Plasma-Engraved Co$_3$O$_4$ Nanosheets with Oxygen Vacancies and High Surface Area for the Oxygen Evolution Reaction

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Abstract: Co$_3$O$_4$, which is of mixed valences Co$^{3+}$ and Co$^{4+}$, has been extensively investigated as an efficient electrocatalyst for the oxygen evolution reaction (OER). The proper control of Co$^{3+}$/Co$^{4+}$ ratio in Co$_3$O$_4$ could lead to modifications on its electronic and thus catalytic properties. Herein, we designed an efficient Co$_3$O$_4$-based OER electrocatalyst by a plasma-engraving strategy, which not only produced higher surface area, but also generated oxygen vacancies on Co$_3$O$_4$ surface with more Co$^{3+}$ formed. The increased surface area ensures the Co$_3$O$_4$ has more sites for OER, and generated oxygen vacancies on Co$_3$O$_4$ surface improve the electronic conductivity and create more active defects for OER. Compared to pristine Co$_3$O$_4$, the engraved Co$_3$O$_4$ exhibits a much higher current density and a lower onset potential. The specific activity of the plasma-engraved Co$_3$O$_4$ nanosheets (0.055 mA cm$^{-2}$ at 1.6 V) is 10 times higher than that of pristine Co$_3$O$_4$, which is contributed by the surface oxygen vacancies.

Electrocatalytic water splitting provides a sustainable strategy to supply clean energy through hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), where an effective catalyst is a necessity. In principle, OER is a thermodynamic uphill reaction involving a stepwise four-electron transfer at a high overpotential. Noble metal/metal oxides, such as Pt, RuO$_2$, and IrO$_2$, are still considered as being the most active electrocatalysts. However, the high cost and element scarcity of these noble metals or metal oxides seriously hinder their large-scale application for water splitting. Co-based oxides can act as active OER electrocatalysts with relatively low cost and earth-abundance. Bulk cobalt oxides are normally less active for OER due to their poor conductivity and low surface area. The electrocatalytic activity of cobalt oxide is mainly determined by its surface area and electronic states. Various approaches have been adopted to improve the catalytic activity of cobalt oxides for OER. Anchoring Co$_3$O$_4$ nanocrystals on carbon-based supports could significantly enhance their electrocatalytic activity for OER contributed by the small crystalline size and conductive support.

As discussed above, the electrocatalytic activity of Co$_3$O$_4$ was mainly affected by its surface area and electronic states. The higher surface area of Co$_3$O$_4$ provides more accessible sites for electrochemical reactions. The surface area could be increased through a nanostructure strategy. On the other hand, the electronic states, especially the surface electronic states, of Co$_3$O$_4$ could be tuned by doping with a third element, facet control, or oxygen vacancies. Tuning oxygen vacancies of metal oxides could significantly alter their catalytic activity. Co$_3$O$_4$ is of mixed valences with the presence of Co$^{3+}$ and Co$^{4+}$. The proper control of the ratio of Co$^{3+}$/Co$^{4+}$ in the Co$_3$O$_4$ could lead to significant modifications on its electronic and thus catalytic properties.

Herein, we designed a highly efficient Co$_3$O$_4$-based OER electrocatalyst with oxygen vacancies and high surface area by a one-step plasma-engraving strategy. The pristine Co$_3$O$_4$ nanosheets were deposited on a Ti substrate by the electrodeposition of Co(OH)$_2$ followed by thermal annealing. The pristine Co$_3$O$_4$ nanosheets were subjected to the Ar plasma treatment. It is well known that the Ar plasma is often used for etching and cleaning. The Ar plasma treatment on Co$_3$O$_4$ nanosheets could effectively engrave the nanosheet structure to expose more surface sites, as illustrated in Scheme 1. More surprisingly, the plasma-engraved Co$_3$O$_4$ shows the presence of oxygen vacancies on its surface, as characterized by XRD and XPS. The increased surface area and the generated surface oxygen vacancies of Co$_3$O$_4$ by the plasma engraving significantly contributed to the excellent electrocatalytic performance for OER. Compared to the pristine Co$_3$O$_4$ nanosheets, the plasma-engraved Co$_3$O$_4$ nanosheets exhibit...
a much higher current density of 44.44 mA cm\(^{-2}\) at 1.6 V vs. reversible hydrogen electrode (RHE) and a much lower onset potential of 1.45 V. The specific activity of plasma-engraved Co\(_3\)O\(_4\) nanosheets obtained by normalizing the OER current with the BET surface area (0.055 mA cm\(^{-2}\) at 1.6 V) is 10 times higher than that of pristine Co\(_3\)O\(_4\) nanosheets. It should be pointed out that the Ar plasma treatment is very time-saving with only 120 s to produce highly efficient electrocatalysts, and the similar strategy could be extended to engrave NiO nanosheets with improved electrocatalytic performance for OER as well.

For the preparation of Co\(_3\)O\(_4\) nanosheets, Co(OH)\(_2\) was electrochemically deposited on Ti foil followed by the thermal annealing to form Co\(_3\)O\(_4\) nanosheets, which were treated by Ar plasma for 120 s. To observe the effect of the plasma treatment on the surface morphology of Co\(_3\)O\(_4\) nanosheets, the SEM characterizations were performed. Figure 1 shows the SEM images of pristine and the plasma-engraved Co\(_3\)O\(_4\) nanosheets. As shown, a continuous and compact surface was observed for pristine Co\(_3\)O\(_4\) nanosheets. For the plasma-engraved Co\(_3\)O\(_4\), the rough, discontinuous and loose surface was observed, in which the interconnected Co\(_3\)O\(_4\) nanoparticles were observed. The SEM comparison clearly demonstrated that the plasma treatment could effectively engrave Co\(_3\)O\(_4\) nanosheets to increase the surface area. We also engraved Co\(_3\)O\(_4\) nanosheets for different times (Supporting Information, Figure S1). It could be found that more Co\(_3\)O\(_4\) species were etched off with the increase of the plasma-engraving time. To further investigate the structural change of Co\(_3\)O\(_4\) nanosheets after the plasma treatment, TEM characterizations were performed on both pristine Co\(_3\)O\(_4\) and plasma-engraved Co\(_3\)O\(_4\), as shown in Figure 2. Like the SEM observation, solid and compact nanosheets were observed on pristine Co\(_3\)O\(_4\). For plasma-engraved Co\(_3\)O\(_4\), the interconnected Co\(_3\)O\(_4\) nanostructures with amounts of nanoholes were observed. Obviously, it can be seen that the plasma-engraved Co\(_3\)O\(_4\) have a much higher surface area per unit mass, resulting in enhanced electrochemical performance, as discussed below. To investigate the possible extension of the plasma-engraving strategy, we also treated NiO nanosheets by Ar plasma (Supporting Information, Figure S2), from which it could apparently be seen that the plasma could also effectively engrave NiO nanosheets with more exposed surface area per unit mass. This phenomenon could be more clearly observed in TEM images (Supporting Information, Figure S3).

The high-resolution TEM (HRTEM) is used to study the crystalline structure of Co\(_3\)O\(_4\) nanosheets before and after the plasma engraving. From the HRTEM images (Supporting Information, Figure S4), the lattice spacing (220) of pristine Co\(_3\)O\(_4\) nanosheets is 0.29 nm (Figure S4a,c), which is the same with the plasma-engraved Co\(_3\)O\(_4\) nanosheet (Figure S4b,d). The lattice spacing of NiO nanosheet is the same (0.21 nm) before and after the plasma treatment (Supporting Information, Figure S5). XRD characterizations were also performed on both Co\(_3\)O\(_4\) and NiO to observe the crystalline change before and after the plasma treatment. The XRD patterns (Supporting Information, Figure S6) of pristine Co\(_3\)O\(_4\) and NiO nanosheets can be indexed to those in the JCPDS data (JCPDS No. 43-1003) and (JCPDS No. 44-1159), respectively. After the plasma treatment, the XRD patterns show no obvious change. Both HRTEM and XRD results indicated that the bulk crystalline phases of Co\(_3\)O\(_4\) nanosheets were not significantly changed by the plasma engraving, although a higher surface area was obtained.

As observed by the SEM and TEM, it is believed that the plasma-engraved Co\(_3\)O\(_4\) nanosheets would expose more surface area. To confirm this hypothesis, the N\(_2\) sorption isotherms (Figure 2) were obtained for the two samples. The Brunauer–Emmett–Teller (BET) surface area of plasma-engraved Co\(_3\)O\(_4\) is much higher than that of pristine Co\(_3\)O\(_4\) (160.26 vs. 95.27 m\(^2\)g\(^{-1}\)). This comparison confirms that the plasma engraving could significantly increase the surface area of Co\(_3\)O\(_4\), resulting in more exposed sites for the electrocatalysis, as discussed below.

Since the electrocatalysis reaction mainly occurs on the surface of electrocatalysts, it is essential to investigate the surface properties of Co\(_3\)O\(_4\) before and after the plasma treatment.\(^{10}\) The X-ray photoelectron spectroscopy is an ultra-sensitive tool to detect the surface properties of electrocatalysts.\(^{11}\) XPS characterizations were performed on the
pristine and the plasma-engraved CoO$_x$. The survey spectra (Supporting Information, Figure S7) show the presence of Co and O in both the samples. The fine-scanned Co 2p XPS spectra of the pristine and the plasma-engraved Co$_x$O$_y$ were given in Figure 3a, in which the peaks of Co 2p$_{3/2}$ and Co 2p$_{1/2}$ are located at around 780 eV and 796 eV, respectively, for both samples. Compared to the pristine Co$_x$O$_y$, the Co 2p peaks of the plasma-engraved Co$_x$O$_y$ exhibit two new satellite peaks centered at about 786 eV and about 803 eV (Figure 3a), which is attributed to the Co$^{3+}$ oxidation state, indicating that a portion of Co$^{2+}$ ions is reduced to Co$^{3+}$ with generating oxygen vacancies.[13] To get further insight into the surface properties, the fine-scanned Co 2p spectra of both pristine and plasma-engraved Co$_x$O$_y$ were fitted to investigate the electronic states of Co atoms with different valences (Figure 3b,c). The two fitted peaks for Co 2p$_{3/2}$ are Co$^{2+}$ (ca. 779.5 eV) and Co$^{3+}$ (ca. 780.8 eV), respectively.[13] The relative atomic ratio of Co$^{2+}$/Co$^{3+}$ on the surface of the Co$_x$O$_y$ 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$^{3+}$ (1.2) on the plasma-engraved Co$_x$O$_y$ is higher than that (1.0) of pristine Co$_x$O$_y$, indicating that relatively more Co$^{2+}$ present in the plasma-engraved Co$_x$O$_y$, that is, surface oxygen vacancies were generated by Ar plasma, which can be confirmed by the fine-scanned O 1s XPS spectra. Figure 3d shows two oxygen peaks contributions of O 1s region of pristine Co$_x$O$_y$ and Figure 3e shows four oxygen peaks contributions of O 1s region of the engraved Co$_x$O$_y$. O1 at 529.8 eV is typical for metal–oxygen bonds, whereas O4 at the higher value of 532 eV resulted from Co$_3$O$_4$ reduction by Ar plasma attributed to the high-binding energy peak from surface oxygen defect species.[10,8,13] The appearance of the O4 peak in the O 1s region of the plasma-engraved Co$_x$O$_y$ indicates the presence of oxygen vacancies on the surface of Co$_x$O$_y$. The fine-scanned XPS results of Co 2p region and O 1s region of pristine and plasma-engraved Co$_x$O$_y$ nanosheets indicated that Co$^{3+}$ is partially reduced to Co$^{2+}$, producing oxygen vacancies. The partial reduction from Co$^{3+}$ to Co$^{2+}$ resulted from the Ar plasma treatment. Previously, Ar plasma has been used to reduce metal ions to metal nanoparticles, indicating its reducing capability.[15] Since XRD and HRTEM characterizations show no obvious change of the bulk phase of Co$_x$O$_y$ after the plasma treatment while XPS spectra indicates the appearance of oxygen vacancies, it is believed that the oxygen vacancies are only present on the surface of Co$_x$O$_y$. It is understandable as the plasma is a surface treatment technology.[16] Previous density-functional theory (DFT) calculations revealed that the oxygen vacancies create new defect states located in the band gap of Co$_x$O$_y$ and the two electrons on the defect states are easily excited, resulting in improvement of the conductivity of Co$_x$O$_y$. The oxygen vacancies on the surface of Co$_x$O$_y$ formed by the plasma-engraving may improve the electronic conductivity, create more electrochemically active sites, and thus enhance the electrocatalytic activity for OER.

To investigate the electrocatalytic performance for OER, the linear sweep voltammetry (LSV) curves of pristine Co$_x$O$_y$ nanosheets and plasma-engraved Co$_x$O$_y$ nanosheets are probed in alkaline electrolyte (0.1 M KOH), as shown in Figure 4a. Since Co$_x$O$_y$ nanosheets were grown on Ti foil substrate, the supported electrocatalysts could be used as the working electrode directly. The onset potential for OER on Ar-plasma engraved Co$_x$O$_y$ nanosheets is 1.45 V versus RHE which is lower than pristine Co$_x$O$_y$ nanosheets (1.5 V vs. RHE). Furthermore, to reach the current density of 10 mA cm$^{-2}$ (based on geometric electrode area), the pristine Co$_x$O$_y$ nanosheets requires a potential of 1.77 V versus RHE, while the plasma-engraved Co$_x$O$_y$ nanosheets only 1.53 V, suggesting the excellent electrocatalytic performance of Ar-plasma engraved Co$_x$O$_y$ nanosheets for OER. More apparently, the current density of OER on the plasma-engraved Co$_x$O$_y$ nanosheets is 44.44 mA cm$^{-2}$ at 1.6 V, which is much higher than that of pristine Co$_x$O$_y$ nanosheets (2.57 mA cm$^{-2}$). The enhanced activity should be attributed to the unique surface properties of the plasma-engraved Co$_x$O$_y$ nanosheets with high surface area and oxygen vacancies. It is interesting to observe the specific activity (current per BET area) of the electrocatalysts for OER to understand the synergetic role of the surface area and oxygen vacancies. Thus, the current of the LSV curves in Figure 4a were normalized by the BET surface area to exclude the contribution of the increased surface area to the significantly enhanced electrocatalytic activity of plasma-engraved Co$_x$O$_y$ for OER. The specific activity could exclusively specify the role of surface oxygen vacancies. Figure 4b shows the LSV curves after normalizing...
The current in Figure 4a by the BET surface area. After the BET normalization, the specific activity of Ar-plasma engraved CoO nanosheets is 0.055 mA cm\(^{-2}\) at 1.6 V, which is 10 times higher than that of pristine CoO nanosheets (0.0054 mA cm\(^{-2}\)). indicating the advanced catalytic activity of the CoO surface after the plasma treatment contributed by the surface oxygen vacancies.

The Tafel slope is usually used to study the catalytic mechanism of electrocatalysis for OER. In Figure 3c, the Tafel slope of Ar-plasma engraved CoO is calculated to be 68 mV/dec, much lower than that of pristine CoO (234 mV/dec). The Tafel slope comparison confirmed that the OER performance of Ar-plasma engraved CoO is better than that of the pristine CoO. Furthermore, the turnover frequency (TOF) is also a very important kinetic parameter for OER. TOF is the intrinsic properties of the catalysts, which is important for evaluating the performance of the catalysts. As summarized in the Supporting Information, Table S1, the TOF of Ar-plasma engraved CoO is 0.21 s\(^{-1}\) at the over-potential of 0.3 V, while the TOF of the pristine CoO was 0.02 s\(^{-1}\). These electrochemical results indicated that the OER performance of CoO was significantly improved by the plasma- engraving strategy with surface oxygen vacancies and high surface area. We tested the OER performance of treated CoO for different plasma time (Supporting Information, Figure S8). It could be found that, initially, the activity increased with the increase of treatment time due to the increased surface area and the generation of oxygen vacancies. The best treatment time is found to be 120 s. The longer treatment results in poorer activity for OER because the over-treatment removed CoO\(_2\) active species.

The electrochemical surface area (ECSA) is calculated by the cyclic voltammograms (CV) technique. In the Supporting Information, Figure S9, the double-layer capacitance (C\(_{dl}\)) of the Ar-plasma engraved CoO nanosheets is about 94.97 mF cm\(^{-2}\), which is much higher than pristine CoO nanosheets (about 1.75 mF cm\(^{-2}\)). This result is consistent with the SEM, TEM, and BET characterizations. Moreover, the stability of electrocatalysts is very important for OER. As shown in the Figure 4e, Ar-plasma engraved CoO nanosheets was tested by taking CV curves for 2000 cycles at a scan rate of 50 mV s\(^{-1}\). There was only little decay of the activity based on the polarization curves after 2000 cycles. Furthermore, the electrochemical impedance spectroscopy (EIS) of Ar-plasma engraved CoO nanosheets and the pristine CoO nanosheets was tested at the onset potential (Figure 4d). The charge transfer resistance (R\(_{ct}\)) is closely related to the OER process. As can be seen in the Supporting Information, Figure S10, the R\(_{ct}\) of Ar-plasma engraved CoO nanosheet is 7.7 \(\Omega\), which is much smaller than that of pristine CoO nanosheet (18.8 \(\Omega\)), indicating that Ar-plasma engraving CoO nanosheets have relatively lower charge transfer resistance for OER.

As demonstrated in the Supporting Information, Figure S3, the plasma- engraving strategy could also be used to tailor NiO nanosheets. We also tested the electrochemical activity of NiO for OER. The LSV curves of pristine NiO and plasma engraved NiO for different time are shown in the Supporting Information, Figure S11a, and suggest that the OER performance of plasma engraved NiO is better than pristine NiO. The Tafel slope of Ar-plasma engraved NiO is lower than pristine NiO (Figure S11b). The EIS test of Ar-plasma engraved NiO and the pristine NiO indicates that the Ar-plasma engraved NiO shows lower charge transfer resistance (7 \(\Omega\)) than pristine NiO (11.1 \(\Omega\)). Figure S11c, Figure S12). Like CoO, the plasma-treated NiO nanosheets also show reasonable stability (Figure S11d). The electrochemical surface area of Ar-plasma engraved NiO nanosheet is also higher than the pristine NiO nanosheets (Supporting Information, Figure S13). All of these electrochemical results conclude similarly like the CoO-related studies above.

Previous studies on the facet-dependence of the CoO(OH) for electrocatalysis have demonstrated that the population of Co\(^{2+}\) and Co\(^{3+}\) on different exposed facets of CoO(OH) nanostructures is the key to influence the catalytic performance. The relative population of Co\(^{2+}\) over Co\(^{3+}\) is directly related to the oxygen vacancies. The high OER catalytic activity of CoO(OH) has been attributed to high Co\(^{3+}\) population. Liu et al. performed the in-operando identification of geometrical-site-dependent OER activity of spinel CoO(OH) and concluded that Co\(^{2+}\) was the active sites for OER and Co\(^{3+}\) could promote the formation of cobalt oxyhydroxide (CoOOH) as active sites for OER. Therefore, increasing the population of Co\(^{2+}\) (oxygen vacancies) in CoO(OH) could significantly enhance the electrocatalytic activity for OER. Herein, the as-developed plasma- engraving strategy not only increased the surface area of CoO(OH) nanosheets, but also led to the formation of oxygen vacancies.
vacancies on the surface of Co₃O₄ nanosheets. The synergistic effect of the surface oxygen vacancies and high surface area of Co₃O₄ nanosheets result in a superior electrocatalyst for OER.

In summary, we have demonstrated a simple but efficient plasma-engraving strategy to produce Co₃O₄ nanosheets with oxygen vacancies and high surface area. The electrocatalytic performance of Co₃O₄ for OER is mainly affected by its surface area and the oxygen vacancies, both of which could be simultaneously realized by the plasma-engraving method. In addition to the usual contribution of the high surface area, the specific activity results (mA per BET area) imply the significant role of the oxygen vacancies. The plasma-engraving method is green, efficient and safe. The electrocatalytic activity for OER of metal oxides could be significantly enhanced through proper surface engraving by plasma. With the plasma engraving, although less electrocatalyst resided, more active sites, and better catalytic activity were realized by obtaining the high surface area and oxygen vacancies. Therefore, the as-developed plasma-engraving strategy could produce highly competitive non-noble electrocatalysts for oxygen production from water splitting. This work provides a new strategy to design advanced electrocatalysts by increasing the surface area and generating surface oxygen vacancies simultaneously.

Acknowledgements

The authors acknowledge the support from the National Natural Science Foundation of China (51402100 and 21573066).

Keywords: Co₃O₄ · electrocatalysis · oxygen evolution · oxygen vacancies

How to cite: Angew. Chem. Int. Ed. 2016, 55, 5277–5281
Angew. Chem. 2016, 128, 5363–5367


Received: January 21, 2016
Published online: March 17, 2016