Interfacial assembly of 2D polydopamine/graphene heterostructures with well-defined mesopore and tunable thickness for high-energy planar micro-supercapacitors

Jieqiong Qin , Zhi Yang , Jiaxin Ma , Liangzhu Zhang , Feifei Xing , Hongtao Zhang , Shuxia Tian , Shuanghao Zheng , Zhong-Shuai Wu

 PII:
 S1001-8417(23)00668-X

 DOI:
 https://doi.org/10.1016/j.cclet.2023.108845

 Reference:
 CCLET 108845



Received date:11 June 2023Revised date:5 July 2023Accepted date:24 July 2023

Please cite this article as: Jieqiong Qin, Zhi Yang, Jiaxin Ma, Liangzhu Zhang, Feifei Xing, Hongtao Zhang, Shuxia Tian, Shuanghao Zheng, Zhong-Shuai Wu, Interfacial assembly of 2D polydopamine/graphene heterostructures with well-defined mesopore and tunable thickness for high-energy planar micro-supercapacitors, *Chinese Chemical Letters* (2023), doi: https://doi.org/10.1016/j.cclet.2023.108845

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2023 Published by Elsevier B.V. on behalf of Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.



Chinese Chemical Letters

journal homepage: www.elsevier.com

Interfacial assembly of 2D polydopamine/graphene heterostructures with well-defined mesopore and tunable thickness for high-energy planar micro-supercapacitors

Jieqiong Qin^{a,*}, Zhi Yang^a, Jiaxin Ma^{b,c}, Liangzhu Zhang^b, Feifei Xing^{b,c}, Hongtao Zhang^a, Shuxia Tian^d, Shuanghao Zheng^b, Zhong-Shuai Wu^{b,*}

^a College of Science, Henan Agricultural University, Zhengzhou 450002, China

^b State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^c University of Chinese Academy of Sciences, Beijing 100049, China

^d Mechanical and Electrical Engineering Institute, Zhengzhou University of Light Industry, Zhengzhou 450002, China

ARTICLE INFO	ABSTRACT	
Article history:	Two-dimensional (2D) me	esoporous pseudocapacitive polymer/graphene heterostructure
Received 11 June 2023	combine the advanced merits	its of 2D materials and mesoporous materials, possessing uniqu
Received in revised form 5 July 2023	nanosheet structure, large sp	pecific surface area (SSA), abundant oxygen/nitrogen-containin
Accepted 10 July 2023	groups, desirable electrical co	conductivity and admirable electrochemical redox activity, and hol
Available online	great potential for constructin	ng high-performance planar micro-supercapacitors (MSCs). Herein
	we demonstrate the interfacia heterostructures with well-d	ial assembly of 2D mesoporous polydopamine/graphene (mPDC defined mesopore structure (12 nm) and adjustable thickness
Keywords:	(7.5-14.1 nm) for planar high	h-energy pseudocapacitive MSCs. Attributed to medium thickness
2D materials	exposed mesopore of 12 nm	n and large SSA of 108 m ² /g, the mPDG with 10.8 nm thickness
Mesopores	reveals prominent mass capa	pacitance of 419 F/g and impressive cycling stability with ~969
Heterostructures	capacitance retention after 50	5000 cycles. Furthermore, the symmetric mPDG-based MSCs wit
Polydopamine	"water-in-salt" gel electrolyte	e present wide voltage window of 1.6 V, superior volumetric energ
High energy density	density of 11.5 mWh/cm ³ , o	outstanding flexibility and self-integration ability. Therefore, the
Micro-supercapacitors	work offers a new platform high-performance MSCs.	of controllably synthesizing 2D mesoporous heterostructures for

With the continuously increasing requirement for portable and wireless electronic products, substantial endeavors have been devoted to developing flexible and reliable micro-electrochemical energy storage systems, mainly including micro-supercapacitors (MSCs) and micro-batteries [1-5]. Owing to the faster charge-discharge rate, longer cycle life and higher power density than micro-batteries, MSCs have garnered much attention [6-8]. To boost the energy density of MSCs, two-dimensional (2D) graphene-based heterostructures have been proved as one of promising active electrode materials [9-11]. They can effectively restrain the restacking of graphene and strongly couple with functional components, yielding satisfactory electrical conductivity, high electrochemical activity, rapid ion-electron transport and outstanding flexibility for MSCs. So far, various 2D heterostructures of carbon/graphene [12,13], metal oxide (hydroxide)/graphene [14-16], metal sulfide/graphene [17,18] and polymer/graphene [19-21] have been reported as active materials for MSCs, in which 2D pseudocapacitive polymer/graphene (*e.g.*, polypyrrole/graphene, polyaniline/graphene and polyethylene dioxythiophene/graphene) stands out because of fully integrating the high pseudocapacitance of polymer with extraordinary conductivity and flexibility of graphene.

By virtue of abundant oxygen/nitrogen-containing groups (*e.g.*, -OH, -COOH and -NH-), redox-active properties of catechol/ortho-quinone groups, unique adhesion and good biocompatibility, polydopamine (PDA) is considered as a high-pseudocapacitive material for surface modification of graphene (Fig. S1 in Supporting information) [22-25]. Through synergistically combining the high-conductive graphene and high-pseudocapacitive polydopamine, the resultant 2D PDA/graphene heterostructures have been widely used as active electrodes or functional protection materials of various metal-ion batteries [26-30]. However, their electrochemical and structural stability are severely hindered by the swell effect of PDA in charging-discharging process [23,30]. In this regard, the introduction of mesopore structure (2-50 nm) into 2D PDA/graphene will be an effective approach to provide increasing active sites, buffer the reversible volume changes, and enhance effective contact areas, ultimately realizing improved cycling stability as well as power and energy densities for MSCs [31-33]. Nonetheless, precisely controllable assembly of 2D mesoporous PDA/graphene heterostructures for MSCs is underdeveloped so far.

^{*} Corresponding authors.

E-mail addresses: qinjieqiong@henau.edu.cn (J. Qin), wuzs@dicp.ac.cn (Z.-S. Wu)

Herein, we develop 2D mesoporous pseudocapacitive PDA/graphene (mPDG) heterostructures with well-defined mesopore structure and tunable thickness for high-energy planar MSCs. Using silica nanospheres as mesopore template and graphene oxide (GO) as 2D substrate, a series of mPDG heterostructures are successfully prepared by a dual-template interfacial assembly strategy. Remarkably, their sheet thickness can realize univariate regulation by precisely tailoring the amount of PDA monomer, which is of significance for elucidating their structure-activity relationship. Benefiting from medium thickness, exposed mesopore structure and larger specific surface area (SSA), mPDG with 10.8 nm thickness (mPDG-2) exhibits higher specific capacitance (419 F/g) and longer cycle life than mPDG with other thickness and non-mesoporous PDA/graphene (nPDG). Furthermore, mPDG-based MSCs with polyvinyl alcohol (PVA)-H₂SO₄ gel electrolyte (defined as mPDG-HMSCs) offer impressive volumetric capacitance of 34.3 F/cm³ and energy density of 3.1 mWh/cm³. What is more, mPDG-based MSCs with silica-lithium bis(trifluoromethane sulfonyl)imide (SiO₂-LiTFSI) gel electrolyte (mPDG-LMSCs) display high output voltage of 1.6 V and enhanced volumetric energy density of 11.5 mWh/cm³. Finally, both mPDG-HMSCs and mPDG-LMSCs present good mechanical flexibility and facile self-integration, demonstrating their tremendous application potential in on-chip wearable microelectronics.

The fabrication of 2D mPDG heterostructures by a dual-template interfacial assembly strategy is displayed in Fig. 1. Specifically, GO nanosheets are firstly modified by polydiallyldimethylammonium chloride to produce positively-charged GO templates. Then, negatively charged SiO₂ nanospheres as mesopore templates are uniformly assembled on the modified GO surface according to their electrostatic interaction. Subsequently, dopamine (DA) monomers are added and adsorbed on the surface of GO-SiO₂ to form GO-SiO₂-DA composites. After initiating by tris(hydroxymethyl)aminomethane, the PDA layer is successfully polymerized and coated on GO-SiO₂, named as GO-SiO₂-PDA. Finally, 2D mPDG heterostructures are obtained by hydrothermal reduction and removing templates of SiO₂. Notably, the sheet thickness and mesopore structure of mPDG can be precisely regulated by changing the additive amount of DA monomers. With different amounts of DA (150, 300 and 600 mg), the resulting mPDG heterostructures are denoted as mPDG-1, mPDG-2 and mPDG-3, respectively.



Fig. 1. Illustration of the fabrication of 2D mPDG heterostructures with tunable thickness and mesopore structure.

The morphological and structural characterizations of 2D mPDG heterostructures are presented in Fig. 2 and Figs. S2-S4 (Supporting information). For mPDG-2, scanning electron microscope (SEM) image exhibits uniform and flat 2D morphology with exposed mesopore arrays (Fig. 2a). Transmission electron microscope (TEM) images further confirm the homogeneous mesopore structure with ~12 nm pore size (Figs. 2b and c). Meanwhile, mPDG-1 and mPDG-3 reveal unformed and partially encapsulated mesopores, respectively, deriving from the half and double amount of DA precursor compared with mPDG-2 (Fig. S2 in Supporting information). Atomic force microscope (AFM) measurements confirm the varying thickness of 7.5 nm for mPDG-1, 10.8 nm for mPDG-2, and 14.1 nm for mPDG-3 (Figs. 2d and e, Fig. S3 in Supporting information). In addition, their nitrogen adsorption-desorption isotherms display a typical H₃-type hysteresis loop, verifying the mesopore structure of mPDG (Fig. 2f and Fig. S4 in Supporting information). The calculated SSA of mPDG-1, mPDG-2 and mPDG-3 is 80, 108 and 98 m²/g, and the corresponding pore volume is 0.27, 0.38 and 0.34 cm^{3}/g , respectively. Moreover, it is observed that the mesopore diameter of mPDG-2 is ~10.7 nm, which is consistent with its TEM result. Consequently, it is demonstrated that dual-template interfacial assembly strategy can realize the precise regulation of sheet thickness and mesopore structure. Furthermore, X-ray photoelectron spectroscopy (XPS) measurement manifests the C, O and N elements in mPDG-2 (Fig. S5 in Supporting information) [23,28,29]. As shown in Fig. 2g, four peaks in the C 1s XPS spectrum are identified as C-C, C-O/C-N, C=O, and O-C=O at 284.7, 285.9, 288.0 and 290.6 eV, respectively [23,28,29]. The two primary peaks for the O 1s spectra are 531.4 eV for O=C and 533.1 eV for O-C (Fig. 2h) [23,28,29]. The N 1s XPS spectrum exhibits three different binding energy from -N=, -NH- and -NH₂ at 398.9, 400.3 and 401.3 eV, respectively (Fig. 2i) [23,28,29]. The Fourier transform infrared spectroscopy (FTIR) spectrum of mPDG-2 exhibits distinct characteristics of PDA and graphene (Fig. S6 in Supporting information). The two feature peaks located at 2930 and 2850 cm⁻¹ can be assigned to the indole functional groups, the peak centered at 1460 cm⁻¹ is induced by N-H [27,34], and the peak located at 1630 cm⁻¹ is attributed to C=C in aromatic rings [35,36]. It is indicated

that mPDG possesses abundant oxygen/nitrogen-containing groups, which is beneficial to provide high pseudocapacitance and excellent electrolyte wettability.



Fig. 2. Morphological and structural characterizations of 2D mPDG heterostructures. (a) SEM image, (b, c) TEM images, (d) AFM image and (e) corresponding height profile, (f) nitrogen adsorption-desorption isotherm and pore size distribution profile, (g) C 1s, (h) O 1s, and (i) N 1s XPS spectra of mPDG-2.

Because of uniform 2D morphology, adjustable mesopore structure, large SSA and abundant oxygen/nitrogen-containing groups, the mPDG heterostructures are expected to work as active materials for MSCs to achieve high performance. To demonstrate the impact of sheet thickness on electrochemical performance, mPDG-1, mPDG-2 and mPDG-3 are examined in H₂SO₄ electrolyte via a three-electrode system. In Figs. 3a and b, the cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) profiles of mPDG-2 show pronounced pseudocapacitive behavior originating from redox-active PDA [34,37]. When the scan rate or current density increases, the CV curves and GCD profiles deliver incremental response current or discharge time, demonstrative of excellent electrochemical reversibility of mPDG. Compared with mPDG-1 and mPDG-3, the mPDG-2 presents a larger integral area at 50 mV/s and a longer discharge time at 1 A/g (Fig. S7 in Supporting information and Fig. 3c). Confirmed by Fig. 3d, mPDG-2 yields higher specific capacitance at 0.5-5 A/g than those of mPDG-1 and mPDG-3. Specifically, mPDG-2 reveals superior gravimetric capacitance of 419 F/g compared with mPDG-1 (363 F/g) and mPDG-3 (295 F/g) at 0.5 A/g. Furthermore, mPDG-2 can retain ~96% of initial capacitance over 5000 cycles, exceeding those of mPDG-1 (~91%) and mPDG-3 (~88%), which proves its better cycling stability derived from fully exposed mesopore structure (Fig. 3e). The initial capacitance increase can be attributed to the electro-activation process of mPDG induced by the enhanced ion accessibility and increased charge accommodation in 2D mesoporous heterostructures during the long charge-discharge process [38-40]. Moreover, the mesopore structure endows mPDG-2 with a larger CV curve, longer discharge time, and thus much higher capacitance and rate performance than nPDG (Fig. S8 in Supporting information). Meanwhile, the nPDG presents only ~62% capacitance retention for 5000 cycles, which is far lower than mPDG-2, affirming that mesopore structure is able to alleviate the volume change of electrode materials in charge-discharge process. According to electrochemical impendence spectra (EIS), mPDG-2 reveals a measured internal resistance (R_s) of 0.8 Ω and the corresponding charge-transfer resistance (R_{ct}) of 2.1 Ω , which are lower than mPDG-3 ($R_s = 1.3 \Omega$, $R_{ct} = 3.5 \Omega$) and slightly higher than mPDG-1 ($R_s = 0.8 \Omega$, $R_{ct} = 1.6 \Omega$) (Fig. 3f). Similarly, the slope in low frequency of mPDG-2 is larger than mPDG-3 and less than mPDG-1, indicative of the advantage of thin sheet thickness and exposed mesopores for enhancing ion-electron transport.



Fig. 3. Electrochemical performance of 2D mPDG working in a three-electrode system. (a) CV curves at 2-50 mV/s, and (b) GCD profiles at 0.5-10 A/g for mPDG-2. (c) GCD profiles measured at 1 A/g, (d) specific capacitances at varying current densities, (e) cycling stability over 5000 cycles at 1 A/g, and (f) EIS plots (inset: magnified high-frequency region) of mPDG-1, mPDG-2 and mPDG-3.

Considering excellent performance merits, the mPDG-2 is selected as active electrode material for fabricating planar interdigital MSCs by a mask-assisted filtration technology [41-43], in which highly conductive exfoliated graphene (EG) is used as flexible metal-free current collector, and carbon nanotube (CNT) is applied as conductive additive to improve electrical conductivity of electrode. As exhibited in Fig. 4a, the interdigital microelectrodes display excellent uniformity and robust mechanical flexibility. The top and cross-section views clearly show a uniform and flat EG layer on the surface, and a sandwich-like layered structure with a thickness of ~4 µm (Figs. 4b and c, Fig. S9 in Supporting information). After drop-casting and solidifying PVA-H₂SO₄ electrolyte, the planar quasi-solid-state mPDG-HMSCs are obtained. Then, the CV curves of mPDG-HMSCs at 0-0.8 V display obvious pseudocapacitive feature and stepwise improved current with increasing scan rate (Fig. 4d). The GCD curves at 0.05-1 mA/cm² present similar shape and gradually increased charge-discharge times, indicating reversible electrochemical behavior of mPDG-HMSCs (Fig. S10 in Supporting information). Remarkably, mPDG-HMSCs deliver large areal capacitance and volumetric capacitance of 13.8 mF/cm² and 34.3 F/cm³ at 2 mV/s, respectively (Fig. 4e), both of which surpass those of graphene/sulfonated polyaniline (rG/SPANI: 3.31 mF/cm², 16.55 F/cm³) [44], laser-reduced GO (laser-rGO: 0.51 mF/cm², 3.1 F/cm³) [45], rGO/CNT (5.1 mF/cm², 6.1 F/cm³) [46] and laser-scribed graphene (LSG: 2.3 mF/cm², 3.1 F/cm³) [47] for MSCs. The EIS plots of mPDG-HMSCs are shown in Fig. S11 (Supporting information). The mPDG-HMSCs also reveal impressive cycling stability of ~89% capacitance retention over 5000 cycles (Fig. S12 in Supporting information). Further, the mechanical flexibility and self-integration of mPDG-HMSCs were assessed to verify their potential applications in smart microelectronics. As shown in Figs. 4f and g, mPDG-HMSCs present nearly coincident CV curves under varying bending angles, showing ~97% retention at the bending angle of 180°. With continuous bending, mPDG-HMSCs can still maintain ~88% of initial capacitance for 1000 bending cycles, demonstrative of admirable mechanical flexibility (Fig. S13 in Supporting information). In addition, the CV curves and GCD profiles of three serially-connected mPDG-HMSCs illustrate similar shapes and stepwise voltage increase from 0.8 (one cell) to 2.4 V (three cells), as exhibited in Fig. 4h and Fig. S14 (Supporting information). Meanwhile, parallelly-connected mPDG-HMSCs display a linear increase of capacitance, verifying outstanding performance uniformity and accessible self-integration ability for high current/capacitance output (Fig. 4i and Fig. S15 in Supporting information).



Voltage (V)

а

g

Fig. 4. Characterization and electrochemical performance of mPDG-HMSCs. (a) Photograph at a bending state, (b) top-view SEM image, and (c) cross-section SEM image of mPDG-based microelectrodes. (d) CV curves at 5-100 mV/s, (e) areal capacitance and volumetric capacitance versus scan rate of mPDG-HMSCs. (f) CV curves at 50 mV/s, and (g) capacitance retention of mPDG-HMSCs under varying bending angles of 0°-180° (insets: photographs of the device at 0° and 180°). (h, i) CV curves at 50 mV/s of three connected mPDG-HMSCs in (h) series and (i) parallel.

According to the formula of $E = CV^2/2$, the energy density (E) of MSCs is directly proportional to specific capacitance (C) and the square of cell voltage (V) [48,49]. Thus, expanding the cell voltage with high-voltage electrolyte is a straightforward strategy to enhance the energy density of mPDG-based MSCs. To this purpose, a low-cost, highly safe SiO₂-LiTFSI "water-in-salt" (WIS) gel electrolyte was used to assemble high-voltage mPDG-LMSCs [43,50]. The CV curves and GCD profiles of mPDG-LMSCs verify a high voltage of 1.6 V (Fig. 5a and Fig. S16 in Supporting information) and the EIS plots reveal low resistance (Fig. S17 in Supporting information). Notably, the areal capacitance and volumetric capacitance of mPDG-LMSCs are 12.9 mF/cm² and 32.4 F/cm³, respectively (Fig. 5b). Besides, mPDG-LMSCs deliver impressive cycle stability of ~83% retention over 5000 cycles (Fig. S18 in Supporting information). With varying bending angles, mPDG-LMSCs present almost unchanged CV curves and ~96% capacitance retention even at 180°, demonstrative of superior mechanical flexibility (Fig. 5c). Further, serially-connected mPDG-LMSCs offer a progressive voltage expansion from 1.6 V for one cell to 4.8 V for three cells, while parallelly-connected mPDG-LMSCs disclose a stepwise current/capacitance increase, manifesting adjustable voltage and capacitance outputs (Figs. 5d and e, Figs. S19 and S20 in Supporting information). As demonstrated, two serially-connected mPDG-LMSCs can effectively drive a liquid crystal display with the logo of "Henan Agricultural University", and readily light up a red diode (Fig. 5f and Fig. S21 in Supporting information).



Fig. 5. Electrochemical performance of mPDG-LMSCs. (a) CV curves, (b) areal capacitance and volumetric capacitance versus scan rate of mPDG-LMSCs. (c) Capacitance retention versus bending angle for mPDG-LMSCs (Inset: CV curves at 50 mV/s). (d, e) CV curves of three connected mPDG-LMSCs in (d) series and (e) parallel. (f) Photograph of the logo of "Henan Agricultural University" powered by two serially-connected mPDG-LMSCs.

Further, the Ragone plot of mPDG-HMSCs and mPDG-LMSCs is provided to compare their energy density and power density with recently reported polymer/graphene-based MSCs (Figs. 6a and b). Expectedly, mPDG-LMSCs show the highest areal and volumetric energy densities of 4.6 µWh/cm² and 11.5 mWh/cm³, which exceed those of mPDG-HMSCs (1.2 µWh/cm² and 3.1 mWh/cm³). What is more, this value (11.5 mWh/cm³) is considerably larger than other polymer/graphene-based MSCs, *e.g.*, rG/SPANI (1.5 mWh/cm³) [44], mesoporous polypyrrole-rGO (mPPy-rGO: 2.3 mWh/cm³) [51], mPPy/rGO anchored with polyoxometalate (mPPy/rGO-POM: 4.8 mWh/cm³) [52], dual-mesoporous polypyrrole-graphene (DM-PG: 2.5 mWh/cm³) [53] and polypyrrole@rGO (PPy@rGO, 8.9 mWh/cm³) [20], as well as commercially available supercapacitors and Li thin-film batteries (Table S1 in Supporting information). Meanwhile, mPDG-LMSCs possess high areal and volumetric power densities of 424.6 µW/cm² and 1061.5 mW/cm³, respectively.



Fig. 6. Ragone plot of mPDG-HMSCs and mPDG-LMSCs. (a) Areal energy density and power density, and (b) volumetric energy density and power density of mPDG-HMSCs and mPDG-LMSCs with recently reported polymer/graphene-based MSCs and commercially available energy storage devices.

The admirable electrochemical performance of mPDG-LMSCs is attributed to the controllable synthesis of mPDG heterostructures and the effective utilization of WIS gel electrolyte. First, 2D mPDG heterostructures as active materials not only couple the advantages of mesoporous materials and 2D materials, but also combine the high pseudocapacitance of PDA with the excellent conductivity and stability of graphene, ensuring high capacitance of MSCs. Second, mPDG-2 with fully exposed mesopores provides unimpeded ion-electron transfer and adaptable volume expansion in charge-discharge process, greatly enhancing the rate performance and cycle life of devices. Last but not least, the WIS gel electrolyte of SiO₂-LiTFSI endows high operating voltage, robust interfacial coupling of electrolyte and microelectrodes, and ultimately enhanced energy density and mechanical flexibility of the as-prepared planar MSCs.

In summary, we have demonstrated 2D mPDG heterostructures with well-defined mesopores and tunable thickness for safe, high-energy planar MSCs. Using GO and silica nanospheres as 2D and mesopore templates, the sheet thickness and mesopore structure of mPDG can be accurately regulated by changing the amount of DA. Particularly, the prepared mPDG-2 reveals remarkable specific mass capacitance (419 F/g at 0.5 A/g) and long cycle life (~96% retention over 5000 cycles). With mPDG-2 as active material, the mPDG-HMSCs exhibit outstanding volumetric capacitance (34.3 F/cm³) and energy density (3.1 mWh/cm³). More importantly, the mPDG-LMSCs with WIS gel electrolyte offer a large operating voltage of 1.6 V, as well as an amazing volumetric energy density of 11.5 mWh/cm³, surpassing most recently reported symmetric MSCs and comparable to some asymmetric MSCs. Further, the extraordinary flexibility and self-integration capability of mPDG-HMSCs and mPDG-LMSCs endow them with great potential for flexible microelectronic applications. Therefore, this work offers many possibilities for the precise fabrication of 2D mesoporous heterostructures for high-performance MSCs.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 22109040, 22125903, 22279137), Top-Notch Talent Program of Henan Agricultural University (No. 30500947), the "Transformational Technologies for Clean Energy and Demonstration" Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDA21000000), DICP (No. DICP 1202032), Dalian National Laboratory for Clean Energy (DNL), CAS, DNL Cooperation Fund, CAS (Nos. DNL202016, DNL202019), International Postdoctoral Exchange Fellowship Program (Talent-Introduction Program) (No. YJ20210311), China Postdoctoral Science Foundation (No. 2021M703145), the Joint Fund of the Yulin University and the Dalian National Laboratory for Clean Energy (Nos. YLU-DNL Fund 2021009).

References

- [1] M. Beidaghi, Y. Gogotsi, Energy Environ. Sci. 7 (2014) 867.
- [2] S. Zheng, X. Shi, P. Das, et al., Adv. Mater. 31 (2019) 1900583.
- [3] S. Bi, H. Cao, R. Wang, et al., J. Energy Chem. 63 (2021) 25-39.
- [4] F. Liu, X. Feng, Z.S. Wu, J. Energy Chem. 76 (2023) 459-461.
- [5] K. Chen, X. Li, J. Zang, et al., Nanoscale 13 (2021) 12370-12378.
- [6] N.A. Kyeremateng, T. Brousse, D. Pech, Nat. Nanotechnol. 12 (2017) 7-15.
- [7] J. Zhang, G. Zhang, T. Zhou, et al., Adv. Funct. Mater. 30 (2020) 1910000.
- [8] S. Wang, J. Ma, X Shi, et al., Nano Res. Energy 1 (2022) e9120018.
- [9] Z.S. Wu, X.L. Feng, H.M. Cheng, Natl. Sci. Rev. 1 (2014) 277-292.
- [10] Y. Da, J. Liu, L. Zhou, et al., Adv. Mater. 31 (2019) e1802793.
- [11] S. Dai, Z. Liu, B. Zhao, et al., J. Power Sources 387 (2018) 43-48.
- [12] G. Moreno-Fernández, J.L. Gómez-Urbano, M. Enterría, et al., J. Mater. Chem. A 7 (2019) 14646-14655.
- [13] J. Liang, A.K. Mondal, D.W. Wang, et al., Adv. Mater. Technol. 4 (2018) 1800200.
- [14] J. Qin, Z.S. Wu, F. Zhou, et al., Chin. Chem. Lett. 29 (2018) 582-586.
- [15] R. Chen, M. Yu, R.P. Sahu, et al., Adv. Energy Mater. 10 (2020) 1903848.
- [16] C. Jing, B. Dong, Y. Zhang, Energy Environ. Mater. 3 (2020) 346-379.
- [17] D. Vikraman, K. Karuppasamy, S. Hussain, et al., Compos. Part B: Eng. 161 (2019) 555-563.
- [18] S.E. Moosavifard, J. Shamsi, M.K. Altafi, et al., Chem. Commun. 52 (2016) 13140-13143.
- [19] Y. Shi, L. Peng, Y. Ding, et al., Chem. Soc. Rev. 44 (2015) 6684-6696.

[20] L. Chi, S. Zheng, J. Ma, et al., Carbon 194 (2022) 240-247.

- [21] M. Tahir, L. He, W. Yang, et al., J. Energy Chem. 49 (2020) 224-232.
- [22] H. Lee, T. Han, K.Y. Cho, et al., ACS Appl. Mater. Interfaces 8 (2016) 21366-21372.
- [23] T. Liu, K.C. Kim, B. Lee, et al., Energy Environ. Sci. 10 (2017) 205-215.
 [24] K. Qu, Y. Wang, A. Vasileff, et al., J. Mater. Chem. A 6 (2018) 21827-21846.
- [25] X. Yue, H. Liu, P. Liu, Chem. Commun. 55 (2019) 1647-1650.
- [26] T. Liu, K.C. Kim, R. Kavian, et al., Chem. Mater. 27 (2015) 3291-3298.
- [27] P.J. Kim, V.G. Pol, Adv. Energy Mater. 8 (2018) 1802665.
- [28] T. Liu, B. Lee, B.G. Kim, et al., Small 14 (2018) e1801236.
- [29] J. Qin, H. Shi, K. Huang, et al., Nat. Commun. 12 (2021) 5786.
- [30] S. Jiang, F. Xing, J. Zhang, et al., Chem. Eng. J. 452 (2023) 139095.
- [31] Y. Yan, G. Chen, P. She, et al., Adv. Mater. 32 (2020) e2004654.
- [32] A.E. Allah, J. Wang, Y.V. Kaneti, et al., Nano Energy 65 (2019) 103991.
- [33] R. Zhang, H. An, Z. Li, et al., Chem. Eng. J. 289 (2016) 85-92.
- [34] X. Yue, H. Liu, P. Liu, Chem. Commun. 55 (2019) 1647-1650.
- [35] Y. Zhu, S. Murali, W. Cai, et al., Adv. Mater. 22 (2010) 3906-3924.
- [36] Z. Li, S. Wu, W. Lv, et al., Small 12 (2016) 2674-2688.
- [37] T. Liu, B. Lee, B.G. Kim, et al., Small 14 (2018) 1801236.
- [38] S. Liu, P. Gordiichuk, Z.S. Wu, et al., Nat. Commun. 6 (2015) 8817.
- [39] Y. Song, T.Y. Liu, X.X. Xu, et al., Adv. Funct. Mater. 25 (2015) 4626-4632.
- [40] Q. Wu, T. He, Y. Zhang, et al., J. Mater. Chem. A 9 (2021) 24094-24147.
- [41] H. Xiao, Z.S. Wu, L. Chen, et al., ACS Nano 11 (2017) 7284-7292.
- [42] F. Zhou, H. Huang, C. Xiao, et al., J. Am. Chem. Soc. 140 (2018) 8198-8205.
- [43] J. Qin, S. Wang, F. Zhou, et al., Energy Storage Mater. 18 (2019) 397-404.
- [44] B. Song, L. Li, Z. Lin, et al., Nano Energy 16 (2015) 470-478.
- [45] W. Gao, N. Singh, L. Song, et al., Nat. Nanotechnol. 6 (2011) 496-500.
- [46] M. Beidaghi, C. Wang, Adv. Funct. Mater. 22 (2012) 4501-4510.
- [47] M.F. El-Kady, R.B. Kaner, Nat. Commun. 4 (2013) 1475.
- [48] S. Zheng, Z.S. Wu, S. Wang, et al., Energy Storage Mater. 6 (2017) 70-97.
- [49] Y. Zhu, S. Zheng, J. Qin, et al., Fund. Res. (2022) 10.1016/j.fmre.2022.03.021.
- [50] Y. Zhu, S. Zheng, P. Lu, et al., Natl. Sci. Rev. 9 (2022) nwac024.
- [51] H. Tian, J. Qin, D. Hou, et al., Angew. Chem. Int. Ed. 58 (2019) 10173-10178.
- [52] J. Qin, F. Zhou, H. Xiao, et al., Sci. China Mater. 61 (2018) 233-242.
- [53] J. Qin, J. Gao, X. Shi, et al., Adv. Funct. Mater. 30 (2020) 1909756.

Graphical abstract



The interfacial assembly of 2D polydopamine/graphene heterostructures with well-defined mesopore structure of 12 nm and adjustable thickness of 7.5-14.1 nm is demonstrated for high-energy pseudocapacitive micro-supercapacitors.

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

