## Modified Co<sub>4</sub>N by B-doping for high performances hybrid

## supercapacitors

Zonghua Wang<sup>1</sup>, Guangmeng Qu<sup>1</sup>, Chenggang Wang, Xixi Zhang, Guotao Xiang,

Peiyu Hou, Xijin Xu\*

School of Physics and Technology, University of Jinan, Shandong 250022, P.R.

China

Corresponding authors: (Xijin Xu) <u>sps\_xuxj@ujn.edu.cn</u>

<sup>1</sup>The authors contribute equally to the manuscript.



Fig. S1 SEM image of Co(OH)<sub>2</sub>.



Fig. S2 XRD spectrum image of  $Co_4N$ .



Fig. S3 SAED pattern of B-Co<sub>4</sub>N-20.



Fig. S4 EDS spectrum of B-Co<sub>4</sub>N-20.



Fig. S5 XPS survey of B-Co<sub>4</sub>N-20.



**Fig. S6** Plots of N<sub>2</sub> adsorption-desorption isotherm and pore size distribution of (a) Co<sub>4</sub>N/NF (b) B-Co<sub>4</sub>N-20/NF (c) pure Ni foam



Fig. S7 CV curves of (a) B-Co<sub>4</sub>N at 10 mV/s (b) Co<sub>4</sub>N (c) B-Co<sub>4</sub>N-12 (d) B-Co<sub>4</sub>N-16 (e) B-Co<sub>4</sub>N-24.



Fig. S8 GCD curves of a) B-Co<sub>4</sub>N at 1 A  $g^{-1}$  (b) Co<sub>4</sub>N (c) B-Co<sub>4</sub>N-12 (d) B-Co<sub>4</sub>N-16 (e) B-Co<sub>4</sub>N-24.



Fig. S9 Ratio image of B-Co<sub>4</sub>N.



Fig. S10 Equivalent circuit image of EIS fitting.



Fig. S11 SEM images of B-Co<sub>4</sub>N-20/NF after 5000 cycles.



Fig. S12 XRD spectrum of  $B-Co_4N-20/NF$  after 5000 cycles.



Fig. S13 XPS B1s spectrum of B-Co<sub>4</sub>N-20/NF after 5000 cycles.

| Materials                              | Morphology           | Electrolyte                         | Capacitance  | Cycle retention                     | Ref.      |
|--|----------------------|-------------------------------------|--|-------------------------------------|-----------|
| CoS/N-doped C dots                     | Flower-like          | 3.0M KOH                            | 697 F g <sup>-1</sup> (1A g <sup>-1</sup> )  | 80.3% (10000 th)                    | 1         |
| CoS                                    | Flower-like          | 6.0M KOH                            | 348 F g <sup>-1</sup> (1A g <sup>-1</sup> )  | 97.2% (1000 th)                     | 2         |
| Co <sub>9</sub> S <sub>8</sub>         | Nanosheets           | 1.0M KOH                            | 954.5 F g <sup>-1</sup> (1A g <sup>-1</sup> )  | 87.4% (1000th)                      | 3         |
| Co <sub>3</sub> O <sub>4</sub>         | Nanocrystals         | 0.5M H <sub>3</sub> PO <sub>4</sub> | 1049 F g <sup>-1</sup> (1mV s <sup>-1</sup> )  | 100%(20000th)*                      | 4         |
| СоР                                    | Hollow microspheres  | 6.0M KOH                            | 449.4 F g <sup>-1</sup> (1A g <sup>-1</sup> )  | 80.9%(3000th)                       | 5         |
| СоР                                    | Microcubes           | 6.0M KOH                            | 560 F g <sup>-1</sup> (1A g <sup>-1</sup> )  | 91.2%(10000th)                      | 6         |
| CoSe                                   | Nanosheets           | 2.0M KOH                            | 70.6 (1A g <sup>-1</sup> )   | 95.4%(20000th)                      | 7         |
| CoSe <sub>2</sub>                      | Nanoparticles        | 6.0M KOH                            | 120.2 mAh g <sup>-1</sup> (1A g <sup>-1</sup> )  | 92 % (10000th)                      | 8         |
| Co <sub>0.85</sub> Se                  | Hollow spheres       | 2.0M KOH                            | 1220 F g <sup>-1</sup> (1A g <sup>-1</sup> )   | 88.8 % (10000th)*                   | 9         |
| CoS <sub>2</sub>                       | Hollow dodecahedrons | 2.0M KOH                            | 375.2 C g <sup>-1</sup> (1A g <sup>-1</sup> )  | 92.1 % (5000th)*                    | 10        |
| CoNi-MOF                               | Nanosheets           | 1.0M KOH                            | 1044 F g <sup>-1</sup> (1A g <sup>-1</sup> )   | 94 % (5000th)                       | 11        |
| Co <sub>3</sub> O4/Co(OH) <sub>2</sub> | Nanopolyhedron       | 1.0M KOH                            | 184.9 mAh g <sup>-1</sup> (1A g <sup>-1</sup> )  | 91 % (5000th)                       | 12        |
| VN                                     | Nano-tree-like       | 0.5M K <sub>2</sub> SO4             | 37.5 mF cm <sup>-2</sup>   | 85 % (20000th)                      | 13        |
| TiN/MoN <sub>x</sub>                   | Moss-like nanosheet  | 1.0M KOH                            | 174.83 F g <sup>-1</sup> (1.5A g <sup>-1</sup> )   | 93.8 % (1000th)                     | 14        |
| C/Mo <sub>x</sub> N                    | Nanofibers           | 1.0M H <sub>2</sub> SO <sub>4</sub> | 251 F g <sup>-1</sup> (1A g <sup>-1</sup> )  | 78.6 % (15000th)*                   | 15        |
| W <sub>2</sub> N                       | Film                 | 1.0M H <sub>2</sub> SO <sub>4</sub> | 163 F g <sup>-1</sup> (0.5 mA cm <sup>-2</sup> )   | 94 % (10000th)                      | 16        |
| CrN                                    | Nanoparticles        | 1.0M LiPF <sub>6</sub>              | 75 F g <sup>-1</sup> (30 mA g <sup>-1</sup> )  | 100 % (120th)                       | 17        |
| TiN                                    | Nano-pyramid         | 1.0M KOH                            | 385 F g <sup>-1</sup> (1A g <sup>-1</sup> )  | 92.6 % (30000th)*                   | 18        |
| Ni <sub>3</sub> N                      | Nanosheets           | 1.0M KOH                            | 845 F g <sup>-1</sup> (10 mV s <sup>-1</sup> )   | 50 % (2000th)                       | 19        |
| h-BN/C                                 | Nanosheets           | 2.0M KOH                            | 250 F g <sup>-1</sup> (0.5A g <sup>-1</sup> )  | 86 % (1000th)                       | 20        |
| TiN                                    | Nanoparticles        | 1.0M H <sub>2</sub> SO <sub>4</sub> | 120 F cm <sup>-3</sup> (0.83mA cm <sup>-3</sup> )  | 99 % (3000th)                       | 21        |
| B-Co <sub>4</sub> N-20/NF              | Nanoneedles          | 3.0M KOH                            | 817.9 C g <sup>-1</sup> (1A g <sup>-1</sup> )<br>743.5 C g <sup>-1</sup> (1A g <sup>-1</sup> ) | 93.06% (5000th)<br>98.59% (5000th)* | This work |

Table S1. The summary of some recent similar works.

\*corresponding two-electrode device



Fig. S14 CV curves and GCD curves of AC/CF.

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