storage system, the Mars battery is driven by a realistic Mars atmosphere, exhibiting a high energy density of 373.9 Wh kg^{-1} and a long cycle life of over 1350 h even at a low temperature of 0 °C. The wide-temperature electrochemical performance including voltage gap of 1.6 V, rate of 0.4 A g^{-1}, and power capability of 3.9 W m^{-2} is investigated during the diurnal temperature span. Moreover, the application poten-

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tial of low-temperature Mars batteries was demonstrated in electronic devices, and a pouch battery with a size of 2 cm × 2 cm was developed with a cell-level energy density of up to 765 Wh kg^{-1} and 630 Wh L^{-1}. This work is dedicated to proposing a Li-Mars gas battery to work in the natural environment of Mars and advancing a versatile multi-energy complementary energy supply system for Mars exploration.

First-class Mars batteries adopting native atmosphere source for Mars exploration. The positioning and working principle of Mars batteries in a multi-energy supply system for Mars exploration are illustrated in Fig. 1a, which as a portable rechargeable battery enriches the energy storage system and even is capable of updating LIBs to drive multiple terminals (e.g., rovers, helicopters, and even human landing on Mars). The current application of portable rechargeable LIBs on Mars rovers is summarized (Table S1 online). The development of Mars batteries aims to benchmark the monopolization of secondary LIBs carried in exploration devices from the 1997 American Sojourner rover to the 2021 Chinese Zhurong rover. In contrast, the unique feature of Mars batteries is the direct inhalation of Mars atmosphere as fuel (active components: 95.32% CO_2, 0.13% O_2, and 0.08% CO) during discharge, thus showing the advantage of extremely light battery weight to carry into space. After the electricity depletion, they achieve secondary charging by the external solar and nuclear energy sources, preparing for the next discharge. To access the potential of the proposed Mars battery, the electrochemical performance, the atmosphere utilization, and the temperature suitability are evaluated in detail below.

The first-class performance of Mars battery is markedly unveiled due to the inexhaustible native fuel of Mars atmosphere in Fig. 1b–d. Compared with the Li-CO_2 battery with a voltage of 1.1 V and a capacity of 1519 mAh g^{-1}, the Mars battery is boosted by ~40% to 1.5 V and 2107 mAh g^{-1} in the positive presence of trace O_2 and CO in atmospheric compositions (Fig. 1b). The cyclic

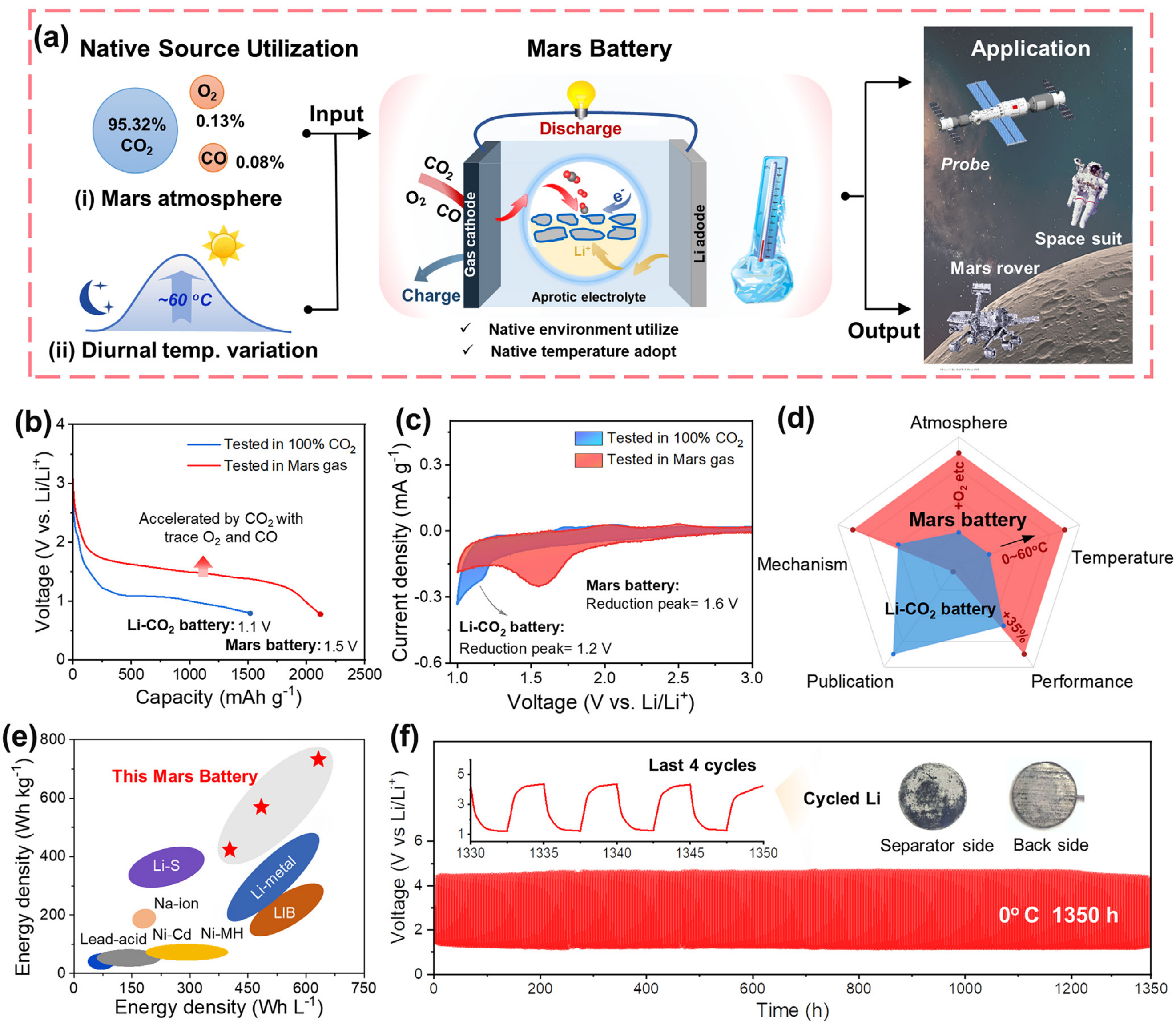

Fig. 1. (Color online) First-Class Mars batteries updated energy supply system for Mars exploration. (a) Schematic illustration of the positioning and working principle in the energy supply system for Mars exploration. Performance comparison between Mars batteries and Li-CO_2 batteries. (b) Capacity-voltage curves at 100 mA g^{-1}. (c) CV curves at a scan rate of 0.1 mV s^{-1}. (d) Multidimensional performance. Performance advantages of Mars batteries. (e) Ragone plots for cell-level specific (Wh kg^{-1}) and volumetric (Wh L^{-1}) energy densities with representative commercial and reported batteries, and the starts represent the minimum, middle, and maximum values at 0, 25, and 60 °C, respectively. (f) Ultralong working lifespan at low-temperature of 0 °C with 500 mAh g^{-1} (depth of discharge/charge of around 20%) per cycle at 100 mA g^{-1}, and the inset shows last four times of cycling curve and photographs of both sides of Li anode after cycle.

voltammetry (CV) curves show that the reduction reaction potential of the Mars battery starts at 1.6 V and can exhibit a reduction current higher than that of the Li-CO_2 battery (Fig. 1c), suggesting a much higher reaction rate in Mars battery. The presence of active components on the Mars surface has a positive impact on the electrochemical process (Fig. 1d). Diverse differences between Mars batteries and Li-CO_2 batteries are thoroughly summarized (Table S2 online). It is demonstrated to emphasize that the Li-CO_2 battery completely cannot be equated with the Mars battery, the latter exhibiting superior electrochemical performance with complex mechanism in Mars exploration.

To resist the extreme temperatures on the Mars surface, mature physical temperature control systems for batteries have been applied and loaded in Mars rovers (e.g., Perseverance, Zhurong). These approaches include thermal insulation, preheating techniques, thermal radiation, and hibernation protocol, shortening the subzero temperature region (Table S3 online). Considering the diurnal temperature span of 60 °C and the minimum operating temperature of Mars batteries, the performance and process of Mars batteries at 0–60 °C deserve to be further investigated. Under the operating temperature of 0 °C, the Mars battery achieves cell-level specific and volumetric energy densities of 373.9 Wh kg^{-1} and 393 Wh L^{-1}, respectively. The cell-level evaluation of batteries contains the anode, separator, cathode, and electrolyte components. The capacity-voltage curve of the Mars battery, components specifications, and evaluation details are shown in Fig. S1 (online) and Table S4 (online). After the cathode optimization and structure design, the highest energy densities of 765 Wh kg^{-1} and 630.1 Wh L^{-1} are further achieved, as shown in the following section. It follows that the energy densities of cell-level Mars batteries far exceed those of all reported commercial LIBs and other advanced rechargeable batteries (Fig. 1e) [12,13]. Notably, the Mars battery shows a steadily ultralong working lifespan exceeding 1350 h (nearly two Mars months) with 270 cycles at a current density of 100 mA g^{-1} (Fig. 1f). Disassembling the battery after cycling, the relatively clean Li anode excludes the possibility of severe side

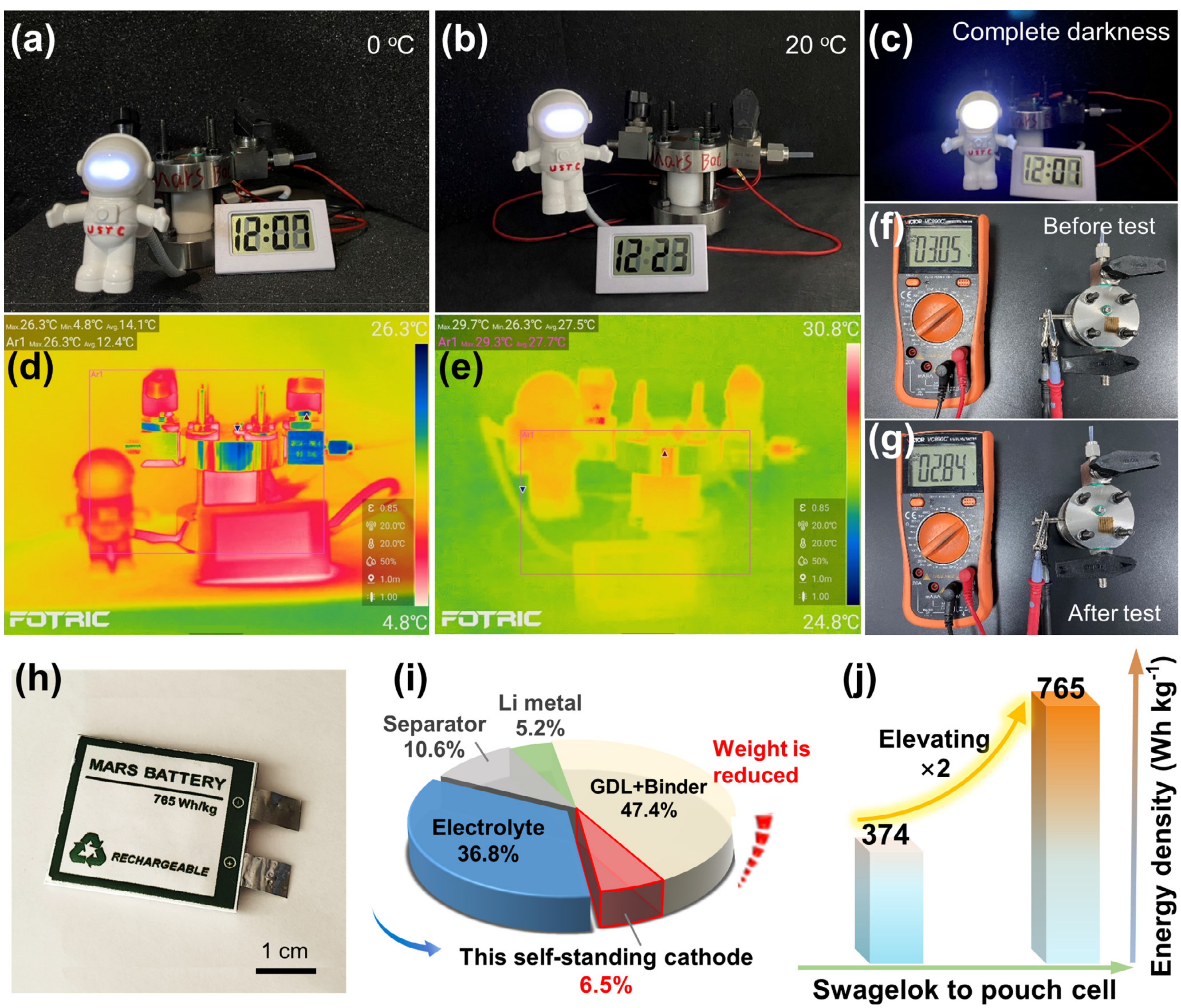

Fig. 2. (Color online) Application demonstration and development potential of all-temperature Mars batteries. (a–c) The battery powers an astronaut mode and an electronic watch at 0, 20 °C, and complete darkness surrounding, respectively (see in Movie S1 online). Synchronous IR images at (d) 0 and (e) 20 °C, respectively. (f, g) The open-circuit voltages before and after test, respectively. (h) A photograph of a high energy–density pouch battery with a size of 2 cm × 2 cm, and it is a double-layered folded cell structure assembled with a high-loading free-standing RuO_2/CNT cathode. (i) Pie chart of weight distribution. (j) Comparison chart of the energy density of the Mars battery with optimized components at 60 °C.

reactions and demonstrates the stability of the battery system. Li_2CO_3 as a reversible product is proved during cycle in X-ray diffraction (XRD) and scanning electron microscopy (SEM) results (Figs. S2 and S3 online). The high energy density and ultralong cycling life demonstrate that Mars batteries are expected to be the next-generation energy conversion and storage device contributing to Mars exploration.

The wide-temperature electrochemical performance was tested from 0 to 60 °C with a fixed capacity of 1000 mAh g^{-1} at a current of 100 mA g^{-1} (Fig. S4 online). The capacity-limited operation mode can effectively prevent the disruption of the solid–liquid interface making the best performance for cycling. As the temperature rises from 0 to 60 °C, the Mars battery exhibits a gradually increasing discharge voltage plateau from 1.2 to 2.1 V and a decreasing charge plateau from 4.3 to 3.7 V. A slight trend of polarization at the terminal of charge curves at 0 and 20 °C disappears with increasing temperature. The electrochemical performance is unsatisfactory at –20 °C, and the Coulombic efficiency of 63.85% failed to the ideal 100% for 0 to 60 °C (Fig. S5 online). The wide-temperature rate and power density region are then predicted. The output power maximizes to 3.9 W m^{-2} with 400 mA g^{-1} at 60 °C, which is a superior power value supplying the electronic devices (Fig. S6 online). The energy efficiency can be up to 56.8%. The operating temperature is closely linked with the voltage, rate, and power capabilities. Therefore, the multi-faceted temperature-dependent performances can guide to switchover of the multiple working modes of Mars batteries under different working conditions.

A proof-of-concept application potential of Mars batteries. For proof-of-concept purposes, ease of understanding, comparability, and verifiability are of utmost importance. The RuO_2/carbon nanotube (CNT) material is prepared as the efficient catalyst for the redox reaction of CO_2, O_2, and CO, and the preparation and successful evidence are detailed (Supplementary materials and Figs. S7–S9 online). The porous RuO_2/CNT cathode material could facilitate Li^+ ion/electron transfer and Li_2CO_3 product storage in electrochemical reactions. The tetraethylene glycol dimethyl ether (TEGDME)-based electrolyte due to its low volatility and high stability to the Li anode is used in the semi-open Mars batteries (Table S5 online). Its freezing point of –30 °C and high ionic conductivity of 2.7 mS cm^{-1} at 0 °C during cycling are determined, which meet the wide temperature range of 0–60 °C and even of –20 °C (Fig. S10 online). The prospect of Mars batteries for practical applications is reflected in two aspects: (i) The feasibility of powering electronics at low temperatures, and (ii) the wide scope of improvement in energy density. A proof-of-concept demonstration of low-temperature Mars batteries was carried out at 0 and 20 °C. As shown in Fig. 2a, b, the Mars battery utilizes Mars gas in the environment simultaneously powering an astronaut model and an electronic watch in the low-temperature range of 0 and 20 °C in a bright environment. Fig. 2c contrasts the power supply effect in the dark, and the whole test process is recorded in Movie S1 (online). An infrared (IR) camera is used to monitor the environmental temperature of batteries and electronic devices operating at 0 °C (Fig. 2a, d) and 20 °C (Fig. 2b, e). The slight increase in measurement temperature is attributed to the need to open the thermostat to focus the shot during calorimeter operation. The open-circuit voltage of the Mars battery drops from 3.05 V before the test to 2.84 V after the test, demonstrating the feasibility of Mars batteries powering electronic devices (Fig. 2f, g).

To achieve a higher cell-level energy density, a pouch battery is designed with a bi-side cell structure with a size of 2 cm × 2 cm and assembled with a novel free-standing cathode based on RuO_2/CNT material with a high loading of 1 mg cm^{-2} (Supplementary materials for the preparation details). The photographs of the pouch battery are shown in Fig. 2h and Fig. S11 (online). The bi-side cell structure is beneficial for accelerating mass transport of active gases to the reaction sites. The overall battery weight is reduced by 47.4% (Fig. 2i), resulting from the weight of the free-standing cathode being lighter than the conventional cathode coated on carbon paper or cloth (Fig. S12 online). Photographs of the flexible cathode and the corresponding SEM images are provided in Fig. S13 (online). The capacity and voltage of the pouch battery are 30.8 mAh and 1.8 V, respectively (Fig. S14 online). By controlling the temperature, the cell-level specific and volumetric energy density of the pouch battery is maximized to a surprising 765 Wh kg^{-1} and 630.1 Wh L^{-1}, respectively (Fig. 2j). Battery parameters including the component specifications and performances are detailed in Table S4 (online). As a result, the model and pouch structure demonstrate the potential of Mars batteries for low-temperature capability and high cell-level energy density, respectively.

In summary, we have developed a Mars battery for space exploration powered directly by the Mars atmosphere and evaluated the wide-temperature electrochemical performance to suit the serious temperature fluctuations on Mars. The Mars battery has a high energy density of 373.9 Wh kg^{-1} and a long cycling lifespan of 2 Martian months at 0 °C. The wide-temperature performance exhibits a voltage gap of 1.6 V, rate of 0.4 A g^{-1}, and power capability of 3.9 W m^{-2}. Through the optimized structure and integrated cathode, the cell-level performance of Mars batteries is further raised to 765 Wh kg^{-1} and 630.1 Wh L^{-1}. Owing to its electrochemical performance and environmental adaptability, this system shows great potential for application and development and is promising for the next generation of Mars power sources.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Xu Xiao designed research, performed research, analyzed data, and wrote the paper. Zhuojun Zhang performed research and wrote the paper. Aijing Yan performed research. Peng Tan designed research and provided supervision.

Appendix A. Supplementary materials

Supplementary materials to this short communication can be found online at https://doi.org/10.1016/j.scib.2024.06.033.

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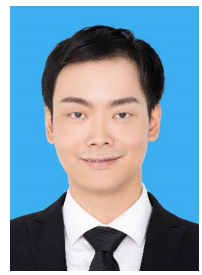

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