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Communication

A new Type of Porous Graphite Foams and Their Integrated Composites with Oxide/Polymer Core/Shell Nanowires for Supercapacitors: Structural Design, Fabrication and Full Supercapacitor Demonstrations

Xinhui Xia, Dongliang Chao, Zhanxi Fan, Cao Guan, Xiehong Cao, Hua Zhang, and Hong Jin Fan

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A new Type of Porous Graphite Foams and Their
Integrated Composites with Oxide/Polymer
Core/Shell Nanowires for Supercapacitors:
Structural Design, Fabrication and Full
Supercapacitor Demonstrations

Xinhui Xia,^{†‡} Dongliang Chao,[†] Zhanxi Fan,[§] Cao Guan,[†] Xiehong Cao,[§] Hua Zhang,[§] and
Hong Jin Fan^{†,*}

[†] *Division of Physics and Applied Physics, School of Physical and Mathematical Sciences,
Nanyang Technological University, Singapore 637371, Singapore,*
[§] *School of Materials Science & Engineering, Nanyang Technological University, Singapore
639798, Singapore,*
[‡] *State Key Laboratory of Silicon Materials, Key Laboratory of Advanced Materials and
Applications for Batteries of Zhejiang Province, and Department of Materials Science and
Engineering, Zhejiang University, Hangzhou 310027, China*

ABSTRACT

We attempt to meet the general design requirements for high-performance supercapacitor electrodes by combining the strategies of light-weight substrate, porous nanostructure design and conductivity modification. We fabricate a new type of 3D porous and thin graphite foams (GF) and use as the light and conductive substrates for the growth of metal oxide core/shell nanowire arrays to form integrated electrodes. The nanowire core is Co_3O_4 and the shell is a composite of conducting polymer (Poly (3,4-ethylenedioxythiophene), PEDOT) and metal oxide (MnO_2). To show the advantage of this integrated electrode design (viz., GF+ Co_3O_4 /PEDOT- MnO_2 core/shell nanowire arrays), three other different less-integrated electrodes are also prepared for comparison. Full supercapacitor devices based on the GF+ Co_3O_4 /PEDOT- MnO_2 as positive electrodes exhibit the best performance compared to other three counterparts due to an optimal design of structure and a synergistic effect.

KEYWORDS: Graphite foam · Graphene foam, Conducting Polymer · Core/shell · Nanowire arrays · Supercapacitor

TOC

1. Introduction

Intensive research has been devoted to developing new or high-performance electrochemical energy storage devices in order to respond to the increasing energy demand and environmental pollution.^{1, 2} Supercapacitor has emerged as a promising device for electrochemical energy storage.^{3, 4} Over recent years, great progress has been achieved in the field of supercapacitor through advances in understanding charge storage mechanisms and the development of high-quality nanostructured materials.⁵⁻⁸ Despite this, supercapacitor is still struggling for high energy density without sacrificing the high power density to make them as the primary power source. Just like battery, a full supercapacitor device consists of four parts: positive and negative electrodes, separator and electrolyte. Among them, electrode materials are considered as the key components to the performance of supercapacitor. Hence, designing and fabricating high-quality electrode materials plays a decisive role in developing next-generation high-performance supercapacitors.

Design consideration for high-performance electrode. Because of their high power density, fast recharge capability and long cycle life, supercapacitors are unique and different from common batteries. Based on the previous literature and uniqueness of supercapacitors,⁵⁻⁷ the basic principles for designing high-performance electrode materials can be elaborated as follows.

First, high power density. This is a most important requirement. It is unwise to achieve high energy densities at the cost of power density. The power density is tightly related to the transport kinetics of electrons and ions.⁵ Hence, electrodes with meso- or nanoporous structures and good conductivity are highly desirable for high power densities. Porous nanostructures facilitate the sufficient contact between electrolyte and active materials, and shorten the ion transport path; these two features lead to fast reaction kinetics. To date, numerous nanostructures, such as nanowires,⁹⁻¹² nanotubes,¹³⁻¹⁵ nanorods,^{16, 17} nanoflakes,^{18, 19} nanospheres,^{20, 21} nanowalls,^{22, 23} and core/shell nanoarrays,²⁴⁻³⁰ have been prepared and improved electrochemical performances have been demonstrated in these systems. As for the conductivity issue, the active material with a high conductivity will lower the polarization and accelerate the reaction kinetics. In this regard, researchers generally adopt conductive scaffolds (e.g., carbon nanotube,^{31, 32} graphene,³³⁻³⁵ and porous metal films^{36, 37}) or conductive coatings (e.g., metals,^{11, 38, 39} carbons,⁴⁰ conducting polymers⁴¹⁻⁴³) to improve the conductivity of the whole electrode.

Second, high capacitance and energy density. From the definition of energy density (E) of a supercapacitor, $E = \frac{1}{2}CV^2$ (C : capacitance of the electrode; V : potential across the electrode), one can immediately notice that, an effective way to boost the energy density is to utilize electrochemical materials with high capacitance and high working voltage. For this reason, the scientific community shifts its attention from pure carbon materials to pseudocapacitive materials (such as metal oxides/hydroxides, metal sulfides and conducting polymers);^{7, 8, 12, 44} the latter have specific capacitances several times larger than carbon materials.

On the other hand, most of the transition metal based pseudocapacitive materials result in a compromise of rate capability and reversibility, because they rely on faradic redox reactions and they suffer from low conductivity. This feature makes them kinetically unfavorable for high rate purpose. In this regard, one can turn to the above-mentioned two design strategies. The porous nanostructure design and conductivity engineering (e.g., combination between pseudocapacitive materials and highly conductive backbones) can effectively improve the utilization of active materials and result in higher capacitance. As for the working voltage, generally speaking, asymmetric supercapacitors are believed to have a higher working voltage than the symmetric ones. Notice that the voltage is dependent on several factors including the intrinsic electrochemical reactions, electrolyte species and macroscopic structure of cell.

Third, low weight. The mass unit of energy density and power density is Wh/kg and W/kg, respectively. So light-weight electrode materials are non-trivial in improving the energy density and power density. This is particularly the issue in portable electronics. Currently, in commercial supercapacitors, the weight of conductive substrates (such as nickel foam or aluminum foil) accounts for a large mass portion in the device, but these conductive substrates do not contribute to the capacitance. This translates to an effectively lower energy density and power density. In recent years, new kinds of light substrates based on three-dimensional (3D) porous graphene or graphite foams have attracted increasing attention and become promising new light-weight substrates,^{45, 46, 47} Several composites based on 3D porous graphene or graphite foams, such as graphene/Ni(OH)₂,⁴⁸ graphene/Co₃O₄,⁴⁹ graphite/Ni(OH)₂,⁵⁰ and graphite/LFP,⁵¹ have been fabricated and exhibited enhanced energy and power densities.

Finally, high structural stability. In order to fulfill the long cycling life (more than 10⁴ times), the electrode materials must have strong structural stability. It is generally accepted that

nanoarrays grown directly on current collectors possess better mechanical and structural stability compared to powders. Further, an elastic thin shell around the nanowires can provide effective strain accommodation during cycles, leading to a high cycling life.^{52, 53}

Based on above guidelines, an *ideal electrode supercapacitor material should be highly porous, electrical conductive, light, electrochemical active and stable*. In the present work, we attempt to combine all these strategies together; we develop new high-performance integrated electrodes by using novel thin sheets of 3D porous graphite foams and by combining different active materials into core/shell nanowire arrays. For demonstration, we prepared Co₃O₄/PEDOT-MnO₂ core/shell nanowire arrays directly on the 3D porous graphite thin foams. *Unique features of our design are as follows*: Superlight and conductive new 3D porous graphite foam skeleton; stable and porous core/shell nanowire arrays architecture; conductivity modification by conducting polymer (PEDOT), and high voltage asymmetric supercapacitor. More specifically, (1) New graphite foams with smaller pores. The previous demonstrated porous graphite or graphene foams prepared from commercial nickel foam template have a thickness of around ~50 μm and pore size of 200–500 μm . In the present work, our new 3D porous graphite foams are light-weight, highly conductive, and consist of interconnected homogeneous ultrathin graphite building blocks. The pore size is around 5–10 μm . (2) New core/shell array. Core/shell nanowire arrays are uniform deposited onto the 3D graphite foams. In particular, the shell structures are homogeneous composites of MnO₂ and (Poly (3,4-ethylenedioxythiophene), PEDOT) prepared by co-electrodeposition method. PEDOT has merits of good conductivity, high stability and mechanical flexibility; but its electrochemical energy density is low. MnO₂ is a low-cost active material and provides high energy storage, but it has poor conductivity. In our design, the composite shell renders a synergistic effect and assures a high capacitance and good conductivity. The PEDOT not only contributes capacitance, but also facilitates the electron diffusion into MnO₂ and acts as a protective layer to protect MnO₂ from degradation during long cycling. (3) Asymmetric supercapacitors using the above integrated electrodes are assembled and indeed show drastic performance improvement as compared to other less-integrated counterparts. The capacitance retention after 20,000 cycles reaches ~90 %.

2. Results and discussion

Fabrication and characterization of integrated electrodes.

The fabrication process of the new 3D porous graphite foams and their integrated composites with $\text{Co}_3\text{O}_4/\text{PEDOT-MnO}_2$ core/shell nanowire arrays is schematically illustrated in Figure 1, together with the corresponding SEM images. Firstly, we fabricate highly porous electrodeposited 3D Ni films as the template for CVD-grown 3D porous graphite foams. Clearly shown in the SEM images (Figure 1a and S1a-c), the as-prepared Ni films exhibit highly porous structure with interconnected Ni branches composed of numerous Ni particles ranging from 500 nm to 1 μm . The typical large pore size of the Ni films is about 5–10 μm (Figure 1a and S1a-c). The free-standing interconnected Ni branches have a typical width of 5–10 μm . As shown in the TEM image (Figure S1d), the Ni particles ranging from 500 nm to 1 μm are connected with each other. In addition, the selected area electronic diffraction (SAED) pattern can be indexed with typical polycrystalline Ni phase (JCPDS 04-0850) (Figure S1e), supported by the XRD pattern (Figure S1f).

In the second step, the 3D porous Ni films are acted as the template for the following growth of CVD-graphite foams. After CVD and etching the Ni template, it is observed that the whole 3D porous structure of the graphite foams is well preserved and still keeps pore size of 5–10 μm (Figure 1b and 2a, b). The graphite branches have a width of 2–10 μm and are interconnected with each other forming self-supported 3D porous graphite foams. The pore and branch sizes are much smaller than those of CVD-graphite/graphene foams prepared via commercial Ni foam template (branches with a width of ~ 50 μm and pore size of 200–500 μm). Moreover, it is observed that all the pores in the graphite foams, whether on the surface or in the inner space, are connected with each other and reach out in all directions forming 3D porous networks (Figure 1b and 2a, b). Ripples and wrinkles of graphite are observed on the graphite branches (Figure 2b). Additionally, the hollow space of the graphite foams is verified in Figure 2c due to the removal of Ni template. The obtained ultrathin 3D porous graphite foams are lightweight with a density of ~ 4 mg/cm^3 , close to that of graphite foams prepared by commercial nickel foam template (~ 5 mg/cm^3).⁴⁷ In addition, the obtained GF shows a porosity of ~ 99.8 % and a specific surface area of ~ 980 m^2/g (Figure S2), higher than those obtained from commercial nickel foam (~ 850 m^2/g).⁴⁷ The pore size distribution shows a main peak at 9 μm . The phase and composition of the as-prepared 3D porous graphite foams are verified by XRD and EDS spectrum results (Figure 2d). The 3D porous graphite foams exhibit two typical diffraction peaks at 26.4° and 54.5° ,

which correspond to the (002) and (004) planes of graphitic carbon, respectively (JCPDS 75-1621) (Figure 2d). Only carbon peak is detected in the EDS spectrum (inset in Figure 2d), indicating that the nickel template is completely dissolved and only graphitic carbon is left. The ultrathin 3D porous graphite foams are also confirmed by Raman spectrum (inset in Figure 2c). Two strong peaks at $\sim 1560\text{ cm}^{-1}$ (G band) and $\sim 2700\text{ cm}^{-1}$ (2D band) are noticed. The intensity ratio of G/2D band is always used to determine the layer numbers of graphene. Here, the intensity ratio of G/2D indicates that the as-prepared porous graphite foams are ultrathin, only composed of a few layers of graphene. Additionally, no D band at $\sim 1350\text{ cm}^{-1}$ is observed implying that the as-prepared graphite foams are of defect-free high-quality graphite, and ensure better electrical conductivity than the commonly reduced graphene oxide sheets.^{49, 51} TEM image shows a typical ultrathin graphite sheet with wrinkled edge (Figure 2e). Furthermore, the measured lattice spacing of 0.34 nm is in consistent with the (002) interplanar distance of graphitic carbon (inset in Figure 2e). The selected area electron diffraction (SAED) pattern (Figure 2f) shows a typical hexagonal pattern characteristic of graphitic carbon. All these results above indicate that the high-quality ultrathin 3D porous graphite foams can be successfully by CVD using the electrodeposited 3D porous Ni films template.

In the third step, we assembled $\text{Co}_3\text{O}_4/\text{PEDOT-MnO}_2$ core/shell nanowire arrays on the ultrathin 3D porous graphite foams by the combination of hydrothermal synthesis and anodic electro-deposition methods to form integrated electrode for supercapacitor applications. After hydrothermal synthesis, it can be seen that the whole 3D porous graphite foams are decorated and covered by porous Co_3O_4 nanowires with average diameters of $\sim 100\text{ nm}$ (Figure 1c and S3a-c). The Co_3O_4 nanowires consist of numerous nanoparticles, and show mesoporous structure. The growth of Co_3O_4 nanowires on the 3D porous graphite foams is also verified by EDS and Raman spectra, and XRD pattern (Figure S3d-f). Then, the binary shell of PEDOT- MnO_2 is electrodeposited on the surface of Co_3O_4 nanowires to form free-standing $\text{Co}_3\text{O}_4/\text{PEDOT-MnO}_2$ core/shell nanowires with diameters of $\sim 320\text{ nm}$ (Figure 1d, 3a and S4a). Notice that the 3D porous structure is well preserved and show large feature pore size of $3\text{--}8\text{ }\mu\text{m}$. The Co_3O_4 nanowires are uniformly coated by the binary PEDOT- MnO_2 shell with a relatively lower roughness. In the XRD pattern (Figure 3b), except for the diffraction peaks from graphite foam (JCPDS 75-1621), Co_3O_4 (JCPDS 42-1467) and MnO_2 (JCPDS 30-0820), there are no obvious peaks of PEDOT observed in the XRD pattern, indicating that the deposited PEDOT is

amorphous, supported by the SAED pattern as below. This core/shell nanowire structure is clearly shown in the TEM image (Figure 3c and d). The Co_3O_4 nanowire core is well wrapped by the PEDOT- MnO_2 shell. The EDS mapping of S, Mn, O, C and Co from Figure 3e clearly demonstrates the ternary core/shell nanowire structure. It is worth mentioning that the shell is a binary composite of MnO_2 and PEDOT. The MnO_2 and PEDOT are co-electrodeposited at the same time to form homogeneous binary shell structure. The PEDOT in the composites is verified by the FTIR spectrum (Figure S4b), and Raman spectrum (Figure S4c and d). The SAED pattern in Figure 3c can be well indexed as crystalline ϵ - MnO_2 (JCPDS 30-0820) and no characteristic pattern of PEDOT is noticed, indicating that the electrodeposited PEDOT is amorphous, which is consistent with the XRD result above. Notice that the MnO_2 is well embedded within the PEDOT matrix, forming a composite shell (see Figure S4 e and f). In our experiment, we constructed uniform binary PEDOT- MnO_2 shell to take the advantages of both components and offer special properties through the reinforcement or modification of each other. It is anticipated that the PEDOT can modify the conductivity and structural stability of the MnO_2 to make it deliver enhanced performance.

For comparison, we also prepared three other counterparts on the 3D porous graphite foams (Figure S5-7): (1) $\text{Co}_3\text{O}_4/\text{MnO}_2$ core/shell nanowire arrays, (2) $\text{Co}_3\text{O}_4/\text{PEDOT}$ core/shell nanowire arrays, and (3) PEDOT/ MnO_2 composites. The $\text{Co}_3\text{O}_4/\text{MnO}_2$ core/shell nanowires have diameters of ~ 350 nm and MnO_2 nanoflake shell with polycrystalline structure (Figure S5). For the $\text{Co}_3\text{O}_4/\text{PEDOT}$ core/shell nanowires, the PEDOT layer is well coated on Co_3O_4 nanowire core forming core/shell nanowires of ~ 300 nm. The amorphous nature of PEDOT shell is confirmed by the SAED pattern (Figure S6). For the PEDOT/ MnO_2 composites, just a dense PEDOT/ MnO_2 layer is coated on the 3D porous graphite foams to form a 3D porous composite film (Figure S7). Note the fact that the 3D porous structures are all well maintained in the three counterpart electrodes.

Electrochemical properties and supercapacitor performance

To demonstrate the potential applications of these integrated electrodes with ultrathin 3D porous graphite foams and core/shell nanowire arrays, asymmetric supercapacitor full devices were assembled with the above integrated electrodes as the positive electrode and commercial activated carbon in 3D porous graphite foams as the negative electrode (see specific fabrication

process in Supporting Information). For convenience, the $\text{Co}_3\text{O}_4/\text{PEDOT-MnO}_2$ core/shell nanowire arrays on the 3D porous graphite foams are designated as **GF+CPM**; $\text{Co}_3\text{O}_4/\text{MnO}_2$ core/shell nanowire arrays as **GF+CM**; $\text{Co}_3\text{O}_4/\text{PEDOT}$ core/shell nanowire arrays as **GF+CP**; PEDOT/ MnO_2 composites as **GF+PM**. In our experiment, the hydrothermal-synthesized Co_3O_4 nanowires are used as the core backbone for the growth of binary MnO_2 -PEDOT shell. And the capacitance contribution from Co_3O_4 nanowires is very low or negligible because the electrolyte used in the asymmetric supercapacitors is neutral 1M Na_2SO_4 solution, not alkaline electrolyte (Co_3O_4 nanowires are active in alkaline electrolyte).

The CV curves and charge/discharge profiles of the supercapacitors are shown in Figure S9. In order not to exceed the current range of electrochemical working station, the CV test was conducted using small-size full supercapacitor devices (Figure S8). The CV potential range of the full asymmetric supercapacitor device is from 0–1.8 V. For the GF+CPM, nearly rectangular CV profiles are observed at increasing scanning rates from 50 to 800 mV/s. Furthermore, the CV curves of GF+CPM exhibit nearly mirror-image current response on the reverse voltage at all different scanning rates, which is indicative of a good reaction reversibility and excellent capacitive behavior. In comparison with other counterparts, the GF+CPM shows much higher reaction current densities and bigger enclosed area of the CV curves, indicating its enhanced electrochemical reactivity and energy storage. Comparing the CV curves of GF+CPM (Figure S9a) and GF+CM (Figure S9c), it is found that the combination of PEDOT and MnO_2 into the same shell can effectively improve the electrochemical performance of MnO_2 , especially for stability at high scanning rate. The core/shell wire arrays in GF+CPM have better reaction activity than the common dense GF+PM due to an effectively larger surface area and thus an increase in the mass load of PEDOT/ MnO_2 . In addition, the full device can be bent with a small loss of its initial capacity (flexibility test was shown in Figure S10).

All four positive electrodes exhibit nearly straight charge/discharge curves at different current densities (Figure 4). The charge/discharge potential window is from 0.8 to 1.8 V, for the consideration of practical applications. This working voltage range is possible to achieve for full supercapacitors based on MnO_2 in neutral 1M Na_2SO_4 solutions.⁵⁴⁻⁵⁶ This working voltage is also higher than that of pure carbon based aqueous-system supercapacitors (~1 V). The enlarged voltage is beneficial for the improvement of energy and power densities. The photos of positive electrode and supercapacitor device are shown in Figure 4a-c. In our experiment, the CV and

charge/discharge behaviors of the supercapacitors are close to those of electric double layer capacitors (EDLC). The specific capacitances of the positive electrodes (Figure 5d, based on the mass of the whole positive electrode) were calculated from the charge/discharge curves at different current densities. The specific equations and reactions are given for readers after Figure S8.

Our results demonstrate clearly that, compared to the other three composites, the GF+CPM has the best electrochemical performance as supercapacitor electrodes: highest specific capacitance, capacity retention at different current densities, energy density, and cyclic stability. The performance of as-prepared asymmetric supercapacitor is controlled by the positive electrode. The results are shown in Figure 4 and also tabulated in Table S1 (Supporting Information). The enhanced electrochemical performance is also supported by the EIS analysis (Figure S11a). We also calculated the Ragone plot of the whole full supercapacitor device (this includes the mass of positive electrode, negative electrode and separator) (Figure S11b). The energy density dramatically decreases because of larger mass, but the GF+CPM still exhibits the highest energy density of ~9.8 Wh/kg at a power density of 20 kW/kg than the other three counterparts. These values from the supercapacitor with GF+CPM are about 2–3 times than those of commercial carbon-based supercapacitors (3–4 Wh/kg). In addition, the GF+CPM also shows better electrochemical performances compared to those in the literature (shown in Table S2 in supporting information). Liu and Lee reported MnO_2 /PEDOT nanowire arrays grown on ITO glass via AAO template.⁵⁷ Their nanowires could easily collapse after etching the AAO template leading to a larger resistance.

The cycle life is one of the most important parameters for the practical application of supercapacitors. The cycling stability of the four electrodes was conducted at a current density of 5 A/g for 20000 cycles (Figure 4f). The GF+CPM exhibits a remarkable cycling stability and delivers a capacitance of 353 F/g with capacitance retention of 90.2 % after 20000 cycles, higher than all the rest three electrodes.. The cycling stability is highly related to the structural stability of the electrodes. We disassembled the supercapacitors after 20000 cycles to check the morphology of the positive electrodes (Figure S12). The macroporous structures from the graphite foam in the electrodes are well preserved, and the core/shell nanowires are still strongly adhered to the graphite foam. The core/shell nanowires architecture in the GF+CPM is intact and little degraded, better than those in the GF+CM, whose MnO_2 shell exhibits some degradation.

The other two electrodes (GF+CP and GF+PM) also show good morphology stability. It is thus indicated that the introduction of PEDOT can protect the MnO₂ from degradation during cycling.

To further evaluate the practical application of the assembled supercapacitors with GF+CPM, a tandem cell was constructed by connecting three supercapacitor units in series. This tandem cell can work between 3 and 5.4 V and could easily power and light up a letter pattern of 25 green LED lights connected in parallel. This physical demonstration further demonstrates the great potential of the GF+CPM for electrochemical energy storage with high energy and power densities.

3. Conclusion

In summary, we have proposed the general rules for designing high-performance electrodes of supercapacitors and made demonstrations by combining ultrathin 3D porous graphite foams and their composites with core/shell nanowire arrays. The strategies of porous nanostructure design and conductivity modification are combined together into single electrodes. Particularly important features of our electrodes are two: a new-type of ultrathin 3D porous graphite foams that are used as the light and conductive substrates for the integrated electrode. Second, the conducting polymer (PEDOT) and metal oxide (MnO₂) in the homogeneous binary shell can work synergistically to obtain enhanced rate capability and structural stability. Through comprehensive compare experiments, we have demonstrated that asymmetric supercapacitors based on the highly-integrated electrodes exhibit superior electrochemical properties with higher specific capacitance, higher energy and power densities, better cycling stability to their less-integrated counterparts. It is envisaged that the proposed rules can guide the design of better-performance electrodes for applications in electrochemical energy storage devices and electrochemical catalysts.

Supporting Information Available:

Experimental details on synthesis of 3D porous graphite foams and different kinds of positive electrodes, and details on electrochemical measurements for supercapacitors. **Figure S1**, SEM-TEM images and XRD pattern of electrodeposited 3D porous Ni films. **Figure S2**, BET

measurement of 3D GF. **Figure S3**, SEM-TEM images and XRD-EDS-Raman results of Co_3O_4 nanowire arrays grown on the 3D porous graphite foams. **Figure S4**, SEM-TEM image, EDS-FTIR results of $\text{Co}_3\text{O}_4/\text{PEDOT-MnO}_2$ core/shell nanowire arrays grown on the 3D porous graphite foams (GF+CPM). **Figure S5**, SEM-TEM images, XRD-EDS results of $\text{Co}_3\text{O}_4/\text{MnO}_2$ core/shell nanowire arrays grown on the 3D porous graphite foams (GF+CM). **Figure S6**, SEM-TEM images of $\text{Co}_3\text{O}_4/\text{PEDOT}$ core/shell nanowire arrays grown on the 3D porous graphite foams (GF+CP). **Figure S7**, SEM images of PEDOT-MnO₂ dense composite films on the 3D porous graphite foams (GF+PM). **Figure S8**, Photos of small-size cathode (GF+CPM) and corresponding full supercapacitor devices for CV test. **Figure S9**, CV curves and charge/discharge curves of four supercapacitors based on different positive electrodes. **Figure 10**, flexibility test of the full supercapacitor. **Figure S11**, Nyquist plots of four positive electrodes and Ragone plot of four full supercapacitor devices with different positive electrodes. **Figure S12**, Morphologies of four positive electrodes after 20000 cycles. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors.

* Email: fanhj@ntu.edu.sg (H.J. F)

Notes

The authors declare no competing financial interest.

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Figure 1 Schematics of the fabrication process of thin 3D porous graphite foams (GF) and their integrated composites with Co₃O₄/PEDOT-MnO₂ core/shell nanowire arrays. (a) Porous Ni films as the substrate. (b) 3D GF by CVD growth from the Ni film substrate followed by etching. (c) Co₃O₄ nanowires by hydrothermal growth on the GF. (d) PEDOT-MnO₂ composite shell by electro-codeposition. The bottom row is the corresponding SEM images of the structures.

Figure 2 Morphological and structural characterizations of the thin 3D porous graphite foams. (a-c) SEM images. Inset in (a) is a cross-sectional image and inset in (c) is Raman spectrum; (d) XRD pattern (Inset: EDS spectrum); (e) TEM image (Insets: magnified image and HRTEM image) and (f) SAED pattern.

Figure 3 Morphological and structural characterizations of $\text{Co}_3\text{O}_4/\text{PEDOT-MnO}_2$ core/shell nanowire arrays grown on the 3D porous graphite foams. (a) SEM image; (b) XRD pattern; (c, d) TEM images (SAED pattern in inset); (e) Dark field TEM image of $\text{Co}_3\text{O}_4/\text{PEDOT-MnO}_2$ core/shell nanowire and corresponding EDS mapping of S, O, Mn, C and Co.

Figure 4 Photos of (a) GF+CPM electrode and (b) asymmetric full supercapacitor device. (c) Specific capacitance of four positive electrodes at different current densities (The capacitance of the positive electrode is obtained based on the mass of the whole weight of electrode). (d) Ragone plot of four positive electrodes. (e) Cycling life at current densities of 5 A/g. (f) Photograph of 25 green LEDs that are powered by the tandem supercapacitor device.