Plasma engraved Bi$_{0.1}$(Ba$_{0.5}$Sr$_{0.5}$)$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3}$–δ perovskite for highly active and durable oxygen evolution

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The development of highly active and cost-effective catalysts based on noble metal free oxygen electro-catalysis is critical to energy storage and conversion devices. Herein, we highlight a plasma-treated Bi$_{0.1}$(Ba$_{0.5}$Sr$_{0.5}$)$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3}$–δ perovskite (denoted as P-Bi$_{0.1}$BsCF) as a promising catalyst for oxygen evolution reaction (OER) in alkaline media. H$_2$/Ar plasma engraving could significantly increase electrochemically active O$_2^2$\nobreakdash−$/\text{O}^−$ concentration and tune the electronic structure of Co ions efficiently, and consequently tailor the intrinsic electrocatalytic ability for OER. Of note, P-Bi$_{0.1}$BsCF, with unique crystalline core/amorphous shell structure, exhibits an enhanced intrinsic OER activity and higher stability than the noble metal IrO$_2$ catalyst, which outperforms most of the reported perovskite catalysts. The present work provides new insights into exploring efficient catalysts for OER, and it suggests that, in addition to the extensively applied for surface treatment of various catalysts such as carbons and metal oxides, the plasma engraved perovskite materials also exhibits great potential as precious metal-free catalysts.

The pursuit of highly active and cost-effective catalysts is of prime significance for sustainable energy conversion and storage in order to develop renewable energy production. Implementing these emerging clean energy solutions, such as water splitting, direct solar and metal air batteries et al., highly relies on a variety of electrocatalytic reactions, such as oxygen evolution reaction (OER). Given that OER is in general impeded by its intrinsically sluggish kinetics due to a multistep four electron process, and consequently requires a considerable overpotential relative to its thermodynamic potential of 1.23 V vs. reversible hydrogen electrode (RHE). To address this, precious metal-based materials, e.g. RuO$_2$ and IrO$_2$, are currently employed as the efficient state-of-art OER catalysts. However, high cost, low abundance as well as poor durability during long term operation badly hinder their widespread application.

Over these years, a tremendous number of alternatives based on non-precious metals materials have been intensively explored, including oxides (hydroxides)$^{2–5}$, carbon (carbon based hybrid)$^{6,7}$, metal oxides/carbon composite catalysts$^{8–10}$, chalcogenides$^{11,12}$ and phosphates$^{13,14}$. Among these candidates, perovskite oxides have drawn much attention as competitive electrocatalysts due to their flexible states of transition metals, fascinating oxygen ion mobility and exchange kinetics, and unique tailorable properties$^{15–17}$. For example, Suntivich et al.$^{18,19}$ reported that Ba$_{0.3}$Sr$_{0.7}$Co$_{0.8}$Fe$_{0.2}$O$_3$ (BSCF) perovskite provided a higher intrinsic OER activity in alkaline solution comparable to commercial IrO$_2$ electrocatalyst, A site of Ba/Sr displays the fastest oxygen transport kinetics, while the Co-rich compositions on the B site offers faster oxygen exchange kinetic. The rational design of B-site transition metal ratio could tune the $\sigma^*$ orbital filling ($\pi^*$–orbital occupation), and thus benefited OER process$^{18}$.

Although BSCF is known to have superior intrinsic activity, large particle sizes rendered from traditional bottom-up method$^{14}$ limit their large-scale practical application due to low gravimetric mass activity. The poor stability caused by surface amorphization of BSCF particles under OER conditions is another tough issue for industrial application$^{20}$. It is known that the surface area could be increased through a nanostructure strategy or surface modification, while the stability of perovskites could be improved by intrinsic methods resort
such as chemical substitution or electronic configuration modification. Jung et al.\textsuperscript{19} introduced a nano-sized La$_x$(Ba$_{0.5}$Sr$_{0.5}$)$_{1-x}$CoO$_3$-δ with superior activity and stability, where the electronic states was managed by chemical substitution of A-site cations with lanthanum and particle growth was controlled by sintered temperature. In(Ba$_{0.5}$Sr$_{0.5}$)$_{1-x}$CoO$_{3-\delta}$ (La = Nd, Sm, Gd)\textsuperscript{21} and Fe$_{0.5}$(Ba$_{0.5}$Sr$_{0.5}$)$_{1-x}$CoO$_{3-\delta}$Fe$_2$O$_3$\textsuperscript{22} have also been developed as highly active catalysts base on A-site chemical substitution strategy.

In this work, we highlight a feasibility of Bi introduced into A site of BSCF lattice (Bi$_x$(Ba$_{0.5}$Sr$_{0.5}$)$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_3$), denoted as Bi$_x$BSCF to modify the electronic structure of perovskites. As known, bismuth oxide is usually used as an oxygen-ion conducting electrolyte in solid oxide fuel cells. Bi could also be introduced to A site of BSCF perovskite and tailor oxygen electrocatalysis ability\textsuperscript{23}. Furthermore, surface modification is another effective strategy to improve the activity and durability of electrocatalysts. It is reported that the cold plasma process is an efficient approach for surface modification and functionalization, which can generate roughed surface, surface vacancies, defects and other active functional groups\textsuperscript{24-28}. Therefore, for the first time, we propose the pollution-free and facile plasma modification on perovskite oxides to tailor the near-surface structure. The optimized 5\% H$_2$/Ar plasma-treated Bi$_{0.1}$BSCF catalyst, which denoted as P-Bi$_{0.1}$BSCF, demonstrates a higher intrinsic activity and durability towards OER, relative to the well-known BSCF perovskite as well as commercial IrO$_2$ catalyst. An electrochemically active amorphous layer created by plasma engraving is achieved, and its effect is furthermore elaborated for OER.

**Methods**

**Catalysts synthesis.** Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$ and Bi$_{0.1}$(Ba$_{0.5}$Sr$_{0.5}$)$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_3$ (denoted as BSCF and Bi$_{0.1}$BSCF, respectively) perovskite oxides were synthesized by using a EDTA-citrate sol-gel process\textsuperscript{17}. Briefly, the starting materials of Ba(NO$_3$)$_2$, Sr(NO$_3$)$_2$·4H$_2$O, Bi(NO$_3$)$_3$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and Co(NO$_3$)$_2$·6H$_2$O (Sinopharm Chemical Reagent Co., Ltd.) were mixed in deionized water in accordance with their stoichiometric amounts, employing EDTA and citric acid as chelating agents. With the introduction of aqueous ammonium hydroxide solution (NH$_4$OH, 8\%), Sinopharm Chemical Reagent Co., Ltd. were mixed in deionized water in accordance with their stoichiometric amounts, employing EDTA and citric acid as chelating agents. The pH value was tuned at ~7. Such solution was stirred and then heated at 100°C to yield a gel, then calcination at 250°C overnight to form a solid precursor. The solid precursor of BSCF was sintered in air at 1000°C, whereas Bi$_{0.1}$BSCF was calcined in air at 850°C for 4 h to obtain the powders. The commercial IrO$_2$ (99.5\%, Aladdin Industrial Corporation) catalysts was studied for comparison.

The freshly-prepared Bi$_{0.1}$BSCF catalyst was subsequently conducted via a plasma cleaner (MING HENG, PDC-MG) with a gas flow of air, Ar or 5\% H$_2$/Ar for the plasma ignition (commercial 13.56 MHz RF source). Different irradiation time (0 min, 2 min, 3 min, 5 min and 8 min) with powers of ~130 W and pressure of 90 Pa was applied during plasma process. The optimized 5\% H$_2$/Ar plasma-treated Bi$_{0.1}$BSCF for 3 min was used for detailed studies, which denoted as P-Bi$_{0.1}$BSCF.

**Materials characterization.** Phase structures of the as-prepared catalyst powders were determined by XRD on Bruker (D8 Focus, Cu K$_\alpha$ radiation). Program FullProf was employed for the diffraction refinement. SEM images were performed on a SU-8010 SEM, whereas high resolution TEM images equipped with EDS were conducted on a Tecnai G2 F20 U-TWIN TEM. XPS measurements of the catalysts were carried out on a Kratos Axis Ultra DLD instrument. The obtained XPS spectra were calibrated by referencing C 1s to 284.6 eV, and simulated using the XPSPEAK41 software. We analyzed the specific surface areas by Brunauer Emmet Teller (BET) equilibrium. Approximately 2.0 g samples were weighed and degassed at 250°C for 4 h before nitrogen physisorption at the temperature of liquid nitrogen (77 K). The ability of perovskites to adsorb OH$^-$ after exposure to water (100\% humidity) at room temperature for 2 h was estimated from the Fourier transform infrared spectra (FTIR, Nicolet iS50; Thermo Scientific America). Oxygen temperature programmed desorption (O$_2$-TPD) measurement was surveyed to analysis the oxygen desorption properties.

**Electrochemical evaluation.** The as-prepared BSCF, Bi$_{0.1}$BSCF, P-Bi$_{0.1}$BSCF and commercial IrO$_2$ (~5 μm, Sigma Aldrich 99.9\%) catalysts were, respectively, ground in mortar to disperse well. The mixture, including 40 mg perovskite catalyst, 8 mg Ketjen black (KB, EC-600JD), 5 mL ethanol and 0.25 mL 5 wt.\% Nafion solution were ultrasonicating to obtain a homogeneous ink. A 2 μL catalyst ink was then deposited onto the polished glassy carbon electrode surface with a uniform loading of ~0.2832 mg cm$^{-2}$ (~0.2266 mg cm$^{-2}$). Electrodes containing IrO$_2$ were also prepared with a similar loading of 0.2587 mg cm$^{-2}$. The OER electrochemical characteristics were conducted in N$_2$-saturated 0.1 M KOH electrolyte with a standard three electrode cell configuration (Pine Research Instrumentation). 1 M Hg/Hg$_2$Cl$_2$ electrode and platinum sheet were applied as the reference and counter electrode, respectively. The potentials in this work were iR corrected, where the value of R is the ohmic electrolyte resistance via high frequency AC impedance. Cyclic voltammetry (CV) curves for OER were recorded on the rotating disk electrode from 1.3 to 2.0 V vs. RHE at 1600 rpm, with the scan rate of 10 mV s$^{-1}$.

**Results and Discussion**

Fig. 1a,b show the Rietveld refined powder XRD pattern of pristine Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$ and Bi$_{0.1}$(Ba$_{0.5}$Sr$_{0.5}$)$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_3$ (denoted as BSCF and Bi$_{0.1}$BSCF, respectively). Upon Rietveld refinements, the fitted lattice parameters of BSCF and Bi$_{0.1}$BSCF are summarized in Table S1 (ESI). One can see that both BSCF and Bi$_{0.1}$BSCF present a cubic perovskite structure with the space group of Pm-3m. Schematic representation of A-site doping perovskite structure of Bi$_{0.1}$BSCF is described in Figure S1 (ESI). The phase structure of Bi$_{0.1}$BSCF in this study agrees well with the reported literature\textsuperscript{25}. The typical diffraction peak (110) of Bi$_{0.1}$BSCF moves to a higher angle compared to pristine BSCF, indicating that the introduction of Bi into BSCF lattice causes lattice contraction. This might be attributed to the substitution of the larger Sr$^{2+}$ (0.158 nm) and Ba$^{2+}$ (0.175 nm) ions by smaller Bi$^{3+}$ (0.124 nm).
Additionally, upon XRD analysis (Fig. 1c), no obvious structural change of P-Bi0.1BSCF is observed after plasma treatment for 3 min using 5% H2/Ar as the generating gas.

Shown in Fig. 2 is the SEM morphology of the as-prepared BSCF, Bi0.1BSCF, and P-Bi0.1BSCF catalysts. It is clearly seen that the particle size of Bi0.1BSCF is 0.5~1 um (Fig. 2c,d) and is smaller than that of initial BSCF (Fig. 2a,b), which is probably due to its much lower sintering temperature. Accordingly, Bi0.1BSCF has a larger surface area of 3.0771 m² g⁻¹, which is 4.3 times larger than that of BSCF (0.7132 m² g⁻¹) as estimated via BET method (Fig. S2, ESI). Although the SEM morphology of P-Bi0.1BSCF does not change obviously after 5% H2/Ar plasma engraving (Fig. 2e,f), the BET surface area of P-Bi0.1BSCF increase by 14% compared to the freshly prepared Bi0.1BSCF. This demonstrates that the plasma treatment could engrave the surface of Bi0.1BSCF perovskite and thereby increase the specific surface area.

To further investigate the crystalline structural change of BSCF after Bi-doping and plasma treatment, HR-TEM are performed on BSCF, Bi0.1BSCF and P-Bi0.1BSCF catalysts, as shown in Fig. 3. The cubic perovskite structure of BSCF and Bi0.1BSCF is also confirmed by Fourier transformed pattern. The lattice diffraction fringes in Fig. 3b are 0.397 and 0.176 nm, which are well indexed to the (100)BSCF and (021)BSCF interplanar spacing, respectively. In the case of Bi0.1BSCF, the lattice diffraction fringes in Fig. 3d is 0.395 nm, which agrees well with
the (100) interplanar spacing. One can see that the surfaces of BSCF and Bi0.1BSCF particles are highly crystalline with little amorphous region. After exposure in 5% H2/Ar-plasma for 3 min, the perovskite structure of P-Bi0.1BSCF is still observed in Fig. 3f (d (110) spacing of 0.281 nm). Together with XRD characterization of plasma-engraved Bi0.1BSCF, the results reveal that no crystalline changes after plasma treatment. In addition, STEM and the corresponding EDS mapping analysis suggests that the elements of P-Bi0.1BSCF are uniformly distributed without surface segregation phenomenon after plasma engraving process. Moreover, it is apparent that P-Bi0.1BSCF displays a unique core-shell structure, a disordered amorphous shell with a thickness of approximately 8–10 nm is generated after plasma modification. Similar phenomenon is reported by Li and his co-workers that the TiO2 nanosheets shows a crystalline TiO2 core/amorphous TiO2−δ shell structure via NH3-plasma surface modification with oxygen deficient on shell region29.

Figure 4a presents the CV curves of pristine BSCF, Bi0.1BSCF and P-Bi0.1BSCF catalysts under the OER potential window. Similar measurements are performed on the IrO2 and KB for comparison. The catalytic activity contribution of KB is subtracted according to the composition of electrode. The performance of commercial IrO2 catalyst is comparable to that reported elsewhere30,31. The CV of Bi0.1BSCF shows a comparably lower onset potential (1.49V) and a higher current density than the IrO2 and BSCF catalyst, indicating a better OER catalytic activity of Bi0.1BSCF. After plasma engraving, P-Bi0.1BSCF catalyst manifests an apparent enhancement in OER activity with a significantly improved current density. The optimized processing parameters for plasma engraving is 5% H2/Ar working atmosphere only for 3 min (Fig. S3, ESI). Moreover, P-Bi0.1BSCF catalyst exhibits a quite small overpotential (η) at a current density of 10 mA cm−2 of 370 mV, which is superior to that of Bi0.1BSCF (411 mV), BSCF (525 mV), and IrO2 (464 mV). Notably, the overpotential of P-Bi0.1BSCF favorably outperforms the reported perovskite-based OER catalysts32–39, e.g. BaCo0.7Fe2−Sn0.1O3−δ (410 mV)36, SrNb0.1Co0.7Fe2−O3−δ (SNCF) (500 mV)39, summarized in Table S2 (ESI).
Corresponding Tafel plots of the investigated samples are compared in Fig. 4b to evaluate the kinetics performance of OER. The Tafel slopes are 68, 74, 87, and 78 mV dec\(^{-1}\) for P-Bi\(_{0.1}\)BSCF, Bi\(_{0.1}\)BSCF, BSCF, and IrO\(_2\), respectively. Furthermore, the mass activity (MA) and specific activity (SA) are illustrated to evaluate the intrinsic activity, as shown in Fig. 4c. For instance, at an overpotential of 0.4 V, P-Bi\(_{0.1}\)BSCF displays 8.9 times higher MA and 2.7 times higher SA relative to BSCF, respectively. The results confirm the positive contribution from the Bi-dopant and plasma engraving to the intrinsic activity. In addition,

The durability of electrocatalysts is another vital parameter for OER. In current study, we performed continuous CV curves for P-Bi\(_{0.1}\)BSCF, Bi\(_{0.1}\)BSCF, BSCF, and commercial IrO\(_2\) catalysts for 600 cycles, as shown in

**Figure 3.** Bright-field TEM, High-resolution TEM image and corresponding fast-Fourier transformed pattern of (a,b) BSCF; (c,d) Bi\(_{0.1}\)BSCF; (e,f) P-Bi\(_{0.1}\)BSCF; (g) EDS mapping of P-Bi\(_{0.1}\)BSCF.
Fig. 4d. BSCF and IrO₂ show a 25% and 27% reduction of its 2nd activity over 600 cycles, respectively, and the poor stability of BSCF results from the leaching of A site cations to the alkaline medium 20. In contrast to BSCF, only 10% and 12% reduction is observed in the Bi₀.¹BSCF and P-Bi₀.¹BSCF catalysts under the same condition, respectively. The TEM image of post-OER P-Bi₀.¹BSCF in Fig. S₄ shows that the structure of P-Bi₀.¹BSCF is maintained and the thickness of amorphous shell did not change much after continuous CV tests compared to as-synthesized P-Bi₀.¹BSCF. In addition, the XPS spectra before and after long-term OER testing shows that the oxidation state of Bi³⁺ does not change 40,4¹ (Fig. S₅), which also reveals the durability of P-Bi₀.¹BSCF catalyst.

To understand the source responsible for the excellent OER activity of P-Bi₀.¹BSCF, the surface state of BSCF, Bi₀.¹BSCF and P-Bi₀.¹BSCF catalysts is intensively studied by XPS analysis. The O₁s XPS spectra for BSCF, Bi₀.¹BSCF and P-Bi₀.¹BSCF is deconvoluted to four characteristic peaks (Fig. 5a). The first one at a lower binding energy (529.6 eV) represents the lattice oxygen (O²⁻), followed by the surface oxidative oxygen O₂⁻/O⁻ (530.5 eV), hydroxyl groups OH⁻ or adsorbed O₂ (531.5 eV), and adsorbed molecular H₂O of the oxide surface (532.9 eV) 4². The relative content of the lattice and surface oxygen species derived is listed in Table S₃ (ESI). The content of surface oxidative oxygen O₂⁻/O⁻ increases from 35.68% with BSCF to 42.17% with Bi₀.¹BSCF. Moreover, the O₂⁻/O⁻ concentration is further increased to ~49.23% by plasma engraving, indicating the existence of abundant active oxygen species on the amorphous region of P-Bi₀.¹BSCF oxide surface. Importantly, the electrochemically active O₂⁻/O⁻ are proved to be beneficial for catalyzing OER 4³,4⁴. Also, the highly oxidative oxygen species on the surface are reported to be closely relevant to the oxygen vacancies 4⁵, and surface oxygen vacancies play a key role for perovskite oxides in catalyzing OER 4⁶. It reveals that the plasma engraving could create more electrochemical active sites on the amorphous shell. The similar phenomenon of surface amorphization and simultaneous increased activity for efficiently electro-catalyzing OER is also found in other catalysts 4⁷–5₀.

The core-level spectra of Co 2p & Ba 3d for these three catalysts are presented in Fig. 5b. The overlapping between Co 2p and Ba 3d spectra makes it difficult to identify the surface Co valence by peak fitting, while the Co oxidation state could be inferred from the shift of peak position. Compared to BSCF, the positions of Co peaks for the Bi₀.¹BSCF shift to lower binding energies, suggesting that the surface valence of Co slightly decrease owing to high valence Bi-substitution. After 5% H₂/Ar plasma engraved, the two main peaks of P-Bi₀.¹BSCF shift to higher binding energies obviously, which indicates the presence of surface cobalt in a higher oxidation state. It is reported that the high valence of Co could also play a positive role in the improvement of OER activity 5¹. No distinctive variation was observed in the Fe state of catalyst surface (Fig. 5c). On the basis of the XPS results, the
increased $\cdot O_2^2-/O^-\cdot$ concentration together with electronic structure tuning of Co induced by plasma engraving might be responsible to the enhancement in OER performance.

The redox property of BSCF, Bi$_{0.1}$BSCF, and P-Bi$_{0.1}$BSCF is studied by O$_2$-TPD, as shown in Fig. 6a. The desorption peak of the Bi$_{0.1}$BSCF catalyst, associated with the reduction of Co iron, occur at approximately 251 °C, which is lower than that of BSCF (275 °C). It’s worth noting that, after 5% H$_2$/Ar plasma engraved, the desorption temperature of P-Bi$_{0.1}$BSCF catalyst reduce remarkably to nearly 198 °C, this indicates an excellent oxygen desorption capability and reflects a higher oxygen surface exchange ability for P-Bi$_{0.1}$BSCF perovskite. The result is consistent with the EIS analysis that P-Bi$_{0.1}$BSCF has better ionic and charge transfer abilities. Besides O$_2$ desorption capability, the P-Bi$_{0.1}$BSCF catalyst also shows good OH$^-$ adsorption. As observed by FTIR spectroscopy (Fig. 6b), a broad IR band centers at approximately 3466 cm$^{-1}$ appeared, which corresponds to H-bonded OH$^-$ stretching vibration. Obviously, Bi$_{0.1}$BSCF exhibited a stronger OH$^-$ absorption ability than initial BSCF, and the
OH\(^{-}\) absorption ability is further improved via plasma treatment. According to the adsorbate evolution mechanism\(^5\), OH\(^{-}\) absorption on the active sites of perovskites is the prerequisite for OER, and thereby the large OH\(^{-}\) absorption can continually offer raw materials for the following OER process\(^3\). Due to the complex interplay between oxygen deficiency and surface-active redox centre of perovskite oxides, detailed mechanistic insights into the OER electrocatalysis of P-Bi\(_{0.1}\)BSCF materials in alkaline media are currently limited. Nevertheless, with the superior activity, stability and cost-effectiveness, Bi\(_{0.1}\)BSCF promises a novel precious-metal-free catalyst for the alkaline OER, and plasma engraving proved to be a facile and effective surface modification method to further improve the activity.

**Conclusion**

In summary, a plasma engraving strategy is, for the first time, proposed for the surface modification of perovskite materials towards electrocatalyzing OER. After 5\% H\(_2\)/Ar plasma engraving only for 3 min, an amorphous layer with abundant electrochemical active oxygen species is generated on Bi\(_{0.1}\)BSCF perovskite surface. Moreover, the increased oxygen surface exchange ability and OH\(^{-}\) absorption ability of P-Bi\(_{0.1}\)BSCF are achieved. Owing to the unique properties via Bi-doping as well as plasma engraving, P-Bi\(_{0.1}\)BSCF exhibits a fast kinetics process with a small Tafel slope of 68 mV dec\(^{-1}\) and high stability for OER, that is superior to most of the state-of-the-art perovskite-based electrocatalysts. The foregoing results open a new avenue for engineering perovskite oxides via plasma method for highly efficient OER, which is promising for a variety of electrochemical energy storage applications.

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**Author Contributions**
B.B. He conceived and designed the research. J. Sun and Z.H. Zhang carried out the electrochemical tests. Y.S. Gong performed the BET measurements. B.B. He wrote the manuscript with the help of H.W. Wang, L. Zhao and R. Wang. All authors reviewed the manuscript.

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