

## Electronic Supplementary Information (ESI)

### B/N co-doped carbon nanosphere frameworks as high-performance electrodes for supercapacitors

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#### 1. Supplementary Methods:

##### *Preparation of the electrode*

The Ti foil was cut into rectangle pieces with dimension of 1.5x1 cm and 1x0.5 cm rectangle end was left as current collector. Around 1 mg sample with weight ratio (B/N-CNS: super-P: PVDF=85:10:5) was coated on the Ti foil surface. The electrodes were dried in vacuum at 70 °C for 12 h.

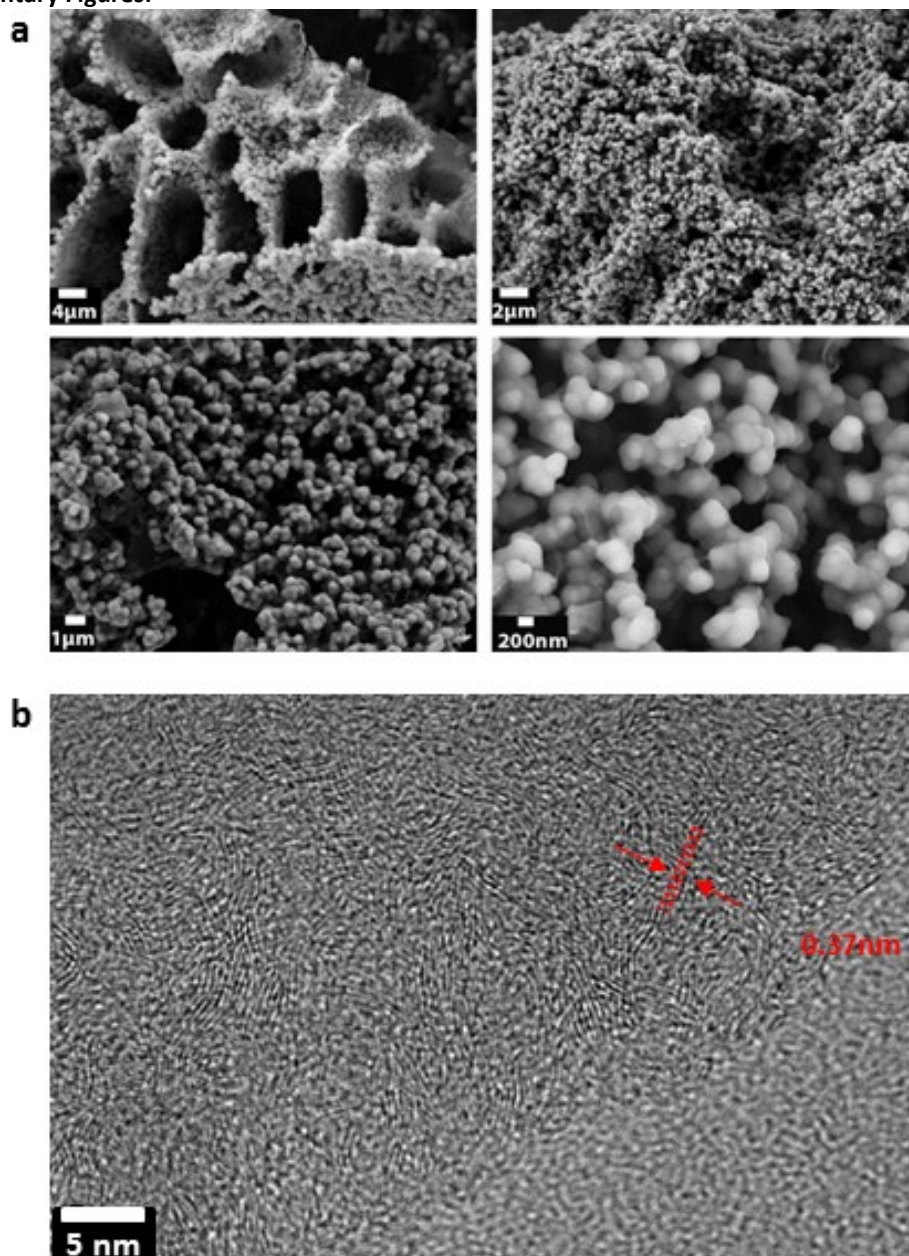
##### *Preparation of the solid gel electrolyte*

The gel electrolyte was prepared by mixing 1 g H<sub>2</sub>SO<sub>4</sub> and 1 g PVA in 10 ml deionized water at 85 °C for 1 h under vigorous stirring. The resulting gel solution was cooled to room temperature. The electrode was soaked in the gel solution for 5 minutes. After that, the gel electrolyte was further dipped onto the surface of the electrode to ensure the contact.

##### *Preparation of the sandwich-structured symmetrical supercapacitor*

After the electrode was sufficiently infiltrated with the gel electrolyte and solidified for 12 h at room temperature, the as-prepared two electrodes were symmetrically integrated into one cell. And a piece of adhesive tape was adhered on the outer layer of the Ti foil to prevent the short circuit (Fig. S6).

## 2. Supplementary Figures:



**Fig. S1** a) SEM images showing the morphology of B/N co-doped carbon nanospheres frameworks at different magnifications. b) HRTEM image of B/N co-doped carbon nanosphere frameworks.

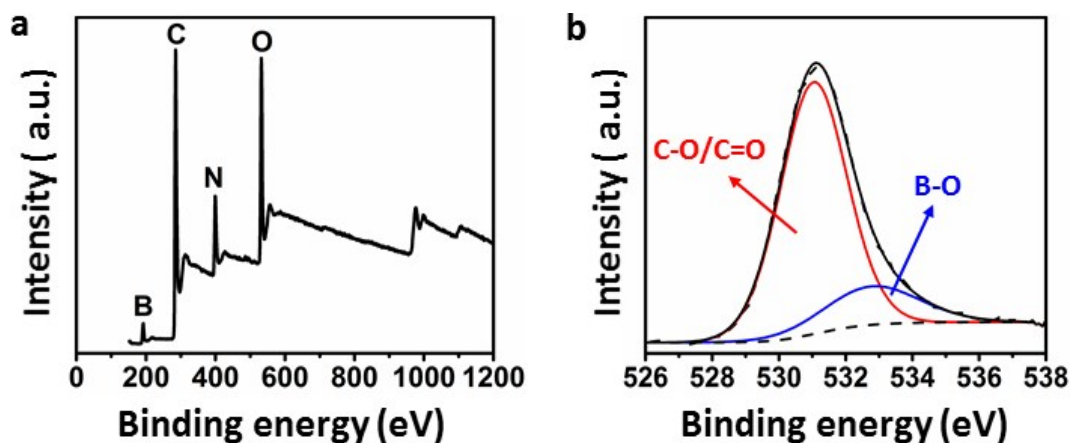


Fig. S2 a) XPS survey spectrum and b) O 1s spectrum of B/N co-doped carbon nanosphere frameworks.

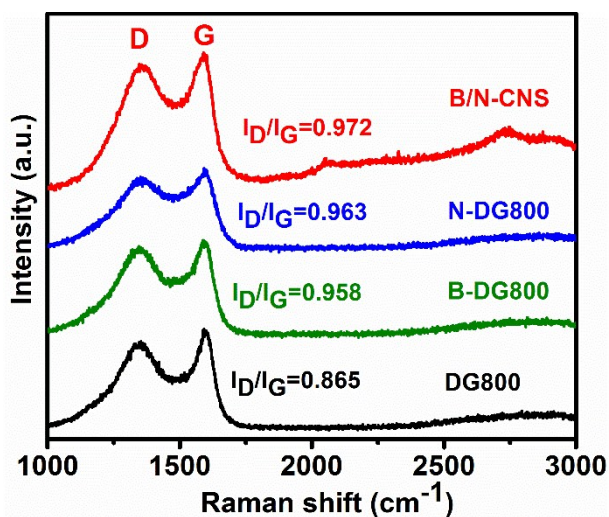
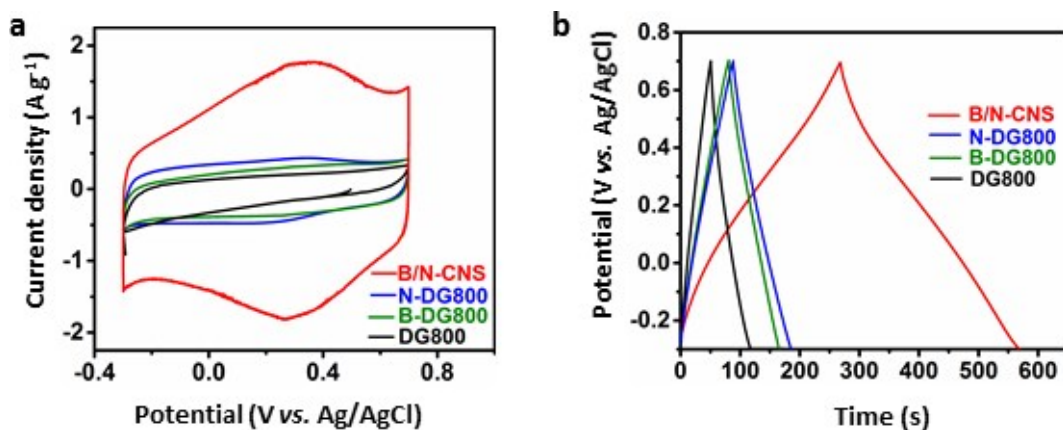
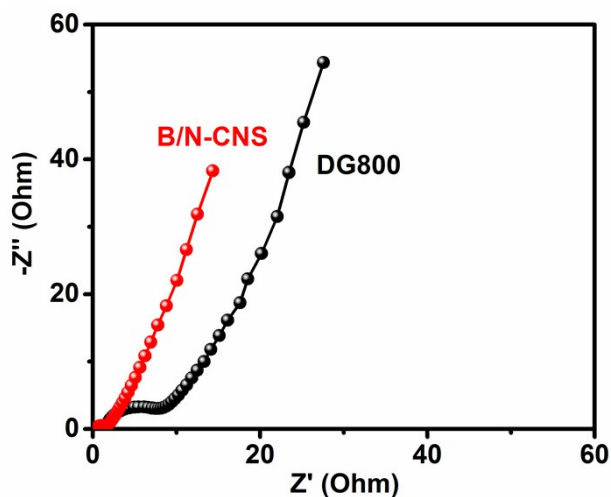


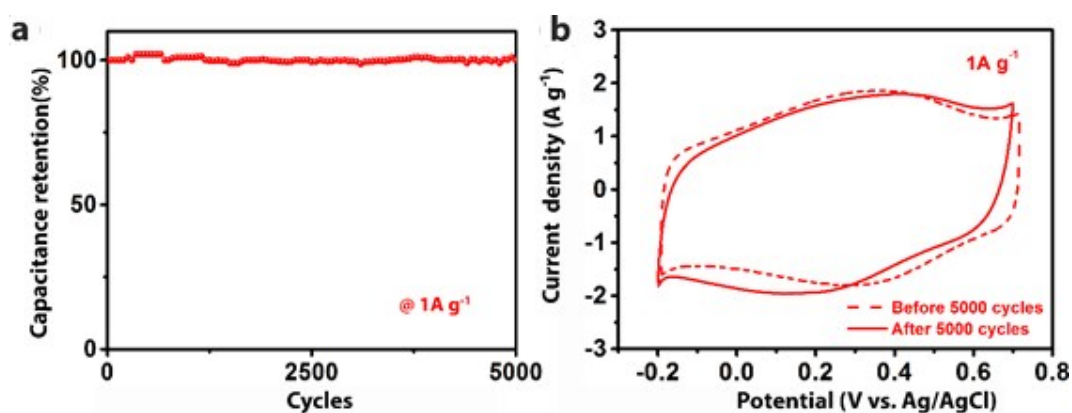
Fig. S3 Raman spectra of B/N co-doped carbon nanosphere frameworks (B/N-CNS), N doped carbon (N-DG800), B doped carbon (B-DG800) and pure carbon (DG800).



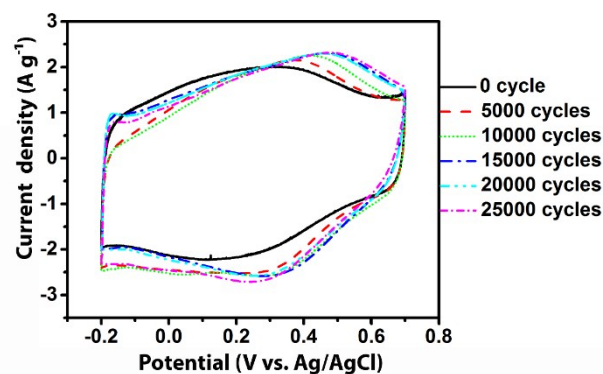
**Fig. S4** a) CV curves (at  $5 \text{ mV s}^{-1}$ ) and GCD curves (at  $1 \text{ A g}^{-1}$ ) of B/N co-doped carbon nanosphere frameworks (B/N-CNS), N doped carbon (N-DG800), B doped carbon (B-DG800) and undoped carbon (DG800).



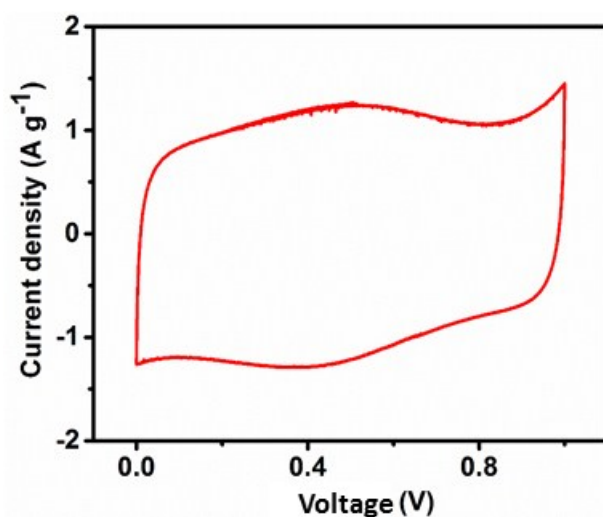
**Fig. S5** Nyquist plots of electrochemical impedance of B/N co-doped carbon nanosphere frameworks (B/N-CNS) and undoped carbon (DG800) in the frequency range of 100 kHz to 10 mHz.



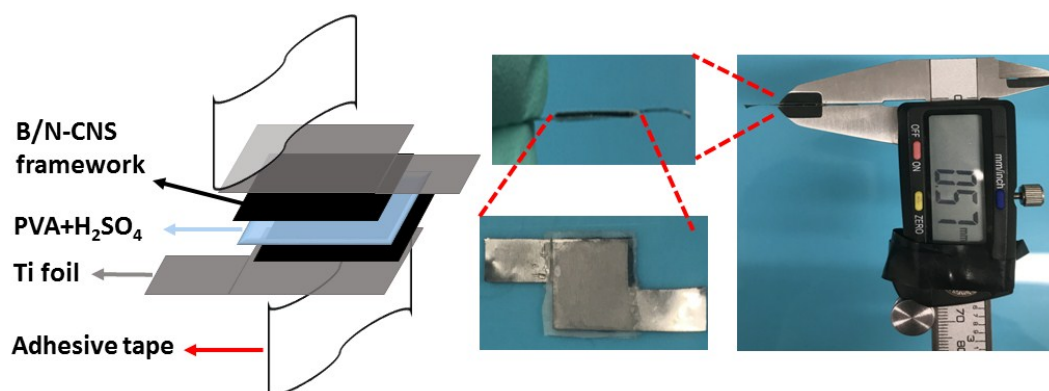
**Fig.S6** Long cycle stability of B/N-CNS framework electrodes in  $1 \text{ M H}_2\text{SO}_4$  electrolyte at  $1 \text{ A g}^{-1}$ . a) Capacitance retention within 5000 cycles at  $1 \text{ A g}^{-1}$ . b) CV curves before and after 5000 cycles at  $1 \text{ A g}^{-1}$ .



**Fig. S7** The CV curves ( $5 \text{ mV s}^{-1}$ ) after 5000, 15000, 20000 and 25000 cycles of charge-discharge at  $10 \text{ A g}^{-1}$ . It could be observed that the area of the CV curves increased within 10000 cycles and remained nearly unchanged after 10000 cycles, in accordance with the retention rate.



**Fig. S8** The CV curve of symmetric supercapacitor based on two electrodes of B/N-CNS framework at a scan rate of  $5 \text{ mV s}^{-1}$  with a 1 V voltage window. The CV curve shape is symmetrical.



**Fig. S9** Schematic configuration and pictures of the all-solid sandwich-structured symmetric supercapacitor cell. The loading mass was around 1 mg B/N-CNS framework for a single Ti foil. The thickness and weight for one

cell was around 0.57 mm and 200 mg, respectively. Two cells in series connection were able to power a LED bulb.

### 3. Supplementary tables:

**Table S1** Capacitive performance comparison of B/N-CNS framework and other reported B, N doped carbon nanomaterials.

Samples	Maximum specific capacitance (F g <sup>-1</sup> )*	Corresponding current density (A g <sup>-1</sup> )	Cycles	Retention (%)	Corresponding current density (A g <sup>-1</sup> )	Refs
B/N-CNS framework	423	0.2	30000	106	10	This work
B/N-carbon nanosheets film	358	0.1	10000	105	5	3
Polyaniline/boron-doped graphene	247	0.5	10000	90	10	4
B/N co-doped porous carbon	304	0.1	10000	93	2	5
N/B co-doped local graphitized carbon framework	247	0.5	4000	96.2	1	6
BCN-3:1 nanosheets	244	1	2500	96	5	7
BCN 700 nanosheets	130.7	0.2	2000	97.5	5	8
Vertical aligned-BCN nanotubes	320.1	0.2	1000	95	1	9

\* The maximum specific capacitances calculated here and estimated in the literature are based on the GCD process with corresponding discharge current density.

### References

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Journal Name

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