


Cite this: *RSC Adv.*, 2017, 7, 25732

# Nitrogen-doped reduced graphene oxide intertwined with $V_2O_3$ nanoflakes as self-supported electrodes for flexible all-solid-state supercapacitors

Z. Q. Hou, \* Z. Y. Wang, L. X. Yang and Z. G. Yang

Flexible all-solid-state supercapacitors (SCs) have great potential applications in flexible and wearable electronics because of their safety, high power density, flexibility, and portability. Herein, a self-supported film electrode comprising nitrogen-doped reduced graphene oxide intertwined with vanadium trioxide nanoflakes ( $V_2O_3$ /N-rGO) was fabricated. The  $V_2O_3$  nanoflakes have abundant active sites accessible to charge storage, and nitrogen-doped reduced graphene oxide provides a flexible support. The  $V_2O_3$ /N-rGO film electrodes exhibit high conductivity, short diffusion length for ions and electrons, and robust flexibility, resulting in excellent capacitive properties and flexibility. The flexible  $V_2O_3$ /N-rGO film electrode has a high areal capacitance of  $216 \text{ mF cm}^{-2}$  at a current density of  $1 \text{ mA cm}^{-2}$ . All-solid-state flexible SCs assembled by sandwiching two self-supported  $V_2O_3$ /N-rGO hybrid electrodes with alkaline poly(vinyl alcohol) (PVA) and LiCl gel electrolyte show an ideal volumetric capacitance of  $8.1 \text{ F cm}^{-3}$ , an energy density of  $0.55 \text{ mW h cm}^{-3}$ , and a power density of  $0.035 \text{ W cm}^{-3}$  at a current density of  $0.1 \text{ A cm}^{-3}$ , based on the entire cell. This indicates that the self-supported  $V_2O_3$ /N-rGO film electrodes have great potential applications in portable and wearable flexible electronics due to their high capacitance, high energy/power density, and good mechanical flexibility.

Received 10th March 2017  
Accepted 29th April 2017

DOI: 10.1039/c7ra02899g

rsc.li/rsc-advances

## 1. Introduction

The flexible and wearable electronic products such as bendable mobiles phones, flexible sensors, and wearable devices have gained intense research focus due to the increasing demand of flexible energy storage devices in our daily life.<sup>1–4</sup> An ideal flexible supercapacitor should not only provide a flexible, lightweight, easily portable, and environmentally friendly power source, but also possess excellent electrochemical properties including a fast charge–discharge rate, high power density, and long cyclic life. Thus, the electrochemical properties of the flexible SCs should not be affected by the mechanical actions such as folding, bending, and other deformation actions. To fulfill these requirements, the key is to design a flexible electrode with robust mechanical strength and high capacitance because the electrode materials are the key components of SCs.

Generally, SCs can be classified into electrical double-layer capacitors (EDLC) and pseudocapacitors based on the charge storage mechanism. The charge storage of EDLCs is achieved *via* reversible ion adsorption/desorption on a large-surface-area

that usually produce limited specific capacitance. The electrode materials such as carbon nanotubes and graphene usually provide low specific capacitance. In addition, the pseudocapacitors store charge through a fast reversible faradaic process of redox reactions, which may provide higher specific capacitance. Pseudocapacitive materials such as transition metal oxides ( $MnO_2$ ,<sup>5,6</sup>  $NiO$ ,<sup>7</sup>  $Co_3O_4$ ,<sup>8</sup>  $Fe_2O_3$ ,<sup>9</sup>  $MoO_3$ ,<sup>10</sup> and  $V_2O_5$  (ref. 11)) and conduction polymers including polypyrrole<sup>12</sup> and polyaniline<sup>13</sup> can deliver higher capacitance than carbon materials. However, the low electron conductivity of metal oxides and kinetic irreversibility associated with conducting polymers lead to a low rate capability and cycling stability. In recent years, transition metal carbides or nitrides have been demonstrated as electrode materials for SCs due to their high electrical conductivity, impressive specific capacitance, and chemical stability.<sup>14–18</sup> However, the synthesis of transition metal carbides or nitrides usually require high temperature and long reaction times, which do not meet the requirements for green synthesis methods.

Thus, capacitor materials with the good conductivity and high specific capacitance as well as fabricated using green synthesis methods are highly desired. Fortunately, vanadium-based oxide phases of  $V_2O_3$  exhibit quasi-metallic conductivity of  $10^3 \Omega^{-1} \text{ cm}^{-1}$ , close to that of  $Ru_2O_3$ .<sup>19</sup> Therefore,  $V_2O_3$ , as well

School of Chemistry and Chemical Engineering, Zhoukou Normal University, Henan 466001, P. R. China. E-mail: houzq@hust.edu.cn



as VN, may also be a great candidate to develop fast ECs with high-power and high-energy densities. Li *et al.* have reported that  $\text{V}_2\text{O}_3/\text{C}$  composites exhibit a specific capacitance of  $205 \text{ F g}^{-1}$  at  $0.05 \text{ A g}^{-1}$  over a potential range of  $-0.4$ – $0.6 \text{ V}$ .<sup>20</sup> However, a graphene-bridged  $\text{V}_2\text{O}_3/\text{VO}_x$  core-shell composite as an electrode material was fabricated by Xuan Pan, which exhibited a specific capacitance of  $590 \text{ F g}^{-1}$  at  $5 \text{ mV s}^{-1}$  and high-power and high-energy densities.<sup>19</sup> The reason is that  $\text{V}_2\text{O}_3$  has a high conductivity, and  $\text{V}_2\text{O}_3/\text{VO}_x$  core-shell structure provides high capacitance. Hence,  $\text{V}_2\text{O}_3$  could be a great candidate for developing fast supercapacitors with excellent electrochemical performance.

Herein, we report the synthesis of nitrogen-doped reduced graphene oxide intertwined with  $\text{V}_2\text{O}_3$  nanoflakes to form a self-supported film electrode suitable for flexible all-solid-state SCs. The self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrode comprised nitrogen-doped reduced graphene oxide intertwined with  $\text{V}_2\text{O}_3$  nanoflakes ( $\text{V}_2\text{O}_3/\text{N-rGO}$ ) without the introduction of any mechanical support or foreign binder. The flexible  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrodes have several advantages to achieve high electrochemical performance. First, the  $\text{V}_2\text{O}_3$  nanoflakes provide more active sites accessible to charge storage, leading to high specific capacitance. In addition, nitrogen-doped reduced graphene oxide also participates in charge storage. Second, nitrogen-doped reduced graphene oxide intertwined with  $\text{V}_2\text{O}_3$  nanoflakes has a robust mechanical infrastructure, which is compatible with the intrinsic rigidity of  $\text{V}_2\text{O}_3$ , leading to robust flexibility and mechanical integrity of the  $\text{V}_2\text{O}_3/\text{N-rGO}$  film. Third, the interconnected framework of the  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrodes provide high conductivity and short diffusion length for ions and electrons, resulting in impressive capacitance. Fourth, the contact between  $\text{V}_2\text{O}_3$  and N-rGO results in a much higher contact area at the interface, which can be beneficial for good dispersion without size variation or any agglomeration and retaining the structure during the charge-discharge process, which can help in achieving excellent cycling stability.<sup>21–24</sup> As a consequence, the self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrodes deliver a high areal capacitance of  $216 \text{ mF cm}^{-2}$  at a current density of  $1 \text{ mA cm}^{-2}$ . The all-solid-state flexible SCs fabricated by sandwiching two self-supported film electrodes with a LiCl/PVA gel electrolyte show an ideal volumetric capacitance of  $8.1 \text{ F cm}^{-3}$  at a current density of  $0.1 \text{ A cm}^{-3}$ , a high energy density of  $0.55 \text{ mW h cm}^{-3}$  at a power density of  $0.035 \text{ W cm}^{-3}$ , and excellent cycling stability. These values are higher than most of the previously reported results obtained from quasi and all-solid-state flexible SCs, demonstrating the great commercial potential of the present all-solid-state flexible SCs in portable or wearable devices.

## 2. Experimental

### 2.1 Preparation of the $\text{V}_2\text{O}_5$ gel

All chemical reagents were purchased and used without further purification. The flaky  $\text{V}_2\text{O}_5$  xerogel was prepared using a typical hydrothermal method. For example,  $0.24 \text{ g}$  of  $\text{V}_2\text{O}_5$  powder was dispersed in  $20 \text{ mL}$  of  $\text{H}_2\text{O}$  followed by the addition of  $10 \text{ mL}$  of  $\text{H}_2\text{O}_2$  (30%) under vigorous stirring for  $2 \text{ h}$ .<sup>25</sup> The obtained

orange solution was transferred to a  $50 \text{ mL}$  Teflon-lined autoclave. The autoclave was sealed and heated in an oven at  $205^\circ\text{C}$  for  $16 \text{ h}$ . Finally, the brownish red gel was obtained.

### 2.2 Fabrication of the self-supported $\text{V}_2\text{O}_3/\text{N-rGO}$ hybrid film

The flexible self-supported hybrid films were fabricated using a vacuum filtration method. First, the desired GO powders were sonicated in  $15 \text{ mL}$  of DI water for  $60 \text{ min}$  using a probe sonicator. Then, the desired  $\text{V}_2\text{O}_5$  gel was added dropwise to the GO suspension and sonicated for  $30 \text{ min}$  to ensure sufficient mixing of the materials. The suspension was filtered through a filter membrane ( $220 \text{ nm}$  pore size). After vacuum drying at  $70^\circ\text{C}$  for  $60 \text{ min}$ , the self-supported  $\text{V}_2\text{O}_5$  gel/GO hybrid film was peeled from the filtration membrane and was further annealed at  $500^\circ\text{C}$  for  $30 \text{ min}$  under an  $\text{NH}_3$  atmosphere to obtain the self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  hybrid film. For comparison, the  $\text{V}_2\text{O}_3/\text{N-rGO}$  hybrid films were prepared by the annealing of  $\text{V}_2\text{O}_5$  gel/GO films (with various mass ratios of  $\text{V}_2\text{O}_5$  gel and GO) under an  $\text{NH}_3$  atmosphere *via* the same procedure.

### 2.3 Fabrication of the half-cell and flexible all-solid-state symmetric devices

To optimize the electrochemical performance of the  $\text{V}_2\text{O}_3/\text{N-rGO}$  electrodes, the  $\text{V}_2\text{O}_3/\text{N-rGO}$  electrodes were investigated using three-electrode cells because they were simple and maneuverable. In the three-electrode configuration, the cell was equipped with  $\text{V}_2\text{O}_3/\text{N-rGO}$  as the working electrode, a saturated SCE as the reference electrode, and a Pt plate as the counter electrode in a  $1 \text{ M Na}_2\text{SO}_4$  electrolyte. All the all-solid-state supercapacitor devices studied for material performance in this study were fabricated using a two-electrode standard method. The LiCl/PVA gel was prepared as follows:  $3 \text{ g}$  of PVA was mixed with  $30 \text{ mL}$  of LiCl ( $5 \text{ M}$ ) aqueous solution and heated at  $85^\circ\text{C}$  for  $1 \text{ h}$  under vigorous stirring.<sup>6</sup> Herein, two pieces of the self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  hybrid electrodes with a separator were sandwiched with LiCl/PVA gel as the solid-state electrolyte. Prior to assembly, the two self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  hybrid electrodes and separator were immersed in the LiCl/PVA solution for  $10 \text{ min}$ . The devices were solidified at room temperature for  $1 \text{ h}$  and then placed under  $40^\circ\text{C}$  and vacuum conditions to remove excess water.

### 2.4 Characterization

The morphology, structure, and composition of the samples were determined *via* field-emission scanning electron microscopy (FE-SEM, FEI, Nova 450 Nano), high-resolution transmission electron microscopy (HRTEM, TECNAI), X-ray diffraction using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) (XRD, Philips, X' Pert Pro), and XPS (ESCALB MK-II).

### 2.5 Electrochemical measurements

The three-electrode set-up in  $1 \text{ M Na}_2\text{SO}_4$  used for the single electrode tests comprised Hg/Hg $_2\text{SO}_4$  and platinum flake as the reference and counter electrodes, respectively. The mass loading of the active materials in each electrode was  $1.05 \text{ mg}$



$\text{cm}^{-2}$ . The electrochemical performances of the  $\text{V}_2\text{O}_3/\text{N-rGO}$  hybrid electrodes and all-solid-state symmetrical devices were tested using an electrochemical station (CHI 660E). The areal capacitance  $C_s$  ( $\text{mF cm}^{-2}$ ), volumetric capacitance  $C_{\text{vol}}$  ( $\text{F cm}^{-3}$ ), energy density  $E$  ( $\text{mW h cm}^{-3}$ ), and power density ( $\text{mW cm}^{-3}$ ) were calculated using the following equations:<sup>16</sup>

$$C = I\Delta t/\Delta E \quad (1)$$

$$C_s = C/S = I\Delta t/S\Delta E \quad (2)$$

$$C_v = C/V = I\Delta t/V\Delta E \quad (3)$$

$$E = CU^2/2V \quad (4)$$

$$P = Elt \quad (5)$$

where  $C$  is the total capacitance,  $C_s$  is the area capacitance,  $C_v$  is the volumetric capacitance,  $S$  ( $\text{cm}^2$ ) is the effective electrode area,  $I$  (A) is the charging/discharging current,  $\Delta t$  (s) is the discharging time,  $\Delta E$  (V) is the potential window during the discharging process after the IR drop,  $A$  ( $\text{cm}^3$ ) is the volume of the entire device including the electrolyte and electrodes, and  $U$  (V) is the operating voltage.

### 3. Results and discussion

Fig. 1 demonstrates the fabrication process of the flexible  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrodes and the flexible all-solid-state SCs. First, the GO powders were sonicated in DI water and the  $\text{V}_2\text{O}_5$  xerogel was synthesized using a hydrothermal method.<sup>25</sup> Then, a mixture of the GO suspension and  $\text{V}_2\text{O}_5$  xerogel was obtained *via* ultrasonication. Second, the freestanding  $\text{V}_2\text{O}_5$  xerogel/GO films were obtained by vacuum filtering the mixture and subsequently peeled off from the filter membrane after drying at  $70^\circ\text{C}$  for 1 h. Finally, the flexible  $\text{V}_2\text{O}_3/\text{N-rGO}$  hybrid films were produced by thermally annealing the  $\text{V}_2\text{O}_5$  xerogel/GO films at  $500^\circ\text{C}$  for 30 min under an  $\text{NH}_3$  atmosphere. The all-solid-state flexible SCs based on two symmetrical  $\text{V}_2\text{O}_3/\text{N-rGO}$  hybrid film electrodes were assembled using the LiCl/PVA gel electrolyte.

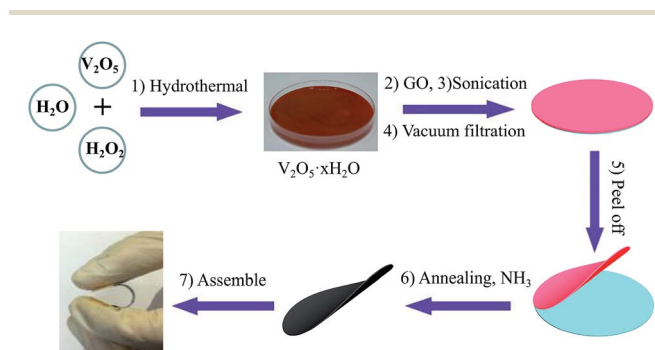


Fig. 1 Schematic of the fabrication of the flexible and self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrodes and the assembly of the all-solid-state flexible SCs devices.

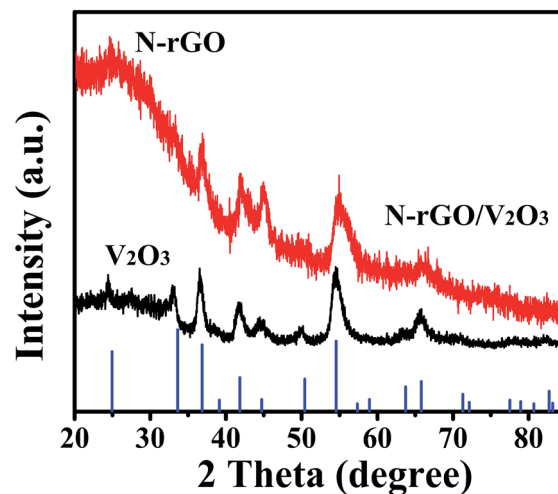


Fig. 2 The XRD patterns of the composites and the standard  $\text{V}_2\text{O}_3$  (corundum structure) pattern (JCPDS Card No. 34-0187).

The XRD pattern of the product obtained by annealing the  $\text{V}_2\text{O}_5$  xerogel and the freestanding  $\text{V}_2\text{O}_5$  xerogel/GO film in an  $\text{NH}_3$  atmosphere at  $500^\circ\text{C}$  for 30 min is presented in Fig. 2. The XRD pattern of the product obtained by annealing  $\text{V}_2\text{O}_5$  xerogel can be well attributed to the hexagonal structure of  $\text{V}_2\text{O}_3$  (JCPDS no. 34-0187), as shown in Fig. 1a.<sup>25</sup> For the composites obtained by annealing  $\text{V}_2\text{O}_5$  xerogel/GO, the XRD pattern shows the features of broad peaks above a diffuse background, indicating a poor crystalline quality (Fig. 1b). The XRD diffraction peak at  $26^\circ$  corresponds to N-doped reduced graphene oxide<sup>26</sup> (See XPS characterization). The other diffraction peaks can be indexed to the hexagonal structure of  $\text{V}_2\text{O}_3$  (JCPDS no. 34-0187). This suggests that the  $\text{V}_2\text{O}_5$  xerogel and GO in the  $\text{V}_2\text{O}_5$  xerogel/GO film after thermal treatment produce  $\text{V}_2\text{O}_3$  and N-rGO, respectively. In addition, the diffraction peaks of  $\text{V}_2\text{O}_3$  are broadened due to the doping of N-rGO. This indicates that  $\text{V}_2\text{O}_3/\text{N-rGO}$  was obtained by annealing the  $\text{V}_2\text{O}_5$  xerogel/GO film under an  $\text{NH}_3$  atmosphere at  $500^\circ\text{C}$  for 30 min.

Fig. 3a shows the SEM images of the self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  film. It can be observed that the surface of the film shows a wrinkled structure due to GO and graphene-like  $\text{V}_2\text{O}_5$  xerogel. The cross-section SEM image shows that the self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  film has a thickness of about  $20\ \mu\text{m}$ , and the  $\text{V}_2\text{O}_3$  nanosheets intertwined with N-rGO nanosheets were uniformly distributed in the self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  film (Fig. 3b). The  $\text{V}_2\text{O}_3/\text{N-rGO}$  film was further characterized by TEM and HR-TEM. The TEM images depicted in Fig. 3c show that the composite has a wrinkled structure due to the N-rGO nanosheets. The nanosheets are clearly observed in Fig. 3c. Fig. 3d indicates that the  $\text{V}_2\text{O}_3$  nanosheet is a single-crystal, and the lattice fringe spacing is  $0.205\ \text{nm}$ , which is consistent with the spacing of the (202) plane of  $\text{V}_2\text{O}_3$ . In addition, N-rGO becomes disorientated due to the structural distortions caused by the intercalation of the nitrogen atoms into its graphitic plans.<sup>26</sup> This provides more information about the  $\text{V}_2\text{O}_3/\text{N-rGO}$  composite structure.





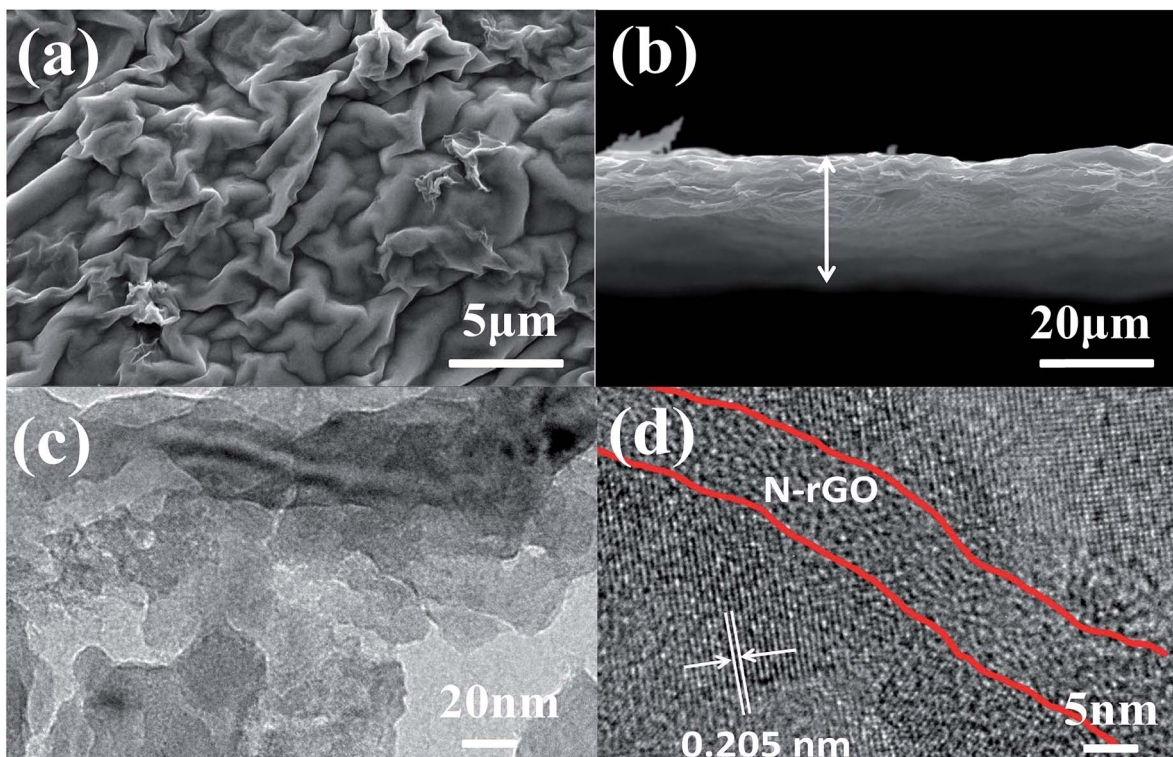


Fig. 3 (a) and (b) SEM images of the  $V_2O_3$ /N-rGO samples. (c) and (d) TEM and HR-TEM images of the  $V_2O_3$ /N-rGO samples, respectively.

To further investigate the  $V_2O_3$ /N-rGO sample, Raman spectroscopy was conducted to characterize the composition (Fig. 4). The Raman peaks at  $1355$  and  $1588\text{ cm}^{-1}$  originate from N-doped reduced graphene oxide. The Raman peaks at  $645$ ,  $901$ , and  $990\text{ cm}^{-1}$  were attributed to  $VO_x$  (ref. 25, 27 and 28) in the  $V_2O_3$  sample. The reason is that the surface of  $V_2O_3$  is naturally oxidized to  $V^{4+}$  and  $V^{5+}$  under ambient conditions.<sup>19</sup> This indicates that the Raman spectra of the  $V_2O_3$ /N-rGO composites exhibits little  $V^{4+}$  and  $V^{5+}$  coated on  $V_2O_3$  and the characteristic peaks of N-doped reduced graphene oxide.

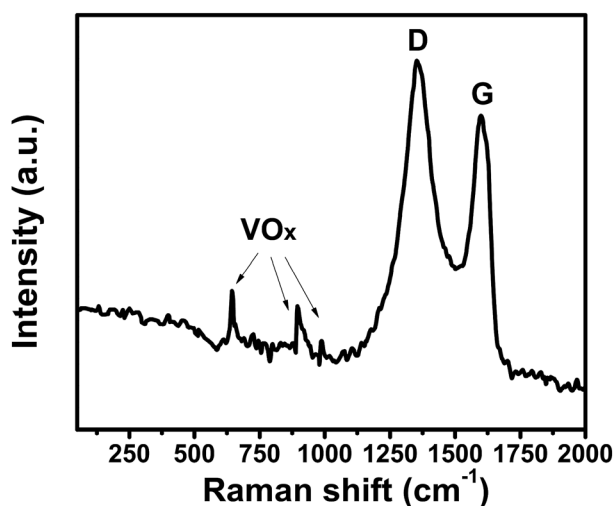


Fig. 4 The Raman spectra of the N-rGO/ $V_2O_3$  samples.

Fig. 5a is the spectra of the typical XPS survey scans of the  $NH_3$ -treated graphene–vanadium oxide xerogel composites, in which C, N, O, and V can be apparently identified. The XPS survey spectra indicates that  $V_2O_3$ /N-rGO contains only C, V, N, and O graphite-like  $sp^2$  C, N- $sp^2$  C, and N- $sp^3$  C corresponding to  $284.9$ ,  $286.7$ , and  $287.7\text{ eV}$ , respectively.<sup>29</sup> In addition, most of the C atoms in the N-doped graphene are arranged in

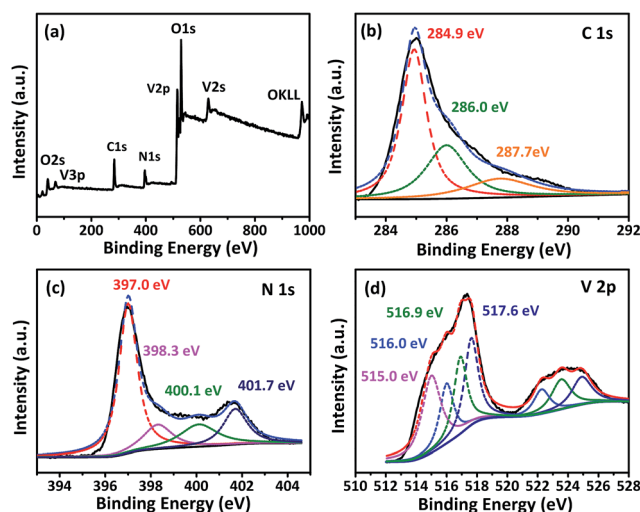


Fig. 5 (a) The XPS survey scan spectra of the  $NH_3$ -treated graphene–vanadium oxide xerogel composites. The (b) C 1s (c) N 1s, and (d) V 2p spectra of the  $NH_3$ -treated graphene–vanadium oxide xerogel composites.

a conjugated honeycomb lattice without other detectable impurities on their surface. Fig. 5b compares the high-resolution C 1s XPS spectra of the samples. It indicates that the carbon element of the sample originates from the main peak at 284.9 eV. The high-resolution N 1s spectra show five different states (Fig. 5c). The peak at 397.0 eV was attributed to the N atom from vanadium oxynitride (P1). The other three peaks at 398.3, 400.1, and 401.7 eV were ascribed to pyridinic nitrogen, pyrrolic nitrogen, and quaternary nitrogen in the outer shell.<sup>29</sup> The high-resolution V 2p XPS peak in Fig. 5d shows the four chemical states of V: the peak at 515.0 eV was attributed to V–N–O<sup>14</sup> and the peaks at 516.0, 516.9, and 517.6 eV were attributed to V<sup>3+</sup>, V<sup>4+</sup>, and V<sup>5+</sup>, respectively. The existence of V<sup>4+</sup> and V<sup>5+</sup> in the V<sub>2</sub>O<sub>3</sub>/N-rGO samples is a result of the inevitable oxidation of surface V<sub>2</sub>O<sub>3</sub> when it is exposed to air.<sup>19</sup>

The electrochemical properties of the flexible V<sub>2</sub>O<sub>3</sub>/N-rGO films were evaluated using a three-electrode system in a 1 M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte with Hg/Hg<sub>2</sub>SO<sub>4</sub> as the reference

electrode and Pt plate as the counter electrode. Fig. 6a shows the CV curves obtained for the electrodes with various ratios of V/G = 1, V/G = 2, and V/G = 3 at a scan rate of 50 mV s<sup>-1</sup>. The CV curve obtained for the V<sub>2</sub>O<sub>3</sub>/N-rGO film electrode (V/G = 1) was close to rectangular in shape at a potential of -0.2–0.6 V. In addition, the CV area of the V<sub>2</sub>O<sub>3</sub>/N-rGO film electrode (V/G = 3) is the greatest among all the samples, revealing its great specific capacitance. Herein, the flexibility of the film becomes poor for the V/G = 4 electrode; thus, the optimal ratio of V/G for the V<sub>2</sub>O<sub>3</sub>/N-rGO film electrodes was determined to be 3. Fig. 6b indicates the most specific capacitance of the flexible V<sub>2</sub>O<sub>3</sub>/N-rGO films electrode (V/G = 3) in the potential range between -0.2 and 0.6 V at a scanning rate ranging from 10 to 200 mV s<sup>-1</sup>. The galvanostatic charge–discharge (GCD) curves exhibit a slight curvature and symmetrical triangular shape without evident voltage drops between 1 and 10 mA cm<sup>-2</sup>, suggesting good pseudocapacitive behavior. The flexible freestanding V<sub>2</sub>O<sub>3</sub>/N-rGO electrode shows a substantial areal capacitance of 216 mF cm<sup>-2</sup> (206 F g<sup>-1</sup> based on the entire mass of the electrode) at a current density of 1 mA cm<sup>-2</sup> (Fig. 6c). It is higher than the previously reported results: MVN@VN NWs electrode (196 F g<sup>-1</sup> at 1.44 mA cm<sup>-2</sup>),<sup>14</sup> Fe<sub>2</sub>O<sub>3</sub> nanotube-based electrodes (180.4 mF cm<sup>-2</sup> at 1.1 mA cm<sup>-2</sup>),<sup>30</sup> self-supported mesoporous VN/CNTs hybrid electrode (178 mF cm<sup>-2</sup> at 1.1 mA cm<sup>-2</sup>),<sup>31</sup> MMNBNs/rGO hybrid electrode (142 mF cm<sup>-2</sup> at 1 mA cm<sup>-2</sup>),<sup>16</sup> and hydrogenated ZnO core/shell nanoscale electrodes (138.7 mF cm<sup>-2</sup> at 1 mA cm<sup>-2</sup>).<sup>32</sup> Moreover, 55% of the capacitance was retained when the current density was increased 10 times from 1 to 10 mA cm<sup>-2</sup>. This indicates that the V<sub>2</sub>O<sub>3</sub>/N-rGO electrode suffers from severe capacitance decay because of the solubility of V<sub>2</sub>O<sub>3</sub> during the process of the electrochemical measurements. Thus, the electrolyte becomes slightly yellow due to the formation of V<sup>5+</sup>.

The self-supported V<sub>2</sub>O<sub>3</sub>/N-rGO film electrode has good flexibility, high specific capacitance, low rate capability, and low cycling stability, caused by the solubility of V<sub>2</sub>O<sub>3</sub> in the aqueous solution system. However, the high solubility can be improved using a solid-state electrolyte. Thus, the self-supported V<sub>2</sub>O<sub>3</sub>/N-rGO film electrode is a promising candidate for high performance flexible SCs. To meet the practical requirements of a flexible electrode, a flexible all-solid-state SC composed of two self-supported V<sub>2</sub>O<sub>3</sub>/N-rGO film electrodes and a LiCl/PVA gel electrolyte was assembled, as illustrated in Fig. 1. Fig. 7a depicts the CV curves obtained for the assembled V<sub>2</sub>O<sub>3</sub>/N-rGO//V<sub>2</sub>O<sub>3</sub>/N-rGO symmetrical devices in the voltage range of 0–0.7 V at the scanning rates between 10 and 500 mV s<sup>-1</sup>. The CV curves exhibit a nearly rectangular shape and mirror image with respect to the zero-current line, even at a large scanning rate from 100 to 500 mV s<sup>-1</sup>, indicating superior capacitive behavior and high rate capability. The GCD curves obtained for the all-solid-state SCs at various current densities from 0.1 to 0.5 A cm<sup>-3</sup> are shown in Fig. 7b. The capacitance of the devices was calculated to be 8.1 and 6.9 F cm<sup>-3</sup> at the current density of 0.1 and 0.5 A cm<sup>-3</sup>, respectively. These values are higher than those for the previously reported flexible solid-state SCs such as hydrogenated ZnO@MnO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> asymmetrical SCs (1.21 F cm<sup>-3</sup> at 6.3 mA cm<sup>-3</sup>),<sup>33</sup> functionalized carbon-nanotube-based

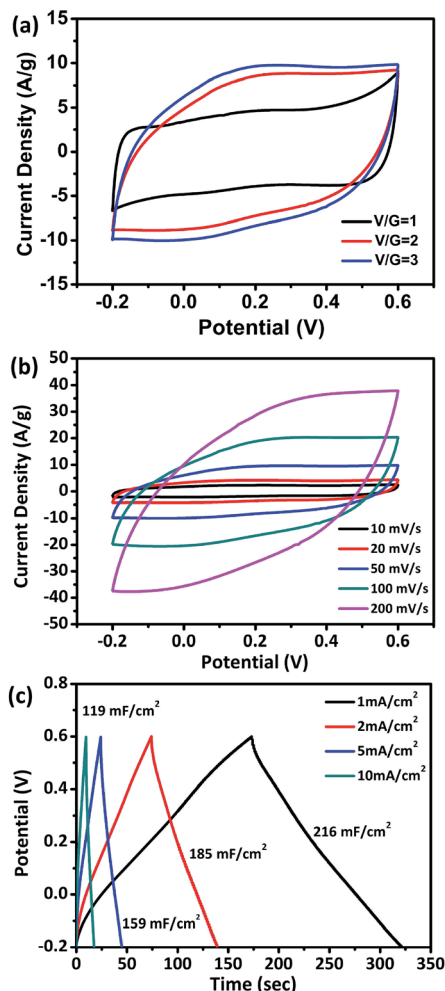


Fig. 6 (a) The CV curves obtained for various ratios of the self-supported V<sub>2</sub>O<sub>3</sub>/N-rGO film electrodes at 50 mV s<sup>-1</sup>. (b) The CV curves obtained for the self-supported V<sub>2</sub>O<sub>3</sub>/N-rGO film electrodes at different scan rates. (c) The GCD curves obtained for the self-supported V<sub>2</sub>O<sub>3</sub>/N-rGO film electrodes at different current densities.



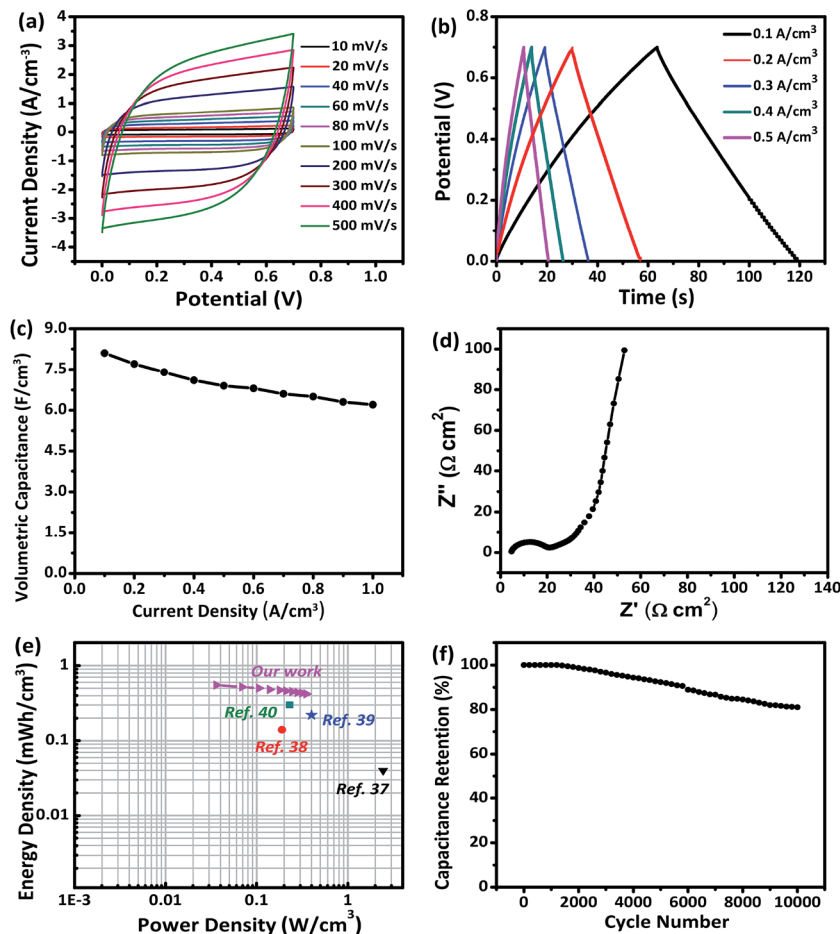


Fig. 7 The electrochemical performance of the all-solid-state SCs devices based on the self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrodes. (a) The CV curves obtained at different scanning rates from 10 to 500  $\text{mV s}^{-1}$ . (b) The GCD plots obtained at various volumetric current densities. (c) The volumetric capacitance as a function of current density. (d) Nyquist plot. (e) Ragone plot. (f) Cycling stability.

SCs ( $3.0 \text{ F cm}^{-3}$  at  $0.133 \text{ mA cm}^{-3}$ ),<sup>34</sup> N-rGO-based SCs ( $3.4 \text{ F cm}^{-3}$  at  $20 \text{ mA cm}^{-3}$ ),<sup>35</sup> and a free-standing mesoporous VN/CNTs film electrode-based SCs ( $7.9 \text{ F cm}^{-3}$  at  $25 \text{ mA cm}^{-3}$ ).<sup>31</sup> Moreover, the device had superior rate capability with 76% capacity retention when the current density was varied from 0.1 to  $1 \text{ A cm}^{-3}$  (Fig. 7c). The electrochemical impedance spectra of the solid-state devices are presented in Fig. 7d. The Nyquist plot exhibits a nearly vertical line along the imaginary axis in the low frequency region, and the equivalent series resistance of the devices was about  $5 \Omega \text{ cm}^2$ , revealing the excellent capacitor behavior of the device. The energy density  $E$  and power density  $P$  are the key parameters for the flexibility of the SCs in practical applications. Herein, the  $E$  and  $P$  values of the all-solid-state SCs were calculated and are listed in Fig. 7e. The  $E$  and  $P$  values of other previously reported devices are also presented in Fig. 7e for comparison. The volumetric energy density ( $0.55 \text{ mW h cm}^{-3}$ ) of the devices described in this study is higher than that of some previously reported devices constructed from quasi and all-solid-state SCs such as carbon nanotube-based SCs H-ZnO NW-based SCs ( $0.04 \text{ mW h cm}^{-3}$ , PVA/LiCl),<sup>36</sup> carbon microfiber bundles coated with multi-walled CNT-based SCs ( $0.14 \text{ mW h cm}^{-3}$ , PVA/ $\text{H}_3\text{PO}_4$ ),<sup>37</sup> carbon/ $\text{MnO}_2$  core-shell fiber-based SCs

( $0.22 \text{ mW h cm}^{-3}$ , PVA/ $\text{H}_3\text{PO}_4$ ),<sup>38</sup> and H- $\text{TiO}_2/\text{MnO}_2$ //H- $\text{TiO}_2/\text{C}$ -based SCs ( $0.3 \text{ mW h cm}^{-3}$ , PVA/LiCl).<sup>39</sup> The all-solid-state device based on the  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrodes and a LiCl/PVA gel electrolyte exhibited remarkable long-term cycling stability at a current density of  $1 \text{ A cm}^{-3}$ , and there was only a 19% decrease in the capacitance after 10 000 cycles, as presented in Fig. 7f, indicating its relatively high stability. Thus, the all-solid-state SCs exhibit excellent energy storage performance due to the excellent capacitive properties of the self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrode coupled with the matching PVA/LiCl gel electrolyte.

To evaluate the potential of our devices as flexible energy storage components in flexible/wearable electronics, CV tests were performed under different bending conditions. Fig. 8a exhibits no obvious change in the CV curves obtained under various bending conditions of  $45^\circ$ ,  $90^\circ$ ,  $135^\circ$ , and  $180^\circ$ , revealing the excellent flexibility. To further demonstrate the feasibility, three identical devices were connected in series or parallel to construct devices. The three units were denoted as A, B, and C, respectively. The charging/discharging voltage window of the three devices connected in series was 2.1 V with almost the same discharging time as a single device. The





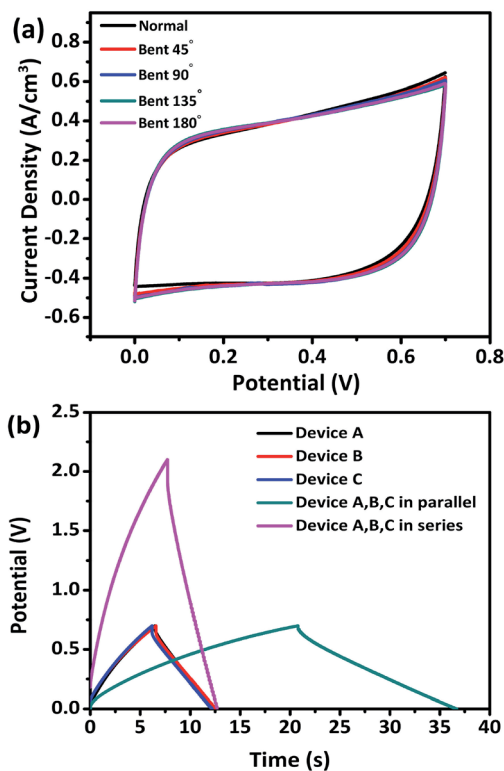


Fig. 8 (a) The CV curves obtained for an all-solid-state supercapacitor device at a scan rate of  $50 \text{ mV s}^{-1}$  under different bending states. (b) The GCD curves obtained for the as-fabricated all-solid-state SCs with various device configurations at a fixed current of  $1.57 \text{ mA}$ .

charging time of the three devices in parallel was about 2.82 times longer than that of a single device, which is close to the theoretical value of 3, thereby conforming to the theorem of series and parallel connections of capacitors (Fig. 8b). This demonstration indicates the great potential of the  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrodes for practical applications in flexible electrochemical energy-storage devices.

## 4. Conclusions

In summary, a self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrode comprising nitrogen-doped reduced graphene oxide intertwined with  $\text{V}_2\text{O}_3$  nanoflakes was prepared using a facile and effective method; this method consisted of the hydrothermal formation of  $\text{V}_2\text{O}_5$  xerogel with subsequent mixing with a GO suspension, vacuum filtration, and annealing under an  $\text{NH}_3$  atmosphere. The  $\text{V}_2\text{O}_3$  nanosheets have abundant active sites for charge storage, and nitrogen-doped reduced graphene oxide intertwined with  $\text{V}_2\text{O}_3$  provide a flexible support. This indicates that the  $\text{V}_2\text{O}_3/\text{N-rGO}$  electrodes have abundant active sites, good mechanical integrity, and flexibility, resulting in high ion diffusion and electron transfer, and high capacity and high rate capability. The flexible  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrodes exhibit a high areal capacitance of  $216 \text{ mF cm}^{-2}$  at a current density of  $1 \text{ mA cm}^{-2}$ . The all-solid-state flexible SCs fabricated by sandwiching two self-supported  $\text{V}_2\text{O}_3/\text{N-rGO}$  film electrodes with

a PVA/LiCl gel electrolyte deliver an ideal volumetric capacitance of  $8.1 \text{ F cm}^{-3}$ , an energy density of  $0.55 \text{ mW h cm}^{-3}$ , and a power density of  $0.035 \text{ W h cm}^{-3}$ . Moreover, the flexible all-solid-state devices have excellent cycling stability with 81% of the initial capacitance retention after 10 000 cycles. Hence, the flexible all-solid-state devices have promising potential in portable/wearable electronics due to their environmentally friendliness, good flexibility, and facile connectivity in series and parallel.

## Acknowledgements

This work was supported by the Key Research Project of Henan Higher Education Institute (15A430055).

## Notes and references

- 1 G. Q. Ma, Z. Wang, B. Gao, T. P. Ding, Q. Z. Zhong, X. Peng, J. Su, B. Hu, L. Y. Yuan, P. K. Chu, J. Zhou and K. F. Huo, *J. Mater. Chem. A*, 2015, **3**, 14617–14624.
- 2 X. Wang, X. Lu, B. Liu, D. Chen, Y. Tong and G. Shen, *Adv. Mater.*, 2014, **26**, 4763–4782.
- 3 L. Li, Z. Wu, S. Yuan and X. B. Zhang, *Energy Environ. Sci.*, 2014, **7**, 2101–2122.
- 4 J. Kristy, D. Genevieve and G. Yury, *J. Mater. Chem. A*, 2014, **2**, 10776.
- 5 J. Liu, L. Zhang, H. B. Wu, J. Lin, Z. Shen and X. W. Lou, *Energy Environ. Sci.*, 2014, **7**, 3709–3719.
- 6 X. Lu, T. Zhai, X. Zhang, Y. Shen, L. Yuan, B. Hu, L. Gong, J. Chen, Y. Gao, J. Zhou, Y. Tong and Z. L. Wang, *Adv. Mater.*, 2012, **24**, 938–944.
- 7 Z. Yang, F. Xu, W. Zhang, Z. Mei, B. Pei and X. Zhu, *J. Power Sources*, 2014, **246**, 24–31.
- 8 X. Wang, M. Li, Z. Chang, Y. Yang, Y. Wu and X. Liu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 2280–2285.
- 9 Z. Ma, X. Huang, S. Dou, J. Wu and S. Wang, *J. Phys. Chem. C*, 2014, **118**, 17231–17239.
- 10 H. Ji, X. Liu, Z. Liu, B. Yan, L. Chen, Y. Xie, C. Liu, W. Hou and G. Yang, *Adv. Funct. Mater.*, 2015, **25**, 1886–1894.
- 11 B. Saravanakumar, K. K. Purushothaman and G. Muralidharan, *ACS Appl. Mater. Interfaces*, 2012, **4**, 4484–4490.
- 12 Q. Wang, J. Yan, Z. Fan, T. Wei, M. Zhang and X. Jing, *J. Power Sources*, 2014, **247**, 197–203.
- 13 H. Tang, J. Wang, H. Yin, H. Zhao, D. Wang and Z. Tang, *Adv. Mater.*, 2015, **27**, 1117–1123.
- 14 B. Gao, X. Li, X. Guo, X. Zhang, X. Peng, L. Wang, J. Fu, P. K. Chu and K. Huo, *Adv. Mater. Interfaces*, 2015, **2**, 1500211.
- 15 W. Bi, Z. Hu, X. Li, C. Wu, J. Wu and Y. Xie, *Nano Res.*, 2015, **8**, 193–200.
- 16 G. Ma, Z. Wang, B. Gao, T. Ding, Q. Zhong, X. Peng, J. Su, B. Hu, L. Yuan, P. K. Chu, J. Zhou and K. Huo, *J. Mater. Chem. A*, 2015, **3**, 14617–14624.
- 17 M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall'Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon,



- M. W. Barsoum and Y. Gogotsi, *Science*, 2013, **341**, 1502–1505.
- 18 Y. Zhong, X. Xia, F. Shi, J. Zhan, J. Tu and H. J. Fan, *Adv. Sci.*, 2016, 1500286.
- 19 X. Pan, G. Ren, M. Nadim Ferdous Hoque, S. Bayne, K. Zhu and Z. Fan, *Adv. Mater. Interfaces*, 2014, **1**, 1400398.
- 20 H.-Y. Li, K. Jiao, L. Wang, C. Wei, X. Li and B. Xie, *J. Mater. Chem. A*, 2014, **2**, 18806–18815.
- 21 H. N. Ma, J. He, D. B. Xiong, J. S. Wu, Q. Q. Li, V. Dravid and Y. F. Zhao, *ACS Appl. Mater. Interfaces*, 2016, **8**, 1992–2000.
- 22 Y. F. Zhao, H. N. Ma, S. F. Huang, X. J. Zhang, M. R. Xia, Y. F. Tang and Z. F. Ma, *ACS Appl. Mater. Interfaces*, 2016, **8**, 22997–23005.
- 23 Z. Y. Chen, D. B. Xiong, X. J. Zhang, H. N. Ma, M. R. Xia and Y. F. Zhao, *Nanoscale*, 2016, **8**, 6636–6645.
- 24 Y. F. Zhao, W. Ran, J. He, Y. Z. Huang, Z. F. Liu, W. Liu, Y. F. Tang, L. Zhang, D. W. Gao and F. M. Gao, *Small*, 2015, **11**, 1310–1319.
- 25 Z. Hou, K. Guo, H. Li and T. Zhai, *CrystEngComm*, 2016, **18**, 3040–3047.
- 26 L. T. Qu, Y. Liu, J. B. Baek and L. M. Dai, *ACS Nano*, 2010, **4**, 1321–1326.
- 27 B. Hu, Y. Zhang, W. Chen, C. Xu and Z. L. Wang, *Adv. Mater.*, 2011, **23**, 3536–3541.
- 28 W. J. Shen, K. W. Sun and C. S. Lee, *J. Nanopart. Res.*, 2011, **13**, 4929–4936.
- 29 D. C. Wei, Y. Q. Liu, Y. Wang, H. I. Zhang, L. Q. Huang and G. Yu, *Nano Lett.*, 2009, **9**, 1752–1758.
- 30 P. H. Yang, Y. Ding, Z. Y. Lin, Z. W. Chen, Y. Z. Li, P. F. Qiang, M. Ebrahimi, W. J. Mai, C. P. Wong and Z. L. Wang, *Nano Lett.*, 2014, **14**, 731–736.
- 31 X. Xiao, X. Peng, H. Y. Jin, T. Q. Li, C. C. Zhang, B. Gao, B. Hu, K. F. Huo and J. Zhou, *Adv. Mater.*, 2013, **25**, 5091–5097.
- 32 P. Yang, X. Xiao, Y. Li, Y. Ding, P. Qiang, X. Tan, W. Mai, Z. Lin, W. Wu, T. Li, H. Jin, P. Liu, J. Zhang, C. P. Wong and Z. L. Wang, *ACS Nano*, 2013, **7**, 2617–2626.
- 33 X. Lu, Y. Zeng, M. Yu, T. Zhai, C. Liang, S. Xie, M.-S. Balogun and Y. Tong, *Adv. Mater.*, 2014, **26**, 3148–3155.
- 34 X. Xiao, T. Q. Li, Z. H. Peng, H. Y. Jin, Q. Z. Zhang, Q. Y. Hu, B. Yao, Q. P. Luo, C. F. Zhang, L. Gong, J. Chen, Y. Gogotsi and J. Zhou, *Nano Energy*, 2014, **6**, 1–9.
- 35 S. Y. Liu, J. Xie, H. B. Li, Y. Wang, H. Y. Yang, T. J. Zhu, S. C. Zhang, G. S. Cao and X. B. Zhao, *J. Mater. Chem. A*, 2014, **2**, 18125–18131.
- 36 P. H. Yang, X. Xiao, Y. Z. Li, Y. Ding, P. F. Qiang, X. H. Tan, W. J. Mai, Z. Y. Lin, W. Z. Wu, T. Q. Li, H. Y. Jin, P. Y. Liu, J. Zhou, C. P. Wong and Z. L. Wang, *ACS Nano*, 2013, **7**, 2617–2626.
- 37 V. T. Le, H. Kim, A. Ghosh, J. Kim, J. Chang, Q. A. Vu, D. T. Pham, J. H. Lee, S. W. Kim and Y. H. Lee, *ACS Nano*, 2013, **7**, 5940–5947.
- 38 X. Xiao, T. Li, P. Yang, Y. Gao, H. Jin, W. Ni, W. Zhan, X. Zhang, Y. Cao, J. Zhong, L. Gong, W. C. Yen, W. Mai, J. Chen, K. Huo, Y. L. Chueh, Z. L. Wang and J. Zhou, *ACS Nano*, 2012, **6**, 9200–9206.
- 39 X. Lu, M. Yu, G. Wang, T. Zhai, S. Xie, Y. Ling, Y. Tong and Y. Li, *Adv. Mater.*, 2013, **25**, 267–272.

