Simultaneously engineering the mesoscale mass transfer and surface reactions on the electrode can promote the kinetics of oxygen evolution reaction (OER). Herein, it is reported that the simultaneous modulation of the mesoscale diffusion and Mo–Fe–C sites formation over monodispersed hollow Fe@MoS$_2$–C sub-micro reactors for boosted OER performance. According to finite element simulation and analysis, the hollow nanostructured MoS$_2$–C host possesses better mesoscale diffusion properties than its solid and yolk–shell counterparts. Notably, the sulfur vacancies and intercalated carbon in the sub-micro reactor offer a unique microenvironment for Fe anchoring on Mo–Fe–C sites. The stability and activity of the sites are revealed by theoretical calculations. The resultant Fe@MoS$_2$–C presents an OER overpotential of 194 mV, which is much better than those of the Fe-based single-atom catalysts reported in the data. This monodispersed sub-micro reactor involves the modulation of mesoscale diffusion and single-atom sites, and it may have broad prospects for complex electrocatalytic reactions.

1. Introduction

Electrochemical refinement technologies, including carbon dioxide/nitrogen/oxygen reduction reaction processes, water splitting systems, and metal–air batteries are sustainable means for realizing the carbon neutrality.[1,2] As one of the key half-reactions in the electrocatalytic process, the electrochemical oxygen evolution reaction (OER) has more prospective applications than other anodic reactions.[3] However, the kinetic process of the OER is always sluggish due to the high energy barriers involving in the multistep electrochemical water oxidation process,[4] thereby hindering catalytic efficiency. Though noble metal-based materials, such as IrO$_2$ and RuO$_2$, are state-of-the-art catalysts for electrochemical water oxidation, the scarcity, high cost, and inferior stability have limited their widespread application in the alkaline electrolysis field.[5] Therefore, the design of highly active nonprecious-metal OER electrocatalysts with long-term durability is important, but remains highly challenging.[3,6-9]

Optimizing the mass transfer behaviors of chemical species and the surface reactions over electrodes to develop highly efficient electrocatalysts is crucial for facilitating the electrochemical OER kinetics process.[10,11] In fact, considerable efforts have been devoted to the engineering of electrodes to tailor the diffusion behavior, and sufficiently rapid macroscale electrolyte transfer to electrodes has been achieved.[12,13] However, for the water-splitting
reaction at the gas–liquid–solid triple-phase interface, optimizing the electrocatalysts at the mesoscale could maximize their utilization, which is an important strategy for promoting the catalytic process.\[14\] 2D layered molybdenum sulfide (MoS\(_2\)) has potential electrocatalytic application, while its 2D configuration could be easily self-stacked leading to disillusionary mass transfer property.\[15\] As a result, mass diffusion could become the determining factor of the electrocatalytic process. For this reason, it is of great significance for the innovative design of the geometric configurations of MoS\(_2\) materials to optimize mass diffusion at the mesoscale. For example, benefiting from the 3D hierarchical nanoarchitectures\[16\] self-assembled by 2D nanosheets, the mass transfer properties of electrodes could be enhanced to some extent. The design of nanoarrays could provide a shorter electron or ion transfer path and increase the accessibility of catalytic sites.\[17–19\] Meanwhile, 3D ordered channels are available for electrolyte diffusion, thereby enhancing electrocatalysis.\[10,20\] The diffusion mobility and paths could be improved by the alternate intercalation of monolayer carbon in the (002) facets of MoS\(_2\).\[21\] Notably, multilevel nanostructured materials with porous shell layers and inner spaces can yield catalysts that can be readily infiltrated by electrolytes, with rich paths for mass diffusion.\[22–25\] However, it is still an ambiguous conclusion how the mesoscale diffusion affects the catalytic activity, due to the challenges for design, and the limitations of suitable synthetic methods for such a material model.

In addition, the improvement of the surface reactions on the electrode has focused on regulating the active sites of the catalysts.\[26–28\] Single-atom catalytic sites (SACs) possess 100% atomic utilization efficiency, quantum size effects, and highly tunable electronic states, endowing the materials with superb electrocatalytic properties.\[29–33\] The interactions between the support and the metal, which are closely related to the coordination environment, could play a key role for the activity, durability, and selectivity of electrocatalysts.\[34–36\] Therefore, the support could have a noticeable impact on the efficiency of SACs. Over the past decade, the structure–property relationships of carbon-supported SACs with unsaturated, saturated, and super-saturated coordination environments have been systematically studied.\[37–41\] Recently, noncarbon supports, such as metal oxides, metal chalcogenides, and metal hydroxides, have been demonstrated potentially for the construction of SACs than carbon supports.\[42–45\] Because of the multifarious anchoring mechanisms\[46,47\] it may be more profitable to maximize the atomic utilization and stability of SACs in noncarbon hosts. According to previous literature, engineering MoS\(_2\)-based materials via self-tailoring,\[48–49\] doping,\[50–51\] and interface formation\[52–53\] can create abundant sites, which could possibly be used for the preparation of transition metal decorated SACs afford for electrocatalytic applications.\[54–56\] Specifically, it is feasible to simultaneously obtain preeminent electronic structures and mass transfer properties via the engineering of 3D nanostructured nanoreactors, owing to the abundant exposed active sites, and increased contact area between catalysts and electrolyte, and shortened mass transport length.\[57–59\] The sub-micro reactor distinguishes the nanoreactor in size and refers that the monodispersed particle is with particle size from 100 to 1000 nm on three-dimensional scale, which could combine mass transfer with active sites at the mesoscale, beyond the traditional catalyst. Inspired by this, the modulation of single-atom catalytic sites on mesoscale diffusion-enhanced MoS\(_2\)-based material platforms to design sub-micro reactors could be of great importance for boosting electrochemical water oxidation.

In this study, we reported the simultaneously modulation of the mesoscale diffusion and Mo–Fe–C active site formation over monodispersed hollow Fe@MoS\(_2\)–C sub-micro reactors for highly efficient electrochemical water oxidation. Based on the controllable preparation of monodispersed MoS\(_2\) developed in our lab,\[22,23\] a series of MoS\(_2\)–C material platforms assembled by carbon-intercalated MoS\(_2\) nanosheets were prepared through a modified micelle-confined microemulsion technology. According to finite element simulation and analysis (FEA), the hollow nanostructured configuration possessed much better mesoscale mass transfer properties than solid and yolk–shell structures. The monodispersed hollow MoS\(_2\)–C host with a dual coordination environment for Fe anchoring was used to develop the Fe@MoS\(_2\)–C sub-sub-micromicro reactor. The resultant catalyst exhibited a significantly lower OER over-potential than those of Fe-based SACs reported so far, and it also exhibited superior durability. Density functional theory (DFT) revealed the high activity and stability of the Mo–Fe–C sites.

2. Results and Discussion

2.1. Structural Characterization, FEA, and OER Assessment of MoS\(_2\)–C

Three kinds of monodispersed MoS\(_2\)–C materials were successfully synthesized by a micelle-confined microemulsion technology (Figure S1, Supporting Information). The configurations of the materials can be changed dramatically from solid to yolk–shell to hollow spheres. Specifically, the solid spheres with diameters of \(\approx 540\) nm were assembled from nanosheets by adding 1.2 mL hydrochloric acid (Figure 1a, and Figure S1a, S2, Supporting Information). The spheres were converted to yolk–shell configurations after regulating the amount of hydrochloric acid to between 0.8 and 0.6 mL. The diameter and the wall thickness of the yolk–shell sphere (\(\approx 650\) nm) remained unchanged, while the core gradually decreased with the decline in the hydrochloric acid (Figure 1b, and Figure S1b–d, S3, Supporting Information). By reducing the amount of hydrochloric acid to 0.5–0.3 mL, the monodispersed and uniform hollow spheres with diameters of \(\approx 750\) nm could be prepared (Figure 1b, and Figure S1e–g, S4, Supporting Information). As indicated by the transmission electron microscopy (TEM) results, the wall thicknesses of the spheres were \(\approx 20, 40,\) and 75 nm for the hollow MoS\(_2\)–C-1, MoS\(_2\)–C, and MoS\(_2\)–C-3, respectively.

According to the X-ray diffraction (XRD) profiles, the main peaks of the as-prepared materials could be attributed to 2H-MoS\(_2\) (JCPDS 37–1492). Interestingly, a (002) peak of the MoS\(_2\) at 14.2° was not found, while a new peak at 9.4° corresponding to an expanded layer of 0.96 nm appeared, demonstrating the intercalation of nonmolecular carbon. Based
on Fourier-transform infrared spectroscopy (FT-IR), the carbon intercalation could be derived from the graphitization of cetrimonium bromide (CTAB, Figure S6, Supporting Information). The specific surface areas were 41.2, 59.1, and 90.7 m² g⁻¹ for the solid, yolk-shell, and hollow MoS₂–C, respectively, and mesopores were present, supplying diffusion channels for electrolyte (Figure S7a–c, Supporting Information). The average pore sizes were 13.1, 16.2, and 21.0 nm for the solid, yolk–shell, and hollow MoS₂–C, respectively (Figure S7d, Supporting Information).

FEA was conducted to investigate the mass transfer properties at the mesoscale and to obtain a better understanding of the superiority of the engineered MoS₂–C hosts. Based on the experimental characterization, the models were correspondingly constructed for solid, yolk–shell, and hollow MoS₂–C materials. Diagrams of the models are shown in Figure S8a–c (Supporting Information). The simulated velocity fields are shown in Figure 1d–f, and the corresponding flow velocity at the outer boundary (path 1) and mid-position (path 2) is shown in Figure S8d–i (Supporting Information). The flow rate of the fluid was greatly influenced by the geometric configurations of the materials. As shown from the simulated results of path 1, the flow rate in the hollow sphere was much larger than those in the solid and yolk–shell spheres, except that very few positions were approximately equal to those of the yolk–shell spheres. More importantly, the hollow model had a clear advantage in terms of the flow velocity over the solid and yolk–shell spheres for path 2. The pressure distribution of the material in the fluid was another important index to evaluate the mesoscale mass diffusion. As shown by the comparison of the pressure fields (Figure 1g–i), a significant pressure difference was generated between the outside and inside in the hollow-structured model. In contrast, the pressure difference became weaker in the solid and yolk–shell models. In general, the higher flow velocity and pressure difference in the hollow-nanostructured catalyst could be conducive to the
full and rapid contact between the electrode and electrolyte, thereby promoting the mass transfer of the electrolyte at the mesoscale.

The static contact angles (CAs) are 61.9° and 57° for the solid and yolk–shell MoS$_2$–C, respectively (Figure S9, Supporting Information). In contrast, the CA of the hollow spheres decreased to 42.6°. According to the comparison of the surficial microstructure (Figure S2–S4, Supporting Information), the enhanced hydrophilicity may have been due to the vertical self-assembly of the layer-expanded nanosheets onto the hollow spheres. There was no doubt that the higher surface wettability of the hollow-structured catalyst would ensure fast electrolyte penetration and accelerate the migration of hydroxyl groups. Next, we studied the electrochemical water oxidation performances of the as-prepared materials to reveal the structure–property relationships. In contrast, the hollow MoS$_2$–C catalyst with optimal mesoscale diffusion properties delivered an overpotential of 303 mV (10 mA cm$^{-2}$) and a Tafel slope of 79 mV, which was better than those of the hollow MoS$_2$–C–1, hollow MoS$_2$–C–3, solid MoS$_2$–C, and yolk–shell MoS$_2$–C catalysts (Figure 1j and Figure S10, Supporting Information). This result indicated that the mesoscale diffusion could be modulated via the engineering of the microstructure of the catalyst, thus promoting the electrocatalytic OER activity. Nonetheless, the OER activity of the hollow MoS$_2$–C was still inferior to those of the catalysts reported to date (Table S3, Supporting Information) because of the simple and scanty active sites.

2.2. Preparation and Characterization of Monodispersed Hollow Sub-Micro Reactors

To further improve the OER performance, a series of monodispersed sub-micro reactors were designed via the elaborate functionalization of the hollow MoS$_2$–C. The carbon-intercalated MoS$_2$–C host was first prepared by the treatment of the hollow precursor, which was subsequently thoroughly mixed with Fe salt. The resultant powder was treated via a calcination process to obtain the monodispersed Fe@MoS$_2$–C sub-micro reactor (Figure 2a). According to the comparison for the XRD profiles (Figure 2b and Figure S11, Supporting Information), the expanded layer was reduced from 1.1 nm for MoS$_2$–CTAB to 0.96 nm for MoS$_2$–C and Fe@MoS$_2$–C, and it was further decreased to 0.62 nm corresponding to the typical value of (002) facet in Fe@MoS$_2$ and MoS$_2$.

As shown by the field-emission scanning electron microscope (FESEM) images, the MoS$_2$–CTAB precursor exhibited a monodispersed feature with a diameter of ~840 nm, and the nanosheets were vertically assembled onto the well-defined spheres, forming a quasi-nanorarray (Figure S12, Supporting Information). After the calcination, the morphology remained constant, while the size of the MoS$_2$–C decreased to ~750 nm. The self-assembled array on the MoS$_2$–C could supply rich channels for electrolyte diffusion and gas release, which was consistent with the Brunauer–Emmett–Teller (BET) and CA results (Figure S13, Supporting Information). After introducing Fe, the structure, size, and nanoray of the MoS$_2$–C remained unchanged, exhibiting a stable nanoarchitecture (Figure 2c–e and Figure S14, Supporting Information). Notably, the diameters of the hollow MoS$_2$ and Fe@MoS$_2$ microspheres were reduced to ~670 nm, and the vertical nanosheets tended to collapse compared with those in the MoS$_2$–C and Fe@MoS$_2$–C (Figure S15 and S16, Supporting Information). Significantly, the monodispersed and uniform microspheres could be controllably prepared on a large scale using the low magnification FESEM images and the size distributions (Figure S12–S16, Supporting Information).

TEM and high-resolution TEM (HRTEM) images of the MoS$_2$–CTAB showed its hollow structure, and an expanded space was observed due to the intercalation of CTAB (Figure S17, Supporting Information). The hollow nanostructured configurations remained almost constant after the heat treatment, while the expanded lattice was reduced to 0.96 nm in the MoS$_2$–C and to a typical spacing of 0.62 nm in the MoS$_2$ (Figure S18–S20, Supporting Information). As shown in the high-angle annular-dark-field (HAADF) image and the corresponding energy-dispersive X-ray spectroscopy (EDS) mappings of MoS$_2$–C, the elements Mo, S, and C were homogeneously distributed in the microsphere, implying that the composition in the core was the same as that in the shell. After introducing Fe, neither the hollow nanostructures nor the expanded layer was affected (Figure 2f,g). The aberration-corrected HAADF and corresponding annular-field (ABF) images revealed that the monomolecular carbon was successfully intercalated in the (002) facet of MoS$_2$ to generate a superlattice (Figure 2h,i). The low- and high-magnification HAADF images and the EDS mapping for Fe@MoS$_2$–C indicated that the element distribution in the nanosheet-assembled hollow sub-micro reactor was homogeneous (Figure 2j and Figure S19, Supporting Information). No aggregation was evident in the EDS mapping image of Fe. Verified from the corresponding EDS spectrum (Figure S19f, Supporting Information), weak peaks attributed to the Fe signal could be seen in the Fe@MoS$_2$–C sub-micro reactor, and the atomic percentage was calculated to be 0.8% (weight percentage: 0.93%). We performed the spherical aberration-corrected HAADF scanning transmission electron microscopy (HAADF-STEM) to further visually estimate the Fe distribution (Figure 2k). Speckled bright dots (yellow circles) existed in the interlayer and at the edge, demonstrating that single-atom Fe was atomically isolated in the sub-micro reactor. The Raman spectra of MoS$_2$–C and Fe@MoS$_2$–C (Figure S21, Supporting Information) displayed typical vibration peaks of 2H–MoS$_2$ and defective carbon. In contrast, both the out-of-plane $A_{1g}$ and in-plane $E_{2g}$ vibrations of Mo–S were blue-shifted in the Fe@MoS$_2$–C further confirming the interaction between MoS$_2$ and single-atom Fe.

Electron paramagnetic resonance (EPR) was carried out to study the sulfur vacancies before and after carbon intercalation. Compared with MoS$_2$, MoS$_2$–C delivered larger signal at $\approx$3484 G (Figure S22, Supporting Information), indicating that introducing monolayer carbon in the interlayer could lead to the enhancement of the sulfur vacancies. The correlation between Fe and the MoS$_2$–C host was revealed by X-ray photoelectron spectroscopy (XPS). According to the comparison of the Mo 3d spectra, a pair of peaks at 229.0 and 232.2 eV attributed to Mo$^{4+}$ were fitted, and they were positively shifted by 0.3 eV after introducing Fe (Figure 3a). Meanwhile, the binding energies of S 2p (163.1 and 162.0 eV) also increased by 0.2 eV in the
Fe@MoS$_2$–C compared with those of the MoS$_2$–C (Figure S23b, Supporting Information). In the high-resolution Fe 2p spectrum of the Fe@MoS$_2$–C, two peaks at 712.9 and 726.0 eV belonged to the Fe 2p3/2 and Fe 2p1/2 of the oxidation states of Fe$^{x+}$ species ($x < 3$), respectively. Compared with Fe$^{3+}$, the lower valence states of Fe atoms could be due to the electron transfer between Mo and Fe. The couple peaks at 717.6 and 730.6 eV were satellite peaks (Figure 3b). Another two weak peaks at 706.9 and 720.6 eV, which were respectively assigned as Fe 2p of the Fe–C bonds, were also identified. A new peak at 283.7 eV was evident in the C1s spectra (Figure 3c). The above XPS analysis indicated the strong electronic interactions between Mo and Fe as well as the formation of Fe–C bonds in the Fe@MoS$_2$–C. Similar peak shifts were found in the Fe@MoS$_2$ and MoS$_2$ except that the peaks associated with Fe–C disappeared (Figure S24, Supporting Information). Based on the inductively coupled plasma mass spectrometry (ICP-MS) result (Table S1, Supporting Information), the concentrations of Fe were 54.5 and 27.5 µg L$^{-1}$ in the Fe@MoS$_2$–C and Fe@MoS$_2$, respectively, which corresponded to 1.09 and 0.55 wt.%.
We collected the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the Fe K-edge to determine the electronic states and the local structural information around the Fe in the Fe@MoS\(_2\)-C. According to the XANES spectroscopy results of the Fe K-edge (Figure 3d), the white line intensity was between those of the Fe metal foil and Fe\(_2\)O\(_3\) references, signifying the oxidation state of Fe between Fe\(^0\) and Fe\(^{3+}\) in the Fe@MoS\(_2\)-C, which was consistent with the XPS analysis. Atomic coordination information of Fe was revealed by Fourier-transformation EXAFS spectroscopy. Compared with the radial distance space spectra \(\chi(R)\) of the Fe foil and Fe\(_2\)O\(_3\) reference, a prominent peak at \(\approx 1.69\) Å belonging to the first shell of the Fe–C scattering signal was clearly identified, while no Fe–Fe signal was evident at \(\approx 2.23\) Å, demonstrating the atomic dispersion of Fe in the Fe@MoS\(_2\)-C (Figure 3e). Notably, a weak signal at \(\approx 2.64\) Å assigned to the scattering signal of the Fe-Mo pair can also be found. Accordingly, the electron transfer could be existed between Fe and Mo, which was in agreement with XPS spectra. The high-resolution wavelet-transform EXAFS was obtained to intuitively show the formation of Fe–C and Fe–Mo pairs. Specifically, the Fe@MoS\(_2\)-C delivered the highest intensity at \(\approx 1.69\) Å attributed to the Fe–C pairs (Figure 3f). To better understand the local geometry, EXAFS fitting was carried out, and the parameters and \(k\)-space are shown in Table S2 and Figure S25 (Supporting Information), respectively. The fit indicated that the Fe–C distance was 2.11 Å with a coordination number of around 3. In addition, a significant lobe appeared above 2 Å, which indicated that the Mo could be coordinated with metal Fe, forming the Fe-Mo pair. Based on the above detailed XAFS results, atomically dispersed Fe was anchored by the C and Mo atoms of the hollow MoS\(_2\)-C, forming a sub-micro reactor.

2.3. Electrocatalytic OER Evaluation

The OER performances of the as-prepared monodispersed hollow Fe@MoS\(_2\)-C, Fe@MoS\(_2\), MoS\(_2\)-C, MoS\(_2\), S-Fe@MoS\(_2\)-C, and Y-Fe@MoS\(_2\)-C sub-micro reactors were systematically compared, and the commercial IrO\(_2\) was tested for comparison. As shown by the polarization curves in 1 M KOH (Figure 4a), the Fe@MoS\(_2\)-C catalyst delivered an overpotential of 194 mV at 10 mA cm\(^{-2}\), which was lower than those of Fe@MoS\(_2\) (239 mV), MoS\(_2\)-C (303 mV), and MoS\(_2\) (362 mV), exhibiting the highly improved OER activity after carbon intercalation and single-atom Fe anchoring. The corresponding Tafel slope of 63 mV dec\(^{-1}\) was also lowered for the Fe@MoS\(_2\)-C catalyst compared with those of the Fe@MoS\(_2\), MoS\(_2\)-C, and MoS\(_2\) (Figure 4b). In addition, the activity of the hollow Fe@MoS\(_2\)-C catalyst for water oxidation was much higher than those of the S-Fe@MoS\(_2\)-C and Y-Fe@MoS\(_2\)-C materials based on the polarization curves and Tafel slopes (Figure S26, Supporting Information), which could be attributed to the highly enhanced mesoscale mass transfer behavior in the monodispersed hollow sub-micro reactors. Importantly, the overpotential of
the Fe@MoS₂-C catalyst was reduced by 138 mV compared with that of commercial IrO₂. Furthermore, the monodispersed hollow Fe@MoS₂-C sub-micro reactor exhibited the lowest OER overpotential of the Fe-based SACs reported in the literature (Figure 4c and Table S3, Supporting Information). The oxygen bubble formation and removal on solid and hollow nanostructured Fe@MoS₂-C catalysts were recorded to investigate the difference on the electrodes. The bubbles generated and left the hollow structured catalyst (Movie S2, Supporting Information) much rapid than those of solid structured catalyst (Movie S1, Supporting Information). This continuous release of bubbles could minimize the “dead area”, thereby offering a constant catalytic performance. The corresponding digital images every 5 s for 35 s are shown in Figure S27 and Figure S28 (Supporting Information). By contrast, at the same period, the bubbles updated more rapidly on the hollow structured catalyst, thus leading to superior current increase. Based on the above analysis, the high OER activity was co-determined by the mesoscale mass transfer and catalytic sites, and the contribution of catalytic sites played the dominant role.

According to the electrochemical impedance spectroscopy (EIS) curves (Figure S29a, Supporting Information), the Fe@MoS₂-C catalyst exhibited the lowest charge transfer resistance, revealing the fastest charge transfer kinetics. The double-layer capacitance was 35.8 mF cm⁻² for the Fe@MoS₂-C, which was much higher than the values of 23.0 mF cm⁻² for the Fe@MoS₂, 8.3 mF cm⁻² for the MoS₂-C, and 3.5 mF cm⁻² for the MoS₂, verifying that the Fe@MoS₂-C had the highest number
of active sites (Figure S29b, S31, Supporting Information). To further assess the durability of the Fe@MoS$_2$–C catalyst, we conducted electrolytic measurement using the chronoamperometric method. The overpotentials of the sub-micro reactor exhibited almost no attenuation during continuous measurements at 10, 50, 100, and 200 mA cm$^{-2}$ (Figure S29c, Supporting Information). As shown in Figure S30 (Supporting Information), the Fe@MoS$_2$–C after the multistep chronoamperometric test delivered overpotential of 197 (10 mA cm$^{-2}$) and 235 mV (100 mA cm$^{-2}$), exhibiting negligible attenuation in terms of catalytic activity. The multistep chronoamperometric result and the LSV polarization curve demonstrated that the Fe@MoS$_2$–C catalyst could possess the superior durability and rate capabilities for electrochemical water oxidation.

Furthermore, the OER activity in a strongly alkaline environment was investigated to estimate the potential application in industrial environments. The OER activity was gradually improved in the increase of the alkaline concentration of the electrolyte, and an overpotential of 155 mV could be achieved when the alkalinity approximated to that of industrial conditions (Figure S32a, Supporting Information). Accordingly, the Tafel slope was reduced to 43 mV dec$^{-1}$ in 6 M KOH (Figure S32b, Supporting Information). The stability of the Fe@MoS$_2$–C catalyst was studied in 6 M KOH, which exhibited slight attenuation in the electrolytic OER test for 120 h at 100 mA cm$^{-2}$, further revealing its excellent durability under strongly alkaline conditions (Figure 4d). Notably, the polarization curve and Tafel slope after electrolysis for 120 h were close to those of the catalyst before catalysis (Figure S33, Supporting Information).

2.4. Operando Raman Spectroscopy, Durability of Catalyst, and Theoretical Calculations

The operando Raman analysis of the Fe@MoS$_2$–C electrode was conducted in 1M KOH at different voltages to investigate the operando Raman spectra, structural characterization after catalysis, and DFT calculations. a) Operando Raman, b) Fe K-edge EXAFS spectra of the Fe$_2$O$_3$ reference and Fe@MoS$_2$–C, c) wavelet transform of the Fe@MoS$_2$–C after catalysis, d) TEM image, e) HRTEM image, f) HAADF image and corresponding EDS mapping, g) theoretical stability of the single-atom Fe, h) EDDs of the MoO$_x$–C, MoO$_x$–Fe, and MoO$_x$–Fe–C. The scale bars in f are 200 nm. Isovalue in h is 0.005 e Å$^{-3}$.
the structural evolution (Figure 5a). The Raman signal revealed distinct changes during the OER test compared to that of the initial state. In contrast, two peaks at 3779 and 401.0 cm\(^{-1}\) corresponding to the stretching vibrations of Mo–S could be clearly observed before applying a voltage, and these vibrations gradually decreased with the enhancement of the D and G bands of carbon from 0 to 0.7 V. In particular, two weak peaks at 8173 and 989.7 cm\(^{-1}\) corresponding to Mo–O vibrations appeared at 0.3 V, signifying that slight oxidation could occur in situ on the MoS\(_2\) during the OER process. The Mo–O vibrations were gradually raised along with the increase in the applied voltage. The operando Raman data verified that the Fe@MoS\(_2\)-C catalyst could undergo reconstruction. According to the XPS results of the Fe@MoS\(_2\)-C after catalysis (Figure S34, Supporting Information), the positions of Fe\(^{2+}\), satellite, and Fe–C peaks were positively shifted in the Fe 2p, and two weak peaks belonging to the high valence state of Mo could be found in the Mo 3d (Figure S34, Supporting Information).

We collected the XAFS of the Fe@MoS\(_2\)-C catalyst after catalysis (120 h at 100 mA cm\(^{-2}\)) to reveal the catalytic sites. Compared with that of fresh catalyst (Figure 3d), the near-edge absorption energy of Fe was between those of the Fe foil and the Fe\(_2\)O\(_3\) references, yet it was close to the high-valance Fe\(^{3+}\) of the Fe\(_2\)O\(_3\) reference (Figure S35a, Supporting Information), indicating that the Fe could be affected by the oxygen species. According to the EXAFS, the primary scattering signal at 1.60 Å showed slight negative changes in intensity compared to that of the fresh catalyst, which can be explained as the co-contribution of Fe–C and Fe–O pairs (Figure 3e). Meanwhile, the position of Fe–O for the catalyst after catalysis was lower than 1.69 Å of Fe–C for the fresh catalyst and higher than 1.55 Å of Fe–O for the Fe\(_2\)O\(_3\) reference, which indicated that the Fe–O pair could be derived from the adsorbed water molecules or hydroxyl groups in the OER process. According to the EXAFS fitting result (Table S4 and Figure S35b, Supporting Information), the coordination numbers of Fe–C and Fe–O were around 3 and 1, respectively. Considering the closeness of the fitted Fe–C (2.08 Å) and Fe–O (2.06 Å) peaks, these two peaks likely overlapped in the catalyst after catalysis. The signal of the Fe–Mo pair remained, while it also exhibited a marginal shift due to the formation of hexavalent Mo in the surficial reconstruction, which was in accordance with the XPS results. Furthermore, scattering signals of the Fe–O/Fe–O and Fe–Mo pairs also appeared in the wavelet transform contour plots. The above XAFS results revealed that the catalytic site of Fe atom could participate in the adsorption and desorption of oxygen intermediates during the catalytic OER.

The mechanical stability of the hollow sub-micro reactor was confirmed by the unchanged configuration after the catalytic testing (Figure 5d). The expanded layer still existed revealing the stability of the carbon intercalation. Beyond that, a thin layer with a thickness of ~10 nm and poor crystallinity was generated outside the sphere (Figure 5e) due to in situ surface oxidation during the water oxidation process.\(^{[86]}\) The HAADF image and EDS mapping revealed that Mo, S, C, and Fe were homogeneously distributed, while the O accumulated outside the sphere to some extent (Figure 5f). According to the EDS spectrum (Figure S36, Supporting Information), the percentage of Mo, S, C, and Fe elements remained nearly constant, and the weight percentage of O element was 7.94%. The XRD pattern after catalytic process still demonstrated the expanded layer and the typical peaks of MoS\(_2\), further indicating the as-prepared catalyst is very durable (Figure S37, Supporting Information). These results were consistent with the operando Raman and XPS results, indicating the steadfastness of single-atom Fe and the reconstruction.

We employed DFT calculations to assess the electronic structures, Mo–Fe–C sites, and kinetics process (Figure S38, Supporting Information). The stability of the single-atom Fe was first investigated via the calculation of the adsorption energy (\(E_{\text{ads}}\)) and the cohesive energy (\(E_{\text{coh}}\)). According to the criteria, both the \(E_{\text{ads}}\) and \(E_{\text{coh}}\) should be negative values for the atom to stabilize on the host.\(^{[61]}\) As a result, the calculated \(E_{\text{ads}}\) values of Fe atoms in the MoO\(_x\) and MoO\(_{x–}\text{C}\) were ~4.16 and ~4.47 eV, respectively, while the corresponding \(E_{\text{coh}}\) values were 0.12 and ~0.19 eV (Figure 5g). The result indicated that single-atom Fe could be stabilized in MoO\(_{x–}\text{C}\) when there were dual-anchoring sites of vacancies and carbon atoms.

As shown from the partial electronic density of states (PDOS), the peaks of the Fe d orbital overlapped with those of the Mo d and C p orbitals in the MoO\(_{x–}\text{Fe–C}\) to some extent, confirming the Mo–Fe–C sites (Figure S39, Supporting Information). Furthermore, the d states of Fe dominated the PDOS near the Fermi levels in the MoO\(_x\)-Fe and MoO\(_{x–}\text{Fe–C}\). The PDOS diagram (Figure S40, Supporting Information) showed that the d-band center of Fe atoms in the MoO\(_{x–}\text{Fe–C}\) was at ~1.19 eV, which was slightly upshifted compared with that of the MoO\(_x\)-Fe. Similarly, the d-band center of the Mo atoms was shifted to ~1.01 eV from ~3.05 eV after introducing Fe and carbon. The upshifted d-band center originating from the decrease in the antibonding electrons could promote charge transfer leading to effortless adsorption and desorption of the intermediates. The electron density difference (EDD) results showed that the electron redistribution occurred at the interface of MoO\(_{x–}\text{Fe–C}\), and an enhanced electron transfer channel of “MoO\(_x\) → Fe → carbon,” had formed (Figure 5h). The specific amounts of charge transfer were identified by population analysis (Figure S41, Supporting Information).

The chemisorption models and processes were shown in Figure S42, S43 (Supporting Information), and the free energy changes were calculated to investigate the kinetic barriers (Figure S44, Supporting Information). As shown from the energy diagram, the formation of OOH\(^*\) intermediates (Step 3) was the rate-determining step (RDS) for MoO\(_x\). The RDS had not changed while the energy barrier was reduced to 3.06 from 3.88 eV after introducing carbon intercalation. Because of the electron accumulation, the decomposition of OOH\(^*\) intermediates was more difficult, and the RDS changed to the dissociation of OOH\(^*\) intermediates for MoO\(_x\)-Fe (Step 4). Compared with MoO\(_{x–}\text{C}, MoO\(_{x–}\text{Fe} delivered a much lower barrier of 2.50 eV, revealing that Fe was more predominant than carbon intercalation. Interestingly, benefitting from the enhanced electron channel of “MoO\(_x\) → Fe → carbon,” the dissociation of OOH\(^*\) intermediates for the MoO\(_{x–}\text{Fe–C}\) became more toilless than that of the MoO\(_x\)-Fe. Furthermore, the energy barrier of 1.98 eV (Step 3) was the RDS for the MoO\(_x\)-Fe–C, which was the lowest compared with those of the MoO\(_x\), MoO\(_{x–}\text{C}, and MoO\(_{x–}\text{Fe–C.}
According to the comparisons of the barrier for RDS at Mo and Fe sites (Figure S45, Supporting Information), Fe site is the active site for the OER process. In general, the Mo–Fe–C sites could stabilize single-atom Fe, promote charge transfer, and regulate kinetics process, thereby leading to an enhanced electrochemical OER.

3. Conclusion

In summary, we simultaneously modulated the mesoscale mass transfer and surface reaction active sites of the electrode to achieve highly efficient electrochemical water oxidation process via constructing monodispersed hollow Fe@MoS$_2$–C sub-micro reactor. Specifically, a series of MoS$_2$–C hosts with sulfur intercalated in the (002) facet of MoS$_2$ resulting in a superlative mass transfer could be highly improved in the hollow that the flow velocity and differential pressure related to mesoscale diffusion and particular local sites, the Fe@MoS$_2$–C sub-micro reactor delivered a significantly lower OER yield the Fe@MoS$_2$–C sub-micro reactor. Benefiting from the unique microenvironment for Fe anchoring on Mo–Fe–C sites vacancies and intercalated carbon in the hollow host offered a lattice and increasing the number of sulfur vacancies. The sulfur vacancies and intercalated carbon in the hollow host offered a unique microenvironment for Fe anchoring on Mo–Fe–C sites yield the Fe@MoS$_2$–C sub-micro reactor. Benefitting from the rich mesoscale diffusion and particular local sites, the Fe@MoS$_2$–C sub-micro reactor delivered a significantly lower OER overpotential than those of the Fe-based SACs reported to date; moreover, it also exhibited excellent stability in continuous electrolysis tests. DFT calculations demonstrated the stability of Mo–Fe–C coordination, the electron transfer channel of “MoO$_x$ → Fe → carbon,” and the favorable d-band center in the dual-anchoring model. The kinetics calculations further signified that the dual-anchoring site could change the RDS and optimize the adsorption and desorption of oxygen intermediates, thereby reducing the reaction barriers for water oxidation. Our work contributes to understanding the relationship between mass transfer and catalytic activity and might provide insight into the design of advanced electrocatalysts through the engineering of monodispersed sub-micro reactors.

4. Experimental Section

Synthesis of MoS$_2$–C and MoS$_2$ Hosts: The MoS$_2$–C materials were prepared through a micelle-confined microemulsion technology. Specifically, the water phase solution (Na$_2$MoO$_4$·2H$_2$O: 1 mmol; glucose: 0.6 g; H$_2$O: 300 mL) was stepwise added into the oil solution (CTAB: 15 mmol; n-butanol: 100 mL) and strongly stirred for 2 h. 50 mL of ethylene glycol and 0.4 mL of hydrochloric acid (32.36 mol L$^{-1}$) were introduced in order and stirred for 5 h. The milky white emulsion was subsequently transferred into a high-pressure autoclave and kept at 220 °C for 24 h. The black powder was produced after the filtration, abstersion (distilled water and absolute ethanol), and drying at 60 °C overnight to obtain the precursor, named as MoS$_2$-CTAB. The MoS$_2$-CTAB was treated at 700 °C with 2 °C min$^{-1}$ in Ar for 5 h to produce the hollow MoS$_2$–C host, named as MoS$_2$–C. Similarly, the hollow MoS$_2$ host was synthesized via disposing of the MoS$_2$-CTAB at 850 °C with 10 °C min$^{-1}$ in Ar for 5 h.

Keeping the based condition constant, a series of MoS$_2$–C materials with different nanostructured configurations were prepared by changing the amounts of hydrochloric acid to 1.2, 0.8, 0.7, 0.6, 0.5, and 0.3 mL, named as solid MoS$_2$–C, yolk–shell MoS$_2$–C-1, yolk–shell MoS$_2$–C-2, yolk–shell MoS$_2$–C-3, hollow MoS$_2$–C-1, and hollow MoS$_2$–C-3, respectively.

Synthesis of Monodispersed Sub-Micro Reactors: Hollow MoS$_2$–C hosts (100 mg) were dispersed in a mixed solution (H$_2$O: 40 mL; ethanol: 20 mL) followed by slowly adding Fe(NO$_3$)$_3$·9H$_2$O solution (5 mL, 1 mol L$^{-1}$). The mixed solution was stirred for 12 h, and the resultant product was separated by centrifugation and dried at 60 °C (vacuum oven) overnight. Finally, the product was treated at 700 °C in Ar for 3 h to obtain the monodispersed hollow Fe@MoS$_2$–C subnano reactor. Similarly, the Fe@MoS$_2$ sub-micro reactor was produced by replacing the hollow MoS$_2$–C with the hollow MoS$_2$ host.

Accordingly, the monodispersed solid Fe@MoS$_2$–C and yolk–shell Fe@MoS$_2$–C sub-micro reactors were prepared through changing hollow MoS$_2$–C host with the solid MoS$_2$–C and yolk–shell MoS$_2$–C materials, named as S–Fe@MoS$_2$–C and Y–Fe@MoS$_2$–C, respectively.

FEA Methods: The finite element simulation and analysis (FEA) were performed with the COMSOL Multiphysics, and the corresponding 2D mode was collected. According to the experimental data, the model of the solid sphere was constructed with a diameter of 540 nm and a pore size of 13 nm; the model of the yolk–shell sphere was plotted with a diameter of 650 nm and a pore diameter of 16 nm; the model of the hollow sphere was constructed with a diameter of 750 nm and a pore diameter of 20 nm. The error of the pore diameter in the models was ±0.2 nm. The calculated domain was simulated via filling water in a rectangular region (6000 w nm × 6010 h nm). The water was poured from the left boundary, and outflowed from right boundary. The inflow velocity was set to 0.25 m s$^{-1}$ at the entrance. The flow field was done on the “Laminar Flow” module. In order to represent the adhesion of the materials on an electrode, the calculated models were all put on the coboundary of the domain in the stationary simulation. The flow field and pressure field were calculated by the Navier–Stokes equations:

$$\nabla \cdot \mathbf{u} = 0
$$

$$\rho \left[ \nabla \cdot \left( \nabla \mathbf{u} \right) \right] = \nabla \cdot \left( -p I + \mu \left( \nabla \mathbf{u} + \left( \nabla \mathbf{u} \right)^T \right) \right) + \mathbf{f}
$$

Where $\mathbf{u}$, $\rho$, $p$, and $\mathbf{f}$ represent the flow velocity, fluid density, pressure, and volume force vector, respectively.

Computational Details: The DFT calculations were executed in the CASTEP with the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. This calculation was performed to represent the exchange and correlation effects. Partial sulfur atoms were substituted by oxygen atoms to match with the self-reconstruction. A sulfur atom was removed to represent the sulfur vacancy. The MoS$_2$ (001) surfaces were modeled by a 3 x 3 unit cell with two layers of 6.5 Å and the atoms periodically repeated with the vacuum was set 15 Å in z-direction. The model that sulfur atoms were substituted by oxygen atoms and removed in MoS$_2$ cell was named MoO$_x$. The graphite was modeled by a 4 x 4 unit cell and inserted into the extended layer of MoO$_x$ with a distance of 9.5 Å forming the MoO$_x$–C. Fe atoms were put into the vacancy of sulfur in MoO$_x$ and MoO$_x$–C to construct the MoO$_x$–Fe and MoO$_x$–Fe–C models. The spin-polarized were added because of the special property of Fe. The k-point and energy cut-off was set to 3 x 3 x 1 and 490.0 eV. The self-consistent field, maximal force, maximal stress, and maximal displacement were set to 2.0 x 10$^{-4}$ eV atom$^{-1}$, 0.05 eV Å$^{-1}$, 0.1 GPa, and 0.002 Å. The green and yellow regions in the EDDs mean the electron accumulation and depletion area, respectively.

The adsorption energy ($E_{\text{ads}}$) of the single-atom Fe on the host was computed by the following equation:

$$E_{\text{ads}} = E_{\text{Fe@host}} - E_{\text{host}} - E_{\text{single-atom}}$$

where $E_{\text{Fe@host}}$, $E_{\text{host}}$, and $E_{\text{single-atom}}$ are the total energies of MoO$_x$, MoO$_x$–C, MoO$_x$–Fe, MoO$_x$–Fe–C, or Fe, respectively.

The bulk cohesive energy ($E_{\text{coh}}$) of the Fe atom on the host was calculated by the following equation:
\[ E_{\text{coh}} = \frac{E_{\text{bulk}}}{n} - E_{\text{single-atom}} \]  \hspace{1cm} (4)

where \( n \) represents the number of Fe atoms. when \( E_{\text{ads}} < E_{\text{coh}} < 0 \) and \( E_{\text{ads}} < 0 \), there is no metal leaching or aggregating, showing that the Fe atoms are stable in the host.

The overall OER process in the alkaline medium involving four-electron reaction steps was identified as follows:

1. \( \text{OH}^- + \star \rightarrow \text{OH}^- + e^- \) \hspace{1cm} (5)
2. \( \text{OH}^- + \text{OH}^- \rightarrow \text{O}_2(g) + \text{H}_2\text{O}(l) + e^- + \star \) \hspace{1cm} (6)
3. \( \text{O}_2^- + \text{OH}^- \rightarrow \text{OOH}^- + e^- \) \hspace{1cm} (7)

and the Gibbs free energy change (\( \Delta G \)) for each step was calculated by the following equation:

\[ \Delta G = E^{0}_{\text{DFT}} - E^{0}_{\text{DFT}} + \frac{1}{2} E^{0\text{p}}_{\text{DFT}} - E^{0\text{p}}_{\text{DFT}} + \Delta ZPE - T\Delta S \]  \hspace{1cm} (8)

Where the \( E_{\text{DFT}}, E'_{\text{DFT}}, E^{0\text{p}}_{\text{DFT}}, \) and \( E^{0\text{p}}_{\text{DFT}} \) are the total energies of the catalyst, \( \text{O}^n, \text{OH}^n, \) and \( \text{OOH}^n \) adsorbed on the catalyst surface, \( \text{H}_2 \), and \( \text{H}_2\text{O} \) molecule obtained from DFT calculation. \( \Delta ZPE \) and \( T\Delta S \) are the change in zero-point energies and entropy at 298 K (7).

The theoretical overpotential (\( \eta \)) is calculated by the following equation:

\[ \eta = -\min(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4) \]  \hspace{1cm} (9)

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
