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In Situ Integration of Anisotropic SnO₂ Heterostructures inside Three-Dimensional Graphene Aerogel for Enhanced Lithium Storage

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S Supporting Information

ABSTRACT: Three-dimensional (3D) graphene aerogel (GA) has emerged as an outstanding support for metal oxides to enhance the overall energy-storage performance of the resulting hybrid materials. In the current stage of the studies, metals/metal oxides inside GA are in uncrafted geometries. Introducing structure-controlled metal oxides into GA may further push electrochemical properties of metal oxide–GA hybrids. Using rutile SnO₂ as an example, we demonstrated here a facile hydrothermal strategy combined with a preconditioning technique named vacuum-assisted impregnation for *in situ* construction of controlled anisotropic SnO₂ heterostructures inside GA. The obtained hybrid material was fully characterized in detail, and its formation mechanism was investigated by monitoring the phase-transformation process. Rational integration of the two advanced structures, anisotropic SnO₂ and 3D GA, synergistically led to enhanced lithium-storage properties (1176 mAh/g for the first cycle and 872 mAh/g for the 50th cycle at 100 mA/g) as compared with its two counterparts, namely, rough nanoparticles@3D GA and anisotropic SnO₂@2D graphene sheets (618 and 751 mAh/g for the 50th cycle at 100 mA/g, respectively). It was also well-demonstrated that this hybrid material was capable of delivering high specific capacity at rapid charge/discharge cycles (1044 mAh/g at 100 mA/g, 847 mAh/g at 200 mA/g, 698 mAh/g at 500 mA/g, and 584 mAh/g at 1000 mA/g). The *in situ* integration strategy along with vacuum-assisted impregnation technique presented here shows great potential as a versatile tool for accessing a variety of sophisticated smart structures in the form of anisotropic metals/metal oxides within 3D GA toward useful applications.

KEYWORDS: anisotropic SnO₂ heterostructures, lithium-ion battery, *in situ* integration, three-dimensional graphene aerogel, vacuum-assisted impregnation

INTRODUCTION

The manipulation ability of graphene building blocks enables the creation of sophisticated functional architectures, where the intriguing properties of graphene are effectively harnessed for a wide range of applications.^{1–4} Since the first exfoliation of single-layer graphene,⁵ multifarious smart nanostructures based on it have been realized, including nanoparticles/nanorods/nanowires anchored on the graphene surface,^{6–9} encapsulated nanospheres,^{10,11} layer-by-layer assembled thin films,^{12,13} stacked papers,^{14–17} and vertically aligned sheets.¹⁸ Recently, three-dimensional (3D) graphene including graphene aerogel (GA)¹⁹ and graphene foam²⁰ has emerged as an attractive support to fabricate novel functional materials. On account of their interconnected porous framework, high surface area, and mechanical flexibility, these 3D graphene materials present promising applications, especially for serving as advanced energy materials. However, the application potential of graphene foam was greatly restricted by complex and costly synthetic procedures. On the contrary, the synthesis of GA could be achieved via a one-step facile route by either

hydrothermal treatment or *in situ* reduction,^{21,22} which is apparently more cost-effective, scalable, and approachable in terms of industrial applications.

With respect to energy applications, metal oxides are competitive candidates but at the same time suffer from poor electric conductivity. Hence, combining metal oxides with graphene of high electron mobility can hopefully retain the advantages of both species. Recently, researchers demonstrated that 3D graphene–metal oxide hybrids could exceed their 2D counterparts both in energy conversion and storage.^{23–25} In the case of a lithium-ion battery, 3D GA brings three substantial improvements: (1) an interconnected graphene framework facilitates the electron transport across the electrode, (2) numerous multidimensional channels in GA could effectively accelerate the lithium diffusion within the bulk electrode, and (3) an elastic matrix of GA could accommodate the volume

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Scheme 1. Synthetic Process of SnO₂ NCs@GA through a Hydrothermal Route along with Vacuum-Assisted Impregnation as Preconditioning

expansion of metal oxides during long-term cycling. To date, various metal oxides/sulfides such as Co₃O₄,²⁶ SnO₂,²⁷ Fe₃O₄,²³ and MoS₂²⁸ have been successfully coupled with GA for high-performance lithium storage. Nevertheless, these metal oxides/sulfides in GA present uncrafted geometries, and in most cases, they are nanoparticles in the rough. Thus, controlled aqueous growth of well-defined morphologies inside 3D GA still remains a challenge. On the other hand, it was well-documented that the geometric shape and surface features could significantly influence the physiochemical properties of metal oxides. Controlled anisotropic morphologies such as nanorods, nanowires, and nanosheets are expected to enhance electrochemical energy-storage performance of metal oxides over their particle-like counterparts.^{29–31} Therefore, highly ordered nanostructures prepared through *in situ* growth may unfold the full application potential of GA based hybrids. Herein, we present a novel synthetic strategy to construct the purposely designed, coral-like SnO₂ embellished GA heterostructures with enhanced lithium-storage performance. Furthermore, the strategy shows great promise as a general approach to be applied to other metal oxides such as Fe₂O₃, TiO₂, and ZnO.

In this work, we developed a facile strategy, namely, a vacuum-assisted impregnation, to fully saturate the porous hydrophobic GA with aqueous precursor solution, followed by an *in situ* hydrothermal reaction to grow anisotropic SnO₂ crystallites inside 3D architecture of GA prepared beforehand (Scheme 1). Here, selective nucleation of SnO₂ nanocorals (NCs) on the surface of reduced graphene oxide (RGO) was achieved through the conjugation of oxygen-containing species. Without vacuum-assisted impregnation as the pretreatment, GA would be floating in aqueous precursor solution, resulting in failure to introduce SnO₂ crystallites into the interior pore channels of GA. Alternatively, surfactants or prefunctionalization with hydrophilic groups could be applied to modify the surface properties of GA, which could slightly improve its saturation in aqueous solution.^{32–34} In the present case, by rapidly lowering the systematic pressure below 50 mbar, the air

inside pore channels of GA would be pumped out, and thus aqueous solution could enter the inner territories of GA. Ultimately, it was found that this technique could improve the effectiveness of impregnation and at the same time secure the purity of precursors. As observed from samples of different reaction times, Na₄SnO₄ was first formed and eventually transmuted into SnO₂. After the hydrothermal treatment, the product was annealed at 600 °C under nitrogen atmosphere for 3 h to improve the graphitic lattice, as well as the crystallinity and phase purity of SnO₂ NCs. As both GA and SnO₂ were extensively studied as potential energy materials,^{35–37} we finally manifested superior properties of obtained SnO₂ NCs@GA as stable lithium-storage materials as compared to its counterparts including SnO₂ NCs@graphene sheets (SnO₂ NCs@GS) and SnO₂ nanoparticles@GA (SnO₂ NPs@GA) in terms of enhanced specific capacity and rate capability. Overall, these results confirmed that the performance improvement of SnO₂ NCs@GA could be achieved through the combination of 3D porous GA and coral-shaped SnO₂, showing integrated advantages of individual elements, i.e., (1) accelerated electron transport and lithium-ion diffusion, as well as accommodated volume expansion of SnO₂ during cycling, and (2) additional contact surface for lithium ions to access.^{23,38}

RESULTS AND DISCUSSION

The preparation of SnO₂ NCs@GA was described in the Supporting Information (SI). The phase purity and crystallographic structure of the developed SnO₂ NCs@GA hybrid were investigated by means of powder X-ray diffraction (XRD, Figure 1a). Major diffraction peaks of the hydrothermally synthesized product (pattern I) can be readily indexed to cassiterite SnO₂ (PDF 41-1445), except for four additional minor peaks (2θ = 31.6°, 45.3°, 56.5°, and 75.3°) that are assigned to hydroromarchite Sn₆O₄(OH)₄ (PDF 46-1486). Diffraction signal of graphene in the hybrid is weak and indistinguishable as compared with that of SnO₂, while pure GA shows a hump peak around 25° that resulted from poor ordering of sheets along the stacking direction (Figure S2b in

Figure 1. (a) Powder XRD patterns of SnO₂ NCs@GA: (I) hydrothermally synthesized, and (II) after calcination. (b) XPS spectrum of SnO₂ NCs@GA. (c) TGA curves of SnO₂ NCs@GA.

the SI). After calcination of the hydrothermal product at 600 °C in N₂ flow, the final SnO₂ NCs@GA hybrid was obtained with decreased labile oxygen-containing groups for graphene as well as improved crystallinity for SnO₂. The powder XRD peaks of Sn₆O₄(OH)₄ in pattern II (Figure 1a) were eliminated, confirming that Sn₆O₄(OH)₄ was totally converted into SnO₂.

In order to verify the chemical composition of the annealed product, we further conducted X-ray photoelectron spectroscopy (XPS in 0–1200 eV range) as a cross-reference. As displayed in Figure 1b, the presence of carbon, oxygen, and tin was traced from the hybrid material. It can be seen from the inset high-resolution spectrum that two peaks at 486.4 and 494.9 eV correspond to Sn 3d_{5/2} and Sn 3d_{3/2}, respectively. The peak position and interpeak interval (8.5 eV) collectively

confirm that SnO₂ is the major form of tin oxide in this material after the calcination treatment.³⁹

Composition percentage of graphene as well as thermal behavior for the hybrid material after calcination were probed by thermogravimetric analysis (TGA) that was performed with a ramping rate of 20 °C/min in air flow (Figure 1c). The weight derivative line of SnO₂ NCs@GA suggests that the decomposition of RGO is a two-step process where the first stage denotes the rapid combustion of defective graphene sheets at the vicinity of 500 °C, followed by further disintegration of defect-free graphene around 600 °C. It is noteworthy that the combustion of graphene starts at a relatively high temperature, i.e., 500 °C, which implies the improved crystallinity of graphene after calcination. On the basis of the TGA curve, the mass fraction of SnO₂ was calculated to be 70.18%, which is comparable to other graphene/metal oxide hybrid materials.

The structural and morphological details of the as-prepared SnO₂ NCs@GA were examined by means of field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The bare GA demonstrates a hierarchical interconnected graphene matrix featured with macropores (Figure 2a). The inset image in Figure 2a shows the macroscopic shape of the monolithic GA, whose size was controlled by several factors including reaction temperature, volume/concentration of GO, and shape of polytetrafluoroethylene (PTFE) containers. As indicated by N₂ adsorption/desorption isotherms (Figure 3a), a mesoporous structure was generated in addition to the macroporous skeleton during the self-assembly process of forming GA. The N₂ adsorption/desorption plots present the characteristics of both type II and type IV isotherms, corresponding to unlimited monolayer-multilayer adsorption taking place in macroporous adsorbents and capillary condensation in mesopores, respectively.⁴⁰ It also reveals an H3 hysteresis loop with sharp increase of adsorption at the region of relatively high pressure ($P/P_0 = 0.8–0.99$),⁴¹ indicating the dominance of mesopores that arise from plate-like RGO sheets. On the basis of Barrett–Joyner–Halenda (BJH) calculations (inset in Figure 3a), the majority of the pore volume is contributed by mesopores with an average diameter of around 4 nm. Such a combination of macroporous and mesoporous structures in GA leads to a remarkable specific surface area of 366.9 m²/g, as probed by the Brunauer–Emmett–Teller (BET) method.

For the morphology of SnO₂ NCs@GA (Figure 2b–f), it is immediately apparent that the porous graphene skeleton became solid after hydrothermal crystallization, and uniformly embellished with highly dispersed SnO₂ NCs. From the magnified images (Figure 2d–f), it can be observed that these SnO₂ NCs are trapped and segregated inside a formicary-like graphene matrix. Moreover, part of the SnO₂ NCs was wrapped by the assembled flexible RGO sheets (Figure 2f). It is commonly accepted that the graphene wrapping can accommodate the volume expansion of SnO₂ during the charge/discharge process,^{42,43} and curtail the distance of electron transportation from semiconductive SnO₂ to the graphene electron highway.⁴⁴ After embedding with SnO₂ NCs, specific surface area of the hybrid sharply decreased to 60 m²/g (Figure 3b), which is attributed to the high density of SnO₂. The good consistency in pore size distribution (insets in Figure 3a,b) indicates that the graphene network remains unimpaired during SnO₂ growth. It is noteworthy that the featured incorporation of mesopores and macropores within the hybrid system could

Figure 2. FESEM images of (a) GA and (b–f) SnO₂ NCs@GA. Inset photos in parts a and b show the shape and size of monolithic GA and hybrid.

Figure 3. N₂ adsorption/desorption isotherms for (a) GA and (b) SnO₂ NCs@GA.

Figure 4. (a) TEM image of SnO₂ nanorods wrapped by graphene. (b,c) High-magnification TEM images of SnO₂ nanorods.

Figure 5. FESEM images of the products collected at various reaction stages: (a) 0.5 h, (b) 1 h, (c) 4 h, and (d) 12 h.

enable easier and faster lithium diffusion between electrolyte and active materials, hence augmenting the lithium-storage performance. In addition, it should be mentioned that the N_2 adsorption/desorption isotherms were carried out with finely ground powder samples of GA and SnO_2 NCs@GA, and the obtained results implied that their microscopic architectures were not squished by the grinding procedure.

The low-magnification TEM image (Figure 4a) exhibits individual SnO_2 nanorods in the coral assembly, which are partially wrapped by graphene sheets with thicknesses of a few layers (details of the graphene wrapping behavior are specified in Figures S5 and S6 of the SI). The diameter of the nanorods was determined to be ca. 100 nm. The high-magnification TEM images (Figure 4b,c) denote two sets of dominant crystal lattices in the nanorods with respective interfringe spacing of 0.33 and 0.26 nm, corresponding to the (110) and (101) facets from tetragonal rutile SnO_2 . It was confirmed that the anisotropic growth along the c -axis is thermodynamically preferred, since the surface energy of (001) plane is the highest one.⁴⁵

To further investigate the growth mechanism and formation process of such a nanostructure inside GA, we conducted several control experiments. Generally, we found no formation of SnO_2 NCs when GA was absent, and the solution remained transparent throughout hydrothermal treatment. The observation is probably due to the oxygen-containing groups on RGO being able to reduce the surface-energy barrier as compared to homogeneous nucleation, hence enabling a heterogeneous nucleation. As displayed in Figure 5a–d, samples collected from various reaction stages were inspected by FESEM in order to give a detailed demonstration of the structural and morphological evolution during the whole crystal growth process. Within the initial 30 min (Figure 5a), an irregular spherical Na_4SnO_4 phase was formed as the first stage, due to its fast kinetics of crystallization.⁴⁶ After reacting for 1 h (Figure 5b), a phase transformation from intermediate Na_4SnO_4 to thermodynamically more stable SnO_2 started, as indicated by the formation of primary nanorods. At this preliminary stage, the SnO_2 crystals already illustrated a coral-like contour, which

would direct their further growth. When the reaction time was prolonged to 4 h (Figure 5c), the ripening of SnO_2 nanorods continued, while Na_4SnO_4 still existed. After 12 h of reaction (Figure 5d), no spheres were observed, indicating that almost 100% of Na_4SnO_4 was converted into SnO_2 NCs along with a modicum of $Sn_6O_4(OH)_4$. In addition to FESEM visualizations, powder XRD spectra (details shown in Figure S7 of the SI) collected at various stages of reaction collectively verified the maturation mechanism we proposed.

SnO_2 has been extensively studied as a host structure for reversible lithium insertion/desertion.^{47,48} There are two principle electrochemical processes involved:

According to these processes, the theoretical capacity of SnO_2 was calculated to be 790 mAh/g.

To evaluate the lithium-storage properties of SnO_2 NCs@GA, galvanostatic cyclic measurements were performed at the current density of 100 mA/g, and the discharge/charge voltage profiles of the first, second, and 50th cycles are exhibited in Figure 6a. Impressively, for the first cycle, SnO_2 NCs@GA electrode shows a considerable discharge capacity of 2569 mAh/g, while the reversible charge capacity is 1176 mAh/g. This irreversibility is probably contributed by the reduction of SnO_2 , reaction of oxygen functionality with lithium ions, and formation of solid–electrolyte interphase (SEI) during the initial cycle.⁴⁹ The second cycle shows reversible discharge and charge capacities of 1236 and 1112 mAh/g, respectively. Despite the initial loss, the high capacity of SnO_2 NCs@GA electrode was largely retained, as shown in Figure 6b. From the 20th cycle onward, the specific capacity stabilizes at ~900 mAh/g. Furthermore, after 50 cycles, its charge capacity still remains at 861 mAh/g (73.21% of its initial cycle), which is even beyond the theoretical capacity (790 mAh/g) of SnO_2 . In accordance with the results from other SnO_2 /carbon hybrids reported in the literature,^{50,51} the excessive specific capacity could be originated from the enhanced electrochemical activity

Figure 6. (a) Galvanostatic discharge/charge profiles of SnO₂ NCs@GA at a current density of 100 mA/g for the 1st, 2nd, and 50th cycles. (b) Cycling performance of SnO₂ NCs@GA, SnO₂ NPs@GA, and SnO₂ NCs@GS at a current density of 100 mA/g. (c) Columbic efficiency of SnO₂ NCs@GA at 100 mA/g. (d) Rate performance of SnO₂ NCs@GA, SnO₂ NPs@GA, and SnO₂ NCs@GS at different current densities. (e) Nyquist plots of SnO₂ NCs@GA, SnO₂ NPs@GA, and SnO₂ NCs@GS based anodes. Inset shows Randles equivalent circuit.

of graphene supported/wrapped SnO₂. It should be noted that over 97% columbic efficiency of SnO₂@GA electrode was attained beyond 60 cycles, as revealed in Figure 6c.

To further demonstrate the superior performance of the anisotropic metal oxide/3D graphene hybrid, we then compared SnO₂ NCs@GA with two control samples, namely, SnO₂ NPs@GA and SnO₂ NCs@GS. Before the electrochemical measurements, we conducted TGA characterization to ensure that the weight ratios of SnO₂ in these three materials are at the same level (Figure S8 in the SI). As shown in Figure 6b, the SnO₂ NCs@GA based anode shows better overall performance over the other two groups, which could be

explained by its higher surface area and additional active sites. As for their long-term performance, the reversible discharge capacity of SnO₂ NCs@GA electrode maintains at 872 mAh/g even beyond 50 cycles, which is much higher than 618 mAh/g from SnO₂ NPs@GA and 751 from SnO₂ NCs@GS. In addition, these three electrodes demonstrate very stable cyclic curves, indicating that graphene is an excellent candidate for metal oxide coupling.

The rate performance of SnO₂ NCs@GA was evaluated at various current densities, namely, 100, 200, 500, and 1000 mA/g (Figure 6d). By increasing the current density, it was observed that the specific capacities at all conditions degraded

Figure 7. Schematic comparison of SnO_2 NCs@GS, SnO_2 NPs@GA, and SnO_2 NCs@GA in terms of lithium access and electron transport. Compared with sphere-shaped nanoparticles, the NCs consisting of 1D nanorods provide additional active sites for lithium access, attributing to their increased electrode–electrolyte contact area. SnO_2 NCs grown on graphene sheets (SnO_2 NCs@GS) suffer from severe self-stacking, which results in shrinking of surface area (as shown in Figure S8b of the SI). The graphene wrapping in SnO_2 NCs@GA can also accelerate the electron transport by providing more shortcuts to the graphene highway.

mildly, implying the excellent rate capability of SnO_2 NCs@GA. The corresponding charge capacities gained from each cycle at 100, 200, 500, and 1000 mA/g are 1044, 847, 698, and 584 mAh/g, respectively. Even at a current density as high as 1000 mA/g, a notable specific capacity of 533 mAh/g could still be stabilized at the 10th cycle. After 10 cycles, the current density was set back to 100 mA/g, and the charge capacity could be retrieved to 824 mAh/g, which is equivalent to 78.93% of initial reversible capacity. In addition to SnO_2 NCs@GA, the rate capabilities of SnO_2 NCs@GS and SnO_2 NPs@GA were also examined to provide a more balanced assessment on the lithium-storage performance of the three structures. At each first cycle where current density was 100, 200, 500, 1000 mA/g initially and then fell back to 100 mA/g, the respective charge capacities for SnO_2 NCs@GS were 964, 672, 513, 425, and 693 mAh/g. Meanwhile, specific charge capacities delivered by SnO_2 NPs@GA at the same conditions were 815, 588, 466, 390, and 545 mAh/g, respectively. It was shown that the SnO_2 NCs@GA has a better rate capability than SnO_2 NCs@GS and SnO_2 NPs@GA, and it is in good agreement with their cycling performance. It should be noted that, at higher current rates, the SnO_2 NCs@GA showed even better relative specific capacity. For example, at the first cycle of 200 mA/g, SnO_2 NCs@GA were capable of delivering a reversible charge capacity that was 26% and 44% higher than those of SnO_2 NCs@GS and SnO_2 NPs@GA, respectively. Later on, at a first cycle of 1000 mA/g, it was increased to 37% and 49% higher than SnO_2 NCs@GS and SnO_2 NPs@GA, respectively.

Alternating current (AC) impedance results shed some light on understanding the mechanisms underlying the improved performance of the SnO_2 NCs@GA electrode, which could be specified from two aspects. First, in typical Nyquist plots for anodic materials, the depressed semicircle in the high-medium frequency region is associated with the transportation of charges through the electrode–electrolyte interface. For the SnO_2 NCs@GA anode shown in Figure 6e, its semicircle is obviously smaller than those for other samples, indicating lower contact impedance (R_f) as well as lower charge-transfer resistance (R_{ct}) over its two counterparts. Second, in the low-frequency region, the slope of the fitted line is determined by the diffusion behavior of lithium ions inside the bulk electrode. It was clearly demonstrated that the Warburg line for SnO_2 NCs@GA is much steeper than that of SnO_2 NPs@GA, implying more rapid ion diffusion in the case of SnO_2 NCs@GA probably due to increased exposure to electrolyte. On the basis of electrochemical impedance spectroscopy (EIS), it was

confirmed that the combination of 3D graphene and anisotropic SnO_2 could enhance both the electron and lithium-ion transport within the electrode.

In accordance with the specialized structure and morphology of SnO_2 NCs@GA, it is reasonable to attribute the enhanced lithium-storage properties to the advances from both 3D architecture and the patterned growth of metal oxide. On one hand, in a comparison with 2D graphene architecture, a stable 3D structure remarkably improves not only the overall conductivity by providing large surface area with multidimensional channels for electron transport, but also the lithium-ion diffusion in electrolyte with the mesoporous structure. On the other hand, compared with nanoparticles with a similar size, SnO_2 NCs assembled from nanorods have larger surface area exposed to electrolyte and therefore additional approaches for lithium ions to access (as explained in Figure 7). Moreover, a synergistic interaction observed from morphological characterizations is associated with a unique combination of the two advanced structures by SnO_2 NCs and 3D GA. As already demonstrated in SEM and TEM images, flexible graphene sheets randomly attach onto the surface of SnO_2 NCs, and successively wrap and encapsulate SnO_2 . Such wrapping methodology significantly improves the transfer of electrons from semiconducting SnO_2 to conductive graphene. Furthermore, elastic graphene sheets could also accommodate the volume changes during the charge–discharge cycles. As a consequence, by rationally coordinating these two structures, we could further push the specific capacity and rate capability of SnO_2 /graphene hybrid materials.

CONCLUSIONS

In conclusion, a novel hydrothermal strategy combined with vacuum-assisted impregnation has been developed to perform the *in situ* construction of metal oxides with crafted geometry inside 3D GA. As an illustration, the coral-shaped SnO_2 structures have been successfully introduced into 3D GA to afford SnO_2 NCs@GA. Although this work cannot provide new solutions to address the inevitable SnO_2 pulverization,^{52,53} the present strategy indeed offers accessibility to a variety of sophisticated 3D composites. This unique combination of the two devised structures has led to synergistic enhancement in energy-storage applications (Table S1 in the SI). In a comparison with 2D graphene structure and 3D structure coupled with rough nanoparticles, SnO_2 NCs@GA has shown increased reversible capacity and durability. As demonstrated by the rate capability results, SnO_2 NCs@GA has also exhibited

impressive performance for rapid charge/discharge. Thus, this strategy allows the introduction of shape-controlled nanocrystals with high exposure of desired facets into GA, potentially enabling other significant applications in catalysis or lithium–air batteries.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b07081.

Preparation and characterization details (PDF)

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Notes

The authors declare no competing financial interest.

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