

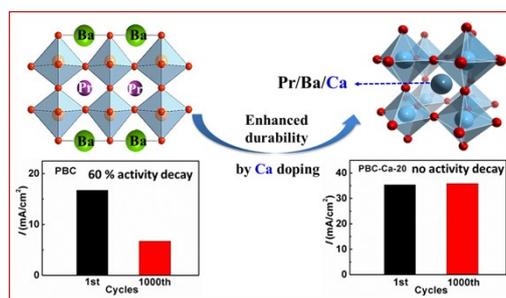
## Electronic Supplementary Information

### Enhanced durability and activity of perovskite electrocatalysts $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ by Ca doping for oxygen evolution reaction at room temperature

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Enhanced durability and activity was achieved by introducing Ca into perovskite electrocatalyst for oxygen evolution reaction.

## Experimental details

**Materials.** Praseodymium (III) nitrate hexahydrate, cobalt (II) nitrate hexahydrate, barium nitrate, calcium (II) nitrate tetrahydrate, citric acid monohydrate and edetic acid (EDTA) were obtained from Aladdin Chemical Co. Nafion solution (5%) was purchased from Sigma-Aldrich. Commercial RuO<sub>2</sub> catalyst was bought from Sigma-Aldrich. All chemicals were used as received without any further purification. Water used for preparation of aqueous solution was purified using a Millipore-Q water purification system.

**Synthesis of catalyst Pr<sub>0.5</sub>Ba<sub>0.5-x</sub>Ca<sub>x</sub>CoO<sub>3-δ</sub>.** Pr<sub>0.5</sub>Ba<sub>0.5-x</sub>Ca<sub>x</sub>CoO<sub>3-δ</sub> (x = 0.05, 0.13, and 0.20) powders were synthesized by a standard combined EDTA-citrate complexing sol-gel process, as detailed elsewhere.<sup>1</sup> In a typical preparation process, Pr(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O, Ba(NO<sub>3</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O were used as the raw materials for the cation sources. Stoichiometric amounts of these metal nitrates were added to deionized water (>18.2 MΩ cm) at the concentration of 0.20 M, followed by the addition of citric acid, EDTA and ammonium hydroxide with vigorous stirring, and the pH was maintained at 8 ~ 9. The beaker containing the mixture was stirred for about 24 h at room temperature. After the solvent evaporation at 60 °C, the mixture was further heated to remove the organics. The powder was then calcined at 1000 °C in air for 10 h. Finally, the product was milled into fine powder for further characterizations. The double Pr<sub>0.5</sub>Ba<sub>0.5</sub>CoO<sub>3-δ</sub> (PBC) perovskite was also prepared by the above method without the addition of Ca(NO<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O.

The as-prepared Pr<sub>0.5</sub>Ba<sub>0.5-x</sub>Ca<sub>x</sub>CoO<sub>3-δ</sub> perovskite were denoted as PBC-Ca-x, in which P, B, and C indicating Pr, Ba, and Co, respectively, followed by the molar percentage of calcium (x\*100). For example, PBC-Ca-20 refers to Pr<sub>0.5</sub>Ba<sub>0.3</sub>Ca<sub>0.2</sub>CoO<sub>3-δ</sub>.

**Catalyst characterization.** X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer with Cu-Kα radiation (λ=1.54178 Å) at 40 kV and 40 mA for phase identification. The experimental diffraction patterns were

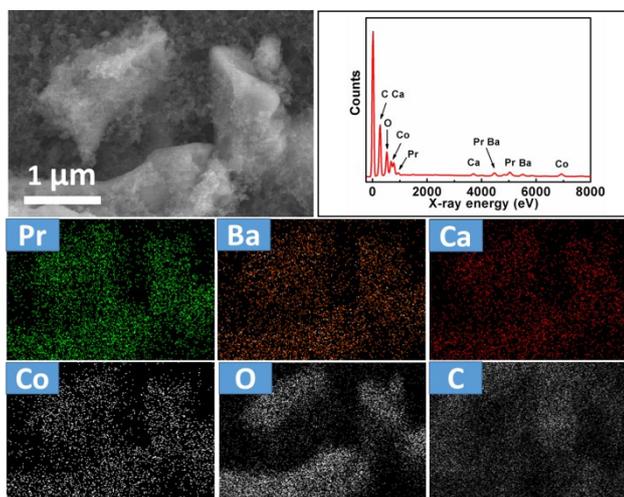
collected at room temperature with step size of  $0.02^\circ$  in  $2\theta$  over the scanning angular range of  $20-80^\circ$ . The surface morphology of the perovskite film on glassy carbon electrode was characterized by using a Hitachi S-4800 field emission scanning electron microscope with energy dispersive spectroscopy analysis (EDS).

**Electrochemical measurement.** All electrochemical measurements were performed with a CHI 842d electrochemical workstation (CHI Instrument, Shanghai Chenhua, China) using a three electrode cell arrangement. The working electrode was a glassy carbon rotating disk electrode (RDE) with an area of  $0.126\text{ cm}^2$ . A Pt foil and Ag/AgCl (versus saturated KCl) were used as the counter and reference electrodes, respectively. The reference electrode was calibrated in the high purity hydrogen-saturated  $0.1\text{ M KOH}$ . The potentials reported in our work are calibrated with respect to the reversible hydrogen electrode (RHE).

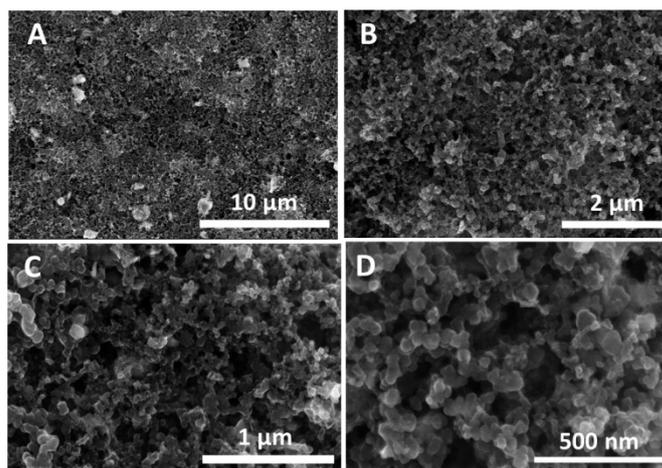
The catalytic electrodes were prepared by drop-casting a catalyst ink suspension on the glassy carbon electrode (GCE). The glassy carbon rotating disk electrode was polished with alumina powder and then rinsed with deionized water.  $5\text{ mg}$  catalysts and  $1\text{ mg}$  carbon black were redispersed in a  $1\text{ mL}$  mixture containing water, isopropanol, and Nafion ( $v/v/v = 4: 1: 0.05$ ), followed by sonication for at least  $30\text{ min}$  to obtain a homogeneous solution. Before CV or rotating disk electrode (RDE) experiments, the as-obtained suspension was applied to the GCE with a catalyst loading of  $0.39\text{ mg cm}^{-2}$ .

The electrolyte with a concentration of  $0.1\text{ M}$  was prepared using deionized water and KOH pellets. Oxygen evolution reaction (OER) test were performed in  $0.1\text{ M KOH}$  electrolyte solution by purging with  $\text{O}_2$  for at least  $30\text{ min}$  before each measurement and maintained under  $\text{O}_2$  atmosphere throughout. Linear sweeping voltammetry (LSV) was carried out in the electrolyte at a scan rate of  $10\text{ mVs}^{-1}$  and a rotating speed of  $1600\text{ rpm}$ . All potential values in this study are iR-corrected to compensate for the effect of solution resistance. The stability tests were conducted in  $\text{O}_2$ -saturated  $0.1\text{ M KOH}$  by potential cycling with the upper potential of  $1.74\text{ V}$  vs. RHE and a scan rate of  $100\text{ mVs}^{-1}$  for  $1000$  cycles. LSVs were performed at the

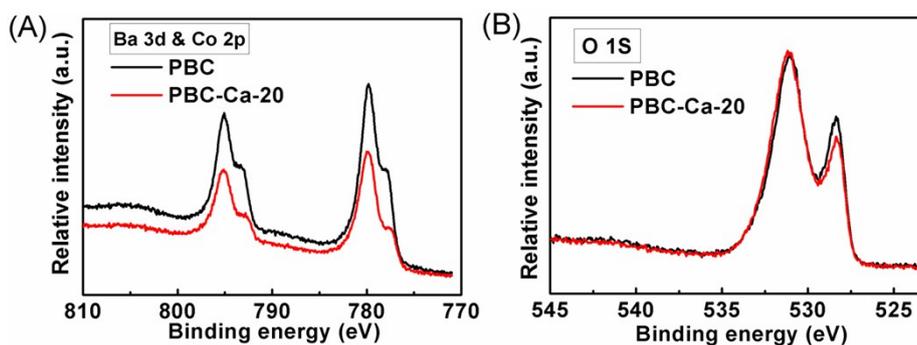
resulting electrodes after potential cycling.



**Figure S1.** EDS profile and elemental mapping of the composite of PBC-Ca-20 perovskite and carbon black. All scale bars are 1 μm.



**Figure S2.** SEM images of the composite of PBC-Ca-20 perovskite and carbon black. Scale bars: 10 μm, 2 μm, 1 μm and 500 nm in (A), (B), (C) and (D) respectively.

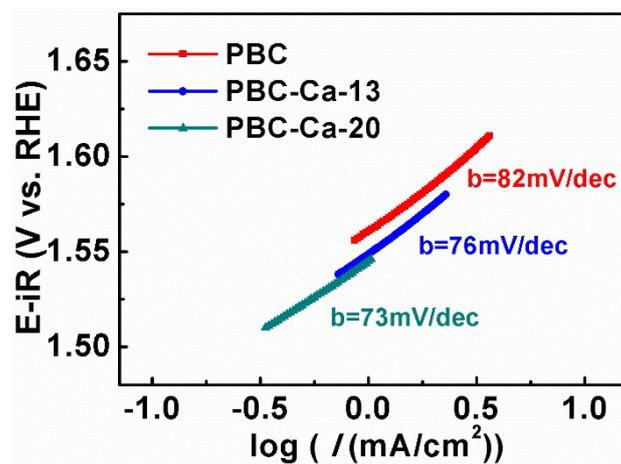


**Figure S3.** XPS spectra for Ba 3d & Co 2p (A) and O 1s (B) in perovskites PBC and PBC-Ca-20, respectively.

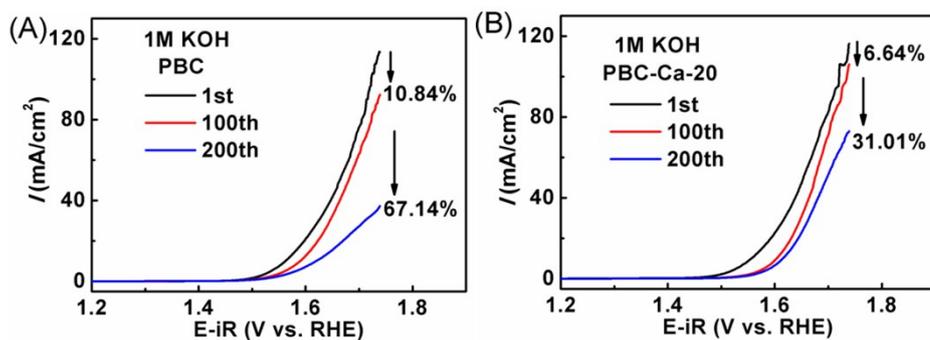
*There is no significant difference of peaks in the range of 770-810 eV between PBC and PBC-Ca-20. Moreover, Co-2p and Ba-3d peaks have strong overlap in this range, it's difficult to distinguish the valence change of Co after doping PBC with Ca.*

*For both samples the O1s spectra presented two peaks centered at 528.3 and 531.1 eV, respectively. The peak at 528.3 eV is associated with the lattice oxygen (metal-oxygen bonds), and the broad peak centered at 531.1 eV is usually related to the adsorbed oxygen species in the form of hydroxyl groups (-OH),  $O_2^{2-}/O^-$ , or molecular water.<sup>2-4</sup>*

*It is necessary to point out that the peak area at 528.3 eV in O1s spectrum of PBC-Ca-20 is smaller than that of PBC. Thus, the **RELATIVE** peak area of PBC-Ca-20 at 531.1 eV slightly increased compared to that of PBC although the real peak area at 531.1 eV for both samples looks almost the same. This indicates the addition of Ca enhanced the ability of catalyst surface to be hydroxylated, and thus enhancing the activity.*

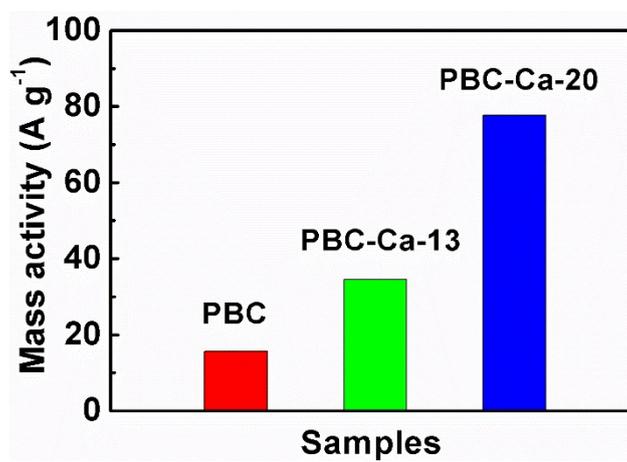


**Figure S4.** The Tafel plots for the PBC, PBC-Ca-13 and PBC-Ca-20 catalysts, which is derived from the corresponding polarization curves in Figure 2.



**Figure S5.** LSV curves (a scanning rate of  $10 \text{ mV s}^{-1}$ ) of (A) PBC and (B) PBC-Ca-20 catalysts before and after 100 and 200 potential cycles of accelerated stability testing in  $\text{O}_2$ -saturated 1 M KOH solution with the upper potential of 1.74 V (vs. RHE) and the scan rate of  $100 \text{ mV s}^{-1}$ .

*After testing 200 potential cycles in 1 M KOH, the OER current of PBC and PBC-Ca-20 at the potential of 1.74 V (vs. RHE) decreased by ca. 67.14% and 31.01%, respectively. This indicates that Ca-doped PBC-Ca-20 still shows better stability than PBC in 1 M KOH solution although its stability in the practical conditions needs to be further improved.*



**Figure S6.** The mass activity of the PBC, PBC-Ca-13 and PBC-Ca-20 based on the respective residual current values after 1000 continuous OER electrolysis cycles.

**Table S1** Comparison of the electrocatalytic OER activity of PBC-Ca-20 with other perovskite OER catalysts recently reported in alkaline solutions.

Catalyst	Current density j (mA cm <sup>-2</sup> )	$\eta$ (vs.RHE) at corresponding j	Tafel slope (mV dec <sup>-1</sup> )	Electrolyte	References
Ca <sub>2</sub> Mn <sub>2</sub> O <sub>5</sub>	4.0	550	149	0.1 M KOH	<i>J. Am. Chem. Soc.</i> , <b>2014</b> , 136, 14646.
Pr <sub>0.5</sub> Ba <sub>0.5</sub> CoO <sub>3-δ</sub>	10	370	-	0.1 M KOH	<i>Nat. Commun.</i> , <b>2013</b> , 4, 2439.
Ba <sub>0.5</sub> Sr <sub>0.5</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3-δ</sub>	10	510	94	0.1 M KOH	<i>J. Phys. Chem. Lett.</i> , <b>2012</b> , 3, 3264
SrCo <sub>0.9</sub> Ti <sub>0.1</sub> O <sub>3-δ</sub>	10	510	88	0.1 M KOH	<i>ACS Appl. Mater. Interfaces</i> , <b>2015</b> , 7, 17663.
CaMnO <sub>3-δ</sub>	4.0	620	-	0.1 M KOH	<i>Inorg. Chem.</i> , <b>2014</b> , 53, 9106.
La <sub>0.8</sub> Sr <sub>0.2</sub> MnO <sub>3-δ</sub>	3.7	610	-	0.1 M KOH	<i>J. Power Sources</i> , <b>2013</b> , 214, 225.
La <sub>0.3</sub> (Ba <sub>0.5</sub> Sr <sub>0.5</sub> ) <sub>0.7</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3-δ</sub>	10	400	-	0.1 M KOH	<i>Angew. Chem. Int. Ed.</i> , <b>2015</b> , 53, 4582
BaMnO <sub>3</sub> @5%C	10	610	-	0.1 M KOH	<i>Electrochim. Acta</i> , <b>2015</b> , 174, 551.
<b>Pr<sub>0.5</sub>Ba<sub>0.3</sub>Ca<sub>0.2</sub>CoO<sub>3-δ</sub></b>	<b>10</b>	<b>440</b>	<b>73</b>	<b>0.1 M KOH</b>	<b>This work</b>

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