Mechanism of Hydrogen Generation Catalyzed by a Single Atom and Its Spin Regulation

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Cite This: J. Am. Chem. Soc. 2025, 147, 6193–6202 ACCESS Indext More Information Supporting Information ABSTRACT: Single-atom catalysts exhibit the excellent catalytic activity and selectivity, making them widely applicable in the fields of advanced materials, environmental science, and chemical synthesis. However, understanding the mechanism of single-atom

synthesis. However, understanding the mechanism of single-atom catalytic reactions, such as the hydrogen generation reaction, is still challenging, which notably hampers the optimization and precise control of the reaction. Here, we immobilize a single-metal atom model catalyst into a single-molecule electrical detection platform for in situ monitoring of the catalytic hydrogen generation process at the single-event level. In combination with theoretical and experimental studies, the catalytic mechanisms of the hydrogen generation reaction, especially the selection of the catalytic center

mization and precise e a single-metal atom al detection platform en generation process with theoretical and ms of the hydrogen of the catalytic center ontrol, are elucidated. In addition, a hydrogen generation process via quantum spin

through charge, spin, and orbital quantum control, are elucidated. In addition, a hydrogen generation process via quantum spininduced catalysis is observed, in which the turnover frequency increases by about 65 times at a magnetic field of 50 mT. This study provides valuable insights into the intrinsic mechanism of single-metal atom catalysis and opens up unique avenues for their precise control, thus offering a useful strategy for efficiently developing clean energy.

INTRODUCTION

Single-atom catalysts can achieve 100% atom utilization to maximize the use of catalytic active sites and improve catalytic efficiency,^{1–5} and have shown significant advantages in various fields such as biocatalysis,^{6,7} chemical synthesis,^{8–10} and energy storage.^{11,12} In particular, utilizing single-atom catalysis can enable low-carbon, high-efficiency, and pollution-free hydrogen production.^{13–16} However, the electronic structure of the catalytic site is highly sensitive to the external environment, such as defects, heteroatoms, ligands and supports, leading to different reaction pathways and efficiencies.¹⁷ Precise control of the catalytic sites, especially their charge and spin states, can greatly improve the catalytic performance and selectivity.^{18,19} Therefore, monitoring and regulating the reaction process of single-metal atom catalytic sites at the single-event level is invaluable for elucidating the catalytic mechanism and designing effective catalysts.

Single-molecule detection, especially single-molecule electrical detection, enables the visualization of molecular properties and dynamic behaviors of individual molecules with high temporal resolution.^{20–27} Using the molecule as the primary conductive channel in the single-molecule electrical platform, the device conductance detected during the reaction is precisely synchronized with the molecular structure.^{28,29} To date, single-molecule junctions have been utilized to study a wide range of chemical reactions, revealing their intrinsic mechanisms.^{24–27,30–33} In addition, single-molecule junctions can effectively introduce electric or magnetic fields to manipulate the charge and spin state distributions of fixed single-molecules, which is expected to regulate the corresponding chemical reactions. Therefore, when a single metal atom is introduced into a single-molecule junction through coordination assembly, the resulting single-molecule device is expected to be an ideal platform for monitoring and regulating single-atom catalysis.

The cobalt porphyrin molecule has a large conjugated ring structure consisting of four pyrrole subunits linked via methine bridges and a central cobalt metal ion. It exhibits high efficiency in catalytic reactions such as hydrogen generation and demonstrates the significant chemical stability during reactions, making it an ideal model for single-metal atom catalysis studies. In this work, we use cobalt porphyrin to simulate the single-metal atom catalytic center and achieve real-time monitoring of its catalytic hydrogen generation process through a graphene-molecule-graphene single-mole-

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Figure 1. Structure and characterization of single-molecule devices. (A) Schematic diagram of a cobalt porphyrin-based GMG-SMJ with the benzyl alcohol hydrogen evolution process (left) and corresponding catalytic reaction (right). (B) Gas chromatography after the ensemble catalytic reaction (top) and gas chromatography of solvent (bottom). (C) I-V curves before (black) and after molecular reconnection (green) at 290 K. (D) Reproducible IETSs for the cobalt porphyrin-based GMG-SMJs measured five times at 2 K. The lock-in second-harmonic technique is adopted at an alternating current modulation of 10.6 mV and a frequency of 661 Hz. Infrared and Raman spectra of used cobalt porphyrin molecule are calculated as well. The peaks corresponding to specific vibrational modes are marked in the IETSs ($V = h\omega/e$). The peaks of ν (C=C) (Ar) (~200 mV), ν (Co–N) (~120 mV), ν (C–H) (Al) (~370 mV), and ν (C–H) (Ar) (~390 mV) should be assigned to the molecular bridge. In particular, the peaks of ν (C=O) (~230 mV) and ν (N–H) (~440 mV) should be assigned to the amide bond.

cule junction (GMG-SMJ) platform. In combination with experimental and theoretical studies, external electric and magnetic fields are introduced into the single catalytic site to study the effects of charge, spin, and orbital states on catalytic reactions.

RESULTS AND DISCUSSION

Device Fabrication and Characterization. The singlemolecule device is prepared with the methods in the previous protocol.^{34,35} First, graphene is grown using chemical vapor deposition (CVD) and transferred onto a silicon wafer. Then, the graphene field-effect transistor is fabricated through multistep photolithography and thermal evaporation. The cobalt porphyrin molecule is synthesized specifically for this study with terminal amino groups. The molecule is covalently bonded to carboxyl-modified graphene point electrodes, forming stable GMG-SMJ (Figure 1A). Detailed procedures for molecular synthesis and single-molecule device fabrication are provided in the Supporting Information (Figures S1-S6). The catalytic reaction equation is shown on the right of Figure 1A. Compared to the gas chromatography of standard hydrogen (Figure S7) and N,N-dimethylformamide (DMF) solvent (Figure 1B, bottom), the ensemble gas chromatography demonstrates efficient hydrogen generation after the catalytic reaction (Figure 1B, top), proving the validity of cobalt porphyrin. The successful connection of a single cobalt porphyrin molecule can be verified through the currentvoltage (I-V) curves before and after molecular connection (Figure 1C). Binomial distribution analysis has indicated that approximately 15% of these devices exhibited successful

reconnection, and the probability of single-molecule connection is ~93%. In addition, the characteristic signals of the molecule in the super-resolution optical microscope (Figure S8) and inelastic electron tunneling spectroscopies (IETSs) (Figure 1D) further confirm the single-molecule connection. 36,37

Real-Time Measurement of Single-Metal Atom Catalysis. To elucidate the complex mechanism of singlemetal atom catalysis, the catalytic hydrogen generation on cobalt porphyrin is selected as the target system. A classic example of the hydrogen generation reaction is the formation of aldehyde from alcohol and the release of hydrogen in the presence of the catalyst (Figure 1A).³⁸ As a strong base and commonly used reducing agent in organic reactions, potassium tert-butoxide (KOtBu) is capable of reducing Co(II) to Co(I) (Figure 2A).^{39,40} Current-time (I-t) curves are conducted on cobalt porphyrin-based GMG-SMJs (Figure 2B) in DMF solvent and KOtBu solution (10⁻⁵ M in DMF solvent) at 290 K with nitrogen atmosphere protection. After the addition of a 10^{-5} M KOtBu solution, the device conductance shows a slight decrease (Figure 2B). Electrical tests exhibit a single conductance before the addition of KOtBu in the GMG-SMJ, which can be attributed to the Co(II) species. After the KOtBu addition, a new conductance state appears and dominates. Concentration-dependent experiments with KOtBu show that the proportion of the lower conductance state increases with increasing concentration, indicating more reduction by KOtBu (Figure S9), and the lower conductance state can be attributed to the Co(I) species. In addition, the coordination effect of KOtBu cannot stabilize the intermedi-



Figure 2. Single-metal atom catalysis on cobalt porphyrin-based GMG-SMJs. (A) Proposed mechanism for the Co(II)–Co(I) redox process. (B) I-t curves, corresponding enlarged curves, and histograms at 290 K with a bias voltage of 0.34 V in DMF solvent (top) and 10⁻⁵ M KOtBu solution (bottom). (C) Proposed mechanisms for the complete single-metal atom catalysis process. (D) I-t curves at 290 K with a bias voltage of 0.34 V (left) and corresponding histograms (right) after adding benzyl alcohol. (E) Enlarged I-t curves(left) and transmission spectra (right) of five states.

ates (Table S1). Therefore, the structures calculated in this study no longer take into account the influence of KOtBu. By varying the base promoters with different basicities including KOMe, KOtPr, and KOtBu (Figure S10), the degree and rate of the reduction process increase sequentially due to their increased electron-donating abilities (Figures S11 and 12). In the crystal field of the Co(I) complex, more empty orbitals are available, which facilitates the catalytic process of hydrogen generation.

When benzyl alcohol is added, five conductance states appear at the bias voltage of 0.34 V as shown in Figure 2D. The magnified view clearly illustrates the hydrogen generation reaction process (Figures 2E,left and S13). These fluctuations can be attributed to the catalytic cycle as shown in Figure 2C. Based on the reaction process with the addition of KOtBu (Figure 2B), the orange conductance state can be attributed to the Co(II) species, and the red conductance state corresponds

to the Co(I) species. Upon the addition of benzyl alcohol, the light blue conductance state emerges from the red conductance state, which can be attributed to the Co(III)OH intermediate in oxidative addition, and then is converted to the blue conductance state. Due to the entire catalytic cycle, the blue state can be attributed to the Co(III)HH intermediate. There are two transition pathways for the blue conductance state. On one hand, the Co(III)HH intermediate (blue conductance state) can revert to Co(I) species (red conductance state), which can be denoted as direct hydrogen generation. On the other hand, the Co(III)HH intermediate (blue conductance state) can revert to the Co(III)OH intermediate (light blue conductance state) through the reaction with benzyl alcohol and generate hydrogen, completing the assisted hydrogen generation reaction. In addition, an additional green conductance state emerging from the Co(I) species is observed, which is preliminarily attributed to the Co(III)CH

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Figure 3. Effects of temperature and voltage on single-metal atom catalysis in cobalt porphyrin-based GMG-SMJs. (A) I-t curves, corresponding enlarged curves, and histograms at 0.25, 0.31, 0.32, 0.34, and 0.36 V with the temperature of 290 K. (B) I-t curves, corresponding enlarged curves, and histograms at 290, 295, 300, 305, and 310 K with the bias-voltage of 0.34 V. (C) Proportions of five conductance states at different temperatures. The error bars are derived from the statistics of three independent devices. (D) Proportions of five conductance states at different bias voltages. The error bars are derived from the statistics of three independent devices. (E) Proportions of five conductance states for different substituent groups of benzyl alcohol. The error bars are derived from the statistics of three independent devices. (F) Rate constants of Co(I)–Co(III)OH and Co(I)–Co(III)CH for different substituent groups of benzyl alcohol. The error bars are derived from the statistics of three independent devices. (G) Radial bar plots of proportions for Co(I) and Co(III)OH (white numbers in the circle) with increased deuterated benzyl alcohol ratios (black numbers on the outer ring). (H) Arrhenius plots for Co(I)–Co(III)OH (left) and plots of three independent devices.

intermediate based on the catalytic reaction mechanism reported in previous studies.^{41,42} Based on the above speculations, it is found that the Co(III)CH intermediate

does not enter the catalytic cycle. Theoretical simulations of the transmission spectra of the five hypothesized structures show that the order of conductance at the Fermi level is



Figure 4. Charge, spin, and orbital control of single-metal atom catalysis. (A) Charge population of intermediate states. (B) Spin population of intermediate states. (C) Molecular orbital occupation diagram and part of the frontier orbitals treated by wave function biorthogonalization. The energies are given in eV.

Co(III)HH > Co(III)OH > Co(III)CH > Co(II) > Co(I)(Figures 2E and S14). Co(I) and Co(II) do not have high-spin states, and the conductance order dominated by perturbed highest occupied molecular orbitals (p-HOMO) is Co(II) > Co(I) (Figure 2E,right). For Co(III)CH, Co(III)OH, and Co(III)HH, the formation of high-spin Co-C, Co-O, and Co-H intermediates leads to the emergence of new conductivity peaks near the Fermi level, significantly increasing their conductivity (Figures S15–S19). The order of the singly occupied molecular orbital (SOMO) peaks of Co(III)CH, Co(III)OH, and Co(III)HH is Co(III)HH > Co(III)OH > Co(III)CH (Figure 2E, right), which also corresponds to their respective conductivities. In addition, through calculations of the direct dehydrogenation step between cobalt porphyrin and benzyl alcohol, a reaction barrier of up to 88 kcal/mol demonstrates that no side reaction to produce phenoxy anion

occurs (Figure S20). These are consistent with the experimental predictions, which confirms the proposed reaction mechanism.

Temperature and Voltage Dependence of Single-Metal Atom Catalysis. First of all, temperature-dependent and bias voltage-dependent experiments are conducted on the cobalt porphyrin-based single-molecule devices to monitor the conductance state evolution. I-t curves are recorded for three devices at ten different biases (0.20, 0.25, 0.30, 0.31, 0.32, 0.33, 0.34, 0.35, 0.36, and 0.37 V) (Figures 3A and S21), with two additional sets shown in the Supporting Information (Figures S22–S25). At 0.25 V, two conductance states predominate, corresponding to Co(II) and Co(I), respectively. As the bias increases to 0.3 V, another conductance state (Co(III)OH) appears. At 0.32 V, all five conductance states can be observed. The extent and rate of the reaction increase with increasing bias voltage, which suggests the efficient catalysis of the reaction in the electric field. Temperature-dependent I-t curves are recorded for three devices at ten different temperatures (290, 295, 300, 305, 310, 315, 320, 325, 330, 335 K) (Figures 3B and S26), and the other two sets can be found in the Supporting Information (Figures S27–S30). As the temperature increases, the reaction rate is progressively intensified. As temperature and bias voltage increase, the proportion of Co(II) decreases, and the proportions of Co(III)OH, Co(III)CH, and Co(III)HH increase (Figure 3C,3D).

Next, a series of dependent experiments (alcohol typedependent and isotope-dependent experiments) are conducted to confirm the attributions and the reaction mechanisms. Alcohol type-dependent experiments are conducted at 290 K and 0.34 V to study the effect of electron-withdrawing substituents on the para-position of benzyl alcohol on the single-metal atom catalysis (Figures S31-S33). The electronwithdrawing ability is determined by the electrostatic potential (Figure S34). As the electron-withdrawing strength of the substituent increases, the proportions of the high conductance states (Co(III)HH, Co(III)OH, and Co(III)CH) increase, while the proportion of the lowest conductance state (Co(I))decreases (Figure 3E). The conversion rates from Co(I) to Co(III)OH (k(Co(I)-Co(III)OH)) and from Co(I) to Co(III)CH (k(Co(I)-Co(III)CH)) increase with increasing electron-withdrawing strength (Figure 3F). This is because the electron-withdrawing group at the para-position reduces the electron density of the O-H/C-H bonds, weakening the bonds and accelerating the insertion reaction.

Isotope-dependent experiments are conducted at 290 K and 0.34 V (Figures \$35-37). The extent and rate of the hydrogen generation reaction decrease with increasing deuterated benzyl alcohol ratio (n_D) (Figures 3G and S38), which can be explained by the fact that it requires more energy to break as the proportion of O-D bond increases.⁴³ Proton inventory for the Co(I)-Co(III)OH process shows a linear relationship between $k_{\rm n}/k_{\rm H}$ ($k_{\rm n}$ denotes the reaction of the system with different proportions of deuterated benzyl alcohol, and $k_{\rm H}$ denotes the reaction of the system with benzyl alcohol) and $n_{\rm D}$, indicating that a single proton transfer is involved (Figure S39). Kinetic isotope effect (KIE), on behalf of $k_{\rm H}/k_{\rm D}$, is calculated as \sim 1.61, which indicates the presence of a bondbreaking process. Proton inventory for the Co(III)HH-Co(III)OH process also shows a linear relationship between $k_{\rm n}/k_{\rm H}$ and $n_{\rm D}$, further indicating the involvement of a single proton transfer to generate hydrogen and the new pathway for hydrogen generation (Figure S40). The lifetime (τ) of each species is determined by single-exponential fitting of the time intervals in the idealized I-t curves using the QuB software. The conversion rate constant from Co(I) to Co(III)OH (k = $1/\tau$) is calculated from the measured lifetimes. The equilibrium constant K for the Co(I)-Co(III)OH process is determined by the peak area ratios in I-t histograms at ten different temperatures, and the thermodynamic parameters for the Co(I)-Co(III)OH transition are derived using the Van't Hoff equation: $\Delta H = 1.24 \pm 0.80$ kcal/mol, $\Delta S = 0.07$ cal/ (mol K), and $\Delta G = 1.22 \pm 0.78$ kcal/mol (Figure 3H).

Quantum Control of Single-Metal Atom Catalysis. There are two probable reaction pathways for single-metal atom catalysis, involving different intermediates (O center: Co(III)OH and C center: Co(III)CH). The identification of carbon and oxygen center is of crucial importance to

understanding the reaction mechanism of single-metal atom catalysis. The reaction mechanisms of a single-metal atom with different C or O reactive sites are analyzed through charge distribution, spin distribution, and orbital occupancy. First, the charge population analysis of the intermediates in the hydrogen generation process is carried out (Figure 4A). By comparing Co(III)OH with Co(III)CH, it can be observed that the electronegativity of the O center (-0.63 a.u.) in the Co(III)OH is greater than that of the C center (-0.16 a.u.) in Co(III)CH. This results in a more stable σ -bonding and antibonding system with the Co center, stabilizing the Co(III)OH other than Co(III)CH. The electronegativity of H changes from 0.07 to -0.52 a.u. during the process from Co(III)OH to Co(III)HH, whereas the electronegativity of H needs to change from 0.32 to -0.52 a.u. during the process from Co(III)CH to Co(III)HH. The larger change in local electronegativity indicates a greater barrier to overcome, making the transition from Co(III)CH to Co(III)HH more difficult. The local electronegativity differences in the transition states also support this conclusion (Figure S41). Therefore, charge regulation of the single-metal atom catalysis mechanism contributes to the reaction pathway with the O-centered intermediate.

Spin delocalization can modulate the catalytic activity and selectivity to determine the reaction mechanism. For 3d metals, the crystal field splitting energy is quite small, making it easier to form open-shell structures.44-46 The electronic structure of the molecule can be affected by spin multiplicity and the degree of spin delocalization, resulting in different bond lengths.^{47,48} By examining the spin population of complexes, a significant amount of spin localization is observed in the intermediates of the single-metal atom catalysis (Figures 4B and S42). The stability of intermediates can be judged by the degree of spin delocalization from the Co center to its ligands (porphyrin ring and benzyl alcohol). In Co(I), there is no spin delocalization from the Co center to benzyl alcohol due to the great distance between these two species, indicating that bond formation does not occur in the benzyl alcohol ligand in Co(I) at the beginning. However, significant spin delocalization from the Co center to the O center and H atom can be observed in Co(III)OH and Co(III)HH, respectively, indicating that these intermediates are more stable. Spin delocalization enhances the interaction between the Co center and the ligand, shortens the Co-O bond length and stabilizes the Co(III)OH intermediate. In the Co(III)CH intermediate, no spin delocalization from the Co center to the C center is observed, indicating that the stability of Co(III)CH is poor. This well explains why no further hydrogen generation reaction can occur at the C center. The spin population of transition states can also confirm the above inference (Figure S43). Therefore, the spin delocalization can be utilized to regulate single-metal atom catalysis by efficiently selecting active centers.

Furthermore, orbital occupancy is also investigated to elucidate the mechanism. To study the bond formation between these two species, a molecular orbital occupancy diagram is drawn using the wave function biorthogonalization (Figure 4C). Co(II) is reduced to Co(I) by KOtBu, then the whole system undergoes a carbon center or an oxygen center process. A σ (Co-O) bond is formed by an O-centered process, with bonding and antibonding orbital energies of -7.22 and -7.03 eV, respectively. In contrast, a σ (Co-C) bond is formed through a C-centered process, with bonding



Figure 5. Spin-regulated single-metal atom catalysis under magnetic fields. (A) Energy diagram for single-metal atom catalysis. The energies are given in kcal/mol. Core structures of intermediates are given. The spin state and total charge are marked out. (B) I-t curves, corresponding enlarged curves, and histograms at 10, 20, 30, 40, and 50 mT under 290 K and 0.34 V. (C) Proportions of Co(I) and Co(III)OH states under different magnetic fields. The error bars are derived from the statistics of three independent devices. (D) DOS of Co 3*d* and O 2*p* in Co(III)OH. (E) DOS of Co 3*d* and H 1*s* in Co(III)HH.

and antibonding orbital energies of -6.14 and -5.06 eV, respectively, which are significantly higher than orbital energies that occur via the O-centered mechanism. This further proves that the single-metal atom catalysis can be regulated through orbital occupancy that occurs at the O center.

Quantum Spin Regulation of Single-Metal Atom Catalysis. By theoretically simulating the potential energy surface, it can be determined that the ligands induce high-spin intermediates (Table S2). For the Co(III)CH pathway, the reaction energy barrier is notably higher than that of the Co(III)OH pathway. In the observed catalytic cycle, the hydrogen generation pathway from Co(III)HH to Co(III)OH can be detected (Figure 2C-E), which is verified in the calculated potential energy surface (Figure 5A). The energy barrier of the hydrogen generation process from the Co(III) HH to Co(III)OH (2.97 kcal/mol) is notably lower than that of the reversible process from Co(III)OH to Co(III)HH (~5.18 kcal/mol), enabling the hydrogen generation process to proceed smoothly. In addition, the electric field can notably lower the energy of TS2, thereby reducing the barrier from Co(III)OH to Co(III)HH (Figure S44). The linear dependence observed in isotope-dependent experiments for the hydrogen generation process from Co(III)HH to Co(III)OH (Figure S40) suggests that a single proton transfer also confirms the speculated mechanism.

To further investigate the spin catalysis on single-metal atom catalytic reactions, magnetic field-dependent experiments are conducted (Figures 5B, S45, and 46), which shows that the magnetic field can efficiently promote the hydrogen generation reaction and accelerate the reaction rate (Table S3). Under a

magnetic field of 50 mT, the turnover frequency (TOF) can reach up to $\sim 6.5 \times 10^5$ h⁻¹, an increase of ~ 65 times compared to the case without magnetic field. With increasing magnetic field strength, the proportion of Co(I) decreases, while the proportion of Co(III)OH increases significantly (Figure 5C). To further explain the mechanism of the spincatalyzed hydrogen generation reaction, the spin-polarized density of states (DOS) before and after spin polarization is calculated. The results indicate that there is no significant change in the overlap between Co 3d and O 2p orbitals of Co(III)OH (Figure 5D), but there is an increased overlap between Co 3d and H 1s orbitals in Co(III)HH (Figure 5E). This further suggests that Co(III)HH is the key step in singlemetal atom catalysis, which is consistent with the ratedetermining step in the potential energy surface. Applying an external magnetic field in catalytic reactions can modulate the spin state and orbital hybridization of the magnetic center, synergistically affecting ligand-induced spin selectivity. By altering the spin-orbital configuration, the ferromagnetism of the Co center is activated, significantly affecting its catalytic performance. Here, spin polarization is utilized to reflect the influence of the magnetic field. In this process, the DOS of bonding orbitals shows efficient magnetic field regulation, indicating the successful occurrence of spin-catalyzed reactions under a magnetic field.

CONCLUSIONS

In this work, a representative hydrogen generation reaction catalyzed by a single-metal atom is monitored on a singlemolecule electrical detection platform at the single-event level, which helps to understand the complex catalytic reaction process. Both experimental and theoretical studies consistently clarify the controversial mechanism of the hydrogen generation reaction, elucidating the effects of charge, spin, and orbitals on the selection of the oxygen-centered mechanism. In addition, under a magnetic field, an effect of quantum spin-induced catalysis has been discovered, which significantly increases the TOF by a factor of approximately 65 times in comparison with that under no magnetic field. This work contributes to a deeper mechanistic understanding of single-atom catalytic reactions and provides promising prospects for their further applications, driving the innovation in chemistry, materials, and energy.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c17722.

Experimental section including molecular synthesis and the fabrication process of single-molecule junctions, statistical analysis of single-molecule connections, basicity-dependent experiments, theoretical calculations, different electrical characterizations, and atomic coordinates (PDF)

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The authors declare no competing financial interest.

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