## M<sub>X</sub>P(M=Co/Ni)@Carbon Core-Shell Nanoparticles Embedded in 3D

## **Cross-linked Graphene Aerogels Derived from Seaweed Biomass for**

## **Hydrogen Evolution Reaction**

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Figure S1 (a) XRD patterns of CoP-NPs@CA and CoP@C-NPs/GA-x, (b) Ni<sub>2</sub>P-NPs@CA and Ni<sub>2</sub>P@C-NPs/GA-x



Figure S2 (a) Raman spectra of CoP-NPs@CA and CoP@C-NPs/GA-x, (b) Ni<sub>2</sub>P-NPs@CA and Ni<sub>2</sub>P@C-NPs/GA-5.



Figure S3 FESEM images of different mass ratio of graphene oxide (a) Ni<sub>2</sub>P-NPs@CA, (b) Ni<sub>2</sub>P@C-NPs/GA-5.



Figure S4 (a) High-magnification TEM images of the synthesized Ni<sub>2</sub>P@C-NPs/GA-5, (b) HRTEM images of Ni<sub>2</sub>P@C-NPs/GA-5.



**Figure S5** Stability tests of Ni<sub>2</sub>P@C-NPs/GA-5 using the chronopotentiometric measurements (without iR corrections) with the fixed current density of 10 mA cm<sup>-2</sup> in (a) 0.5 M H<sub>2</sub>SO<sub>4</sub> and (b) 1 M KOH solutions.



**Figure S6** CVs performed at various scan rates in the region of 0.10–0.20 V versus RHE for CoP-NPs@CA electrocatalyst (a) in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolytes and (b) in 1 M KOH electrolytes.



**Figure S7** CVs performed at various scan rates in the region of 0.10-0.20 V versus RHE for Ni<sub>2</sub>P-NPs@CA (a) in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolytes and (c) in 1 M KOH electrolytes, Ni<sub>2</sub>P@C-NPs/GA-5 (b) in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolytes and (d) in 1 M KOH electrolytes. Ni<sub>2</sub>P-NPs/CA and Ni<sub>2</sub>P@C-NPs/GA-5 in current density at 0.15 V versus RHE

plotted against the scan rate and ftted to a linear regression allows for the estimation of  $C_{dl}$  (e) in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolytes and (f) in 1 M KOH electrolytes.



**Figure S8** Nyquist plots of Ni<sub>2</sub>P-NPs@CA and Ni<sub>2</sub>P@C-NPs/GA-5 over the frequency range from 100 kHz to 0.1Hz (a) at  $\eta$ =135 mV with an AC voltage of 10 mV in in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolytes,(b) at  $\eta$ =377 mV with an AC voltage of 10 mV in 1 M KOH electrolytes.

	Loading (mg.cm <sup>-2</sup> )	η <sub>10</sub> (mV)	Tafel slop (mV dec <sup>-1</sup> )	C <sub>dl</sub> (mF cm <sup>-2</sup> )	Reference
Porous CoP concave					
polyhedron	0.35	133	51	/	1
CoP@C	0.31	130	64	9.30	2
CoP@NC-T	0.31	124	59	9.90	2
CoP Hollow Polyhedron	0.10	159	59	/	3
CoP/CNTs	/	139	52	/	4
Co@NC/NG	0.29	/	79	37.30	5
Co@NGF	0.28	125	94	/	6
Ni <sub>2</sub> P/N-doped Graphene	0.18	102	59	/	7
CoSe2@DC	0.36	132	82	51.10	8
Ni <sub>5</sub> P <sub>4</sub> -Ni <sub>2</sub> P nanosheet	68.2 (electrode)	120	79	/	9
Ni <sub>12</sub> P <sub>5</sub> /CNT	0.18	240	81	/	10
МоР	0.36	125	54	/	11
Mo <sub>2</sub> C@NC	0.28	124	60	73.20	12
SV-MoS <sub>2</sub>	/	170	60	/	13
CoP NPs	0.35	221	87	/	14
Free CoP NPs	/	167	88	2.57	15
CoP-RGO	/	157	70	5.23	15
Mo <sub>3</sub> S <sub>13</sub> @rGO-CNTs	/	179	67	/	26
aerogels GCA-MoSe <sub>2</sub> -2 aerogels	/	228	68	1.31	27
MoSe <sub>2</sub> /carbon fiber aerogel	/	179	62	/	28
CoP@C-NPs/GA-5	0.28	120	57	55.83	Our work

Table S1 Comparison of catalytic parameters of different HER catalysts in 0.5 M H2SO4 .

	Loading	$\eta_{10}$	Tafel slop	C <sub>dl</sub>	Reference
	(mg.cm <sup>-2</sup> )	(mV)	(mV dec <sup>-1</sup> )	(mF cm <sup>-2</sup> )	
CoP@C	0.31	170	83		2
CoP/NF	/	182	109	/	16
CoP nanowire arrays/CC	0.92	209	129	/	17
CoP nanoparticle/Ti	0.18	170	66		18
NiMoN/CC	1.10	109	95	21	19
Ni-P/CP	25.80	117	85		20
FeP nanorod arrays/CC	1.50	218	146	/	21
NiFeVS/NF	38.25 (electrode)	161	96	32.30	22
WP <sub>2</sub>	/	225	84		23
Lepidocrocite VOOH hollow nanospheres	0.80	164	104		24
Fe <sub>2</sub> O <sub>3</sub> /Fe@CN	0.28	330	114	16.20	25
CoP@C-NPs/GA-5	0.28	225	66	18.85	Our work

 Table S2 Comparison of catalytic parameters of different HER catalysts in 1 M KOH.

## References

- 1. M. Xu, L. Han, Y. Han, Y. Yu, J. Zhai, S. Dong, J. Mater. Chem. A, 2015, 3, 21471.
- 2. F. Yang, Y. Chen, G. Cheng, S. Chen, W. Luo, ACS Catalysis, 2017,7,1602355.
- 3. M. Liu, J. Li, ACS Appl. Mater. Interfaces, 2016, 8, 2158.
- 4. C. Wu, Y. Yang, D. Dong, Y. Zhang, J. Li, Small, 2017, 13, 1602873.
- 5. W. J. Zhou, J. Zhou, Y. C. Zhou, J. Lu, K. Zhou, L. J. Yang, Z. H. Tang, L. G. Li, S. W. Chen, *Chem. Mater.*, 2015, **27**, 2026.

6. D. Hou, W. Zhou, K. Zhou, Y. Zhou, J. Zhong, L. Yang, J. Lu, G. Li, S. Chen, J. Mater. Chem. A, 2015, 3, 15962.

- 7. Y. Pan, N. Yang, Y. Chen, Y. Lin, Y. Li, Y. Liu, C. Liu, Journal of Power Sources, 2015, 297, 45-52.
- 8. W. Zhou, J. Lu, K. Zhou, L. Yang, Y. Ke, Z. Tang, S. Chen, Nano Energy, 2016, 28, 143.
- 9. X.Wang, Y. V.Kolen'ko, X. Q. Bao, K.Kovnir, L. Liu, Angew. Chem. Int. Ed. 2015, 54, 8188-8192.
- 10. Y. Pan, W. Hu, D. Liu, Y. Liu, C. Liu, J. Mater. Chem. A, 2015, 3, 13087-13094.
- 11. Z. Xing, Q. Liu, A. M.Asiri, X. Sun, Adv. Mater. ,2014, 26, 5702-5707.
- 12. Y. Liu, G. Yu, G. D. Li, Y. Sun, T. Asefa, W. Chen, X. Zou, Angew. Chem. Int. Ed., 2015, 54, 10752–10757.
- 13. H. Li, C. Tsai, A. L. Koh, L. Cai, A. W. Contryman, A. H. Fragapane, J. Zhao, H. S. Han, H. C. Manoharan, F. Abild-Pedersen, J. K. Nørskov, X. Zheng, *Nat.Mater.*, 2016, **15**, 48–54.
- 14. P. Jiang, Q. Liu, C. Ge, W. Cui, Z. Pu, A. M. Asiri, X. Sun, J. Mater. Chem. A, 2014, 2, 14634.
- 15. M. Li, X. Liu, Y. Xiong, X. Bo, Y. Zhang, C. Han, L. Guo, J. Mater. Chem. A, 2015, 3, 4255.
- 16. Y. Xua, C. Yuan, Z. Liua, X. Chen, Catalysis Science & Technology, 2018, 8, 128-133.
- 17. J. Tian, Q. Liu, A. M. Asiri, X. Sun, J. Am. Chem. Soc., 2014, 136, 7587-7590.
- 18. D. H. Ha, B. Han, M. Risch, L. Giordano, K. P. C. Yao, P. Karayaylali, Y. Shao-Horn, *Nano Energy*, 2016, 29, 37–45.
- 19. Y. Q. Zhang, B. Ouyang, J. Xu, S. Chen, R. S. Rawat, H. J. Fan, Adv. Energy Mater., 2016, 6, 1600221.
- 20. X. Wang, W. Li, D. Xiong, D. Y. Petrovykh, L. Liu, Adv. Funct. Mater., 2016, 26, 4067-4077.
- 21. Y. Liang, Q. Liu, A. M. Asiri, X. Sun, Y. Luo, ACS Catal., 2014, 4, 4065-4069.
- 22. X. Shang, J. Chi, Z. Liu, B. Dong, K. Yan, W. Gao, J. Zeng, Y. Chai, C. Liu, *Electrochimica Acta*, 2017, 256 241–251.
- 23. H. Du, S. Gu, R. Liu, C. Li, J. Power Source, 2015, 278, 540-545.
- 24. H. Shi, H. Liang, F. Ming, Z. Wang, Angew. Chem. Int. Ed., 2017, 56, 588-592.
- 25. D. F. Su, J. Wang, H. Y. Jin, Y. T. Gong, M. M. Li, Z. F. Pang, Y. Wang, J. Mater. Chem. A ,2015, 3, 11756.
- 26.Y. Shang, X. Xu, B. Gao, Z. Ren, ACS Sustainable Chem. Eng., 2017, 5, 8908-8917.
- 27. Y. Shi, W. Gao, H. Lu, Y. Huang, L. Zuo, W. Fan, T. Liu, ACS Sustainable Chem. Eng., 2017, 5, 6994-7002.
- 28. Y. Zhang, L. Zuo, L. Zhang, Y. Huang, H. Lu, W. Fan, T. Liu, ACS Appl. Mater. Interfaces, 2016, 8, 7077-7085.