

**Two-step facile synthesis of $\text{Co}_3\text{O}_4@\text{C}$ reinforcing PbO_2 coated
electrode to promote efficiently oxygen evolution reaction for zinc
electrowinning**

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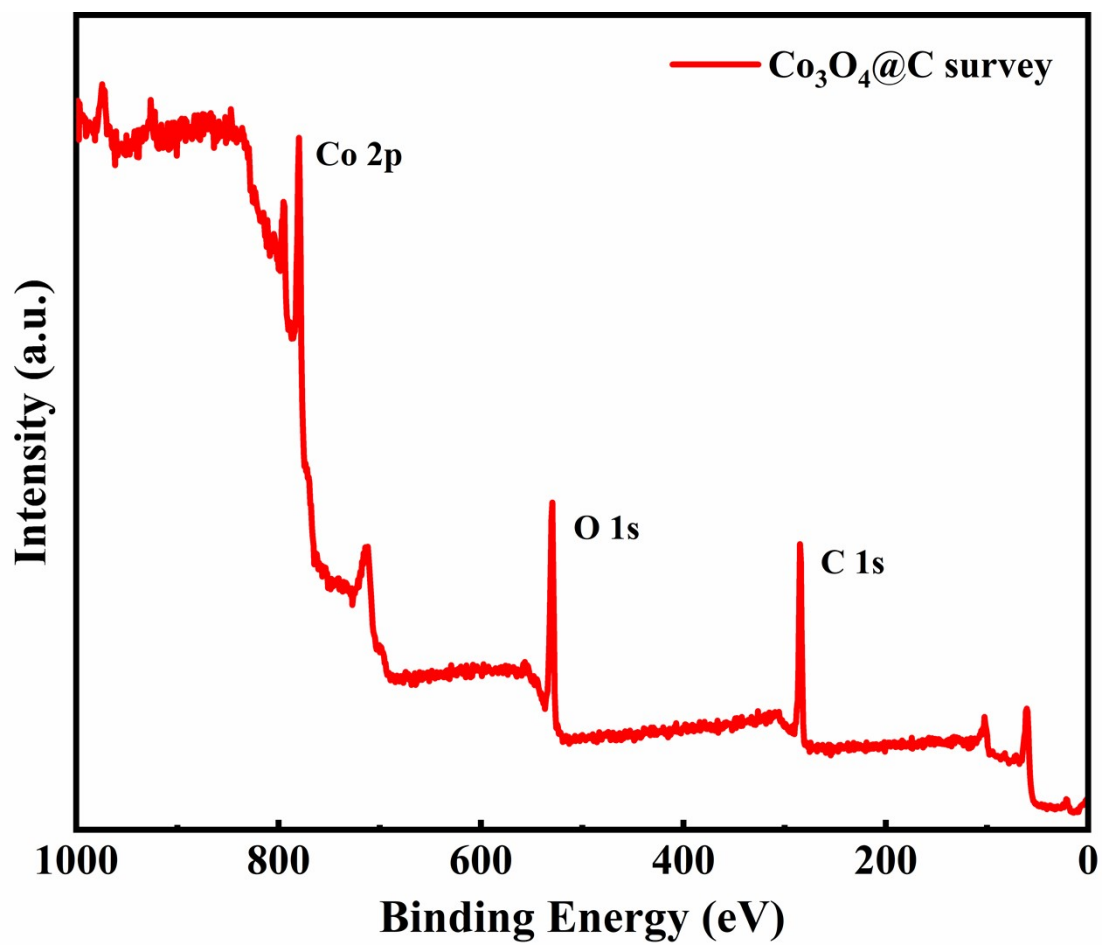


Fig. S1 The full XPS spectrum.

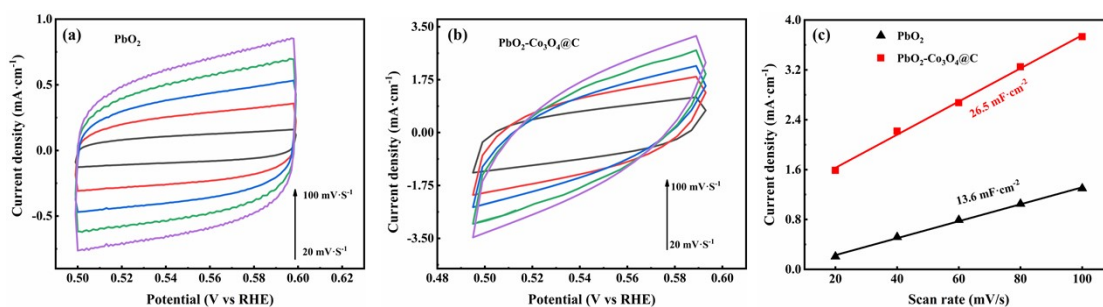


Fig. S2 CV curves of (a) PbO_2 and (b) $\text{PbO}_2\text{-Co}_3\text{O}_4\text{@C}$ deposit at different scan rates; and (c) Double-layer capacitance measurements for determining electrochemically active surface area of PbO_2 and $\text{PbO}_2\text{-Co}_3\text{O}_4\text{@C}$ deposit.

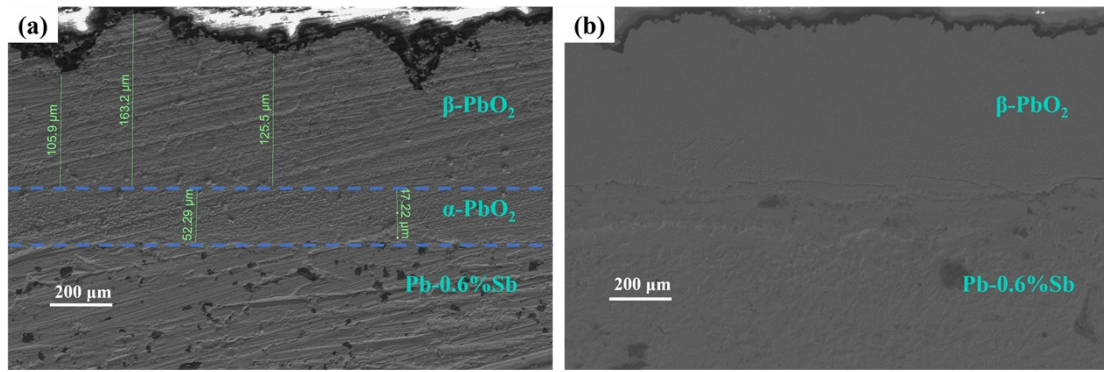


Fig. S3 Cross-section SEM images of (a) $\text{Pb-0.6\%Sb}/\alpha\text{-PbO}_2/\beta\text{-PbO}_2$ and (b) $\text{Pb-0.6\%Sb}/\beta\text{-PbO}_2$.

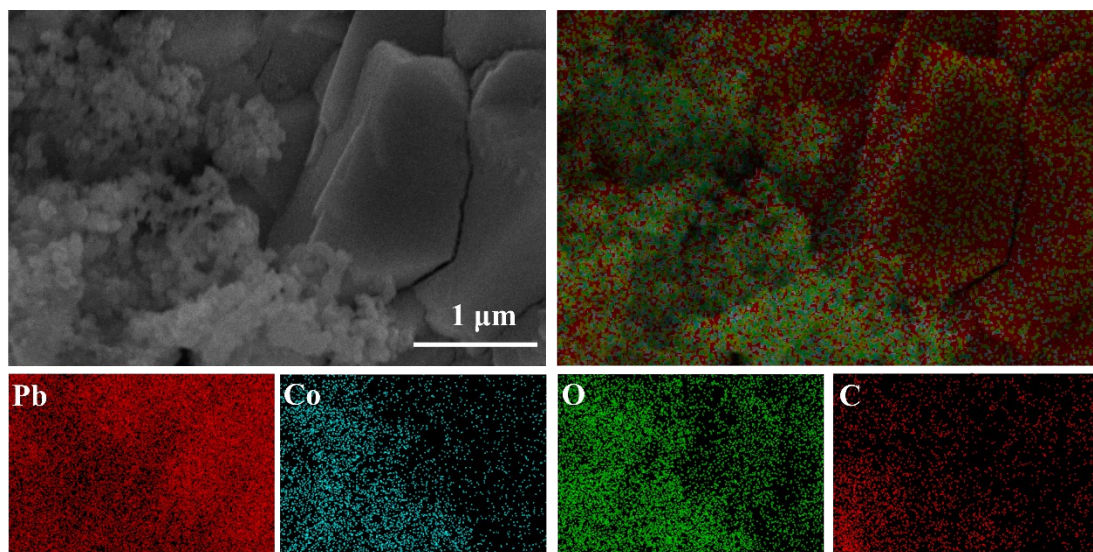


Fig. S4 The SEM image and element mapping of $\text{PbO}_2\text{-Co}_3\text{O}_4@\text{C}$ deposit.

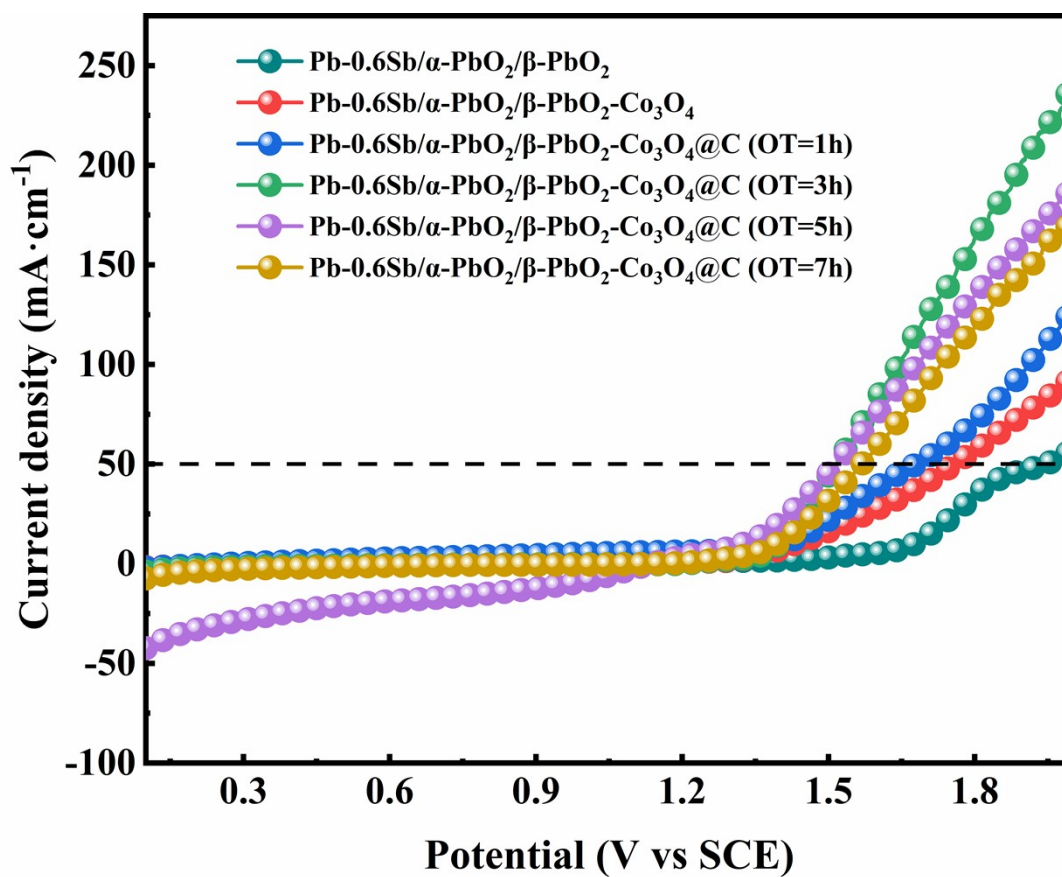


Fig. S5 The LSV curves of PbO₂ coated electrodes without and with reinforcement of different Co₃O₄@C composite.

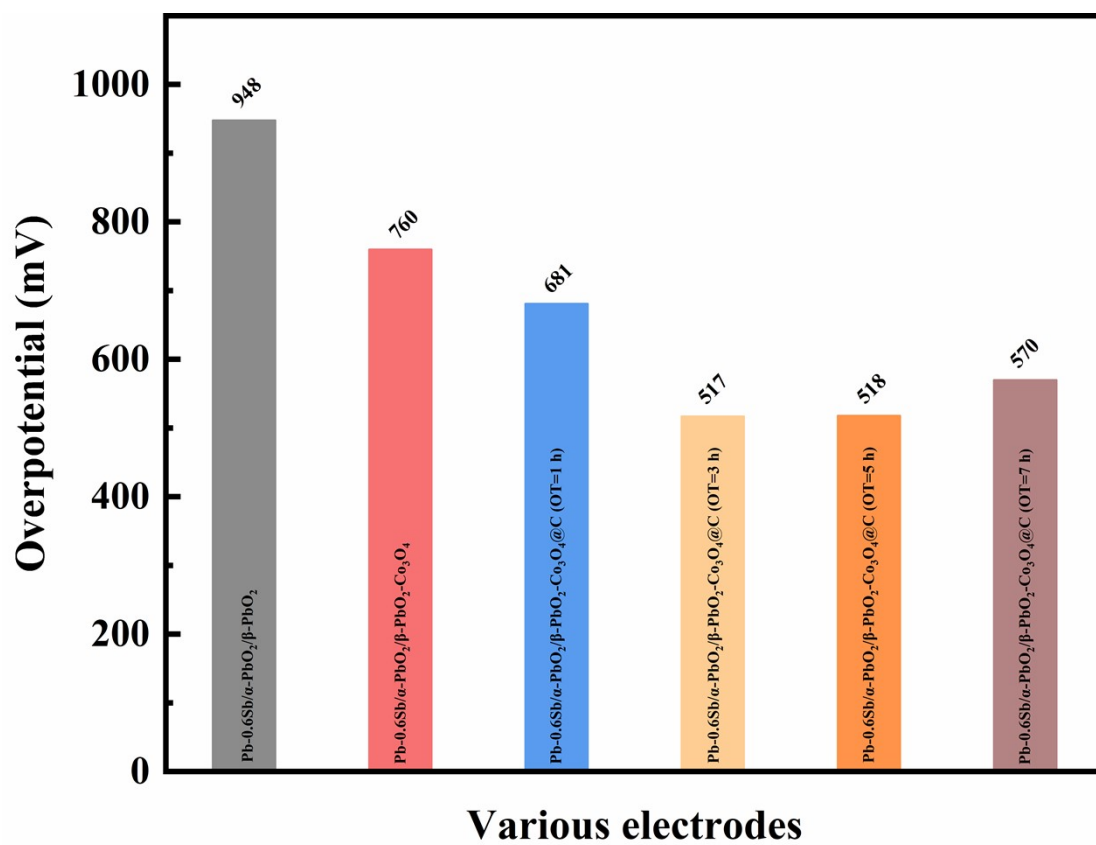


Fig. S6 The OER overpotential of different electrodes.

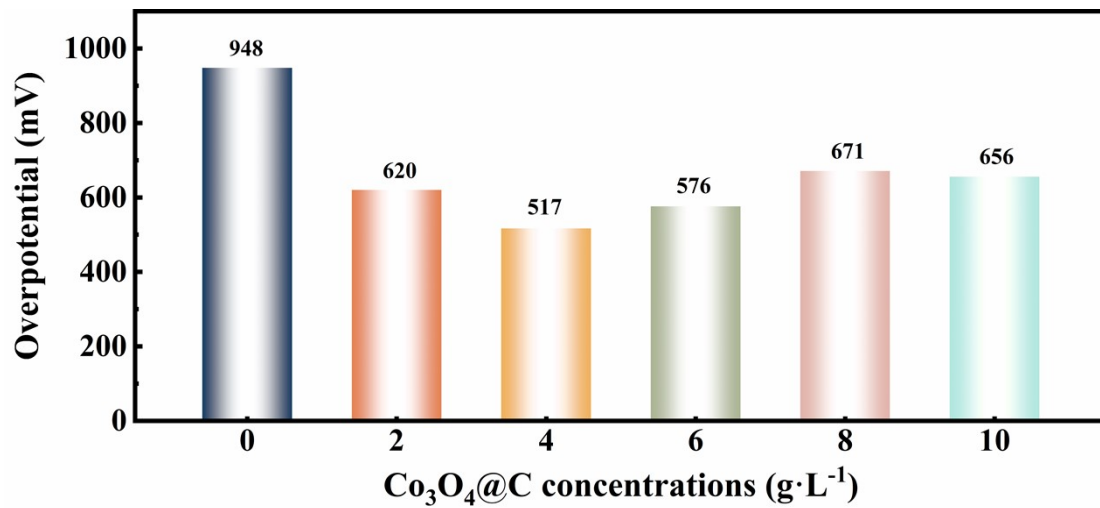


Fig. S7 The relationship between $\text{Co}_3\text{O}_4@\text{C}$ concentration and overpotential at 500 $\text{A}\cdot\text{m}^{-2}$.

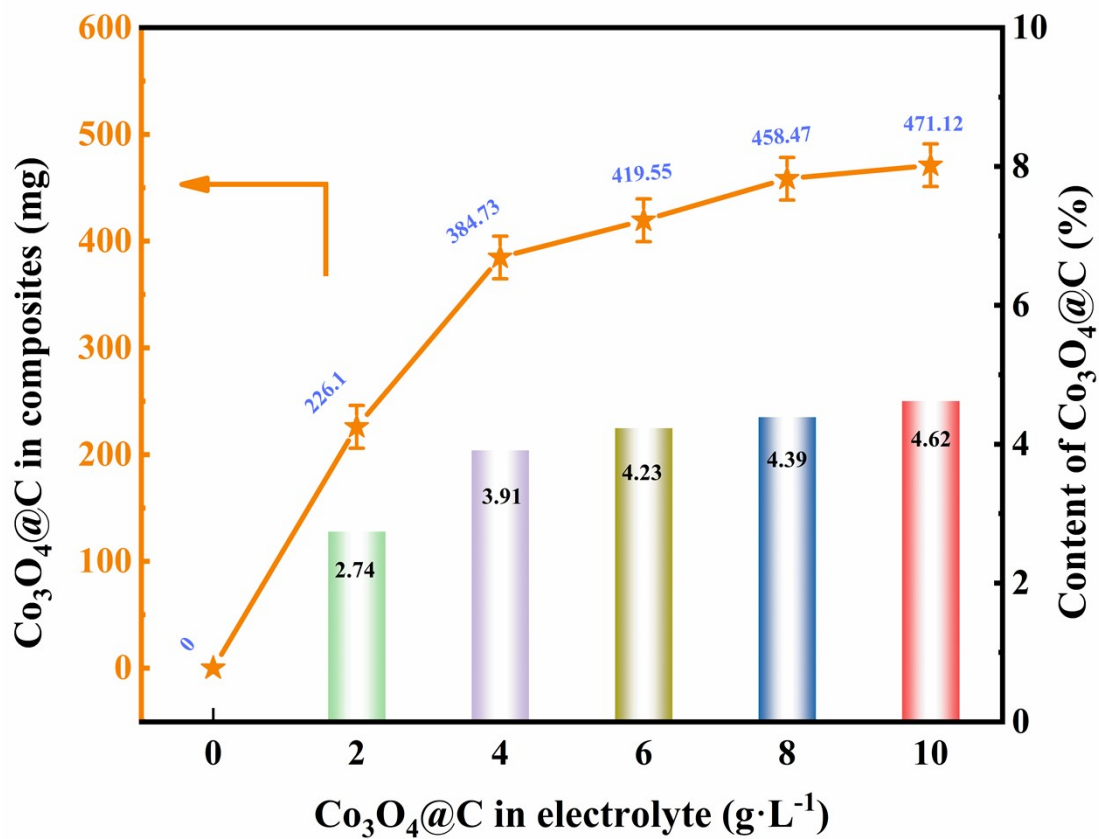


Fig. S8 The graph between Co₃O₄@C in electrolyte and in coated electrode.

Table. S1 Parameters involved in the Tafel fitting of the prepared coated electrodes.

| Concentration (g L ⁻¹) | a | b | R ² |
|------------------------------------|-------|-------|----------------|
| 0 | 1.197 | 0.487 | 0.997 |
| 2 | 0.806 | 0.183 | 0.996 |
| 4 | 0.714 | 0.156 | 0.998 |
| 6 | 0.789 | 0.167 | 0.996 |
| 8 | 0.928 | 0.209 | 0.997 |
| 10 | 0.923 | 0.196 | 0.997 |

Table. S2 Related circuit parameters for PbO₂ electrodes with various Co₃O₄@C concentrations according to the EIS shown in Fig. 6(d).

| concentrations | R_s | R_f | n_1 | CPE1 | R_{ct} | n_2 | CPE2 |
|----------------|----------|----------|-------|--------------------------|----------|-------|--------------------------|
| | Ω | Ω | | Yo [S-sec ⁿ] | Ω | | Yo [S-sec ⁿ] |
| 0 | 1.03 | 0.65 | 0.896 | 0.016 | 19.45 | 0.887 | 2.229×10 ⁻⁵ |
| 2 | 0.87 | 0.70 | 0.875 | 0.021 | 3.17 | 0.889 | 6.366×10 ⁻⁵ |
| 4 | 0.84 | 0.12 | 0.871 | 0.025 | 2.18 | 0.892 | 6.203×10 ⁻⁵ |
| 6 | 0.85 | 0.68 | 0.850 | 0.022 | 2.82 | 0.872 | 7.847×10 ⁻⁵ |
| 8 | 0.92 | 0.63 | 0.876 | 0.019 | 9.27 | 0.879 | 5.786×10 ⁻⁵ |
| 10 | 0.90 | 0.71 | 0.862 | 0.023 | 4.19 | 0.894 | 6.213×10 ⁻⁵ |

Table. S3 Comparison of the overpotential of various electrodes at $500 \text{ A}\cdot\text{m}^{-2}$

| Electrodes | Concentration of H_2SO_4 | η (mV) | Reference |
|-----------------------------------------------------------------------------------------------------|---------------------------------------------|-------------|-----------|
| Bi-PbO ₂ | 0.5M | 1046 | [1] |
| Pb-0.76%Ag | 1.53M | 1038 | - |
| Al/Pb-PANI-WC | 1.53M | 941 | [2] |
| Pure Pb | 1.8M | 936 | [3] |
| CF/PbO ₂ | 1.53M | 931 | [4] |
| PANI/CeO ₂ /WC | 1.53M | 856 | [5] |
| PbO ₂ -CeO ₂ | 1.63M | 826 | [6] |
| Ti/Cu-PbO ₂ | 0.5M | 751 | [7] |
| Pb-0.3Ag/PbO ₂ -Co ₃ O ₄ | 1.53M | 747 | [8] |
| Ti/TiO ₂ -NTs/PbO ₂ | 1.53M | 630 | [9] |
| Pb-0.6Sb/ α -PbO ₂ / β -PbO ₂ -Co ₃ O ₄ @C | 1.53M | 517 | This work |

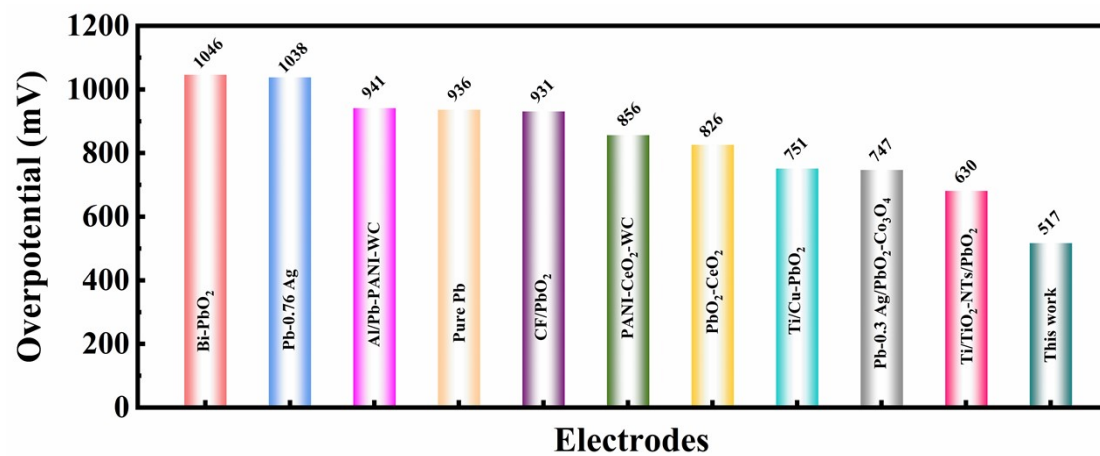


Fig. S9 The comparison chart of the overpotential of various works at 500 A m⁻².

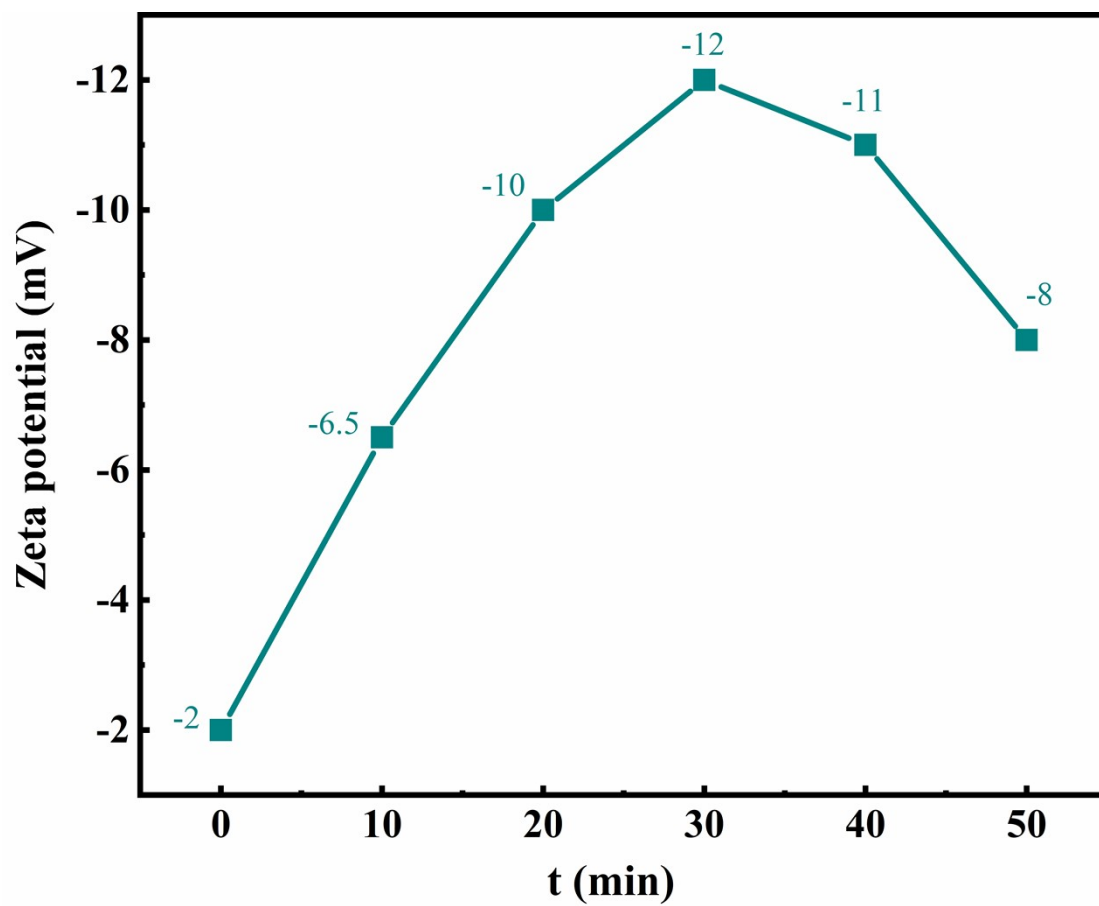


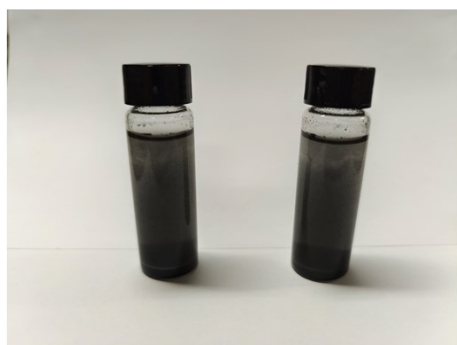
Fig. S10 The zeta potential of $\text{Co}_3\text{O}_4@\text{C}$ particles in $\beta\text{-PbO}_2$ plating bath at different ultrasonic dispersion time.



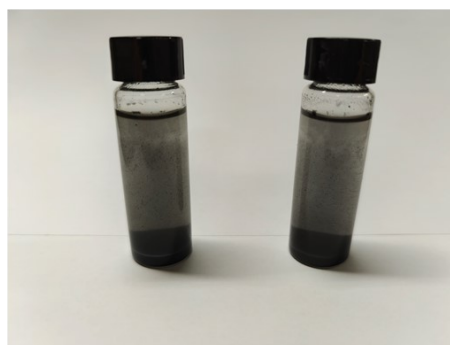
(a) 0 min



(b) 30 min



(c) 60 min



(d) 90 min

Fig. S11 Photographs of sedimentation of $\text{Co}_3\text{O}_4@C$ particles in $\beta\text{-PbO}_2$ plating bath.

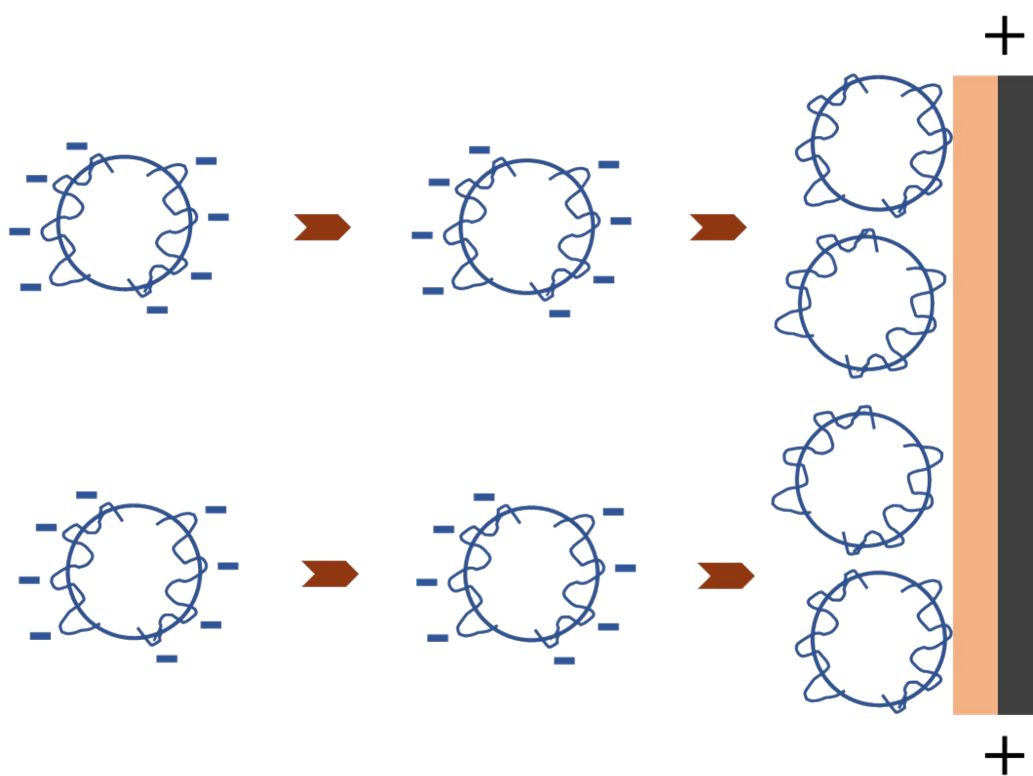


Fig. S12 Diagram of the migration of $\text{Co}_3\text{O}_4@\text{C}$ particles on the electrode surface.

References

1. W. Yang, W. Yang and X. Lin, *Applied Surface Science*, 2012, **258**, 5716-5722.
2. R. D. Xu, L. P. Huang, J. F. Zhou, P. Zhan, Y. Y. Guan and Y. Kong, *Hydrometallurgy*, 2012, **125-126**, 8-15.
3. I. Ivanov, Y. Stefanov, Z. Noncheva, M. Petrova, T. Dobrev, L. Mirkova, R. Vermeersch and J. P. Demaerel, *Hydrometallurgy*, 2000, **57**, 125-139.
4. J. Liu, J. Xu and Z. Han, *ECS Journal of Solid State Science and Technology*, 2020, **9**, 041012.
5. L. Jin, H. Huang, Y. Fei, H.-t. Yang, H.-y. Zhang and Z.-c. Guo, *Hydrometallurgy*, 2018, **176**, 201-207.
6. W. Wang, Z. Wang, T. Yuan, R. Li, H. Li, W. Lin and D. Zheng, *Hydrometallurgy*, 2019, **183**, 221-229.
7. X. Hao, S. Dan, Z. Qian, Y. Honghui and W. Yan, *RSC Advances*, 2014, **4**, 25011-25017.
8. S. He, R. Xu, L. Sun, Y. Fan, Z. Zhao, H. Liu and H. Lv, *Hydrometallurgy*, 2020, **194**, 105357.
9. C. Chen, X. Wang, R. Xu, Y. Zhang, S. Feng, A. Ju and W. Jiang, *RSC Advances*, 2021, **11**, 6146-6158.