Thermo-induced nanocomposites with improved catalytic efficiency for oxygen evolution

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Water electrolysis is a sustainable and environmentally benign process for energy conversion and production. The oxygen evolution reaction (OER), the anode reaction, is slower during water electrolysis than the hydrogen evolution reaction, the cathode reaction, because of the necessary four-electron transfer process. Therefore, exploring highly efficient OER catalysts is crucial for advancing the electrochemical water splitting reaction.

Metal-organic frameworks (MOFs) are widely used in areas such as recognition [1–3], adsorption [4–7], and catalysis [8–11] because of their porous architecture and highly specific surface areas. Unfortunately, the low conductivity of MOFs has limited their applications in electrochemical processes. Several approaches have been employed to improve the conductivity and electrochemical properties of MOFs, including use of bimetallic templates [12,13], inorganic heteroatom doping [14–16], incorporation of conductive molecules [17,18], and thermolysis [19–21]. Therefore, application of MOFs in electrochemical catalysis has gained considerable attention because these compounds can be easily modified and have a specific framework [22–27].

Metal nanoparticles (MNPs) are also promising candidates for catalysis [28,29]. Unfortunately, their catalytic activities are typically limited because of their high surface energy and ability to easily aggregate [30,31]. Optimizing MNPs and maximizing their dispersion are important to improve their catalytic activity. MOFs are perfect hosts for MNPs because the intrinsic pores and cavities of MOFs can confine MNPs and prevent their aggregation [32]. The adjustable and tailorable size of the channels in MOFs enables the versatile incorporation of MNPs. An increasing number of researchers have focused their efforts on combining the advantages of MOFs and MNPs, especially for electrocatalysis [33,34]. The numerous pores in the MOFs can guarantee mass transfer, while

MNPs can accelerate electron transfer. The synergy between these two components can negate their individual shortcomings and effectively improve their electrocatalytic performance.

Zeolitic imidazolate frameworks (ZIFs), a subfamily of MOFs, consist of functionalized imidazolate ligands and coordination metal ions. Compared with many other MOFs, ZIFs exhibit outstanding thermal stability and chemical robustness [35]. Hence, ZIFs have attracted considerable attention and are employed in various fields such as sensing [36], catalysis [37,38], bio-simulation [39], and energy storage [40,41]. The thermal treatment of ZIFs is a common functionalization method. Because of the applicability of calcined ZIF-derived materials in catalysis [42], energy conversion [43], and sensing [44], these materials have attracted considerable attention. In this work, we chose ZIF-67 as the parent framework because of its easy-to-synthesize Co-based framework. Moreover, because of their high conductivity and catalytic activity, Au NPs were directly loaded in ZIF-67 *via* a “bottle-around-ship” strategy [45], yielding the composite Au@ZIF-67. Under the confinement of ZIF-67, Au NPs were dispersed uniformly and their aggregation was effectively prohibited. As a result of the loading of Au NPs, the conductivity of the obtained product was significantly enhanced. The synergetic effect of the Au NPs and the porous ZIF-67 negated their individual shortcomings and strengthened their corresponding advantages, thus efficiently improving the electrocatalytic performance of the composite. Furthermore, the composite was calcined at different temperatures. The synthetic route is presented in Scheme 1. The composite obtained after 500°C thermal treatment exhibited excellent electrochemical activity and optimal electrocatalytic performance for OER compared with the composites treated at other temperatures.

Au NPs were prepared *via* the sodium citrate reduction

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Scheme 1 Schematic of the syntheses of Au@ZIF-67 and Au@ZIF-67-*x*.

of HAuCl_4 according to the method previously reported by Lu *et al.* [46]. The diameter of the acquired Au NPs was ~ 13 nm, as determined through scanning electron microscopy (SEM, Fig. S1). Au@ZIF-67 was synthesized using the “bottle-around-ship” strategy with an Au NP solution of the desired concentration, 2-methylimidazole, and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The detailed synthesis can be found in the Supplementary information. Different concentrations of 2-methylimidazole and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in methanol were tested to determine the optimal loading amount of Au NPs. Fig. S2a–d show the transmission electron microscopy (TEM) images of different composites and reveal that Au NPs were embedded in ZIF-67 showing different loading amounts of Au NPs. From the elemental mapping analysis *via* energy dispersive X-ray spectroscopy (EDS, Fig. S2g), Au, C, N, O, and Co were found to be evenly distributed, demonstrating the successful encapsulation of Au NPs.

To evaluate the catalytic efficiency for the OER, linear sweep voltammetry (LSV) was carried out on a glass carbon electrode in a standard three-electrode system in a N_2 -saturated 1.0 mol L^{-1} KOH electrolyte. Although the same amount of Au NPs (1 mL Au NPs solution) was loaded, the composites exhibited different electrocatalytic activities for OER. Au@ZIF-67 formed from 1 mL of Au NP solution, 15 mL of 2-methylimidazole (240 mmol) in methanol, and 15 mL of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (200 mmol) in methanol displayed the lowest charge transfer resistance (R_{ct}) and the lowest operating potential to deliver a current density of 10 mA cm^{-2} , as shown in Fig. S3.

Different amounts of Au NPs embedded in ZIF-67 were used to determine the catalytic performances of the composites. The amount of encapsulated Au NPs increased as the Au NP loading amount increased from 1 to 3 mL (Fig. S2e, f). The operating potential *versus* RHE required to achieve a current density of 10 mA cm^{-2} increased with increasing amount of encapsulated Au NPs (Fig. S4). This is likely because as the loading amount of Au NPs increases, more volume of the ZIF-67 crystals

is occupied, resulting in a decrease in mass transfer and low catalytic performance for the OER. Comparing the average pore size of Au@ZIF-67 as determined by the Barrett-Joyner-Halenda (BJH) method (1.07 nm; shown in Fig. S5a) with that of ZIF-67 (1.71 nm) reported previously [47], the presence of Au NPs in the crystal structure can be confirmed.

Most MOFs are thermally unstable and easily collapse at high temperatures. To further explore the synergetic effect of the Au NPs and the porous framework of the MOFs on the catalytic efficiency for the OER, Au@ZIF-67 (the sample discussed above with the highest electrocatalytic activity) calcined at different temperatures were investigated in detail. Au@ZIF-67 was annealed at 350, 400, 450, 500, 550, 600, and 700°C under N_2 atmosphere for 1 h, resulting in Au@ZIF-67-*x* (where *x* denotes the annealing temperature). As shown in Fig. 1a–g, Au@ZIF-67-*x* preserves the rhomboidal dodecahedral morphology when heated at 500°C , and the frameworks shrink when the temperature increases continuously thereon. As revealed from the TEM images in Fig. 1h–n, the Au NPs are dispersed homogeneously within the crystal structure of both the parent ZIF-67 and the pyrolyzed ZIF-67. The collapse of Au@ZIF-67 within the temperature range is in agreement with the thermogravimetric analysis results (Fig. S6). Additionally, the similar thermal behavior of Au@ZIF-67 and ZIF-67 confirms the maintenance of framework integrity after Au NP encapsulation. The powder X-ray diffraction (XRD) data (Fig. S7) show that the main peaks of Au@ZIF-67, Au@ZIF-67-350, Au@ZIF-67-400, Au@ZIF-67-450, and Au@ZIF-67-500 match well with those of ZIF-67, while the peaks of ZIF-67 cannot be found in the XRD patterns of Au@ZIF-67-550, Au@ZIF-67-600, or Au@ZIF-67-700. This suggests that the long-range-ordered structure of ZIF-67 can be inherited upon Au NP loading; however, the framework collapses after calcination at high temperatures. The peaks of Au NPs can be hardly observed in these samples, which is attributed to the low concentration and small size of Au NPs. Nevertheless, the localized surface plasmon resonance band of the Au NPs at 560 nm in the ultraviolet–visible (UV-vis) absorption spectra was clearly observed for Au@ZIF-67 and Au@ZIF-67-*x* but not in ZIF-67 (Fig. 2a and Fig. S8), confirming the successful Au loading [48,49]. The presence of Au NPs was also verified by EDS elemental mapping results (Fig. 1o and Fig. S2).

Furthermore, Fourier transform infrared (FTIR) spectroscopy was conducted to investigate the internal structure of the composites subjected to thermal treatment. The absorption bands at 600–1350 and

Figure 1 (a–g) SEM and (h–n) TEM images of Au@ZIF-67-350, Au@ZIF-67-400, Au@ZIF-67-450, Au@ZIF-67-500, Au@ZIF-67-550, Au@ZIF-67-600, and Au@ZIF-67-700. (o) TEM-EDX elemental mapping images of Au, C, N, O, and Co in Au@ZIF-67-500.

1350–1500 cm^{-1} are attributed to plane bending and entire stretching of the imidazole ring, respectively (Fig. 2b). The weak band at 1580 cm^{-1} is ascribed to the C–N stretching vibration of the imidazole backbone. The sharp band at $\sim 420 \text{ cm}^{-1}$ corresponds to the Co–N coordination of ZIF-67. The main absorption peaks of the as-prepared Au@ZIF-67 are similar to those of the parent ZIF-67, implying the preservation of the structural integrity. Notably, the relative intensity of the 420 cm^{-1} band decreased substantially in the Au@ZIF-67-500 spectrum, indicating a possible cleavage of the Co–N bond due to the thermal treatment [50]. Detailed discussions will be revealed in the following text.

X-ray photoelectron spectroscopy (XPS) was used to determine the surface structure and electronic state changes of the elements introduced by Au encapsulation and subsequent calcination. From the high-resolution Co 2p spectra (Fig. 2d), typical $2p_{1/2}$ and $2p_{3/2}$ peaks due to spin-orbit coupling can be observed [51–53]. Comparing the spectra of ZIF-67 and Au@ZIF-67, there is almost no shift in the binding energy of Co ions, demonstrating that the loading of Au NPs does not affect the electronic state of the surface Co ion. Nevertheless, a negative shift in the binding energy appeared for the Co ion of Au@ZIF-67-500. To determine the factor that causes the change in the binding energy of the Co ion, ZIF-67 was directly calcined at 500°C for 1 h (the composite is denoted as ZIF-67-500). The XRD pattern in Fig. S7 confirms the maintenance of framework integrity in ZIF-67-500. The XPS data of ZIF-67-500 displayed the same shift observed for Au@ZIF-67-500. Additionally, a new peak corresponding to the binding energy of Co(0)

emerged in both ZIF-67-500 and Au@ZIF-67-500 spectra, which can be attributed to the thermal treatment. The electron density around Co ions increased because of the appearance of Co(0), leading to a slight reduction in the binding energy of $\text{Co}^{2+/3+}$. Thus, the polarization between Co(0) and Co ions gave rise to surface electron redistribution, as demonstrated by XPS. The binding energies of C, N, and O displayed similar behavior, confirming the redistribution of the surface electrons (Fig. S9). XPS data were also recorded for Au@ZIF-67-350, Au@ZIF-67-400, and Au@ZIF-67-450 (Fig. S10). Neither the Co(0) peak nor the shift in the binding energy was observed for these composites, demonstrating that low-temperature calcination could not cause Co reduction. Thermal energy from 500°C annealing is sufficient to reduce Co and introduce a small change in the surface structure. Along with Co reduction, the Co–N coordination bond in the parent ZIF-67 was partially cleaved, which can be confirmed by the above-mentioned FTIR results. Furthermore, the BJH result showed that the average pore size of Au@ZIF-67-500 was 1.12 nm (Fig. S5b), which is slightly larger than that of Au@ZIF-67 mentioned above, which also supports the observation of the partial cleavage of the Co–N bond.

To clarify the difference in the catalytic performance for the OER observed for the composites, a series of electrochemical measurements were conducted. First, the LSV results presented in Fig. 3a were achieved under the above-mentioned conditions. Au@ZIF-67-500 showed the lowest potential to achieve the current density of 10 mA cm^{-2} . The overpotential of Au@ZIF-67-550 increased to $\sim 200 \text{ mV}$, implying a substantial decline in the

Figure 2 (a) UV-vis absorption spectra of ZIF-67, Au@ZIF-67-500, and Au@ZIF-67-500. (b) FTIR spectra of ZIF-67, ZIF-67-500, Au@ZIF-67, and Au@ZIF-67-x. (c) Full XPS spectra and (d) high-resolution spectra of Co 2p in ZIF-67, Au@ZIF-67, ZIF-67-500, and Au@ZIF-67-500.

electrocatalytic activity for the OER. The performance of the composites annealed at <500°C was lower than that of Au@ZIF-67-500, denoting that 500°C was the optimal calcination temperature. Additionally, compared with Au@ZIF-67 (1.624 V, Fig. S4) and ZIF-67-500 (1.619 V, Fig. 3a), Au@ZIF-67-500 (1.597 V) presented the lowest potential to achieve the target current density, demonstrating its highest performance. It can be concluded that both Au NP loading and favorable calcination temperature are necessary for improving the catalytic performance for the OER.

The LSV curve of Au@ZIF-67 calcined at 500°C for 4 h was determined to verify the catalytic efficiency. Long-term thermal treatment at 500°C caused the framework to shrink further, as shown in the corresponding TEM and SEM images (Fig. S11). LSV results (Fig. S12) showed a considerable increase in the operating potential to achieve the same current density. This can be explained by the fact that mass transfer is blocked without the support of the stubborn skeleton of ZIF-67, resulting in low electrocatalytic activity.

The Tafel slopes of the different samples were plotted to further reveal the catalytic kinetics for the OER on the

basis of the polarization curves (Fig. 3b). The value of Au@ZIF-67-500 is 87 mV dec⁻¹, which is the lowest value among all composites. The lowest overpotential and smallest Tafel slope indicate that Au@ZIF-67-500 exhibits the highest catalytic activity toward the OER. Additionally, electrochemical impedance spectroscopy was conducted to study the electron transfer rate of the composites. Nyquist plots of the selected samples are shown in Fig. 3c, in which the R_{ct} can be easily determined from the diameter of the semicircles [54]. The lower the R_{ct} , the higher the electrical conductivity. Au@ZIF-67-500 showed a considerably lower R_{ct} than ZIF-67-500. Consequently, Au NP encapsulation significantly accelerated the electron transfer, which promoted the electrochemical activity of the OER catalysts. In addition to electrocatalytic efficiency, the durability of the composites is an important factor that determines their practical application scope. As presented in Fig. S12a, the potential of Au@ZIF-67-500 decreased by only 8 mV to deliver the 10 mA cm⁻² current density after 1000 cycles. Moreover, the dependent current density–time (i – t) curve showed almost no decline in current density after the 12,000-s test (Fig. S12b). Therefore,

Figure 3 (a) LSV polarization plots for catalytic activity for the OER. (b) Tafel plots from the corresponding LSV measurements. (c) Electrochemical impedance spectroscopy of ZIF-67-500, Au@ZIF-67-350, Au@ZIF-67-400, Au@ZIF-67-450, Au@ZIF-67-500, and Au@ZIF-67-550. Inset: the partially enlarged electrochemical impedance spectroscopy plot. (d) Estimation of C_{dl} of different composites from cyclic voltammetry measurements.

Au@ZIF-67-500 was found to display high stability toward the OER, guaranteeing its practical application as an OER catalyst.

It is well known that the electrochemical active surface area (ECSA) of a catalyst has a strong influence on the catalytic performance for OER. With regard to electrochemical catalysts, the double-layer capacitance (C_{dl}) is proportional to the magnitude of ECSA. Consequently, cyclic voltammetry in the potential range without a Faradic effect was measured at different scan rates to calculate the C_{dl} values of the different composites (Fig. S13). As shown in Fig. 3d, Au@ZIF-67-500 displayed the highest C_{dl} , illustrating that it has the largest active surface area and affirming its superior catalytic activity for the OER. The normalized LSV pattern from the ECSA results (Fig. S14) further demonstrates the highest catalytic performance of Au@ZIF-67-500 among all the tested composites. Furthermore, the specific surface area of Au@ZIF-67-500 determined by the Brunauer-Emmett-Teller method is $622.2 \text{ m}^2 \text{ g}^{-1}$, guaranteeing the efficient mass transfer in the framework.

In conclusion, Au NPs were successfully loaded on ZIF-67 via the “bottle-around-ship” strategy as verified by

TEM, EDS elemental mapping, and UV-vis spectroscopy. The resulting Au@ZIF-67 composite showed distinctly improved catalytic activity for the OER compared with the parent ZIF-67. Furthermore, Au@ZIF-67-500, which was obtained from Au@ZIF-67 under thermal treatment at 500°C , displayed higher catalytic performance for the OER than Au@ZIF-67 and ZIF-67-500. After the thermal treatment at the appropriate temperature, the porous framework of ZIF-67 was inherited in Au@ZIF-67-500, which guaranteed mass transfer within the structure during OER catalysis. Additionally, the reduction of Co at high temperature induced polarization between Co(0) and Co ions, resulting in surface electron redistribution. Upon Au NP loading, electron transfer was further accelerated and the conductivity of Au@ZIF-67-500 substantially increased. The synergetic effect from Au NP loading, thermally induced Co reduction, and maintenance of the integrity of the porous framework is attributable for the efficient electrocatalysis of the OER. In this work, simple synthesis and controllable treatment realized a considerable improvement of the electrocatalytic performance of the nanocomposites. We believe that such a facile method would realize the development

of novel catalysts and facilitate their practical application.

Received 21 October 2020; accepted 4 December 2020;
published online 4 March 2021

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Acknowledgements This work was supported by the National Natural Science Foundation of China (NSFC, 21901221 and 21671170), the Natural Science Foundation of Jiangsu Province (BK20190870), Changjiang Scholars Program of the Ministry of Education (Q2018270), Lvyangjinfeng Talent Program of Yangzhou and Six Talent Peaks Project of Jiangsu Province. The authors acknowledge the technical support from the Testing Centre of Yangzhou University and State Key Laboratory of Coordination Chemistry of Nanjing University.

Author contributions Zhu R conceived the experiments and wrote the paper; Zhang Y collected and analyzed the data; Ding J synthesized the materials and performed the measurements; Pang H supervised the project and contributed the funding. All authors discussed the results and commented on the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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热引发纳米复合物提高催化析氧反应效率

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摘要 电解水能够为我们提供清洁可持续的能源, 这对生态环境系统大有裨益。因此, 在电解水体系中, 开发新型有效的析氧催化剂迫在眉睫。本文首先通过自下而上的方法合成 $\text{Au}@ \text{ZIF}-67$, 再对其进行控温处理得到纳米复合物 $\text{Au}@ \text{ZIF}-67-500$ 。通过扫描电子显微镜、透射电子显微镜、X射线光电子能谱和紫外光谱等一系列测试手段揭示了材料的纳米结构形貌及其表面电子分布。在 $1.0 \text{ mol L}^{-1} \text{ KOH}$ 电解液中, 利用三电极体系进行了电催化性能的测试。结果显示, 该纳米复合物在催化析氧反应过程中呈现出良好的催化活性和较好的稳定性。这一结果可以归功于三方面的协同作用: 金纳米粒子的包覆、多孔结构和有效的热控制。这种通过简单方法制备的析氧催化剂对能量转换领域具有一定的借鉴意义。