

Supporting Information

Activity Manifestation via Architectural Manipulation by Cubic Silica Derived Co₃O₄ Electrocatalysts towards Bifunctional Oxygen Electrode Performance

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Preparation of Silica template:

In this work, we desire four silica materials used as templates such as SBA-15 (Santa Barbara Amorphous), KIT-6 (Korean Institute of Science and Technology), MCM-41 and MCM-48 (Mobile Corporation Materials). Among them, SBA-15 and MCM-41 are 2D hexagonal symmetry (*P6mm*) mesoporous silica; similarly, KIT-6 and MCM-48 are 3D cubic symmetry (*Ia3d*) mesoporous silica templates.

Materials used: Pluronic P123 (triblock copolymer, structuring agent), Tetraethoxysilane (TEOS 98%, Silica source), Cetyltrimethyl ammonium bromide (CTAB, structuring agent), n-butanol and Ethanol are purchased from Sigma-Aldrich; Hydrochloric acid (HCl 37%) and Ammonium solution (NH₃ OH, 30%) are obtained from Merck chemicals. The following chemicals were purchased in analytical grade and used as received for template preparation.

In typical **SBA-15** preparation, 16 g P₁₂₃ was dissolved in 120 ml de-ionised (DI) water and 400 ml of 2 M HCl was added in drop wise under constant stirring, then 36.8 ml of TEOS was added in drop wise and continuously stirred at 35 °C for 24h. The white precipitate product was obtained; the solution was transferred into polypropylene (PP) bottle in hydrothermally treated at 100 °C for 24 h. After cooling down to room temperature, the resulting white precipitate collected by filtered, washed with distilled water and ethanol several times. Then the product was dried in air at 60 °C for overnight. Finally, the resultant product was calcined at 550 °C in air for 6h with the ramp rate heating of 2 °C/min.

Similarly, for **KIT-6** preparation, 10g of P₁₂₃ was dissolved in 1400 ml of DI water and 64 ml of HCl was added in drop wise under constant stirring, then 50 ml of n-butanol was added and continuously stirred for 90 min. After that 92 ml of TEOS was added in drop wise and continuously stirred at 35 °C for 24 h. The white precipitate product was obtained, the solution was transferred into PP bottle and hydrothermally treated at 100 °C for 24 h. After cooling down to room temperature, the resulting white precipitate collected by filtered, washed with distilled water and ethanol several times. Then the product was dried in air at 60°C for overnight. Finally, the resultant product was calcined at 500 °C in air for 4 h with the ramp rate heating of 2 °C/min.

In typical **MCM-41** preparation, 14.6 g of CTAB was dissolved in 520 ml of DI water and 65 ml of ethanol was added and vigorously stirred until CTAB completely dissolved. Then, 42 ml NH_3OH and 45 ml of TEOS was drop wise added into the above mixture and continuously stirred for 120 min at 35 °C. The milky white suspension was transferred into a PP bottle and hydrothermally treated for 24 h at 100 °C. Then the milky white product was collected by filtration and dried overnight. Finally, the resultant powder was calcined at 550 °C in air for 6 h with the ramp rate heating of 2 °C/min.

For **MCM-48** preparation, 15.6 g of CTAB was dissolved in 720 ml DI water and 300 ml ethanol was added under vigorous stirring until CTAB completely dissolved. Then, 72 ml NH_3OH solution was added and stirred for about 30 min. At this stage 22 ml of TEOS was drop wise added into the above solution and continuously stirred for 10 h at 35 °C. The white gel suspension was formed, and then the white product was filtered and dried in air at 60 °C overnight. Finally, the resultant powder was calcined at 550 °C in air for 6 h with the ramp rate heating of 2 °C/min.

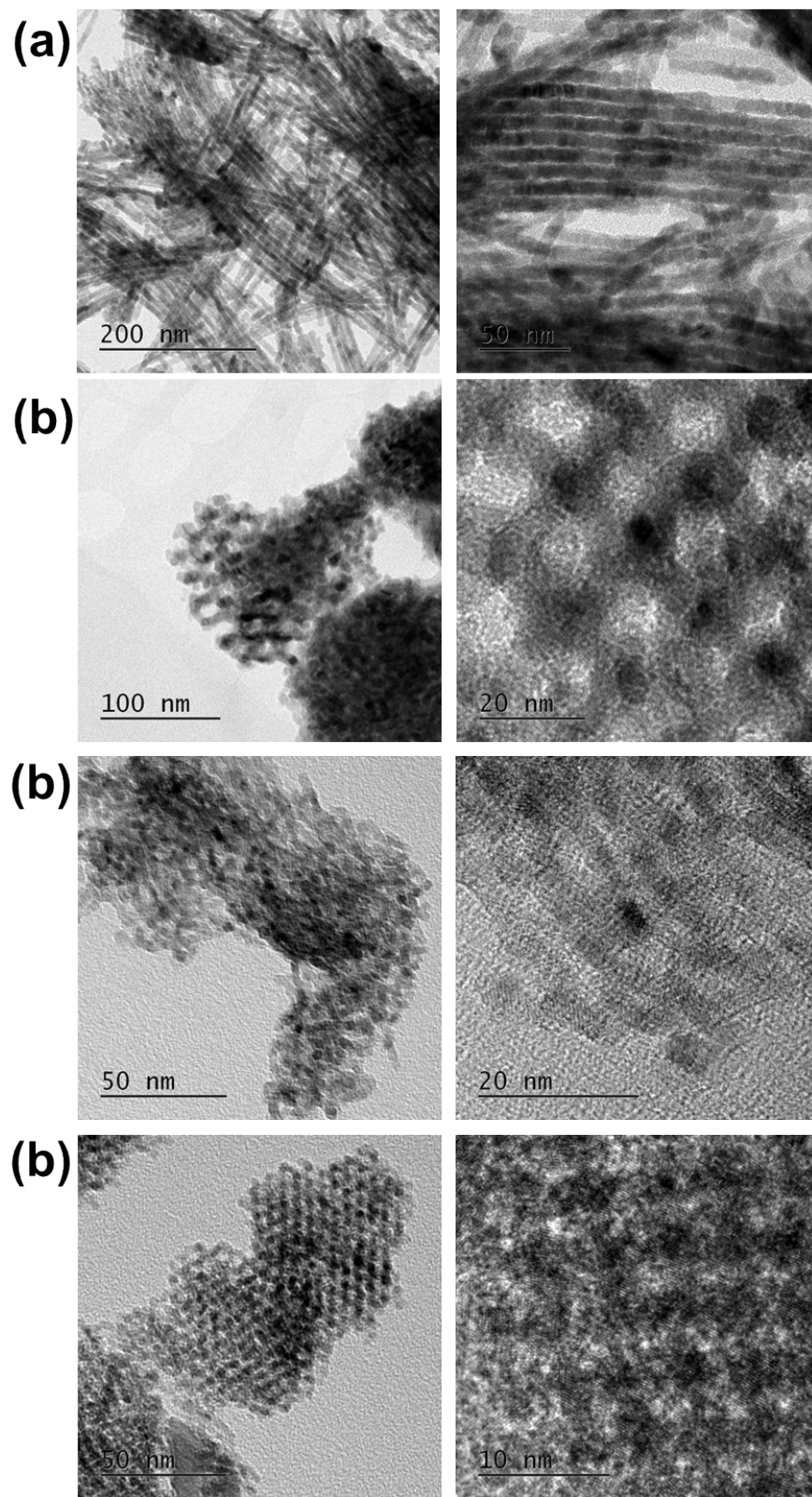


Fig. S1. Pore morphology for four replicated materials (a) $\text{Co}_3\text{O}_4\text{-S1}$, (b) $\text{Co}_3\text{O}_4\text{-K6}$, (c) $\text{Co}_3\text{O}_4\text{-M1}$ and (d) $\text{Co}_3\text{O}_4\text{-M8}$.

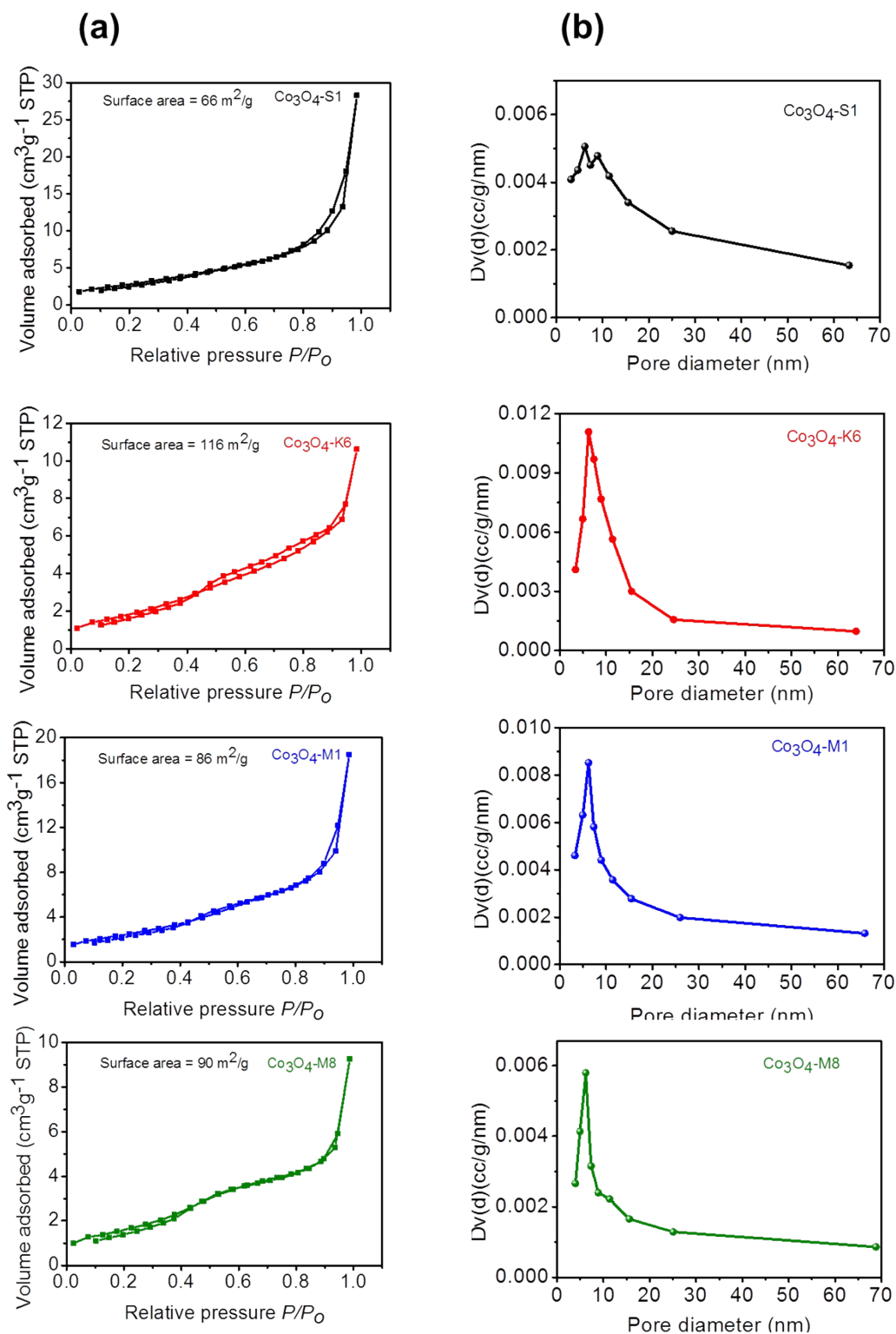


Fig. S2. (a) BET isotherm and (b) pore size distribution for four replicated materials Co_3O_4 -S1, Co_3O_4 -K6, Co_3O_4 -M1 and Co_3O_4 -M8.

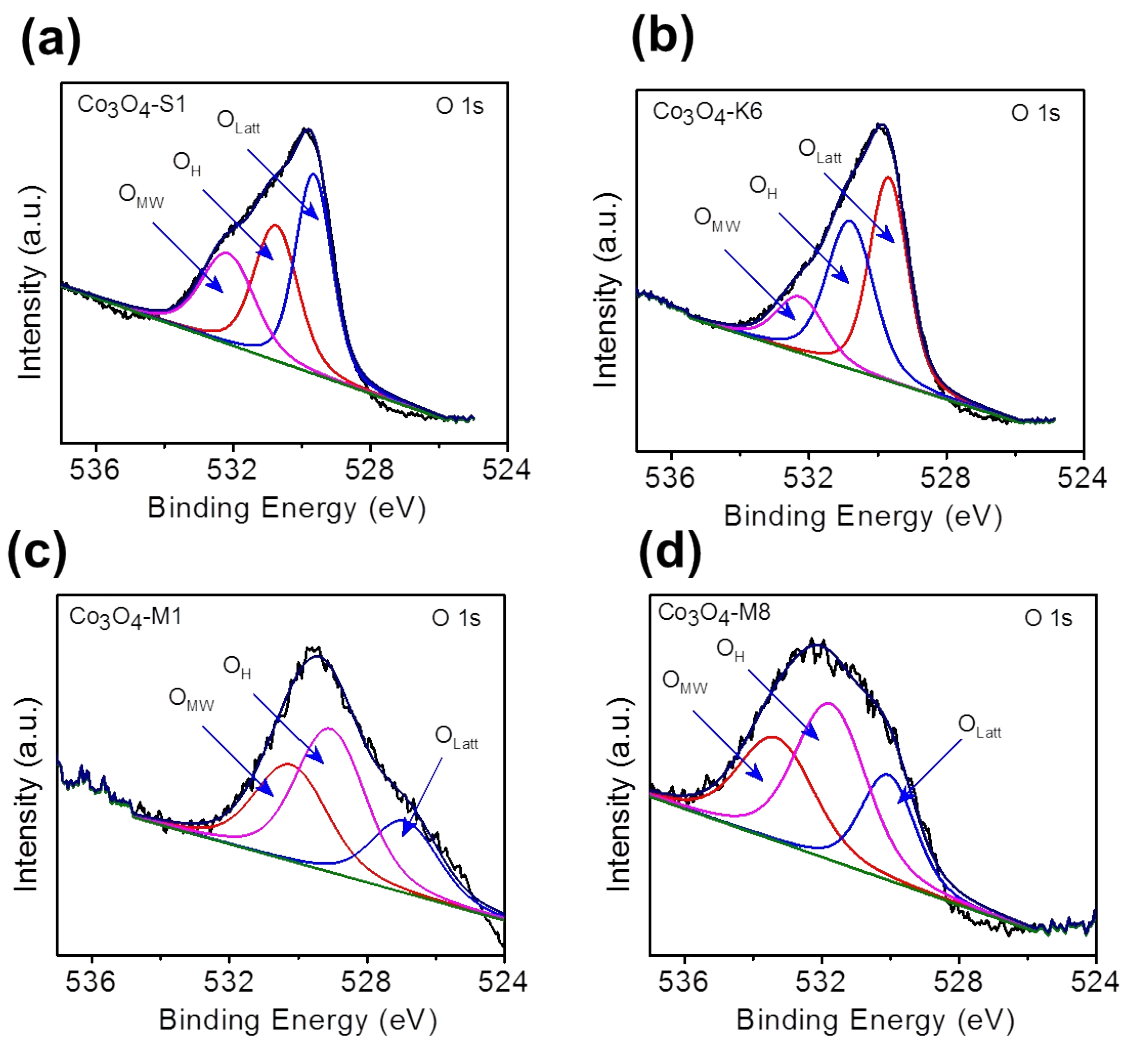


Fig. S3. XPS O 1s spectra for $\text{Co}_3\text{O}_4\text{-S1}$, $\text{Co}_3\text{O}_4\text{-K6}$, $\text{Co}_3\text{O}_4\text{-M1}$ and $\text{Co}_3\text{O}_4\text{-M8}$ materials.

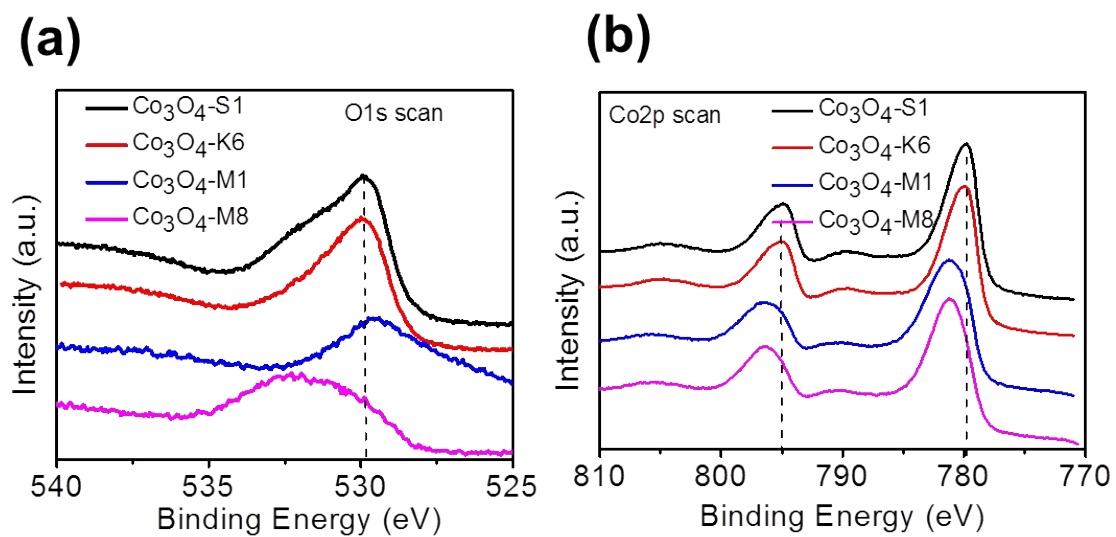


Fig. S4. XPS O 1s and Co 2p spectra for Co_3O_4 materials prepared in this work.

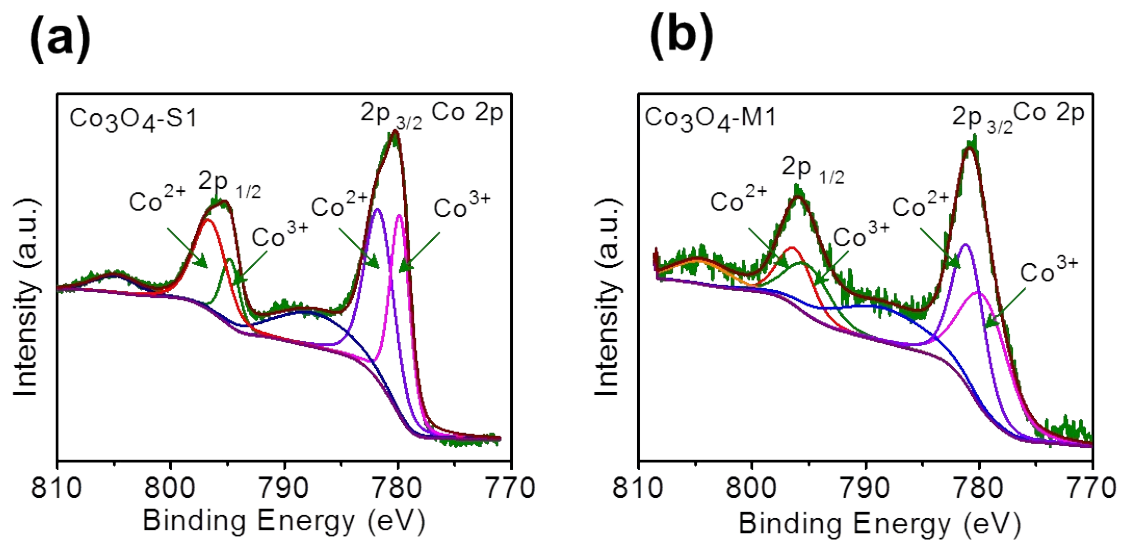
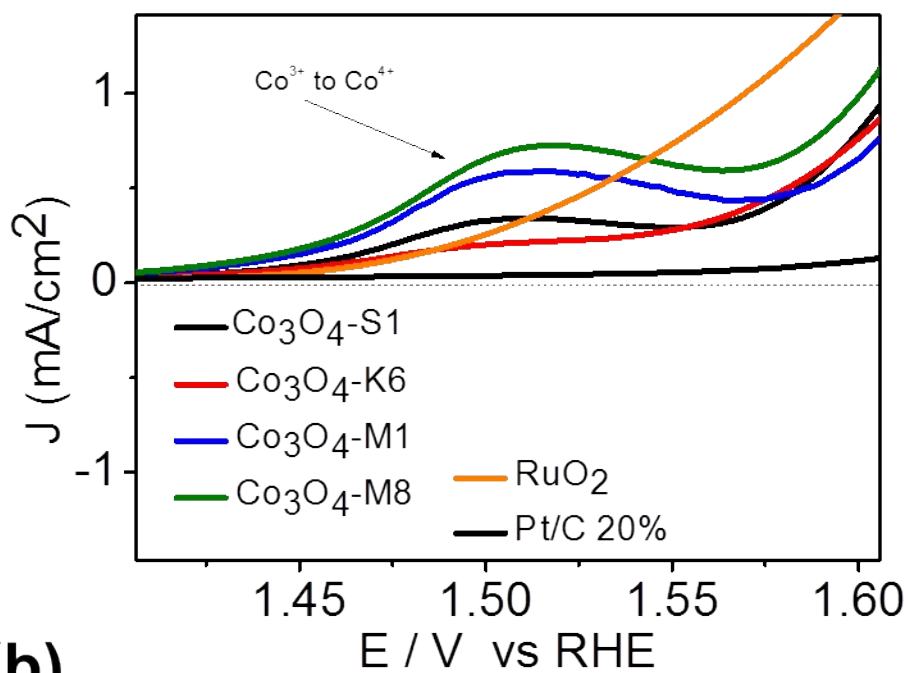


Fig. S5. XPS Co 2p spectra for Co₃O₄-S1 and Co₃O₄-M1 materials prepared in this work.

Table S1. Summary of atomic percentages of various species obtained from deconvoluted Co 2p and O 1s spectra.

| Materials | Co 2p _{3/2} (at%) | | O 1s (at%) | | |
|------------------------------------|----------------------------|------------------|-------------------|-----------------|-----------------|
| | Co ³⁺ | Co ²⁺ | O _{Latt} | O _{OH} | O _{MW} |
| | (779.8 eV) | (781.8 eV) | (529.6 eV) | (530.5 eV) | (532.1 eV) |
| Co ₃ O ₄ -S1 | 24.06 | 30.24 | 40.5 | 32.88 | 26.62 |
| Co ₃ O ₄ -K6 | 24.46 | 29.05 | 44.54 | 39.78 | 15.68 |
| Co ₃ O ₄ -M1 | 29.04 | 24.44 | 22.02 | 45.82 | 32.16 |
| Co ₃ O ₄ -M8 | 36.03 | 27.48 | 23.03 | 45.36 | 31.61 |

(a)



(b)

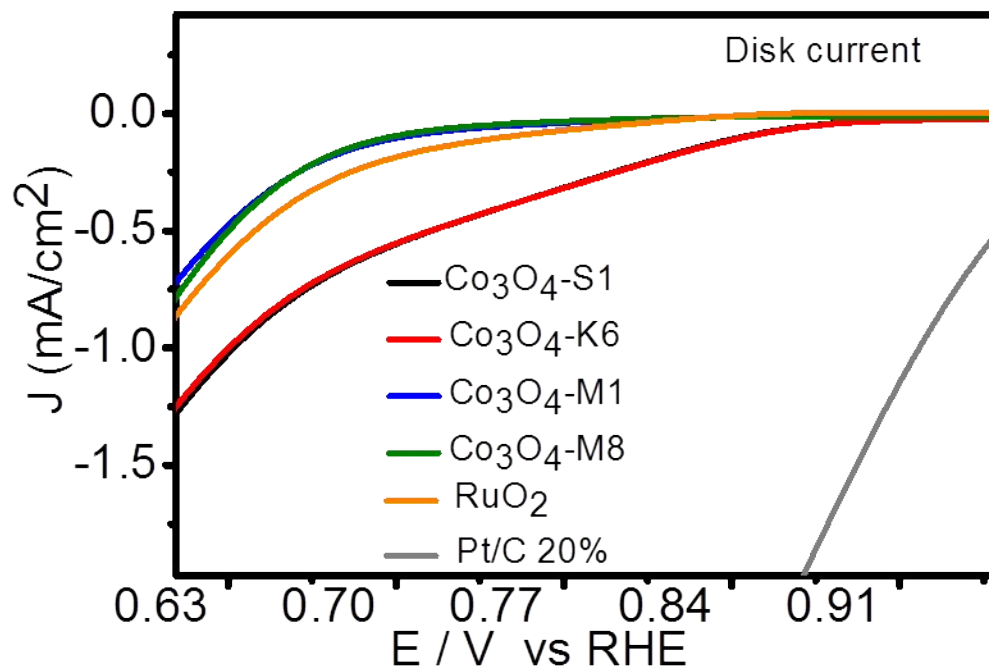


Fig. S6. LSV curves of (a) OER and (b) ORR performance (onset nearer view) for Co_3O_4 -S1, Co_3O_4 -K6, Co_3O_4 -M1, Co_3O_4 -M8, RuO_2 and Pt/C materials.

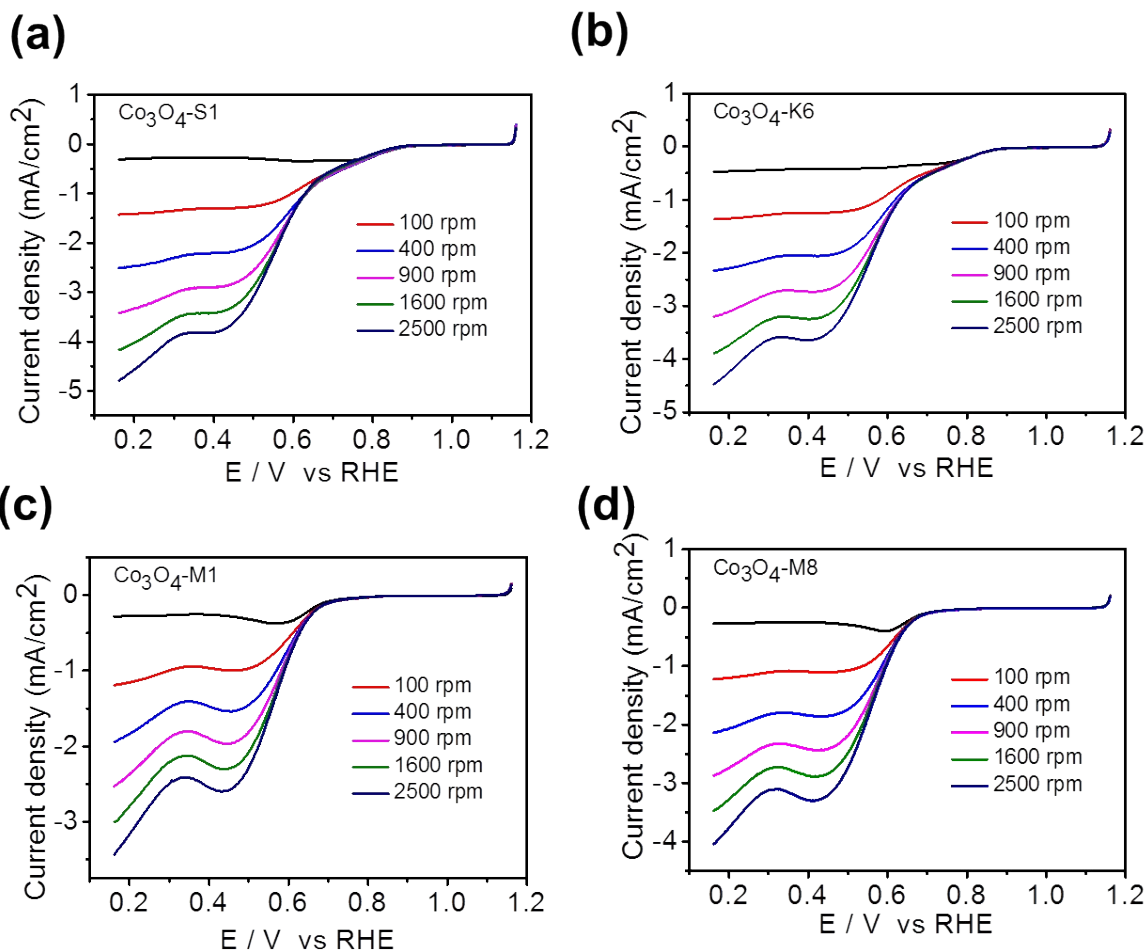


Fig. S7. The disk current performance (RPM effect) for (a) $\text{Co}_3\text{O}_4\text{-S1}$, (b) $\text{Co}_3\text{O}_4\text{-K6}$, (c) $\text{Co}_3\text{O}_4\text{-M1}$ and (d) $\text{Co}_3\text{O}_4\text{-M8}$ materials.

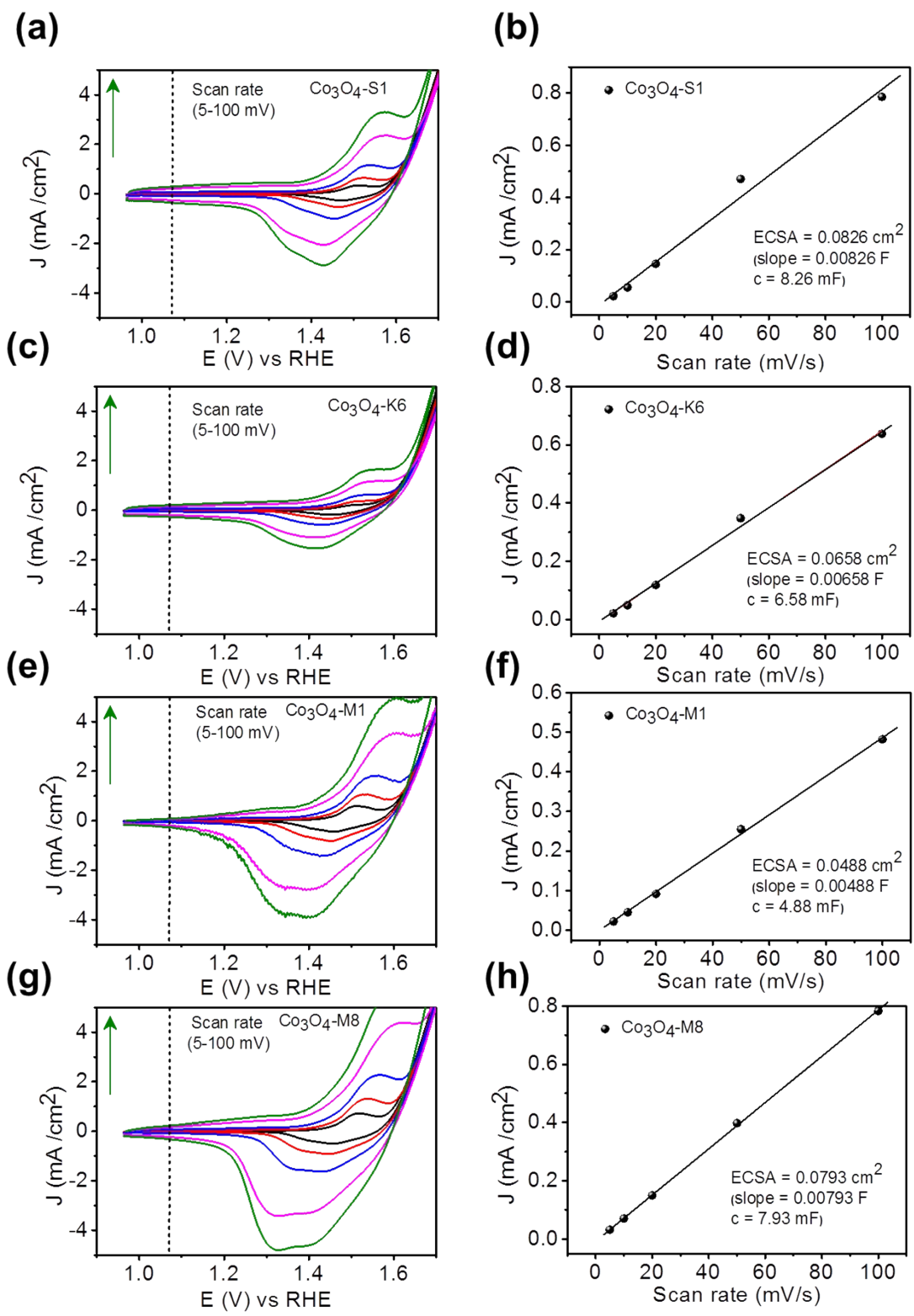


Fig. S8. Electrochemical active surface area (ECSA) for various silica template derived Co_3O_4 materials.

Table S2. Comparison of bifunctional electrocatalytic performance of various silica derived Co_3O_4 materials with previous literature data.

| Materials | BET surface area (m^2/g) | Pore volume (m^3/g) | OER | | | ORR | | | ΔE (OER@10mA -ORR@E1/2) | Reference |
|--------------------------------|--|---------------------------------------|---|---|------------------------------|-------------------|---|---|---------------------------------|-------------------------------------|
| | | | E (V/RHE) OER $j@10\text{mA}/\text{cm}^2$ | Tafel slope ($\text{mV}/\text{dec}^{-1}$) | R_{ct} (Ω) | $E_{1/2}$ (V/RHE) | E (V/RHE) OER $j@-3\text{mA}/\text{cm}^2$ | Tafel slope ($\text{mV}/\text{dec}^{-1}$) | | |
| Co_3O_4 | - | - | 1.583 ($\eta=353$ mV) | 84 | - | - | - | - | - | ¹ Feng, NPG asia2018 |
| Co_3O_4 | - | - | 1.83 | - | - | - | - | - | 1.34 | ² Nanoscale 2013,5, 5312 |
| Co_2MnO_4 | | | 1.82 | - | - | - | - | - | 1.33 | |
| meso- Co_3O_4 | - | - | ~ 1.76 (525) | - | - | - | - | - | - | ³ ACS cat 2014,4 3701 |
| c- Co_3O_4 -20 | 107 | - | ~ 1.77 (537) | - | - | - | - | - | - | ⁴ Chemmat 2014, 26, 6127 |
| h- Co_3O_4 -20 | 110 | - | ~ 1.73 (502) | - | - | - | - | - | - | |
| Co_3O_4 -100 | 113 | - | ~ 1.87 (636) | - | - | - | - | - | - | ⁵ Nanores 2013,6, 47 |
| Co_3O_4 -35 | 156 | - | ~ 1.76 (525) | - | - | - | - | - | - | |
| Meso- Co_3O_4 | 150 | - | ~ 1.76 (525) | - | - | - | - | - | - | |
| CoO/CNT | 170 | - | ~ 1.78 (550) | - | - | - | - | - | - | ⁶ Nanores 2012,5, |

| | | | | | | | | | | |
|--|-----|-------|---------------|-----|-----|-----------|------|-----|------|--|
| | | | | | | | | | | 521 |
| Co ₃ O ₄ | - | - | 1.78 | - | - | 0.46 | - | - | 1.32 | ⁷ CEC 2018,5,1 976-84 |
| Co ₃ O ₄ | - | - | - | - | - | - | - | - | 1.66 | ⁸ JECS 2016,16 3,F3041 -50. |
| Co ₃ O ₄ /C | - | - | 1.67 (425) | - | - | ~0.6 0 | 0.58 | - | 1.06 | ⁹ Chemca tchem 2018,10, 4162 |
| Co ₃ O ₄ - S1 | 67 | 0.244 | 1.78 | 107 | 97 | 0.55 | 0.49 | 125 | 1.23 | This work |
| Co ₃ O ₄ - K6 | 116 | 0.193 | 1.78 | 118 | 120 | 0.56 | 0.48 | 105 | 1.22 | |

References

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