SPECIAL ISSUE: Innovative Electrode Materials for Supercapacitors

Mesoporous polypyrrole-based graphene nanosheets anchoring redox polyoxometalate for all-solid-state micro-supercapacitors with enhanced volumetric capacitance

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ABSTRACT Micro-supercapacitors (MSCs) have emerged as one competitive candidate of high-performance, flexible, safe, portable and wearable energy storage devices. However, improving their electrochemical performance from electrode materials to assembled devices still remains huge challenges. Here, we for the first time synthesized two-dimensional (2D), ultrathin, mesoporous polypyrrole-based graphene nanosheets uniformly anchored with redox polyoxometalate (mPPy@rGO-POM) by soft template approach. Further, using a layer-by-layer deposition and mask-assisted technique, the compactly stacked and sandwich-like hybrid film (mPGM) based on pseudocapacitive mPPy@rGO-POM nanosheets and electrochemically exfoliated graphene was directly fabricated as binder- and additive-free interdigital electrodes for all-solid-state planar micro-supercapacitors (mPGM-MSCs). Notably, the resulted mPGM-MSCs exhibited outstanding areal capacitance (115 mF cm^{-2}), remarkably enhanced volumetric capacitance (137 F cm^{-3} at 1 mV s^{-1}) in comparison with MSCs based on the films of mPPy@rGO without POM anchoring (95 F cm^{-3}), and non-porous polypyrrole-graphene (68 F cm^{-3}). Further, mPGM-MSCs disclosed robust mechanical flexibility with $\sim 96\%$ of capacitance retention at a highly bending angle of 180° , and impressive parallel or serial interconnection for boosting capacitance or voltage output. As a consequence, our proposed strategy of filling the redox species into mesoporous graphene and other 2D nanosheets will open up new ways to manufacture high-compact and flexible energy storage devices ranging from supercapacitors to batteries.

Keywords: mesoporous, graphene, redox, all-solid-state, micro-supercapacitors

INTRODUCTION

The ever-increasing consumption of energy demands highly efficient energy storage devices, such as supercapacitors that provide high power density, long-term cycle life, and fast charge and discharge process [1–5]. Recently, micro-supercapacitors (MSCs) with multiple compatible characteristics of lightweight, tailored size, robust mechanical flexibility, and ultrahigh power delivery have attracted tremendous attentions [6–8]. Despite dramatic developments in innovating nanostructured electrode materials and fabricating novel devices, there are still enormous challenges in realizing MSCs with high volumetric capacitance and energy density [9,10]. Therefore, the exploitation of high-compact film electrode materials with developed electronic and ionic conducting networks is crucial for MSCs, but still underdeveloped in this research field [11–14].

Conducting polymers, such as polypyrrole (PPy) have been extensively utilized in energy storage devices (e.g., MSCs) [15–17]. Unfortunately, the incident volume change and unsatisfied electrical conductivity of conducting polymers result in low power density, poor rate capability and cyclability for MSCs. To overcome these drawbacks, the introduction of mesoporous structure and conductive network (e.g., graphene) to construct two-dimensional (2D) graphene-based mesoporous polymer nanosheets with high specific surface area, ultra-thinness, interconnected pore structure, good electrical conductivity and excellent flexibility could remarkably improve their electrochemical performance for MSCs [18–

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20]. On the other hand, the presence of mesopores in such 2D nanosheets is favorable for the anchoring of highly redox species in order to construct densely compact films for MSCs with enhanced volumetric performance.

Polyoxometalates (POMs), as redox-active molecular metal oxide clusters containing high-valent transition metals (e.g., V, Mo and W), possess a variety of structures, sizes and compositions [21]. In particular, Keggin cluster $[\text{PMo}_{12}\text{O}_{40}]$ (POM) has been reported as a prospective candidate for supercapacitors with high capacitance, due to its abundance, stable redox states, fast and reversible multi-electron transfer reactions [22,23]. However, POMs exhibit intrinsically poor conductivity and high solubility in aqueous and polar organic solvents. In general, POMs require anchoring onto a chemically stable, large surface area substrates ranging from conducting polymers to graphene, activated carbons or carbon nanotubes to form hybrid materials, in order to prevent the dissolution of POMs into electrolyte, provide the necessary electrical conductivity and utilize the high pseudocapacitance [24–26]. Nevertheless, rational design of anchoring POMs on 2D mesoporous graphene nanosheets for compact MSCs has not yet been reported.

Herein, we reported the designed synthesis of 2D mesoporous polypyrrole-based graphene (mPPy@rGO) nanosheets with open and wormlike mesopores, which were well suitable for the homogeneous and efficient anchoring of redox POM clusters. After POM anchoring, the as-obtained 2D hybrid nanosheets (mPPy@rGO-POM) remained uniform, ultrathin and mesoporous structure and presented notable multiple redox peaks, indicative of strong pseudocapacitive behavior from POM clusters. Further, employing layer-by-layer deposition and interdigital mask-assisted techniques, we directly constructed sandwich-like stacked-layer hybrid film (mPGM) with pseudocapacitive mPPy@rGO-POM and capacitive electrochemically exfoliated graphene (EG) nanosheets for all-solid-state MSCs (mPGM-MSCs). Remarkably, the resulted all-solid-state mPGM-MSCs with a polymer gel electrolyte exhibited superior areal capacitance (115 mF cm^{-2}), enhanced volumetric capacitance (137 F cm^{-3}), unprecedented flexibility with ~96% of initial capacitance even bended at 180° , and efficient integration through parallel and serial interconnection.

EXPERIMENTAL SECTION

Materials synthesis

Graphene oxide (GO) was chemically synthesized from

natural graphite flakes according to a modified Hummers method [27,28].

The mesoporous polypyrrole-based graphene oxide (mPPy@GO) nanosheets were first synthesized by *in-situ* polymerization of pyrrole on GO surface using poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymers (P123) as soft template. Typically, 0.2 g of P123 was dissolved in 1 mL tetrahydrofuran and 8 mL deionized water to generate aggregation. After stirring, 1.5 mg of GO, 30 mg of pyrrole and 12 mg NaOH were added into the solution. Then, 90 mg of ammonium persulfate was added to initiate polymerization of pyrrole. Afterwards, mPPy@GO nanosheets were obtained after washing and centrifugation.

Through the reduction of mPPy@GO by hydrothermal treatment at 180°C for 12 h [29,30], mPPy@rGO nanosheets were obtained. For comparison, polypyrrole-based graphene nanosheets without mesoporous structure (PPy@rGO) were also synthesized, without using P123, while other steps were kept the same as mPPy@rGO.

In order to prepare POM anchored mPPy@rGO nanosheets (mPPy@rGO-POM), 50 mg of mPPy@rGO was added to 50 mL of phosphomolybdic acid aqueous solution (10 mmol L^{-1}) [24,31,32]. This suspension was stirred for 2 h and kept for 5 h at room temperature. Finally, the sample was rinsed with water several times and freeze-dried to yield mPPy@rGO-POM nanosheets.

The EG nanosheets were prepared by electrochemical exfoliation of graphite in aqueous solution, as described in our previous studies [33,34].

Devices assembly

The interdigital electrodes for MSCs were directly fabricated by one-step mask-assisted technique we developed recently [33]. First, the stable ink of 2 mL EG dispersion in ethanol solution (0.05 mg mL^{-1}) was vacuum filtrated as current collectors on nylon membrane ($0.22 \mu\text{m}$, Agela Technologies Ltd.), with the help of a customized interdigital mask (8 interdigital fingers with 15 mm length, 1 mm width, and 0.5 mm width of interspacing). Then, 2 mL dispersion of PPy@rGO (0.25 mg mL^{-1}), mPPy@rGO (0.25 mg mL^{-1}) or mPPy@rGO-POM (0.34 mg mL^{-1}) in aqueous solution was immediately added onto the top of the EG layer and continuously filtrated. Subsequently, the same volume of EG dispersion was filtered to form the second EG layer on the top of the active material layer. After removing the mask, the interdigital patterns of film electrodes of PG, mPG or mPGM, respectively,

Figure 1 Scheme of the fabrication of mPPy@rGO-POM nanosheets.

were obtained. After drop-casting and solidification of gel electrolyte of polyvinyl alcohol (PVA)/H₂SO₄ [35,36], the resulted MSCs were correspondingly denoted as PG-MSCs, mPG-MSCs and mPGM-MSCs, respectively. For comparison, we also constructed the EG-MSCs based on the deposition of EG dispersion of 8 mL, while other steps were kept the same as mPGM-MSCs.

Materials characterization

The morphology and structure of as-obtained nanosheets were characterized by scanning electron microscopy (SEM, JSM-7800F), transmission electron microscopy (TEM), high-resolution TEM (HRTEM, JEM-2100), atomic force microscopy (AFM, Veeco nanoscope multimode II-D), physical adsorption instrument (Quadrascorb SI), Raman spectrometer (LabRAM HR 800, 532 nm), Fourier transform infrared spectrometer (FT-IR, Bruker Optics hyperion 3000) and thermogravimetric analysis (TGA, STA 449 F3). The thickness of the film electrodes was measured using a surface profiler (Veeco Dektak 150). The electrical conductivity of film electrodes was examined by a standard four-point probes system (RTS-9).

Electrochemical measurement

The electrochemical properties of PPy@rGO, mPPy@rGO and mPPy@rGO-POM nanosheets were measured using an electrochemical workstation (CHI 760E) in a three-electrode system. The working electrode was prepared by mixing 80 wt.% active material, 10 wt.% ketjen black and 10 wt.% poly(tetrafluoroethylene) in ethanol. The working electrode was evaluated in 1 mol L⁻¹ H₂SO₄ as electrolyte, using platinum plate as counter electrode and saturated calomel electrode (SCE) as reference electrode. The cyclic voltammetry (CV) and galvanostatic

charge/discharge (GCD) measurements were performed with a potential range from -0.2 to 0.8 V vs. SCE.

The electrochemical properties of all-solid-state PG-MSCs, mPG-MSCs, mPGM-MSCs and EG-MSCs, using PVA/H₂SO₄ gel electrolyte, were also measured by CV curves at different scan rates from 1 to 100 mV s⁻¹, GCD profiles at varying current densities, and electrochemical impedance spectroscopy (EIS) in the frequency range from 0.01 Hz to 100 kHz using CHI 760E electrochemical workstation.

RESULTS AND DISCUSSION

Fig. 1 shows the schematic of the synthesis of 2D mPPy@rGO-POM nanosheets *via* self-assembly of triblock copolymer (P123), *in-situ* polymerization of pyrrole monomer and anchoring of redox POM clusters. First, free-standing GO nanosheets were employed as 2D substrates for bottom-up patterning of mesoporous polypyrrole layers. In this case, the oxygen-bearing groups of GO surface primarily interacted with P123 micelles driven by hydrogen bonding to form wormlike islands. Then, pyrrole monomers were polymerized rounding building blocks of micelles. After removing the P123 template and hydrothermal reduction, mPPy@rGO nanosheets were attained. Finally, the redox POM clusters were uniformly immersed into the mesopores, and strong anchoring on the surface of mPPy@rGO nanosheets.

The morphology and structure of as-prepared mPPy@GO nanosheets were firstly characterized by SEM, TEM, AFM, and N₂ adsorption-desorption isotherm measurements. As shown in Fig. 2a, b, mPPy@GO nanosheets presented uniform, ultrathin, flat and graphene-like structure with wormlike mesopores, demonstrative of successful replication of well-defined polypyrrole patterns from the vacant spacing between the GO and P123 mi-

Figure 2 Morphology and structure of mPPy@GO nanosheets. (a, b) SEM images. (c, d) TEM images. (e) AFM image (up) and corresponding height profile (down). (f) N_2 adsorption-desorption isotherm and pore size distribution (inset).

cells. The homogeneous mesoporous structures were also demonstrated by TEM images (Fig. 2c, d). The typical AFM image and height analysis (Fig. 2e) revealed ultrathin structure of mPPy@GO nanosheets with a uniform thickness of ~ 3.7 nm. The mesoporous feature of mPPy@GO nanosheets was further confirmed by N_2 physisorption measurement (Fig. 2f). The adsorption-desorption isotherm displayed a type IV curve with a H_2 -type hysteresis loop [37]. The specific surface area and pore volume were calculated to be $142 \text{ m}^2 \text{ g}^{-1}$ and $0.44 \text{ cm}^3 \text{ g}^{-1}$, respectively. The narrow pore size distribution was mainly presented ranging from 5 to 10 nm for mPPy@GO nanosheets, consistent with SEM and TEM observations.

After reduction of mPPy@GO nanosheets by hydrothermal treatment, the resulting mPPy@rGO nanosheets, imaged by TEM characterization (Fig. 3a, b), revealed the similar ultrathin and wormlike mesoporous structure to mPPy@GO. In a sharp contrast, heterogeneous and non-porous polypyrrole was observed on the surface of graphene nanosheets (PPy@rGO, Fig. S1) without the usage of structure-directing P123, highlighting the crucial role of P123 template for the formation of mesopores. Furthermore, after anchoring POM clusters, the resultant mPPy@rGO-POM nanosheets still well retained the wormlike mesoporous structure (Fig. 3c). HRTEM image disclosed the uniform distribution of POM clusters, with

ultrasmall sizes of 1–2 nm (Fig. 3d) [23], homogeneously anchored on the surfaces and in the pores of mPPy@rGO nanosheets, and the corresponding EDX analysis determined the presence of Mo, P and O elements of POM, and C, N and O elements corresponding to the graphene and polypyrrole, respectively, derived from mPPy@rGO-POM nanosheets (Fig. 3e). Raman spectra of mPPy@GO, mPPy@rGO and mPPy@rGO-POM nanosheets were given in Fig. 3f. The D and G peaks of graphene appearing at 1350 and 1590 cm^{-1} were partially overlapped with the peaks of polypyrrole at 1340 and 1570 cm^{-1} ascribed to C=C stretching modes [16,22]. The relative intensity ratio I_D/I_G of D and G bands was 1.03 for mPPy@GO and 1.06 for mPPy@rGO, indicative of the reduction of GO [29,35]. Four main peaks presented at 997 , 826 , 667 and 287 cm^{-1} evidenced the existence of POM clusters (Fig. S2) in mPPy@rGO-POM, demonstrative of the integration of POM into mPPy@rGO nanosheets. In addition, FT-IR spectra of mPPy@rGO and mPPy@rGO-POM exhibited characteristic functional groups of polypyrrole vibration peaks, and Mo-O stretching modes (around 1000 cm^{-1}) for mPPy@rGO-POM (Fig. S3) [38]. The weight content of POM clusters anchored on mPPy@rGO-POM nanosheets was determined to be $\sim 26.5 \text{ wt.}\%$, derived from the TGA curve (Fig. S4) [22,38].

Due to the unique sandwich-like structure, high-conductive graphene, mesoporous polypyrrole patterns and

Figure 3 (a, b) TEM images of mPPy@rGO nanosheets after reduction. (c, d) TEM and HRTEM images of mPPy@rGO-POM nanosheets. (e) EDX spectrum of mPPy@rGO-POM nanosheets. Cu element is derived from TEM grid used. (f) Raman spectra of mPPy@GO, mPPy@rGO and mPPy@rGO-POM nanosheets.

uniform POM modulation, the as-obtained mPPy@rGO-POM nanosheets were expected to serve as a novel class of promising electrode materials for MSCs. To this end, we firstly evaluated their electrochemical properties of PPy@rGO, mPPy@rGO and mPPy@rGO-POM nanosheets in a three-electrode configuration (Fig. S5). Notably, both CV and GCD curves of mPPy@rGO-POM nanosheets showed strong pseudocapacitive behaviors of polypyrrole and redox POM species, in comparison with mPPy@rGO and PPy@rGO. It is worth noting that, although mPPy@rGO-POM nanosheets delivered similar gravimetric capacitance to mPPy@rGO, mPPy@rGO-POM nanosheets with high mass density of POM anchoring into mesopores hold enormous potentials for compact MSCs in term of volumetric performance metrics.

To demonstrate this assumption of constructing the compact film, we selected the pseudocapacitive mPPy@rGO-POM nanosheets as the core active materials and EG nanosheets as both film-assisted agents and metal-free current collectors, and employed an interdigital mask-assisted technique to fabricate the interdigital films (mPGM) for mPGM-MSCs. Specifically, the stable inks of EG (0.05 mg mL^{-1} in ethanol, 2 mL), mPPy@rGO-POM (0.34 mg mL^{-1} in deionized water, 2 mL) and EG

(0.05 mg mL^{-1} in ethanol, 2 mL) were continuously deposited in a controlled sequence [33]. Remarkably, the resulting interdigital mPGM film exhibited a sandwich-like structure of EG/mPPy@rGO-POM/EG, outstanding uniformity, immense continuity, robust mechanical flexibility (Fig. 4a, b), high mass density of 0.58 g cm^{-3} and excellent electrical conductivity of $43\text{--}162 \text{ S cm}^{-1}$ (Fig. S6), and thereby can be directly employed as binder- or additive-free planar electrodes, without metal-based current collectors, for mPGM-MSCs. It is noted that the EG nanosheets are flat, transparent and ultrathin, with a layer number of ≤ 3 (Fig. 4c, d). The resultant sandwich-like mPGM film possessed well-developed ionic and electronic networks, in which the rich mesoporous arrays could enhance the ionic diffusion, and two EG layers serve as the main conductive backbones and the rGO nanosheets were as branch-like conductive pathways for speeding electron transport (Fig. 4e). Top-view SEM images of mPGM film revealed highly uniformity, large-area continuity, and excellent structural integrity of the EG layer (Fig. 4f). Cross-section SEM images clearly exhibited micrometer thickness, and compactly layer-stacked sandwich-like structure of EG/mPPy@rGO-POM/EG (Fig. 4g, h). The homogeneous distribution and dense arrangement of mPPy@rGO-POM nanosheets were fur-

Figure 4 (a, b) Photographs of mPGM film taken at (a) flat and (b) bending states. (c, d) TEM and HRTEM images of EG nanosheets. (e) Cross-section schematic of sandwich-like mPGM film, showing an EG/mPPy@rGO-POM/EG structure. (f) Top-view SEM image of mPGM film. (g, h) Cross-section SEM images of mPGM film at low and high magnification. (i–m) Cross-section elemental mapping analyses of mPGM film, showing the presence of (i) C, (j) O, (k) Mo, (l) N and (m) P elements.

ther validated by elemental mapping analysis from cross-section of sandwich-like mPGM film (Fig. 4i–m). After drop-casting and solidification of PVA/H₂SO₄ gel electrolyte onto the interdigital electrodes, all-solid-state mPGM-MSCs were obtained.

To highlight the superiority of mesoporous structure and POM anchoring of mPPy@rGO-POM nanosheets on the improvement of electrochemical performance, we also adopted the same procedure to construct the PG-MSCs based on the sandwich-like film of EG/PPy@rGO/EG, and mPG-MSCs based on EG/mPPy@rGO/EG film, while other steps were kept the same as mPGM-MSCs. Fig. 5a shows the CV curves of all-solid-state mPGM-MSCs, mPG-MSCs, and PG-MSCs tested at 10 mV s⁻¹. It can be observed that the CV curves of mPGM-MSCs, in comparison with mPG-MSCs and PG-MSCs, exhibited the impressive pseudocapacitive behavior originating from redox POM clusters, and the increased current integration (Fig. 5a). The areal capacitance and volumetric capacitance of mPGM-MSCs, mPG-MSCs and PG-MSCs as a function of scan rate were presented in Fig. 5b, c.

Apparently, mPGM-MSCs delivered high areal capacitance of 115 mF cm⁻² and outstanding volumetric capacitance of 137 F cm⁻³ at 1 mV s⁻¹, both of which were much higher than those values of mPG-MSCs (79 mF cm⁻² and 95 F cm⁻³), PG-MSCs (74 mF cm⁻² and 68 F cm⁻³), and EG-MSCs (0.4 mF cm⁻² and 2.2 F cm⁻³, Fig. S7). Meanwhile, the mPGM-MSCs, even tested at scan rate of 100 mV s⁻¹, still presented higher volumetric capacitance of 52 F cm⁻³ than those of mPG-MSCs (44 F cm⁻³) and PG-MSCs (30 F cm⁻³). As a result, mPGM-MSCs offered higher energy density (4.8 mW h cm⁻³) and power density (645.1 mW cm⁻³) than those of mPG-MSCs (3.3 mW h cm⁻³ and 544.2 mW cm⁻³), and PG-MSCs (2.4 mW h cm⁻³ and 380.4 mW cm⁻³) in Fig. 5d. These results revealed that the presence of mesoporous patterns and further anchoring of redox POM clusters could significantly enhance the electrochemical energy storage of MSCs.

To further evaluate the electrochemical properties of mPGM-MSCs as a function of mPGM film thickness, we investigated the CV curves of mPGM-MSCs based on the

Figure 5 (a) CV curves tested at 10 mV s⁻¹, (b) areal capacitance, (c) volumetric capacitance as a function of scan rate, and (d) Ragone plot of mPGM-MSCs, mPG-MSCs, and PG-MSCs. (e) CV curves and (f) Ragone plot of mPGM-MSCs based on the varying volume from 1, 2 to 4 mL mPPy@rGO-POM ink.

varying volume of 1, 2, and 4 mL mPPy@rGO-POM ink (Fig. 5e). Correspondingly, the resultant thickness of mPGM film is 4.3, 8.4 and 16.7 μm , respectively. It is disclosed that these three mPGM-MSCs showed the stepwise increased areal capacitance at low scan rate (e.g., 1–20 mV s⁻¹) while the volumetric capacitance decreased shortly, in particular, at high scan rate (e.g., 100 mV s⁻¹) (Fig. S8). When 1 mL ink of mPPy@rGO-POM was used, mPGM-MSCs presented lower areal capacitance of 63 mF cm⁻² and high volumetric capacitance of 147 F cm⁻³ at scan rate of 1 mV s⁻¹, and better rate capability than those of mPGM-MSCs based on 2 mL ink (115 mF cm⁻² and 137 F cm⁻³ at 1 mV s⁻¹) and 4 mL ink (206 mF cm⁻² and 123 F cm⁻³ at 1 mV s⁻¹). This phenomenon could be well explained by high electrical conductivity of thinner mPGM film (Fig. S6), resulting in higher electron transport and volumetric energy density of compact mPGM-MSCs (Fig. 5f).

To validate the outstanding mechanical flexibility, we further evaluated the electrochemical performance of mPGM-MSCs under different bending degrees [39]. Due to high flexibility of 2D nanosheet-based electrodes, our

mPGM-MSCs exhibited impressive repeatability under different bending degrees and retained ~96% of initial capacitance when the cell was tested at highly bending angle of 180° (Fig. 6a, b). Moreover, mPGM-MSCs disclosed good cycling stability, showing 80% of capacitance retention after 2000 cycles (Fig. S9). To satisfy the growing demands for smart integrated electronics, we further fabricated the integrated mPGM-MSCs packing from three parallelly or serially interconnected devices to boost the capacitance or voltage output (Fig. 6c-f) [40]. As shown in Fig. 6c, d, both CV and GCD curves of parallelly-connected mPGM-MSCs from device 1 to 3 presented a stepwise linear increase in the capacitance, while the integrated mPGM-MSCs connected in series illustrated the progressive voltage extension from 1.0 to 3.0 V (Fig. 6e,f). Dramatically, our three serially-connected mPGM-MSCs could readily power a red light emitting diode, highlighting the enormous potentiality for smart power source units with variable current and voltage outputs.

Therefore, the exceptional performance of all-solid-state planar mPGM-MSCs can be attributed to the ela-

Figure 6 (a) CV curves measured at 50 mV s^{-1} of mPGM-MSCs under different bending angles, and (b) capacitance retention as a function of bending angle of mPGM-MSCs. Insets in (b) are optical images of mPGM-MSCs taken at 0° and 180° . (c) CV curves tested at 50 mV s^{-1} and (d) GCD profiles obtained at 0.5 mA cm^{-2} of three parallelly-connected mPGM-MSCs. (e) CV curves at 50 mV s^{-1} and (f) GCD profiles at 0.2 mA cm^{-2} of three serially-connected mPGM-MSCs. Inset in (f) is a photograph of three serial mPGM-MSCs to power a light-emitting diode.

borated design of mPPy@rGO-POM nanosheets with developed mesopores and abundant redox POM clusters, and advanced fabrication of sandwich-like stacked-layer film with synergetic effect of pseudocapacitive mPPy@rGO-POM nanosheets and capacitive EG nanosheets [41]. First, mPPy@rGO-POM nanosheets feature high conductive pathways, enriched mesopores, ultrathin thickness, large surface-area-to-volume ratio for fast ion diffusion and electron transport, and uniformly anchored POM clusters for introducing large additional pseudocapacitance. Second, the densely packed film with sandwich-like structure offers higher electronic conducting networks composed of 2D capacitive EG layers and mass-density-enhanced mPPy@rGO-POM pseudocapacitive layer, more accessible active surfaces and extra interfaces to facilitate electrolyte ions transport and enhance volumetric charge storage. Last but not least, ultra-thinness and excellent flexibility of 2D nanosheets are particularly favorable for significantly improving the electrochemical performance of all-solid-state mPGM-MSCs in a planar geometry [42].

CONCLUSIONS

In summary, we have successfully synthesized a novel class of mPPy@rGO-POM nanosheets with enriched mesopore arrays and anchored redox species of POM clusters for all-solid-state planar MSCs with improved volumetric capacitance and energy density. The as-prepared 2D mPPy@rGO-POM nanosheets possessed ultrathin thickness of $\sim 3.7 \text{ nm}$, wormlike mesoporous structure with a size of $5\text{--}10 \text{ nm}$, and uniformly anchored POM species. Furthermore, the fabricated mPGM-MSCs based on interdigital patterned films of stacked-layer mPPy@rGO-POM and EG nanosheets demonstrated impressive areal capacitance of 115 mF cm^{-2} , enhanced volumetric capacitance of 137 F cm^{-3} , excellent mechanical flexibility, and outstanding parallel or serial integration. As a consequence, our proposed strategy of synthesizing 2D mesoporous nanosheets anchored with highly redox species will open up numerous possibilities for constructing next-generation, flexible, and high-performance energy storage devices in both supercapacitors and batteries.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Additional detailed calculations, and figures are available in the online version of the paper.

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可控制备磷钼酸复合介孔聚吡咯/石墨烯纳米片应用于高比容量全固态微型超级电容器

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摘要 微型超级电容器是一种新型的、柔性化、易集成、可穿戴便携的电化学储能器件, 但提高电极材料和器件的性能仍面临着巨大的挑战. 本文成功首次制备出一种二维磷钼酸复合介孔聚吡咯/石墨烯纳米片, 具有超薄、比表面积大、孔道结构发达、导电性好、赝电容高的特点. 然后, 在十指交叉形状的掩模版协助下, 采用交替沉积的方法, 一步制备出电化学剥离石墨烯和磷钼酸复合介孔聚吡咯/石墨烯纳米片三明治层状结构、高致密、高导电的复合薄膜图案化电极. 该复合薄膜图案化电极应用于全固态平面微型电容器, 表现出显著提高的面电容(115 mF cm^{-2})和体电容(137 F cm^{-3}), 以及优异的机械柔性和可串/并联直接集成的特征. 总之, 本文通过对石墨烯基二维材料的合理设计和微型超级电容器的高效组装实现了器件性能的极大提高, 为发展新一代的微型储能器件提供了一定的科学依据.