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Improvement of oxygen evolution activity on isolated Mn sites by dual-heteroatom coordination

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ABSTRACT

The coordination of dual-heteroatom is an effective strategy to enhance the performance of oxygen evolution reaction (OER) of single-atom catalysts. Here, we synthesize Mn-SG-500 with isolated Mn sites coordinated with two sulfur and two oxygen atoms on graphene, and perform in-depth research on the structure-activity relationship for the OER. Under alkaline conditions, the Mn-SG-500 displays higher OER activity than commercial RuO₂. Combining *in-situ* structure analysis and theoretical calculations, we identify Mn-S₂O₂ as the catalytic active center, on which the oxidation of *O to *OOH is the rate-control step. The improved OER activity is attributed to the redistribution and optimization of Mn charges caused by the co-coordination of S and O. This work is helpful for further structure design and performance management of single-atom catalysts with dual-heteroatom doping.

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1. Introduction

Developing and utilizing renewable energy (such as wind energy and solar energy) can mitigate the depletion of traditional fossil fuels [1,2]. However, due to geographical and weather restrictions, the storage and transformation of renewable energy break through various restrictions to increase the accessibility of energy utilization, which is the main direction of energy development at present [3,4]. OER is an important half-reaction of electrolytic water and rechargeable zinc-air battery, which has a high reaction barrier and a large overpotential, greatly limiting the performance improvement of energy storage systems [5,6]. Therefore, a great deal of research has been focused on developing efficient and stable OER catalysts.

Single atom catalysts (SACs) are cutting-edge heterogene-

ous materials, in which the metal atom is the catalytic active center and has a high atomic utilization [7-10]. Due to large specific surface area, strong metal-carrier interaction, and high electrical conductivity, graphene materials show obvious advantages in SAC carriers [11-13]. Ir and Ru oxides have been widely studied and used in electrocatalytic OER, but their large-scale production has been limited by high cost [14–16]. To comply with sustainable development and reduce costs, transition metals, namely iron [17,18], cobalt [19,20], and nickel [21] have been loaded onto graphene carriers for OER [22,23]. As a natural OER active center, the excitation of the intrinsic electrocatalytic activity of Mn atoms to the maximum extent has received extensive attention [24]. Metal atoms in carbon-support SACs used in electrochemical fields such as electrocatalysis and energy storage are typically connected in the form of M-N, as stronger metal-support interaction to en-

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sure that metal atoms do not overflow [25]. Guan et al. [26] anchored manganese atoms on graphene to make the Mn sites exhibit excellent OER activity by combining with four nitrogen atoms. Nevertheless, in addition to structural stability, it is essential to regulate the *d*-orbital electrons of the central metal atom to improve the intrinsic catalytic activity of the catalyst. It has been shown that the adsorption of intermediates on M-N₄ structure is not optimal due to the strong electron donating effect of nitrogen [27]. Changing the type and number of coordination atoms is an effective strategy to modulate the crystal field of single atomic sites, adjust the *d*-electron structure and spin state of the metal, and optimize the adsorption strength of reaction intermediates. Li et al. [28] substituted two nitrogen atoms in Mn-N4 with two carbon atoms to regulate the adsorption of reaction intermediates on the catalyst and reduce OER overpotential. Zeng et al. [29] introduced boron dopants into Mn-N4, which reduced the *d*-orbital charge density of Mn, reduced the adsorption strength of reaction intermediates on Mn, and improved the electrocatalytic activity. Yao et al. [30] found that pre-adsorbed oxygen atoms at the Ru-N₄ site further optimized the adsorption and desorption of active intermediates, improving the OER activity. Hence, the introduction of dual-heteroatoms has a positive effect on the activity of single atom sites [31]. Compared with nitrogen atom, the introduction of S has a stronger conductivity enhancement effect on graphene, effectively promoting the reduction of graphene oxide. The oxygen atoms on graphene are conducive to improving surface hydrophilicity and enhancing mass transfer efficiency, especially for water-based electrolytes. However, the enhancement of OER activity by dual-heteroatom on single atom electrocatalyst has been simply attributed to the coordination effect [32]. The electronic effect should be more deeply understood, which is beneficial to better understanding the electrocatalysis mechanism.

To analysis the electronic effect caused by dual-heteroatoms, we designed isolated Mn sites coordinated with sulfur and oxygen on graphene to study the OER activity. Under alkaline conditions, Mn-SG-500 (Mn-O/S loaded on graphene) exhibited an overpotential of 332 mV at 10 mA cm⁻² and a Tafel slope of 56 mV dec-1, indicating enhanced OER activity compared to related materials such as Mn-G-500 (Mn-O/C loaded on graphene). In addition, the valence of Mn increased during the OER, and the Mn(IV) was the active center as analyzed by in-situ Raman and ex-situ X-ray photoelectron spectroscopy (XPS). Theoretical calculations showed that Mn-S₂O₂G demonstrated the best stability and the lowest theoretical overpotential, on which the rate-limiting step is the oxidation of *0 to *00H. The electron donating effect of oxygen and sulfur significantly increases the charge density around Mn. The electronic regulation strategy of double nonmetallic doping could be extended to the design of other transition metal SACs. For example, introducing sulfur into Fe-N-C was conducive to the generation of low-spin Fe3+ and promoted OH* desorption process [33]. Isolated Ni atom with three nitrogen and one sulfur coordination reduced the OER barrier by redistributing the charge [34]. The bonding of cobalt sites with oxygen intermediates was weakened due to the co-coordination of nitrogen and phosphorus [35].

2. Experimental

2.1. Synthesis of catalysts

Graphene oxide was synthesized according to the method described in the literature [36]. Mn-SG-500 was synthesized by freeze-drying and high-temperature calcination. Firstly, 1.8 mg MnCl₂·4H₂O and 100 mg of GO were dispersed into 50 mL of deionized water, and stirred ultrasonically for 30 min to form a uniformly dispersed colloidal solution, which was then freeze-dried to obtain solid A. After grinding the solid A and sulfur powder evenly, it was calcined in a tube furnace at 500 °C in a nitrogen atmosphere (the heating rate is 10 °C min⁻¹), and a black powder, namely Mn-SG-500, is obtained. The catalysts Mn-SG-*T* (*T* = 400, 600, and 700) were obtained at annealing temperature of 400, 600, 700 °C respectively. Mn-G-500 was obtained by direct high-temperature calcination of solid A in a tubular furnace without the addition of sulfur powder.

In order to ensure the experimental contrast, SG and G are also synthesized by lyophilization and calcined two-step. Graphene oxide and sulfur powder were evenly ground and calcined in a tube furnace at 500 °C in a nitrogen atmosphere to obtain SG-500. G-500 was obtained by direct high-temperature calcination of graphene oxide without the addition of sulfur powder.

2.2. Material characterizations

Transmission electron microscope (TEM) was performed on a Hitachi HT7700. High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) imaging was conducted with an aberration-corrected JEM-ARM 200F microscope. Energy-dispersive spectrometer (EDS) analysis and corresponding elemental mapping were performed using the FEI TEM. X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD-6000. XPS spectra were performed on a Thermo VG ESCALAB 250. X-ray absorption structure (XAS) of Mn K-edge was conducted at BL14W1 beamline of Shanghai Synchrotron Radiation Facility. Raman spectra were performed on a confocal microscopic Raman spectrometer (HORIBA LabRAM HR Evolution).

2.3. Electrochemical measurement

The OER test was performed on a workstation (CHI 760E) using a three-electrode system in 1 mol L⁻¹ KOH. The linear sweep voltammetry (LSV) curve is recorded with 95% *iR*-compensation at a scan speed of 5 mV s⁻¹. The Tafel slope is obtained by plotting the LSV curve using the equation $\eta = a + b \log j$, where η refers to overpotential, b is the Tafel slope, and a is the intercept. The applied potential was converted to a reversed hydrogen electrode (RHE) scale by equation: E (RHE) = E (SCE) + 1.0684. The activation energy (E_a) is calculated by Arrhenius formula: $\frac{\partial (\log i_a)}{\partial (x/r)} = \frac{\Delta H^2}{2.3038}$. The LSV curves of the catalyst

at different temperatures were obtained without *IR* compensation, and then the temperature and the current at the overpotential of 300 mV were mapped as $1/T(K^{-1})-\log[I(A)]$ to obtain E_{a} .

2.4. Computational methods

Vienna ab initio Simulation Package (VASP) was used for the density functional theory (DFT) calculations [37,38]. The exchange-correlation functional was performed by using the projector-augmented wave (PAW) method and Perdew-Burke-Ernzerhof (PBE) potential. The Brillouin zone consists of $1 \times 2 \times 2$ Monkhorst-Pack point mesh. In this work, the Brönsted's model was used to explore the OER mechanism. The models are generally reported to proceed based on the following four steps:

$$H_2O + * \rightarrow *OH + H^+ + e^-$$
 (1)

$$*0H \to *0 + H^+ + e^-$$
 (2)

$$^{*}0 + H_2 0 \rightarrow ^{*}00H + H^+ + e^-$$
 (3)

$$^{*}\text{OOH} \rightarrow \text{O}_2 + \text{H}^+ + ^{*} + e^-$$
 (4)

The Gibbs free energies of *OH, *O and *OOH on the surface of the modified electrode was evaluated using DFT calculations. The Gibbs free energy changes were calculated at the standard conditions.

3. Results and discussion

3.1. Structural characterization

The synthesis process of Mn-SG-500 is shown in Fig. 1(a). In simple terms, Mn2+ ions were uniformly anchored onto the surface of the graphene oxide by abundant oxygen-containing functional groups to get precursor (Mn²⁺⁻G). Then the Mn-SG was obtained by mixing Mn2+-G with sulfur powder and annealing under nitrogen at 500 °C. TEM image shows that the synthesized Mn-SG possesses two-dimensional nanosheet structure and no metal-based nanoparticles are observed on the nanosheet (Fig. 1(b)). In addition, HAADF-STEM image with atomic resolution shows uniformly dispersed bright spots, representing that manganese was loaded on graphene in the form of isolated single atom (Fig. 1(c)). The content of manganese and sulfur in Mn-SG-500 was 1.1 wt% and 5.2 wt%, respectively, as detected by element analysis. From the XRD pattern, the peaks located at 25° and 45° belong to the (002) and (101) planes of graphene, and the doping of sulfur and manganese introduces defects, which significantly weaken the peak intensity (Fig. S1). In addition, no peaks of manganese-based nanoparticles appear in the XRD pattern, indicating that no manganese aggregates exist. In addition, the EDS confirms uniform dispersion of Mn, S and O (Figs. 1(d) and (e)).

The chemical environment of Mn in Mn-SG was analyzed by XAS. As shown in Fig. 2(a), the Mn-SG has Mn-K edge regions between MnO and Mn_2O_3 , but closer to MnO, displaying that the valence of Mn in Mn-SG is close to +2. The EXAFS spectra (Fig. 2(b)) show the absence of Mn-Mn in Mn-SG, further verifying isolated single-atom Mn distribution. According to the best fitting results, the Mn–S distance is 2.34 ± 0.07 Å and the coor-



Fig. 1. (a) Synthetic illustration of Mn-SG. (b) TEM image of Mn-SG-500. (c) HAADF-STEM image of Mn-SG-500. STEM image (d) and EDS elemental mappings (e) of Mn-SG-500.

dination number is 1.7 ± 0.4 , and the Mn–O distance is 1.94 ± 0.05 Å and the coordination number is 1.8 ± 0.4 (Fig. 2(c)). The bond of Mn–S is longer than that of Mn–O bond, which is due to the strong interaction of Mn–O coordination caused by the large electronegativity of O. Fig. 2(d) shows the difference in charge density obtained from S and O by calculating simulated Mn atom, where yellow and green represent the accumulation and depletion of charge, respectively.

3.2. Electrocatalytic performance

The OER performance of Mn-SG was studied in a three-electrode system in 1 mol L⁻¹ KOH. Fig. 3(a) shows the LSV curves of the Mn-SG-500, Mn-G-500, SG-500, G-500, and commercial RuO₂. The results display that when the current density reaches 10 mA cm⁻², the overpotential of Mn-SG-500 is 332 mV, which is smaller than Mn-G-500 (391 mV), SG-500 (403 mV), and G-500 (422 mV), and even better than RuO₂ (353 mV). Further, the Tafel slope was calculated to study the kinetics of the catalyst during OER process. The results show that the Mn-SG-500 has the smallest Tafel slope of 58 mV dec⁻¹, which is smaller than Mn-G-500 (85 mV dec⁻¹), SG-500 (92 mV dec⁻¹), G-500 (112 mV dec⁻¹) and RuO₂ (68 mV dec⁻¹), indicating that Mn-SG-500 has the fastest OER kinetics (Fig. 3(b)). Besides, in the range of non-Faraday current, the cyclic voltammetry (CV) curves of the catalyst at different scanning rates



Fig. 2. (a) XANES spectra at Mn K-edges of the Mn-SG-500 and referred samples. (b) FT-EXAFS spectra. (c) FT-EXAFS fitting spectrum. (d) $Mn-S_2O_2$ configuration.

were measured to calculate the double layer capacitance (C_{dl}) and electrochemical active surface area (ECSA) (Figs. S2–S5). The Mn-SG-500 has more opportunities to expose available active sites during electrocatalysis due to the large ECSA (269 cm⁻²), far exceeding that of other catalysts. Due to the large radius of sulfur, the introduction of sulfur to GO is difficult, and the doping process is inevitably accompanied by oxygen atoms, which are inherited from GO. Therefore, in the case of excessive sulfur components, the incorporation of sulfur can be controlled by changing the doping temperature. In order to select the optimum doping content of sulfur, a series of Mn-SG-*T* catalysts were synthesized (T = 400, 600, and 700) (Fig. S6). The Mn-SG-500 has a larger ECSA than Mn-SG-400 (85 cm²), Mn-SG-600 (232 cm²) and Mn-SG-700 (184 cm²) (Figs. S7–S9).

In addition, the activation energy (E_a) of the synthesized catalyst was calculated according to Arrhenius formula. With the increase of reaction temperature from 25 to 55 °C, the reaction activity of the catalyst increases (Fig. S10). The E_a of Mn-SG-500 was calculated to be 32.6 ± 2.8 kJ mol⁻¹, which is smaller than Mn-G-500 (37.1 ± 1.5 kJ mol⁻¹), SG-500 (42.3 ± 0.38 kJ mol⁻¹) and G-500 (45.9 ± 3.2 kJ mol⁻¹), indicating that the combined action of Mn and S species accelerates the OER process (Fig. 3(c)). The differential pulse voltammetry (DPV) diagram shows that when the OER process occurs, the valence of manganese species has changed from +2 to +4, and the tetravalent manganese species is the active substance of OER, which can be obtained by applying high voltage (Fig. 3(d)). Additionally, the addition of sulfur reduces the activation potential of Mn from 1.39 to 1.348 V and promotes OER. Moreover, the coordination of Mn and S has an obvious effect on the reduction of charge transfer resistance ($R_{Mn-SG-500} = 10.9 \Omega$ cm⁻²), which is conducive to the rapid transfer of charge (Fig. 3(e)).

The stability of Mn-SG-500 was measured by chronoamperometry test at 1.6 V. Notably, the current density does not decrease and remains above 10 mA cm⁻² after 25 h, indicating the excellent electrocatalytic stability of the Mn-SG-500 (Fig. 3(f)). Besides, the structure of Mn-SG-500 after OER has been characterized by XRD, Raman and XPS. The XRD pattern shows that there is no formation of manganese-based nanoparticles



Fig. 3. OER polarization curves (a) of G-500, SG-500, Mn-G-500, Mn-SG-500 and RuO₂, and the corresponding Tafel slopes (b). (c) Activation energy of G-500, SG-500, Mn-G-500, and Mn-SG-500. (d) DPV curves of Mn-G-500 and Mn-SG-500. (e) Nyquist plots of the EIS test for the G-500, SG-500, Mn-G-500, and Mn-SG-500 (inset: the equivalent circuit used for fitting the Nyquist plots). (f) Chronoamperometry test for the Mn-SG-500.

after OER (Fig. S11). The carbon structure of Mn-SG-500 after OER was studied by *in-situ* Raman spectroscopy (Fig. S12). For the initial Mn-SG-500, the sp^3 carbon (D band) and sp^2 carbon (G band) peak is centered at 1339 and 1586 cm⁻¹, respectively, and the peaking area ratio was 1.31. As the applied voltage increased from 0.2 to 0.55 V, the I_D/I_G ratio gradually increases, indicating that the number of active edges and defect sites of the catalyst graphene layer increases under high potential.

To further understand the valence state change of Mn sites, the Mn-SG-500 under different voltage conditions was collected for XPS characterization (Fig. S13, and Fig. 4). For the fresh Mn-SG-500, the Mn 2*p* spectrum includes three peaks at 640.6, 653.3, and 644.4 eV, characteristic of Mn²⁺ (Fig. 4(a)). With the increase of applied voltage, a new peak corresponding to Mn4+ appears at 641.9 eV, indicating that Mn2+ was oxidized to higher valence state during the reaction. Besides, in the fresh Mn-SG-500, the peak intensity of the S 2p spectrum at 167.7 eV $(C-SO_x-C)$ is much smaller than that at 164 eV, indicating that the sulfur in the fresh catalyst exists more in the form of -2 valence state rather than sulfur oxide (Fig. 4(b)) [39]. In addition, the peak at near 164 eV can be deconvolved into two different chemical environments, S-Mn (162.9 eV) and S-C (163.7 eV) [40-42]. In the O 2s spectrum, the fresh Mn-SG-500 has three different types of oxygen chemical bonds at the binding energy of 530.2, 531.6, and 532.9 eV, corresponding to O-Mn, O=C, and O-C bond, respectively (Fig. 4(c)) [43]. During the OER process, a new peak is observed at around 534.9 eV due to H–O–H bond, which is attributed to catalyst affinity for H₂O or O2. With the increase of reaction voltage, the relative contents of Mn-S and Mn-O do not decrease, indicating that the catalyst has structural stability in the OER process.

3.3. OER mechanism analysis

To elucidate the OER mechanism of the four-electron reaction and the electrocatalytic activity of Mn-S_xO_yG, we conducted corresponding theoretical calculations using DFT. A considerable number of potential models including Mn-S₄G, Mn-S₃OG, Mn-S₂O₂G, Mn-SO₃G, Mn-O₃G and Mn-O₄G were meticulously constructed. Based on the calculations of formation energy, the Mn-SO₃G model exhibits the lowest formation energy values, indicating that it is the most stable structure among the considered models. To assess the catalytic activities of different electrocatalysts, we calculated the theoretical overpotential (η) for the catalytically active sites in each model. In the case of the O–S model, the S and C atoms adjacent to the O atom, known as electron donors, exhibit high potential barriers for the rate-limiting step in the OER.

To delve deeper into the catalytic mechanism, the population distributions of the relevant doped graphene materials are illustrated in Figs. 5(a)-(h). Fig. 5(i) illustrates a notable disparity in the theoretical overpotential values on these five models, in with Mn-S₂O₂G displays a significantly lower value of 2.2 eV compared to Mn-S₃OG and Mn-S₃G in the *O-*OOH reaction step. This difference in overpotential can be attributed to the symmetrical structure of Mn-S₂O₂G. Consequently, the determination of the overpotential for Mn-S₄G and Mn-SO₃G shifts to the Mn–O bond rupture step, rather than the oxidation of *O to *OOH observed in Mn-S₂O₂G. It is disappointing that Mn-S₄G, Mn-SO₃G, Mn-O₃G and Mn-O₄G all exhibit higher overpotential values than Mn-S₂O₂G due to the strong binding of *OOH on the surfaces.

Fig. 5(j) showcases an elegant volcano plot that portrays various active sites on different models. The OER overpotential values have been meticulously calculated, yielding remarkable results: 1.03 V for the Mn-S₄G model, 1.17 V for Mn-S₃OG, 0.96 V for Mn-S₂O₂G, 1.48 V for Mn-SO₃G, 1.24 V for Mn-S₃G, 1.20 V for Mn-O₃G and 1.21 V for Mn-O₄G. Significantly, the Mn-S₂O₂G model emerges as the clear victor with the lowest overpotential value. This implies a substantial decrease in the potential barrier of the third step, unequivocally highlighting the outstanding catalytic process of Mn-S₂O₂-doped graphene compared to its counterparts. Furthermore, based on our meticulous DFT calculations (Fig. 5(k)), an intriguing band alignment emerges. The enlightening results derived from the projected density of states (DOS) analysis uncover a noteworthy characteristic of the Mn-S₂O₂G, showcasing an exquisite alignment of the conduction and valence bands. This exceptional feature sets the



Fig. 4. Ex-situ Mn 2p (a), S 2s (b), and O 1s (c) XPS spectra of fresh Mn-SG-500 and Mn-SG-500 after OER at overpotentials of 0.25, 0.35, 0.45 and 0.55 V, respectively.



Fig. 5. Population distributions for the DFT-calculated representative models: (a) $Mn-S_4G$, (b) $Mn-S_3OG$, (c) $Mn-S_2O_2G$ para-position (d) $Mn-S_2O_2G$ ortho-position, (e) $Mn-S_0G_3G$, (f) $Mn-S_3G$, (g) $Mn-O_3G$ and (h) $Mn-O_4G$. (i) The optimized structures of three reaction intermediates of $Mn-S_2O_2G$ and the reaction paths of free energy diagram for the OER on $Mn-S_4G$, $Mn-S_3OG$, $Mn-S_2O_2G$, $Mn-S_3G$, $Mn-O_3G$ and $Mn-O_4G$. (j) OER volcano plot of the overpotential η *vs.* the difference between the adsorption free energy of *O and *OOH for the seven models. (k) The projected DOS for the $Mn-S_2O_2G$. (l) The charge density differences of Mn in $Mn-S_2O_2G$. Yellow and blue areas represent charge density accumulation and depletion in the 3D map, respectively.

stage for an effortless transfer of photoexcited charge carriers, thereby propelling the catalytic reaction process with remarkable efficiency. Moreover, we conducted a comprehensive exploration of the charge density in Mn-S₂O₂G model. Remarkably, Fig. 5(l) showcases the significant amplification of electron density surrounding the active Mn site. This augmentation can be attributed to the exceptional bonding electron coupling effect facilitated by the distinctive structural characteristics of single-atom metal-sulfur-oxygen doping.

4. Conclusions

In summary, we have successfully synthesized a Mn-based SAC with oxygen and sulfur dual-heteroatom coordination on graphene. The Mn-SG-500 displays higher OER activity than commercial RuO₂, and its overpotential (η_{10}) is reduced by 59 mV compared with the sulfur-free sample Mn-G-500. According to the XAS, *in-situ* characterization and theoretical calculations,

Mn-SG-500 has the optimal active configuration of sulfur and oxygen dual-heteroatom coordination Mn-S₂O₂. Mn⁴⁺ is a key species for the OER and the rate-control step is the oxidation of *O to *OOH. The analysis of OER performance of Mn SACs with O/S-dual-coordination environment encourages the study of the optimal electronic structure of other transition metal-based catalysts, promoting the development of advanced OER catalysts for energy storage and conversion.

Electronic supporting information

Supporting information is available in the online version of this article.

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Graphical Abstract

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Improvement of oxygen evolution activity on isolated Mn sites by dual-heteroatom coordination

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Through oxygen and sulfur dual-heteroatom doping, the OER activity of isolated Mn sites is significantly improved, on which the $Mn-S_2O_2G$ structure exhibits lower OER energy barrier.

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双杂原子配位提高单原子锰位点的析氧活性

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摘要:可再生能源的储存和转化可以增加能源利用的可及性,是目前能源发展的主要方向. 析氧反应(OER)是电解水与可充电锌-空气电池的重要半反应,然而其较高的反应势垒降低了能源利用效率. 因此,开发高效和稳定的OER催化剂是提升能源利用的关键. 由于具有低成本和高原子利用率的优势,非贵金属基单原子催化剂已被广泛应用于电催化析氧反应. 研究表明,单原子催化剂的OER活性与其电子结构密切相关. 改变配位原子的种类和配位数可以调节单金属原子的d电子结构和自旋状态,进一步优化反应中间体的吸附. 锰(Mn)是自然界光合作用系统的析氧中心,近年来模拟Mn结构以最大程度激发催化活性受到了广泛的关注.

本文采用双杂原子配位方法来调节孤立锰位点的电子结构从而提升其OER性能. 以氧化石墨烯、氯化锰和硫粉为前驱体, 合成了双杂原子配位的单原子锰催化剂Mn-SG-500 (退火温度为500°C), 其中单锰原子与两个硫原子和两个氧原子配位. 能谱分析(EDS)和X射线衍射(XRD)谱图中均未观察到锰基纳米粒子, 高角环形暗场-扫描透射电子显微镜(HAADF-STEM)图像显示均匀分散的亮点, 表明锰以单原子形式负载在石墨烯上. Mn的扩展X射线吸收精细结构(EXAFS)光谱结果表明, Mn-SG-500中的Mn表现出接近+2的化合价, 且不存在Mn-Mn键, 进一步说明Mn以单原子形式存在. 拟合结果显示, Mn-S键长为2.34±0.07Å, 配位数为1.7±0.4; Mn-O键长为1.94±0.05Å, 配位数为1.8±0.4. 电化学测试结果表明, 在碱性条件下, Mn-SG-500在电流密度为10 mA cm⁻²时的过电位为332 mV, Tafel斜率为56 mV dec⁻¹. 与无硫掺杂样品Mn-G-500相比, 其过电位(η₁₀)降低了59 mV. 根据Arrhenius公式计算, S/O和Mn共配位降低了OER活化能. 此外, 在1.6 V (vs. RHE)电压下, Mn-SG-500连续运行25 h仍可保持电流密度在10 mA cm⁻²以上. 差分脉冲伏安(DPV)结果表明, 在OER过程中, 锰的价态由+2变为+4, 说明四价锰是析氧反应的关键物种. 反应后的Mn 2p XPS谱图也证实了Mn(IV)的生成. 此外, 硫的加入使Mn⁴⁺到Mn²⁺的还原电位从1.39 V降至1.348 V, 提高了OER活性. 通过理论计算进一步揭示Mn-SG-500上OER催化活性中心为Mn-S₂O₂, 速率控步为*O氧化成*OOH, 其理论过电位为0.9 V, 远小于硫或氧单独配位的Mn-S₄和Mn-O₄.

综上所述,催化剂Mn-SG-500的析氧活性提高是由于S和O的共配位引起了Mn电荷的重新分配和优化,这对其它过渡 金属基催化剂的进一步结构设计和性能优化具有参考意义,也为相关催化领域的研究提供借鉴.

关键词: 双杂原子配体; 原位拉曼; 析氧反应; 单原子催化剂; 理论计算

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