Supporting Information

Nickel-cobalt bimetallic tungstate decorated 3D hierarchical porous carbon derived from lignin for high-performance supercapacitor applications

Feiyan Shi [a †], Shuai Zhao [c †], Junyu Yang [b], Yao Tong[a, *], Jiajun Li [a], Shangru Zhai [a], Xinyu Zhao [a], Shenghan Wu [a], Hongsheng Li [a], Qingda An [a, *], Kai Wang[b, *]

[a]*Faculty of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, Liaoning, China*

[b]*Dalian National Laboratory for Clean Energy; Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

[c]*School of Science, Chongqing University of Technology, Chongqing 400054, China*

F. Shi and S. Zhao contributed equally to this work.

*Corresponding authors:

E-mail address: anqingdachem@163.com; wangkai@dicp.ac.cn; tongyao@dlpu.edu.cn.

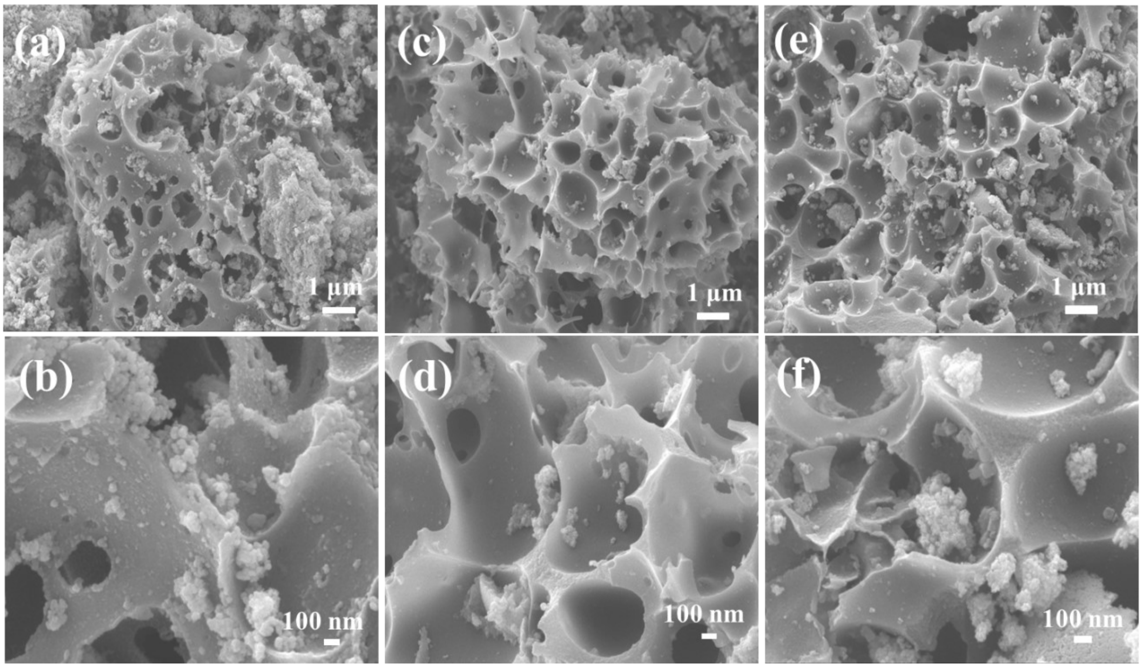

Fig. S1. (a) low and (b) high magnification SEM images of $Ni_{3.5}Co_{0.5}WO_4$/HPC; (c) low and (d) high magnification SEM images of $Ni_{2.5}Co_{1.5}WO_4$/HPC and (e) low and (f) high magnification SEM images of $Ni_2Co_2WO_4$/HPC.

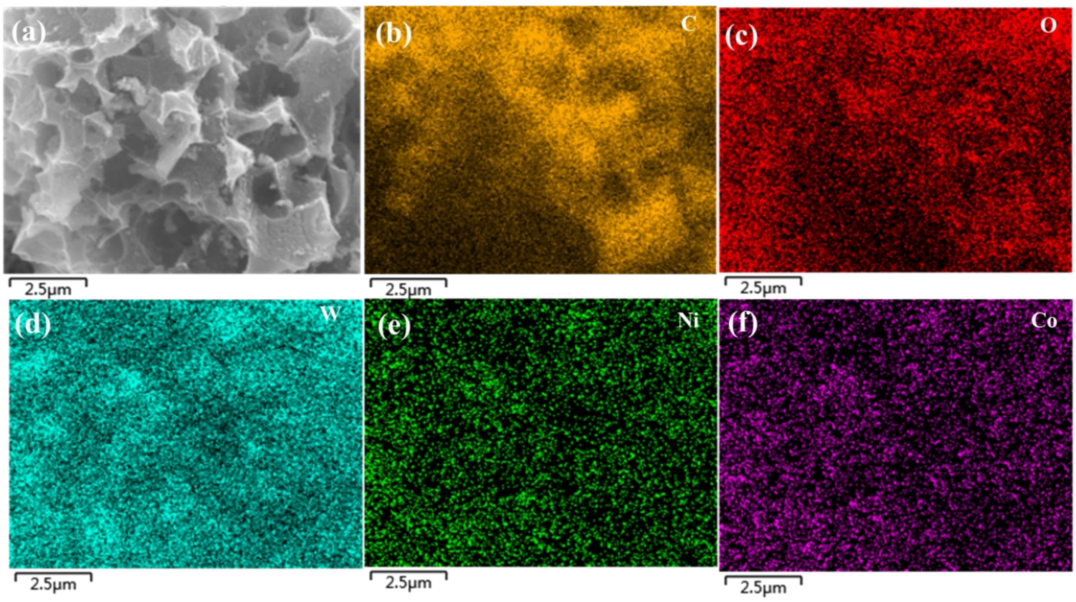

Fig. S2. (a) SEM images of the $Ni_3Co_1WO_4$/HPC, (b-f) EDS spectrum of $Ni_3Co_1WO_4$/HPC nanocomposite.

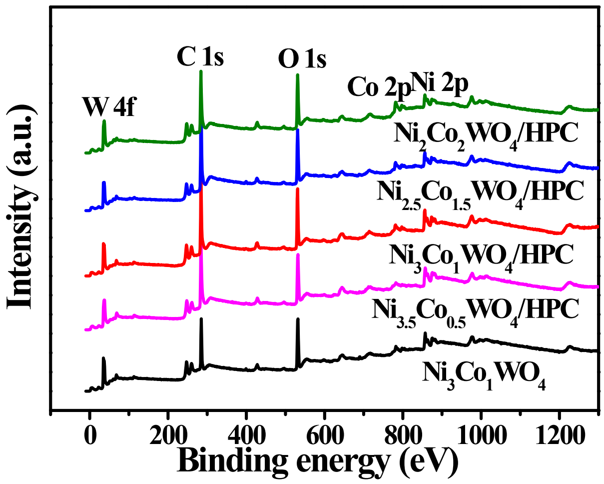

Fig. S3. The high resolution XPS spectra of Survey spectrum.

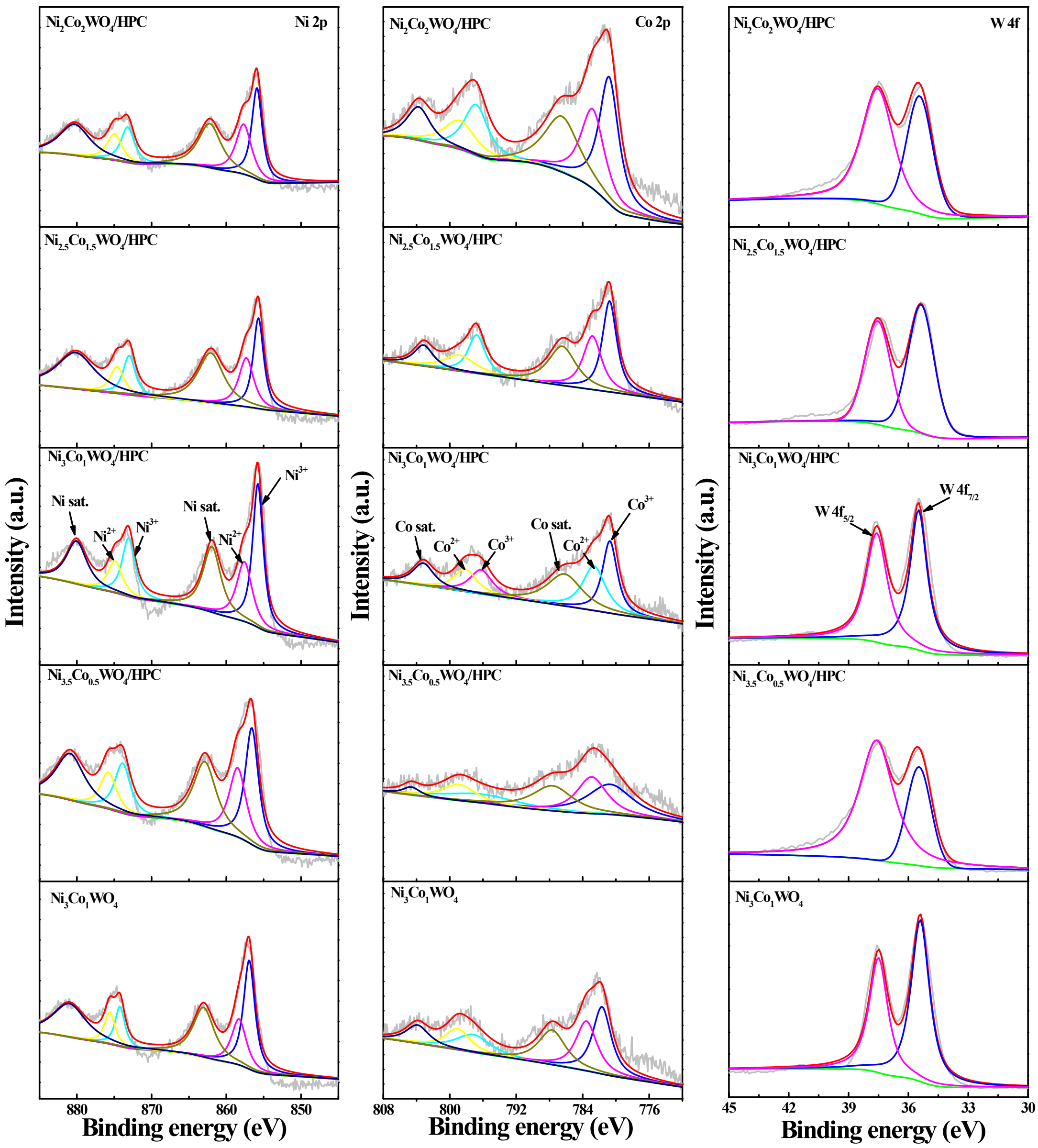

Fig. S4. High resolution XPS spectrum of Ni, Co and W in $Ni_{4-x}Co_xWO_4$/HPC and $Ni_3Co_1WO_4$.

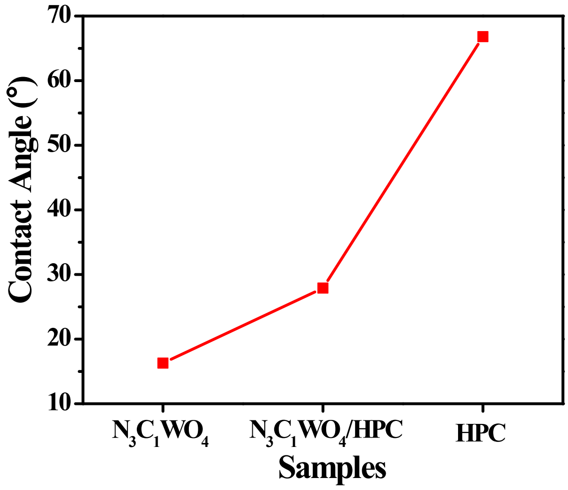

Fig.S5. The contact angles of the Ni_3Co_1W, Ni_3Co_1W/HPC and HPC.

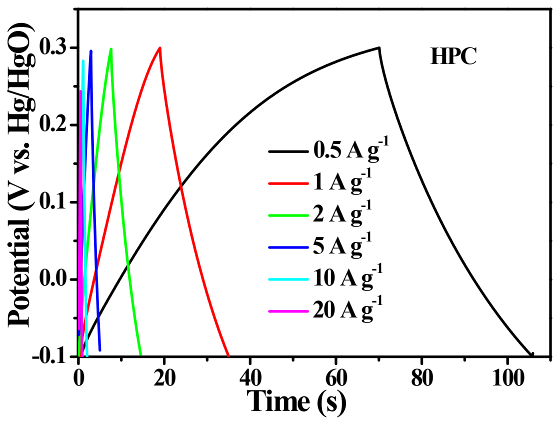

Fig.S6. GCD curves of HPC in a three-electrode system in 6 M KOH.

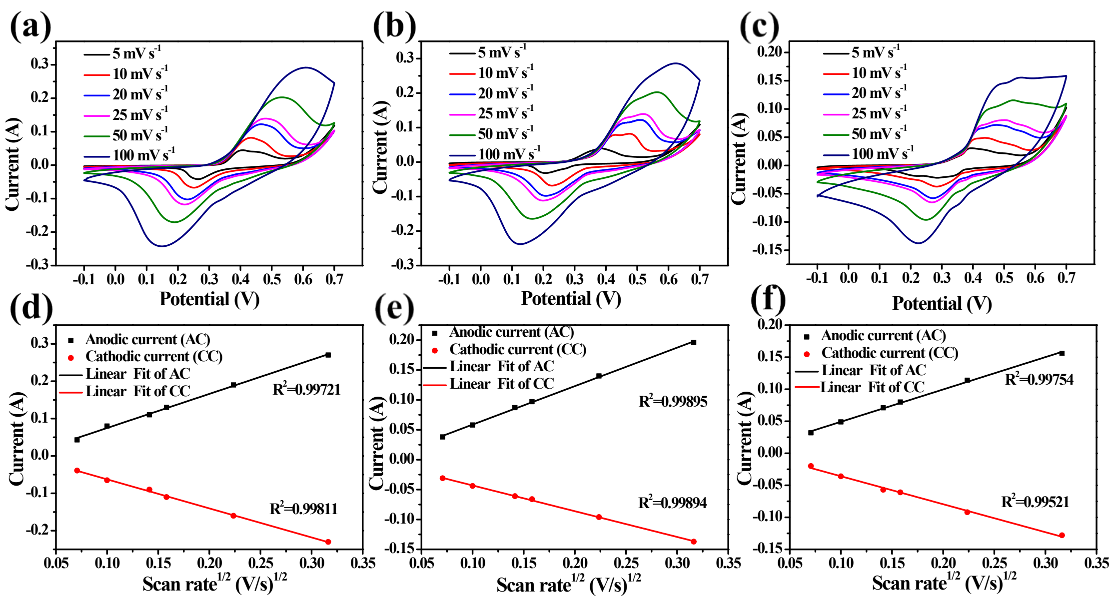

Fig. S7. CV curves at different scan rates of (a) $Ni_{3.5}Co_{0.5}WO_4$/HPC, (b) $Ni_{2.5}Co_{1.5}$ WO_4/HPC, (c)

$Ni_2Co_2WO_4$/HPC, the variation of the current of the cathodic and anodic peaks for the electrodes as a function of the square root of scan rate of (d) $Ni_{3.5}Co_{0.5}WO_4$/HPC, (e) $Ni_{2.5}Co_{1.5}$ WO_4/HPC, and (f) $Ni_{2.5}Co_{1.5}$ WO_4/HPC.

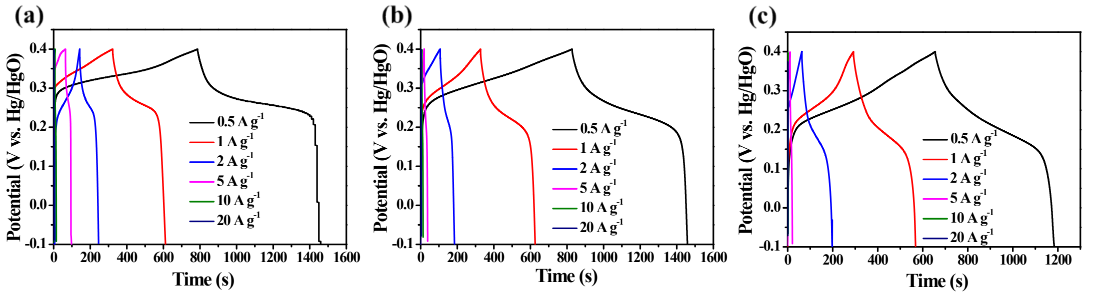

Fig.S8. GCD curves of (a) $Ni_{3.5}Co_{0.5}WO_4$/HPC, (b) $Ni_{2.5}Co_{1.5}WO_4$/HPC and (c) $Ni_2Co_2WO_4$/HPC determined in a three-electrode system in 6M KOH.

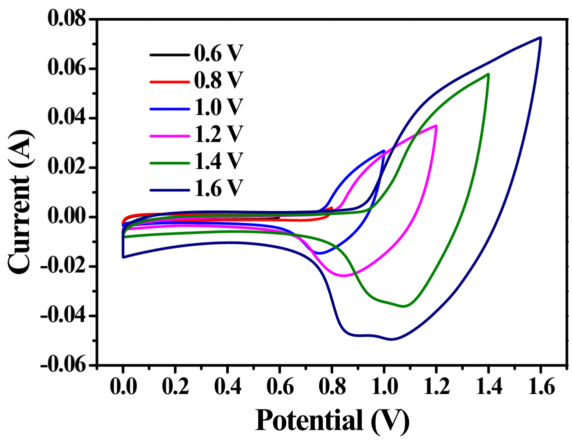

Fig.S9. CV curves of Ni_3Co_1W/HPC nanocomposite in different potential windows in a two-electrode system in 6M KOH.

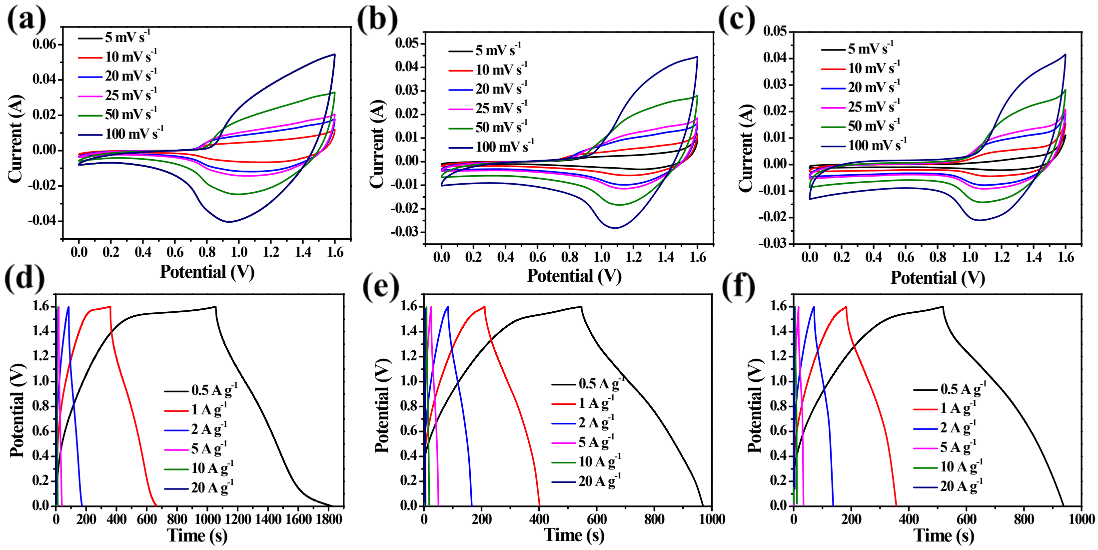

Fig.S10. CV curves of (a) $Ni_{3.5}Co_{0.5}WO_4$/HPC, (b) $Ni_{2.5}Co_{1.5}$ WO_4/HPC and (c) $Ni_2Co_2WO_4$/HPC, GCD curve of (d) $Ni_{3.5}Co_{0.5}WO_4$/HPC, (e) $Ni_{2.5}Co_{1.5}WO_4$/HPC and (f) $Ni_2Co_2WO_4$/HPC determined in a two-electrode system in 6M KOH.

Table S1. Pore textural properties of the pure $NiCoWO_4$ and $NiCoWO_4$/HPC composites.

Sample	**S_{BET} (m^2 g^{-1})**	**S_{micro} (m^2 g^{-1})**	**V_{total} (cm^2 g^{-1})**	**V_{micro} (cm^2 g^{-1})**
$Ni_3Co_1WO_4$	53	-	0.086	-
$Ni_{3.5}Co_{0.5}WO_4$/HPC	282	49	0.44	0.021
$Ni_3Co_1WO_4$/HPC	300	91	0.38	0.041
$Ni_{2.5}Co_{1.5}WO_4$/HPC	281	76	0.29	0.034
$Ni_2Co_2WO_4$/HPC	235	75	0.33	0.033

Table S2. XPS of all the samples.

Samples	Ni^{3+} (at %)	Ni^{2+} (at %)	Ni^{3+}/ Ni^{2+}	Co^{3+} (at %)	Co^{2+} (at %)	Co^{3+}/ Co^{2+}	W (at %)
$Ni_3Co_1WO_4$	5.01	2.74	1.83	1.9	1.62	1.17	5.42
$Ni_{3.5}Co_{0.5}WO_4$/HPC	3.32	1.66	2.00	0.75	0.61	1.23	2.82
$Ni_3Co_1WO_4$/HPC	3.29	1.99	1.65	0.96	0.92	1.04	2.81

Table S3. The fitted result of EIS data.

Sample	**R_{ct}**	**R_s**
$Ni_{3.5}Co_{0.5}WO_4$/HPC	0.54	0.44
$Ni_3Co_1WO_4$/HPC	0.47	0.36
$Ni_{2.5}Co_{1.5}WO_4$/HPC	0.96	0.45
$Ni_2Co_2WO_4$/HPC	1.26	0.45

Table S4. The OH^- diffusion coefficients in $NiCoWO_4$/HPC

Sample	Diffusion coefficients of OH^- ($D_{OH^-} \times 10^{-8}$/$cm^2 \cdot s^{-1}$)	
	Ni^{2+}/Ni^{3+}	$Co^{2+}/Co^{3+}/Co^{4+}$
$Ni_{3.5}Co_{0.5}WO_4$/HPC	7.38	4.65
$Ni_3Co_1WO_4$/HPC	7.95	5.01
$Ni_{2.5}Co_{1.5}WO_4$/HPC	5.2	3.28
$Ni_2Co_2WO_4$/HPC	4.08	2.57

Table S5. The comparison of the electrochemical property of various Co/Ni-based metal tungstates.

Nano-structure	**Preparation method**	**Electrolyte**	**Sc ($F\cdot g^{-1}$/ $C\cdot g^{-1}$)**	**Specifc current**	**Cycling stability**	**Ref.**
$NiWO_4$ nano-structure	Preparation method	2 M KOH	586.2	0.5 $A\cdot g^{-1}$	91.4% over 5000 cycles at 2 A·g–1	1
RGO/$CoWO_4$ nanocomposites	Hydrothermal	2 M KOH	159.9/112.0	5 $mV\cdot s^{-1}$	94.7 % over 1000 cycles at 1 $A\cdot g^{-1}$	2
$CoWO_4$@$NiWO_4$ nanocomposites	Co-precipitation	1 M KOH	746/410	1 $A\cdot g^{-1}$	91.3 % over 2000 cycles at 2 $A\cdot g^{-1}$	3
$NiWO_4$/Ni foam nanostructures	Precipitation	2 M KOH	797.8/359.0	1 $A\cdot g^{-1}$	206 % over 6000 cycles at 50 $mV\cdot s^{-1}$	4
$NiWO_4$ nanoparticles	Precipitation	2 M KOH	173/104	5 $mV\cdot s^{-1}$	90 % over 1000 cycles at 2 $mA\cdot cm^{-1}$	5
Co_3O_4@$CoWO_4$/rGO core–shell arrays	Hydrothermal- annealing	6 M KOH	386/193	0.5 $A\cdot g^{-1}$	\	6
$NiWO_4$/RGO nanocomposite	Solvothermal	2 M KOH	1031.3/618.8	0.5 $A\cdot g^{-1}$	100 % over 5000 cycles at 20 $mV\cdot s^{-1}$	7
$NiWO_4$-$CoWO_4$ nanocomposite	Precipitation	2 M KOH	491.8/196.7	0.5 $A\cdot g^{-1}$	\	8
$CoWO_4$/NRGO	Situ sonochemical approach	2M H_2SO_4	597	5 $mV\cdot s^{-1}$	97.1 % over 4000 cycles at 200 $mV\cdot s^{-1}$	9
$CoWO_4$ nanoparticles	Hydrothermal- annealing	1 M H_2SO_4	378/265	5 $mV\cdot s^{-1}$	95.5 % over 4000 cycles at 200 $mV\cdot s^{-1}$	10
$CoWO_4$@$NiWO_4$-A	Co-precipitation	1 M KOH	677.5	1 $A\cdot g^{-1}$	82 % over 5000 cycles at 5 $A\cdot g^{-1}$	11
Co_3O_4/$CoWO_4$ heterojunctions	Hydrothermal	6 M KOH	396.9	1 $A\cdot g^{-1}$	70.2 % over 2000 cycles at 7 $A\cdot g^{-1}$	12

Nano-structure	Preparation method	Electrolyte	Sc ($F\cdot g^{-1}$/ $C\cdot g^{-1}$)	Specifc current	Cycling stability	Ref.
$NiCo_2O_4$@$NiWO_4$ core-shell nanowire	Hydrothermal- annealing	6 M KOH	1384/692	1 $A\cdot g^{-1}$	87.6 % over 6000 cycles at 1 $A\cdot g^{-1}$	[13]
$Ni_{0.85}Co_{0.15}WO_4$ Nanosheet	Co-precipitation	1 M KOH	360	0.1 $A\cdot g^{-1}$	\	[14]
$NiWO_4$ nanowires	Solvothermal	6 M KOH	1190/595	0.5 $A\cdot g^{-1}$	\	[15]
$CoNiWO_4$/P-S-GNS nanocomposite	Hydrothermal	6 M KOH	1298.6	0.5 $A\cdot g^{-1}$	95.5 % over 7000 cycles	[16]
2D CNWO porous thin sheets	Hydrothermal	6 M KOH	1392/626.4	1 $A\cdot g^{-1}$	105.27 % over 10,000 cycles at 10 $A\cdot g^{-1}$	[17]
CoWO4/Ni anocomposite	Co-precipitation	6 M KOH	271	1 $A\cdot g^{-1}$	86.4 % over 1,500 cycles at 5 $A\cdot g^{-1}$	[18]
$Ni_{0.5}Co_{0.5}WO_4$	Hydrothermal	3 M KOH	34.55	1 $A\cdot g^{-1}$	92 % over 10,000 cycles at 10 $A\cdot g^{-1}$	[19]
$NiWO_4$ nanoparticles	Hydrothermal	2 M KOH	427	1 $A\cdot g^{-1}$	99 % over 1000 cycles	[20]
P-$NiWO_4$@$CoWO_4$	Hydrothermal	6 M KOH	1683.4	1 $A\cdot g^{-1}$	84 % over 1000 cycles at 1 $mA\cdot cm^{-1}$	[21]
$Ni_3Co_1WO_4$/HPC	**Co-precipitation**	**6 M KOH**	**1084**	**0.5 $A\cdot g^{-1}$**	**80.74 % over 10,000 cycles at 10 $A\cdot g^{-1}$**	**This work**

References

1. Z. L. L Niu, Y Xu, J Sun, W Hong, X Liu, J Wang, and S Yang, *ACS Applied Materials Interface*, 2013, **5**, 8044-8052.
2. X. Xu, J. Shen, N. Li and M. Ye, *Electrochimica Acta*, 2014, **150**, 23-34.
3. X. Xu, J. Gao, G. Huang, H. Qiu, Z. Wang, J. Wu, Z. Pan and F. Xing, *Electrochimica Acta*, 2015, **174**, 837-845.
4. G. He, J. Li, W. Li, B. Li, N. Noor, K. Xu, J. Hu and I. P. Parkin, *Journal of Materials Chemistry A*, 2015, **3**, 14272-14278.
5. S. R. E. U Nithiyanantham, S Anantharaj, and Subrata Kundu, *Crystal Growth & Design*, 2014, DOI: 10.1021/cg501366d.
6. Y. Y. Xiaowei Xu, Man Wang, Pei Dong, Robert Baines, Jianfeng Shen, Mingxin Ye, *Ceramics International*, 2016, DOI: 10.1016/j.ceramint.2016.03.192.
7. X. Xu, L. Pei, Y. Yang, J. Shen and M. Ye, *Journal of Alloys and Compounds*, 2016, **654**, 23-31.
8. C. S. Yidan Wang, Lengyuan Niu, Zhenkun Sun, Fengping Ruan, Man Xu, Shen Shan, Can Li, Xinjuan Liu, Yinyan Gong, *Materials Chemistry & Physics*, 2016, **182**, 394-401.
9. H. R. Naderi, A. Sobhani-Nasab, M. Rahimi-Nasrabadi and M. R. Ganjali, *Applied Surface Science*, 2017, **423**, 1025-1034.
10. K. Adib, M. Rahimi-Nasrabadi, Z. Rezvani, S. M. Pourmortazavi, F. Ahmadi, H. R. Naderi and M. R. Ganjali, *Journal of Materials Science: Materials in Electronics*, 2016, **27**, 4541-4550.
11. D. A. M Feng, H Zhang, G Ma, C Zhang and Z Ma, *International Journal of Chemical Studies*, 2017, **5**, 1954-1960.
12. X. Z. K Ding, J Li, P Yang, X Cheng, *ChemElectroChem*, 2017, **4**, 3011-3017.
13. S. Chen, G. Yang, Y. Jia and H. Zheng, *Journal of Materials Chemistry A*, 2017, **5**, 1028-1034.
14. Y. Huang, C. Yan, X. Shi, W. Zhi, Z. Li, Y. Yan, M. Zhang and G. Cao, *Nano Energy*, 2018, **48**, 430-440.
15. J. Tian, Y. Xue, X. Yu, Y. Pei, H. Zhang and J. Wang, *RSC Advances*, 2018, **8**, 41740-41748.
16. A. S. Rajpurohit, N. S. Punde, C. R. Rawool and A. K. Srivastava, *Chemical Engineering Journal*, 2019, **371**, 679-692.
17. B. Huang, H. Wang, S. Liang, H. Qin, Y. Li, Z. Luo, C. Zhao, L. Xie and L. Chen, *Energy Storage Materials*, 2020, **32**, 105-114.
18. K. Thiagarajan, D. Balaji, J. Madhavan, J. Theerthagiri, S. J. Lee, K. Y. Kwon and M. Y. Choi, *Nanomaterials (Basel)*, 2020, **10**.
19. S. Prabhu, C. Balaji, M. Navaneethan, M. Selvaraj, N. Anandhan, D. Sivaganesh, S. Saravanakumar, P. Sivakumar and R. Ramesh, *Journal of Alloys and Compounds*, 2021, **875**, 160066.
20. R. Packiaraj, P. Devendran, K. S. Venkatesh and N. Nallamuthu, *Inorganic Chemistry Communications*, 2021, **126**, 108490.
21. Q. H. Wenkang Miaoa, Hongming Zhanga, Kangli Chena, Lu Zhanga, Yuan Lia,⁎ and S. H. , *Journal of Alloys and Compounds*, 2021, **877**, 160301.