Controllable synthesis of Fe–N$_4$ species for acidic oxygen reduction

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Abstract
Controllable design and synthesis of catalysts with the target active sites are extremely important for their applications such as for the oxygen reduction reaction (ORR) in fuel cells. However, the controllably synthesizing electro-catalysts with a single type of active site still remains a grand challenge. In this study, we developed a facile and scalable method for fabricating highly efficient ORR electro-catalysts with sole atomic Fe–N$_4$ species as the active site. Herein, the use of cost-effective highly porous carbon as the support not only could avoid the aggregation of the atomic Fe species but also a feasible approach to reduce the catalyst cost. The obtained atomic Fe–N$_4$ in activated carbon (aFe@AC) shows excellent ORR activity. Its half-wave potential is 59 mV more negative but 47 mV more positive than that of the commercial Pt/C in acidic and alkaline electrolytes, respectively. The full cell performance test results show that the aFe@AC sample is a promising candidate for direct methanol fuel cells. This study provides a general method to prepare catalysts with a certain type of active site and definite numbers.

KEYWORDS
atomic Fe–N$_4$ site, controllable synthesis, fuel cells, oxygen reduction reaction

1 | INTRODUCTION

It is predicted that the global population will be over 9 billion people by 2050. At that time, we need 50% more fuel and have to reduce 80% carbon dioxide emissions to maintain political, social, and fuel sustainability.$^1$ It is therefore of pivotal importance to explore and utilize clean energy to meet the fuel requirement for the sustainable development of humanity. As an emerging technique, the hydrogen fuel cell is believed to be one of the cleanest energy technologies for a sustainable future. However, the sluggish cathodic oxygen reduction reaction (ORR) in fuel cells is the rate-limiting step that significantly impedes the overall cell efficiency.$^{2,3}$ Currently, the most efficient ORR
catalyst is still based on platinum (Pt) and its alloys, particularly in acidic media.\(^4\)\(^6\) Undoubtedly, Pt should be replaced by low-cost but more efficient alternatives due to its scarcity and poor stability. Therefore, tremendous efforts have been devoted in the last decade to explore efficient nonprecious metal-based ORR catalysts, such as Fe and Co-based electrocatalysts.\(^7\)\(^10\)

Recently developed atomic metal catalysis strategy provides a feasible way of exploiting active ORR catalysts.\(^11\)\(^15\) At present, the stabilization of the atomic metal species is mostly based on a bottom-up strategy, where the metal precursors are adsorbed, reduced, and anchored by the defect-rich support.\(^16\)\(^17\) Generally, the concentration of metal precursors should be extremely low to avoid the aggregation of atomic metal species during the fabrication process.\(^18\)\(^19\) In addition, the type and density of the active sites still could not be fully controlled. For example, a mixture of different types of possible active sites such as metal-nonmetal with various coordination are formed, and may also contain clusters/nanoparticles. Therefore, it is almost impossible to identify the real active site for a certain reaction.\(^20\)\(^21\) Furthermore, the controllable fabrication of electrocatalysts with a single type of active site accompanied by sufficient numbers for highly efficient catalysis is still challenging.\(^22\)\(^23\) These issues not only restrict the fundamental understandings of the reaction mechanism but also limit the further improvement of the ORR performance. This is because it is very hard to investigate the configuration of the possible active sites and the structure-performance relationship in such a mixed system.

Addressing the aforementioned drawbacks, this study aims to develop a controllable and scalable method for synthesizing an electrocatalyst with a single type of active site. The use of Fe porphyrin as the precursor guarantees that every atomic Fe species is coordinated with four nitrogen atoms (e.g., Fe–N\(_4\)). Meanwhile, the heat-treatment temperature should not be too high to prevent the broken of Fe–N bonds. This approach is crucial to retain the Fe–N\(_4\) configuration. Accordingly, the synthesized sample is supposed to contain a sole active site of Fe–N\(_4\) on the carbon support, without any other configurations as the possible active site. This is a feasible and reliable methodology to study the reactivity of Fe–N\(_4\). The aberration-corrected high-resolution transmission electron microscopy (AC-TEM) and extended X-ray absorption fine structure (EXAFS) characterizations of the synthesized samples confirm the atomic state of the Fe species on the highly porous carbon support. The EXAFS fittings show that each Fe atom is coordinated with four nitrogen atoms (coordination number is 4). The corresponding electrocatalytic performance test results show that the atomic Fe–N\(_4\) in activated carbon (aFe@AC) exhibits excellent ORR activity in both acidic and alkaline electrolytes. The full cell evaluation results further reveal that the aFe@AC is a promising catalyst for direct methanol fuel cells (DMFCs).

## EXPERIMENTAL SECTION

### 2.1 Sample preparation

The synthesis of the Fe-based samples is followed by a wetness impregnation method. Specifically, the Fe source is porphine iron(III) chloride (Fe-Por, a small Fe molecular) purchased from Sigma-Aldrich. A highly porous activated carbon (AC) prepared from a Taixi coal (Ningxia Huahui Activated Carbon Company Limited, China) is used as the carbon support to anchor and coordinate the Fe species, and tetrahydrofuran is the solvent. For synthesizing the samples with different Fe contents, 10/20/40 mg Fe-Por and 80 mg AC were dissolved into 20 and 40 mL tetrahydrofuran, respectively. The solution contains Fe-Por was dropped into the AC solution slowly under fast stirring conditions at room temperature in the fume hood. Subsequently, the obtained mixture was continuously stirred at room temperature in the fume hood for 12 hours. The collected solid was drying in a vacuum oven at 80°C for 12 hours after the solvent was evaporated. The final Fe-containing catalysts were obtained by treating the dried sample under a nitrogen atmosphere at 600°C for 2 hours in a tubular furnace. For comparison, graphene anchored Fe species sample (aFe@G) was also prepared under the same conditions as synthesizing the aFe@AC (20 mg Fe-Por and 80 mg graphene were dissolved into 20 and 40 mL tetrahydrofuran, respectively. The following steps are the same).

### 2.2 Characterizations

The specific surface area and pore size distribution of the prepared samples were measured at the liquid nitrogen temperature (77 K) using a TriStar II 3020 automated surface area and a pore size analyzer. Chemical compositions of the prepared samples were acquired using a Kratos Axis ULTRA X-ray photoelectron spectrometer incorporating a 165 mm hemispherical electron energy analyzer, the energy scale was calibrated to the C 1s peak maximum at 284.5 eV. Raman spectra of the synthesized samples were recorded on a Renishaw InVia spectrometer equipped with a Leica DMLM microscope and a 514 nm argon-ion laser as the excitation source with a grating of 2400 l/mm. The crystalline structures of the
prepared samples in this study were characterized in a Bruker Advance X-ray diffractometer using nickel-filtered Cu Kα X-ray source radiation (λ = 1.5405 Å). The ultraviolet-visible (UV-Vis) spectra of the prepared samples were recorded on the Agilent 8453 UV-Vis spectrophotometer. The Fe content in the resulting samples was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) on the Perkin Elmer Optima 8300 ICP-OES instrument. The morphology of the samples was examined using TEM and high-resolution TEM (Philips Tecnai F20). High-angle annular dark-field (HAADF) images and bright-field images were collected from a probe-corrected JEOL ARM200F with an acceleration voltage of 80 kV.

X-ray absorption spectra at Fe K-edge EXAFS were recorded at beamline 17C1 of National Synchrotron Radiation Research Center, Hsinchu, Taiwan. The storage ring was operated at 1.5 GeV with a stored current of 360 mA. BL17C1 utilizes the radiation from a superconducting wavelength shifter (Eg = 7.5 keV). Beamline employs a double Si (111)-crystal monochromator for energy selection with a resolution of ΔE/E higher than 2 × 10⁻⁴. EXAFS data were collected in a fluorescent mode at room temperature. Two ion chambers filled with N2 and Ar were used as the detectors of I₀ and Iₚ, respectively. A standard compound, Fe foil, was measured simultaneously by using the third ionization chamber so that energy calibration could be performed scan by scan. Raw X-ray absorption data were analyzed following the standard procedures, including pre-edge and postedge background subtractions, normalization with respect to the edge jump, Fourier transformation and nonlinear least-squares curve fitting.

### 2.3 Electrochemical measurement

A typical three-electrode system was applied to evaluate the electrochemical performance of the synthesized samples on the CHI 760E workstation (CH Instruments Inc). For the ORR measurement, a glassy carbon (4 mm in diameter), a graphite rod, and an Ag/AgCl (in saturated KCl solution) electrode are the working, counter, and reference electrodes, respectively. Two milligrams of the finely ground catalyst was dispersed into the 1 mL mixed solution of distilled water (680 μL), ethanol (300 μL) and Nafion 117 solution (5%, 20 μL). Then, 10 μL of the mixture was dropped onto a polished glassy carbon electrode after sonication it for at least 60 minutes to form a homogeneous ink. The loaded electrode was placed in a 60°C oven for 10 minutes to dry and then was taken out to cool down before the ORR test. The catalyst loading is 0.16 mg/cm². Cyclic voltammetry and linear sweep voltammetry (LSV) measurements were conducted on the CHI 760E workstation with an RKDE-3A rotator (ALS Co., Ltd.) in an oxygen-saturated 0.1M HClO₄ or 0.1M KOH solution. The commercial Pt/C (20 wt% Pt on Vulcan XC-72, Pt particle size is around 3 nm; Premetek; Figure S1) was tested under the same conditions. All potentials were referred to the reversible hydrogen electrode (Figure S2) and all the tests were performed without IR compensation.

The DMFC performance of the aFe@AC and the commercial Pt/C (20 wt%) samples were tested on the Arbin fuel cell test system in acidic conditions. For the catalyst spray ink preparation, a mixture of the catalyst and solvent (water/isopropanol) with the addition of 5% Nafion (30% total volume) was sonicated to form a homogeneous ink. The resulting catalyst loading is 3.0 mg/cm², and the used membrane is Nafion 115. The testing parameters are as follows. O₂ pressure: atmosphere pressure, O₂ flow rate: 200 mL/min, methanol concentration: 1.0M, methanol flow rate: 35 mL/min. The test temperature is 80°C.

3 RESULTS AND DISCUSSION

The schematic illustration of the catalyst preparation is shown in Figure 1A. Here, a highly porous activated carbon with a specific surface area of 3483 m²/g (Figure S3) is used to absorb and anchor the Fe porphyrin precursor. The Fe porphine molecular can be entered into the pores of the activated carbon during the wetness impregnation process. This is because the molecular size of the Fe porphine is smaller than the pore size of the activated carbon (around 1.2 nm; Figure S4). This strategy is essential to prevent the aggregation of the Fe molecular since the single Fe porphine site is confined and isolated by the pores of activated carbon. After absorption and assembling, the obtained mixture is treated under a nitrogen atmosphere at 600°C for 2 hours. The heat treatment will combine the Fe–N₄ sites with the porous carbon substrate to form an integrity. The resulting sample is denoted as aFe@AC. Comprehensive characterization techniques were used to reveal the states of Fe species in the aFe@AC.

The X-ray photoelectron spectroscopy (XPS) survey spectrum in Figure 1B shows that the sample aFe@AC contains elements C, N, O, and trace Fe. The calculated N and Fe contents on the surface of the aFe@AC are 1.28 and 0.17 at% (equals to 0.78 wt% Fe), respectively. The XPS tested Fe content is lower than the ICP measured result of 1.93 wt%, as the XPS is mainly used for the surface analysis. The XPS N 1s and Fe 2p high-resolution spectra are presented in Figure 1B as well (inset). The Fe species are
supposed to be coordinated with N in the aFe@AC due to the Fe–N₄ coordination of Fe in the porphyrin precursor (Figure S5). The microstructure of the aFe@AC is revealed by the TEM image shown in Figure 1C. The highly porous structure is consistent with the nitrogen adsorption-desorption isotherm and pore size distribution curve of the carbon support. In addition, no visible Fe particles are detected in the aFe@AC (Figure 1C), indicating that the incorporated Fe should be in the form of atomic Fe species. The wide peak at around 26° in the X-ray powder diffraction pattern of the aFe@AC sample (Figure S6) shows the graphitic character of carbon materials, proving its excellent conductivity. The Raman spectrum of the aFe@AC sample further proves its good conductivity (Figure S7) as it shows a prominent graphitic peak at around 1593 cm⁻¹.24-26 Meanwhile, the existence and homogeneous distributions of N and Fe in the sample aFe@AC are verified by the energy-dispersive X-ray spectroscopy elemental mappings.

The uniform distribution of the Fe species in the aFe@AC sample (Figure 1D) provides the opportunity to investigate the reactivity of Fe–N₄ for the ORR both in acidic and alkaline solutions.

The atomic state of the incorporated Fe in the aFe@AC sample is further revealed by the HAADF-scanning transmission electron microscope (STEM). Figure 2A shows that the atomic Fe species are distributed homogeneously on the porous carbon support. The HAADF-STEM image of the aFe@AC also confirms that the Fe species did not aggregate during the preparation process. This should be attributed to the highly porous carbon with narrow size distribution that could anchor and isolate the atomic Fe species. Thereafter, the X-ray absorption spectroscopy measurements were used to probe the atomic structures of the Fe species in the aFe@AC. The corresponding X-ray absorption near-edge structure (XANES) spectrum of the aFe@AC is presented in Figure 2B. For comparison, the XANES spectra of the
reference samples Fe foil and FeO were also measured. Apparently, the white line peak of the aFe@AC sample is different from those of the Fe foil and FeO (Figure 2B), suggesting the absence of metallic Fe and Fe oxide in the aFe@AC. The corresponding EXAFS spectrum of the aFe@AC in Figure 2C further supports this conclusion. Specifically, a distinct Fe–N peak at 1.63 Å is observed in the R-space spectrum of the aFe@AC (Figure 2C), indicating the atomic dispersion of the Fe species on the carbon support.\(^{27-29}\) Besides, an obvious Fe–Fe peak at 2.15 Å is detected from the Fe foil, and the Fe–O and Fe–Fe peaks at 1.63 and 2.64 Å are detected from the FeO reference sample, respectively (Figure 2C). This is a potent support to show that the aFe@AC sample is free of Fe–Fe and Fe–O bonds.

Furthermore, the EXAFS fitting is applied to determine the structural and the detailed chemical configurations of the Fe species in the aFe@AC. The corresponding fitted R-space curve in Figure 2D shows that the coordination number of the Fe species within the aFe@AC sample is 4. This is a strong evidence to prove that the Fe–N\(_4\) structure remains unchanged after the heat treatment, otherwise the coordination number should be varied. The detailed fitting parameters of the aFe@AC and the reference samples Fe foil and FeO can be found in Table S1. The proposed structure of the aFe@AC is illustrated by the inset in Figure 2D. Through the above characterizations, it can be concluded that the Fe atom is coordinated by four N atoms in the aFe@AC, which confirms our hypothesis regarding the Fe–N coordination. Consequently, we further adjust the concentration of Fe–N\(_4\) site, aiming to investigate the density of the ORR active site and the performance relationship as well as to compare it with the previously reported results.\(^{28,30}\)

The electrocatalytic oxygen reduction performance of the prepared samples was first evaluated in an oxygen-saturated...
A 0.1 M HClO₄ solution by a rotating disk electrode. Figure 3A shows the LSV curves of the prepared samples and the commercial Pt/C (20 wt% Pt) measured under the rotation speed of 1600 rpm. To study the influence of the density of the Fe–N₄ on electrocatalysis, lower and higher Fe contents were also loaded on the carbon support. The resulting samples were denoted as aFe@AC-L and aFe@AC-H, respectively. From Figure 3A, it can be observed that before the heat treatment, the precursor of the aFe@AC shows very low ORR activity in acidic solutions. After treated it at 600°C for 2 hours, it shows greatly enhanced ORR performance. For example, the half-wave potential of the resulting sample aFe@AC is only 59 mV more negative than that of the Pt/C in 0.1 M HClO₄ solution. As can be seen from Table S2, our catalyst aFe@AC shows comparable or even better ORR performance than the reported state-of-the-art Fe–N–C counterparts, suggesting its excellent ORR activity in acidic media. Besides, both the heat-treated samples with lower Fe content (aFe@AC-L) and higher Fe content (aFe@AC-H) show good ORR performance as well, although they are less active than that of the aFe@AC. The more intuitive comparison of the ORR activity of these samples is given in the form of half-wave potential in Figure 3B. It can be seen that the concentration of the Fe species has a distinct influence on the ORR activity of the obtained samples. Specifically, with the increase of the Fe content, the ORR activity was first increased; however, when the Fe content was further increased, the ORR performance was decreased slightly.

The UV-Vis spectra of these samples prove that after the heat treatment, the typical Fe porphyrin peak located at 407 nm has been disappeared (Figure S8). It means that the Fe porphyrin precursor has completely decomposed and integrated with the carbon support at the heat-treatment temperature of 600°C. The ICP test results reveal that the Fe contents in the aFe@AC-L, aFe@AC, and aFe@AC-H samples are 0.87, 1.93, and 3.81 wt%, respectively. From the corresponding TEM images, it can be found that no visible Fe particles were observed in the samples aFe@AC-L (Figure S9) and aFe@AC (Figure 1C); however, Fe nanoparticles were detected in the aFe@AC-H sample (Figure S10). In

**FIGURE 3**  A, LSV curves of the prepared samples and the commercial Pt/C tested in an oxygen-saturated 0.1 M HClO₄ solution. B, Half-wave potential comparison of the prepared samples tested in an oxygen-saturated 0.1 M HClO₄ solution. C, LSV curves of the aFe@AC sample tested at different rotation speeds with the scan rate of 10 mV/s in an oxygen-saturated 0.1 M HClO₄ solution. D, i-t stability of the aFe@AC and the commercial Pt/C tested at 0.5 V (vs RHE) at 1600 rpm in an oxygen-saturated 0.1 M HClO₄ solution. E, LSV curves of the aFe@AC and the commercial Pt/C tested in an oxygen-saturated 0.1 M KOH solution. F, Electrochemical activity is given as the kinetic current density (J_K) at different potentials for the aFe@AC and the commercial Pt/C tested in an oxygen-saturated 0.1 M KOH solution. LSV, linear sweep voltammetry; RHE, reversible hydrogen electrode.
addition, the XANES spectra in Figure S11 suggest that the aFe@AC-L sample is lack of metallic Fe–Fe peak but a weak Fe–Fe peak can be noted from the spectrum of the aFe@AC-H sample. The corresponding EXAFS spectra in Figure S12 further demonstrate that all the Fe species are in atomic Fe–N₄ state in the sample aFe@AC-L, while both the atomic Fe species and metallic Fe clusters/nanoparticles are presented in the aFe@AC-H sample. These results are fully consistent with the corresponding TEM images, showing the formation of Fe nanoparticles when further increase the Fe concentration. Combine the ORR performance with the corresponding characterizations of the fabricated samples, it is apparent that when the Fe content is increased, the density of the atomic Fe species is increased as well. That is why the ORR performance of the obtained samples is improved accordingly. However, the further increase of the Fe content resulted in the aggregation of the Fe species, forming less active Fe nanoparticles. This reasonably explains why higher Fe content sample aFe@AC-H shows inferior ORR activity to that of the lower Fe content counterpart aFe@AC. Apparently, the density of the ORR active site can also be controlled by this synthetic strategy.

To show the advantages of the highly porous structures of the used activated carbon, we also utilized less porous graphene with similar pore sizes (Figure S13) to anchor the atomic Fe species. The Brunauer-Emmett-Teller surface area of the graphene is 469 m²/g (Figure S14), which is much lower than that of the activated carbon, 3483 m²/g. Under the same synthetic conditions for preparing the aFe@AC sample, the obtained sample aFe@G using graphene as the carbon support shows much lower ORR activity than that of the aFe@AC in acidic solutions (Figure S15). This result is a strong support to prove the advantages of the highly porous activated carbon for anchoring and isolating the atomic Fe species. More detailed investigations were carried out on the aFe@AC catalyst as it shows the highest ORR activity among the prepared samples. Figure 3C presents the LSV curves of the aFe@AC tested under the rotation speed from 400 to 2500 rpm in an oxygen-saturated 0.1M HClO₄ solution. The limiting current density is increasing with the increase of the rotation speed, suggesting the ORR is a diffusion-controlled reaction process. The reaction kinetics is uncovered by the corresponding Tafel plots. The small Tafel slope of 42 mV per decade at low overpotentials confirms the excellent ORR kinetics of the aFe@AC, which is smaller than that of the commercial Pt/C (45 mV per decade; Figure S16).

The amperometric i-t stability was measured for the aFe@AC and the Pt/C samples in acidic solutions as well. From Figure 3D, it is obvious that the aFe@AC is much more stable than that of the Pt/C under the acidic ORR conditions. The aFe@AC could maintain 88.0% of its initial current after 12 hours continuous test; however, the Pt/C only retains 42.8% under the same testing conditions (Figure 3D). This fully suggests that the atomic Fe species could catalyze the ORR in a relatively longer time, showing the advantages of the aFe@AC catalyst for practical fuel cell applications. Meanwhile, for methanol powered fuel cells, the cathodic ORR catalyst should also be capable of resisting the cross-over of the methanol. For this purpose, we measured the cross-over effect of the methanol in acidic ORR conditions. It can be observed from Figure S17 that the aFe@AC is free from the methanol poisoning, further demonstrates its flexibility as a cathodic ORR catalyst in fuel cells with a wide range of fuel options.

Since the aFe@AC shows excellent ORR performance in acidic media, we also evaluated its ORR activity in alkaline solutions. The corresponding LSV curves in Figure 3E shows that the aFe@AC sample has outperformed the commercial Pt/C for the ORR in 0.1M KOH solution. For example, its half-wave potential is 47 mV more positive than that of the Pt/C. In addition, the aFe@AC also exhibits a higher limiting current density than that of the Pt/C (Figure 3E). It means that the controllably synthesized active site of Fe–N₄ is effective in catalyzing the ORR, both in acidic and alkaline electrolytes. The alkaline kinetic current density (Jₖ) at different potentials for the aFe@AC and the Pt/C is presented in Figure 3F. The Jₖ at 0.70 and 0.80 V (vs reversible hydrogen electrode) are 99.0 and 42.4 mA/cm², respectively, which are much higher than those of the Pt/C (68.1 and 12.8 mA/cm², respectively), indicating the fast mass transfer of the aFe@AC for the ORR under lower overpotentials. The corresponding LSV curves of the aFe@AC at different rotation speeds are shown in Figure S18, which also exhibit excellent reaction kinetics. As can be seen from the above discussions, the designed and controllably fabricated ORR electrocatalyst with atomic Fe–N₄ species as the active site is an ideal cathodic catalyst for both the acidic and alkaline ORR catalysis.

In view of the aFe@AC sample shows excellent ORR performance in acidic electrolytes and it is free from methanol poison, we thereafter measured its activity as a cathode catalyst in an acidic DMFC. As a comparison, the commercial Pt/C (20 wt%) was also tested under the same conditions. It can be observed from Figure 4 that the DMFC using aFe@AC as the cathode catalyst shows significantly higher open-circuit voltage than that of the Pt/C (0.98 V vs 0.81 V). This further confirms the excellent methanol poisoning resistance of the aFe@AC in practical
methanol fuel cell applications. However, both the aFe@AC and Pt/C show a fast voltage drop with the increase of the current density, which is due to the electrochemical activation of the electrode reactions and the Ohmic resistance of the cell. In addition, the aFe@AC shows a maximum power density of 44.4 mV/cm² at the test temperature of 80°C, which is lower than that of the commercial Pt/C (71.3 mV/cm²; Figure 4). Therefore, further research should be devoted to improve the electrocatalytic performance of the non-Pt-based ORR catalysts to make them more effective in the real fuel cell systems, such as to further increase the density of the active sites in the catalysts.

4 CONCLUSION

In summary, we have successfully synthesized electrocatalysts with a sole atomic Fe–N₄ coordination site as the active center for the ORR via a controllable preparation method. The AC-TEM and EXAFS characterizations confirm the atomic dispersion of the Fe species on the carbon support in a coordination structure of Fe–N₄. The ORR test results show the high activity of Fe–N₄ in both acidic and alkaline electrolytes but increase the density of Fe–N₄ site without segregations (forming nanoparticles to reduce the activity of electrocatalyst) becomes crucial. This study develops a feasible approach on controllably synthesizing electrocatalysts with the designed active sites. It provides a method to synthesize a single type of other coordination structures thus search for active sites with higher activities for electrochemical reactions.

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CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

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**SUPPORTING INFORMATION**
Additional supporting information may be found online in the Supporting Information section.

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