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Hierarchical vertical graphene nanotube arrays via universal carbon plasma processing strategy: A platform for high-rate performance battery electrodes

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Abstract

Tailoring graphene-based nanostructures with numerous edges and large porosity is critical in developing high-capacity and fast rate-response Na-ion battery. Here, we report a rapid and generalized strategy for preparation of hierarchical vertical graphene nanotube (hVGT) array via carbon plasma processing of CuO nanowires. A plausible mechanism is provided with the successful extension of such approach to grow hVGT array on different nanostructure templates such as Ni₃S₂, NiO and Co₃O₄. Benefiting from such unique structural advantages including high electrical conductivity, strong mechanical stability and highly porous structure, the self-supported MoS₂ nano-crystals anchored hVGT (MVGT) nano-frameworks deliver satisfactory Na-ion storage properties with enhanced rate capability and long-term cycling stability. Hence, it is worth emphasizing that this deterministic and plasma-based dry-synthesis method to fabricate hVGT architecture could provide new avenues in designing and fabricating high-performance carbon-based electrodes for energy storage devices.

Graphical Abstract :

Universal plasma-based strategy is validated for the facile synthesis of hierarchical vertical graphene nanotubes in superior Na-ion storage behavior.

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Keywords: Carbon plasma • universal strategy • hierarchical framework • vertical graphene nanotube • high capability and stability

1. Introduction

Vertical graphene nanosheets (VGSs), grown onto micro-sized substrates, have attracted considerable interests owing to the non-agglomerated three-dimensional (3D) inter-

networked morphology, controlled inter-sheet connectivity, and exposed ultra-thin and ultra-long edges [1, 2]. Advanced functional properties, including readily accessible surface areas, unusual surface functionalities and enhanced loading density also become quite accessible [1, 3-7]. The VGSs-based nano-frameworks have achieved considerable performance enhancement in different areas of applications, especially energy storage and conversion [3, 8-10].

However, the advantages of currently investigated VGSs are quite limited. Firstly, the amount of VGSs is largely restricted due to the planar substrate, even in terms of the quasi-planar substrates with micro-sized sub-structures (such as carbon cloth and Ni foam) as a result of limited plasma penetration into inner part of porous structure. It has been demonstrated that the thickness of VGS array reduces with the depth inside the 3D substrate [11]. Secondly, the loading density of other active materials is also limited since smaller exposed surface of VGS on quasi-planar substrates reduces inwardly. The heights of VGS array are typically confined to hundreds of nanometers, which largely restricts its chemically available area [12]. Moreover, to our best knowledge, few current reports actually intend on following through the advantage of light-weight feature of VGS, i.e., without getting rid of the porous metal or carbon cloth substrates. Hence, the technical challenge on employing high-quality VGS for energy storage remains formidable. New methodologies and nanotechnologies are required for achieving highly porous substrates with sufficient nano-scaled VGSs.

Here, we provide a facile strategy to directly grow vertical graphene onto nano-sized substrate, using CuO nanowires (NWs) as the backbones. Natural carbon-plasma leads to the reduction of CuO to metallic copper NWs and simultaneously achieves densely decorated hierarchical vertical graphene nanosheets on their surfaces (Cu-VGS). The growth mechanism has been investigated for the successful extension of a series of nano-sized architectures for VGS growth, including Ni_3S_2 , NiO and Co_3O_4 . Furthermore, free-standing hierarchical vertical graphene nanotube (hVGT) is achieved by removing metallic skeleton for the exploitation of hVGT application in energy storage. MoS_2 , serving as a promising Na^+ host, is further deposited onto hVGT surface via pulsed laser deposition (PLD). Based on the robust and highly porous structure, such hierarchical

arrays have been confirmed with superior capacity and high-rate stability. Herein, our research provides a carbon plasma-based dry and universal synthesis process for the potential construction of hierarchical structure for the applications in energy storage, catalysis, and sensing.

2. Experimental Section

Synthesis of CuO nanowires: All reagents were analytically pure and used without further purification. Compressed Cu foams were cut into standard pieces ($2\text{ cm} \times 1\text{ cm}$) with a small rectangular extension ($0.5\text{ cm} \times 0.5\text{ cm}$) at the middle of one side acting as the current collector (see Supporting Information Figure S1). The substrates were washed in acetone, ethanol, and distilled water for 20 min separately and then dried with N_2 gun. After that, anodization of Cu into $\text{Cu}(\text{OH})_2$ was conducted in 1 M NaOH with a CHI 760D using chronopotentiometry technique under 20 mA anodizing current for 10 min. The samples were then annealed in air under $300\text{ }^\circ\text{C}$ for 1 h to obtain CuO NWs.

Synthesis of CuO-deposited VGS and free-standing hVGTs: The Cu-deposited VGS (Cu-VGS) were synthesized via 13.56 MHz radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) system. In a typical process, as-obtained CuO nanowires substrate was placed inside the quartz tube reactor between the two capacitively coupled RF electrodes. Afterwards, the tube was evacuated using combination of rotary and turbo pump. The reactor chamber was then heated to $450\text{ }^\circ\text{C}$. Once the desired temperature was achieved, a small amount of sustainable tea-tree oil vapor, serving as carbon precursor, was continuously introduced into the reaction tube by its self-evaporation at ambient temperature. The RF plasma discharge was switched off after 10 min plasma deposition to finally obtain Cu-VGS. Subsequently, 3 M FeCl_3 solution was introduced to remove the metallic Cu skeleton of Cu-VGS, and the free-standing hVGT was obtained accordingly for Na-ion storage application. The mass density of hVGT was $\sim 0.8\text{ mg cm}^{-2}$.

The VGS growth mechanism on CuO nano-framework was investigated using different C-plasma processing durations ranging from 10 to 120 s with sample designated as CuO/Cu-C-X ($X = 10\text{s}, 30\text{s}, 60\text{s}, \text{ and } 120\text{s}$). Additionally, to validate the universal behavior of such facile approach, same parameters have also been applied for the successful growth of VGSs onto the surfaces of Ni_3S_2 , NiO and Co_3O_4 nano-frameworks

with designations of Ni_3S_2 -VGS, NiO -VGS and Co_3O_4 -VGS respectively. Ni_3S_2 , NiO and Co_3O_4 nanostructures have been fabricated onto Ni foam using hydrothermal methods based on typical literatures [13-17].

Fabrication of hVGTs-MoS₂ core-shell structure (designated as MVGT): In order to deposit MoS₂ onto hVGT surface using dry-synthesis process, a Lotis-TII (LS-2137U) 2nd harmonic Nd:YAG laser (532 nm, 10 Hz, 10 ns) is used to ablate the MoS₂ target (99.99 purity 2.5 cm diameter disc target purchased from Kurt J. Lesker) in the PLD chamber at room temperature. The deposition was carried out in Ar atmosphere at $\sim 1 \times 10^{-7}$ mbar. The laser fluence and the deposition duration were set to 29 J cm^{-2} and 300 s, respectively. The mass loading of MoS₂ onto hVGT was approximately 0.15 mg cm^{-2} .

Characterization and electrochemical measurements: Field-emission scanning electron microscopy (FESEM) analysis was carried using JEOL JSM-6700F scanning electron microscope at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) measurements were performed by JEOL-2010 UHR high resolution transmission electron microscope at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were collected using a D8 advanced diffractometer equipped with Cu K α radiation ($\lambda = 0.15406 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) analysis was conducted using Thermal Scientific Theta Probe system XPS with a monochromatic Al K α (1486.7 eV) X-ray source. Binding energy of C 1s peak from sp²-bonded carbon at 284.5 eV was used as a reference for correction. Raman spectra were obtained using a WITEC-CRM 200 Raman system with an excitation laser of 532 nm (2.33 eV). The Si peak at 520 cm^{-1} was used as a reference to calibrate the wavenumber.

To measure the electrochemical performance of all synthesized materials, coin-type cells (CR 2032) were assembled in an argon-filled glove box with both moisture and oxygen contents below 0.1 ppm. The coin cells were assembled using metallic sodium foil as the counter-electrode, 1M NaPF₆ in ethylene carbonate (EC)-diethyl carbonate (DEC)-fluoroethylene carbonate (1:1:0.05 in volume) as the electrolyte, and glass fiber as the separator. The hVGTs-MoS₂ were directly used as working electrode without the addition of any conductive or binding materials. The galvanostatic charge-discharge (GCD) tests were performed using a NEWARE battery testing system at different current rates. Cyclic

voltammetry (CV) measurements were conducted on Solartron 1470E electrochemical workstation using a potential range of 0.005-3.0 V (vs. Na/Na⁺). The electrochemical impedance spectroscopy (EIS) was performed in the frequency range of $1 \times 10^6 - 0.01$ Hz.

3. Results and discussion

3.1 Growth mechanism of hVGTs via carbon plasma processing and its universality

Figure 1: SEM images and XRD characterization of CuO and Cu-VGS. (a) and (b) SEM images of CuO and Cu-VGS; (c) XRD comparisons.

The CuO NWs, serving as starting materials, were achieved via electrochemical anodization process followed by thermal annealing. Figure 1a shows the uniform CuO nanowires arrays with homogeneous size distribution (ca. 150 nm in width). After RF carbon-plasma based processing for 10 min, the whole surface of CuO is completely covered by interconnected VGS arrays with typical heights of 150~200 nm (Figure 1b). As shown in Figure 1c, strong diffraction peaks located at 35.5° , 38.6° , and 67.6° are observed before VGS growth, corresponding to the lattice facets of (002), (111) and (220) of CuO (JCPDS No. 48-1548). Notably, copper oxides have been totally reduced after vertical graphene deposition for 10 min, with the evidence of the absence of oxide-related diffraction peaks. Such results indicated that our facile strategy is capable of delivering hierarchical vertical graphene on nanowire surfaces along with simultaneous reduction of copper oxides to metallic copper at relatively low temperature and without any specific hydrogen feed.

Figure 2: The schematic illustration, SEM and TEM images of carbon plasma processing with different duration. (a) Intrinsic CuO nanowires without treatment. (b-e) 10, 30, 60, 120 s duration C-plasma treated samples.

To further extend such plasma-based strategy for other nano-substrates, the growth mechanism of VGSs onto NWs has been investigated. The morphology and structure variation on copper oxide nanowires are deduced on the basis of images shown in Figure 2 at different carbon-plasma processing durations. As shown in Figure 2a, the bare CuO NWs exhibit smooth surface with typical lattice spacings of 2.55 and 2.79 Å, corresponding to (111) and (110) facets respectively. After plasma treatment of 10 s, randomly separated nano-assemblies with sizes of ~100 nm have been observed from images in Figure 2b. Such nano-assemblies show a lattice spacing of 2.13 Å, which is attributed to the metallic copper. With the increase of C-plasma processing duration of 30 s (Figure 2c), the proportion of metallic nano-assemblies enhances. Meanwhile, the homogeneous carbon shell could be found on the surface of metallic nano-structure. With plasma processing duration of 60 s, most of the oxide NWs has been converted to metallic phase, which can also be confirmed by XRD results (Figure S2).

Besides, XRD pattern also confirmed the above results. Typically, CuO nanowires exhibit characteristic peaks at 35.5° and 38.7° , corresponding to (-111) and (111) planes [18]. With C-plasma processing of 10 s, a new peak at 36.44° appears, accompanied with the absence of both peaks in CuO. Such peak can be assigned to the (111) plane of Cu_2O , indicating the rapid reduction of CuO to Cu_2O phase [19]. With elongated treatment duration, the peak intensity of Cu_2O gradually reduces until the total disappearance, which demonstrates the complete reduction of copper oxide towards metallic Cu. Simultaneously, the thickness of graphitic carbon shell is also observed, which serves as the preliminary stage for the growth of hVGT. As the C-plasma processing duration is increased to 120 s, the uniformly distributed vertical graphene is observed to form onto the Cu NWs surfaces. Notably, the reduction of CuO by our carbon-based sustainable oil was carried out in RF-plasma at $<450^\circ\text{C}$. In comparison, the normal thermal treatment at the same temperature can only deliver slight conversion and the substrate remains in the oxide form [20, 21].

As reported, the high temperature ($>600^\circ\text{C}$) reduction of NiO by CH_4 proceeds via the fragmentation of adsorbed CH_4 on active sites of the oxide surface to form active adsorbed carbon (C_{ad}) and H_2 [22]. In our low temperature C-plasma, a relatively higher concentration of carbon-based radicals is formed through electron impact dissociation. The resulting radicals recombine in the gas phase and form higher hydrocarbons. It was then adsorbed onto the substrate surface and further fragmented to form active adsorbed carbon. This effective plasma decomposition of carbon precursor allows CuO NW reduction at much lower temperatures. The generated active carbon reduces CuO to metallic copper and CO, which further reduces CuO to generate CO_2 . Meanwhile, the excessive free carbon (adatoms) begin to deposit onto metallic surface to achieve buffer layer. With elongated plasma duration, vertical graphene is successfully grown onto the substrate.

To further confirm the universality of our approach for the VGS growth on other nano-sized structures, other metal- sulfide and oxide nano-architectures such as Ni_3S_2 , NiO and Co_3O_4 have also been used. Figure S3a displays the uniform Ni_3S_2 nanosheets on Ni foam, followed by the densely distributed hierarchical vertical graphene onto nanosheets after

plasma processing with same operational parameters as that of Cu-VGS (Figure S3b). The XRD pattern in Figure S3c shows the disappearance of well-defined peaks corresponding to Ni_3S_2 after plasma treatment, indicating the reduction of Ni_3S_2 to metallic nickel. Notably, only small amount of structural pulverization of nanosheets is observed after the VGS growth, demonstrating the excellent structural maintenance through such strategy. Besides, we also succeeded in expanding such fabrication to NiO and Co_3O_4 nanostructures via same synthesizing strategy. It can be observed in Figure S3d and S3g that NiO and Co_3O_4 deliver vertical nanoflake and nanowire structures on Ni foam based on wet-chemical approaches. After carbon plasma processing, hierarchical VGS can be observed on the corresponding nano-framework without any structural pulverization (Figure S3e and Sh). Meanwhile, the related XRD results (Figure S3f and S3i) exhibit similar results like Ni_3S_2 and CuO , further manifesting the universal feature of our C-plasma processing strategy.

3.2 Structural and morphological characterization of MVGTs

To further investigate the superior features of such hierarchical vertical graphene, we achieved the free-standing hVGT nano-structures via CuO nanowires as the template, followed by the MoS_2 decoration as active materials for sodium-ion storage. The synthesis procedure of the MoS_2 decorated free-standing hVGT arrays electrode is illustrated in Figure 3a. Upon vertical graphene deposited onto nanowires, the metallic substrate was removed to deliver VGS nanotube structure, referred as hVGT, which retains its original hierarchical structure without pulverization (Figure S4a). Noticeably, the VGS nanotube arrays deliver a uniformly vertical nanosheet structure, which are ideal backbones for anchoring active materials. Subsequently, the MoS_2 nano-crystalline structures were deposited onto the hVGT surfaces using PLD, forming hVGT- MoS_2 nanotube. The MoS_2 nano-crystals are compatible with the VGSs, and the whole deposition is very uniform (Figure 3b). Notably, the MVGT still preserves the 3D interconnected network with little pulverization after MoS_2 deposition (Figure S5). The sponge skeleton derived from porous copper foam is observable. Under the π - π interaction between graphene nanosheets and sponge structure, such MVGT is expected to deliver enhanced mechanical stability [23, 24]. After several times of binding, our

MVGT could completely recover its original shape, further indicating its mechanical flexibility and strength.

Figure 3: Synthesis procedure of the MVGT. (a) The schematic illustration of the fabrication of MVGT; (b) SEM images of free-standing hVGT nanotube array; (c) and (d) TEM images of hVGT and MVGT nano-framework.

The detailed microstructures of hVGTs and MVGTs core-shell frameworks are visualized by TEM analysis. Figure 3c and S4b show the TEM images of hierarchical graphene sheets, in which VGSs are grown perpendicularly to the original CuO nanowires, delivering large amounts of dual vertically-aligned graphene on quasi-planar substrate of Cu foam. The single nanosheet of hVGTs is almost transparent to the electron beam. Lattice spacing of ~ 0.37 nm is observed, which is identified as graphene sheets of hVGT arrays (Figure S4c). Figure 3d shows TEM images of MVGTs after PLD deposition of MoS_2 . The corresponding lattice fringes with an interplanar spacing of 0.64 nm and 0.27 nm are observed, which are attributed to the interplanar spacing of the (002) and (100) planes of hexagonal 2H-structured MoS_2 [25]. Such hierarchical structure is further explored by the element mapping images of EDX analysis (Figure S4d). The Mo and S signals of MoS_2 are uniformly distributed among C signals. It is justified that the hierarchical MVGT core-shell structure could be realized with hierarchical vertical

graphene core and MoS₂ shell. Our architecture delivers great flexibility and could be directly applied as electrodes without any post-process or additives (e.g., carbon black and polymer binder). All these characteristics are beneficial for enhanced sodium ion storage. More importantly, the developed method is fast, dry and facile, and thus scalable.

The phases, compositions, and crystallographic structures of samples are monitored using XRD, Raman, and XPS characterizations. Both hVGT and MVGT frameworks contain characteristic XRD peaks at 26° and 43° resulting from free-standing hVGT (Figure 4a). Additionally, MVGTs exhibit distinct (002), (100), and (103) diffraction peaks of MoS₂, indicating a hexagonal structure (JCPDS 00-006-0097). Although no obvious difference is observed from the SEM morphologies, the existence of MoS₂ nano-crystalline architecture is reflected in Raman and XPS spectra. For the Raman spectrum of pristine hVGT arrays from 1000 to 3000 cm⁻¹, strong graphitic G-band at about 1580 cm⁻¹ and well-defined disorder induced D-band at about 1350 cm⁻¹ are observed (Figure S6). Besides, well-defined 2D peak at ~2690 cm⁻¹ could be observable, indicating good crystallinity of graphene. Such nano-framework also delivered D+D' peak at 2938 cm⁻¹, which further confirms the presence of numerous defects [26]. In the MVGT nanotube array, the G and D bands (1580 and 1350 cm⁻¹) still exist without apparent changes, indicating the morphology preservation of VGS after MoS₂ coating. Notably, the increased I_D/I_G ratio for MVGT (1.29) compared to that of hVGT (1.04) indicates that defects may be introduced onto the surface of hVGT during the MoS₂ deposition process [27]. Meanwhile, new characteristic peaks located at 376 and 403 cm⁻¹ appear, corresponding to the E_{2g}¹ and A_{1g} Raman modes of MoS₂, respectively, indicating that the hVGT core is composited by MoS₂. Such characteristic peaks further confirm the presence of crystalline 2H-MoS₂. The difference of ~26 cm⁻¹ between E_{2g}¹ and A_{1g} Raman mode peaks suggests a multi-layer feature of the deposited MoS₂ [28].

The surface of MVGT framework is further investigated by XPS. Two binding energy peaks at 229.3 and 232.4 eV are observed in the high-resolution spectrum of Mo 3d, which are assigned to Mo 3d_{5/2} peaks in MoS₂ and MoO₃, respectively (Figure 4c) [29]. Figure 4d shows the two characteristic peaks at 161.4 and 162.6 eV corresponding to S 2p_{3/2} and S 2p_{1/2}, respectively. These peaks can be indexed to Mo-S bonding in MoS₂.

The calculated atomic ratio of S/Mo is about 2.47, indicating that the products are S-rich MoS_{2+x} . Additionally, in C 1s spectra, two strong peaks at 284.5 and 285.3 eV are observable in both architectures (Figure 4e), corresponding to sp^2 C=C and C-O bonds, respectively [30, 31]. A deconvoluted peak at 286.1 eV can be assigned to C-O bonding in hVGT. After MoS_2 anchoring, such peak intensity is typically enhanced for 8 times compared with intrinsic hVGT, indicating the introduction of many broken sp^2 C=C on VGS surfaces, which subsequently forms new C-O bonds after exposure to ambient air. This indicates Mo-O does not come from a MoO_3 phase, but rather from a Mo-O-C bonding at the interface between MoS_2 and hVGT. Moreover, two peaks at 530.9 and 532.8 eV in O 1s region in Figure 4f are associated with Mo-O and C-O bonding, which further corroborates the Mo-O-C bonding. The formation of Mo-O-C bond confirms strong chemical and electronic coupling between MoS_2 and hVGT in the resultant nano-composite. Such unique Mo environment with O- and S-bonding may offer more active defect sites as well as unusual electronic properties.

Figure 4: Structure characterization of hVGT and MVGT. (a) XRD patterns and (b) Raman spectra. (c-f) XPS spectra corresponding to Mo 3d & S 2s, S 2p, C 1s and O 1s.

3.3 Electrochemical performance evaluation of MVGTs

Our MVGT electrodes provide continuous electron and sodium ion transfer channels through the hVGT network without the necessity of extra conductive additives. In the

cyclic voltammetry (CV) curves of the MVGTs electrode (Figure S7a), two broad and strong peaks exist in the first cathodic process at 0.5 and 0.3 V (vs Na/Na⁺). These two peaks can be assigned to the intercalation of sodium ions into the interlayers of MoS₂ to form Na_xMoS₂, and subsequent conversion reaction from Na_xMoS₂ to Mo metal and Na₂S, accompanied by the reduction of electrolyte solution to form solid electrolyte interface (SEI) film, similar to the CV results of MoS₂-based anode materials [32]. Hence, the sodiation processes of MoS₂ can be divided into two stages with the corresponding reactions as:

At high potential, sodium ions firstly intercalate into the lattice of MoS₂ (Eq. 1), followed by subsequent conversion reaction at low potential (Eq. 2) [32-34]. During the anodic process, one strong anodic peak at about 1.85 V is observed, corresponding to the oxidation of metallic Mo to MoS₂. Beyond the first cycle, the reduction peak below 0.5 V disappeared, and the overlapped 2nd and 3rd CV curves suggest high reversibility and cycling stability of Na⁺ storage in the MVGT hybrid array.

Figure 5: Electrochemical performance and Kinetic analysis of MVGT framework. (a) Rate capability, and (b) and cycling stability. (c) Relationship between logarithm cathodic and anodic peak current and logarithm scan rates. (d) Capacitive contribution at 1.0 mV s⁻¹. (e) Contribution ratio of the capacitive and diffusion-controlled charge versus scan rate.

The initial discharge curve of MVGT composite at 0.5 A g⁻¹ consists of two slight plateaus near 1.1 and 0.5 V (Figure S7b), which is consistent with the results of CV curves. During the following discharging process, the potential plateaus in the 1st discharge curve were replaced by long slopes between 3.0 and 0.01 V, indicating the stable SEI formation in the first sodiation process. The initial charge and discharge capacities are 547 and 827 mA g⁻¹ respectively with an initial Coulombic efficiency of ~68.8%, which is mainly ascribed to the formation of SEI layer on the electrode surface and the reaction of the sodium ions with residual oxygen-containing functional groups [35]. As a comparison, the sodium ion storage capacity in hVGT framework is negligible (~22 mA h g⁻¹ at 0.5 A g⁻¹) (Figure S8) when compared with the MoS₂ which is consistent with reported results of Na⁺ in vertical graphene [8].

The rate capabilities of binary MVGT electrodes were evaluated at high current densities from 0.5 to 20 A g⁻¹ in Figure 5a and S7c. Upon cycling at current densities of 0.5, 1, 5,

and 20 A g^{-1} , the MVGT electrode yields discharge capacities of 535, 520, 430, and 314 mA h g^{-1} , respectively with rate retention of 58% from 0.5 to 20 A g^{-1} . The decreased Na^+ diffusion distance and enhanced electrical connectivity resulted in the superior rate performance of MVGT composite. Furthermore, the discharge capacity is capable of recovering to 535 mA h g^{-1} when the current density returns to 1 A g^{-1} . Such a high specific capacity and rate performance are either comparable to or higher than those of previous MoS_2 -based anode materials (see detailed comparison in Table S1, Supporting Information).

Long-term high rate measurement was conducted on the MVGT array electrode (Figure 5b). In terms of previous reports, unsatisfactory cyclability has been regarded as the major bottleneck of MoS_2 as the anode material for Na^+ storage (Supporting Information Table S1). Specifically, ultrathin MoS_2 delivered the capacity retention of 73% after 100 cycles at 320 mA g^{-1} [36]. Such a fast drop in capacity may originate from the poor electrical conductivity of the base nano-sized materials. To address this drawback and enhance the cyclability, nano-sized materials with different conductive additives have been prepared, such as MoS_2 -rGO, MoS_2 -CNT, and MoS_2 -CNF [37-39]. However, the capacity retentions are still unsatisfactory even in short cycles (83% after 20 cycles, 84% after 80 cycles, and 62% after 100 cycles, respectively). Possible reasons include aggregation of active materials and relatively lower conductivity of carbon-based materials due to surface polar functional groups. In comparison, our MVGT electrode delivers much enhanced cyclability. At the current density of 0.5 A g^{-1} , the first and the 800th discharge capacities of the MVGT framework were 560 and 513 mA h g^{-1} , respectively, with corresponding capacity retention of ~92%. The average Coulombic efficiency during these 800 cycles was as high as 99.8%. Additionally, with the current density increasing to 20 A g^{-1} , the integrated MVGT electrode also delivered greatly enhanced long-cycle stability for 3000 cycles. The average capability was around 300 mA h g^{-1} with capacity retention of 88%. In general, achieving fast and stable Na^+ storage properties in sodium-ion batteries is challenging because of large ionic radius of Na^+ . Such outstanding electrochemical properties of the three-dimensional MVGT architecture are related to the reduced stacking layers of the MoS_2 and the highly porous vertical graphene network. The low stacking of the MoS_2 nano-layers relaxed the strain and

lowered the barrier for Na^+ insertion. The interlayer structure of vertical graphene offered sufficient void spaces for volume expansion and fast electron transfer pathways through reactive edges during repeated cycling.

To further understand the enhanced electrochemical performances of MVGT composite, we studied the electrochemical surface area (ECSA) of different samples, which can be determined via double-layer capacitance (C_{dl}). Such method has been largely applied to compare the active surface area of different composites in electrocatalysis and batteries [40-43]. Since it is hard to determine the ECSA in the battery electrolyte. Alternatively, we obtained this value in the 1 M NaOH solution, which can also suggest the surface area of different nano-frameworks. The C_{dl} can be estimated at 0.2 V against the scan rate, where the slop is twice C_{dl} . It was observed that the C_{dl} of MVGT is larger than that of CuO nanowires and porous copper foam because of the highest slop (Figure S9d). This could indicate that the improved electrochemical surface area of MVGT results in enhanced electrochemical performance. Moreover, the EIS spectra of hVGT and MVGT nano-framework were also carried out. As shown in Figure S10, the charge transfer resistance (R_{ct}) of hVGT is 50 Ω , much lower than that of pure nano-structured MoS_2 [38, 44]. This is attributed to great conductivity of hVGT with R_{ct} of 22 Ω . Due to the fast charge-transfer ability of hVGT, the integrated MVGT composite leads to an excellent high-rate performance and long-term cyclability. Above all, these results demonstrate high specific capacity, rate capability and remarkably high-rate stability of MVGT electrode for high-performance SIBs.

To examine the improved rate capability of such hierarchical framework, detailed kinetics analysis was conducted. Figure S5d displays the CV profile of MVGT electrode captured at different voltage scanning rate of 0.2 to 0.8 mV s^{-1} . The rectangular shape of each curve is well preserved with increasing scan rate. For an electrochemical energy storage device, several processes could contribute to total stored charge and they can be characterized by analyzing the CV curves at various sweep rates according to the equation: $i = av^b$, where i is the current response, v is the scan rate and both a and b are adjustable parameters. The value of b is between 0.5 and 1.0, which is determined from the slope of the $\log i$ versus $\log v$ plot (Figure 5c). Particularly, the b -value of 0.5 indicates a total diffusion-controlled process, whereas 1.0 represents a capacitive process.

Hence the high b value of MVGT electrode (0.92 and 0.85 at the anodic and cathodic peaks, respectively) suggests a more favored capacitive kinetics of MVGT. In Figure 5d, the percentage of capacitive contribution to the current at a fixed voltage is quantitatively determined by separating the current response i from the diffusion-controlled and capacitive contribution at the corresponding voltage. Resultantly, as high as 90% of the total capacity is identified as the capacitive contribution for the MVGT electrode, comparable or even higher than previous reports (82% of mesoporous MoS₂ at 1 mV s⁻¹; 85.2% of methyl-functionalized MoS₂ at 1 mV s⁻¹) [45, 46]. Contribution ratios between the two different processes at other scan rates were also quantified (Figure 5e), which exhibit the gradually enhanced capacitive capacity with increasing the scan rate. The final capacitive contribution reaches a maximum value of 91% at 5 mV s⁻¹. Such high capacitive contribution measured for the MVGT-based electrodes further confirms that the highly porous structure and enhanced conductivity of hVGT and the strong chemical coupling enable fast Faradaic reactions, leading to capacitive charge storage.

4. Conclusions

We have provided a generalized approach for the fabrication of hierarchical vertical graphene nanotube via C-plasma based fast and dry-synthesis strategy. A series of nano-frameworks with different morphologies and compositions, such as CuO, Ni₃S₂, NiO and Co₃O₄, were used as the backbones. Densely distributed vertical graphene nanosheets (VGS) have been successfully grown on these nano-framework surfaces with structural preservation, demonstrating the universality of such fabrication strategy. MoS₂ nanocrystalline structures have further been deposited onto the free-standing framework of hVGT for sodium ion storage. The designed MVGT framework has been demonstrated to deliver high capacity and excellent high-rate long-term cyclability due to the unique hierarchical architecture. Enhanced capacitive contribution was ascribed as the source for high-rate and long-term stability. We strongly believe that such carbon plasma strategy can emerge as a novel method to achieve highly porous structure for high-performance electrode materials in energy storage devices.

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