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## **Supporting Information**

## **Open Hollow Co-Pt clusters Embedded in Carbon Nanoflake Arrays for Highly Efficient Alkaline Water Splitting**

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Schem. S1. Schematic illustration of the synthesis of Co-Pt/C nanoflake arrays grown on carbon cloth.



Fig. S1. XRD pattern and SEM images of Co-MOFs.



Fig. S2. SEM images and TEM images of Co/C (a-d), Co-Pt/C-5 (e-h) and Co-Pt/C-10 (i-l).



Fig. S3. (a-c) HRTEM image and the associated fast Fourier transform (FFT) images of Co-Pt/C-5. HRTEM image of (d) Co/C and (e) Co-Pt/C-10.

The HRTEM images and the associated fast Fourier transform (FFT) clearly show that the Co(111) plane with the interplanar distances of 0.203 nm and Pt(111) plane with the interplanar distances of 0.226nm co-exist in Co-Pt/C-5 and Co-Pt/C-10, but only the Co(111) plane can be observed in Co/C, which confirms that the Co nanoparticles turned into the Co-Pt bimetallic open hollow clusters embedding in carbon after the replacement reaction.



Fig. S4. SEM images and STEM images of Co-Pt/C-20.



Fig. S5 High-resolution Pt 4f XPS spectra of Co-Pt/C-10.



Fig. S6. LSV curves of Co-Pt/C-5, Co-Pt/C-10, Co-Pt/C-20 for (a) HER and (b) OER.



Fig. S7. (a) Stability test curves at -0.2 V for HER in an  $N_2$ -saturated 1 M KOH solution. (b) Nyquist plots for HER in an  $N_2$ -saturated 1 M KOH solution.

Table S1. Series resistance and charge transfer resistance from Nyquist plots for HER.

Samples	Co/C	Co-Pt/C-5	Co-Pt/C-10	Pt/C
Series resistance	1.71	1.52	1.38	1.40
Charge transfer	5.01	4.98	3.50	1.68
resistance				1.00



Fig. S8. Comparison of HER performances of some typical Co based and MOF derived electrocatalysts in alkaline electrolyte.

Sources:

Fe-CoP/Ti NA: Fe-doped CoP nanoarray on Ti foil <sup>1</sup> NiCo<sub>2</sub>S<sub>4</sub>/Ni NA: NiCo<sub>2</sub>S<sub>4</sub>nanowire array supported on Ni foam <sup>2</sup> Co–Ni–B<sup>[3]</sup> Co NPs-NC: Co nanoparticles embedded in N-rich carbon <sup>4</sup> CoO<sub>x</sub>@CN: Cobalt Oxide/nitrogen-doped Carbon Hybrids <sup>5</sup> CoP<sub>x</sub>-NC: MOF derived CoP<sub>x</sub> NPs embedded in nitrogen-doped carbon matrices <sup>6</sup> Ni<sub>0.33</sub>Co<sub>0.67</sub>S<sub>2</sub>: Ni<sub>0.33</sub>Co<sub>0.67</sub>S<sub>2</sub> nanowires <sup>7</sup> Co-NG: Atomic cobalt on nitrogenitrogen-doped graphene <sup>8</sup> CoN<sub>x</sub>/C: Molecular Co–N<sub>x</sub> centres in porous carbon <sup>9</sup> Co(OH)<sub>2</sub>/Pt(111) <sup>10</sup> c-CoSe/CC: cubic phase CoSe<sub>2</sub> on carbon cloth <sup>11</sup> Pt<sub>3</sub>Ni<sub>2</sub> NWs-S/C: Pt-Ni sulfide interface nanowires <sup>12</sup> MoC<sub>x</sub>: MoC<sub>x</sub> nano-octahedrons derived by MOF <sup>13</sup> NiO/Ni-CNT: nickel oxide/nickel heterostructures on carbon nanotube <sup>14</sup>



Fig. S9. (a) Curves of stability test at 1.6 V for OER in an  $O_2$ -saturated 1 M KOH solution. (b) Nyquist plots for OER in an  $O_2$ -saturated 1 M KOH solution.

Table S2. Series resistance and charge transfer resistance from Nyquist plots for OER.

Samples	Co/C	Co-Pt/C-5	Co-Pt/C-10	Pt/C
Series resistance	1.95	1.84	1.61	2.73
Charge transfer	17.8	7.01	5.60	5.34
resistance				



Fig. S10. CV curves at scan rates from 1 mV/s to 5mV/s, where no redox peaks are observed in this voltage range, and plots of electrochemical double-layer capacitance.



Fig. S11. Comparison of OER performances of some typical Co based and MOF derived electrocatalysts.

Sources:

NiCo<sub>2</sub>O<sub>4</sub> HNAs: NiCo<sub>2</sub>O<sub>4</sub> hollow nanoarray <sup>15</sup>

Co NPs-NC: Co NPs embedded in porous N-rich carbon <sup>4</sup>

Co/Fe-NC: Spindle-like Co/Fe metal oxides in nitrogen-doped porous carbon <sup>16</sup>

Co<sub>3</sub>O<sub>4</sub>-C NAs: Co<sub>3</sub>O<sub>4</sub>-C nanoarray <sup>17</sup>

CoP/rGO-L: layered CoP/rGO composite <sup>18</sup>

 $Co@Co_3O_4$ -CNT-NC:  $Co@Co_3O_4$  encapsulated in CNTgrafted nitrogen-doped carbon polyhedral <sup>19</sup>

MOF-NCNT: MOF derived nitrogen-doped carbon nanotube 20

Co<sub>3</sub>O<sub>4</sub>/NiCo<sub>2</sub>O<sub>4</sub> DSNCs: Co<sub>3</sub>O<sub>4</sub>/NiCo<sub>2</sub>O<sub>4</sub> double-shelled nanocages <sup>21</sup>

Ni<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> NWAs: Ni<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> nanowire array <sup>22</sup>

Ni-Co CB: Ni-Co cubes <sup>23</sup>

CoCo-LDH: CoCo layered double hydroxides <sup>24</sup>

CoFe<sub>2</sub>O<sub>4</sub><sup>2]</sup>

 $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}^{26}$ 

CoMoO<sub>4</sub> PF: CoMoO<sub>4</sub> porous flowers <sup>27</sup>



Fig. S12. XRD patterns of Co-Pt/C-10 after the stability test of HER and OER, respectively.



Fig. S13. High-resolution (a) Co 2p and (b) Pt 4f XPS spectra of Co-Pt/C-10 after HER stability test.



Fig. S14. High-resolution (a) Co 2p and (b) Pt 4f XPS spectra of Co-Pt/C-10 after OER stability test.

## **Supplementary References:**

- 1 C. Tang, R. Zhang, W. Lu, L. He, X. Jiang, A. M. Asiri and X. Sun, *Advanced materials*, 2017, **29**.
- 2 A. Sivanantham, P. Ganesan and S. Shanmugam, *Advanced Functional Materials*, 2016, **26**, 4661-4672.
- 3 S. Gupta, N. Patel, R. Fernandes, R. Kadrekar, A. Dashora, A. Yadav, D. Bhattacharyya, S. Jha, A. Miotello and D. Kothari, *Applied Catalysis B: Environmental*, 2016, **192**, 126-133.
- 4 X. Li, Z. Niu, J. Jiang and L. Ai, *Journal of Materials Chemistry A*, 2016, 4, 3204-3209.
- 5 H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, *J. Am. Chem. Soc*, 2015, **137**, 2688-2694.
- 6 B. You, N. Jiang, M. Sheng, S. Gul, J. Yano and Y. Sun, *Chemistry of Materials*, 2015, **27**, 7636-7642.
- 7 Z. Peng, D. Jia, A. M. Al Enizi, A. A. Elzatahry and G. Zheng, *Advanced Energy Materials*, 2015, **5**.
- 8 H. Fei, J. Dong, M. J. Arellano-Jiménez, G. Ye, N. D. Kim, E. L. Samuel, Z. Peng, Z. Zhu, F. Qin and J. Bao, *Nature communications*, 2015, **6**, 8668.
- 9 H.-W. Liang, S. Brüller, R. Dong, J. Zhang, X. Feng and K. Müllen, *Nature communications*, 2015, **6**.
- 10 R. Subbaraman, D. Tripkovic, K.-C. Chang, D. Strmcnik, A. P. Paulikas, P. Hirunsit, M. Chan, J. Greeley, V. Stamenkovic and N. M. Markovic, *Nature materials*, 2012, **11**, 550-557.

- 11 P. Chen, K. Xu, S. Tao, T. Zhou, Y. Tong, H. Ding, L. Zhang, W. Chu, C. Wu and Y. Xie, *Advanced materials*, 2016, **28**, 7527-7532.
- 12 P. Wang, X. Zhang, J. Zhang, S. Wan, S. Guo, G. Lu, J. Yao and X. Huang, *Nature Communications*, 2017, **8**.
- 13 H. B. Wu, B. Y. Xia, L. Yu, X.-Y. Yu and X. W. D. Lou, *Nature communications*, 2015, **6**.
- 14 M. Gong, W. Zhou, M.-C. Tsai, J. Zhou, M. Guan, M.-C. Lin, B. Zhang, Y. Hu, D.-Y. Wang and J. Yang, *Nature communications*, 2014, 5, 4695.
- 15 C. Guan, X. Liu, W. Ren, X. Li, C. Cheng and J. Wang, *Advanced Energy Materials*, 2017.
- 16 Y. Han, J. Zhai, L. Zhang and S. Dong, *Nanoscale*, 2016, 8, 1033-1039.
- 17 T. Y. Ma, S. Dai, M. Jaroniec and S. Z. Qiao, *Journal of the American Chemical Society*, 2014, **136**, 13925-13931.
- 18 L. Jiao, Y.-X. Zhou and H.-L. Jiang, Chemical Science, 2016, 7, 1690-1695.
- 19 A. Aijaz, J. Masa, C. Rösler, W. Xia, P. Weide, A. J. Botz, R. A. Fischer, W. Schuhmann and M. Muhler, *Angewandte Chemie International Edition*, 2016, 55, 4087-4091.
- 20 B. Y. Xia, Y. Yan, N. Li, H. B. Wu, X. W. D. Lou and X. Wang, *Nature Energy*, 2016, 1, 15006.
- 21 H. Hu, B. Guan, B. Xia and X. W. Lou, *Journal of the American Chemical Society*, 2015, **137**, 5590-5595.
- 22 Y. Li, P. Hasin and Y. Wu, Advanced materials, 2010, 22, 1926-1929.
- 23 L. Han, X. Y. Yu and X. W. D. Lou, Advanced Materials, 2016, 28, 4601-4605.
- 24 F. Song and X. Hu, *Nature communications*, 2014, 5.
- 25 M. Li, Y. Xiong, X. Liu, X. Bo, Y. Zhang, C. Han and L. Guo, *Nanoscale*, 2015, 7, 8920-8930.
- 26 J. Suntivich, K. J. May, H. A. Gasteiger, J. B. Goodenough and Y. Shao-Horn, *Science*, 2011, **334**, 1383-1385.
- 27 M. Q. Yu, L. X. Jiang and H. G. Yang, *Chemical Communications*, 2015, 51, 14361-14364.