

Bamboo-like Carbon Nanotube/Fe₃C Nanoparticle Hybrids and Their Highly Efficient Catalysis for Oxygen Reduction

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S Supporting Information

ABSTRACT: The design of a new class of non-noble-metal catalysts with oxygen reduction reaction (ORR) activity superior to that of Pt is extremely important for future fuel cell devices. Here we demonstrate a one-pot, large-scale protocol for the controlled synthesis of new one-dimensional bamboo-like carbon nanotube/Fe₃C nanoparticle hybrid nanoelectrocatalysts, which are directly prepared by annealing a mixture of PEG-PPG-PEG Pluronic P123, melamine, and Fe(NO₃)₃ at 800 °C in N₂. The resulting hybrid electrocatalysts show very high ORR activity with a half-wave potential of 0.861 V (vs reversible hydrogen electrode) in 0.10 M KOH solution, 49 mV more positive than that of 20 wt% Pt/C catalyst. Furthermore, they exhibit good ORR activity in acidic media, with an onset potential comparable to that of the Pt/C catalyst. Most importantly, they show much higher stability and better methanol tolerance, with almost no ORR polarization curve shift and no change of the oxygen reduction peak in the cyclic voltammogram in the presence of 1.0 M methanol, than those of the commercial Pt/C catalyst in both alkaline and acidic solutions. This makes them one of the best non-noble-metal catalysts ever reported for ORR in both alkaline and acidic solutions.

Rational design and synthesis of advanced nanocatalysts with unprecedented catalytic efficiency in oxygen reduction reaction (ORR) is extremely important for developing highly efficient fuel cells and lithium air batteries. However, the sluggish ORR at the cathode is a major limiting factor of energy-conversion efficiency in fuel cells. Numerous studies have focused on catalysts with ultra-low Pt content using both electronic and geometric effects to enhance ORR catalysis.¹ Nevertheless, these well-designed Pt-based nanocatalysts still suffer from the very limited supply of Pt in nature, high cost, low stability, and also the issue of methanol crossover.² To get past these bottlenecks, recent significant advances have moved to rational design and synthesis of non-platinum-group metal electrocatalysts as alternatives to Pt for boosting ORR. These have been well demonstrated in the development of metal–nitrogen–carbon catalysts from Fe–N₄ or Co–N₄ macrocycle precursors,³ preparation of N-doped advanced multi-dimensional carbon nanomaterials, and controlled synthesis of graphene/transition metal oxide hybrids etc. for improving the

ORR activity and stability in alkaline solution, yet these are not very effective. These well-established non-noble-metal nanocatalysts still require higher overpotential for ORR than Pt in alkaline solution.⁴ In particular, they show either very limited ORR activity or poor stability in acidic solutions due to the limited catalytic activity of carbon nanomaterials or the poor stability of transition metal oxides.

Here we demonstrate a new one-step soft-template-induced strategy for the controlled synthesis of bamboo-like carbon nanotube (b-CNT)/Fe₃C nanoparticle (NP) hybrids (BCNFNHs) through annealing a mixture of PEG-PPG-PEG Pluronic P123 (P123), melamine, and Fe(NO₃)₃ at high temperature. The resulting BCNFNHs are highly active and stable catalysts for boosting ORR in both alkaline and acidic solutions. The half-wave potential of ORR on BCNFNHs reaches 0.861 V (vs reversible hydrogen electrode) in 0.10 M KOH, which is much more positive than that on 20 wt% Pt/C (half-wave potential of 0.812 V). They also exhibit much higher durability and methanol (MeOH) tolerance than the Pt/C catalyst, showing no ORR polarization curve shift and also no cyclic voltammetric (CV) current changes in the presence of 1.0 M MeOH. Furthermore, the BCNFNHs have an ORR onset potential comparable to that of the Pt/C catalyst in acidic solution. The ORR stability of BCNFNHs in 0.50 M H₂SO₄ solution reveals that there is little shift in the ORR polarization curve after cycling from 0.812 to 0.212 V for 3000 cycles. To the best of our knowledge, the present BCNFNHs are one of the most efficient non-noble-metal catalysts ever reported for ORR.⁵

In a typical synthesis of BCNFNHs, 0.75 g of melamine was dissolved into 7.5 mL of ultra-pure water, followed by addition of 5.0 mL of P123 (0.10 g/mL) and 7.5 mL of 1.0 wt% Fe(NO₃)₃. The resulting homogeneous mixture was stirred for 2 h, further sonicated for 5 h, and then heated at 80 °C to evaporate the solvent. The powder that remained was heated at a rate of 2 °C/min to 180, 240, and 800 °C (or X °C) and held at that temperature for 2, 2, and 1 h, respectively, in nitrogen to obtain BCNFNHs and other control samples. For simplicity, the as-prepared samples were denoted as PMF-X, representing the addition of P123, melamine, and Fe(NO₃)₃, and the use of pyrolysis temperature X °C, during the synthesis process.

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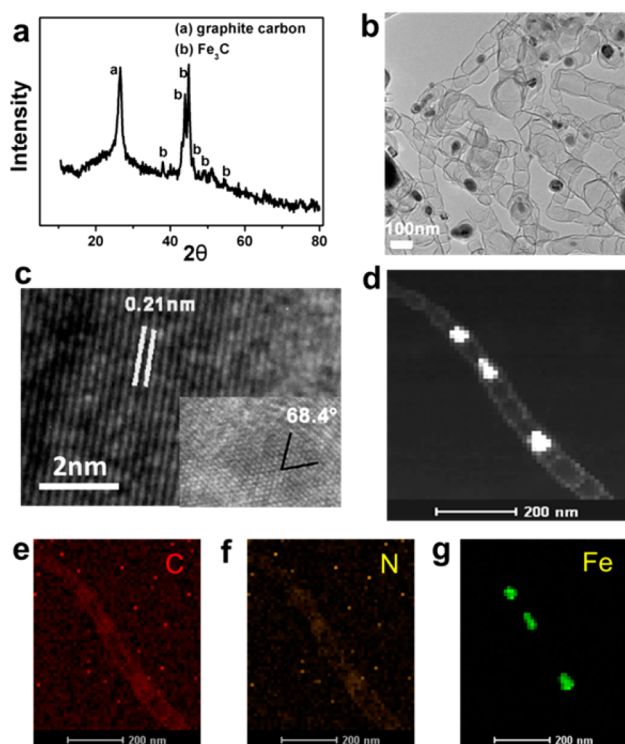


Figure 1. (a) XRD survey, (b) TEM images, (c) HRTEM, (d) HAADF-STEM, and (e–g) its mapping images of the resultant PMF-800.

The morphology and crystal structure of PMF-800 were characterized by X-ray diffraction (XRD) and electron microscopy techniques. Figures 1a and S1 show the XRD patterns of the PMF-800 sample (BCNFNHs) and other control PMF-X samples. A typical strong peak at about 26° is observed, corresponding to the (002) facets of graphite carbon, in agreement with the structural feature of b-CNTs. The peaks located at 37.8° , 43.9° , 45.0° , 46.0° , 49.2° , and 54.5° correspond to the Fe_3C (JCPDS file no. 892867). Figure 1b shows a typical transmission electron microscopy (TEM) image of PMF-800. b-CNTs with a diameter of 50–110 nm are observed. Meanwhile, small Fe-based NPs are distributed either at the tip or inside of b-CNTs. Figure 1c shows a high-resolution TEM (HRTEM) image of PMF-800. The lattice distance is 0.21 nm, corresponding to the (211) crystal planes of the Fe_3C phase. The crystal plane angle of 68.4° is attributed to the (-211) and (211) planes of the Fe_3C phase. We further investigate the elemental distribution of a typical b-CNTs using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), as shown in Figure 1d–g. Along the b-CNTs, it is obvious that Fe (green) concentrates in the inside of the CNTs, while C (red) and N (orange) distribute on the whole CNT surface, further verifying formation of the BCNFNHs.

The Fe_3C content and graphitic qualities of the as-synthesized PMF-800 are evaluated through thermogravimetric analysis (TGA) and Raman spectroscopy techniques. The amount of Fe in PMF-800 is determined to be 38.1 wt%, according to the TGA result (Figure 2a). A Raman spectrum is used to study the degree of graphitization of the PMF-X samples because the D band (1360 cm^{-1}) and G band (1590 cm^{-1}) provide information on the disorder and crystallinity of sp^2 carbon materials, respectively. As given in Figures 2b and S2 and Table S1, PMF-800 shows the lowest $I_{\text{D}}/I_{\text{G}}$ value of 0.81, except for single-walled CNTs, indicating a high degree of graphitization, which can be attributed

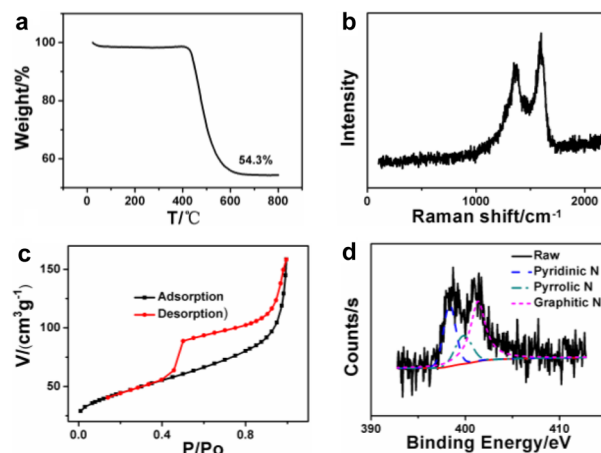


Figure 2. (a) TGA, (b) Raman, (c) N_2 adsorption/desorption isotherm, and (d) high-resolution N 1s XPS spectrum for the resultant PMF-800.

to formation of a bamboo-like microstructure and is in favor of improving the electrical conductivity. Figures 2c and S3 show the nitrogen adsorption/desorption isotherm of PMF-X samples. PMF-800 shows the biggest BET surface area ($151.2\text{ m}^2/\text{g}$) in all the investigated PMF samples. X-ray photoelectron spectroscopy (XPS) analysis (Figure S4) reveals that PMF-800 is mainly composed of C (89.6 at.%), N (3.74 at.%), O (6.22 at.%), and Fe (0.46 at.%), confirming that N and Fe have been successfully doped into the carbon composite. A high-resolution N 1s XPS spectrum (Figure 2d) of PMF-800 shows that there exist pyridinic, pyrrolic, and graphitic N. The amount of pyridinic N has been determined to be about 33.3%. Recently, some of reports have demonstrated that a high proportion of pyridinic N can increase current density, spin density, and the density of π states of the C atoms near the Fermi level, thus boosting O_2 reduction.⁶ Hence, the high proportion of doped pyridinic N in PMF-800 probably leads to enhanced intrinsic ORR activity.

During the synthesis, five important factors impact the formation of well-defined BCNFNHs. (1) The final annealing temperature is critical: when we reduce the final temperature to 700°C , only hollow and short nanotubes can be obtained (Figure S5a), whereas increasing the temperature to 800°C can lead to homogeneous BCNFNHs (Figure S5b). Higher annealing temperatures (900 and 1000°C) just produce irregular NPs (Figure S5c) or carbon nanosheets (Figure S5d). (2) The existence of both P123 and $\text{Fe}(\text{NO}_3)_2$ is the key to forming well-defined BCNFNHs. Without P123 in the synthesis, only nanoshell structures can be produced (named MF-800, Figure S6a). The use of only P123 and $\text{Fe}(\text{NO}_3)_2$ (named PF-800, Figure S6b) or P123 and melamine (named PM-800, Figure S6c) results in only a porous morphology. (3) Pluronic F127 is another interesting surfactant with structure similar to P123 and can form the linear micelle under special conditions. It has been reported to work as an effective soft template for the synthesis of Pt nanowires.⁷ We found that the BCNFNHs could also be prepared when P123 was replaced by F127 (Figures S6d and S7). (4) Meanwhile, the composites (i-PMF) produced by heating to high temperatures for 0 h show completely distinct microstructures from BCNFNHs. Increasing the temperature from 650 to 900°C , the morphologies appeared as corrugated slice sheets (650°C , Figure S8a), hollow or NP-filled carbon nanoshells (700°C , Figure S8b), shorter bamboo-like structure (750°C , Figure S8c), longer b-CNTs (800°C , Figure S8d), and a mixture of b-CNTs and disordered carbon (850 and 900°C ,

Scheme 1. Illustration of the Formation of the BCNFNHs

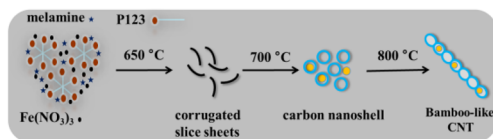


Figure S8e,f). (5) To further investigate the roles of Fe and P123, the effect of temperature on the morphology of the composites was investigated. It is obvious that i-MF-700 (without P123) possesses nanosheet morphology (Figure S9a) and i-MF-750 is the aggregated NPs (Figure S9b), while i-PM-700 (without Fe) and i-PM-750 respectively own a porous carbon plane (Figure S9c) and aggregated carbon thin film (Figure S9d) morphology.

Based on these considerations, a possible mechanism for the formation of BCNFNHs is proposed in Scheme 1. At low temperature (650 °C), ultra-thin carbon nanosheets were formed, and when the temperature reached 700 °C, Fe₃C NPs coated with a few carbon layers appeared. These Fe₃C@C-based NPs produced at high temperature, widely demonstrated for the synthesis of CNTs by the chemical vapor deposition method,⁸ could act as catalyst for the growth of b-CNTs under the assistance of P123 (soft template). Thus, Fe plays a key role in the formation of ultra-thin carbon nanosheets, and the Fe₃C NPs were trapped by the carbon shells at higher temperature (800 °C). Meanwhile, surfactant P123 (or F127) plays the role of 1D soft template (reported for the synthesis of nanowires),^{7,9} which could assist the 1D growth of carbon by catalytically linking rolled carbon nanosheets during the carbonation process. Without surfactant (P123 or F127), only irregular nanosheet structures can be produced (Figures S6 and S9). Thus, both P123 and Fe(NO₃)₃ are key to forming well-defined BCNFNHs, although an in-depth understanding of the mechanism of their formation is left for the future.

The electrocatalytic activity, stability, and MeOH tolerance of the as-synthesized PMF-800 were studied by CV and rotating ring-disk electrode (RRDE) techniques. To perform these tests, the as-prepared catalysts were redispersed in deionized water + isopropanol + 5% Nafion (v:v:v 20:1:0.075) to reach 2 mg/mL. Next, 42 μL of the catalyst ink was cast on the surface of a glassy carbon electrode and dried under an infrared lamp. As shown in Figures S10 and S11, relative to PMF-700, PMF-900, and PMF-1000, PMF-800 displays a superior ORR activity with more positive reduction peak potential, onset potential (E_{onset}), and higher reduction current density in 0.10 M KOH. Figure 3a shows typical RRDE voltammograms of PMF-800 and commercial Pt/C catalyst obtained at room temperature in O₂-saturated 0.10 M KOH solution. We can see that PMF-800 shows much higher electrocatalytic activity toward ORR than commercial Pt/C, as indicated by its 49 mV more positive half-wave potential ($E_{1/2}$) compared to commercial Pt/C. RRDE test results (Figure 3b) also show that the H₂O₂ yield measured with the PMF-800 catalyst remained below 7.7% at all potentials in 0.10 M KOH, corresponding to a high electron-transfer number of 3.99 (Figure 3c), close to that of the Pt/C catalyst (Figure 3b). This negligible H₂O₂ yield clearly confirms that PMF-800 has extremely high ORR catalytic efficiency. Figure 3d shows the Tafel plots of PMF-800 and commercial Pt/C, derived from Figure 3a. PMF-800 has a Tafel slope of 91.2 mV/decade in 0.10 M KOH, close to the 84.8 mV/decade of the Pt/C, indicating that PMF-800 has a good kinetic process for ORR.

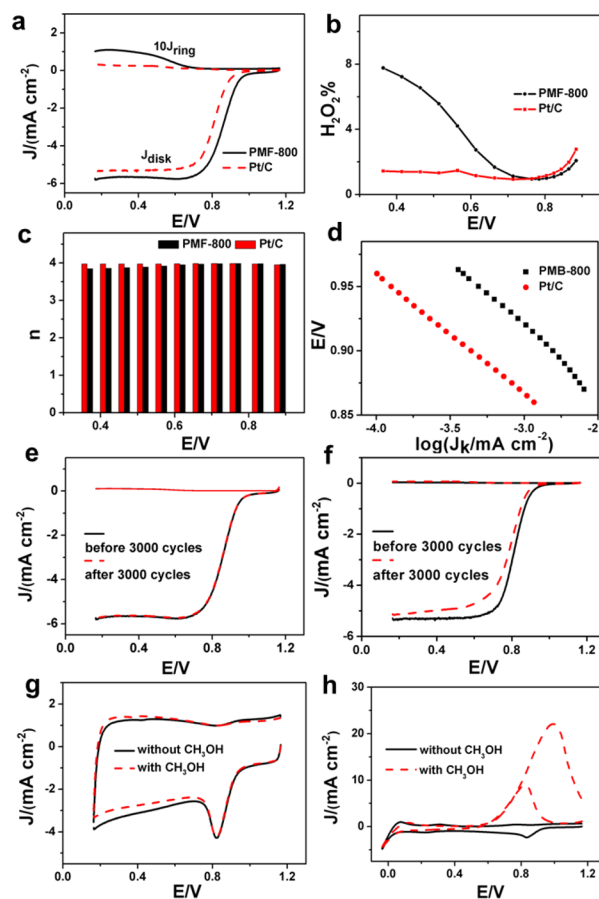


Figure 3. (a) RRDE voltammograms, (b) H₂O₂ yield, and (c) electron transfer number (n) of PMF-800 and Pt/C in O₂-saturated 0.10 M KOH at a scan rate of 5 mV/s, rotation rate = 1600 rpm. Linear sweep voltammograms (LSV) curves of (e) PMF-800 and (f) Pt/C for ORR in O₂-saturated 0.10 M KOH before and after 3000 cycles. CVs of (g) PMF-800 and (h) Pt/C in O₂-saturated 0.10 M KOH without and with 1.0 M CH₃OH. Scan rate: 50 mV/s.

PMF-800 also shows high stability for ORR in alkaline solution, as confirmed by the absence of an ORR polarization curve shift after 3000 cycles between 0.364 to 0.964 V (Figure 3e), while there was a 23 mV loss of half-wave potential for the Pt/C catalyst under the same conditions (Figure 3f), suggesting superior durability of the PMF-800 catalyst. Furthermore, the tolerance of the PMF-800 and Pt/C catalysts toward MeOH was determined by adding 1.0 M MeOH into 0.10 M KOH electrolyte. Figure 3g shows almost no change in the ORR peak current for PMF-800 after addition of MeOH; however, Figure 3h shows the typical inverse MeOH oxidation peaks in CVs for the Pt/C catalyst. These results suggest that PMF-800 has much better catalytic selectivity toward ORR than the commercial Pt/C catalyst.

Interestingly, our PMF-800 catalyst is also active and durable for ORR in acidic solution. As shown in Figure 4a, in acidic media, the ORR polarization curve of PMF-800 exhibits a high E_{onset} (ca. 0.886 V), close to that of the Pt/C catalyst (0.930 V). The H₂O₂ yield on the PMF-800 catalyst in acidic solution is below 4.1% over the whole potential range investigated (Figure 4b), revealing a four-electron-pathway dominated ORR process (Figure 4c). Kinetic currents (Figure 4d) derived from Figure 4a show a Tafel slope of 134 mV/decade at low overpotentials, close to 108.5 mV/decade for the Pt/C catalyst. The PMF-800 catalyst

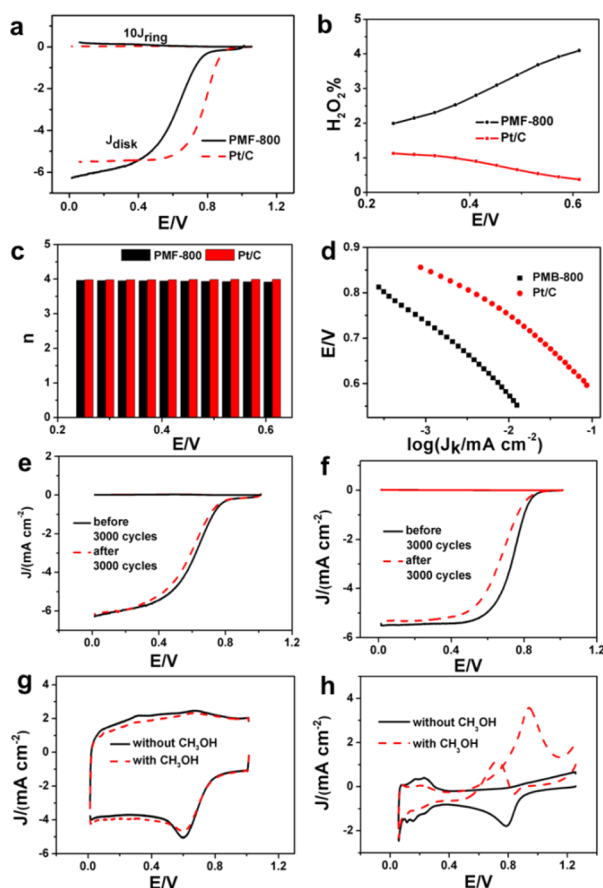


Figure 4. (a) RRDE voltammograms, (b) H_2O_2 yield, and (c) electron transfer number (n) of PMF-800 and Pt/C in O_2 -saturated 0.50 M H_2SO_4 (PMF-800) or 0.10 M HClO_4 (Pt/C) at a scan rate of 5 mV/s, rotation rate = 1600 rpm. LSV curves of (e) PMF-800 and (f) Pt/C for ORR in O_2 -saturated acidic solution before and after 3000 cycles. CVs of (g) PMF-800 and (h) Pt/C in O_2 -saturated acidic solution without and with 1.0 M CH_3OH . Scan rate: 50 mV/s.

shows much better stability for ORR than the Pt/C catalyst, as revealed by a much lower ORR polarization curve change on PMF-800 (Figure 4e) than on the Pt/C catalyst (Figure 4f). PMF-800 is tested for the possible crossover effect caused by MeOH. We found that, in the presence of 1.0 M MeOH, the peak current for PMF-800 is slightly changed (Figure 4g), whereas Pt/C shows a significant MeOH oxidation current (Figure 4h), suggesting that PMF-800 shows high selectivity for ORR with strong tolerance to crossover effect.

Based on the structural and compositional characterizations of PMF-800, we think that four important aspects should be responsible for its superior ORR activity and stability: (1) High percentage of pyridinic N (33.3%) doped into the b-CNTs can promote O_2 adsorption due to the reduced the local work function of carbon caused by the increase current density of the C atoms, and also enhanced hydrophilicity strengthening the electrolyte–electrode interaction. (2) Bamboo-like CNTs can offer more graphene edge, thus introducing more ORR active sites for larger turnover frequency per active site. (3) The Fe_3C NPs wrapped in the b-CNTs are electrochemically active for ORR due to their proper ability to adsorb oxygen.^{4a,10} (4) Recent studies also prove that the encapsulated metal NPs can lead to a unique host–guest electronic interaction and change the local work function of the CNT walls, making the outer surface of the carbon layer more active to ORR.¹¹ Overall, the excellent

electrocatalytic activity, excellent methanol crossover effect, and long-term stability of PMF-800 make it a promising low-cost, highly efficient ORR catalyst.

In summary, we developed a new one-step synthetic strategy for the controlled synthesis of heterostructured bamboo-like CNT/ Fe_3C NP hybrids by simply annealing a mixture of melamine, P123, and $\text{Fe}(\text{NO}_3)_3$. We found that both P123 (soft template) and $\text{Fe}(\text{NO}_3)_3$ (catalyst) play key roles in the formation of BCNFNHs. The BCNFNHs exhibit much higher ORR activity, better stability, and better methanol tolerance for ORR than the commercial Pt/C catalyst in 0.10 M KOH solution. Additionally, our new hybrid catalyst shows a comparable ORR onset potential and much better stability than the Pt/C catalysts in strong acidic solution, making it one of the best-performing non-precious-metal catalysts. This work provides a new protocol to construct novel N-doped CNT/ Fe_3C hybrid nanotubes and opens new avenues for the application of stable Fe_3C NPs-based composite materials in high-efficiency electrocatalysts for ORR.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, figures, and Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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