

2D Nanomaterials

General Interfacial Self-Assembly Engineering for Patterning Two-Dimensional Polymers with Cylindrical Mesopores on Graphene

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Abstract: Free-standing 2D porous nanomaterials have attracted considerable interest as ideal candidates of 2D film electrodes for planar energy storage devices. Nevertheless, the construction of well-defined mesopore arrays parallel to the lateral surface, which facilitate fast in-plane ionic diffusion, is a challenge. Now, a universal interface self-assembly strategy is used for patterning 2D porous polymers, for example, polypyrrole, polyaniline, and polydopamine, with cylindrical mesopores on graphene nanosheets. The resultant 2D sandwich-structured nanohybrids are employed as the interdigital microelectrodes for the assembly of planar micro-supercapacitors (MSCs), which deliver outstanding volumetric capacitance of 102 Fcm⁻³ and energy density of 2.3 mWhcm⁻³, outperforming most reported MSCs. The MSCs display remarkable flexibility and superior integration for boosting output voltage and capacitance.

Dimensionality plays an essential role in determining the physicochemical properties of functional materials in addition to the atom arrangement and elemental composition.^[1-6] For instance, two-dimensional (2D) nanomaterials, such as graphene,^[7,8] transition metal dichalcogenides,^[9-12] and phosphorene,^[13,14] exhibit unique properties absent in their bulk materials. However, these 2D nanosheets easily tend to stack or aggregate together, leading to the limited accessibility of active sites and thus unsatisfied performance in energy-related applications, for example, supercapacitors,^[15–18] Coating electrochemically active moieties on 2D nanomateials to produce sandwich-like heterostructural nanohybrids has proven to be a promising strategy for the prevention of the stacking and thus the improvement of their capacitive performance in supercapacitors.^[19–22] On the other

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hand, mesoporous structure in electrode materials can largely increase specific surface area, reserve the electrolyte, and combine the ionic–electronic conductive pathways.^[23–29] Of particular importance is that the well-defined mesopores can always bring unprecedented and controllable properties.^[25,30–34] Coating well-defined mesoporous electrochemically active materials on free-standing nanosheets, such as graphene, will thereby produce desirable 2D sandwichstructured hybrid nanomaterials for high-performance supercapacitors.^[35,36] Nevertheless, this has remained a great challenge lacking of suitable templates and innovative techniques.

Herein, we demonstrate a general interfacial self-assembly engineering strategy for patterning 2D porous polymers, for example, polypyrrole (PPy), polyaniline (PANi), and polydopamine (PDA), with cylindrical mesopores on reduced graphene oxide (rGO) nanosheets. The interface self-assembly strategy employs cylindrical micelles formed by commercial P123 copolymer (poly(ethylene oxide)₂₀-block-poly(phenylene oxide)₇₀-block-poly(ethylene oxide)₂₀) as the template, and pyrrole, aniline, or dopamine as the monomers, respectively (Figure 1). In the mixed aqueous solution of P123 cylindrical micelles, graphene oxide (GO) and the monomers, the H-bonding interaction drives the close packing of the cylindrical micelles on the GO surface along with the absorption of the monomers in the poly(ethylene oxide) (PEO) domains, which subsequently confine the polymerization and lead to the formation of the polymeric network. After the removal of the P123 template and subsequent hydrothermal treatment, polymeric monolayers with cylindrical mesopores on the surfaces of rGO are obtained. The



2D porous polymer/rGO nanosheets with well-defined cylindrical pores

Figure 1. Illustration of the fabrication of 2D mesoporous polymer/ rGO nanosheets with cylindrical pores by the interface self-assembly strategy. Note that the cylindrical micelles and pores should be freely curved in practice; in the diagram they are drawn as straight structures for convenience. resultant 2D sandwich-like nanohybrids possess an average mesopore diameter of 12 nm and high specific surface area (SSA) up to $157 \text{ m}^2 \text{g}^{-1}$. To the best of our knowledge, this achievement represents the first patterning of 2D polymers with cylindrical pores on free-standing 2D surfaces, and this study develops a new general strategy for the patterning of 2D porous polymer-based free-standing nanosheets.

PPy exhibits high pseudocapacitance from adjustable redox activity when acting as supercapacitor electrodes,^[37] while the cylindrical mesopores parallel to graphene surface would provide in-plane channels that facilitate smooth and fast ion transport. As a proof-of-concept, the 2D nanohybrids composed of mesoporous PPy coated on rGO (mPPy/rGO) are employed as microelectrodes of all-solid-state flexible planar micro-supercapacitors (MSCs). Remarkably, the resultant MSCs deliver superior areal capacitance of 81 mF cm⁻² and volumetric capacitance of 102 F cm⁻³ at 1 mV s⁻¹, large energy density of 2.3 mWh cm⁻³, which outperform those of many recently reported planar MSCs, such as onion-like carbon,^[38] Ni@rGO@MnO2,^[39] PANI nanowires,^[40] and rGO/ PANI.^[41] Moreover, the MSCs show excellent mechanical flexibility without observable capacitance decrease under varied bending angles, and exceptional serial/parallel integration.

GO nanosheets, prepared by the improved Hummers method, $^{[42]}$ have an average lateral dimension of 1 $\mu m \times 1 \ \mu m$ and a uniform thickness of about 1 nm (Supporting Information, Figure S1). The self-assembly behavior of P123 in H₂O is sensitive to temperature,^[43,44] and the formation of robust P123 cylindrical micelles is crucial for the growth of 2D porous polymers on GO nanosheets. In our study, P123 was found to form cylindrical micelles in the aqueous phase at ca. 40°C,^[44] which was thereby employed as the self-assembly temperature (see details in the Supporting Information). As illustrated in Figure 1, after GO and monomers were added to the micelle solutions, the cylindrical micelles were adsorbed on the surfaces of GO via hydrogen-bonding and electrostatic interactions between the PEO coronae and $\mathrm{GO}^{[32,35]}_{,}$ leading to the tight arrangement of cylindrical micelles on both sides of GO nanosheets, while the monomers were adsorbed in the PEO domains.^[32-34] Then, the polymerization of the monomers, triggered by (NH₄)₂S₂O₈, was confined in the PEO domain of the interconnected micelles. The polymerization might drive the migration of the monomer molecules from the PEO coronae to the contact regions of the adjacent micelles,[32-34] yielding a polymeric network around the micelles. The subsequent removal of the P123 template by washing with ethanol and water generated porous polymers with cylindrical pores on GO nanosheets, which were then converted to rGO by hydrothermal treatment at 180°C.^[29] Fourier-transform infrared (FTIR) spectra not only demonstrate the polymerization of the monomers, but also prove the complete removal of the P123 copolymer, in which the characteristic signals around 2800 cm⁻¹ (attributed to P123) disappear (Supporting Information, Figure S2). Raman spectrum indicates the presence of D (1345 cm^{-1}) and G bands (1585 cm^{-1}) from rGO, as well as the signal (1566 cm^{-1}) attributed to the ring C=C stretching mode of PPy (Supporting Information, Figure S3),^[32] proving the coexistence of rGO and PPy in the nanohybrids. It is worth mentioning that the present ingredient concentrations of copolymer and monomer are optimal experimentally. With reduced concentrations, we could not obtain continuous polymeric network on GO surfaces (Supporting Information, Figure S4a); while if their concentrations were increased, additional polymeric aggregates/agglomerates would appear (Supporting Information, Figure S4b). Another control experiment using the similar procedures, except the addition of GO, yielded only irregular polymeric aggregates rather than 2D nanosheets (Supporting Information, Figure S5), confirming the crucial role of GO as 2D template for the formation of the 2D sandwich-like nanohybrids.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs of the mPPy/rGO nanohybrids clearly exhibit a flat sheet-like structure with closely-packed cylindrical mesopores, demonstrating the successful templating of the cylindrical P123 morphology (Figure 2a,b). The average mesopore diameter, measured from both SEM and TEM images, is about 11 nm, which is very close to the average diameter of P123 cylindrical micelles.^[44] High-magnification SEM images also reveal the partial edge connection of the polymeric networks on both sides of rGO (Supporting Information, Figure S6), which tightly sandwich the rGO sheet and thus stabilize the 2D nanohybrids. Atomic force microscopy (AFM) height images clearly show cylindrical pore structure and afford a uniform thickness of about 26 nm for mPPy/rGO (Figure 2c). As the thickness of a single micelle-layer templated polymer layer is close to the micelle diameter (ca. 11 nm), thus the total thickness of two polymer layers is ca. 22 nm, which is very close to the thickness of the mPPy/rGO nanosheets, indicative of the coating of single micelle-layer templated mPPy layers on both sides of GO nanosheets. The mesoporous character of mPPy/rGO is further confirmed by nitrogen adsorption/ desorption analysis (Figure 2d), which gives a type IV isotherm with a H3-type hysteresis loop, a typical feature of mesoporous structure.^[45] The uptake of isotherm at high relative pressure $(P/P_0 \ge 0.9)$ implies the existence of macropores, which most likely derive from the random stacking of the mPPy/rGO nanosheets. The SSA is calculated to be 157 m²g⁻¹ by the Brunauer–Emmett–Teller method, which is higher than that (106 m²g⁻¹) of rGO (Supporting Information, Figure S7). The average mesopore diameter is 12 nm via the Barrett-Joyner-Halenda method, in support of the SEM and TEM results.

The interface self-assembly strategy is also applicable to the coating of other mesoporous polymers, for example, PANi or PDA, on rGO surfaces, yielding free-standing mPANi/rGO or mPDA/rGO nanosheets. The synthetic procedures are similar to those applied for the preparation of mPPy/rGO, except the use of aniline or dopamine monomers. SEM, TEM and AFM micrographs demonstrate that these nanosheets also possess a mesoporous structure with cylindrical pores (Figure 2), resembling that of the mPPy/rGO nanosheets. The average thicknesses of the mPANi/rGO and mPDA/rGO nanosheets are about 27 and 25 nm, respectively (Figure 2g,k). Based on nitrogen adsorption/desorption analyses (Figure 2h,l), the SSAs of mPANi/rGO and mPDA/rGO are



Figure 2. Morphological and structural characterizations of a)–d) mPPy/rGO, e)–h) mPANi/rGO, and i)–l) mPDA/rGO nanosheets with a cylindrical mesopore structure. a),e),i) SEM images; b),f),j) TEM images; c),g),k) AFM height images; d),h),l) nitrogen adsorption–desorption isotherms; insets show the pore size distributions.

132 and 126 m^2g^{-1} , respectively; their average mesopore diameters are both 12 nm.

The mesoporous polymer-based nanosheets possess outstanding flexibility and the parallel cylindrical mesopores would offer in-plane pathways for smooth and fast ion diffusion (Figure 3a), which is a highly appealing feature for 2D planar energy storage devices. For example, the mPPy/ rGO nanosheets exhibit an ion diffusion coefficient of $6.8 \times$ $10^{-8} \text{ cm}^2 \text{s}^{-1}$, much higher than that $(1.8 \times 10^{-8} \text{ cm}^2 \text{s}^{-1})$ of nonporous PPy/rGO sheets in 1M H₂SO₄ electrolyte (Supporting Information, Figures S8,S9). Moreover, PPy has high pseudocapacitance from adjustable redox activity when serving as supercapacitor electrodes. In light of these merits, we selected mPPy/rGO nanosheets as interdigital microelectrode materials to assemble flexible planar MSCs (denoted as mPPy/rGO-MSCs) on a nylon membrane with the help of mask-assisted filtration,^[46-48] and examined their electrochemical performance in H₂SO₄/polyvinyl alcohol (PVA) gel electrolyte. Notably, the resultant interdigital mPPy/rGO microelectrodes present remarkable uniformity, large-area continuity, and outstanding mechanical flexibility, with a valid electrode area of 1.12 cm^2 (Figure 3b). The microelectrodes display an average thickness of 7.1 µm, as confirmed by the 3D cross-section view and high profile tested by a surface profiler (Figure 3c; Supporting Information, Figure S10). Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements were performed to evaluate the electrochemical performance of mPPy/rGO-MSCs (Figure 3d; Supporting Information, Figure S11). It is notable that the features of CV curves (Figure 3d) are well retained even at a high scan rate of 100 mVs⁻¹, manifesting high electrochemical reversibility. The GCD profiles of mPPy/rGO-MSCs (Supporting Information, Figure S11), measured at different current densities, exhibit approximate triangular form with small IR voltage drop. Remarkably, mPPy/rGO-MSCs deliver high areal capacitance (C_A) of 81 mF cm^{-2} and volumetric capacitance (C_v) of 102 F cm⁻³ at 1 mVs^{-1} (Figure 3e; the calculations are given in the Supporting Information, pp S3,S4), which is superior to those of carbon- and conducting-polymer-based MSCs.[49-51] Meanwhile, the resultant microdevice affords high capacitance $(40 \text{ mF cm}^{-2}, 50 \text{ F cm}^{-3})$ even when the scan rate is increased to 100 mVs⁻¹, demonstrative of exceptional rate capability. Moreover, mPPy/rGO-MSCs exhibit good cycling stability with 81% capacitance retention after 3500 charge/discharge cycles (Supporting Information, Figure S12). The initial capacitance drop is likely attributed to the instability of mPPy/rGO microelectrodes induced by the slight structural change of PPy at the early charge/discharge process.^[52] Electrochemical impedance spectrum (EIS) further discloses the merits of cylindrical pore structure within the planar mPPy/rGO-MSCs (Supporting Information, Figure S13). Equivalent series resistance (ESR), including electrolyte and electronic resistances, can be derived from high frequency region on the real axis.^[53] The low ESR (52 Ω) value reflects the high conductivity and successful construction of mPPy/ rGO-MSCs. Furthermore, the negligible semicircle in the curve, pertaining to charge transfer resistance, further verifies



Figure 3. a) Diagram of the roles of cylindrical mesopores parallel to graphene surface in the high electrochemical performance of planar MSCs. b) Photographs of mPPy/rGO microelectrodes taken at flat (up) and bending (down) states. c) 3D cross-sectional view of the mPPy/rGO microelectrode. d) CV curves tested at different scan rates from 1 to 100 mVs⁻¹. e) Areal capacitance (blue) and volumetric capacitance (red) of mPPy/rGO-MSCs as a function of scan rate. f) Ragone plots for mPPy/rGO-MSCs and some commercial energy storage devices for comparison.

the superiority of the mPPy/rGO nanosheets. This is because in mPPy/rGO-MSCs the electrolyte ions can sufficiently penetrate and diffuse along the parallel direction of 2D nanosheet-based microelectrodes through cylindrical mesopores (Figure 3a), while in contrast being limited to the vertical direction in conventional stacked geometry.^[54]

The Ragone plot in relation to the volumetric energy density and power density of mPPy/rGO-MSCs is shown in Figure 3 f. Remarkably, mPPy/rGO-MSCs exhibit high volumetric energy density of 2.3 mWh cm⁻³, which compares well to that of lithium thin film battery (10 mWh cm⁻³),^[55,56] and much higher than those of some commercial energy storage devices (Figure 3 f).^[57,58] Also, this value (2.3 mWh cm⁻³) surpasses those of many recently reported planar MSCs, including onion-like carbon (1.1 mWh cm⁻³),^[38] Ni@r- $(0.6 \text{ mWh cm}^{-3})$,^[39] GO@MnO₂ PANI nanowires $(0.78 \text{ mWh cm}^{-3})$,^[40] and PANi/rGO $(1.51 \text{ mWh cm}^{-3})$,^[41] and so on. Meanwhile, mPPy/rGO-MSCs display large energy density of 1.1 mWh cm⁻³ at a high power density of 503 mW cm⁻³. These consequences confirm that the ultrathin 2D structure and the presence of mesoporous patterns can largely improve the electrochemical capacitive behavior of MSCs.

The rapid development of wearable electronics requires flexible microscale energy storage devices. Therefore, we further investigated the mechanical flexibility of our microdevice. The CV curves of mPPy/rGO-MSCs, recorded under various bending angles (Supporting Information, Figure S14a,b), exhibit circa 90% of initial capacitance when the bending angle is 180°. Furthermore, after continuous bending from 0° to 90° for 3000 cycles, circa 86% of the initial capacitance is retained (Supporting Information, Figure S15a,b). As demand increases for intelligent integrated electronics, multiple integrated mPPy/rGO-MSC packs are required through the interconnection in parallel or in series to boost the capacitance or voltage output (Figure 4). As shown in Figure 4 a,b, the parallel MSCs disclose a stepwise linear growth of the capacitance. In a serial structure, the integrated mPPy/rGO-MSCs exhibit a progressive voltage extension from 0.8 to 2.4 V (Figure 4 c,d), indicative of exceptional



Figure 4. a) CV curves measured at a scan rate of 50 mVs⁻¹, and b) GCD profiles tested at 0.3 mAcm⁻² of three parallell-connected mPPy/rGO-MSCs. c) CV profiles obtained at 50 mVs⁻¹, and d) GCD curves recorded at 0.3 mAcm⁻² of three mPPy/rGO-MSCs connected in series (inset: photograph of three serial-connected mPPy/rGO-MSCs used to power a red light-emitting diode).

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performance uniformity. As a demonstration, our three serialconnected mPPy/rGO-MSCs can easily illume a red-light emitting diode (inset of Figure 4d), demonstrative of great potential as standalone microscale power sources for electronics.

In summary, we have developed a general interfacial selfassembly strategy for the construction of sandwich-like porous polymer-based free-standing nanosheets with cylindrical mesopores. The resultant mesoporous PPy/rGO nanosheets were selected as interdigital microelectrode materials for the assembly of flexible planar MSCs, which exhibited high volumetric capacitance (101 Fcm^{-3}), high energy density (2.3 mWh cm⁻³) and power density (500 mW cm^{-3}), along with outstanding mechanical flexibility and desirable serial/ parallel integration. The interfacial self-assembly protocol affords new opportunities for the preparation of diverse 2D porous polymer-based materials for high-performance energy storage and conversion systems.

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Conflict of interest

The authors declare no conflict of interest.

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