Substitutional Doping for Aluminosilicate Mineral and Superior Water Splitting Performance

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Abstract

Substitutional doping is a strategy in which atomic impurities are optionally added to a host material to promote its properties, while the geometric and electronic structure evolution of natural nanoclay mineral upon substitutional metal doping is still ambiguous. This paper first designed an efficient lanthanum (La) doping strategy for nanotubular clay (halloysite nanotube, HNT) through the dynamic equilibrium of a substitutional atom in the presence of saturated AlCl3 solution, and systematic characterization of the samples was performed. Further density functional theory (DFT) calculations were carried out to reveal the geometric and electronic structure evolution upon metal doping, as well as to verify the atom-level effect of the La doping. The CdS loading and its corresponding water splitting performance could demonstrate the effect of La doping. CdS nanoparticles (11 wt.%) were uniformly deposited on the surface of La-doped halloysite nanotube (La-HNT) with the average size of 5 nm, and the notable photocatalytic hydrogen evolution rate of CdS/La-HNT reached up to 47.5 μmol/h. The results could provide a new strategy for metal ion doping and constructive insight into the substitutional doping mechanism.

Keywords: Aluminosilicate mineral, Halloysite nanotubes, La doping, Photocatalytic hydrogen evolution, DFT calculations

Background

Aluminosilicate minerals (e.g., kaolinite [1–3], zeolite [4, 5], montmorillonite [6, 7], and halloysite [8–13]) have been extensively investigated as catalyst support materials because they are non-toxic to the environment and abundantly available inexpensively from natural deposits. A number of techniques have been used to enhance the functionalities of support materials, such as polymer coating [14, 15], carbon coating [8], and atomic doping [16–19]. Doped aluminosilicate minerals can form in nature, but their synthesis in a laboratory allows for various properties with the specified dopants [20–23]. Incorporating metal ions into the aluminosilicate layer structure makes the corresponding nanomaterial attractive for various applications, including catalysis [24–26], controlled release of pharmaceuticals [27, 28] as well as lithium ion batteries [29, 30]. Recently, based on density functional theory (DFT) computations, the stability, electronic, and mechanical properties of the nanostructured aluminosilicates, like imogolite, halloysite, and chrysotile, have been revealed [31]. However, the substitutional doping mechanism and the electronic structure evolution of a metal into the aluminosilicates are still ambiguous [32, 33].

Towards the goal of improving our understanding of this mechanism, we designed an efficient doping strategy for one of the representative aluminosilicate minerals (halloysite nanotube [34–36], HNT) through the dynamic equilibrium of a substitutional atom in the presence of saturated AlCl3 solution, which contained lanthanum salt. Then, a substitutional atomic doping strategy based on La doping into the HNT structure and the replaced part of the Al atom from the Al–O sheet is presented. Halloysite (HNTs, Al2Si2O5(OH)4·nH2O), as a natural clay mineral, contains octahedral gibbsite Al(OH)3 and tetrahedral SiO4 sheets, and it also consists of hollow cylinders formed by multiple rolled layers. CdS is an attractive semiconductor material that can convert solar energy to chemical energy under visible-light irradiation. Incorporating CdS nanoparticles into La-HNTs and its corresponding water splitting performance could demonstrate the effects of La doping. The

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diffusion process of Al\(^{3+}\) saturated solution and the alumina sheets from halloysite, the change of crystal shapes and surface structures, and the possibility of enhanced catalytic activity were investigated in detail. The microstructures and morphologies of samples were characterized, and the interfacial structure between CdS and La-HNT were investigated. The photocatalytic hydrogen activity was evaluated and the role of La-HNT for enhancing catalytic activity of CdS/La-HNT was also investigated.

Methods

Experimental Section

Materials Preparation

Halloysite nanotubes (HNT) were obtained from Hunan, China. All chemicals were analytical grade and used without further purification. HNT were pretreated via emulsion dispersion, filtering, washing with distilled water, and drying for 8 h at 313 K. La-HNT were synthesized by a modified hydrothermal route. An amount of 34.3 g of AlCl\(_3\) was dissolved into 60 mL deionized water to form AlCl\(_3\) supersaturated solution, while 3 mmol HNT and 6 mmol La(NO\(_3\))\(_3\)·6H\(_2\)O were dissolved in deionized water (5 mL), respectively. Then La(NO\(_3\))\(_3\)·6H\(_2\)O solution and the HNT slurry were added to AlCl\(_3\) supersaturated solution to form a suspension. The resulting suspension was stirred for 10 min in a polypropylene beaker and sonicated for 10 min to break up aggregations of starting material. The volume was limited into 70 mL (L/S = 70–80). The mixture was transferred into a Teflon bottle (100 mL) and treated under auto-generated pressure without stirring at 373 K for 48 h. The autoclave was naturally cooled to room temperature, and the obtained precipitates were filtered and washed several times with deionized water, and finally dried at 353 K in vacuum (denoted as La-HNT). For comparision, acid-treated HNT synthesized by 1.00 g HNT were dissolved in 250 mL of 6 M HCl solution at 373 K in a water bath. The reaction was carried out in a conical flask for 4 h with constant stirring. The conical flask was naturally cooled to room temperature, and the obtained precipitates were filtered and washed several times with deionized water, and finally dried at 353 K in vacuum (denoted as acid-treated HNT).

CdS/La-HNT were synthesized by using the Successive Ionic Layer Adsorption and Reaction (SILAR) method, 3 mmol La-HNT was dissolved into 50 mL 0.5 M Cd(NO\(_3\))\(_2\) ethanol solution for 5 min, rinsed with ethanol, and then dissolved for another 5 min in a 50 mL 0.5 M Na\(_2\)S methanol solution, and rinsed again with methanol. Such an immersion cycle was repeated several times until the desired deposition of CdS nanoparticles was achieved. Then, the obtained precipitates were filtered and washed several times with deionized water, and finally dried at 353 K in a vacuum (denoted as CdS/D-Lax-HNT).

Characterization

X-ray photoelectron spectroscopy (XPS) analysis was performed on using a Thermo Fisher Scientific K-Alpha 1063 spectrometer equipped with an Al Kα monochromatic X-ray source. The test chamber pressure was maintained below 10\(^{-9}\) mbar during spectral acquisition. The XPS binding energy (BE) was internally referenced to the C 1s peak (BE = 284.1 eV). The crystalline phases were identified by XRD analysis using a RIGAKU D/max-2550VB1 18-kW powder diffractometer with Cu Ka radiation (\(\lambda = 1.5418\) Å). The data were collected in the scanning range 2θ = 10–80°, with a scanning speed of 2°/min. FTIR spectra were recorded using a Nicolet 5700 spectrophotometer. The specific surface area was calculated from the nitrogen adsorption isotherms using the Brunauer–Emmet–Teller (BET) equation. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-200CX instrument equipped with an energy dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 200 kV. (PL) spectrum of the sample was detected on a Hitachi H-4500 fluorescence spectrometer using a Xe lamp as the light source. UV–vis spectra of samples in aqueous solution were obtained using a UV-2400 (Shimadzu Corp., Japan) spectrometer. Solid state \(^{29}\)Si and \(^{27}\)Al MAS NMR spectra were recorded using a Bruker AMX400 spectrometer in a static magnetic field of 9.4 T at a resonance frequency of 79.49 MHz. The electrochemical analysis was carried out in a conventional three-electrode cell using a platinum-black wire and saturated calomel electrode (SCE) as the counter electrode and reference electrode, respectively. The working electrode was prepared on FTO (fluorine tin oxide) conductor glass. In detail, 20 mg of sample was added into 10 mL ethanol and formed a uniform suspension. As in a standard spin-coating process, the ethanol suspension was spread onto FTO glass, whose side part was previously protected using Scotch tape. The spinning was at a high speed of 150 rps and then dried in an oven at 70 °C for 1 h. The transient photocurrent responses of different samples were measured in 0.1 M Na\(_2\)S + 0.02 M Na\(_2\)SO\(_3\) aqueous solution under visible-light irradiation (≥420 nm) at 0 V vs. SCE. The illuminated area of the working electrode is 2 cm\(^2\). The photoelectrochemical experiment was performed using a CHI-660A electrochemical workstation (ChenHua Instruments Co. Ltd., Shanghai, China). The electrochemical impedance spectroscopy (EIS) was measured with a CHI-660A electrochemical workstation (ChenHua Instruments Co. Ltd., Shanghai, China), and the electrolyte consisted of 0.01 mol/L potassium hexacyanoferrate (III), 0.01 mol/L potassium hexacyanoferrate (II), and 0.5 mol/L KCl. The applied potential was open circuit potential (OCP).
Photocatalytic Reaction

Water splitting reactions were carried out in a gas-closed circulation within a vacuum. A sample of 100 mg photocatalyst powder was dispersed in a 300-mL aqueous solution of 0.1 M Na₂S and 0.1 M Na₂SO₃. The light source was a 300-W Xe lamp, and the light intensity reaching the surface of the reaction solution was 135 mW/cm². The amount of H₂ evolution was determined using a gas chromatograph (Agilent Technologies: 6890 N).

Computational Details

All calculations were performed with the CASTEP code, based on first-principle density functional theory (DFT). The local density approximation (LDA) potential was used for the calculations. The ultrasoft pseudo-potential plane-wave formalism and an energy cutoff of 400 eV were used. The Monkhorst-Pack grid with $3 \times 3 \times 1$ $k$-points mesh was used for the accurate calculation of DOS results, while Gamma point was used during geometry relaxation. The self-consistent total energy in the ground state was effectively obtained by the density-mixing scheme. For geometry optimizations, the convergence threshold for self-consistent field (SCF) tolerance was set to $1.0 \times 10^{-6}$ eV/atom, all forces on the atoms were converged to less than 0.03 eV/Å, the total stress tensor was reduced to the order of 0.05 GPa, and the maximum ionic displacement was within 0.001 Å. The cell parameters and atomic coordination of the structures were optimized using a Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization algorithm.

Results and Discussion

The integrity of morphology is important to ensure the success of doping because acid can damage the structure of halloysite while saturated AlCl₃ solution will not. TEM images of HNT and La-HNT are shown in Fig. 1. HNT shows a multilayer tubular structure 0.7–1.5 µm in length, with a 50–75-nm outer diameter, and a 10–30-nm inner diameter (Fig. 1a). After La doping, the typical tubular morphology has retained with the La content of 4.2% (Fig. 1b). For the acid-treated HNT, the typical tubular morphology was also retained (Additional file 1: Figure S1a), but amorphous.

The structure of HNT can be influenced by doping due to the larger size of the La atom used to replace the Al atom. For La-HNT, the characteristic data of halloysite (JCPDS card No. 29-1487) can be observed in Fig. 2a and Additional file 1: Table S1, which indicate that the crystalline phase of La-HNT has remained. The slight shift of the first peak in La-HNTs is attributed to the replacement of Al atoms by larger size La atoms, which imparts the enlargement of the (001) interlamellar spacing. However, there is only a broad peak centered at 22° for acid-treated HNT (Additional file 1: Figure S1b), which indicates that there is amorphous silica. The FTIR spectra of HNT and La-HNT are shown in Fig. 2b, and the relative assignment of each vibrational peak are listed in Additional file 1: Table S2. For HNT, these assignments are based on the previous literatures [37–40]. For La-HNT, the O–H deformation vibration of the inner Al–OH groups at 909 cm⁻¹ and the Al–OSi deformation vibration of Al–O tetrahedral sheets at 553 cm⁻¹ shift to 915 and 544 cm⁻¹, respectively. However, the gibbsite octahedral sheet of halloysite is completely destroyed and the Al–O stretching bands disappear for the acid-treated HNT (Additional file 1: Figure S1c). All of these observations prove the successful La doping into the structure of HNT and the change of the HNT structure influenced by La doping. The $^{27}$Al CP/MAS NMR spectra of HNT and La-HNT samples are presented in Fig. 2c. The resonance signal at ~3 ppm is assigned to 6-coordinated Al. The resonance signal at 64 ppm is attributed to the 4-coordinated Al shifting to 58 ppm after La doping, indicating that the environment of the Al atom was influenced by La doping. However, there are three peaks at −111.32, −101.70, and −91.71 ppm in the acid-treated HNT, identified as Si(OSi)₄.
Si(OSi)$_2$OH, and Si(OSi)$_2$(OH)$_2$ (Additional file 1: Figure S1d), respectively. The nitrogen sorption isotherms of HNT and La-HNT are shown in Fig. 2d, and the relative data are summarized in Additional file 1: Table S3. The $S_{BET}$, pore volume, and average pore diameter of La-HNT are 59 m$^2$/g, 0.37 cm$^3$/g, and 25 nm, respectively. The $S_{BET}$ and pore volume values of La-HNT is lower than that of HNT (82 m$^2$/g, 0.41 cm$^3$/g), while its average pore diameter (25 nm) is higher than that of HNT (20 nm). However, the $S_{BET}$ value and pore volume for the acid-treated HNT are three times higher than that of HNT (Additional file 1: Figure S1e). All of these results demonstrate that La doping influences on the structure of HNT, given that the $S_{BET}$ for La-HNT is lower than that of HNT, and there is a decrease in total pore volume. The decreased $S_{BET}$ and pore volume could be assigned to the part of halloysite layers collapsed, and the increased pore size could be associated with the Al atom being replaced by the La atom, consistent with the XRD and FTIR analyses [18]. Hence, it is speculated that La-HNT can serve as an excellent support by changing the chemical and structure performance of halloysite, and thus could contribute to the enhanced catalysis activity for HNT-based catalytic nanocomposite materials.

To confirm the effects of La doping, CdS nanoparticles were deposited on the surface of La-HNT and HNT. Figure 3a–c, e clearly shows that the surface of HNT and La-HNT are well covered with a continuous, dense, and uniform CdS nanoparticle layer with a thickness of about 5 nm. However, the La element has not been detected in the CdS/La-HNT sample (inset in Fig. 3e). The disappearance of the La element in the CdS/La-HNTs may be attributed to the shelter of the CdS nanoparticle layer, plus the relevant low La element. The ratio of CdS in CdS/HNT to CdS/La-HNT is 11 wt.%. Figure 3d, f shows a typical HRTEM image of the layer of CdS nanoparticles coating on the surface of the host with a diameter of 5 nm, corresponding with the particle size of 5 nm calculated by Scherrer’s equation (Additional file 1: Figure S2).

The optical properties of HNT, La-HNT, CdS/HNT, and CdS/La-HNT composites are characterized by UV–vis diffuse reflectance spectroscopy (Fig. 4a). The absorption edges of CdS/HNT and CdS/La-HNT are at 554 and 562 nm, respectively, and CdS/La-HNT shows stronger absorption intensity than CdS/HNT in the visible light region. The La-HNT composites present no absorption in the UV region, and the absorption characteristics are similar to those of HNT in the aspect of wide absorption in the visible light region. The as-obtained $E_g$ values are 2.31 and 2.25 eV for CdS/HNT and CdS/La-HNT, respectively. The catalytic performance of La-HNT for water splitting was evaluated to reveal how the doping process and corresponding microstructure change affects macroscopic properties. Photocatalytic H$_2$ evolution of CdS/HNT and CdS/La-HNT (Fig. 4b) was conducted in an aqueous solution containing SO$_4^{2-}$ and S$^{2-}$ ions as sacrificial reagents under simulated conditions.
solar light irradiation [41–43]. The results show that the photocatalytic H₂ rate of CdS/La-HNT (47.5 μmol/h) is higher than that of CdS/HNT (26.0 μmol/h) under the same reaction conditions (Additional file 1: Table S4), and CdS/La-HNT and CdS/HNT show a higher hydrogenation rate than most of the previously reported CdS-based photocatalysts from the literatures [43–45]. To find out whether the higher photocatalytic H₂ rate derives from La doping, the transient photocurrent responses of CdS/HNT and CdS/La-HNT were measured in Fig. 4c. It can be clearly seen that the photocurrent rises to a high value rapidly under illumination, and the photocurrent decreases to nearly zero when the light is off. The results show that the photocurrent intensity of CdS/La-HNT is higher than that of CdS/HNT, indicating that more efficient separation of charge carriers had been influenced by La doping.
In order to examine the charge transfer and ion transport, the electrochemical impedance spectroscopy (EIS) was employed [2], and the impedance behavior of CdS/HNT and CdS/La-HNT were measured in Fig. 4d. The Nyquist plots showed a semicircle, which occurred due to the electrochemical process at a high frequency level, followed by a line that indicates the diffusive resistance of the electrolyte and active materials. The semicircle confined charge-transfer resistance, which is closely related to the reversibility of the electrochemical reactions. CdS/La-HNT shows a smaller arc than that of CdS/HNT, indicating that La doping led to more efficient charge transfer over CdS/La-HNT.

The smaller semicircle radius of CdS/La-HNTs compared with CdS/HNTs revealed that CdS/La-HNTs nanocomposite has smaller charge-transfer resistance and has good electrochemical resistance. The effects of La doping are also confirmed by the photoluminescence (PL) emission spectra (Fig. 4e), the lower the PL intensity, the higher the efficiency in photogenerated electron-hole separation.

Herein, we investigate the surface structure of HNT to further confirm the environment of the Al atom influenced by La doping. The full range of XPS spectra of HNT and La-HNT are exhibited in Fig. 5a, and the relative atomic concentration is shown in Additional file 1: Table S5. Si and Al elements are detected in HNTs and La-HNTs, while La element is detected only in La-HNT. The concentration ratio of Al/Si is 0.62 in La-HNT, lower than that of HNT (0.88), which may be due to the Al atom being replaced by the La atom. For the acid-treated HNT, only Si 2p and O 1s are detected due to the removal of the alumina sheet (Additional file 1: Figure S1f). Figure 5b shows the La 3d spectra, and their
peak positions are observed at 835.7 eV (La 3d_{5/2}), 839.0 eV (La 3d_{3/2}), 852.3 eV (La 3d_{3/2}), and 855.9 eV (La 3d_{3/2}), respectively. Figure 5c, d shows the Al 2p and Si 2p spectra, and their peak positions are observed at 74.8 eV (Al–OH), 74.3 eV (Al–O), 103.3 eV (Si–OH), and 102.7 eV (Si–O), respectively. Remarkably, the binding energy (BE) values of the Al atom in Al–OH and Al–OSi shifted to 75.1 and 74.6 eV, respectively, while the position of the BE value of Si atoms has not changed. Thus, all of the above results confirm that the La atom replaced part of the Al atom from the Al–O sheet and the environment of Al atoms have been influenced.

Based on the characterization of the La doping into the HNT structure and the replaced part of the Al atom from the Al–O sheet, a substitutional atomic doping model was proposed as follows (Fig. 6). Each layer of HNT consists of a Si tetrahedral sheet and Al octahedral sheet. The distance between the unit cells is difficult to change due to the strong coupling force, so water molecules cannot enter. Thus, halloysite has been identified as the low activity aluminosilicate mineral. In the initial stage, the typical saturated AlCl₃ solution has been chosen because anhydrous AlCl₃ is a strong Lewis acid, capable of forming Lewis acid-based adducts with water, such as AlO₂⁻, HCl, and H₂O⁺. Etching starts by the Lewis acid-based adducts interacting with the alumina in the structure of halloysite, and the reaction extent raise with the concentration of Al³⁺ increasing. As the concentration of Al³⁺ is already over saturated, an inhibition layer will be formed, close to the surface of the halloysite. In this situation, cation substitution could occur in the inhibition layer. The La³⁺ ions following Al³⁺ saturated solution are substituted with the soluble aluminum atoms from halloysite in the inhibition layer according to the principle of the concentration of ion saturated solution conservation. Then, the dynamic
equilibrium of substitutional atomic doping formed and La doped halloysite composites are achieved. The use of an autoclave in the process was to force the doping process because the radius of La\(^{3+}\) ion is larger than that of Al\(^{3+}\). The crystal shapes and surface structures can be obviously changed by doping, and the chemical and structural performance of the supporter would be improved, which brings continuous uniformity to nanoparticle loading and improves the catalysis activity for catalytic nano-composite materials.

Fig. 7 Geometric structure of (a) side view and (b) top view of HNT, and (c) side view and (d) top view of La-HNT

Fig. 8 (a) The PDOS results of La-HNT surface. (b) Charge density difference of the La-HNT interface plotted along the plane designated by the dotted lines shown in the lower panel of Fig. 7c. Blue corresponds to charge depletion and red to charge gain. Isosurfaces are shown in the range \([-0.08, 0.08]\) (e/Å\(^3\)). Contours of constant charge density are separated by 0.005 eV/Å\(^3\).
The first-principle density functional theory (DFT) calculations were performed to further investigate the rationality of the doping mechanism and the effect of the La doping. The structure model of HNT is simulated by using crystalline approximations, and the La-HNT is constructed by replacing the Al atom from halloysite with the La atom. The structure of HNT by using kaolinite structure is simulated (Fig. 7a, b), and the surface structures are constructed by cleaving a 2 × 1 layer structure of two Al–O–Si layer thickness out of the bulk halloysite. A vacuum space of 15 Å is used. The La-HNT is constructed by replacing one Al in the Al sheet of halloysite with an La atom or adding La(OH)₃ on the halloysite surface (Fig. 7c, d). It was found that the Al–O bonds (Al–O) and Si–O bonds perpendicular to the planer layer (Si₃p–O) on the HNT surface are slightly increased compared to that of HNT bulk structure (Additional file 1: Figure S3), i.e., 0.05–0.10 and 0.02–0.03 Å, respectively. At the same time, the Si–O bonds in the planer layer (Si₃p–O) decreased. Additionally, the O–H bond distribution on HNT surface is broadened due to the surface effect. For the La-doped case, a contraction of the Al₃p–O and Si₃p–O bonds, as well as an expansion of the Si₃p–O bond, occurs instead after the atomic structure relaxation of La-HNT surface (Additional file 1: Figure S3). The local structure around La shows that the six La–O bonds possess a bond length (around 2.3–2.5 Å) much longer than Al–O bonds, which increases the space around the La doping site (Additional file 1: Figure S4a). Notably, the elongation of three surface OH bonds with H heading directly towards the O atoms of La(OH)₃ (H-La) induces three reactive surface OH groups around the La atom at the La-HNT surface.

The calculated Mulliken charge for La atom in La-HNT is 1.83 e (Fig. 7d), which corresponds to valence states +3. The PDOS result shows a band gap of 5.2 eV for pristine HNT, and the valence band near the fermi level is mainly composed by O 2p state while conduction band minimum (CBM) is mixed by mainly H 1s, Si 3s 3p, and partially O 2p, Al 3s 3p states (Additional file 1: Figure S4b). The support of La on the HNT surface introduces La 5d states in the CBM (Fig. 8a, purple), and the reactive La dopant with 5d² orbital is confirmed as a donor type impurity. Meanwhile, the three OH groups around La have supplied some lone pair electrons (Fig. 8a, yellow and green) at valence band maximum (VBM), which will enhance the surface absorption ability. The charge density difference around the La-HNT interface shows that there is a charge transfer from the surrounding Al atoms of the HNT surface to La dopants after La doping (Fig. 8b). It is assumed that the La dopants might serve as a charge-transfer bridge between the HNT surface and functional nanoparticles like CdS, and thus the photocatalytic hydrogen evolution rate would be enhanced. Hence, the conformity of the experimentation and simulation has verified the rationality of the simulation model and the substitutional atomic doping model.

Conclusions
In summary, natural halloysite nanotubes have been successfully doped by La atom. The La doping into the structure of HNT leads to crystal shapes and obvious surface structure changes, which brings continuous uniformity for CdS loading and changes the catalysis activity for nanocatalytic composite materials, thus resulting in an enhanced photocatalytic hydrogen evolution rate. The contrast of the photocatalytic hydrogen evolution of CdS/La-HNT and CdS/HNT confirms the high efficiency of the La doping. This result is very encouraging and should be highly applicable for extending the doping technique to other aluminosilicate minerals and the corresponding design of functional materials.

Additional file

Additional file 1: Supporting Information for Substitutional Doping for Aluminosilicate Mineral and Superior Water Splitting Performance. (DOCX 3550 kb)

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Availability of Data and Materials
Supporting information is available from the Springer Online Library or from the author.

Authors’ Contributions
YZ and HMV developed the concept. YZ, HMV, LJF, and TJ conceived the project and designed the experiments. YZ wrote the final paper. YZ and LJF wrote the initial drafts of the work. YZ, LJF, ZS, and ADT performed the experiments. All authors discussed the results and commented on the manuscript.

Competing Interests
The authors declare that they have no competing interests.

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