Bilayered microelectrodes based on electrochemically deposited MnO$_2$/polypyrrole towards fast charge transport kinetics for micro-supercapacitors†

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Micro-supercapacitors (MSCs) are promising power solution facilities for miniaturized portable electronic devices. Microfabrication of on-chip MSC with high specific capacitance and high energy density is still a great challenge. Herein, we report a high-performance MnO$_2$/polypyrrole (PPy) microelectrode based MSC (MnO$_2$/PPy-MSC) by modern micromachining technology. Interdigital Au micro current collectors were obtained by photolithography, physical vapor deposition and lift off. A layer of PPy was electrochemically deposited on Au current collectors followed by deposition of urchin-like MnO$_2$ micro/nanostructures. The electrochemical performance of MnO$_2$/PPy-MSC was explored employing LiClO$_4$/PVA gel electrolyte. The assembled MSC demonstrated a high areal capacitance of 13 mF cm$^{-2}$, an energy density of 1.07 mWh cm$^{-2}$ and a power density of 0.53 mW cm$^{-2}$. In addition, the MnO$_2$/PPy-MSC showed an improved cycling stability, retaining 84% of the initial capacitance after 5000 CV cycles at a scan rate of 500 mV s$^{-1}$. Our proposed strategy provides a versatile and promising method for the fabrication of high-performance MSCs with large-scale applications.

Introduction

With the emerging trend and advancement of miniaturized portable electronics, there is an increasing demand for high-performance microscale energy storage systems with high reliability.1 In this regard, planar micro-supercapacitors (MSCs) are beneficial power sources due to their small size, excellent rate performance and long cycling life.1,2 MSCs are highly promising for wafer-level integration and applications in microsystems due to their great potential of bridging the gap between microbatteries and conventional supercapacitors.4 They are capable of recharging and delivering power faster than those of microbatteries and store more energy than those of capacitors. Based on the inner energy storage phenomenon, MSCs are usually categorized into electrochemical double layer capacitors (EDLCs), and pseudocapacitors.5 EDLC stores charge through ion adsorption/desorption while pseudocapacitor involves rapid reversible redox reaction at the electrode–electrolyte interface.

MSCs have the advantages by virtue of their distinctive interdigital structure with finger microelectrodes.6,7 MSCs based on pseudocapacitive mechanism provide opportunity to achieve higher capacity and energy storage compared with EDLC, but lack fast charge–discharge rate. Various factors are under consideration that have potential to improve overall performance. A decrease in equivalent series capacitance (ESR) will significantly increase the specific capacitance and endow MSC with a high specific energy.8 The ESR can be decreased by fabricating a device with small migration distance of ions that can be controlled by adjusting the width of microelectrodes and the insulating gap.9 The energy and power densities can be considerably improved with reduced ESR and improved electrical conductivity.10,11 Enormous amount of researches have been done in this context with different active materials and techniques.

Conducting polymers and metal oxides/hydroxides have gained attention as the auspicious electrode materials for electrochemical energy storage.12,13 These materials show pseudocapacitive behavior in MSCs, offering a way for achieving high energy density without compromising their high power...
Among conducting polymers, polypyrrole (PPy) is considered highly promising owing to its high electrical conductivity, easy production and high chemical stability. However, due to the polymeric nature and structural properties of PPy, the problems associated with stability and deterioration in cycling life over long-term charge-discharge hinder its large-scale applications. The expedient morphology of metal oxides possesses high performance due to their high electrochemical activity but they have the problem of aggregation. Structured PPy film significantly restricts the aggregation of metal oxides in the production of active electrode material. Manganese dioxide (MnO₂) has been explored as an electrochemically active transition metal oxide with high theoretical specific capacitance (1370 F g⁻¹), low cost and environmental friendliness. Although, its practical applications with high power density are limited due to its poor electrical conductivity (~10⁻⁷ S cm⁻¹) at room temperature. Various composites based on MnO₂ have been developed to yield high electrochemical performance. MnO₂-based supercapacitors exhibit high electrical conductivity by composing with graphene, highly conductive Zn₁SnO₄ (ZTO) nanowires, carbon nanotubes, PPy and PEDOT. Herein, we demonstrate the fabrication of a planar MSC with stacked MnO₂/PPy microelectrodes through facile electrodeposition and study its electrochemical performance. A layer of PPy was electrochemically deposited on Au current collectors followed by electrodeposition of urchin-like MnO₂ micro/nanostructures. We employed electrodeposition method to tailor the thickness and morphology of MnO₂ decorated PPy microelectrodes by optimizing the parameters such as current density, potential and deposition time. The electrochemical performance of MnO₂/PPy-MSC was evaluated by using LiClO₄/PVA gel electrolyte. Our approach provides distinct pathways for access of electrolyte and maximum charge transfer through microelectrodes, while preventing the aggregation of MnO₂. The fabricated MSC exhibits an improved specific capacitance and energy density by the virtue of highly conductive PPy and high capacitive property of MnO₂. A layer of PPy strengthens the conductivity of microelectrodes by fast electron transfer and ensures the high utilization of active material. While, MnO₂ micro/nanostructures have more active sites which facilitate the fast ion diffusion and exchange at electrode-electrolyte interface, providing high capacitance.

Materials characterization and electrochemical measurements

The surface morphology of microelectrodes was characterized by field emission scanning electron microscopy (FE-SEM) through JEOL JSM-7100 microscope. The thickness of active electrode material was assessed using stylus surface profiler (Bruker DEKTAK XT). X-ray diffraction (XRD) measurement was conducted to obtain crystallographic information of the electrode material by means of Bruker D8 Advance X-ray diffractometer with Cu Kα X-ray source (λ = 1.5418 Å). Raman spectra of samples were collected using Renishaw RM-1000 laser Raman microscope. Energy-dispersive X-ray spectroscopy (EDS) test was conducted for elemental analysis using Oxford IES250 system. Fourier transform infrared (FTIR) spectra of samples were acquired by 60-SXB IR spectrometer. The electrochemical tests of MSC were performed by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) using Autolab 302N.

The electrochemical performance of MSC was determined by evaluating the areal capacitance (Cₐ) via GCD using the following equation.

$$C_a = \frac{i \Delta t}{a \Delta V} (\text{mF cm}^{-2})$$

where i (mA) and Δt (s) are the discharging current and time, respectively, a (cm²) is the area of microelectrodes and ΔV (V) is the operational voltage window excluding IR drop.

The areal energy density (Eₐ) and power density (Pₐ) were evaluated by following equations:

$$E_a = \frac{C_a (\Delta V)^2}{7200} (\text{mW h cm}^{-2})$$

$$P_a = \frac{E_a \times 3600}{\Delta t} (\text{mW cm}^{-2})$$

ESR of device was estimated from discharge curve by using the following equation:

$$ESR = \frac{V_{top}}{2I} (\Omega \text{ cm}^2)$$
where $V_{\text{drop}}$ is the voltage drop in the beginning of discharge curve and $I$ is the constant discharge current.

Results and discussion

SEM image (Fig. 2a) reveals the cauliflower-like structure, indicating the incorporation of electrochemically deposited PPy. A layer of PPy participates actively in electron transfer from microelectrodes to current collectors. A fine PPy layer can be obtained by optimizing the deposition time and other parameters. Fig. 2b shows the urchin-like MnO$_2$ structures uniformly deposited onto the PPy layer, and the size of MnO$_2$ structures lies in 500 nm to 1 µm. Usually MnO$_2$ offers high ion diffusion but due to its poor electrical conductivity the ions interaction is limited only to the near surface. It can be observed from the morphology that MnO$_2$ micro/nanostructures offer large intercalation channels and more diffusion pathways for redox reaction. MnO$_2$ micro/nanostructures hold the PPy chains from breaking and create additional active sites for the transfer of ions and electrons during charge and discharge processes.

Fig. S2(a and b, ESI†), respectively shows the optical and SEM images of microelectrodes with no obvious defects. The microelectrodes are not broken or cracked, thus physical practicability of fabrication process is confirmed. The energy-dispersive spectroscopy (EDS) test was performed for elemental analysis and to estimate the relative abundance of elements. Fig. S3 (ESI†) shows the EDS mapping of MnO$_2$/PPy microelectrode and the elements of manganese (Mn), oxygen (O), carbon (C) and nitrogen (N) are uniformly dispersed, confirming the existence of MnO$_2$ and PPy.

The crystal structure of MnO$_2$/PPy microelectrodes was characterized by XRD, as shown in Fig. 3a. It is observed that the sharp diffracting peaks indicate high degree of crystallinity and are indexed to tetragonal structure of MnO$_2$ phase (JCPDS card no. 01-081-2261, $a = b = 4.404$ Å and $c = 2.876$ Å). The crystal structure in correspondence with the morphology shows that the deposited MnO$_2$ exhibits high diffusivity and capacitive properties. The XRD pattern also shows the amorphous nature of composite as it exhibits a broad peak at $\sim$21° in XRD diffractogram. The broadening of peak is due to the scattered X-
rays from the interplanar spacing of polymer chains and could be ascribed to the amorphous PPy. Fig. 3b shows the Raman spectra of PPy and MnO2/PPy. The spectrum of MnO2/PPy at 1570 cm$^{-1}$ corresponds to the C=O symmetry stretching of oxidized PPy. The peaks at 1326 and 1400 cm$^{-1}$ are attributed to pyrrole ring of PPy stretching. The characteristic peaks of PPy at 1047, 980 and 932 cm$^{-1}$ show the C–H in-plane deformation and the ring deformation due to bipolaron and polaron species, respectively. Finally, the peaks observed at 510 and 576 cm$^{-1}$ show the vibration of Mn–O lattice resulting from the deposition of MnO2 onto PPy microstructure matrix. Fig. 3c shows the Fourier transform infrared (FTIR) spectrum ranging from 3900 cm$^{-1}$ to 400 cm$^{-1}$ that confirms the species of as-electrodeposited PPy. The broad signal with high intensity at 3425 cm$^{-1}$ is ascribed to N–H stretching vibration and the peak at 2923 cm$^{-1}$ could be referred to C–H stretching owing to the smaller mass of H atom. The characteristic peak in diagnostic region at 1651 cm$^{-1}$ is referred to stretching vibrations of C=C bonds of PPy rings. Other transmittance peaks in fingerprint region of C–N (1384 cm$^{-1}$), C–C (1195 cm$^{-1}$), N–H (1090 cm$^{-1}$) and C–H (935, 841, 690 cm$^{-1}$) can be observed, confirming the formation of PPy.

The MnO2/PPy-MSC was assembled by applying 1 M LiClO4/PVA gel electrolyte and tested for electrochemical performance from CV, GCD and EIS with 2-electrodes system. Fig. 4a displays the CV curves of MnO2/PPy-MSC under 0.8 V at different scan rates. The quasi-rectangular CV curve shows a successive redox reaction on the electrode surface that corresponds to the capacitive properties of MnO2. The larger enclosed area and reaction on the electrode surface that corresponds to the rates. The quasi-rectangular CV curve shows a successive redox reaction. The voltage drop of charge transfer at different scan rates and current densities are shown in Fig. S4(a and b, ESI†), respectively. Fig. 4(c and d) presents the comparison of CV and GCD of MnO2/PPy-MSC with that of MnO2-MSC. The CV curves at 10 mV s$^{-1}$ demonstrate significant increase in the capacitive performance of MSC with PPy as conducting layer for micro-electrode. The GCD curve at a current density of 0.2 mA cm$^{-2}$ also shows a notable increase in the discharge time and capacitance, consequently the fabricated MSC exhibits an enhanced energy density. Moreover, the electrochemical performance of MnO2/PPy-MSC was also compared with another device fabricated by electrodepositing PPy over the MnO2 (PPy@MnO2-MSC), as shown in Fig. S5(a and b, ESI†).

EIS test was performed to further investigate the resistance and kinetic process of electrode reaction. The typical Nyquist plot at open circuit voltage over a frequency ranging from 100 KHz to 0.01 Hz is shown in Fig. 5a. The impedance spectrum presents a well-defined semi-circle at real axis in a high frequency followed by a sheer graph with steep slope in low frequency Warburg region. The amplified curve in high frequency region is shown in the inset. The intercept at real axis represents the lower internal resistance of about 45 Ω and the diameter of semi-circle indicate the charge transfer resistance ($R_t$) of 6.7 Ω caused by faradaic reaction on the electrode-electrolyte interface and interior. The vertical graph at low frequency is nearly aligned with imaginary axis and represents the ideal capacitive behavior of composite electrode due to the ion diffusion and mobility. Rate capability is significant for the evaluation of the power applications of MSC. Fig. 5b shows the specific capacitances at different corresponding current densities. The MnO2/PPy-MSC demonstrates a rate capability of 62.2% at 1 mA cm$^{-2}$ as compared with the capacitance at current density of 0.1 mA cm$^{-2}$. The percentage of capacitance retention at different current densities with corresponding IR drop is shown in Fig. S6 (ESI†). The sudden voltage drop in the discharge curve is the measure of total resistance of the MSC and is proportional to the discharge current. A smaller voltage drop at a high current density indicates low internal resistance of the tested device. The voltage drop increases at higher current density, as shown by the $V_{\text{drop}}$ graph in Fig. 5b.

CV cycling was conducted at a higher scan rate to evaluate the stability of MnO2/PPy-MSC. The percentage of capacitance...
Fig. 4  (a) Cyclic voltammetry and (b) galvanostatic charge–discharge curves of MnO₂/PPy-MSC. (c) Comparison of CV and (d) GCD of MnO₂/PPy-MSC and MnO₂-MSC.

Fig. 5  (a) Nyquist plot of MnO₂/PPy-MSC, inset is the Nyquist plot in high frequency region. (b) Specific areal capacitances and corresponding voltage drops at different current densities. (c) Cycling performance of MnO₂/PPy-MSC at 0.5 V s⁻¹. (d) Ragone plot of MnO₂/PPy-MSC and analogy with other MSCs.
MnO₂ and PPy demonstrates higher electrochemical perfor-
an nanostructures deposited onto the PPy further improve the oration of electrode material during continuous CV cycles. 4748 Herein, the inclusion of MnO₂ keeps the PPy polymer chains stable and enhances the cycling life of MSC. Consequently, 84% of actual capacitance is retained after 5000 cycles, showing improved stability and cycling performance. 49 The inset graph shows the reduction in current density and enclosed area of the 5000th CV curve during the cycling process. The specific areal energy and power densities are further determined from charge-discharge curves, Fig. 5d shows the results and Ragone plot analogy. MnO₂/PPy-MSC achieves an energy density of 1.07 × 10⁻³ mW h cm⁻² and a power density of 0.53 mW cm⁻², greater than those of MSCs based on interdigital Au/MnO₂/Au, 50 nanoporous gold (NPG)/MnO₂, 51 MWNT/MnO₂, 52 Ag/PEDOT:PSS/MnO₂ (ref. 53) and graphene quantum dots/MnO₂. 54 Fig. S7 (ESI†) shows the corresponding energy and power densities at various current densities. Improved energy density is attributed to the pseudocapacitive properties of MnO₂, high electrical conductivity of PPy and the fine patterning with narrow gap between the fingers.

Conclusions

In summary, we have fabricated a distinctive on-chip microsupercapacitor with enhanced capacitance from a trivial footprint. The fabricated MSC demonstrates improved electrochemical and mechanical performances by highly effective combination of high electrical conductivity of PPy and pseudocapacitive properties of MnO₂. PPy facilitates the fast electron transport and clearly reduce the resistance of MSC. While, MnO₂ micro/nanostructures efficiently increase the ionic penetration by creating more electrochemically active sites and thus enhance the specific capacitance. MnO₂/PPy-MSC shows an areal capacitance of 13 mF cm⁻² in PVA/LiClO₄ gel electrolyte at a current density of 0.1 mA cm⁻². The MnO₂ micro/nanostructures deposited onto the PPy further improve the cycling stability and the MnO₂/PPy-MSC possesses 84% of capacitance after 5000 CV cycles. Cooperative action of layered MnO₂ and PPy demonstrates higher electrochemical performance than that of microelectrodes based on pristine materials. These findings promote new opportunities for polymer/metal oxide based state-of-the-art micro-supercapacitors.

Conflicts of interest

There are no conflicts to declare.

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References

1 S. Wang, Z.-S. Wu, F. Zhou, X. Shi, S. Zheng, J. Qin, H. Xiao, C. Sun and X. Bao, npj 2D Mater. Appl., 2018, 2, 7.
2 D. Qi, Y. Liu, Z. Liu, L. Zhang and X. Chen, Adv. Mater., 2017, 29, 1602802.
3 S. Wang, Z.-S. Wu, S. Zheng, F. Zhou, C. Sun, H.-M. Cheng and X. Bao, ACS Nano, 2017, 11, 4283–4291.
4 C. Lethien, J. Le Bideau and T. Brousse, Energy Environ. Sci., 2019, 12, 96–115.
5 Z. S. Wu, K. Parvez, X. Feng and K. Mullen, Nat. Commun., 2013, 4, 2487.
6 H. Li and J. Liang, Adv. Mater., 2019, 1805864.
7 W. A. Haider, M. Tahir, L. He, W. Yang, A. Minhas-khan, K. A. Owusu, Y. Chen, X. Hong and L. Mai, J. Alloys Compd., 2020, 823, 151769.
8 L. Demarconnay, E. Raymundo-Pinero and F. Béguin, J. Power Sources, 2011, 196, 580–586.
9 N. Liu and Y. Gao, Small, 2017, 13, 1701989.
10 B. Mendoza-Sánchez and Y. Gogotsi, Adv. Mater., 2016, 28, 6104–6135.
11 G. Xiong, C. Meng, R. G. Reifenberger, P. P. Irakozi and T. S. Fisher, Electroanalysis, 2014, 26, 30–51.
12 M. Boota and Y. Gogotsi, Adv. Energy Mater., 2019, 9, 1802917.
13 M. Tahir, L. He, W. A. Haider, W. Yang, X. Hong, Y. Guo, X. Pan, H. Tang, Y. Li and L. Mai, Nanoscale, 2019, 11, 7761–7770.
14 G. Huang, Y. Zhang, L. Wang, P. Sheng and H. Peng, Carbon, 2017, 125, 595–604.
15 H. Wei, C. He, J. Liu, H. Gu, Y. Wang, X. Yan, J. Guo, D. Ding, N. Z. Shen and X. Wang, Polymer, 2015, 67, 192–199.
16 J. Chen, Y. Wang, J. Cao, Y. Liu, Y. Zhou, J.-H. Ouyang and D. Jia, ACS Appl. Mater. Interfaces, 2017, 9, 19831–19842.
17 M. Tahir, L. He, W. Yang, X. Hong, W. A. Haider, H. Tang, Z. Zhu, K. A. Owusu and L. Mai, J. Energy Chem., 2020, 49, 224–232.
18 K. Li, X. Liu, T. Zheng, D. Jiang, Z. Zhou, C. Liu, X. Zhang, Y. Zhang and D. Losic, Chem. Eng. J., 2019, 370, 136–147.
19 K. Li, S. Feng, C. Jing, Y. Chen, X. Liu, Y. Zhang and L. Zhou, Chem. Commun., 2019, 55, 13773–13776.
20 M. Nakayama, K. Kaneshige and K. Komine, ECS Trans., 2017, 75, 19.
21 L. He, H. Liu, W. Luo, W. Zhang, X. Liao, Y. Guo, T. Hong, H. Yuan and L. Mai, Appl. Phys. Lett., 2019, 114, 223903.
22 D. Bélanger, L. Brousse and J. W. Long, Electrochem. Soc. Interface, 2008, 17, 49.
23 C. M. Julien and A. Mauger, Nanomaterials, 2017, 7, 396.
24 L. Peng, X. Peng, B. Liu, C. Wu, Y. Xie and G. Yu, Nano Lett., 2013, 13, 2151–2157.
25 Z. Fan, J. Yan, T. Wei, L. Zhi, G. Ning, T. Li and F. Wei, *Adv. Funct. Mater.*, 2011, **21**, 2366–2375.
26 L. Bao, J. Zang and X. Li, *Nano Lett.*, 2011, **11**, 1215–1220.
27 P. Xu, B. Wei, Z. Cao, J. Zheng, K. Gong, F. Li, J. Yu, Q. Li, W. Lu and J.-H. Byun, *ACS Nano*, 2015, **9**, 6088–6096.
28 L. Sun, X. Wang, K. Zhang, J. Zou and Q. Zhang, *Nano Energy*, 2016, **22**, 11–18.
29 A. Bahloul, B. Nessark, E. Briot, H. Groult, A. Mauger, K. Zaghib and C. Julien, *J. Power Sources*, 2013, **240**, 267–272.
30 P. Tang, L. Han and L. Zhang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 10506–10515.
31 Y. Chen, J. Xu, Y. Yang, Y. Zhao, W. Yang, X. Mao, X. He and S. Li, *Electrochim. Acta*, 2016, **193**, 199–205.
32 S. Gao, L. Zhang, Y. Qiao, P. Dong, J. Shi and S. Cao, *RSC Adv.*, 2016, **6**, 58854–58861.
33 M. Ghosh, V. Vijayakumar, R. Soni and S. Kurungot, *Nanoscale*, 2018, **10**, 8741–8751.
34 R. Della Noce, S. Eugénio, T. Silva, M. Carmezim and M. Montemor, *RSC Adv.*, 2017, **7**, 32038–32043.
35 X. Fan, X. Wang, G. Li, A. Yu and Z. Chen, *J. Power Sources*, 2016, **326**, 357–364.
36 M. Mahmoudian, Y. Alias, W. Basirun and M. Ebadi, *Appl. Surf. Sci.*, 2013, **268**, 302–311.
37 V. Shanthala, S. Shobha Devi and M. Murugendrappa, *J. Asian Ceram. Soc.*, 2017, **5**, 227–234.
38 X. Liu, T. Qian, N. Xu, J. Zhou, J. Guo and C. Yan, *Carbon*, 2015, **92**, 348–353.
39 Y. Liu, J. Zhou, J. Tang and W. Tang, *Chem. Mater.*, 2015, **27**, 7034–7041.
40 N. Ilicheva, N. Kitaeva, V. Duflot and V. Kabanova, *ISRN Polym. Sci.*, 2012, **2012**, 320316.