Synthesis of ultrathin Co_2AlO_4 nanosheets with oxygen vacancies for enhanced electrocatalytic oxygen evolution

Jiayang Wang^{1†}, Yongli Shen^{2†}, Guijuan Wei¹, Wei Xi², Xiaoming Ma¹, Weiqing Zhang^{2*},
Peipei Zhu¹ and Changhua An^{1,2*}

ABSTRACT In this work, we reported the synthesis of two-dimensional spinel structure of ultrathin Co_2AlO_4 nanosheets *via* dealloying and subsequent annealing processes. Oxygen vacancy defects were further introduced into Co_2AlO_4 nanosheets by a mild solvothermal reduction method, resulting in large electrochemical surface area and high active site densities, making the related Co atoms get electrons, and producing more empty orbitals. The positive charge of Co and Al atoms adjacent to the O vacancies in VO-rich Co_2AlO_4 reduced significantly, that is, more electrons are concentrated on the Co and Al atoms. Those electrons closed to the Fermi level have a promoting effect during the H_2O activation. As a result, the obtained ultrathin Co_2AlO_4 nanosheets with oxygen vacancies show a low overpotential of 280 mV at the current density of 10 mA cm^{-2} and a small Tafel slope of $70.98 \text{ mV dec}^{-1}$. Moreover, it also displays a remarkable stability in alkaline solution, which is superior to most of the reported Co_3O_4 electrocatalysts. The present work paves a new way to achieve efficient new energetic materials for sustainable community.

Keywords: Co_2AlO_4 , nanosheets, oxygen vacancies, oxygen evolution

INTRODUCTION

Two-dimensional (2D) nanomaterials have been widely studied and applied due to their excellent physical, electronic, optical and chemical properties with various potential applications among the electronics/optoelectronics, batteries, electrocatalysis, photocatalysis,

supercapacitors, solar cells, and sensing platforms [1–3]. There are many factors affecting the properties of 2D nanomaterials, such as composition, size, crystal phase, defect, doping, surface property and so on [4–7]. Demands for property modulations greatly promoted the development of synthetic methods for the preparation of 2D nanomaterials. To date, top-down and bottom-up methods have been used for the synthesis of a large number of 2D nanomaterials, which can be divided into two categories: layered and nonlayer structured materials [8–12]. Layered materials consist of 2D platelets stacked to form 3D structure by weak van der Waals interaction. Typical examples of layered materials include graphite, hexagonal boron nitride (h-BN), transition metal dichalcogenides (TMDs), $\text{g-C}_3\text{N}_4$, black phosphorus (BP), and transition metal oxides (TMOs), etc.

In recent years, cobalt-based materials, especially spinel type of Co_3O_4 , have been intensively studied for electrochemical energy storage and conversion. Usually, the oxygen evolution reaction (OER) activity of Co-based oxides was mainly dependent on the relative ratio of $\text{Co}^{2+}/\text{Co}^{3+}$. Specifically, Co^{2+} ions were responsible for the formation of cobalt oxyhydroxide (CoOOH), which was an ideal active intermediate for OER activity [13–15]. Whilst, Co^{3+} was conducive to improving the strength between the catalysts' surface and hydroxide groups, reducing the OER activity [16]. On the other hand, Co is a relatively rare and expensive element. Finding a certain alternative element and concurrently promoting the activity is of importance to satisfy the requirements of

¹ Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China

² Tianjin Key Laboratory of Advanced Functional Porous Materials, Institute for New Energy Materials & Low-Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China

[†] These two authors contributed equally to this work.

* Corresponding authors (emails: anch@tjut.edu.cn (An C); zhangweiqing@tjut.edu.cn (Zhang W))

practical applications. It was shown that alternative cheap aluminum (Al) element with earth-abundance, had the great capacity in the catalysis field [17–20]. Therefore, increasing the ratio of $\text{Co}^{2+}/\text{Co}^{3+}$ by substitution of Co^{3+} with Al^{3+} is plausible to enhance the OER activity. Spinel structured Co_2AlO_4 , an isomorphic compound with Co_3O_4 , was traditionally applied as pigment and super-capacitor material [21,22]. It was usually prepared by high temperature solid-phase method and hydrothermal method [21,23]. Since the diffusion processes in these methods were difficult to be controlled, the resulted Co_2AlO_4 often exhibited an aggregated structure with irregular shapes. The development of a robust strategy to synthesize ultrathin Co_2AlO_4 nanosheets with uniform shapes and tailored structures is a prerequisite to achieve high catalytic performance and potential applications.

In this work, we reported the fabrication of reverse spinel-type Co_2AlO_4 nanosheets *via* one-step dealloying of $\text{Co}_5\text{Al}_{95}$ precursor alloy followed by an annealing process. Subsequently, oxygen vacancies on the surface of Co_2AlO_4 nanosheets (VO-rich Co_2AlO_4) were introduced *via* a solvothermal treatment to create large electrochemical surface area (ECSA) and high active site density. As expected, the VO-rich Co_2AlO_4 nanosheets exhibited an impressive catalytic OER performance with a small overpotential of 280 mV at a current density of 10 mA cm^{-2} , a low Tafel slope of $70.98 \text{ mV dec}^{-1}$, and a remarkable stability for 20 h, which were superior to pristine Co_2AlO_4 and the mostly reported Co_3O_4 counterparts. The enhanced catalytic OER performance could be mainly attributed to large $\text{Co}^{2+}/\text{Co}^{3+}$ ratio by replacing Co^{3+} with Al^{3+} , and high active site density by creating oxygen vacancies on the surface of Co_2AlO_4 [24–28].

EXPERIMENTAL SECTION

Chemicals and materials

Cobalt (Co, China New Metal Materials Technology Co. Ltd., 99.99%), and aluminum (Al, China New Metal Materials Technology Co. Ltd., 99.99%), sodium hydroxide (NaOH), potassium hydroxide (KOH), ethylene glycol (EG) and Nafion (5 wt%) were purchased from Sigma-Aldrich and used as received without further purification.

Preparation of Co_2AlO_4 ultrathin nanosheets

The $\text{Co}_5\text{Al}_{95}$ alloy ribbons were prepared *via* a melt-spinning process under N_2 atmosphere. The as-prepared $\text{Co}_5\text{Al}_{95}$ alloy ribbons were then chemically etched in 3 mol L^{-1} NaOH solution at ambient temperature for

20 min under stirring. It was found that the initial ribbons were turned to black fragments after dealloying. Then, the black product was collected and washed with deionized water several times, till the solution became neutral. The product was dried in a vacuum oven at 60°C for 12 h, and further calcined at 300°C for 3 h under Ar atmosphere in order to obtain pure Co_2AlO_4 .

Preparation of VO-rich Co_2AlO_4 nanosheets

The above obtained Co_2AlO_4 nanosheets were treated in a homogeneous solution of NaOH (36 mmol) and EG (12 mL) at 140°C for 12 h under solvothermal condition. After the mixture was cooled down naturally to room temperature, the sample was collected by centrifugation and washed with ethanol several times. Finally, the ultrathin VO-rich Co_2AlO_4 were obtained and dried at 60°C for 12 h in a vacuum oven. For comparison, Co_3O_4 nanosheets were also fabricated following the reference [29].

Materials characterization

The crystal structures of Co_2AlO_4 , VO-rich Co_2AlO_4 and Co_3O_4 products were confirmed by X-ray diffraction (XRD, Rigaku D/max 2500) using Cu K α radiation ($\lambda = 0.154598 \text{ nm}$). The morphologies of the products were investigated using ultrahigh-resolution scanning electronic microscope (SEM, Verios 460L) and high-resolution transmission electronic microscope (TEM with FEG, Talos F200X). The atomic structures of the samples were carried out on an FEI Titan Themis G2 (S)TEM operated at 200 kV. The surface morphology was measured using atomic force microscope (AFM, NT-MDT). The Brunauer-Emmett-Teller (BET) surface areas were analyzed using a nitrogen-adsorption apparatus (ASAP 2020, Micromeritics). The sample was degassed at 120°C prior to the nitrogen adsorption. The chemical statuses and electronic states of the elements were investigated using X-ray photoelectronic spectra (XPS, ESCALAB 250Xi, Thermo Scientific). Hydrogen temperature programmed reduction (H_2 -TPR) experiments were equipped with thermal conductivity detector (TCD) with Automated Catalyst Characterization System (Autosorb-IQ3+ChemStar). The Raman spectra of the monolithic samples were conducted on a HORIBA EVOLUTION Raman Spectrometer.

Electrodes preparation

The electrocatalyst powders (2 mg) were separately dispersed into 100 μL of aqueous Nafion (8% *v/v*) and ethanol (92% *v/v*). The mixture was ultra-sonicated for 30 min to form a homogeneous electrocatalyst ink. Then, all of the electrocatalyst ink was drop-cast onto a piece of

carbon paper (CP) with an area of $1\text{ cm} \times 1.5\text{ cm}$. And the CP with electrocatalyst was dried naturally and used as electrodes.

Electrocatalytic OER measurements

The OER activities of the catalyst were measured in a three-electrode system by using a carbon plate as the counter electrode, and Hg/HgO electrode as the reference electrode. All the electrochemical experiments were conducted in O_2 -saturated 1 mol L^{-1} KOH (pH 14) electrolyte via a CHI 760E electrochemical workstation. All the potentials were calibrated with respect to a reversible hydrogen electrode (RHE, in 1 mol L^{-1} KOH, $E(\text{RHE}) = E(\text{Hg/HgO}) + 0.0591\text{pH} + 0.098$).

Computational methods

All calculations presented in this work were performed using the generalized gradient approximation (GGA)-Perdew, Burke and Ernzerhof (PBE) [30] as implemented in the all-electron DMol³ code [31,32]. The Co_2AlO_4 (half of the Co^{3+} (octahedral coordination Co) is replaced by Al^{3+}) and Co_2AlO_4 with O vacancy were modeled using $8\text{ \AA} \times 12\text{ \AA} \times 10\text{ \AA}$ supercell. The vacuum layer was set to be $30\text{ \AA}$. Double numerical plus polarization (DNP) basis set was used throughout the calculation. The convergence criteria were set to be $1 \times 10^{-5}\text{ Ha}$, $0.001\text{ Ha \AA}^{-1}$, and $0.005\text{ \AA}$ for energy, force, and displacement convergence, respectively. A self-consistent field (SCF) density convergence with a threshold value of $1 \times 10^{-6}\text{ Ha}$ was specified.

RESULTS AND DISCUSSION

Fig. 1a illustrates the schematic fabrication process of ultrathin VO-rich Co_2AlO_4 nanosheets. As shown in step i, ultrathin Co_2AlO_4 nanosheets were firstly obtained by combining dealloying of $\text{Co}_5\text{Al}_{95}$ alloy ribbons in NaOH aqueous solution and annealing the as-prepared products at 300°C under Ar atmosphere. During the dealloying process, partial Al was selectively etched. At the same time, the Co and the reserved Al reacted with NaOH and oxygen dissolved in etching solution. The obtained product exhibited a hierarchal structure assembled with uniform nanosheets (see Supplementary information, Fig. S1). As shown in the powder XRD pattern, the product obtained from the dealloying process has poor crystallinity (Fig. S2). After further annealing, the as-prepared sample formed a Co_2AlO_4 phase with improved crystallinity. As shown in Fig. 1b and Fig. S3a, the pristine Co_2AlO_4 were ultrathin nanosheets, and the thickness of nanosheets was further measured to be varied from 6 to

9 nm using AFM (Fig. S3b). In order to increase the ECSA and density of active sites, the pristine Co_2AlO_4 were post-processed via the solvothermal method to create oxygen vacancies on the ultrathin nanosheets (step ii in Fig. 1a). Fig. 1c shows that the VO-rich Co_2AlO_4 almost retained the hierarchal structures of pristine sample. As revealed in the inset of Fig. 1c, the surface of the VO-rich Co_2AlO_4 became rougher than that of pristine Co_2AlO_4 , implying the exposure of more active sites. The specific surface area of VO-rich Co_2AlO_4 measured by BET method is $54.1\text{ m}^2\text{ g}^{-1}$, which is much larger than that of pristine Co_2AlO_4 ($31.6\text{ m}^2\text{ g}^{-1}$) (Fig. S4). In addition, the thickness of ultrathin nanosheets for VO-rich Co_2AlO_4 was kept the same as that of nanosheets in pristine Co_2AlO_4 . TEM images (Fig. 1d, e) further demonstrated that the Co_2AlO_4 were ultrathin nanosheets, consistent with the SEM observation.

Fig. S5 presents the high-resolution TEM (HRTEM) image of pristine Co_2AlO_4 with interplanar distances of 0.204, 0.287, 0.472 and 0.244 nm, corresponding to the (400), (220), (111) and (311) planes, respectively. Moreover, the discontinuous selected area electron diffraction (SAED) ring patterns embedded with large spots shown in Fig. S6 were indexed to (111), (220), (311), (400), (511) and (440) reflections. The HRTEM image of VO-rich Co_2AlO_4 nanosheets shows that interplanar distances of 0.209 and 0.244 nm correspond to the (400) and (311) planes, respectively (Fig. 2a). Fig. 2b shows the dis-

Figure 1 (a) Schematic illustration for the preparation process of ultrathin VO-rich Co_2AlO_4 nanosheets. (b, c) SEM images (the insets are high-magnification images with scale bars of 100 nm), and (d, e) TEM images of pristine Co_2AlO_4 and VO-rich Co_2AlO_4 nanosheets.

Figure 2 (a) HRTEM image, (b) SAED pattern, and (c–f) HAADF-STEM image and corresponding EDS mapping images of VO-rich Co_2AlO_4 . The mapping indicates the homogeneous distribution of Co (red), Al (blue), and O (green) elements.

continuous SAED ring patterns, which can be indexed to (311), (400) and (440) crystal planes. It was obviously shown that the crystallinity of the Co_2AlO_4 nanosheets with oxygen vacancies decreased. Fig. S7a and Fig. 2c show the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the pristine Co_2AlO_4 and VO-rich Co_2AlO_4 , respectively. Elemental mappings (Fig. S7b–d and Fig. 2d–f) revealed that cobalt, aluminum and oxygen were homogeneously

distributed in the selected area of Co_2AlO_4 and VO-rich Co_2AlO_4 , demonstrating that the Co_2AlO_4 after reduction did not affect its homogeneity.

Crystal structures of pristine Co_2AlO_4 and VO-rich Co_2AlO_4 were checked by XRD. As shown in Fig. 3a, the XRD patterns of both pristine Co_2AlO_4 and VO-rich Co_2AlO_4 exhibited well-defined diffraction peaks located at $2\theta=18.988^\circ$, 31.249° , 36.820° , 44.799° , 55.640° , 59.311° and 65.215° , which were indexed to (111), (220), (311), (400), (422), (511) and (440) planes of pure reverse spinel phase of Co_2AlO_4 (JCPDF: 38-0814). It can be observed that the crystal structure of VO-rich Co_2AlO_4 nanosheets was totally the same as that of pristine Co_2AlO_4 . This observation suggested that the post solvothermal process only resulted in the surface modification and did not destruct crystal structure when it underwent a mild reduction process. Additionally, the diffraction peaks of VO-rich Co_2AlO_4 nanosheets became weakened, which was consistent with the information observed from SAED [33,34].

Surface chemical compositions of the samples were investigated by XPS (Fig. 3b, c and Fig. S8). The full XPS spectra firstly show that both pristine Co_2AlO_4 and VO-rich Co_2AlO_4 only contain the elements of Al, C, O and Co and no other impurities can be detected (Fig. S8a). The atomic percentages of Co, Al and O elements are

Figure 3 (a) XRD patterns, XPS spectra of (b) O 1s, (c) Co 2p, and (d) H_2 -TPR profiles over Co_2AlO_4 and VO-rich Co_2AlO_4 nanosheets.

supplied in Fig. S8b. Obviously, the content of oxygen decreased significantly after post-treatment due to the resulting oxygen vacancies. As revealed from the high-resolution O 1s spectra, the peaks for pristine Co_2AlO_4 and VO-rich Co_2AlO_4 can be fitted into two oxygenated species located at 530.2 and 531.4 eV, which originated from typical metal-oxygen bond and oxygen defects, respectively. The ratios of peak areas for two O statuses indicated that O content on the surface of VO-rich Co_2AlO_4 was less than that for pristine Co_2AlO_4 due to the existence of oxygen vacancies [35–37]. As shown in Fig. 3c, two obvious peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$ can be split into two spin-orbit doublets, which can be assigned to Co^{3+} (780.5 and 795.7 eV) and Co^{2+} (782.1 and 797.4 eV), respectively [26,27]. Based on the peak area, the ratio of $\text{Co}^{2+}/\text{Co}^{3+}$ on the surface of VO-rich Co_2AlO_4 was determined to be 1.78, which was much higher than that of pristine Co_2AlO_4 (0.84). This is because that the formation of oxygen vacancies was balanced by the conversion of Co^{3+} to Co^{2+} [27].

To further confirm the existence of oxygen vacancies on the VO-rich Co_2AlO_4 , H_2 -TPR was carried out for the pristine and VO-rich Co_2AlO_4 . As shown in Fig. 3d, the peaks at 230 and 325°C respectively related to the step-wise change of $\text{Co}^{3+} \rightarrow \text{Co}^{2+} \rightarrow \text{Co}^0$ were observed for pristine Co_2AlO_4 sample [38,39]. For VO-rich Co_2AlO_4 , only one sharp peak appeared at low temperature region of 228°C, and the reduction process of $\text{Co}^{3+} \rightarrow \text{Co}^{2+} \rightarrow \text{Co}^0$ could be finished at a narrow temperature range, showing its easiness to be reduced. Additionally, in case of VO-rich Co_2AlO_4 , there just existed one smaller reduction peak area compared with Co_2AlO_4 , which was generally recognized as a sign of the decreased reducibility of $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ by exposing fraction of surface Co^{3+} species, and the increased reducibility of Co^{2+} to Co^0 [39]. Therefore, it was concluded that the $\text{Co}^{2+}/\text{Co}^{3+}$ ratio increased with exposing decreased Co^{3+} intermediates on the surface. The results further demonstrated that oxygen vacancy defects were produced in the sample, consisting with the analyses of XPS. The peak at 537°C for Co_2AlO_4 was associated with the further reduction of large cobalt-containing spinel particles, where the formation of CoAl_2O_4 or Co_2AlO_4 phase occurred [40]. In terms of VO-rich Co_2AlO_4 , no signals of spinel phases appeared as the temperature increased, indicating the good stability of the defects. Additionally, compared with Co_2AlO_4 , the working electrode made of VO-rich Co_2AlO_4 displayed a distinct oxidation peak at 1.13 V corresponding to $\text{Co}^{2+}/\text{Co}^{3+}$ redox process, indicating the formation of more CoOOH species [26]. This oxidation peak was also

found in the cyclic voltammetric (CV) measurements (Fig. S9), further proving that more Co^{2+} sites were presented in the VO-rich Co_2AlO_4 .

It has been known that oxygen vacancies usually play a very important role in the enhancement of OER activity [21,24,25,27,33]. We carried out density function theory calculations for Co_2AlO_4 and VO-rich Co_2AlO_4 , respectively. It was obvious that the Hirshfeld charge distribution of Co and Al atoms in those two catalysts was different (Fig. 4a, b). Compared with the pristine Co_2AlO_4 , the positive charge of Co and Al atoms adjacent to the O vacancies in VO-rich Co_2AlO_4 reduced significantly, that is, more electrons were concentrated on the Co and Al atoms. As shown in Fig. 4c, d, the density of state (DOS) for Co_2AlO_4 and VO-rich Co_2AlO_4 also reflected the same phenomenon. When there were O vacancies in Co_2AlO_4 , the DOS peak area near the Fermi level increased significantly, indicating more electrons were concentrated on the adjacent Co and Al atoms. And those electrons which were close to the Fermi level had a potential promoting effect during the H_2O activation. The adsorption structure of H_2O on the surface of pristine Co_2AlO_4 and VO-rich Co_2AlO_4 catalysts showed that the vertical distance between H_2O and the catalyst surface was 2 Å, revealing that the adsorption of H_2O on pristine Co_2AlO_4 catalyst was weak (Fig. 4e). On the surface of VO-rich Co_2AlO_4 catalyst, oxygen vacancy strongly adsorbs H_2O molecules. The geometric optimization results show that H_2O molecules cannot exist in O vacancy stably, but split into OH and H directly, facilitating the following oxygen evolution (Fig. 4f).

The electrocatalytic OER of VO-rich Co_2AlO_4 would be readily initiated in comparison with pristine one. Fig. 5a compared the iR -corrected OER polarization curves of Co_2AlO_4 and VO-rich Co_2AlO_4 in 1 mol L^{-1} KOH solution at a scan rate of 10 mV s^{-1} . It was found that the VO-rich Co_2AlO_4 catalysts displayed a noticeable onset potential of 1.51 V vs. RHE, which was smaller than that of pristine Co_2AlO_4 (1.59 V). It was found that the Co_2AlO_4 possessed a similar result to Co_3O_4 nanosheets (Fig. S10) at a current density of 10 mA cm^{-2} (Fig. S11), proving that the feasibility of the substitution of Co^{3+} by Al^{3+} . As shown in Fig. 5b, the overpotential at a current density of 10 mA cm^{-2} over VO-rich Co_2AlO_4 was 280 mV, which was much smaller than the values required for pristine Co_2AlO_4 (360 mV) and carbon paper (560 mV), respectively. As shown in Fig. 5c, the VO-rich Co_2AlO_4 has a smaller Tafel slope of 70.98 mV dec^{-1} relative to the pristine Co_2AlO_4 (79.98 mV dec^{-1}). Moreover, the value was also better than mostly reported Co_3O_4 catalysts

Figure 4 Hirshfeld charge distribution for the first layer atoms in pristine Co_2AlO_4 (a) and VO-rich Co_2AlO_4 (b). Density of state for Co and Al atoms adjoint to the O vacancies: (c) d band of Co atom, (d) p band of Al atom. Optimized structures of H_2O adsorption on pristine Co_2AlO_4 (e) and VO-rich Co_2AlO_4 (f) catalysts.

(Table S1) [27,33,41–55]. The results indicated that the VO-rich Co_2AlO_4 possessed a high OER kinetics.

To further explore the reason for the enhancement of OER performance, electrochemical double-layer capacitance (C_{dl}) and electrochemical impedance spectroscopy (EIS) were measured. As shown in Fig. S12, CV curves of Co_2AlO_4 and VO-rich Co_2AlO_4 were performed at the same voltage range and scan rate. According to the analyses of Fig. S12, the C_{dl} of VO-rich Co_2AlO_4 was $121.69 \text{ mF cm}^{-2}$, which was 3.45-fold that of Co_2AlO_4 (35.24 mF cm^{-2}) (Fig. 5d), indicating the VO-rich Co_2AlO_4 had larger ECSA. Fig. 5e demonstrates the typical Nyquist plots of the Co_2AlO_4 and the VO-rich Co_2AlO_4 electrodes acquired at open circuit in the frequency range of 100,000–0.01 Hz at a 5 mV amplitude. The solution resistance (R_s) of the VO-rich Co_2AlO_4 was 1.99Ω , which was lower than that of Co_2AlO_4 (2.52Ω). In the high frequency region, the magnitude of the charge-transfer resistance (R_{ct}) between the electrode and the electrolyte solution can be compared from the diameter of semi-circle. Obviously, R_{ct} of VO-rich Co_2AlO_4 was smaller than Co_2AlO_4 . Additionally, in the low frequency region, the steeper slope of VO-rich Co_2AlO_4 electrode indicated a lower ion diffusion obstacle and good capacitive merits. Therefore, the VO-rich Co_2AlO_4

nanosheets possessed better conductivity property. The linear sweep voltammetry (LSV) curves of Fig. 5a were normalized by the BET surface area. As shown in Fig. S13, the specific activity of VO-rich Co_2AlO_4 is $0.158 \text{ mA cm}^{-2}_{\text{BET}}$ at 1.6 V, which is 8.78-fold higher than that of Co_2AlO_4 ($0.018 \text{ mA cm}^{-2}_{\text{BET}}$), implying the excellent catalytic performance of the VO-rich Co_2AlO_4 is mainly affected by the oxygen vacancies.

Durability is another important indicator for an electrocatalyst in terms of practical application. Fig. 5f reveals the current density of Co_2AlO_4 and VO-rich Co_2AlO_4 electrocatalysts at a constant potential of 1.615 V (vs. RHE) for reacting 20 h without iR -compensation. It can be seen that the current density over VO-rich Co_2AlO_4 is relatively high compared with Co_2AlO_4 catalyst. Meanwhile, after long-term electrochemical processes, both Co_2AlO_4 and VO-rich Co_2AlO_4 presented an excellent durability. In addition, the LSV stability of Co_2AlO_4 and VO-rich Co_2AlO_4 was tested after 20 h of I - t testing (Fig. S14). As can be seen, the good negligible change was detected in the polarization curves after 20 h, indicating their high stability. Moreover, the XRD patterns and TEM image (Fig. S15) of VO-rich Co_2AlO_4 after the durability test revealed that the shaped nanosheets were retained, further showing the structure was not changed and the

Figure 5 (a) Polarization curves of Co_2AlO_4 , VO-rich Co_2AlO_4 and carbon paper (CP). (b) Corresponding overpotentials required at a current density of 10 mA cm^{-2} . (c) Tafel plots of the samples at a scan rate of 10 mA cm^{-2} . (d) C_{dl} calculations, (e) Nyquist plots, and (f) OER chronoamperometric of Co_2AlO_4 and VO-rich Co_2AlO_4 electrocatalysts.

aggregation of active materials can be restrained during continuous electrochemical reaction.

CONCLUSIONS

In summary, we have developed a facile method to fabricate ultrathin Co_2AlO_4 nanosheets with an average thickness of 8 nm *via* dealloying and annealing processes. After the subsequent alkaline treatment under solvothermal treatment, oxygen vacancies were formed on the surface of ultrathin Co_2AlO_4 nanosheets, resulting in large ECSA and high active site density. Co_2AlO_4 nanosheets with oxygen vacancies exhibited enhanced OER electrocatalytic performance with the onset potential of 1.51 V and overpotential of 280 mV, which were much better than those of pristine Co_2AlO_4 and most reported

Co_3O_4 catalysts. This simple strategy is expected to be extended to the synthesis of other defective metal oxides catalysts with potential applications in the fields of new energy production or environmental disinfection. The relative studies are in progress.

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Author contributions An C conceived the idea of synthesizing Co_2AlO_4 spinel for oxygen evolution reaction; Wang J and An C designed the project; Wang J performed the experiments; Shen Y conducted the theoretical simulations; Wei G, Xi W and Ma X took part in

the characterizations of samples; Wang J, Zhu P and Wei G analyzed the data and discussed the results. Wang J wrote the paper with support from An C and Zhang W.

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

Supplementary information Supporting data are available in the online version of the paper.

Jiayang Wang received her BSc degree in chemical engineering and technology from Shijiazhuang College in 2017. Now she is a master student majored in chemical engineering in Tianjin University of Technology under the supervision of Prof. Changhua An. Her current interests focus on the synthesis of 2D materials for electrochemical hydrogen and oxygen evolution reaction.

Weiqing Zhang received her PhD degree from National University of Singapore (NUS) in 2013. She currently works as an associate professor at Tianjin University of Technology. Her research interests focus on noble metal nanomaterials and their atomic origins for electrochemical energy conversion.

Changhua An received his PhD degree from the University of Science and Technology of China (USTC) in 2003 with Prof. Yitai Qian. After he did postdoc with Prof. Taeghwan Hyeon in Seoul National University from 2004 to 2005, he joined China University of Petroleum as an associate professor. In 2013, he was promoted to full professor of materials science and chemistry. From 2016, he has been a Tianjin distinguished professor at Tianjin University of Technology.

His research interests focus on the synthesis, characterization, and explorations of efficient catalysts in the fields of clean energy production and environmental purification.

氧空位超薄 Co_2AlO_4 纳米片的合成及其增强电催化氧析出反应

王佳阳^{1†}, 申勇立^{2†}, 魏桂涓¹, 刁卫², 马小茗¹, 张维青^{2*}, 朱培培¹, 安长华^{1,2*}

摘要 本文报道了通过脱合金和后续退火工艺合成一种新型超薄二维尖晶石结构的 Co_2AlO_4 纳米片。通过温和的溶剂热还原法将氧空位缺陷引入 Co_2AlO_4 纳米片中,使得电催化表面积增大,活性位密度变高,钴原子得到电子而产生更多的空轨道。这些空轨道有利于接受水分子中氧原子的孤对电子,促进水分子的活化。含有氧空位的超薄 Co_2AlO_4 纳米片在10 mA cm^{-2} 时的过电位为280 mV,塔菲尔斜率为70.98 mV dec^{-1} 。此外,其在碱性溶液中也表现出显著的稳定性,并且优于多数已报道的 Co_3O_4 电催化剂。该工作为制备高效的可持续新能源材料提供了新思路。