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Unveiling the role of surface P–O group in P-doped Co₃O₄ for electrocatalytic oxygen evolution by On-chip micro-device

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ABSTRACT

Transition metal phosphides or partially phosphatized oxides usually suffer from surface reconstruction during oxygen evolution reaction (OER), but still possess enhanced catalytic activity than directly synthesized oxides, which has aroused great interest in exploring the causes of such high catalytic activity. To monitor electronic property of catalyst during the OER can provide crucial insights into catalytic ability. Here we design a planar electrochemical microdevice based on individual thin-film catalyst, and for the first time explore the continuous electric conductance evolution of lattice P-doped oxides during the electrochemical activation process. Moreover, combining on-chip electrochemical impedance spectra measurements, *in situ I-V* measurements, and theoretical simulations of reconstructed lattice P-doped oxides, the effect of P–O groups on new-formed oxides is clarified. The induced electronic coupling between new-formed oxides and P-O groups has been studied and demonstrated. The coupled P–O groups effectively promote the metal–oxygen covalency of new-formed oxides, which accelerates electron transfer between active metallic center and oxygen adsorbates, thus leading to the enhanced electrocatalytic activity. Our study highlights the role of surface P–O groups in Co₃O₄ during the OER, and such unique on-chip electrochemical microdevice platform can also be applied in other related fields to understand the dynamic behavior of energy materials at nanoscale.

1. Introduction

Nowadays, water splitting is recognized as an environmentally friendly route for hydrogen production [1]. Anodic oxygen evolution reaction (OER) in this process, is a crucial half-reaction but severely limits the efficiency of hydrogen evolution for its sluggish four-electron transfer kinetics [2–4]. Transition metal phosphides (TMPs) and phosphorus doped transition metal oxides, are generally recognized as efficient catalysts for the OER in recent years and hold promise to replace the noble metal-based oxides like IrO₂ and RuO₂ [5–9]. However, different from most stable oxides or (oxy)hydroxides, TMPs or P-doped

oxides often suffer from severe surface reconstruction after the OER while show enhanced catalytic activity than the pristine synthesized TM oxides or (oxy)hydroxides [9,10]. It has been widely reported there are three components in OER-reconstructed TMPs or P-doped oxides: internal unreacted structure, surface new-formed TM-O species and residual P–O groups [7]. The internal phosphatized structure and surface TM-O species serve as conductive support and active species, respectively [11]. While the P–O groups are generally considered as unavoidable impurities and rarely involved in the analysis of oxygen evolution mechanism of reconstructed TMPs or P-doped oxides. Interestingly, through rigorous computational simulations, Fabris et al.

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predicted that the presence of surface P–O groups near the active Co sites may affect the OER reaction mechanism of the cobalt-phosphate [12]. Inspired by such work, it is necessary to unveil the intrinsic role of P-O groups in surface TM-O species towards OER, which would affect our understanding of oxygen evolution mechanism.

Generally, the OER activity of catalysts is closely related to their electronic properties. Thus, monitoring the electronic property evolution during the OER is of great importance to predict the catalytic activity. Previously, most of fundamental research used first-principles computations (such as density of states) and advanced spectroscopy technologies (such as X-ray photoelectron spectroscopy) to understand the electronic structure of catalysts [13–17]. Unfortunately, due to the presence of binders, conductive carbon and conductive substrate in traditional OER testing system, it is impossible to accurately measure the actual electric conductance of catalyst during the OER, which hinders the exploration on catalytic mechanism of TMPs or P-doped oxides. In view of this, a planar electrochemical thin-film microdevice is designed to probe the electronic and electrochemical signals of the catalyst. In the device, the catalyst is contacted with two metal microelectrodes in the form of individual thin-film. By this means, the electronic signal from thin-film will be collected in time, which is helpful to understand the catalytic promotion effect of P-O groups in reconstructed phosphorus-containing catalyst [18-21]. In addition, no binders and conductive carbon additives are used in individual thin-film catalyst, avoiding the interference of irrelevant factors. Finally, we aim to establish the correlation between structure, electrical properties and electrochemical performance of the catalysts.

2. Experimental details

2.1. Characterization

X-ray diffraction (XRD) analysis was conducted using a Bruker D2 Xray diffractometer (Cu K α X-ray, $\lambda = 1.5418$ Å). The high-resolution transmission electron microscopy (HRTEM) images and elemental mapping were recorded by JEOL, JEM-2100F microscope equipped with energy-dispersive X-ray spectroscopy (EDX). The silicon nitride membrane we used in HRTEM characterization was from CleanSiN. The scanning transmission electron microscopy (STEM) characterization was carried out in a CEOS probe corrected FEI Themis TEM with 300 kV accelerating voltage. The scanning electron microscopy (SEM) images of the thin-film samples were collected by using a JEOL-7100F microscope with 20 kV acceleration voltage. The energy disperse spectroscopy (EDS) elemental mapping was obtained using an Oxford EDS IE250 system. Xray photoelectron spectroscopy (XPS) analysis was carried out on Escalab 250Xi. The Atomic Force Microscopy (AFM) images were collected by a Scanning Probe Microscopy (Bruker MultiMode VIII). The Raman spectra were obtained by a Horiba Scientific LabRAM HR evolution Raman spectrometer (532 nm laser wavelength). The Fourier transform infrared spectroscopy (FTIR) spectra were collected by a FT-IR spectrometer, model spectrum two. The in situ electrical measurements and I-V curve tests were carried out by using both semiconductor device analyzer (Agilent B1500A) and probe station (Lake Shore, TTPX). Electrochemical measurements of the thin-films were achieved by using Autolab 302N workstation except the ex situ Raman testing, in which the electrochemical curve was obtained by a CHI760E workstation (CH Instruments, China).

2.2. Synthesis of Co₃O₄, P₀-Co₃O₄, P₁-Co₃O₄ and P'₁-Co₃O₄ thin-films

Cobalt metal particles (purity 99.98%) and a piece of clean silicon wafer (with 300 nm dielectric layer) were placed separately in thermal evaporators (Kurt J. Lesker, PVD75). Then, the thickness-controlled Co thin-film was deposited on the silicon wafer by physical vapor deposition (PVD). After that, the prepared Co thin-film was calcined in air at 450 $^{\circ}$ C for 12 h, the final Co₃O₄ thin-film was obtained. 800 mg of

NaH₂PO₂ and the silicon wafer with Co₃O₄ thin-film were placed separately in two porcelains, and further annealed in the tube furnace at 270 °C (denoted as P₀-Co₃O₄, in which P: Co atomic ratio is about 0.034) or 330 °C (denoted as P₁-Co₃O₄, in which P: Co atomic ratio is about 1.052) for 120 min under nitrogen gas atmosphere. After that, the silicon wafer was washed three times alternately with deionized water and alcohol. Finally, the P₁-Co₃O₄ (denoted as P'₁-Co₃O₄) by 50 cyclic voltammetry (CV) cycles in the range of potential between 0 and 0.75 V vs. Hg/ HgO (V_{Hg/HgO}) with scan rate of 50 mV s⁻¹.

2.3. Microfabrication of planar electrochemical thin-film devices

Step 1, a suitable silicon wafer with 300 nm SiO₂ dielectric layer was ultrasonic cleaned and spin-coated with photoresist, then patterned by ultraviolet lithography and deposited Ti and Au through PVD to form the pattern of Ti/Au (5 nm/50 nm) on the Si/SiO2 substrate as the outer electrode. Step 2, the size-controlled Co thin-films (150 µm*150 µm) were obtained by electron beam lithography (EBL) and PVD methods, and undergone same oxidation and phosphating process to form individual Co₃O₄, P₀-Co₃O₄ and P₁-Co₃O₄ thin-films. Step 3, utilizing EBL and PVD to make two metal microelectrodes which were composed of Ti/Au (5 nm/150 nm) and contacted with individual thin-film catalyst as the inner electrodes. In this way, a two-terminal thin-film microdevice was prepared. Step 4, a passive poly (methylmethacrylate) (PMMA) layer was spin-coated as an insulating layer, and then a part of individual thin-film was exposed by EBL to make the thin-film catalyst in contact with the electrolyte as work electrode. Step 5, we dripped the electrolyte (1 M KOH), and configured the reference electrode and the counter electrode to form an electrochemical three-electrode test system.

3. Results and discussion

Herein, we used P-doped Co₃O₄ (called P-Co₃O₄) thin-film as a model to understand the effect of P-O groups in TM-O species towards the oxygen evolution. As shown in Scheme 1a, the P₁-Co₃O₄ thin-film was synthesized through a typical phosphating process at 330 °C. After OERinduced structure evolution, the obtained $P^\prime{}_1\mbox{-}Co_3O_4$ thin-film shared the same oxide species with pure Co₃O₄, but some P-O groups existed on new-formed oxides. The similar component (Co₃O₄/P-O groups) was also prepared through a phosphating process at 270 °C (called P₀-Co₃O₄) as a supplementary sample. Moreover, a planar electrochemical thinfilm microdevice was fabricated to monitor the electrical and electrochemical signals of thin-film catalyst in real time during the OER (Scheme 1b). Though the P'1-Co3O4 (Co3O4/P-O groups) possessed similar electric conductance with pure Co_3O_4 before the OER, the P'₁-Co₃O₄ still showed much better catalytic performance than pure Co₃O₄ due to the coupled P-O groups. In fact, the P'1-Co3O4 showed the lower in-situ resistance and faster kinetic process than pure Co₃O₄ at the high electrochemical potentials. Besides, from the thermodynamic and kinetic perspectives, theoretical simulations on P'1-Co3O4 demonstrated the effects of coupled P-O groups (Co-O-P species) on its high OER activity.

3.1. Characterizations of unreacted thin-film samples

The detailed synthetic process of unreacted thin-film samples $(Co_3O_4, P_0-Co_3O_4 \text{ and } P_1-Co_3O_4)$ is schematically illustrated in Fig. S1. The atomic force microscope (AFM) image of $P_1-Co_3O_4$ thin film is shown in Fig. 1a, and the corresponding height profile depicts an average thickness of ~51 nm (Fig. 1b). In addition, the height line profiles drawn across Co_3O_4 and $P_0-Co_3O_4$ thin-films show average thicknesses of ~45 and 44 nm, respectively (Fig. S2). The high-resolution transmission electron microscopy (HRTEM) reveals interplanar distance of 0.244, 0.287 and 0.468 nm correspond well to the



Scheme 1. (a) Schematic diagram of P–O groups induced OER activity enhancement. (b) Schematic of the individual thin-film-based planar electrochemical microdevice, in which the electronic and electrochemical signals of the thin-film catalyst are collected simultaneously.



Fig. 1. (a) The AFM image of P_1 -Co₃O₄ thin-film. (b) The corresponding height line profile drawn across P_1 -Co₃O₄ thin-film along the orange line. (c) EDX spectra of P_0 -Co₃O₄ and P_1 -Co₃O₄ thin-films. (d) FTIR of Co₃O₄, P_0 -Co₃O₄ and P_1 -Co₃O₄ thin-films. (e) Raman spectra of Co₃O₄, P_0 -Co₃O₄ and P_1 -Co₃O₄ thin-films. (f) The energy disperse spectroscopy (EDS) of two-terminal Co₃O₄ thin-film microdevice, and the obtained G including Co₃O₄, P_0 -Co₃O₄ and P_1 -Co₃O₄ thin-films.

(311), (220) and (111) facets of Co_3O_4 , respectively (Fig. S3d) [22]. The P_0 - Co_3O_4 shows the same polycrystalline structure with Co_3O_4 , which can be seen from the well-defined concentric rings in the selected area electron diffraction (SAED) pattern (Fig. S3b). For P_1 - Co_3O_4 , the energy-dispersive X-ray spectroscopy (EDX) spectra show the significantly increased amount of P dopant compared with P_0 - Co_3O_4 (Fig. 1c). Some lattice planes in P_1 - Co_3O_4 begin to blur or even vanish (Fig. S3c), and an enlarged interplanar distance of (311) facet appears in Fig. S3f, which may be due to the incorporation of lattice phosphorus [9]. These crystal structure analyses are further supported by XRD tests of Co_3O_4 , P_0 - Co_3O_4 has shifted to lower diffraction angle compared with that of Co_3O_4 and P_0 - Co_3O_4 , which is attributed to the enlarged interplanar

distance, suggesting the doping of lattice phosphorus.

The Fourier transform infrared spectroscopy (FTIR) confirms the presence of P–O groups ($H_2PO_4^-$ and $PO_4^{-2}^-$ species) in P₀-Co₃O₄ and P₁-Co₃O₄ thin-films (Fig. 1d). Peaks located at 1079, 1154, and 1239 cm⁻¹ are assigned to $H_2PO_4^-$ [23], and the characteristic absorptions of PO₄⁻² appeared at 978 cm⁻¹ correspond well to reported values [24]. Whether synthetic Co₃O₄ thin-films, or purchased standard Co₃O₄ sample (Fig. S5), do not show characteristic absorption peaks in this wave-number range. Meanwhile, Raman spectra of the three samples are present in Fig. 1e, in which the thin-films are loaded on SiN substrates rather than Si/SiO₂ substrates to avoid unfavorable interference from Si peaks (Fig. S6). Five fingerprint phonon modes of Co₃O₄ are observed and A_{1 g} gives more prominent intensities [25]. There is no much

difference in Raman peaks between Co_3O_4 and $P_0-Co_3O_4$ due to the low content of P dopant, which is in good agreement with above TEM and XRD results. As the phosphating temperature increased to 330 °C, the Raman peaks are completely disappeared in $P_1-Co_3O_4$, indicating that the incorporation of lattice phosphorus destroyed the vibration mode of Co–O bond.

The two-terminal thin-film microdevices are fabricated to measure the electric conductance (G) of pure Co₃O₄, P₀-Co₃O₄ and P₁-Co₃O₄. The detailed assembly process and optical images of the devices are seen in Fig. S7. As shown in Fig. 1f, the Co_3O_4 is connected well with the Au electrodes in the individual Co3O4 thin-film microdevice. The obtained I-V curves and intrinsic conductance are shown in Fig. 1f and S8. The conductance of Co₃O₄ thin-films is reproducible and very sensitive to phosphating temperature, resulting in several orders of magnitude difference in conductance for P₀-Co₃O₄ and P₁-Co₃O₄ (Fig. S9). Notably, there is not always positive correlation between G and P dopant content, instead, a significant decline appeared when Co₃O₄ is converted into P₀-Co₃O₄, from 2.48E-9 S to 4.11E-12 S. This is mainly due to the influence of annealing temperature, according to the I-V curves of Co₃O₄ with 270 and 330 °C annealing, respectively (Fig. S10). By raising the phosphating temperature to 330 °C, the conductance of the P₁-Co₃O₄ thin-film is greatly increased (3.73E-4 S), which is may attributed to the incorporation of lattice phosphorus [9,26].

3.2. Structural evolution of P_1 -Co₃O₄ after electrochemical reconstruction

To get insight to the structure of OER-reconstructed P₁-Co₃O₄, the multiple spectroscopic characterizations are carried out. The Raman spectra illustrate the presence of Co₃O₄ phase in reconstructed P₁-Co₃O₄ after only 1 electrochemical cycle, shown in Fig. 2a and S11. This may be due to the release of lattice phosphorus which restores the vibrational mode of the Co–O bond. The Raman peak at 517 $\rm cm^{-1}$ is assigned to silicon wafer substrate, which is consistent with data in Fig. S6. The new appeared peaks at 481 cm⁻¹ and 688 cm⁻¹ for reconstructed P₁-Co₃O₄ are matched well with E_g and A_{1g} peaks of the Co_3O_4 thin-films. After 50 electrochemical cycle, the obtained P'_1 -Co₃O₄ shows F_{2g} (197 cm⁻¹ and 610 $\mbox{cm}^{-1}\mbox{)},$ E_g (473 $\mbox{cm}^{-1}\mbox{)}$ and A_{1g} (682 $\mbox{cm}^{-1}\mbox{)}$ Raman signals, which are close to that of standard Co₃O₄ rather than Co(OH)₂ (Fig. S12). Thus, the crystal structure of P'1-Co3O4 is considered as Co3O4 instead of hydroxide or oxyhydroxides, which is also consistent with the previous literature [27]. The P₁-Co₃O₄ is very unstable and serves as a precatalyst to form Co_3O_4 species to participate in the OER. In contrast, the Raman peaks of Co₃O₄ remain the same after the electrochemical cycles (Fig. S13), confirming the good stability of pure Co_3O_4 .

To elucidate the crystal structure of the P'_1 -Co₃O₄, the HRTEM analysis was carried out. As shown in Fig. S14a-c, the P'_1 -Co₃O₄ shows polycrystalline layer sheet structure and interplanar distance of 0.236

and 0.246 nm correspond well to the (222) and (311) facets of Co_3O_4 , respectively. And the corresponding fast Fourier transform (FFT) pattern shows that the measured angle of (222) and (311) facets is about 29.53°, close to the ideal angle 29.50° in cubic system (Fig. S14d). Meanwhile, a typical high-angle annular dark-field scanning TEM (HAADF-STEM) image and corresponding elemental mappings for Co, P and O elements were displayed in Fig. S14e-h. The distribution of Co, P and O elements in the whole thin-film is uniform, indicating complete surface reconstruction of P₁-Co₃O₄ thin-films. The EDX spectrum shows very weak P content in P'₁-Co₃O₄ thin-films (Fig. S15).

Furthermore, the X-ray photoelectron spectroscopy (XPS) is employed to probe the surface chemistry of the thin-films. As shown in Fig. 2b, the P 2p spectrum of P₁-Co₃O₄ exhibits component peaks of P $(2p_{3/2})$ and P $(2p_{1/2})$ at 129.59 and 130.49 eV respectively, indicating the incorporation of lattice phosphorus and the formation of Co-P bonds [28]. While the P-O bonds exist in both P₀-Co₃O₄ and P₁-Co₃O₄. After reconstruction, the lattice phosphorus is released but P-O bonds still exist in P'₁-Co₃O₄. No Co–P bonds peaks were observed after removing the surface layer of P'₁-Co₃O₄ by Ar⁺ sputtering (30 s, 2 keV), as shown in Fig. S16. Meanwhile, the Co $2p_{3/2}$ spectra clearly show the changes in the electronic structure related to P dopant (Fig. 2c). The Co (III)-O/ Co (II)-O peaks are detected at 779.38 eV/781.07 eV for Co₃O₄ thin-films. In the presence of P-O bonds, the Co (III)-O/ Co (II)-O peaks in P₀-Co₃O₄ have an obvious positive shift, which indicates the electronic coupling between Co-O and P-O bonds (forming Co-O-P species). For P₁-Co₃O₄, the decreased binding energy compared to Co (III)-O of Co₃O₄ is related to the formation of Co-P bonds [29]. After reconstruction, the P'1-Co3O4 shows the similar binding energy with P0-Co3O4 but not Co_3O_4 in Co $2p_{3/2}$ spectra, which indicates the same electronic coupling between Co-O and P-O bonds. Meanwhile, the XPS survey spectra and O 1s spectra are shown in Fig. S17. In O 1s spectra, the metal-oxygen bonds of both P0-Co3O4, P1-Co3O4 and P1-Co3O4 also have higher binding energy than that of Co₃O₄ due to the presence of coupled P-O bonds. Thus, we present an insight: the Co₃O₄ thin-film is converted into lattice phosphorus doped Co₃O₄ thin-film at 330 °C phosphating temperature, and then reconverted into Co₃O₄ species with P-O bonds coupling after the electrochemical OER evolution. Meanwhile, the Arrhenius plots at 1.58 V (vs RHE) for Co₃O₄, P₀-Co₃O₄ and P'₁-Co₃O₄ allow the electrochemical activation energies to be extracted (Fig. S18) [30]. The calculated activation energy value of the P0-Co3O4 and P'1-Co3O4 are 43.62 and 34.47 kJ/mol, respectively, close to the value of Co3O4 (32.31 kJ/mol). The activation energy is associated with the kinetic barriers involved in the water oxidation, and the similar values indicate that the catalytic active sites in the Co₃O₄, P₀-Co₃O₄ and P'₁-Co₃O₄ are identical [31-33].



Fig. 2. (a) The Raman spectra of P₁-Co₃O₄ thin-film before and after the first electrochemical cycle, and compared with pure Co₃O₄ thin-film. (b-c) High-resolution P 2p and Co 2p_{3/2} spectra, respectively, for Co₃O₄, P₀-Co₃O₄, and P'₁-Co₃O₄.

3.3. Electrical and electrochemical properties evolution after the reconstruction

Generally speaking, the actual OER electrocatalytic performance is simultaneously determined by inherent ability of the active sites and its surrounding local environment [8,34]. More specifically, in the alkaline electrolytes, active sites are in charge of the adsorption of OH, bond formation and breaking, oxygen desorption, and interfacial charge transfer. While the local environment affects the accessibility of active sites, among which the electron transfer between the catalytic surface and the external circuit is one of the most important factors. Thus, it is necessary to acquire the electrical properties of catalysts in time during the OER process. To probe electrical and electrochemical properties evolution of thin-film catalyst during the reconstruction process, a planar electrochemical microdevice is fabricated based on individual thin-film catalyst. The detailed assembly process is schematically illustrated in Fig. S19. The microdevice is configured with an electrochemical three-electrode system including the individual thin-film catalyst (working electrode), a Hg/HgO electrode (reference electrode) and a platinum wire (counter electrode). In addition, a passive poly (methylmethacrylate) (PMMA) layer is used to protect the device from alkaline electrolyte. Then a small window was carved on the PMMA layer to realize the spatial control of the electrocatalytic reaction, so as to ensure that the electrocatalytic reaction only occurred in a certain exposed region (Fig. 3a). The blank device, in which no thin-film catalyst exists, shows very poor OER activity, shown in Fig. S20. By the fabricated microdevice, the initial 50 CV curves of individual P1-Co3O4 thin-film has been measured (Fig. S21), and the current densities at the potential of 0.75 V_{Hg/HgO} are extracted as an electrochemical activity evaluation (Fig. 3b). During OER cycling, the electrochemical performance of P1-Co3O4 continuously increases in the first three cycles which is due to the normal electrode activation (process I). The current density at $\sim 0.75 V_{Hg/HgO}$ drops sharply from 4th to 10th cycle (process II), and then starts to drop slowly (process III), which indicates the activity decay of the catalyst. After the 30th cycle, the current density tends to

stabilize due to the completion of electrode structure evolution (process IV). In contrast, the Co₃O₄ and P₀-Co₃O₄ thin-films show the normal activation and increased current density during the electrochemical cycles (Fig. S22). The dynamic changes of electrochemical activity in P1-Co3O4 exhibit the correlation to the evolution of conductance, shown in Fig. 3c and S23. Before electrochemical activation, the measured conductance of the P₁-Co₃O₄ is 9.13E-4 S. After 1st cycle, the conductance of the P₁-Co₃O₄ begins to decrease but still maintains a high conductance (6.79E-4 S), which is still sufficient to support the electrode activation in process I. To 10th cycle, the conductance is greatly reduced, which results in a sharp decline in catalytic activity during process II. From 10th to 30th cycle, the conductance slowly decays, corresponding to the slowly decreasing electrochemical current in process III. After 30th cycle, the conductance remains almost constant, which makes the electrochemical performance of catalyst stable (process IV). After reconstruction, it is worth noting that the P'1-Co3O4 shows the similar electric conductance (2.73E-9 S) with Co₃O₄, which is several orders of magnitude smaller than that of unreacted P1-Co3O4. In contrast, the I-V characteristics of Co₃O₄ and P₀-Co₃O₄ thin-films have not changed much after the electrochemical CV cycles (Fig. S24).

3.4. Electrical and electrochemical resistance during the OER

Furthermore, based on such unique microdevice platform, *in situ I-V* measurements on individual Co₃O₄, P₀-Co₃O₄ and P'₁-Co₃O₄ thin-films are conducted to obtain the real-time resistance during the OER process. A circuit is designed, in which two working electrodes (WE1 and WE2) are applied to obtain the electrical transporting properties of Co₃O₄, P₀-Co₃O₄ and P'₁-Co₃O₄ in real time (inset, Fig. 3d). The applied potentials in WE1 and WE2 (called V1 and V2) increase synchronously *vs.* RHE, from 1 to 1.8 V, and keep the constant tiny potential difference $\triangle V$ ($\triangle V$ =1 mV). The Current difference ($\triangle I$) between WE1 and WE2 during the OER attributes to $\triangle V$, and in this way the real-time resistance can be calculated (Fig. 3d-e). The result demonstrates that both P'₁-Co₃O₄, P₀-Co₃O₄ and Co₃O₄ keep high resistance at the low



Fig. 3. (a) Optical micrograph of the planar electrochemical microdevice based on individual thin-film catalyst. (b) Electrochemical activity evolution of individual P₁-Co₃O₄ thin-film at the initial 50 electrochemical cycles. Inset: Photograph of the individual thin-film-based planar electrochemical microdevice. (c) Intrinsic conductance evolution of individual P₁-Co₃O₄ thin-film during the electrochemical reconstruction. (d) *In situ I-V* measurements of individual Co₃O₄, P₀-Co₃O₄ and P'₁-Co₃O₄ thin-films. Inset: The schematic of *in situ I-V* measurements based on a planar electrochemical microdevice. (e) The real-time resistance of individual Co₃O₄, P₀-Co₃O₄ and P'₁-Co₃O₄ thin-films during the OER process. (f) Nyquist plots of individual Co₃O₄, P₀-Co₃O₄ and P'₁-Co₃O₄ thin-films. The set potential is 1.6 V vs. RHE. Inset: the amplified Nyquist plot of P'₁-Co₃O₄ thin-films.

potentials. With the electrochemical potential increasing, both P'_1 - Co_3O_4 , P_0 - Co_3O_4 and Co_3O_4 show a decrease in resistance due to the selfgating phenomenon, in which the extra electrons are transferred from the surface absorbed OH⁻ to the catalyst [35]. While the P'_1 - Co_3O_4 and P_0 - Co_3O_4 show the lower *in-situ* resistance ($R_{in\ situ}$) than that of Co_3O_4 at the high potentials. The lower electrode resistance indicates the more charge transfer in the catalyst, which is dynamically beneficial for the OER process.

On-chip electrochemical impedance spectroscopy (EIS) measurements are also carried out for further analysis on charge transfer. As shown in Fig. 3f, two semicircles appear in the spectra of both Co_3O_4 , P_0 - Co_3O_4 and P'_1 - Co_3O_4 at 1.60 V vs. RHE. An equivalent circuit was employed to fit the EIS data obtained from Co_3O_4 , P_0 - Co_3O_4 and P'_1 - Co_3O_4 (Fig. S25). The low frequency element is related to a Faradaic charge transfer process (R_p) at electrocatalytic interface, while the high frequency one indicated charge transport from electrocatalytic interface to Au electrodes (R_{ct}) [35]. Compared with Co_3O_4 , obviously, both R_{ct} (from 274.05 to 9.01 Ω cm²) and R_p (from 291.60 to 8.27 Ω cm²) are greatly reduced in P'_1 - Co_3O_4 , showing a faster charge transfer process. The resistances of the P_0 - Co_3O_4 , including R_{ct} and R_p , are just between the P'_1 - Co_3O_4 and Co_3O_4 .

3.5. Catalytic performance of individual thin-film-based planar OER microdevices

Based on the individual thin-film-based OER microdevices, the catalytic performance of Co₃O₄, P₀-Co₃O₄ and P'₁-Co₃O₄ are obtained. The oxide species for P_0 -Co₃O₄ and P'_1 -Co₃O₄ are the same with Co₃O₄, as evidenced by the previous Raman testing. The polarization curves in Fig. 4a shows that Co_3O_4 exhibits very poor OER activity (570 mV @ 0.8 mA/cm^2). In the presence of P-O groups, both P₀-Co₃O₄ and P'1-Co3O4 show the enhanced OER activity. To elucidate the specific activity of the catalyst, the electrochemical surface area (ECSA) is calculated. As shown in Fig. S26, the electrochemical double-layer capacitance (C_{dl}) of P'₁-Co₃O₄ is 0.41 mF/cm², which is higher than that of P_0 -Co₃O₄ (0.10 mF/cm²) and Co₃O₄ (0.13 mF/cm²). The LSV curves normalized by the ECSA are shown in Fig. S27 to reflect the inherent catalytic properties of Co₃O₄, P₀-Co₃O₄ and P'₁-Co₃O₄. The specific activity of both P_0 -Co₃O₄ and P'_1 -Co₃O₄ are higher than that of Co₃O₄. Compared with P_0 -Co₃O₄, the P'_1 -Co₃O₄ shows the lower overpotential, which attributes to its higher intrinsic conductance than that of P₀-Co₃O₄. It is worth mentioning that it is difficult to further decrease overpotential of P'1-Co3O4 by simply increasing the phosphating temperature (Fig. S28). Meanwhile, the calculated Tafel curves are shown in Fig. 4b. Both P₀-Co₃O₄ and P'₁-Co₃O₄ show the smaller Tafel slope than that of Co₃O₄ (145 mV/dec), exhibiting a faster kinetic process. It indicates the critical effect of coupled P-O groups on the reaction kinetics. Compared with P'1-Co3O4, the larger Tafel slope of P0-Co3O4 is also due to its lower intrinsic conductance than that of P'1-Co3O4.

In fact, both Co₃O₄, P₀-Co₃O₄ and P'₁-Co₃O₄ have poor intrinsic

conductance compared with unreacted P₁-Co₃O₄, which impedes charge transfer process. Therefore, in order to optimize the charge transfer of the whole microdevice, we change the device model, making the thinfilms deposited on Au electrodes directly (Fig. S29). In this way, the electron transport distance between surface active sites and Au electrodes is reduced, and the enhanced electron-transport-effect is clearly presented from *I-V* curves (Fig. S30). The overall catalytic performance of the Co₃O₄, P₀-Co₃O₄ and P'₁-Co₃O₄ thin-films are improved (Fig. S31), and the P'₁-Co₃O₄ @Au exhibits a lowest overpotential (320 mV @ 10 mA/cm²), which is similar to that of reported CoP catalysts [36–38]. To uncover a statistical change trend, six samples for each type of thin-films on Au substrates are tested and shown in Fig. 4c. The average overpotential and Tafel slopes display an obvious decreasing trend after coupling P–O groups for both P₀-Co₃O₄ and P'₁-Co₃O₄ thin-films.

3.6. Theoretical calculation on P–O group coupled Co₃O₄

To further understand the OER activity enhancement mechanism through P-O bonds coupling fundamentally, density functional theory (DFT) simulations are performed based on the exposed (110) surface of Co₃O₄. The surface exposed Co atoms are coupled with P-O bonds referred as P'1-Co3O4 model (Co3O4/P-O groups), as shown in Fig. 5a. Fig. 5b exhibits the total electronic density of states (TDOS) for P'1-Co₃O₄ and Co₃O₄, in which some new hybridized electronic states are generated with P-O bonds coupling. Electron occupied states near the Fermi level for P'1-Co3O4 are close to that of Co3O4, which results in the same intrinsic conductance. In general, the metal-oxygen covalency is regarded as an effective descriptor that determines the experimental OER activity [39,40]. The projected density of states (PDOS) results confirm that the coupled P-O bonds effectively tunes the position of Co 3d and O 2p band centers (ε_d and ε_p), making the energy difference between ε_d and ε_p ($\Delta \varepsilon$) decreases from 1.51 to 1.15 eV (Fig. 5c). In this way, the P'1-Co3O4 exhibits stronger Co 3d-O 2p orbital hybridization and greater Co-O covalency than that of Co₃O₄. The stronger orbital hybridization makes the electron density shift from oxygen anion to Co cation and results in the charge deviation of Co atoms in Co₃O₄, which is reflected by the changed binding energy of Co (III) and Co (II) after P-O groups coupling. The enlarged Co-O covalency promotes electron transfer between the Co atoms and oxygen adsorbates, which results in an accelerated OER dynamics process. This is why the P'1-Co3O4 shows the smaller R_{ct}, R_p and R_{in situ} than Co₃O₄ during the OER. In addition, the energy diagrams of four-steps reaction are illustrated in Fig. S32. The oxygen intermediates (*OH, *O and *OOH) are interacted with the coordinately unsaturated surface Co site with/without P-O coupling. From the perspective of free energy pathways, the rate-determining step (PDS) occurs at the splitting of hydroxyl group towards adsorbed O* (step 2) for both Co₃O₄ and P'₁-Co₃O₄, as shown in Fig. 5d. Through the P-O bonds coupling with surface Co atoms in Co₃O₄, the energy barrier of the PDS reduces from 2.97 to 2.11 eV, which is thermodynamically



Fig. 4. (a) Polarization curves of individual Co_3O_4 , P_0 - Co_3O_4 and P'_1 - Co_3O_4 thin-films, and (b) the corresponding Tafel plots. (c) Statistic-based overpotential @ 10 mA/cm² and corresponding Tafel slope for individual Co_3O_4 , P_0 - Co_3O_4 , and P'_1 - Co_3O_4 thin-films on Au substrates.



Fig. 5. (a) Structural diagram of P'_1 -Co₃O₄. Blue, red, and gray spheres represent Co, O, P atoms, respectively. (b) Total electronic density of states for Co₃O₄ and P'_1 -Co₃O₄. (c) Calculated PDOS of Co₃O₄ and P'_1 -Co₃O₄. The blue and red dotted lines refer to the Co 3d and O 2p band centers, respectively. (d) Calculated free energy diagram of the OER on Co₃O₄ and P'_1 -Co₃O₄.

favorable for the OER process.

4. Conclusion

In summary, we demonstrated the electronic coupling effect between the Co₃O₄ species and surface P–O groups in the reconstructed lattice phosphorus doped Co₃O₄ thin-films. By designing a planar electrochemical microdevice based on individual P1-Co3O4 thin-films, we for the first time measure the electric conductance of reconstructed lattice phosphorus doped Co₃O₄, and establish the correlation between intrinsic conductance and electrochemical activity of lattice phosphorus doped Co₃O₄ during the reconstruction, clearly recognizing the influence of intrinsic conductance on catalytic activity of P-doped Co₃O₄. Moreover, based on such unique microdevice platform, the real-time resistance of reconstructed lattice phosphorus doped Co₃O₄ during the OER is monitored by in situ I-V measurement. Combining with on-chip EIS measurement at 1.6 V vs RHE, it reveals that the reconstructed lattice phosphorus doped Co₃O₄ has a faster charge transfer kinetics than the pristine synthesized Co₃O₄ at high electrochemical potential, even though the two have similar electric conductance before the OER. In the presence of conductive Au substrate, the reconstructed lattice phosphorus doped Co₃O₄ exhibits a lowest overpotential of 320 mV @ 10 mA/cm². Besides, by DFT calculation, we theoretically demonstrated that the coupled P-O groups in Co₃O₄ could shorten the energy difference between Co 3d and O 2p band centers (stronger Co-O covalency), effectively reduce the free energy barrier of the PDS from 2.97 to 2.11 eV, and thus promote the OER activity. Our work highlights the effect of residual P-O groups in TM-O species towards oxygen evolution, and provides new inspiration for the study of other easily reconfigurable catalysts, such as transition metal phosphides, sulfides, selenides, carbides and nitrides.

CRediT authorship contribution statement

Liqiang Mai and Wen Luo conceived the study, provided insights for the experiments and supervised the research. Xunbiao Zhou designed the synthesis method, fabricated the microdevices and performed the electrochemical measurements. Xuelei Pan conducted structural characterization of the thin-film samples. Yan Zhao and Xiaobin Liao performed first-principles calculations. Peijie Wu performed the model diagram of the devices. Xunbiao Zhou, Mengyu Yan and Liang He participated in the all data analysis and wrote the manuscript together with Liqiang Mai and Wen Luo. All authors agreed with the final version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2021.105748.

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