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## Nitrogen Doped and Carbon Coated CoP Hollow Nanospheres with Enhanced

## Electrocatalytic Activity towards Oxygen Evolution Reaction

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Figure S1. (a) Cyclic voltammograms (CV) curves in 1 M KOH for CoP@NC HNS in the region of 0.10~0.30 V vs. RHE at various scan rates. (b) The measured capacitive currents plotted as a function of scan rate.



Figure S2. Decomposed XPS Co 2p spectra of the CoP@NC HNS and SiO<sub>2</sub>@Co(OH)<sub>2</sub>.

The Co region of CoP@NC HNS shown in Figure S2 exhibits that the profiles of Co  $2p_{3/2}$  of CoP can be deconvoluted into two peaks located at 780.8 eV (Co<sup>3+</sup>), and 782.6 eV (Co<sup>2+</sup>). The Co  $2p_{3/2}$  peak of SiO<sub>2</sub>@Co(OH)<sub>2</sub> was at 781.7. Compared with Co(OH)<sub>2</sub>, the peak of metallic Co is visibly red-shifted in CoP, indicating the enriched electrons around Co, which weakens the oxygen bond on the cobalt surface and effectively promotes the kinetics of the Heyrovsky step.



Figure S3. TG curves of SiO<sub>2</sub>@Co(OH)<sub>2</sub> and SiO<sub>2</sub>@Co(OH)<sub>2</sub>-PDA.

The two TG curves shown in the Figure S3 correspond to  $SiO_2@Co(OH)_2$  and  $SiO_2@Co(OH)_2$ -PDA, respectively. The two TG curves have similar trends. According to the TGA curve of  $SiO_2@Co(OH)_2$ , the material experienced the first stage of weight loss (12.9%) before the temperature reached 200 °C. This part of weight loss was due to the removal of water molecules between  $Co(OH)_2$  layers. For  $SiO_2@Co(OH)_2$ -PDA, the first stage of weight loss before the temperature reached 220 °C was 14.6% because of the preliminary carbonization of PDA. Then the weight loss from this segment to the end is due to dehydroxylation and the removal of anions between the layers. The total mass loss was 30.8%.

Composite materials	КОН (М)	J (mA•cm <sup>-2</sup> )	Tafel slope (mA dec <sup>-1</sup> )	Overpotential (mV)
RuO <sub>2</sub> <sup>1</sup>	1.0	10	114	400
$IrO_2^2$	1.0	10	149	395
CoP/rGO-400 <sup>2</sup>	1.0	10	64	340
Amorphous cobalt phyllosilicate (ACP) <sup>3</sup>	1.0	10	60	365
N-doped carbon sheets CoP (CoP/NCS) <sup>1</sup>	1.0	10	57	313
P and N co-doped carbon CoP (CoP@PNC) <sup>4</sup>	1.0	10	64	330
CoP nanoparticles (NPs) <sup>5</sup>	0.1	10	50	330
CoP <sub>3</sub> NAs/CFP <sup>6</sup>	1.0	10	62	334
$Ni_79P^7$	1.0	10	-	326
Sandwich-like CoP/C <sup>8</sup>	1.0	10	53	330
CoP nanorod <sup>9</sup>	1.0	10	71	320
CoP film <sup>10</sup>	1.0	10	47	345
p-CoP/A <sub>12</sub> O <sub>3</sub> <sup>11</sup>	1.0	10	-	357
Co <sub>3</sub> O <sub>4</sub> hollow polyhedrons <sup>12</sup>	1.0	10	61	536
Co <sub>3</sub> O <sub>4</sub> <sup>13</sup>	1.0	10	66	356
CoO/Co <sup>14</sup>	1.0	10	80	350
The Nitrogen doped graphene hollow microspheres supported CoO nanoparticles(CoO/NGHSs) <sup>15</sup>	1.0	10	70	330
CoO nanocrystals embedded into N- doped carbons(NC-CoO/C) <sup>16</sup>	1.0	10	45	362
Microspheric $CoS_2$ (MS $CoS_2$ ) <sup>17</sup>	1.0	10	92	325
$CoNi_2S4@CoS_2/NF^{18}$	1.0	30	238	365
CoS <sub>1.097</sub> nanotubes <sup>19</sup>	1.0	10	-	330
Fe-NiNC-50 <sup>20</sup>	1.0	10	54	340
Meso/micro-FeCo-Nx-CN-30 <sup>21</sup>	1.0	10	57	440
FeCo-DACs/NC <sup>22</sup>	1.0	10	82.7	370
N-doped CoP@NC HNS (this work)	1.0	10	68	320

Table S1. A comparison study on OER performances between this work and the other related reports.

## References

- 1 T. Yin, X. Zhou, A. Wu, H. Yan, Q. Feng and C. Tian, CoP particles embedded in N-doped two-dimensional carbon sheets as efficient electrocatalyst for water splitting, *Electrochimica*. *Acta*, 2018, **276**, 362-369.
- L. Jiao, Y. X. Zhou and H. L. Jiang, Metal-organic framework-based CoP/reduced graphene oxide: high-performance bifunctional electrocatalyst for overall water splitting, *Chem. Sci.*, 2016, 7, 1690-1695.
- 3 S. K. Ju, I. Park, E. S. Jeong, K. Jin, W. M. Seong, G. Yoon, H. Kim, B. Kim, K. T. Nam and K. Kang, Amorphous cobalt phyllosilicate with layered crystalline motifs as water oxidation catalyst, *Adv. Mater.*, 2017, 29, 1606893.
- Z. Zhou, N. Mahmood, Y. Zhang, L. Pan, L. Wang, X. Zhang and J. J. Zou, CoP nanoparticles embedded in P and N co-doped carbon as efficient bifunctional electrocatalyst for water splitting, *J. Energy Chem.*, 2017, 26, 1223-1230.
- 5 C. C. Hou, S. Cao, W. F. Fu and Y. Chen, Ultrafine CoP nanoparticles supported on carbon nanotubes as highly active electrocatalyst for both oxygen and hydrogen evolution in basic media, *ACS Appl. Mater. Interfaces*, 2015, **7**, 28412-28419.
- 6 T. Wu, M. Pi, D. Zhang and S. Chen, 3D structured porous CoP3 nanoneedle arrays as a efficient bifunctional electrocatalyst for the evolution reaction of hydrogen and oxygen, *J. Mater. Chem A*, 2016, **4**. 14539-14544.
- 7 B. K. Kim, S. K. Kim, S. K. Cho and J. J. Kim, Enhanced catalytic activity of electrodeposited Ni-Cu-P toward oxygen evolution reaction, *Appl. Catal. B-Environ.*, 2018, 237, 409-415.
- 8 Y. Bai, H. Zhang, Y. Feng, L. Fang and Y. Wang, Sandwich-like CoP/C nanocomposites as efficient and stable oxygen evolution catalysts, *J. Mater. Chem. A*, 2016, **4**, 9072-9079.
- J. Chang, X. Yao, M. Xiao, J. Ge, C. Liu and X. Wei, Surface oxidized cobalt-phosphide nanorods as an advanced oxygen evolution catalyst in alkaline solution, ACS Catal., 2015, 5, 6874-6878.
- J. Nan, Y. Bo, S. Meili and S. Yujie, Electrodeposited cobalt-phosphorous-derived films as competent bifunctional catalysts for overall water splitting, *Angew. Chem. Int. Ed.*, 2015, 127, 6349-6352.
- 11 W. Li, S. Zhang, Q. Fan, F. Zhang and S. Xu, Hierarchically scaffolded CoP/CoP<sub>2</sub> nanoparticles: controllable synthesis and their application as a well-matched bifunctional electrocatalyst for overall water splitting, *Nanoscale*, 2017, **9**, 5677-5685.
- 12 D. Dong, L. Yang and J. Li, Co<sub>3</sub>O<sub>4</sub> hollow polyhedrons as bifunctional electrocatalysts for reduction and evolution reactions of oxygen, *Part. Part. Syst. Char.*, 2016, **33**, 887-895.
- G. Cao, H. Wu, X. Wen, X. Liu, W. Zang, Z. Hong, J. Ding, P. F. Yuan, S. J. Pennycook and J. Wang, Hollow Mo-doped CoP nanoarrays for efficient overall water splitting, *Nano Energy*, 2018, 48. 73-80.
- 14 X. Yuan, H. Ge, W. Xin, C. Dong, W. Dong, M. S. Riaz, Z. Xu, J. Zhang and F. Huang, Controlled phase evolution from Co nanochains to CoO nanocubes and their application as OER catalysts, ACS Energy Lette., 2017, 2, 1208-1213.
- 15 Z. J. Jiang and Z. Jiang, Interaction induced high catalytic activities of CoO nanoparticles grown on nitrogen-doped hollow graphene microspheres for oxygen reduction and evolution reactions, *Sci. Rep.*, 2016, 6, 27081.

- 16 H. Kim, Y. Kim, Y. Noh, S. Lee, J. Sung and W. B. Kim, Thermally-converted CoO nanoparticles embedded into N-doped carbons as highly efficient bi-functional electrocatalysts for oxygen reduction and evolution reactions, *Chemcatchem*, 2017, 9, 1503-1510.
- 17 M. Guo, K. Xu, Y. Qu, F. Zeng and C. Yuan, Porous Co<sub>3</sub>O<sub>4</sub>/CoS<sub>2</sub> nanosheet-assembled hierarchical microspheres as superior electrocatalyst towards oxygen evolution reaction, *Electrochim. Acta*, 2018, **268**, 10-19.
- 18 Z. Xu, H. Pan, L. Yu, Y. Zhi and Y. Gong, Constructing hexagonal copper-coin-shaped NiCoSe<sub>2</sub>@NiO@CoNi<sub>2</sub>S<sub>4</sub>@CoS<sub>2</sub> hybrid nanoarray on nickel foam as a robust oxygen evolution reaction electrocatalyst, *J. Mater. Chem. A*, 2018, **6**, 18641-18648.
- 19 J. C. Zhang, D. Zhang, R. C. Zhang, N. Zhang, C. Cui, J. Zhang, J. Bei, B. Yuan, T. Wang and H. Xie, Facile synthesis of mesoporous and thin-walled Ni-Co sulfide nanotubes as efficient electrocatalysts for oxygen evolution reaction, ACS Appl. Energy Mater., 2018, 1, 495-502.
- 20 X. Zhu, D. Zhang, C. Chen, Q. Zhang, R. Liu, Z. Xia, L. Dai, R. Amal and X. Lu, Harnessing the interplay of Fe-Ni atom pairs embedded in nitrogen-doped carbon for bifunctional oxygen electrocatalysis, *Nano Energy*, 2020, **71**, 104597.
- 21 Y. S. Wei, L. Sun, M. Wang, J. Hong, L. Zou, H. Liu, Y. Wang, M. Zhang, Z. Liu and Y. Li, Fabricating dual-atom iron catalysts for efficient oxygen evolution reaction: a heteroatom modulator approach, *Angew. Chem. Int. Ed.*, 2020, **59**, 16013-16022.
- 22 M. Liu, N. Li, S. Cao, X. Wang, X. Lu, L. Kong, Y. Xu and X. H. Bu, A "Pre-constrained metal twins" strategy to prepare efficient dual-metal-atom catalysts for cooperative oxygen electrocatalysis, *Adv. Mater.*, 2022, **34**, 2107421.