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Tailoring Oxygen Vacancy on Co$_3$O$_4$ Nanosheets with High Surface Area for Oxygen Evolution Reaction$^\dagger$

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Electrochemical water splitting requires efficient water oxidation catalysts to accelerate the sluggish kinetics of water oxidation reaction. Here, we designed an efficient Co$_3$O$_4$ electrocatalyst using a pyrolysis strategy for oxygen evolution reaction (OER). Morphological characterization confirmed the ultra-thin structure of nanosheet. Further, the existence of oxygen vacancies was obviously evidenced by the X-ray photoelectron spectroscopy and electron spin resonance spectroscopy. The increased surface area of Co$_3$O$_4$ ensures more exposed sites, whereas generated oxygen vacancies on Co$_3$O$_4$ surface create more active defects. The two scenarios were beneficial for accelerating the OER across the interface between the anode and electrolyte. As expected, the optimized Co$_3$O$_4$ nanosheets can catalyze the OER efficiently with a low overpotential of 310 mV at current density of 10 mA/cm$^2$ and remarkable long-term stability in 1.0 mol/L KOH.

Key words: Electrocatalyst, OER, Oxygen vacancy, Co$_3$O$_4$

I. INTRODUCTION

Water oxidation, also known as the oxygen-evolution reaction (OER), is a critical reaction in energy conversion technologies, such as electrolysers, regenerative fuel cells, metal-air batteries, and photoelectrochemical cells [1–7]. However, the kinetics of the OER is sluggish, which requires a high overpotential to experience a complex four-electron oxidation process [8–12]. Although noble metals and their oxides such as RuO$_2$ and IrO$_2$ are currently regarded as the most active electrocatalysts, their scarcity and high cost have seriously impeded their large-scale applications [13–17]. Alternatively, transition-metals-based oxides (TMOs) have exhibited superior performance in OER catalysis due to their reasonable reactivity and stability. Nevertheless, bulk TMOs are normally less active for OER due to the poor conductivity and low surface area. Therefore, developing the ultra-thin TMOs catalysts is immi-

antly necessary to increase the reactivity and number of active sites, thereby improving electrocatalytic performance.

Among them, ultra-thin cobalt oxides are considered as the most promising candidates, due to large surface area, exposed active sites, and short diffusion lengths of ions and electrons. On the other hand, previous investigations suggest that the surface defects can greatly influence the electronic structure and the surface chemistry of faceted catalysts [18–21]. Thereinto, tuning oxygen vacancies of metal oxides has also been proved to be highly efficient for altering their catalytic activity, but the common method of creating oxygen vacancies is generally accompanied by morphological deformation, severe aggregation, and instability [22, 23]. Hence, a powerful synthetic method should include the possibility to directly generate oxygen vacancies on the surface of the nanocatalysts and to integrate the fast electron transfer path into the electrodes for enhancing OER.

Here, we have developed a facile strategy to synthesize Co$_3$O$_4$ nanosheets (NSs) using the pyrolysis approach. Surprisingly, based on a combined characterization of X-ray photoelectron spectroscopy and electron spin resonance spectroscopy, the Co$_3$O$_4$ NSs exhibited the abundant of oxygen vacancies. The increased specific surface area and the presence of oxygen vacancies of Co$_3$O$_4$ NSs significantly contributed to the superior catalytic performance for the OER. In comparison to the bulk Co$_3$O$_4$, Co$_3$O$_4$ NSs display a small overpotential of 310 mV to produce a current density of 10 mA/cm$^2$ and a much lower Tafel slope of 75 mV/decade.

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II. EXPERIMENTAL SECTION

A. Chemicals

All chemicals used were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China) and were of analytical grade and used without purification.

B. Preparation of Co$_3$O$_4$ nanosheets

In a typical procedure, 5 mmol of cobalt(II) acetate tetrahydrate and 2 mmol of ammonium acetate were dissolved in 30 mL of water. After vigorous stirring for 10 min, the mixture was transferred into a 50 mL Teflon-lined autoclave, sealed and heated at 180°C for 10 h. The system was then allowed to cool down to room temperature naturally. The obtained product was collected by centrifuging the mixture, washed with ethanol and water for many times, and then dried in vacuum overnight. Afterward, the precursor was transferred to ceramic boat and calcined at 350°C for 2 h with a heating rate of 5°C/min in argon gas, followed by cooling down to room temperature.

For comparison, the bulk Co$_3$O$_4$ was prepared by the following method. Cobalt(II) chloride hexahydrate (5 mmol) and ammonia solution (2 mL) were dissolved in 30 mL of absolute ethanol under vigorous stirring for 20 min. And then, the pink solution was transferred into a 50 mL Teflon-lined autoclave. The autoclave was sealed and maintained at 180°C for 3 h and cooled down naturally to room temperature. Subsequently, the products were dried in vacuum at 80°C for 6 h after sequential washing with deionized water and absolute ethanol.

C. Physical Characterization

Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) images were taken on a Hitachi SU8010 SEM and a Hitachi J2100F TEM, respectively. X-ray diffraction patterns were recorded by using a Philips X'Pert Pro Super diffractometer with Cu Kα radiation. The X-ray photoelectron spectroscopy (XPS) was acquired on a PHI5000 Versa Probe system. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.8 eV. The N$_2$ gas sorption isotherm and pore size distribution were measured on an ASAP 2020 instrument at liquid nitrogen temperature (77 K). Room-temperature electron spin resonance (ESR) spectra were obtained using a JEOL JES-FA200 ESR Spectrometer.

D. Electrochemical Measurement

Electrochemical measurements were carried out in a three-electrode system at an electrochemical station (CHI760E). A glassy carbon electrode (GCE, 3 mm in diameter) was used as the working electrode, Ag/AgCl/3 mol/L KCl was used as the reference electrode, and a graphite rod was used as the auxiliary electrode. Typically, 5 mg sample and 50 μL Nafion solution (5 wt%) were dispersed in 1 mL water isopropanol solution with volume ratio of 3:1 by sonicating for 1 h to form a homogeneous ink. Then, 5 μL of the dispersion was loaded onto a glassy carbon electrode with 3 mm diameter and dried at ambient temperature. Linear sweep voltammetry with a scan rate of 5 mV/s was conducted in 1 mol/L KOH. All the potentials vs. Ag/AgCl were calibrated to a reversible hydrogen electrode (RHE) scale according to the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \pH + 0.205 \quad (1)$$

Cyclic voltammetry (CV) was conducted at 100 mV/s to investigate the cycling stability. The Nyquist plots were measured with frequencies ranging from 100 kHz to 0.01 Hz at an applied potential of 1.40 V vs. RHE. Electrochemical active surface area (ECSA) was evaluated by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammetry. The double-layer capacitance ($C_{dl}$) was estimated by plotting $\Delta J = J_a - J_c$ at 1.15 V vs. RHE against the scan rates, in which the $J_a$ and $J_c$ are the anodic and cathodic current density, respectively. The slope is twice that of the double-layer capacitance $C_{dl}$.

III. RESULTS AND DISCUSSION

The precursors of Co$_3$O$_4$ NSs were prepared by a hydrothermal reaction. Then, the precursors were brought into a tube furnace and calcined under an Ar atmosphere to obtain the final products. As observed from the X-ray diffraction (XRD) patterns, Co$_3$O$_4$ NSs and bulk Co$_3$O$_4$ present almost the same diffraction peaks at 31.2°, 36.8°, 59.3°, and 65.2°, which can be assigned to the (220), (311), (511), and (440) lattice planes of Co$_3$O$_4$ (JCPDS No. 43-1003), respectively (FIG. 1(a)). The SEM characterizations were performed to observe the surface morphology of the obtained Co$_3$O$_4$ (FIG. 1 (b) and (g)). Compared with the uneven aggregates of bulk Co$_3$O$_4$, a sheet-like morphology was observed for Co$_3$O$_4$ NSs. The transmission electron microscopy (TEM) image further confirms the well-defined nanosheets of Co$_3$O$_4$ NSs. Selected area electron diffraction (SAED) pattern taken from a large area of the Co$_3$O$_4$ NSs gives single crystalline feature with clear diffraction spots. The HRTEM was employed to study the crystalline structure of Co$_3$O$_4$ NSs. From the HRTEM image, the well-defined lattice fringes with a spacing of 0.287 nm were observed, corresponding to the (220) plane of Co$_3$O$_4$ NSs. Energy-dispersive X-ray Spectrum (EDX) analysis reveals that the Co$_3$O$_4$ NSs are principally composed of Ni, Mo and O, suggesting a uniform spatial distribution of these elements.
FIG. 1 (a) XRD patterns of Co$_3$O$_4$ NSs and bulk Co$_3$O$_4$. (b–f) SEM, TEM, HRTEM, and STEM-EDX mapping images of Co$_3$O$_4$ NSs. (g,h,k) SEM, HRTEM, and STEM-EDX mapping images of bulk Co$_3$O$_4$. The inset in (c) shows the corresponding SAED patterns.

As observed by the SEM and TEM, it is believed that the Co$_3$O$_4$ NSs would expose more surface area. To confirm this hypothesis, the N$_2$ sorption isotherms (FIG. 2) were obtained for the two samples. This reveals a distinct hysteresis loop of the Co$_3$O$_4$ NSs, suggesting typical mesoporous structures [24]. The Co$_3$O$_4$ NSs possess the specific surface area of 122.9 m$^2$/g, much larger than that of bulk Co$_3$O$_4$ (38.3 m$^2$/g). This comparison confirms that the structure of nanosheets could significantly increase the surface area of Co$_3$O$_4$, resulting in more exposed sites for the electrocatalysis.

Since the electrocatalysis reaction mainly occurs on the surface of electrocatalysts, it is essential to investigate the surface composition and structure of Co$_3$O$_4$ NSs and bulk Co$_3$O$_4$ by XPS and electron spin resonance (ESR). FIG. 3(a) shows the fine-scanned Co 2p spectra of Co$_3$O$_4$ NSs and bulk Co$_3$O$_4$. They consist

FIG. 2 N$_2$ sorption isotherms of Co$_3$O$_4$ NSs and bulk Co$_3$O$_4$. (FIG. 1 (e) and (f)). Analogously, the lattice fringes with spacing of 0.202 nm are indexed to (400) facet of bulk Co$_3$O$_4$ (FIG. 1(h)). STEM and EDX elemental mapping reveal uniform spatial distribution of Co and O over the whole bulks (FIG. 1(k)).

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FIG. 3 The high-resolution XPS of (a) Co and (c) O. (b) The Co\(^{2+}\)/Co\(^{3+}\) ratio for the Co\(_3\)O\(_4\) NSs and bulk Co\(_3\)O\(_4\). (d) EPR spectra of Co\(_3\)O\(_4\) NSs and bulk Co\(_3\)O\(_4\).

of two spin-orbit doublets characteristic of Co\(^{2+}\) and Co\(^{3+}\) and two shakeup satellites (identified as “sat”). The relative atomic ratio of Co\(^{2+}\)/Co\(^{3+}\) on the surface of the Co\(_3\)O\(_4\) could be obtained by comparing the area that the fitted curve covered. It could be clearly observed that the atomic ratio of Co\(^{2+}\)/Co\(^{3+}\) on the Co\(_3\)O\(_4\) NSs is 1.45, which is higher than that of bulk Co\(_3\)O\(_4\) (1.0), indicating that relatively more Co\(^{2+}\) present on the Co\(_3\)O\(_4\) NSs (FIG. 3(b)). In O 1s spectrum, four peaks can be clearly identified in Co\(_3\)O\(_4\) NSs (FIG. 3(c)). In detail, the peak of O1 at 529.6 eV is assigned to the lattice oxygen, whereas the peak of O4 at 531.9 eV is attributed to a high number of defect sites with lower oxygen coordination [22]. Compared with that in bulk Co\(_3\)O\(_4\), the appearance of the O4 peak in Co\(_3\)O\(_4\) NSs suggested the presence of oxygen vacancies on the surface of Co\(_3\)O\(_4\) NSs. Furthermore, ESR spectra were measured to directly illustrate the vacancies in the Co\(_3\)O\(_4\) samples (FIG. 3(d)) [25]. Co\(_3\)O\(_4\) NSs show much stronger oxygen vacancy-related ESR signal than bulk Co\(_3\)O\(_4\), indicating the abundant oxygen vacancies were formed on the surface of Co\(_3\)O\(_4\) NSs [26]. The detailed analysis indicates that the oxygen vacancies on the surface of Co\(_3\)O\(_4\) NSs may improve the electronic conductivity, create more electrochemically active sites, and thus enhance the electrocatalytic activity for OER.

The electrocatalytic OER performances of Co\(_3\)O\(_4\) NSs and bulk Co\(_3\)O\(_4\) were thereafter studied using linear scan voltammogram (LSV) on glassy carbon (GC) electrodes with a mass loading of 0.35 mg/cm\(^2\) in 1.0 mol/L KOH. As shown in FIG. 4(a), bulk Co\(_3\)O\(_4\) is capable of catalyzing OER with overpotential of 430 mV to drive a geometrical catalytic current density of 10 mA/cm\(^2\). In sharp contrast, Co\(_3\)O\(_4\) NSs has OER activity much superior to that of bulk Co\(_3\)O\(_4\) and only requires a much smaller overpotential of 310 mV to afford 10 mA/cm\(^2\). The enhanced activity should be attributed to the unique surface properties of the Co\(_3\)O\(_4\) NSs with high surface area and oxygen vacancies. Tafel slopes are used to verify that the reaction kinetics for Co\(_3\)O\(_4\) NSs is more favorable. As shown in FIG. 4(b), the Co\(_3\)O\(_4\) NSs show a much lower Tafel slope of 75 mV/decade than the bulk Co\(_3\)O\(_4\) of 93 mV/decade, indicating a fast increase of OER rate with increasing applied potential in Co\(_3\)O\(_4\) NSs. Besides, the OER behavior was also evaluated by estimating the electrochemical active surface areas (ECSAs), which are proportionally positive to \(C_{dl}\). The \(C_{dl}\) value of Co\(_3\)O\(_4\) NSs was 14.16 mF/cm\(^2\), which was about 3.8 times that of the bulk Co\(_3\)O\(_4\) (3.66 mF/cm\(^2\)) (FIG. 4(c)). This further indicated that the formed nanosheets and oxygen vacancies could provide larger active surface areas and more active sites for the OER.
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FIG. 4 (a) Polarization curves and (b) corresponding Tafel slopes of Co$_3$O$_4$ NSs and bulk Co$_3$O$_4$ on GC electrodes in 1 mol/L KOH. (c) The $C_{dl}$ calculations of the Co$_3$O$_4$ NSs and bulk Co$_3$O$_4$. (d) The EIS curves of Co$_3$O$_4$ NSs and bulk Co$_3$O$_4$.

FIG. 5 (a) Stability test of Co$_3$O$_4$ NSs showing initial polarization curve and corresponding curve after 1000 cycles in 1.0 mol/L KOH. (b) Time-dependent catalytic current for Co$_3$O$_4$ NSs in 1.0 mol/L KOH.

To explicate the charge transfer mechanism, electrochemical impedance spectroscopy (EIS) analyses were done on these catalysts as shown in FIG. 4(d). In sharp contrast to bulk Co$_3$O$_4$, the smaller semicircle radius in the Nyquist plot was realized on the Co$_3$O$_4$ NSs, indicating a very fast Faradaic process or charge transfer and superior electrochemical kinetics.

It is well-known that the population of Co$^{2+}$ and Co$^{3+}$ on different exposed facets of Co$_3$O$_4$ nanostructures is the key to influence the catalytic performance due to the direct relation of the oxygen vacancies. Increasing the population of Co$^{2+}$ (oxygen vacancies) in Co$_3$O$_4$ NSs could significantly enhance the electrocatalytic activity for OER. Moreover, previous studies have also demonstrated that Co$^{2+}$ was the active sites for OER and Co$^{2+}$ could promote the formation of cobalt oxyhydroxide (CoOOH) as active sites for OER [27]. To sum up, the synergistic effect of the surface oxygen vacancies and high surface area of Co$_3$O$_4$ NSs result in a superior electrocatalyst for OER.

The electrocatalytic stability of the Co$_3$O$_4$ NSs was confirmed from long-term potential cycling by taking continuous CV at an accelerated scanning rate of 100 mV/s for 1000 cycles (FIG. 5(a)). The polarization curve after 1000 cycles exhibit a slight decrease compared with the initial one of the current density, which meant that Co$_3$O$_4$ NSs exhibited good long-term catalytic durability for OER. Moreover, the excellent durability of Co$_3$O$_4$ NSs toward OER was also investigated using chronoamperometry at a constant voltage of 1.60 V vs. RHE in 1 mol/L KOH. As shown in FIG. 5(b), a stable current density at about 30 mA/cm$^2$ of continuous operation was presented. The current...
density exhibited negligible degradation after a long period of 30000 s, further confirming the robust stability.

IV. CONCLUSION

In summary, we demonstrated a novel strategy to fabricate the Co$_3$O$_4$ nanosheets with oxygen vacancies by the controlled calcination. Physical characterizations confirm the morphology of ultra-thin nanosheets and the presence of oxygen vacancies. Thus, the Co$_3$O$_4$ NSs successfully combined the desired merits including large specific surface areas, high conductivity, and multiple electrocatalytic active sites. These advantages endowed the Co$_3$O$_4$ NSs with excellent OER electrocatalytic activity such as low overpotential, small Tafel slope, and high stability. The present results will open up a new avenue to design advanced electrocatalysts for other energy-related applications, such as metal-air batteries and regenerative fuel cells.

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