# **Supporting information**

## Fabrication of Vanadium Nitride/N-Doped Carbon Hollow

### Nanospheres Composite as an Efficient Electrode Material for

## **Asymmetric Supercapacitors**

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#### Experimental

#### 1. Material characterization

The crystal structures of all the obtained samples were identified by X-ray power diffraction (XRD, Smart Lab). The chemical composition of VN/NCS composite was tested on X-ray photoelectron spectroscope (XPS, ESCALAB 250). The morphologies of the assynthesized samples were obtained from transmission electron microscopy (TEM, JEM-2100 F) and scanning electron microscope (SEM, HITACHI SU8010). Nitrogen absorption-desorption measurement was performed on a MT 3000 analyzer at 77.4 K.

#### 2. Electrochemical measurements

The electrochemical properties of the as-prepared electrode materials were estimated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and the electrochemical impedance spectroscopy (EIS) on CHI660D workstation in a standard three-electrode system in a 2 M KOH electrolyte. Platinum sheet and Hg/HgO electrode were used as a counter electrode and a reference electrode, respectively. After coating the mixture paste of active material (80 wt.%), acetylene black (15 wt.%) and polyvinylidene difluoride (PVDF) (5 wt.%) on the nickel foam, the working electrode was dried for 12 h, and the loading mass of active material on the working electrode is about 2 mg.

The specific capacitance ( $C_s$ ) of the electrode material was assessed by equation (a), where I(A),  $\Delta t(s)$ ,  $\Delta V(V)$  and m(g) in the equation represent the discharge current, discharge time, operating potential window and mass of the active material, respectively. The coulombic efficiency is calculated by the equation (d), where  $t_c$  and  $t_d$  are the charge and discharge times, and  $\eta$  is the coulombic efficiency.

The capacitive contribution of the VN/NCS, NCS, and VN NWs electrodes is calculated by the equation (c), where i, v are the current and the scan rate, respectively, a and b are constants. The detailed calculation process is given as follows:

In the case of EDLC and the diffusion-controlled process, b is equal to 1 and 0.5, respectively. Following this concept, we can divide the equation as:

$$i(V) = kv + k'v^{0.5}$$

where *i* is the current under a fixed voltage (V), *k* and *k'* are constants. By simply plotting the relationship between *i* and  $v^{0.5}$ , we can obtain the slope *k*. Finally, the capacitive contribution

of these samples is plotted and showed in Figure. 6 by calculating the k value at different voltages under different scan rates.

In addition, the energy density (*E*) and the power density (*P*) are utilized to evaluate the electrochemical properties of the V<sub>2</sub>O<sub>3</sub>/C//VN/NC ASC device according to equation (d) and (e), respectively, where C (F g<sup>-1</sup>) is the specific capacitance and  $\Delta V$  (V) is the operating potential window,  $\Delta t$  (s) is the discharge time.

$C_{\rm s} = I/m \times \Delta t/\Delta V$	(a)
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$$\eta = t_{\rm c}/t_{\rm d} \tag{b}$$

$$i = av^b$$
 (c)

$$E = 0.5 \times C \times \Delta V^2 \tag{d}$$

$$P = E/\Delta t \tag{e}$$



Figure S1. XRD pattern of V<sub>2</sub>O<sub>3</sub>/C nanocomposite.



Figure S2. SEM images of (a) NCS and (b) VN NWs.



Figure S3. TEM image of V<sub>2</sub>O<sub>3</sub>/C composite.



Figure S4. The coulombic efficiency of VN/NCS electrode at the various current densities (0.5-20 A  $g^{-1}$ ).



Figure S5. (a) Coulombic efficiency of the ASC device at the current density of 1-10 A g<sup>-1</sup>, (b)

Long-term cycling stability of the assembled ASC device at a current density of 5 A  $g^{-1}$ .



Figure S6. Nyquist plots of the ASC device before and after 5000 cycles.