



Designing coral-like Fe₂O₃-regulated Se-rich CoSe₂ heterostructure as a highly active and stable oxygen evolution electrocatalyst for overall water splitting



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ABSTRACT

The electrocatalytic oxygen evolution reaction (OER) is the bottleneck to overall water splitting because of the slow kinetics of the four-electron transfer process. Therefore, it is of great significance to develop OER electrocatalysts with high activity, long durability, and scalability. Herein, we present a selenium-coated cobalt selenide (CoSe₂@Se) catalyst that was first synthesized by in situ growth on carbon cloth (CC) surface by hydrothermal method, followed by soaking treatment to prepare a three-dimensional coral-like Fe₂O₃-CoSe₂@Se/CC composite. Electrochemical studies revealed that the optimized Fe₂O₃-CoSe₂@Se/CC catalyst only requires 250 mV to reach 10 mA cm⁻² current density, yields a small Tafel slope (50.2 mV dec⁻¹), and has good stability (10 mA cm⁻²@70 h) in the electrocatalytic OER process. The overall water splitting using Fe₂O₃-CoSe₂@Se/CC as anode only requires 1.58 and 1.69 V to achieve 10 and 100 mA cm⁻², respectively, much better than most previously reported catalysts. Analysis showed that the three-dimensional coral-like morphology exposing more active sites and the synergy between different species (giving rise to, respectively, a favorable electronic structure that lowers the electrode overpotential) are the key to the observed improved electrocatalytic performance. This work provides a novel strategy for the rational design of nanostructured OER hybrid catalysts in the future.

1. Introduction

With the increased depletion rate of fossil fuels, exploring renewable energy sources has become exceptionally important [1,2]. Nevertheless, the primary sources of renewable energy, such as wind and solar power, are intermittent because of changes on the seasonal, daily, and regional scales [3,4]. As an alternative, electrochemical water splitting is a very much preferred approach for establishing a sustainable and environmentally clean energy source since it produces carbon-free, renewable, and clean hydrogen for energy generation [5,6]. The critical challenge for water-splitting under alkaline conditions is improving the kinetically slow, rate-limiting four-electron transfer OER process (4OH⁻ → 2H₂O + O₂ + 4e⁻) [7–10], where the OER determines the overall efficiency of a water-splitting system. Currently, IrO₂ and RuO₂ are widely regarded as the benchmark robust

OER electrocatalysts. However, high cost and scarcity seriously hinder their widespread application [11,12]. Therefore, the development of highly active and low-cost OER electrocatalysts to replace precious metals is greatly desirable.

Motivated by this situation, a lot of attention has been given to develop the transition metal based OER catalysts, due to their high earth abundance, special d orbitals, and unique electronic structure [13,14]. In particular, bimetallic composites possess better OER performance compared to monometallic materials because the synergistic effect of electronic tuning will affect the reaction kinetics [11,15]. Thus far, significant efforts have been devoted to developing non-precious metal catalysts of transition metal oxides [16], (oxy)hydroxides [17,18], phosphates [19], sulfides [20], and so on. Interestingly, selenides have high metallic properties, large relative ionic radius, and small ionization energy, all beneficial to OER performance [21]. For

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example, A. T. Sweis and colleagues successfully synthesized a nickel selenide-based compound, and the catalyst reached a current density of 10 mA cm^{-2} at a low overpotential of 290 mV, showing outstanding activity [22]. However, there is no report on the selenide-based OER catalyst showing a stable performance at high current densities ($200 \sim 400 \text{ mA cm}^{-2}$) that are essential for industrial applications [23]. Building on our previous studies [24–27], we constructed a novel Fe_2O_3 -manipulated Se-rich CoSe_2 hybrid OER catalyst working at high current density for the first time.

In this work, we report a $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{@Se/CC}$ hybrid catalyst synthesized on CC through a controllable hydrothermal method and

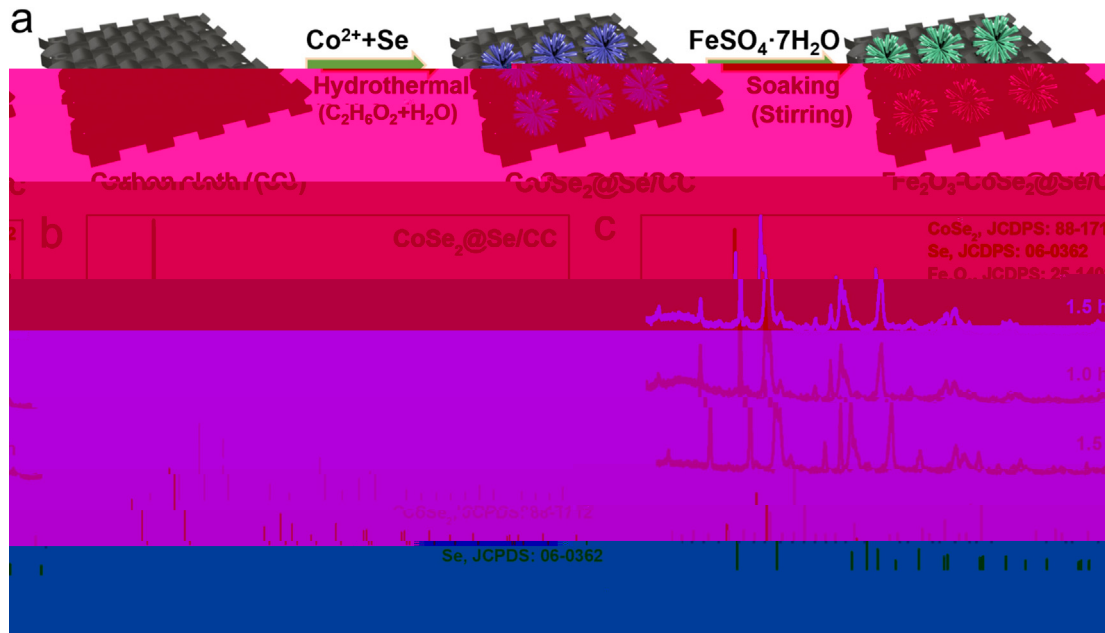


Fig. 1. (a) Schematic diagram of the synthesis process of Fe₂O₃-CoSe₂@Se/CC. X-ray diffraction (XRD) patterns of (b) CoSe₂@Se/CC and (c) Fe₂O₃-CoSe₂@Se/CC for different immersion times of Fe species.

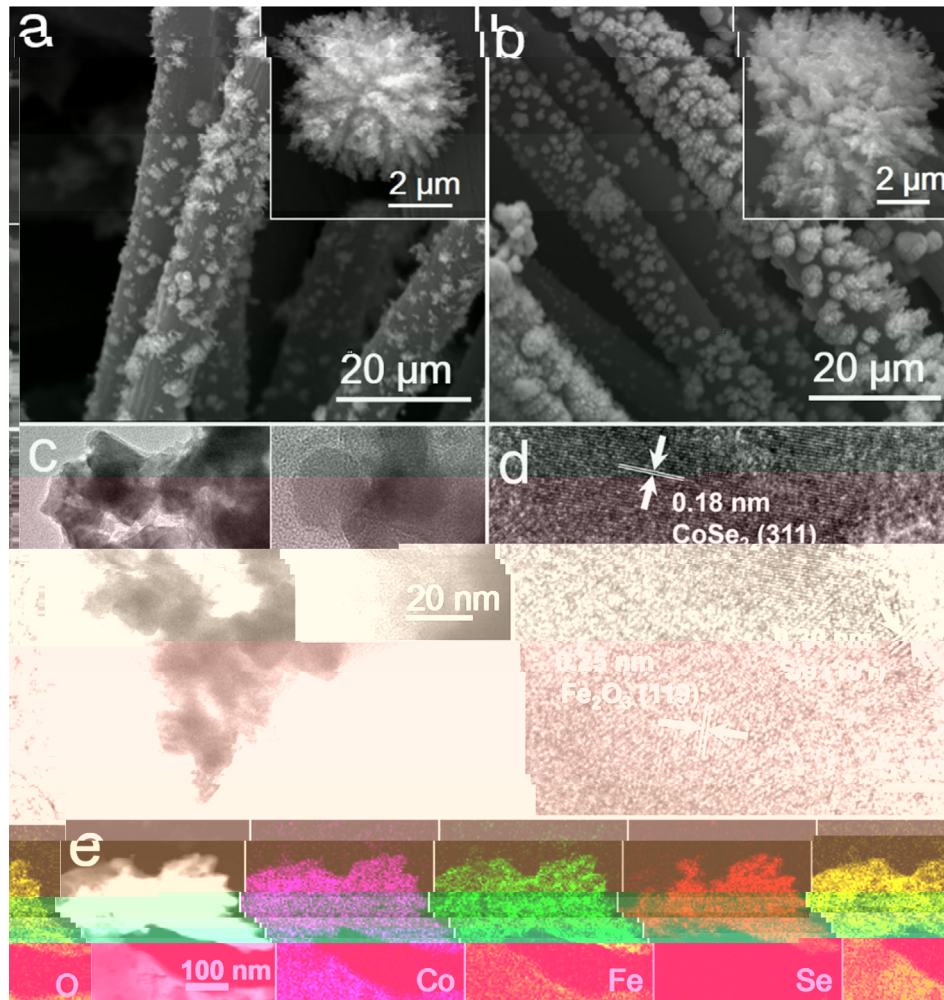


Fig. 2. SEM images of (a) CoSe₂@Se/CC and (b) Fe₂O₃-CoSe₂@Se/CC (Inset: High magnification SEM images). (c) TEM with inset enlarged scale and (d) high-resolution TEM images of Fe₂O₃-CoSe₂@Se. (e) HAADF-STEM image of Fe₂O₃-CoSe₂@Se/CC and corresponding elemental mappings of Co, Fe, Se and O.

thermal decomposition of CoSe₂ (Figure S3b) [31,35,36]. The difference in location is due to the strong interaction between the introduced Fe₂O₃ and CoSe₂@Se. In addition, the mass loss of CoSe₂@Se was significantly different from Fe₂O₃-CoSe₂@Se-1.0 h under the same conditions due to the different composition.

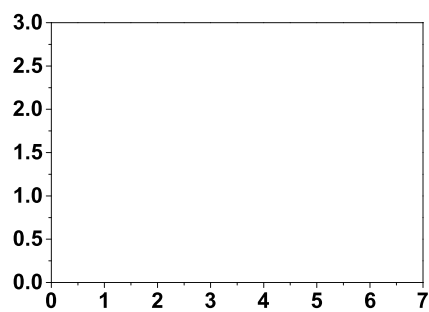
3.3. C

X-ray photoelectron spectroscopy (XPS) characterization was performed to further study the elemental composition and chemical states of different materials. The survey spectrum of Fe₂O₃-CoSe₂@Se/CC show that Fe, Co, Se, C and O are present in the composite (Fig. S4a). Among them, the high-resolution XPS spectrum of C 1s is revised to C=C (284.0 eV), and C—C (284.8 eV) and C—O (286.0 eV) as calibration standards (Fig. S4b) [25,37,38]. The high-resolution Co 2p XPS spectrum reveals the three pairs of peaks in Fig. 3a. For Co 2p_{3/2}, the binding energies at 778.1, 780.5 and 784.9 eV correspond to the Co-Se bond, Co-O bond and a satellite peak [39,40], respectively. Compared to CoSe₂@Se/CC, the binding energy of the Co-O bond of the Fe₂O₃-CoSe₂@Se/CC catalyst has a positive shift of 0.49 eV, indicating that there was strong electron interaction between the introduced Fe₂O₃ and partially oxidized CoSe₂@Se species, resulting in electron enrichment of the Fe₂O₃ species [26,41]. The high-resolution Se 3d region can be deconvoluted into Se 3d_{5/2} and 3d_{3/2} peaks, of which the two prominent Se 3d_{5/2} peaks at 54.2 and 55.1 eV are assigned to Se₂²⁻ and Se [42], while the 58.9 eV binding energy is typical SeO_x species (Fig. 3b) [43]. In Fig. 3c, the high-resolution Fe 2p_{3/2} XPS spectra of Fe₂O₃-CoSe₂@Se/CC catalyst can be deconvoluted at approximately 710.6, 712.9 and 717.0 eV binding energies attributable to Fe²⁺, Fe³⁺ and satellite peak signals [44,45], indicating that the Fe³⁺ species is the dominant component of the material. In addition, the high-resolution O 1s species of the Fe₂O₃-CoSe₂@Se/CC catalyst was also explored (Fig. 3d), in which the four signal peaks generated at 530.2, 530.8, 531.7 and 532.8 eV were attributed to Fe/Co-O, oxygen vacancies, adsorbed C=O bond, and adsorbed H₂O/C—O bond [46], respectively. The analysis found that the area content ratio of oxygen vacancies in Fe₂O₃-CoSe₂@Se/CC is as high as 44.2%, which is much higher than that in CoSe₂@Se/CC

(34.9%, Fig. S4c) indicating around 10% oxygen vacancies contributed by Fe₂O₃. A large number of studies have found that a high percentage of oxygen vacancies can help regulate the adsorption and desorption of reactants on the surface of the catalyst during the OER process, thereby greatly improving the catalytic activity of OER [47,48].

3.4. E

The OER performances of catalysts were further assessed by linear sweep voltammetry (LSV) at a scan rate of 5 mV s⁻¹ in 1.0 M KOH solution, and all LSV polarization curves are processed by R compensation as well as RHE correction (Fig. S1). As shown in Fig. 4a, the Fe₂O₃-CoSe₂@Se/CC-1.0 h electrocatalyst exerts a low overpotential



[53], where the specific capacitance of flat surfaces (C_s) is usually found in the range of 20–60 $\mu\text{F cm}^{-2}$ [24]. As expected, the $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{/Se/CC-1.0 h}$ catalyst retains the maximum ECSA of 1215 cm^2 (normalized to per cm^2 of electrode area), which is much higher than those of $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{/Se-0.5 h}$ (395 cm^2), $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{/Se-1.5 h}$ (260 cm^2), and $\text{CoSe}_2\text{/Se}$ (720 cm^2). The values of C_{dl} and ECSA are close to those of some recently reported Co-based electrocatalysts (Table S3). In addition, as shown in Fig. 4d, the inset R_s represents solution resistance and R_{ct} represents charge transfer impedance. The R_{ct} of $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{/Se/CC-1.0 h}$ catalyst has the smallest charge transfer resistance among all the other catalysts (Table S5), indicating that the hybrid catalyst has the highest conductivity, which intrinsically contributes to the enhancement of OER catalytic performance [54]. More broadly, the OER performance of $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{/Se/CC-1.0 h}$ is also comparable to most of reported Co-based OER catalysts in terms of η_{10} and Tafel slope (Fig. 4e), Table S4 [55–57].

The change of TOF values along with overpotential for different catalysts are discussed in Fig. 5a. As the overpotential increases, the TOF values of all catalysts increase monotonically. Moreover, at OER overpotentials of 300 mV and 350 mV, the TOF values of $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{/Se/CC-1.0 h}$ catalyst are much higher than all control catalysts (Fig. 5b), once again confirming the highest intrinsic catalytic oxygen evolution conversion efficiency [24]. The O_2 gas is collected quantita-

tively by drainage and compared with the theoretical value calculated according to Faraday's law (Fig. 5c) [58,59]. As shown in Fig. 5d, the measured O_2 content maintains a steady increasing trend. For $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{/Se/CC-1.0 h}$, the Faradaic efficiency (FE) of O_2 is similar to the theoretical value.

The industrial application potential is investigated by an electrochemical system with two-electrode configuration using $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{/Se/CC}$ as the anode and Pt/C as the cathode to construct a cell for overall water splitting. In Fig. 6a, the $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{/Se/CC}^{(+)}\text{||Pt/C}^{(-)}$ electrolyzer delivers a current density of 10 and 100 mA cm^{-2} at a cell voltage of 1.58 and 1.69 V in 1.0 M KOH solution, superior to most of the previously reported two-electrode catalytic systems, especially at high current density (Fig. 6b), Table S6.

To evaluate the stability of the catalyst, the chronopotentiometric curves of $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{/Se/CC}$ catalyst were studied in detail. The long-term stability is initially measured at constant current density of 10 mA cm^{-2} (Fig. 6c). It was found that the catalyst retained approximately 84.3% of its initial stability after 70 h of continuous operation at a current density of 10 mA cm^{-2} . The before and after OER samples' SEM, TEM, and XPS characterizations show significant alterations in surface morphology (Fig. S6) and elemental chemical states (Fig. S7). However, there is no significant decline in the OER performance, suggesting the catalyst reaches a particular equilibrium

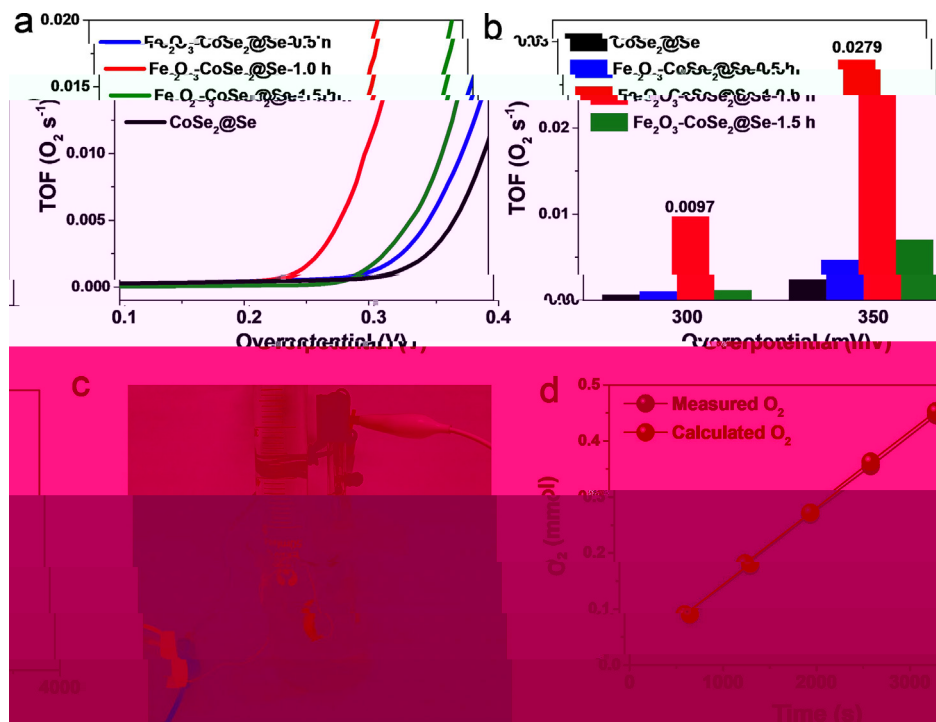


Fig. 5. (a) The turnover frequency (TOF) profiles versus overpotential of various catalysts. (b) The TOF values at different overpotentials. (c) The O_2 collection device by drainage, and (d) the amount of O_2 theoretically calculated and experimentally measured versus time.

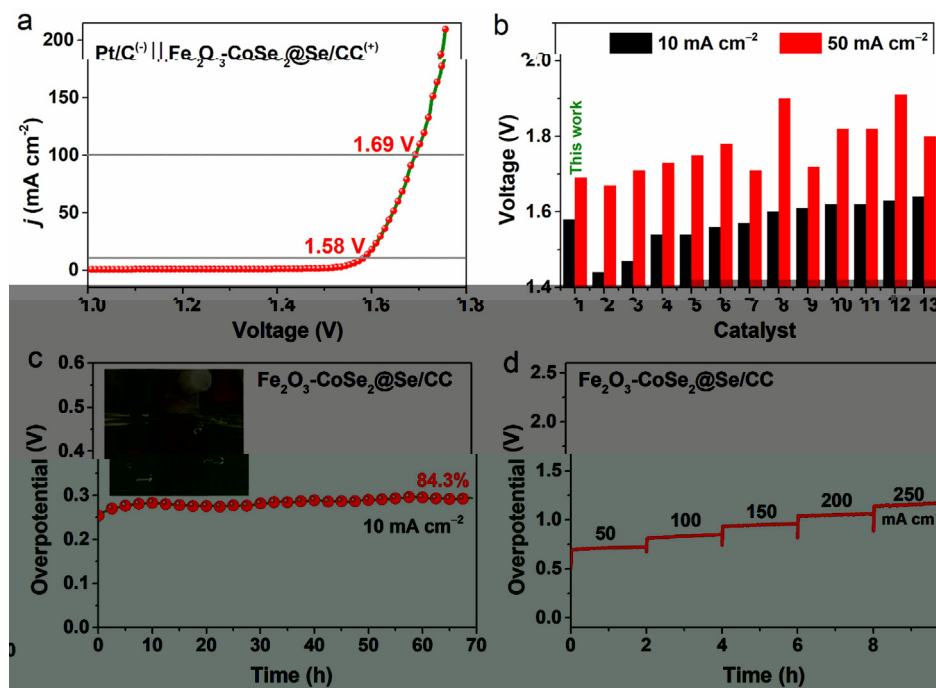


Fig. 6. (a) Overall water splitting of $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{@Se/CC}$ (anode) and commercial Pt/C (cathode) in two-electrode system. (b) Comparison with previously reported two-electrode catalysts at 10 and 50 mA cm^{-2} (Table S6). (c) Stability test at 10 mA cm^{-2} for 70 h in three-electrode system. (d) The multi-step chronopotentiometric curves with the change of current densities from 50 to 250 mA cm^{-2} in 1.0 M KOH.

state during OER that is different from the initial state. On changing the current density from 50 to 350 mA cm^{-2} in steps of 50 mA cm^{-2} every 2 h (Fig. 6d), we observed small increases in overpotential at the different current densities. These results indicate that the $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{@Se/CC}$ electrocatalyst has excellent durability, which may be

attributed to the unique coral-like structure and good electrical conductivity [60]. The above results further highlighted that the 3D coral-like $\text{Fe}_2\text{O}_3\text{-CoSe}_2\text{@Se/CC}$ catalyst possesses excellent OER activity.

Based on the above analysis, a four-electron pathway is suggested for overall OER reaction: $4\text{OH}^- (\text{aq}) \rightarrow \text{O}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{aq}) + 4 e^-$ [45]. Overall, the following features of the electrocatalyst are expected to contribute to its superior performance: (i) The three-dimensional coral-like structure, with a high observed ECSA, helps to expose more active sites as well as improve electrolyte transport and gas emission. (ii) The designed hybrid structure has a smaller electron transfer resistance and provides higher conductivity. This is also reflected in the observed low overpotential. (iii) The $\text{Fe}_2\text{O}_3/\text{CoSe}_2$ heterostructure offers more accessible active sites, thereby synergistically promoting the OER performance [61]. (iv) The observed strong electronic interactions among the different components of the catalyst system along with the high content of oxygen vacancies can modulate the binding energies between the reaction intermediates and the active sites in the OER process, thereby improving the electrocatalytic performance [62].

4. Conclusion

In summary, we successfully prepared a novel catalyst of $\text{Fe}_2\text{O}_3\text{-CoSe}_2@\text{Se}/\text{CC}$ through a conventional hydrothermal growth and soaking treatment. In the case of the optimized hybrid catalyst, XRD confirmed its crystal structure, SEM showed a three-dimensional coral-like structure, and XPS demonstrated strong electronic interactions between different components. The electrocatalytic OER study showed that the hybrid catalyst has excellent electrocatalytic activity and stability in an alkaline three-electrode system, which is also observed in the simulated industrial two-electrode overall water splitting. The study revealed that the hybrid material, with its unique structure, is a promising candidate for industrial electrolysis of water for hydrogen production. Furthermore, this work also provides a feasible route for developing other novel and efficient catalysts.

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Zixia Wan: Investigation, Methodology. **Qiuting He:** Investigation, Data curation. **Yuan Qu:** Data curation. **Jiaxin Dong:** Investigation, Data curation. **Elvis Shoko:** Writing – review & editing. **Puxuan Yan:** Methodology. **Tayirjan Taylor Isimjan:** Writing – review & editing. **Xiulin Yang:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jelechem.2021.115928>.

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