

A Facile Strategy for Fabricating the Hierarchical Nanocomposites of V<sub>2</sub>O<sub>5</sub> Nanowire Arrays on Three-Dimension N-doped Graphene aerogel with Synergistic Effect for Supercapacitor†

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**Computational methods.** Density functional theory (DFT) analysis was applied to investigate the crystal structures of graphene, N-doped graphene and the growth of VO<sub>x</sub> on it. All the calculations in this paper were performed by using the Vienna ab initio simulation package (VASP),<sup>1</sup> the exchange and correlation energy functional was treated by the Perdew-Burke-Ernzerh of variant of the generalized gradient approximation (GGA).<sup>2</sup> Interaction between ion and electrons were described with projector augmented wave pseudo potentials (PAW) approach,<sup>3,4</sup> and the energy cutoff for the plane wave basis set was set to be 400 eV. All calculations were considered in the spin-unrestricted manner, but no magnetic moments were detected. The first Brillouin zone was sampled using a 5 × 5 × 1  $\Gamma$ -centered k-point grid. The vacuum slab was set to be 15 Å.

## EXPERIMENTAL

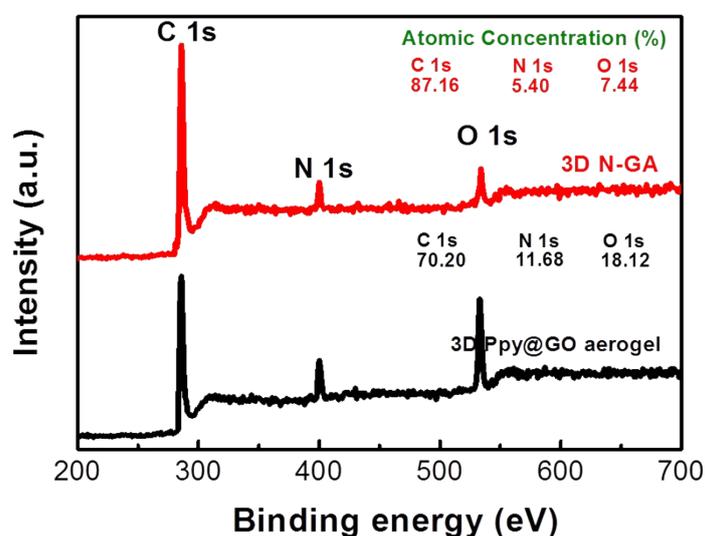
**Synthesis of N-GA.** All the chemicals are obtained as chemically pure grade products and used without any further treatment. Graphene oxide (GO) was prepared from commercially available graphite flakes according to the modified Hummers method in our previous paper. N-doped graphene aerogel (N-GA) was synthesized by following the procedure reported elsewhere with slight modifications. In a typical procedure, 0.5 mL pyrrole monomer was suspended in 10 mL GO aqueous dispersion ( $3 \text{ mg L}^{-1}$ ) and thoroughly dispersed with ultrasonic treatment for 15 min. Then, the pH was adjusted in the range 11.1-11.3 with moderate ethylenediamine under vigorous stirring at room temperature. After 10 min, the resulting suspension was sealed in a glass vial and heated for 8 h at  $90 \text{ }^\circ\text{C}$  for preparation of hydrogel. Finally, N-GA was obtained after heating the pre-freeze-dried graphen gel at  $900 \text{ }^\circ\text{C}$  for 3 h under Ar atmosphere.

**Preparation of the N-GA@V<sub>2</sub>O<sub>5</sub> NWAs.** The prepared N-GA was used as the backbone for the growth of V<sub>2</sub>O<sub>5</sub> NWAs by a facile hydrothermal synthesis method. 0.3 g commercial V<sub>2</sub>O<sub>5</sub> powder and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O in a molar ratio of 1:3 was dissolved in 15 mL of deionized H<sub>2</sub>O under vigorous stirring at  $65 \text{ }^\circ\text{C}$  for 1 h until a clear dark blue solution was formed. Then 2.5 mL of 30 % H<sub>2</sub>O<sub>2</sub> was added and kept continuously stirring for about 20 min, followed by addition of 60 mL ethanol. After putting N-GA cylinder ( $\Phi 2\text{cm} \times 2 \text{ cm}$ ), the solution was then transferred into a Teflon-lined stainless autoclave. The autoclave was sealed and maintained at  $160 \text{ }^\circ\text{C}$  for 2 h. After the autoclave cooled down to room temperature, the product was washed, freeze dried and then thermal treated at  $300 \text{ }^\circ\text{C}$  for 2 h to obtain the N-GA@V<sub>2</sub>O<sub>5</sub> NWAs.

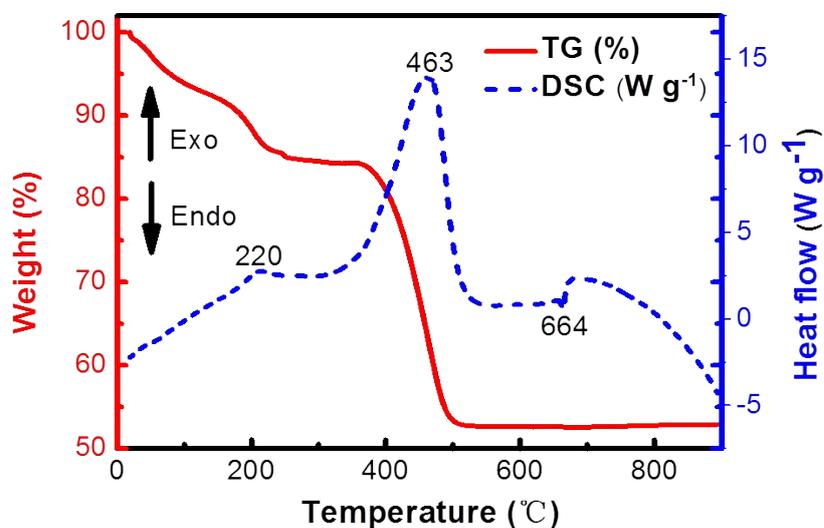
**Characterization.** The as-prepared samples were characterized by SEM (XL30FEG), TEM (JEOL-2100 TEM operating at 200 kV), FTIR spectroscopy (Bruker-TEMSOR27), and rotation anode X-ray powder diffraction (XRD) (Rigaku D/max-C) equipped with Cu K $\alpha$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ). Raman spectra (Jobin-Yvon HR800) were recorded by using a 514 nm argon ion laser (source power 17 mW). X-Ray photoelectron spectroscopy (XPS) was performed using a PHI 5300 spectrometer (Perkin-Elmer) operated at 14 kV. N<sub>2</sub> sorption measurements were operated with Autosorb-1 (Quantchome, USA) at 77 K using Barrett-Emmett-Teller (BET) calculations for the surface area. The pore size distribution plot was recorded from the adsorption branch of the isotherm based on the Barrett-Joyner-Halenda (BJH) model. The thermogravimetry analysis (TGA) and differential thermogravimetry analysis (DTG) were carried out on a SDT Q600 over the temperature range from 50 to 900 °C using a heating rate of 10 °C min<sup>-1</sup> under air atmosphere.

**Electrochemical performance measurements.** Electrochemical measurements were carried out using three-electrode systems by using a 8 M LiCl aqueous solution as electrolyte. The mixture containing 85 wt% active material, 10 wt% conducting acetylene black, and 5 wt% poly(vinylidene fluoride) (PVDF) was well mixed by using N-methylpyrrolidone (NMP) as the solvent. The as-prepared mixed slurry (about 1 mg) was coated onto graphite paper with area of 1 cm<sup>2</sup> and then the electrode was dried at 120 °C for 12 h under vacuum to remove the solvent. Cyclic voltammetry (CV) and galvanostatic charge/discharge curves were measured by a CHI 660D electrochemical workstation with the potential being swept from -0.3 to +0.7 V. For electrochemical

impedance spectroscopy (EIS), the amplitude of the sine perturbation signal was 5 mV, and the frequency was scanned from the highest (100 kHz) to the lowest (10 mHz). The specific capacitance was calculated according to the equation as  $C = I\Delta t/m\Delta V$ , where  $I$  is the discharge current (A),  $\Delta t$  is the discharge time,  $m$  is the total mass of active material, and  $\Delta V$  is the discharge voltage. The energy and powder densities were estimated by using the formula  $E = C(\Delta V)^2/2$  and  $P = Q\Delta V/2t = E/\Delta t$ .

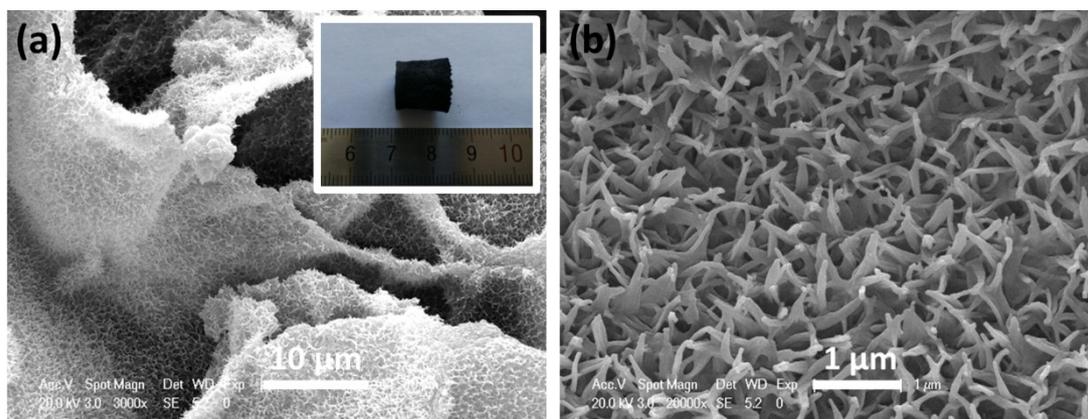


**Figure S1.** XPS spectrum of the 3D Ppy@GO aerogel and 3D N-GA.

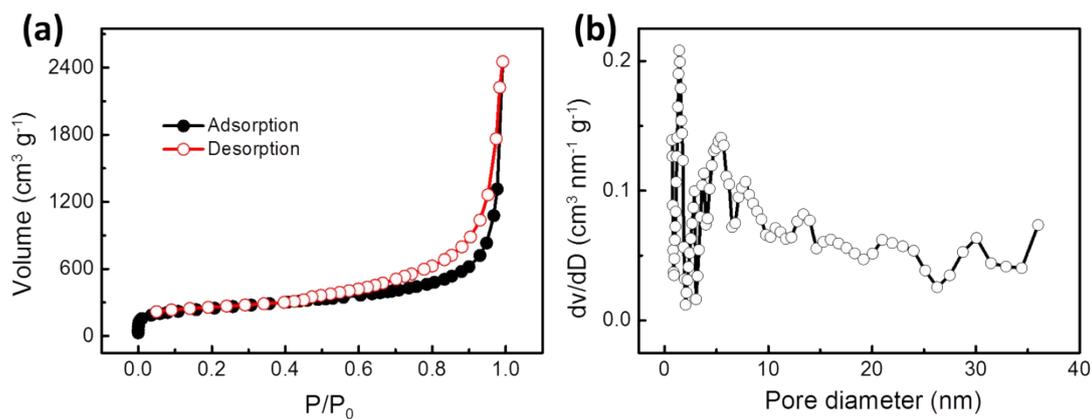


**Figure S2.** TG-DSC curves of N-GA@VO<sub>x</sub> NWAs under an air atmosphere.

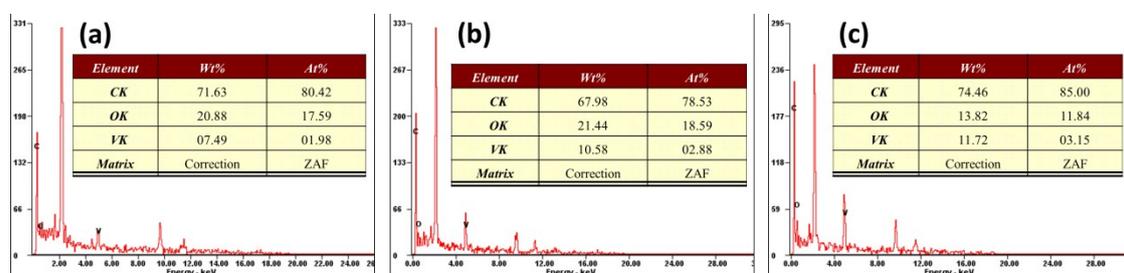
TG-DSC measurements were carried out to investigate the whole sintering process. As shown in DSC curve, three exothermic peaks appeared at 220 °C and 463 °C, which are derived from the oxidation of low valence V<sup>4+</sup> to high valence V<sup>5+</sup> and the decomposition of N-GA in air, respectively. The endothermic peak at 664 °C is caused by the liquefaction of crystal V<sub>2</sub>O<sub>5</sub>. According the analysis of the TG-DSC curves, 300 °C is enough for the oxidation V<sup>4+</sup>, which is corresponding the experimental results that greenish black N-GA@VO<sub>x</sub> NWAs change into yellow N-GA@V<sub>2</sub>O<sub>5</sub> NWAs after thermal treatment at 300 °C in air.



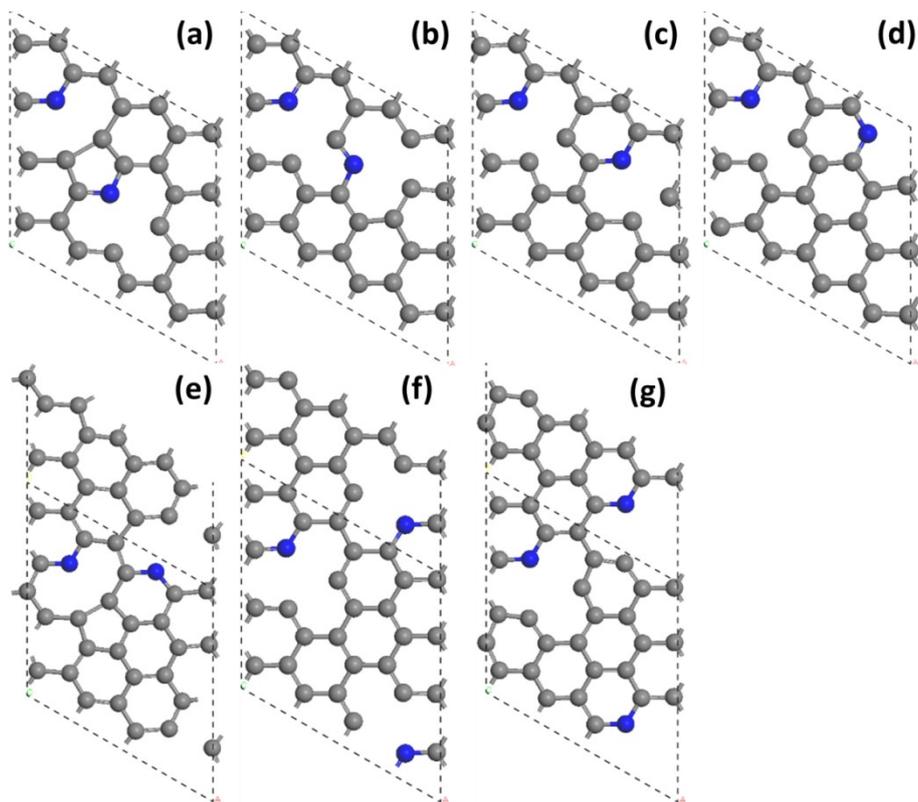
**Figure S3.** (a,b) SEM images of the N-GA@VO<sub>x</sub> NWAs; inset: the photograph (a) of the corresponding sample.



**Figure S4.** (a) Nitrogen sorption isotherms and (b) corresponding pore size distribution of 3D N-GA@V<sub>2</sub>O<sub>5</sub> NWAs.



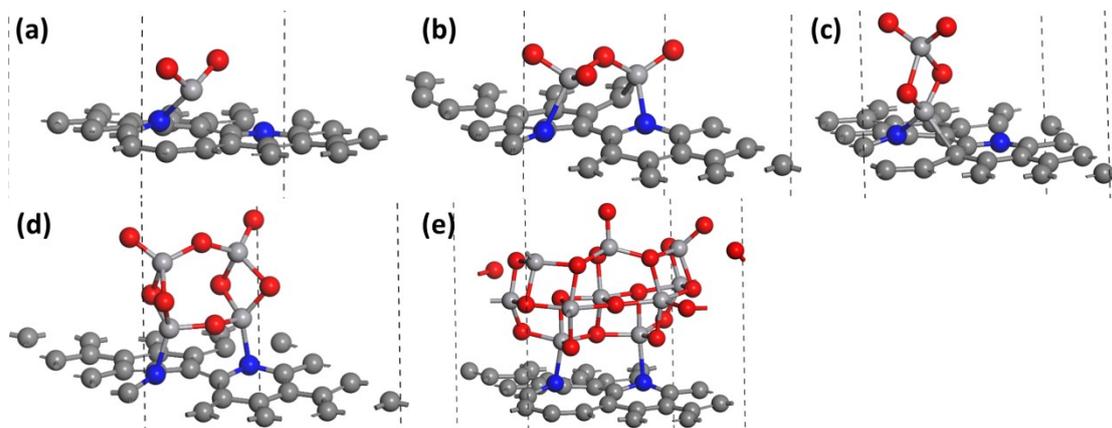
**Figure S5.** The corresponding EDS results of the N-GA@VO<sub>x</sub> NWAs samples fabricated at different reaction intervals: (a) 30 min, (b) 45 min, and (c) 60 min.



**Figure S6.** Structures of the possible 7 isomers for 2 nitrogen atoms doping into graphene lattice.

**Table S1.** The corresponding free energy ( $G_{\text{Fe}}$ ) of possible isomers in Figure S5.

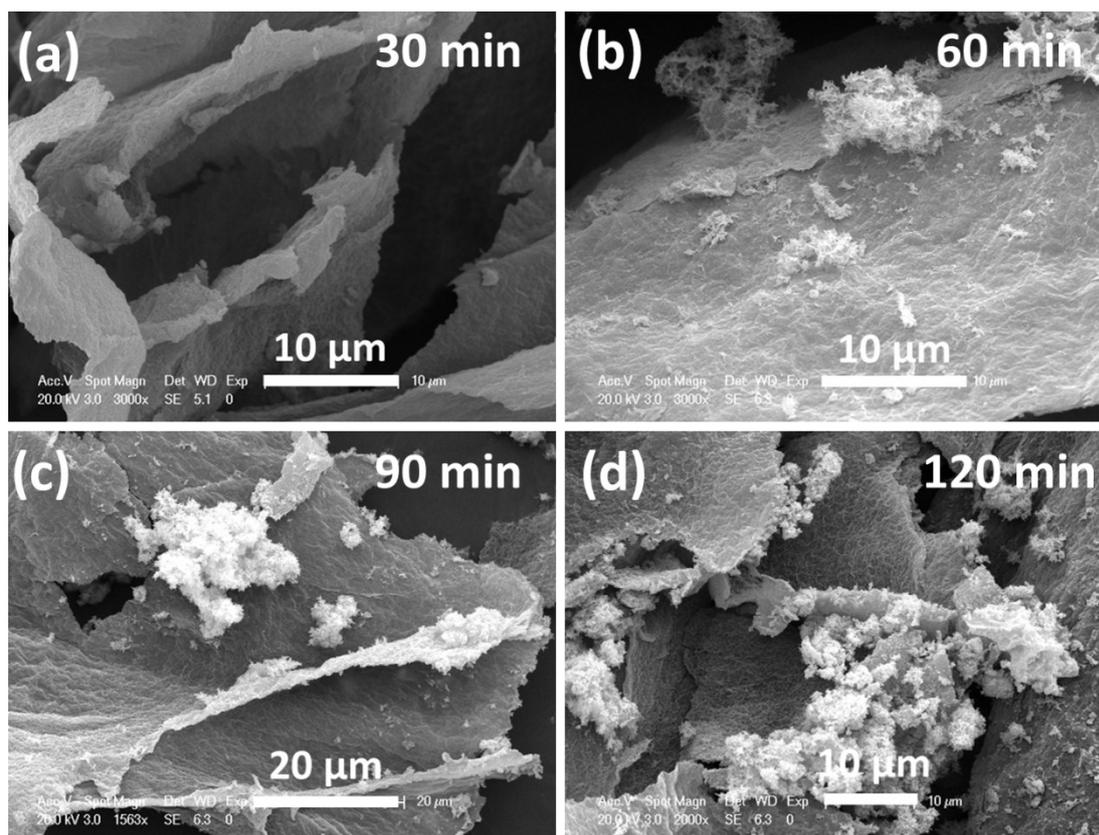
Isomers	a	b	c	d	e	f	g
$G_{\text{Fe}}$ (eV)	- 263.27	-264.42	-263.44	-264.50	-264.73	- 262.92	- 262.37



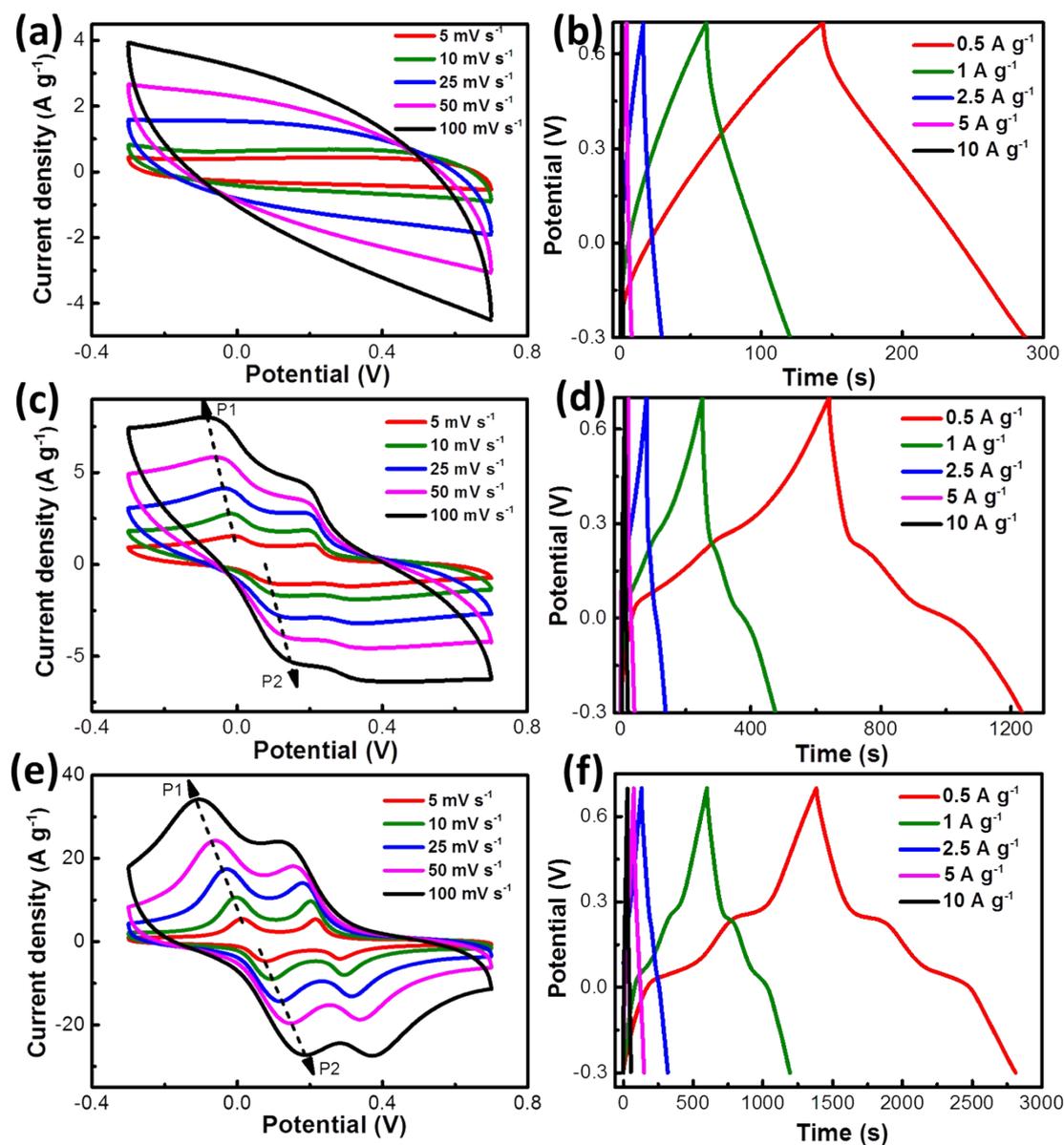
**Figure S7.** Structures of 1, 2, 4, and 10 VO<sub>2</sub> molecules growing on the N-doped graphene (isomer-5).

**Table S2.** The corresponding  $\Delta E$  of configurations in Figure S7.

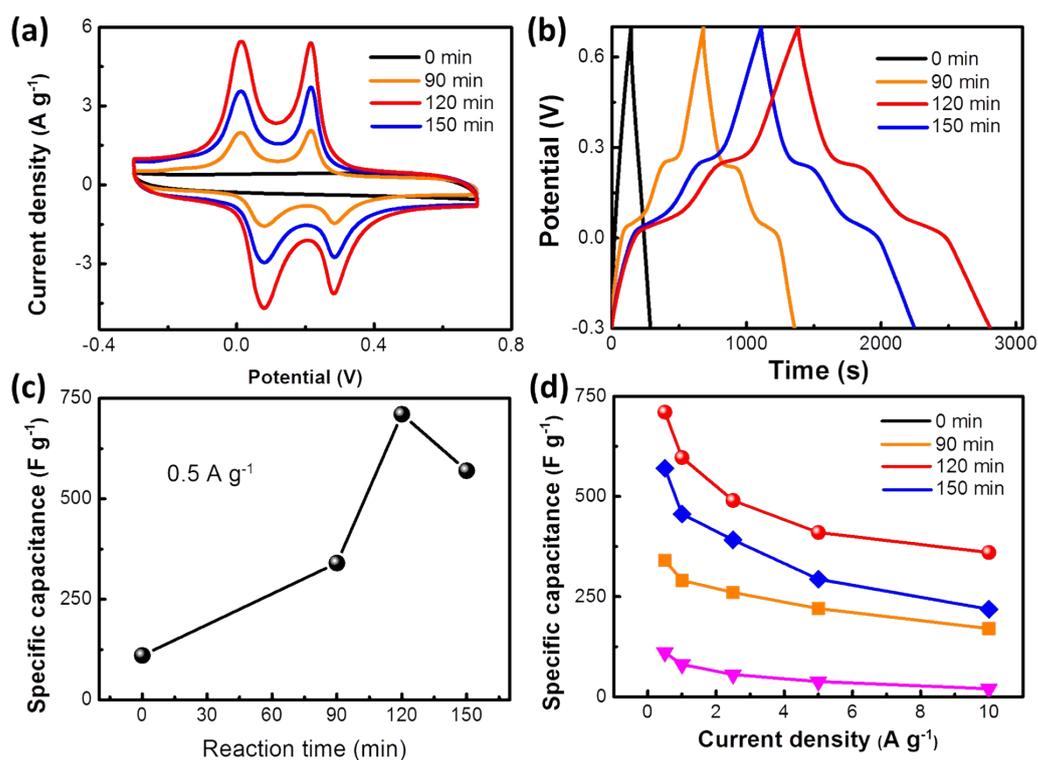
Configurations	a	b	c	d	e
$\Delta E$ (eV)	-3.59	-4.04	-3.87	-4.03	-4.40



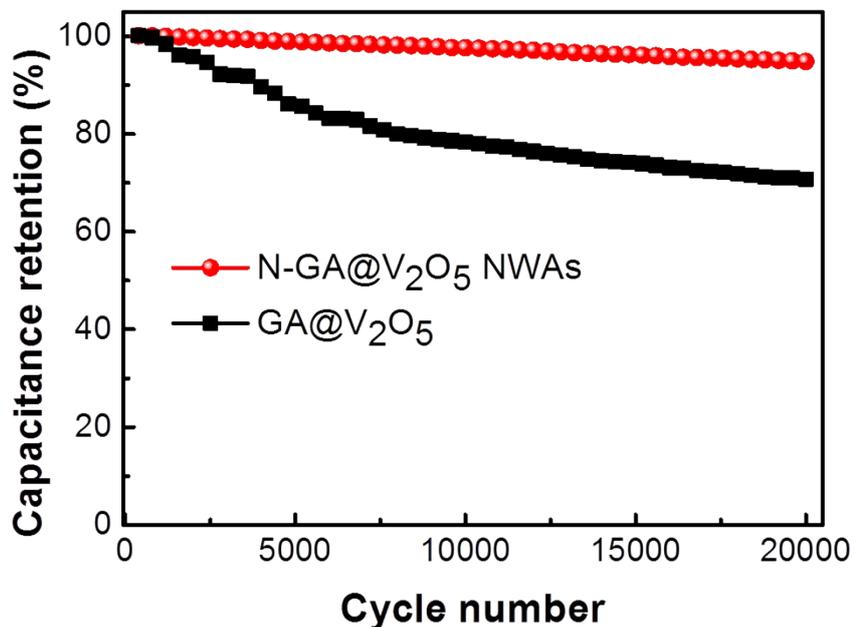
**Figure S8.** (a,b) SEM images of GA@VO<sub>x</sub> without N doping treatment fabricated at different reaction intervals: (a) 30 min, (b) 60 min, (c) 90 min, and (d) 120 min.



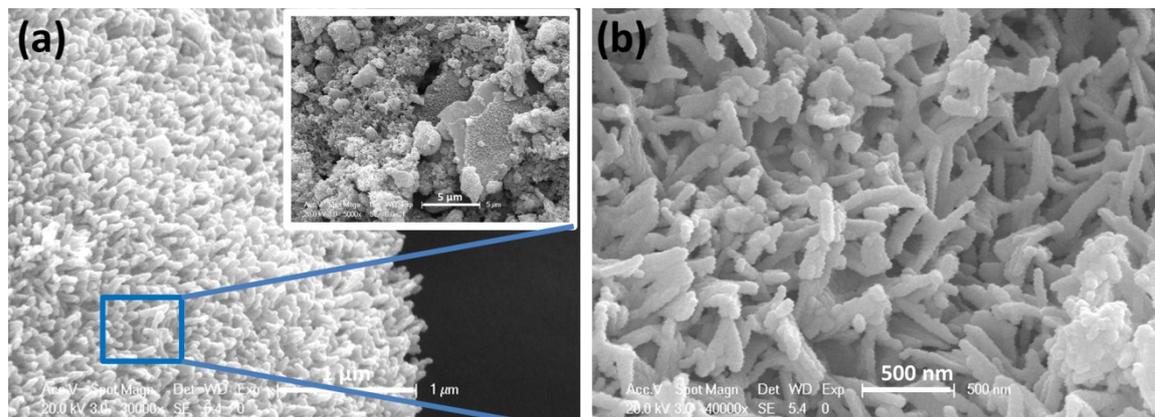
**Figure S9.** (a, c and e) CV curves of the N-GA, GA@V<sub>2</sub>O<sub>5</sub> and N-GA@V<sub>2</sub>O<sub>5</sub> NWAs at different sweep rates; (b, d and f) Galvanostatic charge-discharge curves of the N-GA, GA@V<sub>2</sub>O<sub>5</sub> and N-GA@V<sub>2</sub>O<sub>5</sub> NWAs at the different current density.



**Figure S10.** (a) CV curves of the N-GA@V<sub>2</sub>O<sub>5</sub> NWAs with different reaction times at the sweep rate of 5 mV s<sup>-1</sup>; (b) Galvanostatic charge-discharge curves of N-GA@V<sub>2</sub>O<sub>5</sub> NWAs with different reaction times at the current density of 0.5 A g<sup>-1</sup>; (c) influence of reaction times on the specific capacitance of N-GA@V<sub>2</sub>O<sub>5</sub> NWAs; (d) specific capacitance of the N-GA@V<sub>2</sub>O<sub>5</sub> NWAs with different reaction times as a function of current density.



**Figure S11.** Cycling performance at a constant current density of 10 A g<sup>-1</sup>.



**Figure S12.** (a,b) SEM images of 3D N-GA@V<sub>2</sub>O<sub>5</sub> NWAs after cycling for 20000 cycles.

## REFERENCES

1. G. Kresse and J. Furthmüller, *Computational Materials Science*, 1996, **6**, 15-50.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
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