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Directly Coating a Multifunctional Interlayer on the Cathode via Electrospinning for Advanced Lithium–Sulfur Batteries

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Supporting Information



ABSTRACT: The lithium-sulfur battery is considered as a prospective candidate for a high-energy-storage system because of its high theoretical specific capacity and energy. However, the dissolution and shutter of polysulfides lead to low active material utilization and fast capacity fading. Electrospinning technology is employed to directly coat an interlayer composed of polyacrylonitrile (PAN) and nitrogen-doped carbon black (NC) fibers on the cathode. Benefiting from electrospinning technology, the PAN-NC fibers possess good electrolyte infiltration for fast lithium-ion transport and great flexibility for adhering on the cathode. The NC particles provide good affinity for polysufides and great conductivity. Thus, the polysulfides can be trapped on the cathode and reutilized well. As a result, the PAN-NC-coated sulfur cathode (PAN-NC@cathode) exhibits the initial discharge capacity of 1279 mAh g^{-1} and maintains the reversible capacity of 1030 mAh g^{-1} with capacity fading of 0.05% per cycle at 200 mA g⁻¹ after 100 cycles. Adopting electrospinning to directly form fibers on the cathode shows a promising application.

KEYWORDS: lithium-sulfur battery, electrospinning, interlayer, nitrogen-doped carbon, fibers, cathode

INTRODUCTION

With the rapid development of portable electronic devices, electrical vehicles, and smart grids, high-energy-density storage systems have been receiving increasing attention. In this regard, the lithium-sulfur (Li-S) battery is considered as a prospective candidate because of its appealing theoretical specific capacity (1675 mAh g^{-1}) and theoretical specific energy (2600 Wh kg⁻¹).¹ In addition, elemental sulfur is low cost, naturally abundant, and environmentally friendly. In spite of these outstanding advantages, the viable commercial application of the Li-S battery is still impeded due to its intrinsic problems. One is the low active material utilization, which results from the poor electrical conductivity of sulfur and its final discharged products (Li₂S/Li₂S₂), which block electron transport during the electrochemical reaction. Another issue is the large volumetric expansion caused by the different densities

of sulfur and Li₂S, resulting in cracking of the cathode structure. Furthermore, the Li–S battery suffers from fast capacity fading and poor Coulombic efficiency as well as safety problems, which is mainly associated with the dissolution and shuttle effect of lithium polysulfides (LiPSs, Li_2S_x ($3 \le x \le 8$)). The LiPSs, generated on the cathode, can dissolve into organic electrolytes and even pass through the separator to react with the lithium anode, triggering the loss of active sulfur species and lithium metal corrosion.² Therefore, extensive efforts have been dedicated to improve the conductivity of the cathode, alleviate the volume expansion, and confine the LiPSs within the cathode side.

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Figure 1. Schematic illustration for the cell configurations and the fabrication process of PAN-NC@cathode.

Through tremendous efforts, researchers have found that various materials possess the ability of trapping sulfur species on the cathode by chemical or physical interaction, such as carbonaceous materials, polymers, and polar metal components.^{3–9} Then, the accompanied challenge is how to efficiently assemble these materials with sulfur to make full use of their adsorbing ability for polysulfides. One popular method is to suppress the polysufide dissolution via fabrication of sulfur hosts with special structure, such as hollow, mesoporous, and integrated materials. 10-14 Such a strategy can efficiently confine sulfur species, but elaborate procedures are usually required to synthesize a designed structure and to bring sulfur into the hosts. By contrast, another alternative way is to improve the utilization of dissolved polysufides by inserting trapped materials between the cathode and the separator. A pioneer study is introduced by Su and Manthiram via inserting microporous carbon paper between the cathode and the separator.¹⁵ The inserted interlayer acts as both the upper current collector for the electron pathway and the polysulfide stockroom. This approach adopts the polysufide natural property with gradient distribution, showing its promising potential for practical application. Afterward, a series of materials has been developed as interlayers for Li-S batteries, including multiwalled carbon nanotubes (MWCNTs), reduced graphene oxide (rGO), carbon nanofibers (CNFs), and V_2O_5 .^{16–19} Analogous strategies by modifying the separator or directly coating materials on the cathode are also reported.^{20,21} Table S1 compares the typical references about the property of the prepared interlayers. On the basis of previous research, it can be found that several challenges still remain to be overcome. First, the inserted interlayer has heavy weight,^{15,22} which inevitably sacrifices the energy density of the cell. In addition, a modified sulfur cathode rather than a pure

sulfur cathode is normally used in some cases.^{21,23} Furthermore, the compact interlayers are obtained by roll-pressing or vacuum filtration, which impede the lithium-ion (Li⁺) transport.²¹ Therefore, exploring a facile method to fabricate an effective interlayer is necessary. An ideal interlayer should possess the following properties: (1) lightweight, (2) no influence on the Li⁺ transport, and (3) great conductivity and good affinity for polysulfides.

On the basis of these requirements, in this work, an interlayer composed of polyacrylonitrile (PAN) and nitrogen-doped carbon black (NC) fiber (PAN-NC) is directly coated on the pure sulfur cathode through electrospinning technology. Compared with the traditional direct-coating method, electrospinning can directly form fibers on the cathode, which is beneficial for electrolyte infiltration and Li⁺ diffusion. The proper flexibility of the fibers is able to buffer the volume expansion, guaranteeing its good adhesion with the sulfur cathode during cycling. PAN is chosen to form the fibers because it is lightweight and low cost, which is more suitable for practical application. Additional NC particles can provide strong adsorption for polysulfides based on a Lewis acid-base interaction,²⁴ and fast electron transport can be obtained because of its high electronic conductivity. Pure sulfur powders are used to fabricate the cathode for excluding the interference of a modified sulfur cathode. Thus, the improvements in electrochemical performances can be attributed to the effect of the PAN-NC interlayer. The obtained PAN-NC-coated sulfur cathode (PAN-NC@cathode) exhibits stable cycling performance, maintaining the reversible capacity of 1030 mAh g^{-1} after 100 cycles with the capacity decay of 0.05% per cycle.



Figure 2. (a) Photographs of the prepared electrodes; top-view SEM images of (b) the sulfur cathode, (c, d) the PAN@cathode, and (e, f) the PAN-NC@cathode; TEM images of (g) the PAN fibers and (h) the PAN-NC fibers; (i) cross-sectional SEM image of the PAN-NC@cathode.

RESULTS AND DISCUSSION

A schematic illustration for the cell configurations and the fabrication process of the PAN-NC@cathode is shown in Figure 1. In the case of the traditional cell configuration, because the sulfur cathode is in direct contact with the electrolyte, the formed LiPSs can easily diffuse out from the cathode into the electrolyte and even transport the separator to react with the lithium anode. As a result, the Li-S cell suffers from low active material utilization, fast capacity fading, and serious anode corrosion. By contrast, if a multifunctional interlayer is introduced between the cathode and the electrolyte, which has the capacity for anchoring polysulfides and reutilizing them, enhanced active material utilization and improved electrochemical performances can be obtained. Electrospinning technology is regarded as a popular approach to generate fibers,^{25,26} such as polyethene oxide, poly(acrylic acid), and polyaniline polymer fibers.²⁷⁻²⁹ In general, if the polymer fibers are used as the interlayers for Li-S batteries, an extra calcination step is required to form conductive CNFs because of their naturally poor conductivity.^{30,31} In this work, the NC particles are co-electrospun with PAN to directly form conductive fibers on the sulfur cathode, which significantly simplifies the fabrication process. In such an interlayer, PAN acts as a structure framework to form fibers, on which the NC particles are distributed uniformly. The NC particles cannot only enhance the conductivity of the fabricated fibers but also provide strong adsorption for polysufides. The improved conductivity is confirmed by resistivity measurements (Table S2). Additional N dopants can increase the surface basicity of carbon black, providing strong interaction with polysulfides.⁴

The N content accounts for 2.6% in the NC particles based on elemental analysis. The X-ray photoelectron spectroscopy (XPS) spectra were further used to identify the chemical state of the N dopant. As shown in Figure S1, pristine C only shows the one peak at 288.6 eV, which belongs to the C–C bond. After doping N, an additional peak at 286.3 eV is detected, which is attributed to the C–N bond, demonstrating the existent of N. In addition, the N 1s XPS spectrum of NC particles exhibits that pyrrolic N is dominant, which has been proved showing stronger interaction with polysulfides.^{33,34}

The visible photographs of fabricated electrodes are shown in Figure 2a. The surface of the pristine sulfur cathode is black, which changes to gray if only PAN fibers are coated. PAN-NC@cathode is black with great flexibility and strong adhesion. Figure 2b-f displays the top-view scanning electron microscopy (SEM) images of the obtained pure sulfur cathode, the PAN@cathode, and the PAN-NC@cathode. Obvious particles, which are the mixture of acetylene black, binder, and sulfur powders, are observed in the pure sulfur cathode (Figure 2b). When only PAN is coated by electrospinning, the fibers with a smooth surface are formed on the cathode (Figure 2c, d). After adding NC particles into the PAN solution to coelectrospin, the rough surfaces of the fibers can be clearly seen (Figure 2e), which can provide sufficient surface contact with electrons and sulfur species to reduce charge-transfer impedance.³⁵ The enlarged SEM image (Figure 2f) shows the PAN fibers are covered with NC particles. Transmission electron microscopy (TEM) images are further used to reveal the distribution of the NC particles on the PAN fibers. As shown in Figure S2, NC are nanoparticles with size of ~35 nm. Comparing the TEM images of PAN (Figure 2g) and PAN-NC fibers (Figure 2h),

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we can see that NC particles are uniformly distributed on the PAN fibers. The thickness of the PAN-NC@cathode is analyzed by the cross-sectional image in Figure 2i. The PAN-NC layer with the thickness of ~50 μ m can be observed on the pure sulfur cathode of ~60 μ m. Therefore, it can be seen that the fabricated PAN-NC fibers exhibit the character of a porous conductivity network, in which PAN fibers act as the structure framework and NC particles provide the electron pathway. Furthermore, a nitrogen adsorption–desorption isotherm of the PAN-NC interlayer was measured to obtain the surface area and pore distribution. The result is shown in Figure S3. The Brunauer–Emmett–Teller (BET) surface area and pore volume are measured to be 14.77 m² g⁻¹ and 0.085 cm³ g⁻¹, respectively. The pore size has a broad distribution from 15 to 65 nm.

Before testing electrochemical performances, the contact angle measurements are conducted to investigate the influence of PAN-NC fibers on electrolyte infiltration. The electrolyte of 1 M lithium bis(trisfluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) with LiNO₃ (1 wt %) is chosen as the test liquid. As shown in Figure 3, the electrolyte shows an immediately complete



Figure 3. Contact angles of (a) the sulfur cathode, (b) the PAN-NC@ cathode, (c) the PAN@cathode, and (d) carbon paper.

wetting with a contact angle of 0° for the sulfur cathode, the PAN@cathode, and the PAN-NC@cathode, demonstrating perfect wettability of the PAN-NC and PAN interlayers for the electrolyte. In comparison, the traditional carbon paper shows poor electrolyte wettability with a contact angle of 50.8°. The great electrolyte wettability can guarantee fast Li-ion transport. To verify this hypothesis, the cyclic voltammetry (CV) curves at different scanning rates are measured to determine the diffusion coefficient of Li^+ (D_{Li^+}). The specific measurement results and the calculation are illustrated in Figure S4. The value of $D_{\rm Li^{*}}$ for the pristine sulfur cathode is $4.0 \times 10^{-7} \rm ~cm^{2}$ s⁻¹. When only using PAN electrospun, a lower $D_{\rm Li^+}$ (2.2 \times 10^{-7} cm² s⁻¹) is obtained; if coated with PAN-NC fibers, a higher D_{Li^+} value of 8.1 \times 10⁻⁷ cm² s⁻¹ can be achieved, demonstrating that the NC plays a positive effect on improving Li⁺ diffusion.

To testify the improvements of the designed configuration for the Li–S batteries, a series of electrochemical measurements is carried out. As shown in Figure 4a, the initial CV profiles are performed to detect the impact of the PAN-NC interlayer on

the oxidation/reduction of the sulfur cathode. All cathodes exhibit two typical reduction peaks and one oxidation peak. The first reductive peak at ~ 2.3 V represents the conversion from solid sulfur to the soluble LiPSs (Li₂S_x, $4 \le x \le 8$), and the second reductive peak at ~2.0 V reflects the formation of insoluble products (Li_2S_2/Li_2S). The oxidation peak at ~2.5 V corresponds to the reaction from Li_2S_2/Li_2S to solid sulfur.^{36,37} No additional new peak is detected after coating PAN-NC fibers, which reflects the electrochemical stability during cycling. Notably, the positions of the reduction/oxidation peaks show a slight different between the sulfur cathode and the PAN-NC@cathode. After coating the PAN-NC interlayer, the reduction peaks shift to higher positions, while the oxidation peak shifts to a lower potential, implying enhanced electrochemical reaction kinetics.^{38,39} This can be attributed to the special structure of the PAN-NC interlayer with a porous conductivity network, which can provide great electrolyte infiltration, guaranteeing fast transport for electrons and lithium ions. Furthermore, Figure 4b compares the first galvanostatic discharge/charge profiles of the pure sulfur cathode with the PAN-NC@cathode at 200 mA g⁻¹. Two typical discharge plateaus can be observed in both cathodes. The first plateau at \sim 2.3 V is associated with the solid–liquid transportation from sulfur to soluble Li_2S_{81} and the second long plateau at ~2.1 V belongs to the formation of insoluble $Li_2S_2/Li_2S_1^{40,41}$ which is well consistent with the CV curves. A higher discharge capacity can be achieved by the PAN-NC@cathode (1279 mAh g^{-1}) than by the pure sulfur cathode (1157 mAh g^{-1}), exhibiting an improved active material utilization. The cycling performances of the cathodes are compared at the current density of 200 mA g^{-1} (Figure 4c). The discharge capacity of the pure sulfur cathode suffers from fast decay, with only 467 mAh g^{-1} capacity remaining after 100 cycles. By contrast, higher Coulombic efficiency (CE means the ratio of discharge capacity to charge capacity (i.e., $Q_{discharge} / Q_{charge}$)), and higher discharge capacity is obtained for the PAN-NC@cathode, with a remaining reversible capacity of 1029 mAh g⁻¹ after 100 cycles. Figure S5 shows the discharge and charge plots after 100 cycles. The pristine sulfur cathode exhibits higher charge capacity than discharge capacity, which reflects the existence of the shuttle effect. No overcharged phenomenon is found in the PAN-NC@cathode, implying the assistance of the PAN-NC interlayer in suppressing polysulfide dissolution. The rate performances of different cathodes are assessed at different current densities (100, 200, 500, 1000, and 2000 mA g^{-1}) (Figure 4d). For the pristine sulfur cathode, a poor rate performance with fast capacity fading is exhibited. Only 457 mAh g^{-1} capacity is obtained at 2000 mA g^{-1} , and distorted discharge/charge plots are exhibited (Figure S6). After coating PAN-NC fibers, however, higher discharge capacities of 1281, 956, 857, and 675 mAh g^{-1} can be reached at the densities of 200, 500, 1000, and 2000 mA g^{-1} , respectively. Even at the high current density of 2000 mA g^{-1} , two obvious discharge plateaus are still visible for the PAN-NC@cathode (Figure S6). When the current density returns to 200 mA g^{-1} , a reversible capacity of 1019 mAh g^{-1} can still be obtained. To further prove the improved electrochemical performance at high current density, the PAN-NC@cathode was cycled at 500 mA g⁻¹. As shown in Figure 4e, a stable cycling performance and great Coulombic efficiency can be obtained. After 200 cycles, a typical discharge/ charge plot remains (Figure S7), with a stable discharge capacity of 807 mAh g⁻¹. Even when cycled at the higher current density of 2000 mA g⁻¹ (Figure S8), the PAN-NC@



Figure 4. (a) CV curves at 0.1 mV s⁻¹; (b) initial discharge and charge plots at 200 mA g^{-1} ; (c) cycling performances at 200 mA g^{-1} ; (d) the rate performances; (e) cycling performance of the PAN-NC@cathode at 500 mA g^{-1} .

cathode exhibits a higher discharge capacity than that of the pure sulfur cathode. Furthermore, when increasing the sulfur loading to 4 mg cm⁻², an improved Coulombic efficiency and cycling stability can still be observed in the PAN-NC cathode compared to those of the pristine sulfur cathode (Figure S9). To identify the role of PAN and NC, the PAN-NC/S cathode was fabricated by simply mixing sulfur with PAN and NC. Figure S10 demonstrates that an improved Coulombic efficiency and cycling stability can be obtained in the PAN-NC/S cathode, implying decreased polysulfide dissolution due to the addition of PAN-NC.

For better understanding of the improved electrochemical performance by the added PAN-NC interlayer, the electrochemical impedance spectroscopy (EIS) measurement is carried out to reveal the impedance of the pristine sulfur cathode and the coated sulfur cathode before and after 100

cycles (Figure S11). All Nyquist plots show a depressed semicircle at high frequency and one inclined line at low frequency. The high frequency semicircle is linked to the charge-transfer resistance.⁴² For the fresh electrode, the PAN-NC@cathode shows smaller semicircles than the sulfur cathode, confirming a lower charge transfer; thus, an enhanced active material utilization can be achieved.¹⁵ After 100 cycles, the sulfur cathode shows an increased semicircle, which is much larger than that for the PAN-NC@cathode. Furthermore, exsitu SEM is used to observe the morphological changes of the cathodes after 100 cycles. As shown in Figure 5a, the sulfur cathode suffers from severe agglomeration after long cycling, which explains well the increased resistance of the sulfur cathode (Figure S11). The agglomeration of the sulfur species may cause the loss of electrical contact and block Li⁺ transport, leading to pronounced capacity fading and poor cycle



Figure 5. Top-view SEM images after 100 cycles of (a) the sulfur cathode (insert enlarge image) and (b, c) the PAN-NC@cathode; the elemental mapping images of (d) C, (e) S, and (f) N in the PAN-NC@cathode.



Figure 6. XPS spectra of the sulfur cathode and the PAN-NC@cathode discharged to 1.75 V: (a) Li 1s, (b) S 2p.

stability.^{43,44} For the PAN-NC@cathode (Figure 5b–d), the fibers are still clearly observed after long cycling. The maintained porous structure guarantees good electrolyte penetration and Li⁺ transport. From the elemental mapping analyses (Figure 5e, f), we can see that the C, S, and N elements are homogeneously distributed on the fibers, which is good for the reutilization of the active sulfur species.¹⁵ The observation proves that the PAN-NC interlayer can provide continuously good electron and Li⁺ pathways to improve sulfur species utilization.

To get further information about the interaction between the PAN-NC fibers and the polysulfides, the XPS spectra are used to analyze the cathodes at the fully discharge state. For Li 1s spectra (Figure 6a), the symmetric peak at 55.4 eV belongs to the Li-S bond.⁴⁵ Compared with the sulfur cathode, for the PAN-NC@cathode, a new peak appears at 56.3 eV, which is attributed to the Li-N bond, 32,45 confirming the anchoring ability of the PAN-NC interlayer for polysulfides. In the S 2p XPS spectra (Figure 6b), the peaks attributed to Li₂S (160.2 eV), Li₂S₂ (161.9 eV), polysulfides (161.1 and 161.8 eV), and sulfate (167 eV) can be detected after carefully deconvoluting.⁵ Notably, the peak intensity of the sulfur species in the PAN-NC@cathode is weaker than that of the sulfur cathode, implying less polysulfide diffusion due to the protection of the PAN-NC interlayer. In addition, the peaks of the polysulfides in the PAN-NC@cathode shift to higher binding energies, demonstrating the interaction between S and the PAN-NC fibers because of the positive N dopants.³²

CONCLUSION

In summary, electrospinning technology is adopted to directly coat the PAN-NC interlayer on the sulfur cathode. The PAN-NC@cathode exhibits improved active material utilization, rate performance, and cycling stability. The initial discharge capacity of 1279 mAh g^{-1} is achieved with the reversible capacity of 1030 mAh g^{-1} remaining after 100 cycles at 200 mA g^{-1} . These improvements can be attributed to the coated PAN-NC interlayer. Benefiting from the electrospinning technology, the PAN-NC interlayer possesses porous fiber structure, which can provide excellent electrolyte infiltration and flexibility to buffer the structure change, guaranteeing fast Li⁺ transportation and strong adhesion during cycling. Besides, the PAN-NC interlayer acts as a second current collector because of its good affinity for polysulfides and desirable conductivity for electron transport. The diffused polysulfides can be anchored on the NC matrix, and the fast electron pathway makes it fully reutilized; thus, enhanced active material utilization and cycling stability can be achieved. Therefore, using electrospinning technology to directly coat an interlayer on the cathode of Li-S batteries exhibits a novel design idea for cell configuration, promising its potential application in other battery systems.

EXPERIMENTAL SECTION

Preparation of the NC Particles. The nitrogen treatment of carbon black (super-P) was carried out according to a previous report.²⁴ The carbon black (0.5 g) was mixed with melamine (1 g) in formaldehyde solution (37 wt %, 5 mL). KOH was used to adjust the

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pH value of the solution to 9.0. After subjecting to ultrasound overnight, the mixture was heated at 850 $^\circ C$ for 3 h under a N_2 atmosphere.

Preparation of the Cathode Film. The sublimation sulfur powder was used as the active material. Carboxy methyl cellulose (CMC) and styrene butadiene rubber (SBR) (CMC/SBR = 1:1, mass) was used as the binder. Sulfur, acetylene black, and the binder were mixed with the mass ratio of 6:3:1. After string homogeneously overnight, the slurry was coated onto aluminum foil by using block blade and dried at 60 °C in a vacuum oven overnight. The PAN-NC/S cathode was fabricated by the same procedure with the sulfur/AB/ binder/PAN/NC ratio of 6:3:1:0.305:0.104. The typical mass loading of active sulfur was ~2.0 mg cm⁻².

Preparation of the PAN-NC@Cathode. PAN ($M_r = 150\ 000$) was used as polymer precursor fibers. A certain amount of NC was added into the PAN solution (13 wt %) with *N*,*N*-dimethylformamide as the solvent. The mass ratio of PAN/NC was 3:1. After continuous stirring overnight, the mixed solution was electrospun onto the cathode film under the voltage of 10 kV at the flow rate of 0.02 mL min⁻¹. The PAN@cathode was prepared by using the same process without the addition of NC. The mass of the coated interlayer was ~0.14 mg cm⁻², which was determined by weighing the electrode before and after electrospinning.

Cell Assembly and Electrochemical Measurement. The electrochemical performances were evaluated using CR-2016-type coin cells, which were assembled in an argon-filled glovebox. The electrolyte was composed of 1 M LiTFSI with DOL and DME (DOL/DME = 1:1, v/v). The lithium foil acted as both the counter and reference electrodes. The CV profiles were carried out on a CHI 660D with the scanning rate of 0.1 mV s⁻¹ from 1.5 to 3 V. The electrochemical workstation (Autolab PGSTAT T302N) was used to test CV curves at different rates (0.2, 0.3, 0.4, 0.5, and 0.6 mV s⁻¹) and EIS spectra at the frequency range of 0.1 Hz ~ 100 kHz. The discharge/charge plots were performed on the electrochemical workstation (Autolab PGSTAT T302N).

Characterization and Measurements. The morphologies of all the samples were observed by using SEM (HITACHI S-4800) and TEM (JEM-2100). The contact angle was characterized by Powerach (JC200JC1). The XPS spectra were recorded on a Qtac-100 scanning microprobe. The nitrogen content in the NC particles was analyzed by elemental analyzer (Vario EL III). ASAP 2020 was used to measure the nitrogen adsorption-desorption isotherms to obtain the BET specific surface area and pore distribution.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b08804.

XPS spectra and TEM image of NC particles; nitrogen adsorption–desorption isotherms and corresponding pore size distribution of PAN-NC fibers; CV curves at different scanning rates; calculation of the Li⁺ diffusion coefficient; discharge and charge plots; EIS spectra; comparison of relative references; and resistivity measurements (PDF)

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Notes

The authors declare no competing financial interest.

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