

# 2D Amorphous V<sub>2</sub>O<sub>5</sub>/Graphene Heterostructures for High-Safety Aqueous Zn-Ion Batteries with Unprecedented Capacity and Ultrahigh Rate Capability

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Rechargeable aqueous zinc-ion batteries (ZIBs) are appealing due to their high safety, zinc abundance, and low cost. However, developing suitable cathode materials remains a great challenge. Herein, a novel 2D heterostructure of ultrathin amorphous vanadium pentoxide uniformly grown on graphene  $(A-V_2O_5/G)$  with a very short ion diffusion pathway, abundant active sites, high electrical conductivity, and exceptional structural stability, is demonstrated for highly reversible aqueous ZIBs (A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs), coupling with unprecedented high capacity, rate capability, long-term cyclability, and excellent safety. As a result, 2D A-V2O5/G heterostructures for stacked ZIBs at 0.1 A g<sup>-1</sup> display an ultrahigh capacity of 489 mAh g<sup>-1</sup>, outperforming all reported ZIBs, with an admirable rate capability of 123 mAh  $g^{-1}$  even at 70 A g<sup>-1</sup>. Furthermore, the new-concept prototype planar miniaturized zinc-ion microbatteries (A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs), demonstrate a high volumetric capacity of 20 mAh cm<sup>-3</sup> at 1 mA cm<sup>-2</sup>, long cyclability; holding high capacity retention of 80% after 3500 cycles, and in-series integration, demonstrative of great potential for highly-safe microsized power sources. Therefore, the exploration of such 2D heterostructure materials with strong synergy is a reliable strategy for developing safe and high-performance energy storage devices.

Electrical energy storage, a crucial strategy to achieve the goal of employing low-cost and renewable clean energy sources, does offer a sound and practical way to promote its reliability since the natural sources (e.g., coal, gas, petroleum) are extremely limited.<sup>[1]</sup> In this arena, Li-ion batteries with high energy density have been dominating the energy storage sector achieving great success in the past decades. However, it's never-ceasing demand for practical application is hindered by the availability of lithium sources, high cost (e.g., US\$300 kWh<sup>-1</sup>),<sup>[2]</sup>

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safety issues of organic electrolyte, and dendrites.[3-6] lithium Alternatively, rechargeable aqueous zinc-ion batteries (ZIBs) are increasingly attracting attention owing to their straightforward processing, high capacity of Zn metal anode (820 mAh g<sup>-1</sup>),<sup>[7]</sup> excellent safety, cost effectiveness (US\$65 kWh<sup>-1</sup>),<sup>[8]</sup> higher ionic conductivity of aqueous electrolytes  $(\approx 1 \text{ S cm}^{-1})$  than non-aqueous electrolytes (1-10 mS cm<sup>-1</sup>),<sup>[8]</sup> and two-electron transfer mechanism.<sup>[9]</sup> However, previous works of ZIBs based on the alkaline electrolytes still retain formidable challenges, such as inferior cyclability ( $\leq 1000$  cycles), low coulombic efficiency (≤90%), and limited capacity ( $\leq$ 400 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup>),<sup>[1]</sup> mainly caused by the byproducts and unstable cathodes.

To solve the above issues, much attention has been devoted to exploring highcapacity, electron-ion conductive, and structurally stable cathode materials, such as manganese oxides,<sup>[10–12]</sup> Prussian

blue analogues (e.g., Zn<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>),<sup>[13]</sup> NASICON-type materials (e.g., Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>),<sup>[14]</sup> transition metal sulfide (e.g., VS<sub>2</sub> Mo<sub>6</sub>S<sub>2</sub>),<sup>[15,16]</sup> polymer (e.g., pyrene-4,5,9,10-tetraone,<sup>[17]</sup> polyaniline,<sup>[18]</sup>), and vanadium-based compounds.<sup>[19-21]</sup> Recently, layered vanadium-based materials, including Zn<sub>0.25</sub>V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O,<sup>[8]</sup>  $Li_x V_2 O_5 \cdot nH_2 O_5 (22) Na_{0.33} V_2 O_5 (23) V_2 O_5 \cdot nH_2 O_5 (23) Na_{0.33} V_2 O_5 (23) V_2 V_2$ vanadate,<sup>[24]</sup> have been recognized as a very promising class for high-safety aqueous ZIBs with respectable Zn-storage capacity of 300–400 mAh g<sup>-1</sup> and cyclability (>1000 cycles),<sup>[25]</sup> originating from multivalence nature of vanadium cations and superior stability of layered structure.<sup>[22,26,27]</sup> It is noteworthy that all of the layered vanadium-based materials reported are composed of crystalline frameworks with doped metal ion or structural water, which neither sufficiently accommodates the structural strain during the (de)intercalation process nor provides ample active sites for efficient charge storage.<sup>[28,29]</sup> In a sharp contrast, amorphous frameworks can not only provide more exposed ion channels, accelerate rapid charge transfer across the electrode/electrolyte interface, and further facilitate fast ion intercalation, but also offer low internal energy and outstanding chemical stability.<sup>[30,31]</sup> Moreover, 2D heterostructures by alternating stacking of two type different 2D nanosheets produce







**Figure 1.** Schematic illustration of the fabrication process of 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures and rechargeable-battery chemistry of A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs. a) The synthetic scheme of 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures. Inset is the magnified microstructures. b,c) Schematic of the discharging (b) and charging (c) states of A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs with Zn as anode and A-V<sub>2</sub>O<sub>5</sub>/G heterostructures as cathode.

a strong synergy, which is different from the traditional composites that are created by hybridizing 2D materials with nanoparticles or mixing different 2D materials simply existing in phase separation with the limited degree of synergy.<sup>[32]</sup> In addition, 2D nanosheet heterostructures, upon stacking different 2D nanosheets, for example, high-capacity V<sub>2</sub>O<sub>5</sub> and highconducting graphene, in well-defined sequence, could readily build the high electron–ion conductive frameworks and synergistically combine the merits of individual 2D nanosheets while eliminating their related drawbacks.<sup>[32]</sup> Nevertheless, to the best of our knowledge, reasonable design of ultrathin well-defined V<sub>2</sub>O<sub>5</sub> nanosheet heterostructures with amorphous structure for highly reversible and safe ZIBs has not yet been reported.

In this work, a high-performance 2D heterostructure of ultrathin amorphous  $V_2O_5$  uniformly grown on two sides of graphene (A- $V_2O_5/G$ ) was made by 2D template based on ionadsorption approach, displaying 2D sandwich-like, ultrathin flat nanosheet ( $\approx$ 5 nm) structure with short ion diffusion, numerous active sites, and high electrical conductivity. 2D A- $V_2O_5/G$  heterostructures for ZIBs (A- $V_2O_5/G$ -ZIBs) in ZnSO<sub>4</sub> aqueous electrolytes modified with  $V_2O_5$  sol exhibit ultrahigh capacity of 489 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup>, simultaneously delivering high energy density of 342 Wh kg<sup>-1</sup> and impressive rate capability of 123 mAh g<sup>-1</sup> at 70 A g<sup>-1</sup> with excellent long-term cyclability (86% capacity retention after 3000 cycles). Meanwhile, to meet the demand of high-safety wearable micropower sources, the new-concept planar zinc ion microbatteries (denoted as A- $V_2O_5/G$ -ZIMBs) showcase outstanding performance with a high volumetric capacity of 20 mAh cm<sup>-3</sup>, high safety, extraordinary flexibility, ultralong cyclability, and compatible serial and parallel modularization for boosting the capacity and voltage output.

The synthesis of 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures, ultrathin amorphous V<sub>2</sub>O<sub>5</sub> uniformly anchored on graphene, is schematically illustrated in Figure 1a. Such 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures were prepared from the sandwich-like precursor of homogeneous VOC2O4 adsorbed on both sides of single-layer graphene oxide (GO) templates through V-O-C and C-O-C bonds. The VOC<sub>2</sub>O<sub>4</sub> was synthesized via hydrothermal treatment of V2O5 and H2C2O4 (See details in the Experimental Section). The open lamellar structure of 2D A-V2O5/G heterostructures can provide a great chance for reversibly fast intercalation and deintercalation of Zn<sup>2+</sup> (Figure 1b,c). As shown from Raman spectra in Figure 2a, the characteristic peaks of 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures below 1000 cm<sup>-1</sup> can be completely indexed to the commercial V2O5 and the peaks at 1340 and 1580 cm<sup>-1</sup> were assigned to graphene, indicating the successful loading of V2O5 on graphene nanosheets, which was further confirmed by the X-ray photoelectron spectroscopy (XPS, Figure S1, Supporting Information) results. Whereas the diffraction peaks of V<sub>2</sub>O<sub>5</sub> did not appear in the X-ray diffraction (XRD) pattern of 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures (Figure 2b), implying the formation of amorphous V2O5. The broad diffraction peak at 24.3° was due to the stacked layer of graphene. From scanning electron microscopy (SEM, Figure 2c; Figure S2, Supporting Information) and transmission electron microscopy (TEM, Figure 2d) images, 2D V<sub>2</sub>O<sub>5</sub>/G heterostructures presented an ultrathin flat morphology with nanosheet structure and their lateral size could reach up to 10 µm. High-resolution

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**Figure 2.** Morphological and structural characterizations of 2D A- $V_2O_5/G$  heterostructure. a) Raman spectra of the A- $V_2O_5/G$  heterostructure and  $V_2O_5$ . b) XRD pattern of A- $V_2O_5/G$  heterostructures, showing the obvious amorphous framework. c) SEM images of A- $V_2O_5/G$  heterostructures. d) TEM image of A- $V_2O_5/G$  heterostructures. e) HRTEM image and SAED pattern (inset) of A- $V_2O_5/G$  heterostructures. f) AFM image of A- $V_2O_5/G$  heterostructures, showing a typical thickness of 5 nm.

TEM (HRTEM, Figure 2e) image revealed the sandwich-like structure (A-V<sub>2</sub>O<sub>5</sub>/graphene/A-V<sub>2</sub>O<sub>5</sub>) of 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures. Moreover, selected area electron diffraction (SAED, Figure 2e inset) image displayed concentric diffraction rings without diffraction spots, further confirming the amorphous V2O5 component of 2D A-V2O5/G heterostructures. It was noted that the 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures disclosed a uniform thickness of  $\approx 5$  nm (Figure 2f), suggestive of short ion transfer pathway and ample energy storage active sites. Additionally, as demonstrated by thermogravimetry analysis (TGA, Figure S3, Supporting Information), the content of graphene in 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures was 37%, enabling their high electrical conductivity for fast electron transport, while graphene content of  $C-V_2O_5/G$  was 5% and there is no graphene in C-V<sub>2</sub>O<sub>5</sub>. It is believed that the ultrathin lamellar morphology, open structure, and amorphous V2O5 in 2D A-V2O5/G heterostructures can effectively offer short diffusion pathway, abundant active sites, and highly-developed electron-ion conductivity of Zn<sup>2+</sup> ions, leading to remarkably enhanced capacity and rate capability for aqueous ZIBs.

To evaluate the electrochemical performance of 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures for ZIBs, we first assembled A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs with 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures as cathode and Zn foil as anode, using 3  $\scriptstyle\rm M$  ZnSO<sub>4</sub> (saturated by V<sub>2</sub>O<sub>5</sub>) aqueous electrolyte, measured at current densities from 0.1 to 70 A g<sup>-1</sup>. It was observed that the galvanostatic charge–discharge (GCD) profiles of A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs displayed two typical charge and discharge

plateau at around 1.0/0.8 and 0.6/0.5 V (Figure 3a), respectively, owing to two electron redox process and the extraction/insertion of Zn<sup>2+</sup> ions in A-V<sub>2</sub>O<sub>5</sub>/G. Impressively, A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs delivered a record capacity of 489 mAh  $g^{-1}$  at 0.1 A  $g^{-1}$ , which is the highest value among the state-of-the-art ZIBs reported so far (Table S1, Supporting Information), such as Zn//V<sub>5</sub>O<sub>12</sub>·6 H<sub>2</sub>O (354.8 mAh g<sup>-1</sup> at 0.5 A g<sup>-1</sup>),<sup>[21]</sup> Zn//V<sub>2</sub>O<sub>5</sub> (470 mAh g<sup>-1</sup> at 0.2 A  $g^{-1}$ ),<sup>[33]</sup> Zn//VO<sub>2</sub>(B) (357 mAh  $g^{-1}$  at 0.1 A  $g^{-1}$ ),<sup>[34]</sup> and Zn//LiV<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (146 mAh g<sup>-1</sup> at 0.15 A g<sup>-1</sup>).<sup>[35]</sup> With stepwise increasing current densities, the discharge capacity varied from 489, 330, 299, 266, 254, 250, 247, 237, 221, 175 to 123 mAh g<sup>-1</sup> at 0.1, 0.3, 0.5, 1, 3, 5, 10, 20, 30, 50 to 70 A g<sup>-1</sup> (Figure 3b), respectively. Special emphasis is given to the exceptional rate performance that 123 mAh g<sup>-1</sup> capacity was achieved at ultrahigh current density of 70 A  $g^{-1}$ , corresponding to an extremely short discharge time of 6.3 s. The ultrahigh rate capability of our A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs implied the structural superiority of 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures. After abruptly returning current density to the initial 0.1 A g<sup>-1</sup>, the discharge capacity was easily recovered to 432 mAh  $g^{-1}$  (Figure 3b). In addition, it is revealed that the loading mass of cathode played a key role in the electrochemical performance of A-V2O5/G-ZIBs (Figure S4, Supporting Information).

To highlight the importance of amorphous  $V_2O_5$  and electrically conducting graphene in the performance improvement of  $A-V_2O_5/G$ -ZIBs, we also synthesized the control counterparts of crystalline  $V_2O_5/G$  nanosheets annealed at high temperature







**Figure 3.** Electrochemical performance of A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs. a) The GCD profiles and b) rate capability and columbic efficiency of A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs, obtained from 0.1 to 70 A g<sup>-1</sup>. c) GCD profiles tested at 10 A g<sup>-1</sup>, d) the cyclability obtained at 10 A g<sup>-1</sup>, and e) EIS spectra of A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs, C-V<sub>2</sub>O<sub>5</sub>/G-ZIBs, and C-V<sub>2</sub>O<sub>5</sub>-ZIBs. f) Ragone plot of stacked A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs compared with other zinc-ion batteries. g) Long-term cyclability of A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs tested at current density of 30 A g<sup>-1</sup>.

of 450 °C (denoted as C-V<sub>2</sub>O<sub>5</sub>/G-ZIBs; Figures S5 and S6, Supporting Information) and pure crystalline V2O5 nanosheets (C-V<sub>2</sub>O<sub>5</sub>-ZIBs; Figure S7, Supporting Information), and compared their electrochemical performance for ZIBs (Figure S8, Supporting Information). Obviously, the GCD profile of A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs tested at 10 A g<sup>-1</sup> offered a very impressive capacity of 276 mAh g<sup>-1</sup>, which was much higher than those of  $C-V_2O_5/G-ZIBs$  (217 mAh g<sup>-1</sup>) and  $C-V_2O_5-ZIBs$  (154 mAh g<sup>-1</sup>). Furthermore, A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs displayed exceptional cycling stability, showing an initial capacity of 272 mAh g<sup>-1</sup> increasing to 310 mAh g<sup>-1</sup> after several cycles and satisfactory capacity retention around 93% after 800 cycles. In a sharp contrast, C-V<sub>2</sub>O<sub>5</sub>/G-ZIBs exhibited an initial capacity from 218 mAh g<sup>-1</sup> to 149 mAh g<sup>-1</sup> after 300 cycles with a low capacity retention of 68%, and C-V<sub>2</sub>O<sub>5</sub>-ZIBs kept only 150 mAh g<sup>-1</sup> after 300 cycles with capacity retention of 97% at same current density of 10 A  $g^{-1}$  (Figure 3d), demonstrating the superiority of the

amorphous structure over crystalline V2O5 and the significance of graphene in the heterostructure. This result could be further verified by the electrochemical impedance spectra (EIS, Figure 3e; the equivalent circuit model of A-V2O5/G-ZIBs is shown in Figure S9, Supporting Information), revealing a lower equivalent series resistance value of 2.4  $\Omega$  for A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs in comparison with 2.6  $\Omega$  for C-V<sub>2</sub>O<sub>5</sub>/G-ZIBs and C-V<sub>2</sub>O<sub>5</sub>-ZIBs (2.8  $\Omega$ ) (Figure S10, Supporting Information). More importantly, from medium to high frequency region, A-V2O5/G-ZIBs disclosed a lower charge transport resistance of 20  $\Omega$ , and smaller voltage polarization of 0.64 V at plateau region than that (102  $\Omega$ , 0.8 V) of C-V<sub>2</sub>O<sub>5</sub>/G-ZIBs, further implying the enhanced kinetics in amorphous framework.<sup>[36]</sup> In addition, our A-V2O5/G-ZIBs represented excellent Zn2+ storage property with remarkable energy density of 313 Wh kg-1 and power density of 46 kW kg<sup>-1</sup> (Figure 3f). Remarkably, even when A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs were cycled at current density of as high

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**Figure 4.** Kinetics analysis and mechanism of  $Zn^{2+}$  storage process of A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs. a) The CV curves of A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs tested at different scan rates from 2 to 8 mV s<sup>-1</sup>. b) The plots of log *i* versus log  $\nu$  curves of cathodic and anodic peaks. c) Capacitive contribution (gray part) and diffusion contribution (void part) at 2.0 mV s<sup>-1</sup>. d) Normalized capacitive (gray part) and diffusion-controlled (orange part) contribution ratios from 2 to 8 mV s<sup>-1</sup>. e, f) Ex situ deconvoluted XPS spectra of e) V 2p and f) Zn 2p at pristine, fully discharged, and charged states in the sixth cycle. g,h) Ex situ XRD patterns of A-V<sub>2</sub>O<sub>5</sub>/G cathode for ZIBs tested with 3 M ZnSO<sub>4</sub> after the 1st (g) and 5th (h) cycles, and i) corresponding GCD profiles. j) HRTEM image of 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures cathode obtained after the 5th cycle.

as 30 A g<sup>-1</sup>, the charge/discharge curves at different cycles of 1000th, 2000th, and 3000th almost overlapped with each other, accompanied with high coulombic efficiency of about 99% (Figure S11, Supporting Information). Moreover, A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs unveiled ultralong lifespan, maintaining high capacity of 240 mAh g<sup>-1</sup> and remarkable capacity retention of about 87% after 3000 cycles at 30 A g<sup>-1</sup> (Figure 3g), outperforming most reported ZIBs (Table S1, Supporting Information) based on such as Zn<sub>3</sub>V<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>·2H<sub>2</sub>O (68% retention after 300 cycles),<sup>[4]</sup> V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O (71% after 900 cycles),<sup>[9]</sup> Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O (64% after 1000 cycles),<sup>[22]</sup> and K<sub>2</sub>V<sub>8</sub>O<sub>21</sub> (83% after 300 cycles).<sup>[27]</sup> It is noted that the slight cycling degradation was possibly ascribed to the formation of byproducts on the A-V<sub>2</sub>O<sub>5</sub>/G surface decomposed by ZnSO<sub>4</sub> electrolyte and V<sub>2</sub>O<sub>5</sub>,<sup>[37]</sup> together with the formation).

To further investigate the  $Zn^{2+}$  storage behavior of 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures, cyclic voltammetry (CV) measurements of A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs were performed at different scan

rates from 2 to 8 mV s<sup>-1</sup> (Figure 4a). It was observed that, with the continuous increase of scan rates, the CV curves still retained the initial shapes, verifying exceptional rate performance and structural stability of A-V<sub>2</sub>O<sub>5</sub>/G electrode. The two pairs of redox peaks were consistent with the GCD curves (Figure 3a), corresponding to the (de)intercalation process of Zn<sup>2+</sup>. The surface capacitive effect of A-V<sub>2</sub>O<sub>5</sub>/G cathode was evaluated by the equation<sup>[35,38,39]</sup>  $i = av^b$ , where *i* is the current, v is scan rate, and a and b are adjustable parameters. The bvalue is determined from the slope of log(i) versus log(v) plot, in which b = 0.5 stands for a diffusion-controlled process, and b = 1.0 for a supercapacitor-like process. It was calculated that the b values of peaks 1-4 are 0.82, 0.83, 0.86, and 0.84 (Figure 4b), manifesting a synergetic charge storage process of the diffusion-controlled and capacitive behaviors coexisted in A-V<sub>2</sub>O<sub>5</sub>/G heterostructures.

To specify the capacitive contribution at a certain scan rate, we used the equations of  $i = k_1 v + k_2 v^{1/2}$  and  $i/v^{1/2} = k_1 v^{1/2} + k_2$ 



to evaluate the capacity ratio from capacitive  $(k_1\nu)$  and diffusion-controlled  $(k_2\nu^{1/2})$  process at a particular voltage during cycling.<sup>[40,41]</sup> For instance, at scan rate of 2 mV s<sup>-1</sup>, the shaded area in the whole CV curve stood for the surface-induced capacity, accounting for 77% of the total capacity (Figure 4c). With increasing scan rates from 4 to 8 mV s<sup>-1</sup>, the capacitive contribution ratios increased from 82% to 88% (Figure 4d). Therefore, it is concluded that the high rate performance of V<sub>2</sub>O<sub>5</sub>/G-ZIBs is a result of the prominent capacitive-controlled kinetics process, which is a big advantageous feature and a major difference with the previously reported vanadium based cathode materials with crystalline phase for ZIBs.<sup>[22,26,38,42]</sup>

The reversible ion storage of  $Zn^{2+}$  in 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures was confirmed by ex situ XPS analysis (Figure 4e,f). At the pristine state, it was observed that the V<sup>5+</sup> peak of 2p<sub>3/2</sub> at 517.1 eV appeared in the V 2p XPS region, accompanied by a weak V<sup>4+</sup> component of  $2p_{3/2}$  at 515.4 eV, slightly reduced by the oxygenated graphene during annealing. At the discharge state, the intensity of V<sup>4+</sup> peak increased, while the V<sup>5+</sup> decreased, resulting from the Zn<sup>2+</sup> insertion. Moreover, the pristine V 2p XPS shapes were well recovered upon charging, indicative of high electrochemical reversibility. Meanwhile, there was no signal of the  $Zn^{2+}$  in the initial state of A-V<sub>2</sub>O<sub>5</sub>/G cathode. After being discharged to 0.2 V, two strong and sharp peaks of Zn 2p3/2 signals at 1022 and 1045 eV were presented, originating from the insertion of Zn<sup>2+</sup> ions into the amorphous framework.<sup>[43]</sup> Interestingly, the existence of weak Zn<sup>2+</sup> peaks upon full charging was likely attributed to the surface adsorption of Zn<sup>2+</sup> from residual electrolyte.<sup>[17]</sup> To demonstrate chargestorage mechanism without involving the amorphous phase change of  $A-V_2O_5/G$  during cycling, we carried out the ex situ XRD patterns and HRTEM images of A-V2O5/G cathode for ZIBs tested with 3 M ZnSO<sub>4</sub> electrolyte without saturated V<sub>2</sub>O<sub>5</sub> (Figure 4g-j).<sup>[33]</sup> Notably, it was found that there were no crystalline peaks of V<sub>2</sub>O<sub>5</sub> phase and Zn<sup>2+</sup> intercalation peaks during discharging (from 1.8 to 0.2 V) and charging (from 0.2 to 1.8 V) after the 1st and 5th cycles, suggestive of highly stable amorphous structure of 2D A-V<sub>2</sub>O<sub>5</sub>/G (Figure 4g-i). Also, no crystalline V<sub>2</sub>O<sub>5</sub> nanoparticles were observed from HRTEM images of A-V<sub>2</sub>O<sub>5</sub>/G cathode after the 5th cycle (Figure 4j, Figure S13, Supporting Information), which was in good agreement with XRD patterns. In a sharp contrast, when A-V<sub>2</sub>O<sub>5</sub>/G cathode for ZIBs was tested in the same electrolyte with saturated  $V_2O_5$ , the crystalline V<sub>2</sub>O<sub>5</sub> phase appeared, originating from the slight deposition of V<sub>2</sub>O<sub>5</sub> in the electrolyte (Figures S14 and S15, Supporting Information).

To meet the immense demands of the future flexible and miniature electronics, we also constructed new-concept planar miniaturized zinc ion micro batteries (A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs) based on the interdigital microelectrodes of Zn powder as anode and 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructure film, with a thickness of 7  $\mu$ m, as cathode on one single substrate, fabricated by mask-assisted vacuum filtration deposition strategy (See details in Experimental Section, **Figure 5**a–c).<sup>[44,45]</sup> It could be seen that our planar A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs displayed outstanding mechanical flexibility without any fragmentation of microelectrodes and delamination from the substrate under different bending states, for example, serious bending and twisting. Meanwhile, our microdevice showed an obvious feature of redox

characteristics at 3 mV s<sup>-1</sup> (Figure S16, Supporting Information), indicating the successful construction of planar miniaturized ZIMBs. To fulfill the requirement of high capacity and high voltage, the integrated planar ZIMBs were fabricated via interconnection in series and parallel (Figure 5d), which displayed similar electrochemical behaviors to single cell, and a stepwise increase of average discharging voltage from 1.3 V for one cell to 2.6 V for two cells and 3.9 V for three cells (Figure 5e). In the meantime, the integrated ZIMBs connected in parallel exhibited impressively high capacity increasing from 17 to 51 µAh from one cell to three cells (Figure 5f), demonstrative of high performance uniformity. Furthermore, our planar A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs disclosed excellent rate capability (Figure S17, Supporting Information) from 0.5 to 4 mA cm<sup>-2</sup> and exceptionally long-term cycling stability and high volumetric capacity of 20 mAh cm<sup>-3</sup> at 1 mA cm<sup>-2</sup> after 3500 cycles with capacity retention of 80% (Figure S18, Supporting Information). Remarkably, our A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs show excellent energy density of 21 mWh  $\rm cm^{-3}$  at a power density of 526 mW  $\rm cm^{-3}$ (Figure 5g), which was much higher than commercially available supercapacitors (SC, 1 mWh cm<sup>-3</sup>),<sup>[46]</sup> Zn-ion micro-supercapacitors (Zn-MSC, 11.81 mWh cm<sup>-3</sup>),<sup>[46]</sup> lithium thin-film battery (10 mWh cm<sup>-3</sup>),<sup>[47]</sup> ZnO//NiO (11 mWh cm<sup>-3</sup>),<sup>[48]</sup> and NiO//Fe<sub>3</sub>O<sub>4</sub> (1.83 mWh cm<sup>-3</sup>).<sup>[49]</sup> Notably, A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs exhibited excellent flexibility at a bending angle from 0°, 60°, 90°, 120° to 180° with a capacity retention of 93% at 180° (Figure S19, Supporting Information). Moreover, two planar A-V2O5/G-ZIMBs cells connected in series could readily power a lightemitting diode (LED) for a significantly long time under the flexible state, and light up a display screen of our institute "DICP" logo (Figure 5h,i), demonstrative of great potential as flexible micropower sources.

Such extraordinary performance with high capacity and excellent cyclability of A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs was assigned to the peculiar 2D amorphous V<sub>2</sub>O<sub>5</sub>/G heterostructures, which offers several beneficial features: i) ultrathin sandwich-like structure of V<sub>2</sub>O<sub>5</sub>/ graphene/ $V_2O_5$  combined with the synergy of  $Zn^{2+}$  intercalation and surface-related capacitive process as well as short ion and electron pathways, ii) amorphous feature involving inherent disorder in the structural arrangement with more active sites for Zn ion insertion/extraction,[31,50] iii) amorphous heterostructures providing proper volume accommodation for the structural strain during the charging/discharging process, and iv) 2D ultrathin heterostructures combining the merits of 2D V<sub>2</sub>O<sub>5</sub> and graphene to greatly boost the prominent capacitivecontrolled kinetics process, and to make full use of the ultrathin V2O5 nanosheets and amorphous V2O5 structure as well as graphene at the same time for high capacity contribution.

In summary, we have developed 2D template based ionadsorption approach to successfully synthesize 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures, displaying unprecedented capacity and excellent rate capability and cyclability for the stacked ZIBs and planar ZIMBs, resulting from the unique heterostructure, amorphous nature, and synergy of A-V<sub>2</sub>O<sub>5</sub> and graphene. Impressively, the stacked ZIBs disclosed ultrahigh capacity of 489 mAh g<sup>-1</sup>, outperforming all reported ZIBs, with ultrahigh rate capability of 123 mAh g<sup>-1</sup> even at 70 A g<sup>-1</sup>, while the planar A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs exhibited high volumetric capacity of 20 mAh cm<sup>-3</sup> with long cyclability. Further, the facile www.advancedsciencenews.com

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**Figure 5.** Fabrication and electrochemical performance of planar A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs. a) Schematic illustration of the planar A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs based on asymmetric interdigital microelectrodes of Zn anode and A-V<sub>2</sub>O<sub>5</sub>/G cathode. b) Photograph of the planar A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs. c) Cross-sectional SEM image of the A-V<sub>2</sub>O<sub>5</sub>/G microelectrode. d) Schematic illustration of the integrated planar A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs connected three cells in series (up) and in parallel (bottom). e) GCD profiles of the integrated planar A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs connected e) in series and f) in parallel from 1 to 3 cells. g) Ragone plot of A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs compared with other microscale energy-storage devices (AC: active carbon, CNTs: carbon nanotubes, MSC: microsupercapacitors, SC: supercapacitors). h,i) Photographs of two serially connected planar A-V<sub>2</sub>O<sub>5</sub>/G-ZIMBs for h) lighting up an LED, and i) powering a display of "DICP" logo under flexible state.

integration of our planar A-V<sub>2</sub>O<sub>5</sub>/G ZIMBs in serial and parallel connection verified superior performance uniformity. Therefore, 2D A-V<sub>2</sub>O<sub>5</sub>/G heterostructures equipped with grain boundaries, short ion diffusion path, rich defects, and more active sites for charge storage possess a great potential use in low-cost and aqueous stacked high-performance ZIBs. Besides that, this work of designing 2D heterostructures, derived by architecting graphene and other 2D materials, will open up numerous opportunities to create next-generation high-safety non-lithium-based electrochemical energy storage sources.

## **Experimental Section**

Synthesis of 2D A- $V_2O_5/G$  Heterostructures: First, a dark blue solution of  $VOC_2O_4$  was formed through the solvothermal strategy, where 2 mM

 $V_2O_5$  powder (Sigma-Aldrich) and 6 mm  $H_2C_2O_4$  powder (Sigma-Aldrich) were dissolved into 12 mL deionized water at 75 °C for 2 h. Second, single-layer graphene oxide (GO, 1 mg mL<sup>-1</sup>, 80 mL) nanosheets were used as 2D template or substrate to adsorb the VOC\_2O\_4 monomers (9.6 mL) for 2 h. Third, the resultant solution was frozen by liquid nitrogen, and then freeze-dried for 3 days. Finally, after the dried powders were annealed at 300 °C for 3 h, the 2D A-V\_2O\_5/G heterostructures were obtained. For comparison, the 2D C-V\_2O\_5/G heterostructures were prepared at 450 °C while other steps kept unchanged. The crystalline vanadium oxide (C-V\_2O\_5) was prepared the same approach except for the lack of graphene.

Fabrication of V<sub>2</sub>O<sub>5</sub>/G-ZIBs: The stacked A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs were studied in 2016 coin-type cells assembled in air. The A-V<sub>2</sub>O<sub>5</sub>/G cathode was prepared by mixing the active materials, acetylene black, and polyvinylidene fluoride (the mass ratio is 8:1:1) in *N*-methyl pyrrolidone. Then, the slurry was coated on the stainless steel foil (0.01 mm thick) and dried at vacuum at 80 °C for 12 h. Next, Zn foil, 3 m ZnSO<sub>4</sub> saturated



vanadium oxide aqueous solution, and glass fiber membrane were used as anode, electrolyte, and separator, respectively. It was noted that all the ZIBs had excessive mass loading of anode and specific capacity was calculated based on the cathode.

The planar A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs were fabricated by mask-assisted vacuum filtration.<sup>[44]</sup> First, 1 mL high-quality electrochemically exfoliated graphene (EG, Figure S20, Supporting Information) ethanol dispersion (0.1 mg mL<sup>-1</sup>) was filtrated through the home-made interdigital mask with eight fingers (length of 14 mm, width of 1 mm, interspace of 0.5 mm; Figure S21, Supporting Information) to form highly conductive EG layer on a nylon membrane (0.22  $\mu$ m, Agela Technologies). Second, 1 mL A-V<sub>2</sub>O<sub>5</sub>/G dispersion (0.5 mg mL<sup>-1</sup>, 10 wt% EG) and 1 mL zinc powder dispersion (0.5 mg mL<sup>-1</sup>, 10 wt% EG; Figure S22, Supporting Information) were followed from each side (four fingers) of the mask under constant filtration to establish cathode and anode microelectrodes, respectively. After removing the mask and adding the electrolyte, the planar A-V<sub>2</sub>O<sub>5</sub>/G-ZIBs were achieved.

*Materials Characterization*: The morphology, structure, and composition of the active materials, graphene, the inks, and microelectrodes were analyzed using field-emission SEM (JSM-7800F), HRTEM (JEM-2100), XRD (X'pert Pro, 5°–90°), XPS (Omicron Multiprobe equipped with the monochromatic Al K $\alpha$  source, electron analyzer resolution of 0.9 eV), and TGA (STA 449 F3, measured at air atmosphere, 10° min<sup>-1</sup> from 25 to 650 °C).

*Electrochemical Measurement*: The CV curves obtained at varying scan rates of 2–8 mV s<sup>-1</sup> and EIS tested from 100 kHz to 0.01 Hz with an AC amplitude of 5 mV were conducted by an electrochemical workstation (CHI 760E), and the GCD profiles were measured by LAND CT2001A battery tester between 0.2 and 1.8 V at current densities from 0.1 to 70 A g<sup>-1</sup>.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## Keywords

2D heterostructures,  $V_2O_5$ /graphene, zinc ion batteries

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