Spatially confined synthesis of vanadium nitride nanodots intercalated carbon nanosheets with ultrahigh volumetric capacitance and long life for flexible supercapacitors

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ABSTRACT

High volumetric capacitance electrode materials are highly desirable for miniaturized and portable capacitive storage devices. Herein, a spatially confined strategy to prepare 0D-in-2D pillared lamellar hybrid comprising vanadium nitride nanodots intercalated carbon nanosheets (VNNDs/CNSs) is proposed for promising capacitive material with high volumetric capacitance. The VNNDs/CNSs shows an ultrahigh volumetric capacitance of 1203.6 F cm⁻³ at 1.1 A cm⁻² and rate capability of 703.1 F cm⁻³ at 210 A cm⁻² surpassing those of carbon, transition metal oxides/nitrides. Even the 150 µm-thick film electrode comprising VNNDs/CNSs has a volumetric capacitance of 867.1 F cm⁻³. Moreover, the VNNDs/CNSs electrode exhibits extraordinary cycling stability with 90% capacitance retention after 10,000 cycles. The all-solid-state symmetric flexible supercapacitor based on VNNDs/CNSs electrodes boasts a high volumetric energy density/power density of 30.9 Wh L⁻¹/64,500 W L⁻¹ with 91% capacitance retention after 10000 cycles, rendering promising applications in high-performance flexible supercapacitors. The strategy provides an insight into the rational design of compact, robust and highly conductive electrode materials with high volumetric capacitances and long life.

1. Introduction

Supercapacitors (SCs) are promising energy storage systems for portable electronics and electric vehicles because they have high power densities, fast charging-discharging capability, and long cycling life [1–3]. Although porous carbon (C) materials with large surface areas are widely employed in commercial SCs, the low volumetric capacitance as a result of the small packing density (< 0.8 g cm⁻³) and moderate gravimetric capacitances limits their application in portable and miniaturized capacitive storage because of the limited space of the devices [4–7]. Different from carbon materials with electrical double-layer capacitive storage, pseudocapacitive metal oxides store charges via fast and reversible redox reactions, which potentially provide higher specific capacitance and energy density. However, the intrinsically low electronic conductivity of most metal oxide generally results in poor power capability and low electrochemical utilization [8–12].

Nanostructured transitional metal nitrides such as vanadium nitride (VN) have emerged as promising electrode materials for SCs due to their intrinsic metallic conductivity, large pseudocapacitance, and high density (VN: 6.18 g cm⁻³) [13–24]. Various types of VN materials such as nanoparticles [13,14], nanowires [15–18], nanosheets [19], thin films [20], VN/graphene [21], and VN quantum dots/carbon fibers [22] have been developed for SCs. However, these reported VN nanomaterials generally have small specific surface areas (10–40 m² g⁻¹), resulting in limited electroactive sites for capacitive storage and compromised capacitive performance. Moreover, the gravimetric capacitance of nanostructured VN is generally measured from submicrometer-thick films with low areal mass loadings (generally less than 2 mg cm⁻²) [13–22]. In practical applications, the electrodes generally require a sub-mm-thickness of 100–200 µm. Moreover, the volumetric and areal capacitances are more important than the gravimetric one for portable devices due to the limited packing space. Previous report revealed that the gravimetric capacitance is almost independent of the volumetric or areal capacitance because the gravimetric capacitance measured from sub-µm-thick thin films decreases

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by a factor of 3–5 compared to sub-mm-thick electrodes [25]. Therefore, in practice, high-performance electrodes in sub-mm-thick with high volumetric and areal specific capacitance together with superior rate capability are highly desirable [6,25,26].

Besides the high volumetric capacitance, long cycle life is significantly crucial to the applications of SCs. Previous studies reveal that VN has higher specific capacitance in alkaline electrolyte than in neutral electrolyte, but VN exhibits poor electrochemical stability in the alkaline electrolyte due to electrochemical oxidation and dissolution of VN [13–18,21,22]. Recently, coating or encapsulating of VN with carbon has been demonstrated to mitigate electrochemical oxidation in alkaline media thus improving the cycle life of VN [17,18,21,22]. However, multi-step procedures are normally required to form the core-shell VN nanostructures. It is still a challenge to rationally design VN-based electrode materials with high volumetric capacitance, fast charging-discharging, and long cycle life for high-performance flexible SCs.

In this work, a novel 0D-in-2D pillared lamellar material comprising VN nanodots intercalated carbon nanosheets (VNNDs/CNSs) is designed and synthesized for high volumetric capacitance electrode material by a facile spatially-confined strategy of nitriding organic-inorganic hybrid polyaniline intercalated V2O5 nanosheets. The intercalated polyaniline are in situ converted into 2D CNSs via confining carbonization, while the sandwiched V2O5 nanosheets layers are converted into 0D VNNDs with the diameter of 3–5 nm forming 0D-in-2D pillared lamellar structure. The well dispersed small VNNDs and pillared lamellar structure provide abundant electroactive sites as well as fast ion diffusion for capacitive storage. Simultaneously, the VNNDs encapsulated in CNSs structure impede electrochemical oxidation of VN to achieve long-term cycle life. Moreover, the VNNDs/CNSs hybrid film electrode exhibits large packing density (2.1 g cm$^{-3}$), high VN content (91.3 wt%), excellent wettability to electrolyte, and high conductivity of 225.5 S cm$^{-1}$, which are favorable for capacitive storage. As a result, the VNNDs/CNSs shows an ultrahigh volumetric capacitance of 1203.6 F cm$^{-3}$ at 1.1 A cm$^{-2}$ and rate capability of 703.1 F cm$^{-2}$ at 210 A cm$^{-2}$. Even the 150-μm-thick film electrode comprising VNNDs/CNSs has a volumetric capacitance of 867.1 F cm$^{-3}$ and excellent cyclability. The symmetric all-solid-state flexible SC based on VNNDs/CNSs electrodes boasts a high volumetric energy density of 30.9 W h L$^{-1}$ and 91% capacitance retention after 10,000 cycles, suggesting large potential in next-generation energy storage devices with high energy density.

2. Experimental Section

2.1. Samples preparation

2.1.1. Preparation of V2O5·1.6H2O and hybrid polyaniline/V2O5 (PANI/V2O5) nanosheets

The V2O5·1.6H2O nanosheets were hydrothermally synthesized using a method described previously [18,27]. Typically, 0.91 g of bulk V2O5, 12.5 mL of 30% H2O2, and 75 mL of H2O were mixed to form a clear solution and sealed in a 100 mL Teflon autoclave which was heated to 190 °C for 10 h to produce the V2O5·1.6H2O nanosheets. The hybrid organic-inorganic PANI/V2O5 nanosheets were prepared by stirring the mixture containing 10 mL of the V2O5·1.6H2O dispersion, 100 mL of H2O, as well as 3 mL of the Aniline monomer under ambient conditions for 6 h.

2.1.2. Preparation of VN nanodots intercalated carbon nanosheets (VNNDs/CNSs)

The VNNDs/CNSs were prepared by nitriding the organic-inorganic hybrid PANI/V2O5 nanosheets at 550 °C under Ar/NH3 atmosphere for 2 h with a heating rate of 5 °C min$^{-1}$. For comparison, mesoporous VN nanosheets (VNNSs) and CNSs were also prepared. The VNNSs were prepared by nitriding pure V2O5·1.6H2O nanosheets without PANI intercalation and CNSs were prepared via etching VNNDs/CNSs in 1 M nitric acid to remove VN species. In a typical preparation, 500 mg of VNNDs/CNSs was dispersed in 500 mL of 1 M HNO3 solution under magnetic stirring for 24 h at room temperature. The resulting black powder was collected via centrifuging, filtering and vacuum drying to produce CNSs.

2.2. Materials Characterization

X-ray diffraction (XRD, XPert Pro, PANalytical) was used to determine the crystal structure. Field-emission scanning electron microscopy (FE-SEM, FEI Nova 450 Nano), transmission electron microscopy (TEM, Titan G2 60–300) with energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-6000W) were used to determine the structure, morphology and composition. VN content in the VNNDs/CNSs composite was determined by thermal analysis (TG-DTA, Netsch Corporation STA449). The N$_2$ adsorption-desorption isotherms were measured on a Micrometrics ASAP 2000. An SL200B contact angle instrument (Kino Industry, USA) was employed to assess the surface wettability. The mass loading on the electrode was determined by a microbalance (CPA225D, Sartorius). The conductivity of VNNDs/CNSs electrode was measured with a four-point probe (RTS-8). The I–V curve was tested with Agilent B1500A semiconductor characterization system.

2.3. Electrochemical tests

The capacitive performance of the VNNDs/CNSs was evaluated using a three-electrode configuration with a Pt plate as the counter electrode and Hg/HgO as the reference electrode. The electrodes were prepared by mixing the prepared materials, carbon black, and polyvinylidene fluoride (80:10:10) in N-Methyl pyrrolidone. The mixture was stirred overnight and the slurry was coated onto the carbon paper (30 μm thickness) and vacuum dried at 110 °C overnight. The electrode was pressed at 40 MPa before use. The solid-state device was fabricated by dipping the electrode into the KOH/PVA gel electrolyte for 5 min and pressed together. The KOH/PVA electrolyte was prepared by mixing 6 g of KOH and 6 g of PVA powder with 60 mL of distilled water and heating to 85 °C under vigorous stirring. All electrochemical tests were carried out on the electrochemical station (CHI 760e). Electrochemical impedance spectroscopy (EIS) was conducted by applying an AC voltage with an amplitude of 5 mV in the frequency range between 0.01 and 100 kHz.

The specific capacitance $C_m$ (F g$^{-1}$), volumetric capacitance $C_v$ (F cm$^{-3}$), packing density $\rho$ (g cm$^{-3}$), energy density $E$ (Wh cm$^{-3}$), and power density $P$ (W cm$^{-2}$) are calculated by the following equations.

$$C_m = \frac{\int idU}{S \times m \times \Delta U} \quad (1)$$
$$C_v = \rho C_m \quad (2)$$
$$\rho = \frac{m}{V} \quad (3)$$
$$E = \frac{C \Delta U^2}{2V} \quad (4)$$
$$P = \frac{E}{\Delta t} \quad (5)$$

where $S$ is the integral area based on Galvanostatic charging-discharging (GCD) profiles, $m$ (g) is the mass of VNNDs/CNSs, $I$ (A g$^{-1}$) is current, $\Delta U$ is the potential range, $\Delta t$ (s) is the discharging time, $V$ (cm$^{-3}$) denotes the volume of the VNNDs/CNSs electrode.

3. Results and discussion

Fig. 1a schematically illustrates the synthesis procedures of the 2D VNNDs/CNSs. The V2O5·1.6H2O nanosheets are produced by a facile hydrothermal method as previous report [18,27]. The XRD pattern (Fig. S1a) discloses typical (003) diffraction peaks of the layered V2O5·1.6H2O (JCPDS
SEM and high-resolution TEM (HR-TEM) show that the $V_2O_5\cdot1.6H_2O$ nanosheets have a lateral size of 0.5–2 $\mu$m and thickness of 4–10 nm (Fig. 1b and S1b). The as-synthesized $V_2O_5\cdot1.6H_2O$ nanosheets are dispersed in an aqueous solution containing the aniline monomer (3 mL) which is in situ intercalated/polymerized in the interlamellar space of $V_2O_5$ to yield the polyaniline (PANI) intercalated $V_2O_5$ hybrid nanosheets. The SEM image (Fig. 1c) shows that the PANI/$V_2O_5$ hybrid nanosheets have a morphology similar to that of pristine $V_2O_5\cdot1.6H_2O$ nanosheets. However, the XRD peaks of (001) shift to smaller angles (Fig. S1a) and HR-TEM images (Fig. S1d) disclose that the interlayered distance of $V_2O_5$ increases to 1.40 nm from 1.15 nm of the pristine $V_2O_5\cdot1.6H_2O$. Fourier transformed infrared spectroscopy (Fig. S1c) shows that a large amount of nanodots are well anchored on the 2D nanosheets, these nanodots closely resemble the pillars which are sand-like and are uniformly dispersed in the nanosheets and a well-defined 0D-in-2D pillared lamellar architecture is also revealed which is in agreement with the SEM (Fig. 1a). The HR-TEM image in Fig. 1d shows lattice fringes with spacing of 0.24 nm corresponding to the (111) planes of cubic VN, this crystalline VNNDs encapsulated in non-crystalline CNS. These small sized VNNDs will provide large amount of exposed electroactive sites for more capacitive storage, while the VNNDs intercalated CNSs structure impedes the electrochemical oxidation of VN for long-term cycle life. The STEM image and corresponding EDX elemental maps are depicted in Fig. 2f. C and N elements are uniformly distributed throughout the nanosheets but V is dispersed in an island-like fashion, thereby further indicating successful synthesis of the 0D-in-2D structured VNNDs/CNSs composite via nitriding organic-inorganic PANI/$V_2O_5$ hybrid nanosheets. It is noted that this spatially confined strategy can be extended to prepare other high-performance metal nitrides, sulfides, and phosphides on a large scale.

For comparison, CNSs and VN nanosheets (VNNSs) are also prepared. The CNSs are prepared by acid etching VNNDs/CNSs to remove VNNDs in 1 M $HNO_3$, and the VNNSs are prepared by nitriding pure $V_2O_5$ nanosheets but without PANI intercalation. The EDX and TEM results (Fig. S3) show that only lamellar structured N-doped CNSs are reserved after etching. Without the spatially-confined effect of CNSs deriving from intercalated PANI, the VN in VNNSs (Fig. S4) has larger size than VNNDs/CNSs. These results indicate that N-doped CNSs serves as a 2D encapsulator and supporter to form this 0D-in-2D pillared lamellar VNNDs/CNSs architecture.
The specific surface area (Fig. S5) of the VNNDs/CNSs is measured to be 121.8 m² g⁻¹, which is larger than that of the VNNSs (19.2 m² g⁻¹) but less than that of CNSs (231.6 m² g⁻¹). The larger specific surface area of the VNNDs/CNSs stems from the small size effect of VNNDs and pillared lamellar structure which endow large amount of exposed electroactive sites for the capacitive storage. The conductivity of the electrode film comprising the VNNDs/CNSs is measured by the I-V curve (Fig. S6) and four point probe method, a metallic conductive film and high conductivity of 225.5 S cm⁻¹ is observed, suggesting fast electron transfer and high rate capability. The contact angle measurement indicates that the VNNDs/CNSs has good wettability to the electrolyte as manifested by a small contact angle of 40.8° (Fig. S7). The pillared VNNDs/CNSs hybrid lamellar structure and small contact angle render more electroactive sites to be accessible by ions benefiting the capacitive storage properties. TG analysis shows that the VN content of VNNDs/CNSs is 91.3 wt% (Fig. S8) which is larger than those of previously reported VN/C composites [15–18,21,22]. Moreover, the measured packing density of the VNNDs/CNSs electrode is as large as 2.1 g cm⁻³ (Fig. S9). The large VN content and high packing density of VNNDs/CNSs result in large volumetric capacitance based on the total mass/volume of the electrode.

The supercapacitive performance of the VNNDs/CNSs is evaluated using the three-electrode configuration in a 1 M KOH electrolyte. For comparison, the capacitive properties of VNNSs and CNSs are also determined. Fig. 3a displays the cyclic voltammetry (CV) curves of the VNNDs/CNSs, VNNSs, and CNSs at a scanning rate of 20 mV s⁻¹ between -1.0 and -0.1 V (vs. Hg/HgO). The VNNDs/CNSs shows the largest CV area and largest specific capacitance among the three materials. Prominent Faradaic redox peaks at -0.6 V (cathodic peaks) and -0.57 V (anodic peaks) are observed from the VNNDs/CNSs and VNNSs, but CNSs shows a quasi-rectangular shape without redox peaks, suggesting that the pseudocapacitance from reversible redox reactions is the dominant charge-storage mechanism in VN-based materials. Compared to the VNNSs, the VNNDs/CNSs shows larger peak currents thus revealing enhanced redox reactions due to large amount of exposed pseudocapacitive storage sites of small sized VNNDs. The CV curves of VNNDs/CNSs at different scanning rates are exhibited in Fig. S10. Even at a high scanning rate of 1 V s⁻¹, the VNNDs/CNSs still shows similar CV curves suggesting excellent redox reversibility and high rate capability.

The GCD plots (Fig. 3b) of the VNNDs/CNSs shows a small
curvature and symmetrical triangular shape without an evident voltage drop at current densities of 0.5–100 A g⁻¹ indicative of high Coulombic efficiency and cycling reversibility. The large capacitance and high rate capability of VNNDs/CNSs are very important for SCs. The GCD curves of the VNNDs/CNSs are provided in Fig. S11-S12 and the calculated specific capacitances of the VNNDs/CNSs, VN and CNSs at different current densities are presented in Fig. 3c. The VNNDs/CNSs exhibits higher specific capacitances at all measured current densities compared to the VN and CNSs. The calculated gravimetric capacitances of the VNNDs/CNSs are 573.1, 509.6, 446.3, 408.2, 389.3, 372.3, 356.9, 341.4, and 334.8 F g⁻¹ at 0.5, 1, 2, 5, 10, 20, 50, 80, and 100 A g⁻¹, respectively. We further probed the electron transfer and ion transport properties of the VNNDs/CNSs using EIS measurement (Fig. 3d). The Nyquist plots features a vertical curve in low-frequency region, indicating a nearly ideal capacitive behavior of VNNDs/CNSs. The radius of the semicircle in the high frequency region is 0.21 Ω cm², suggesting excellent accessibility of ions to electroactive sites due to the intrinsic pillared lamellar structure and high conductivity of VNNDs/CNSs.

The long-term cycling stability of the VNNDs/CNSs and VNNSs are further evaluated at 10 A g⁻¹ (Fig. 3e). The VNNDs/CNSs exhibits excellent cycling stability with 90% capacity retention after 10,000 cycles, but in contrast the capacitance of VN fades quickly with only 10% capacity retention. The high cycling stability of the VNNDs/CNSs is also reflected by the color change of the KOH electrolyte (inset in Fig. 3e). The KOH electrolyte becomes brown yellow after 10,000 cycles in the presence of VNNSs due to electrochemical dissolution of VN in KOH. But in contrast, the color of the electrolyte with the VNNDs/CNSs does not change appreciably thereby confirming the high electrochemical stability of VNNDs/CNSs. This excellent cycle stability of VNNDs/CNSs results from the protective effect of CNSs encapsulator in VNNDs/CNSs composite, which is further supported by comparing the TEM images of VNNDs/CNSs before and after cycling. There is no substantial morphological changes after 10,000 cycling (Fig. S13) further proving the excellent electrochemical stability of VNNDs/CNSs.

For portable and miniature devices, the volumetric and areal characteristics are more important than the gravimetric capacitance due to the limited packing space. Fig. 4a compares the volumetric capacitance of the VNNDs/CNSs with those of other capacitive materials. The VNNDs/CNSs has a volumetric capacitance of 1203.6 F cm⁻³ at 1.1 A cm⁻³, which is higher than those of reported C, VN, Mxenes, metal oxides, and sulfides (Table S1) [2,5,7,32–40]. Notably, the tests for the electrodes of VNNDs/CNSs are performed with areal density of 3.5 mg cm⁻² and electrode thickness of 17 µm. In practice, thicker electrodes with sub-mm-thickness (100–200 µm) and higher areal mass loading (> 10 mg cm⁻²) are required [25,26]. Hence, we further investigate the volumetric and areal performance of the VNNDs/CNSs with different thicknesses and areal mass loadings. The side-view SEM images of VNNDs/CNSs electrodes with different thicknesses and their corresponding GCD curves are provided in Fig. S14-S16. The volumetric capacitances of the VNNDs/CNSs electrode films with thickness of 17,
35, 70, and 150 µm are measured to be 1203.6, 1162.8, 1061.5, and 867.1 F cm$^{-3}$ at 1.1 A cm$^{-2}$ (areal mass loadings of 3.5, 7.4, 14.6, and 31.1 mg cm$^{-2}$), respectively, as shown in Fig. 4b. If the underlying carbon paper is included, the volumetric capacitance is as high as 713.4 F cm$^{-3}$ at the current of 15.6 mA (Fig. S17) based on the total thickness of the electrode including 150 µm VNNDs/CNSs film and 30 µm carbon paper supporter, which outperforms previously reported carbon electrodes as well as thick electrodes of 2D carbides [31,32,41]. At a larger current density of 210 A cm$^{-2}$, the VNNDs/CNSs electrode with a thickness of 150 µm still shows a volumetric capacity of 323.5 F cm$^{-3}$.

The areal capacitances of the VNNDs/CNSs with different areal densities of 3.5, 7.4, 14.6 and 31.1 mg cm$^{-2}$ are presented in Fig. 4c showing areal capacitances of 2.0, 4.1, 7.4, and 12.8 F cm$^{-2}$ for the 17, 35, 70 and 150 µm thick electrodes. At a large current density of 1560 mA cm$^{-2}$, the VNNDs/CNSs electrode with a thickness of 150 µm still shows a high areal capacity of 4.3 F cm$^{-2}$. Fig. 4d compares the volumetric and areal capacitances of the VNNDs/CNSs (red line) with those of other materials, revealing the VNNDs/CNSs are superior capacitive performances of VNNDs/CNSs [7,26,31,36,41-46].

The superior capacitive performance of this well-defined 0D-in-2D VNNDs/CNSs stems from several factors as schematically illustrated in Fig. 4e. Firstly, the small sized VNNDs provide more electrochemical active sites for pseudocapacitive storage via fast redox reactions. Secondly, the N-doped CNSs and nano-channels between those VNNDs nano-pillars render good wettability and easy access for the electrolyte and ions to the electrochemical active sites. Thirdly, the intrinsic conductivities of VN and 2D CNSs render a long range conductive pathway for fast electron transfer yielding the superior rate capability. Fourthly, the VNNDs encapsulated in 2D CNSs structure impedes the electrochemical dissolution of VNNDs giving rise to a long cycle life. Fifthly, the large packing density of VNNDs/CNSs and the large mass content of VN in VNNDs/CNSs result in superior volumetric and areal capacitance.

To evaluate the practical application of VNNDs/CNSs in SC, a flexible all-solid-state symmetrical device composed of the VNNDs/CNSs electrodes and gel-like KOH/PVA electrolyte is prepared as shown in Fig. 5a. The all-solid-state SC has robust flexibility and can be operated in a stable voltage window between 0 and 0.9 V. The CV curves (Fig. S18) under different bending conditions have no obvious changes, further confirming the excellent flexibility. GCD curves for individual device, three devices connected in series and parallel at the same current density (7 A g$^{-1}$) were presented in Fig. S19. The charge/discharge voltage of three devices connected in series exhibited 2.7 V with almost the same discharge time compared with a single device and the discharge time of three devices connected in parallel was about 2.95 times larger than a single device which was approached to the theoretical factor 3, confirming to the theorem of series and parallel connections of capacitors. After full charging, the three SCs in series can power a commercial red light-emitting-diode (LED) with a turn-on voltage of 2 V. The CV curves of the device at scanning rates of 10, 20, 50, 100, 200, and 500 mV s$^{-1}$ are displayed in Fig. 5b. The CV curves display a quasi-rectangular and mirror shape without obvious distortion even at a large scanning rate of 500 mV s$^{-1}$ corroborating the high reversibility and rate capability. As shown in Fig. S20, the device has a volumetric capacitance of 261.5 F cm$^{-3}$ at 2 mV s$^{-1}$ which is better than those of previously reported carbon, VN, and other nitrides [15,16,47,48]. The device also exhibits excellent cycle stability with 91% capacity retention after 10,000 cycles (Fig. 5c), which is confirmed by the CV curves.
that remain the similar shape with slight capacitance fading (Inset of Fig. 5c). The volumetric energy density (E) and power density (P) are also key parameters of SCs in practice. Fig. 5d depicts the Ragone plot of the device, the characteristics of the commercial high-energy lithium thin-film battery (4 V/500 µA h), high-power aluminum electrolytic capacitor (3 V/300 µF), and representing SCs are included for comparison. Our SC shows an energy density of 30.9 Wh L⁻¹ that is approximately four times that of the commercial high-energy lithium thin-film battery (4V/500 µA h) and more than those of previously reported SCs made of carbon, metal oxides, nitrides, and Mxenes (Table S2) [2,12,15,34,47–49]. A large power density 64,500 W L⁻¹ is attained at an energy density of 16.1 Wh L⁻¹, which is comparable to that of the commercial high-power aluminum electrolytic capacitor (3 V/300 µF) [2,48]. The excellent volumetric energy/power density reveal large potential in portable and flexible electronics.

4. Conclusion

A 0D-in-2D pillared VCNDs/CNSs hybrid comprising VN nanodots intercalated carbon nanosheets is designed and synthesized by a spatially-confined strategy via nitridation organic-inorganic hybrid PANI/VₓOᵧ nanosheets. The VNNDs have a diameter of 3–5 nm and provide abundant electroactive sites for capacitive charging, while the 2D CNSs not only serve as an encapsulator to prevent the aggregation of VNNDs but also mitigate the electrochemical dissolution of VN giving rise to the large capacity and cycle stability. The VNNDs/CNSs shows an ultrahigh volumetric capacitance of 1203.6 F cm⁻³ at 1.1 A cm⁻³, excellent rate capability of 703.1 F cm⁻³ at 210 A cm⁻³, and 90% capacitance retention after 10,000 cycles. Even with a film thickness of 150 µm and areal mass density of 31.1 mg cm⁻², the film electrode consisting of VNNDs/CNSs delivers a reversible volumetric capacitance as high as 867.1 F cm⁻³ and high areal capacity of 12.8 F cm⁻² at 1.1 A cm⁻² exceeding previously reported sub-mm thickness electrodes of carbon and 2D carbides. The all-solid-state flexible symmetrical SC based VNNDS/CNSs electrodes has a volumetric energy density of 30.9 Wh L⁻¹ and power density of 64,500 W L⁻¹, as well as long cycle life. This work provides insights into the design and development of high-performance electrode materials for high volumetric energy storage.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2018.06.053.

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Supplementary Information

Spatially Confined Synthesis of Vanadium Nitride Nanodots Intercalated Carbon Nanosheets with Ultrahigh Volumetric Capacitance and Long Life for Flexible Supercapacitors

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Fig. S1 (a) XRD patterns of V$_2$O$_5$·xH$_2$O and PANI/V$_2$O$_5$ nanosheets. HR-TEM images of (b) V$_2$O$_5$·xH$_2$O and (c) PANI/V$_2$O$_5$ nanosheets. (d) FTIR spectra of the V$_2$O$_5$·xH$_2$O and PANI/V$_2$O$_5$ nanosheets.

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Fig. S3 EDS (a), TEM image(b) of the CNSs after etching VN from VNNDs/CNSs.

Fig. S4 TEM image of the mesoporous VN nanosheets (VNNSs).

Fig. S5 Nitrogen gas adsorption-desorption isotherms of the VNNDs/CNSs, VNNSs and CNSs.

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Fig. S20 Volumetric capacitances of the solid-state supercapacitor composed of the VNNDs/CNSs electrode.

Table S1 Volumetric and gravimetric capacitances of various electrode materials.

Table S2 Volumetric energy (E) and powder (P) densities of the reported SCs.

References
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**Fig. S8** Thermogravimetric and differential thermal analysis plots of the VNNSs and VNNDs/CNSs.

**Fig. S9** Side-view SEM showing that the thickness (17 μm) of the VNNDs/CNSs. The areal mass density of electrode is 3.51 mg cm⁻², so the mass density of this electrode is 2.1 g cm⁻³.

**Fig. S10** CV curves of the VNNDs/CNSs electrode at different scanning rates.
Fig. S11 Galvanostatic charging-discharging (GCD) profiles of the VNNSs electrode at different current densities.

Fig. S12 GCD profiles of the CNSs electrode at different current densities.

Fig. S13 TEM image of the VNNDs/CNSs electrode after 10,000 cycles.
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**Fig. S17** Volumetric capacitances based on the total volume of the electrode (VNNDs/CNSs+Carbon paper) at different current, the total thickness of the electrode is 47 μm (a), 65 μm (b), 100 μm (c) and 180 μm (d).

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**Fig. S20** Volumetric capacitances of the solid-state supercapacitor composed of the VNNDs/CNSs nanosheets electrode.
<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrolyte</th>
<th>Density [g cm(^{-3})]</th>
<th>Current density or scan rate</th>
<th>(C_s) [F g(^{-1})]</th>
<th>(C_v) [F cm(^{-3})]</th>
<th>Ref</th>
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<tbody>
<tr>
<td>VNNDs/CNSs</td>
<td>1 M KOH</td>
<td>2.1</td>
<td>0.5 A g(^{-1})</td>
<td>573.1 (17 μm)</td>
<td>1203.8</td>
<td>This work</td>
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<tr>
<td>2D Metallic MoN</td>
<td>1 M H(_2)SO(_4)</td>
<td>2.3</td>
<td>2 mV s(^{-1})</td>
<td>-</td>
<td>928</td>
<td>1</td>
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<tr>
<td>MnO(_2)/graphene</td>
<td>1 M H(_2)SO(_4)</td>
<td>2.5</td>
<td>0.25 A g(^{-1})</td>
<td>256</td>
<td>640</td>
<td>2</td>
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<tr>
<td>Graphene foam/MnO(_2)</td>
<td>6 M KOH</td>
<td>0.582</td>
<td>1 A g(^{-1})</td>
<td>395</td>
<td>230</td>
<td>3</td>
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<tr>
<td>Ni(OH)(_2)/graphene</td>
<td>6 M KOH</td>
<td>1.14</td>
<td>0.2 A g(^{-1})</td>
<td>573</td>
<td>655</td>
<td>4</td>
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<tr>
<td>NiCo(_2)O(_4)/NSCS</td>
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<td>2 A g(^{-1})</td>
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<td>790</td>
<td>5</td>
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<tr>
<td>GF/NiCo(_2)S(_4)</td>
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<td>2 mV s(^{-1})</td>
<td>298.5</td>
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<td>1T-MoS(_2) film</td>
<td>1 M H(_2)SO(_4)</td>
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<td>2 mV s(^{-1})</td>
<td>280</td>
<td>700</td>
<td>7</td>
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<tr>
<td>m-WO(_3)(_x)/Carbon</td>
<td>1 M H(_2)SO(_4)</td>
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<td>1 mV s(^{-1})</td>
<td>103</td>
<td>340</td>
<td>8</td>
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<tr>
<td>MoO(_3)(_x) nanobelts/CNTs</td>
<td>1 M H(_2)SO(_4)</td>
<td>1.33</td>
<td>0.5 A g(^{-1})</td>
<td>337</td>
<td>291</td>
<td>9</td>
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<tr>
<td>MXene/CNT</td>
<td>1 M H(_2)SO(_4)</td>
<td>3.0</td>
<td>5 A g(^{-1})</td>
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<td>Ti(_3)C(_2)T(_x) clay</td>
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<td>2 A g(^{-1})</td>
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<td>Ti(_3)C(_2)T(_x) paper</td>
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<td>2 mV s(^{-1})</td>
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<td>PANI/graphene</td>
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<td>Graphene (HPGM)</td>
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<td>0.1 A g(^{-1})</td>
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<td>Dense Carbon</td>
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<td>1 mA cm(^{-2})</td>
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<td>Porous Carbon Layer/Graphene</td>
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<td>0.5 A g(^{-1})</td>
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<td>GNCN film</td>
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<td>5 mV s(^{-1})</td>
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<td>331</td>
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<td>Electrodes</td>
<td>Electrolyte</td>
<td>Windows [V]</td>
<td>$E$ [Wh L$^{-1}$]</td>
<td>$P$ [W L$^{-1}$]</td>
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<td>----------------------------------</td>
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<td>-------------</td>
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<tr>
<td>VNNDs/CNSs</td>
<td>PVA/KOH</td>
<td>0-0.9</td>
<td>30.9</td>
<td>240.1</td>
<td>This Work</td>
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<tr>
<td>VN//VOx</td>
<td>LiCl/PVA</td>
<td>0-0.8</td>
<td>0.61</td>
<td>850</td>
<td>20</td>
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<tr>
<td>VN/CNT</td>
<td>PVA/H$_3$PO$_4$</td>
<td>0-0.7</td>
<td>0.54</td>
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<td>VN@C</td>
<td>PVA/PAAS/KOH</td>
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<td>TiN</td>
<td>PVA/KOH</td>
<td>0-1</td>
<td>0.05</td>
<td>–</td>
<td>23</td>
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<td>Mo$_2$N/rGO</td>
<td>PVA/H$_3$PO$_4$</td>
<td>0-0.7</td>
<td>1.05</td>
<td>35</td>
<td>24</td>
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<tr>
<td>TiN@GNSs/#Fe$_2$N@GNSs</td>
<td>PVA/LiCl</td>
<td>0-1.6</td>
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<td>211.4</td>
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<td>2D MoN</td>
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<td>2</td>
<td>1500</td>
<td>1</td>
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<td>d-Mxene</td>
<td>K$_2$SO$_4$ aqueous</td>
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<td>1.11</td>
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<td>PVA/LiCl</td>
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<td>230</td>
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<tr>
<td>MnO$_2$/graphene//V$<em>6$O$</em>{13-x}$@C</td>
<td>5 M LiCl</td>
<td>0-1.8</td>
<td>0.87</td>
<td>9000</td>
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<td>WO$_3$–x/MoO$_3$–x</td>
<td>PVA/H$_3$PO$_4$</td>
<td>0-1.9</td>
<td>1.9</td>
<td>730</td>
<td>29</td>
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<td>NiCo$_2$O$_4$/NGN/CNTs/#NGN/CNTs</td>
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<td>1600</td>
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<td>17.8</td>
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<td>Functionalized Graphene</td>
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<td>0-2.0</td>
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<td>–</td>
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<td>Reduced graphenefilm</td>
<td>H$_2$SO$_4$/PVA</td>
<td>0-1</td>
<td>0.14</td>
<td>495000</td>
<td>31</td>
<td></td>
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</tbody>
</table>

References


2 X. Zhao, L.L. Zhang, S. Murali, D. Stoller, Q. H. Zhang, Y.W. Zhu, R. S. Ruoff,


