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High-performance Flexible Asymmetric Supercapacitors Based on A New Graphene Foam/Carbon Nanotubes Hybrid Film

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Abstract

In this work, we report the fabrication of a new 3D graphene foam (GF)/carbon nanotubes (CNTs) hybrid film with high flexibility and robustness as ideal supports for deposition of large amount of electrochemically active materials per unit area. To demonstrate the concept, we have deposited MnO₂ and polypyrrole (Ppy) on the GF/CNTs films and successfully fabricated lightweight and flexible asymmetric supercapacitors (ASCs). These ASCs assembled from GF/CNTs/MnO₂ and GF/CNTs/Ppy hybrid films with high loading of electroactive materials in an aqueous electrolyte are able to function with an output voltage of 1.6 V, and deliver high energy/power density (22.8 Wh/kg at 860 W/kg and 2.7 kW/kg at 6.2 Wh/kg). The rate performance can be further improved with less loading of electroactive materials (10.3 kW/kg at 10.9 Wh/kg). The ASCs demonstrate remarkable cycling

stability (capacitance retention of 90.2-83.5% after 10000 cycles), which is among the best reported for ASCs with both electrodes made of non-carbon electroactive materials. Also the ASCs are able to perfectly retain their electrochemical performance at different bending angles. These ASCs demonstrate great potential as power sources for flexible and lightweight electronic devices.

KEYWORDS: Graphene foam, CNTs, Flexible, Asymmetric supercapacitors

1. Introduction

Carbon is a fascinating material that exists in various structural forms by different hybridization ways of atomic orbitals (sp^2 and sp^3). In addition to bulk phases of carbon (graphite, diamond), other nanoscale low-dimensional carbon allotropes, including fullerenes (zero-dimensional), carbon nanotubes (one-dimensional) and graphene (two-dimensional) have been discovered and investigated intensively.^{1, 2} The diversity of macrostructures and bonding schemes provides versatility in properties and applications for various carbon allotropes.^{3, 4} There is no doubt that hybrid structures of different carbon materials would further extend the diversity of carbon-based micro-/macrostructures, with integrated properties inheriting from the constituent structures. Compared with their single components, hybrid structures such as graphene/CNTs,⁵⁻⁸ graphene/fullerenes,⁹ CNTs/fullerenes,¹⁰ CNTs/carbon film¹¹ have shown improved physical and chemical properties, including enhanced electric and thermal conductivity, optical transparency or mechanical flexibility, due to the synergistic effects. These structures have been used in various areas, such as nanoelectronics, drug delivery, sensors, catalysis and energy storage and conversion.¹²⁻¹⁸ Theoretical calculation^{19, 20} has indicated that covalently bonded graphene and carbon nanotubes could lead to superior properties in three dimensions while maintaining

inherited properties in the planer and axial directions. Such hybrid structures would be of particular interest for many applications, especially for implementation in microelectronics and microelectrochemical devices due to their good electrical conductivity,²¹ large specific surface area,²² unique heterogeneous electron transfer and charge carrier rates, and good physical/chemical stability.²³

Many approaches have been attempted to prepare high-quality graphene/CNTs hybrid electrodes for rechargeable lithium-ion batteries and supercapacitors, including solution-based processes,^{7, 12, 24} microwave irradiation,²⁵ and chemical vapor deposition.^{4, 5, 26-28} Graphene/CNTs hybrid films prepared by You et al.²⁴ and Yu et al.²⁹ via simple liquid phase mechanical mixing show enhanced electrochemical performance as supercapacitor electrodes. However, the relatively poor connection between graphene and CNTs impedes its further application in fast charge/discharge energy storage devices. The preparation of high-quality graphene/CNTs hybrid materials with strong bonding connection among them is therefore highly desirable. In-situ growth by chemical vapor deposition is a promising technique to bond graphene and CNTs together. For example, Lee et al.⁶ synthesized graphene/CNTs hybrid films with good flexibility and electrical conductivity via vertically growing CNTs arrays on catalyst-patterned graphene films. More recently, covalently-bonded graphene/CNTs hybrid films were demonstrated by Zhu and coworkers.²⁶ Similar results were also reported by Lin et al.,³⁰ and Yan et al.,³¹ who have demonstrated the growth of CNTs on nickel-supported graphene with high double-layer capacitance. It should be noted that in the above-mentioned studies CNTs are grown only on the graphene surfaces where the catalyst particles are deposited by e-beam evaporation or dip-coating. The insufficient surface area of these graphene/CNTs hybrid films makes it challenging to achieve high loading of electroactive materials per unit area with good contact in the electrodes, which is critically important for flexible devices with high energy density. This limits the wide applications of graphene/CNTs hybrid films as efficient electrodes for flexible and lightweight supercapacitors.

Therefore, it is highly desirable to fabricate graphene/CNTs hybrid films with strongly connected and large quantity of CNTs that could substantially extend the porous architecture and enlarge the surface area.

To increase the amount of CNTs as well as subsequent loading of electroactive materials without sacrificing the good ohmic contact between CNTs and graphene, we rationally develop a facile approach to fabricate a three-dimensional (3D) architecture consisting of graphene foam (GF) and carbon nanotubes (CNTs). CNTs are grown onto GF via catalytic chemical vapor deposition. The catalyst nanoparticless in our study are deposited onto GF by a hydrothermal method so that the subsequent CNTs growth could be substantially improved compared to those using e-beam deposition or dip-coating method. By using the as-prepared 3D GF/CNTs hybrid films as current collectors, MnO_2 nanosheets and polypyrrole (Ppy) are deposited to form GF/CNTs/ MnO_2 hybrid film as the positive electrode and GF/CNTs/Ppy hybrid film as the negative electrode, respectively, with high and tunable loading of active materials. Flexible and lightweight asymmetric supercapacitors (ASCs) have been fabricated based on the above-mentioned electrodes and demonstrated improved electrochemical performance in terms of high energy/power densities, remarkable cycling stability and good mechanical flexibility. An ASC ($1 \times 4 \text{ cm}^2$) could be charged to 1.6 V within 30 seconds, and drive a 0.45 W motor or power three 5-mm-diameter red light-emitting diodes (LED, 1.8 V, 20 mA) simultaneously.

2. Experimental Details

2.1 Synthesis of Graphene Foam (GF)

GF was prepared by using chemical vapor deposition on nickel foam as described in literature.³² Typically, a commercial nickel foam (thickness of 1 mm, areal density of 350 g/m^2) was washed with 5%

HCl to remove the surface oxide layer and then used as the template and catalyst for the growth of ultrathin layer of graphene. A mixed gas of CH₄, H₂ and Ar with 50 sccm, 100 sccm, 800 sccm flow rates, respectively, was passed through the Ni foam at 1000 °C in a tube furnace. After reacting for 2 min, the sample was cooled rapidly to room temperature at a rate of 100 °C/min. An ultrathin layer of graphene was conformably grown and coated on the nickel foam. Free-standing GF foam was obtained via acidic etching of the nickel foam in FeCl₃/HCl mixture solution. GF exhibits similar morphology to that of Ni foam, indicating that intact 3D microstructure was maintained during the etching process. The areal density and quality of GFs could be easily controlled via adjusting the growth time, gas flow rate, and other conditions.

2.2 Synthesis of Graphene Foam (GF)/Carbon nanotubes (CNTs) hybrid film

The above mentioned GF was used as substrate for the subsequent growth of CNTs. The NiCo catalyst was deposited on GF via a hydrothermal process. Briefly, 0.1 mmol of Ni(NO₃)₂ · 6H₂O and 0.2 mmol of Co(NO₃)₂ · 6H₂O were dissolved in 40 ml of deionized (DI) water to form a clear pink solution, followed by the addition of 1.2 mmol of urea. GF was immersed into the above solution to form GF/NiCo precursor composite by keeping at 120 °C for 2 h in an autoclave. Control experiments were conducted by changing the amounts of both nickel and cobalt sources (i.e. 0.2/0.4 mmol, 0.4/0.8 mmol, 0.8/1.6 mmol) in order to control the loading amount of catalyst precursor and thus the amount of grown CNTs. The GF/NiCo precursor was then annealed in air at 350 °C for 1 min and used directly as the catalyst-loaded substrate for the growth of CNTs at 750 °C in a gas flow of C₂H₄, H₂ and Ar with flow rates of 20, 40 and 100 sccm, respectively. H₂ was introduced prior to the growth process in order to activate the catalyst effectively.

2.3 Synthesis of GF/CNTs/MnO₂ hybrid film

MnO₂ nanosheets were grown on the GF/CNTs hybrid film using a hydrothermal method. Briefly, 60

ml (0.1 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0 mM) of KMnO_4 solution was transferred into a 100 ml Teflon-lined autoclave, followed by the immersing of a GF/CNTs hybrid film in the solution and kept at 150 °C for 6 h. The resulting GF/CNTs/ MnO_2 hybrid film was then washed thoroughly, dried, and then used as the positive electrode. The samples are denoted as GF/CNTs/ MnO_2 -n, where n is the loading amount of MnO_2 (mg/cm^2).

2.4 Synthesis of GF/CNTs/Polypyrrole (Ppy) hybrid film

The GF/CNTs/Ppy hybrid film was prepared using a chemical polymerization method as reported previously.³³ Typically, a GF/CNTs film was immersed into a mixture solution of pyrrole (with monomer amount at 100, 250, 500 1000, 1500 and 2000 μl), DI water/ethanol/1M HCl (1:1:1, v/v/v) and sodium p-toluenesulfonate (pTSSNa, dopant), followed by the addition of ammonium persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, oxidant). The chemical polymerization was carried out at 0 - 5 °C for 15 min. The resulting GF/CNTs/Ppy hybrid film was then washed with DI water and dried overnight at 80 °C in a vacuum oven. The samples are denoted as GF/CNTs/Ppy-m, where m is the amount of pyrrole monomer (μl) used during the synthesis.

2.5 Assemble of GF/CNTs/ MnO_2 -GF/CNTs/Ppy ASCs

ASCs with aqueous electrolyte were assembled using a piece of GF/CNTs/ MnO_2 ($1 \times 4 \text{ cm}^2$) and a piece of GF/CNTs/Ppy ($1 \times 4 \text{ cm}^2$), with an electrolyte-soaked (0.5 M Na_2SO_4) separator in between. The ASC devices are denoted as ASC-n, where n is the loading amount of MnO_2 (mg/cm^2).

2.6 Materials characterizations and electrochemical measurements.

Transmission electron microscopy (TEM, JEM-2010, 200 kV), field-emission scanning electron microscopy (FESEM, JEM-6700F, 10.0 kV), Raman spectroscopy (Renishaw, 532 nm excitation laser) were used to characterize the samples. Electrochemical measurements including galvanostatic charge/discharge curves, cyclic voltammetry (CV) curves, electrochemical impedance spectroscopy

(EIS, 100 KHz-0.01 Hz) were conducted on an electrochemical workstation (CHI 760D). The electrochemical performance of individual electrodes was investigated using a three-electrode system (Pt as the counter electrode, saturated calomel electrode (SCE) as the reference electrode) prior to the fabrication of ASCs. The software Z-View was used for EIS fitting. The ASCs were measured using two-electrode method.

2.7 Calculations

The areal capacitance of the positive or negative electrode in three-electrode configuration was calculated from the corresponding CV curves at different scan rates according to the equation:

$$C = \frac{1}{s \nu \Delta V} \int_{V_0}^{V_0 + \Delta V} I dV$$

where I (A) is the response current, ν is the scan rate (V/s), s is the apparent surface area (cm²), V_0 is the lower potential limit, and ΔV is potential window (V).

The areal capacitance (C_s , F/cm²) and specific capacitance (C_m , F/g) of ASCs in two-electrode configuration were calculated from corresponding charge/discharge curves at different current densities according to the equation:

$$C_s = 4 \frac{I}{s} \frac{dt}{dV} \quad \text{or} \quad C_m = 4 \frac{I}{m} \frac{dt}{dV}$$

where I (A) is the response current, s is the specific area (cm²), m is the total mass of the two electrodes, and dt/dV is the inverse of the slope of the discharge curve (V/s). The charge balance between the positive electrode and negative electrode is obtained by the equation: $C_- V_- = C_+ V_+$, where C_- and C_+ are the capacitance of negative and positive electrodes respectively, and V_- and V_+ are the potential window of negative and positive electrodes respectively. The energy density (E) and power density (P) are calculated according to the equations below:¹⁸

$$E = C V_{max}^2 / 8$$

$$P = V_{max}^2 / (4 m R_{ESR})$$

$$R_{ESR} = V_{drop} / (2 I)$$

where V_{max} is the maximum voltage of the ASC, R_{ESR} is the equivalent series resistances (ESR).

3. Results and Discussion

3.1 Fabrication of GF/CNTs hybrid film

The synthesis procedure of the GF/CNTs hybrid film is illustrated in Fig. S1 (see Electronic Supplementary Information (ESI)). Firstly, Ni foam with a porous 3D interconnected network (Fig. S1a) is used as the template and catalyst to grow graphene film via catalytic decomposing of CH_4 at 1000 °C (Fig. S1b).³² Free-standing graphene foam (GF) (Fig. S1c) is obtained by dissolving Ni backbone in a FeCl_3/HCl mixed solution. The resultant GF exhibits similar morphology to that of Ni foam, and an areal density of 0.1 - 0.8 mg/cm^2 could be achieved with growth time ranging from 0.5 to 6 min under the condition mentioned in the experimental section. After that, NiCo-catalyst precursor for the subsequent growth of CNTs is uniformly coated on GF via a hydrothermal process at 120 °C for 2 h. This process leads to the uniform and dense growth of thin nanoneedles onto the surface of GF (Fig. S2, see ESI). The high loading of NiCo catalysts by this hydrothermal method can substantially increase the amount of CNTs and hence the surface-to-volume ratio of the GF/CNTs hybrid film. Comparative experiment using a conventional dip-coating method to load NiCo catalyst leads to much less amount of CNTs grown onto the GF after the subsequent catalytic chemical vapor deposition process (Fig. S3, see ESI), which suggests the advantage of the present catalyst loading method. Moreover, only a small amount of defects is introduced after the deposition of catalyst (Fig. S4, see ESI), indicating that the present hydrothermal method retains the high quality of the pristine GF. As shown in Fig. S1e,

GF/NiCo-precursor is converted to GF/NiCo₂O₄ by heating in air at 350 °C prior to further heating at 750 °C in the presence of H₂/C₂H₄ for the growth of CNTs. The advantage of forming NiCo₂O₄ by heating the precursor at 350 °C in air, instead of direct reducing to NiCo metallic catalyst is to prevent NiCo catalyst particles from agglomeration at high temperatures. The NiCo₂O₄ nanoneedles are then reduced to form well dispersed catalyst islands in the presence of H₂ (Fig. S5, see ESI), and further catalyze the decomposition of C₂H₄ to form 3D GF/CNTs framework (Fig. S1f). Apparent color change of the product can be observed during this synthesis procedure, while the macroscopic 3D framework is well preserved (Fig. S6, see ESI).

3.2 Characterizations of GF/CNTs hybrid film

GF/CNTs hybrid film with a large size (about 9 cm × 5 cm) and good flexibility can be easily fabricated (Fig. 1a1-a2). FESEM images in Fig. 1b,c show the GF/CNTs hybrid film with well-defined interconnected network structure, where the graphene foam is uniformly covered by a layer of entangled CNTs that are in intimate contact with graphene. The FESEM image (Fig. 1d) and TEM images in Fig. 1e,f reveal the detailed structure of the multiple-walled CNTs, with about 15 – 20 walls, 20 – 25 nm in diameter and a few hundred nanometers to several micrometers in length. A bamboo-like structure with complete knots (indicated by the white arrow) is clearly observed from the inset in Fig. 1e, due to the growth of a complete inner graphene layer prior to contraction of the catalyst particle.^{34,}
³⁵ Moreover, most of catalyst particles reside at the top of CNTs as shown in Fig. 1d,f, indicating a tip-growth mechanism,³⁶ which provides further evidence about the excellent interconnection between GF and CNTs. In addition, the corresponding cross sectional images (Fig. 1g) reveal that CNTs are grown on both the outer and inner surfaces of GF backbones. In order to understand the crystalline quality of the resulting GF/CNTs hybrid film, Raman spectra of GF and GF/CNTs are collected (Fig. 1h). The presence of the characteristic G peak at 1580 cm⁻¹, 2D peak at 2710 cm⁻¹, the 2D/G intensity ratio as

well as the absence of the D peak at 1350 cm^{-1} in the spectrum of GF suggest the high quality of GF before CNTs growth.³⁷ A sharp D peak appears after CNTs growth, which indicates the generation of defects during the chemical vapor deposition process. The introduction of defects is further verified by the corresponding selected area electron diffraction (SAED) patterns (Fig. S7b,d, see ESI).³⁸ Nevertheless, the resistance of GF/CNTs hybrid film is $191\text{ }\Omega/\text{sq}$ (corresponding to 178 S/m), which is much smaller than that of pure GF ($352\text{ }\Omega/\text{sq}$, corresponding to 101 S/m), corroborating the good electrical conductivity of GF/CNTs hybrid film (Fig. S7e, see ESI). The densely grown CNTs extend the 3D architecture of GF, and serve as backbone for subsequent active materials deposition. A significant increase in surface area (Fig. 1i, Fig. S8, see ESI) is observed for GF/CNTs hybrid film ($98\text{ m}^2/\text{g}$) compared to that of GF ($30\text{ m}^2/\text{g}$), indicating a substantial increase in the surface-to-volume ratio of the film.³⁷ Moreover, the areal mass loading of CNTs could be easily tuned from 0.19 to 1.1 mg/cm^2 by adjusting the loading amount of catalyst (Fig. S9, see ESI), offering the possibility to further optimize the hybrid film.

3.3 Fabrication of electrode films based on the GF/CNTs hybrid film

The 3D GF/CNTs hybrid film with unique architecture is a flexible, lightweight, highly conductive carbon network, which can be used as an excellent 3D scaffold or substrate for depositing other pseudo-capacitive active materials with high theoretical capacitance to prepare flexible and high-performance electrochemical capacitors.³⁹⁻⁴¹ Manganese dioxide (MnO_2) has been intensively studied in supercapacitor applications because of its remarkable theoretical specific capacitance (nearly 1300 F/g), natural abundance, low cost and environment-friendliness.^{42, 43} Unfortunately, the measured specific capacitance is usually much lower and the cycling stability is generally poor caused probably by its poor conductivity ($10^{-5} - 10^{-6}\text{ s/cm}$), which impede its practical application in flexible energy storage devices.¹⁴ The incorporation of MnO_2 onto a 3D flexible conductive carbon network provides a

feasible approach to overcome the above limitations. However, another challenge of MnO_2 is the narrow electrochemical working voltage window (usually 0.8 – 1.0 V), which would compromise the specific energy density according to the equation: $E = 1/2 CV^2$ (C is specific capacitance; V is cell voltage).⁵ This issue could be addressed by employing organic or ionic liquid electrolytes with large working voltage window to increase output voltage or fabricating ASCs that consist of two different electrodes.^{44, 45} In this work, we demonstrate the fabrication of ASCs with high energy/power density, which are assembled with GF/CNTs/ MnO_2 as the positive electrode and GF/CNTs/Ppy as the negative electrode in neutral aqueous electrolyte.

3.4 Characterizations of GF/CNTs/ MnO_2 hybrid film.

Typical FESEM images of the GF/CNTs/ MnO_2 hybrid film in Fig. 2a,b show that CNTs are fully covered by flower-like MnO_2 nanosheets. MnO_2 nanosheets with small thickness of a few nanometers assemble into a highly porous network (Fig. 2c,d). Furthermore, the appearance of typical MnO_2 Raman peaks at 491 cm^{-1} , 568 cm^{-1} , 640 cm^{-1} as well as the decrease in intensity of G band further verifies the successful deposition of MnO_2 (Fig. S10, see ESI).⁴⁶ This hybrid electrode design provides better electrical and mechanical contact between current collector (i.e., GF/CNTs film) and active material (i.e., MnO_2), and ensures large accessible surface area and fast mass transfer for electrolyte. It is also found that the introduction of CNTs in the GF is crucial to achieve high loading of MnO_2 . For example, the areal density of active material of GF/CNTs/ MnO_2 film is 6.2 mg/cm^2 (at 0.6 mM manganese source), which is 5 times higher than that of GF/ MnO_2 film (Fig. S11, see ESI). The thickness and loading amount of MnO_2 coating layer could be easily adjusted by controlling the concentration of manganese precursor (Fig. S11-S13, see ESI). The high and adjustable loading mass of electroactive MnO_2 on GF/CNTs hybrid film offers the opportunity to optimize the performance and achieve high areal energy density of the fabricated ASC devices.

The electrochemical performance of the GF/CNTs/MnO₂ hybrid film is first evaluated in a three-electrode system using 0.5 M Na₂SO₄ aqueous solution as electrolyte, platinum foil as the counter electrode and SCE electrode as the reference electrode. The freestanding hybrid film is directly used as the working electrode due to its excellent conductivity and integrated structure. As shown in Fig. 3a,b, a series of CV curves within a potential window of 0.0 – 1.0 V are collected at different scan rates for different films (MnO₂ mass loading of 0.6 – 8.4 mg/cm²) in order to evaluate the contribution of MnO₂ to the capacitance of the hybrid film and optimize the loading mass of MnO₂. It is found that the current response increases with an increase in MnO₂ mass loading density in the range of 0.6 – 6.2 mg/cm², corresponding to an increase in the total capacitance.⁴⁷ However, further increasing the mass loading density of MnO₂ to 8.4 mg/cm² decreases the total capacitance. The presence of optimal mass loading density is further verified by areal capacitance *versus* mass density plots shown in Fig. 3e, where the GF/CNTs/MnO₂-8.4 sample exhibits a lower areal capacitance compared to the GF/CNTs/MnO₂-6.2 sample, especially at low scan rates. In order to understand the inferior performance of GF/CNTs/MnO₂ hybrid film with high MnO₂ loading over 8.4 mg/cm², electrochemical impedance spectroscopy (EIS) study of GF/CNTs/MnO₂ hybrid films with different mass loading density of MnO₂ is carried out (Fig. 3f and Table S1, see ESI). The impedance data is analyzed by fitting to an equivalent electrical circuit consisting of the electrolyte resistance (R_s), charge transfer resistance at electrolyte-electrode interface (or polarization resistance, R_{ct}), Warburg element (W) and constant phase element (CPE) (inset in Fig. 3f), instead of pure capacitance due to the depressed semicircle at high frequency region.^{48, 49} It is noteworthy that the charge transfer resistance (R_{ct}) increases with the increase of mass loading density, which could be mainly attributed to two factors: (i) the poor intrinsic electrical conductivity of MnO₂ and (ii) the increase in the thickness of MnO₂ layer that impedes the ion diffusion and migration process. Interestingly, there is only slight increase in R_{ct}

when the MnO₂ loading amount is below 6.2 mg/cm², but there is a sharp jump of R_{ct} from 31.6 Ω (for GF/CNTs/MnO₂-6.2) to 56.2 Ω (for GF/CNTs/MnO₂-8.4) (Table S1, see ESI). It is reasonable to conclude that factor (ii) might take the main responsibility for the sharp increase in R_{ct} when the thickness of MnO₂ layer is close to the diffusion length of Na⁺ at these scan rates.⁵⁰ Typically, the ion diffusion length in GF/CNTs/MnO₂ hybrid films decreases as the scan rate increases, thus resulting in a decrease in the optimal mass loading density. For example, the optimal mass loading density at 75 mV/s is 3.9 mg/cm² whereas it is 2.1 mg/cm² at 200 mV/s.

To investigate the effect of scan rates on electrochemical performance, a series of rate-dependent CV curves of GF/CNTs/MnO₂-2.1 hybrid film with scan rates ranging from 5 to 200 mV/s are plotted in Fig. 3c. The deviation of CV curves from a rectangular shape of ideal double-layer capacitors could be attributed to the relatively large resistance and overpotential.⁴⁷ The specific and areal capacitance of the GF/CNTs/MnO₂ hybrid films with different mass loadings is calculated and plotted in Fig. 3d,e respectively. Particularly, the high specific capacitance of 215 F/g (Fig. 3d), which corresponds to 130 mF/cm² (Fig. 3e), is obtained for sample GF/CNTs/MnO₂-0.6 at a scan rate of 10 mV/s. The areal capacitance obtained here is much higher compared to those of MnO₂-based electrodes in previous reports, such as 62 mF/cm² at 5 mA/cm² for PEDOT/MnO₂,⁵¹ 70 mF/cm² at 2 mA/cm² for TiO₂/MnO₂,⁵² 64 mF/cm² at 0.08 mA/cm² for SnO₂/MnO₂,⁵³ 41 mF/cm² at 0.12 mA/cm² for TiN/MnO₂ coaxial arrays,⁵⁴ 105 mF/cm² at 0.06 mA/cm² for WO_{3-x}/Au/MnO₂ nanowire⁵⁵ and comparable to that of hydrogenated ZnO/MnO₂/Carbon cloth (138.7 mF/cm² at 1 mA/cm²).⁵⁶ At a high scan rate of 100 mV/s, the capacitance still remains as high as 106 F/g, corresponding to 63 mF/cm². Moreover, the GF/CNTs/MnO₂ hybrid film exhibits good cycling stability with nearly overlapped CV curves after 5000 cycles at a scan rate of 20 mV/s (Fig. S14, see ESI), which is better than that of GF/MnO₂ hybrid film with less active material loading. The above electrochemical analysis clearly demonstrates the

remarkable supercapacitive performance of the GF/CNTs/MnO₂ hybrid film.

3.5 Characterizations of GF/CNTs/Ppy hybrid film

Composites of conducting polymers and graphene have been shown as promising electrode materials for supercapacitor applications.^{57, 58} Herein, GF/CNTs/Polypyrrole (Ppy) hybrid film has been prepared and used as a negative electrode to match with the GF/CNTs/MnO₂ hybrid film electrode in an ASC. Uniform coating of Ppy on GF/CNTs film has been achieved via in-situ chemical polymerization (Fig. S15, see ESI).³³ In order to optimize the electrochemical performance and tune the areal capacitance of GF/CNTs/Ppy hybrid film, a series of samples are prepared with different amounts of pyrrole monomer (100, 250, 500 1000, 1500 and 2000 μ l). Similar to GF/CNTs/MnO₂ hybrid films, the GF/CNTs/Ppy hybrid films show higher current response in the CV curves with more Ppy loading due to the increased amount of active materials that contribute to the total capacitance (Fig. S16a,b, see ESI). Similar deviation of CV curves from an ideal rectangular shape is also observed, especially with high Ppy loading and at high scan rates (Fig. S16c,d, see ESI). Corresponding areal capacitance is calculated and plotted as a function of the scan rate (Fig. S16e, see ESI). It is found that the GF/CNTs/Ppy hybrid films exhibit smaller difference in the areal capacitance at high scan rates. This could also be ascribed to the increased R_{ct} and reduced ion diffusion length, which is similar to the case of GF/CNTs/MnO₂ hybrid films as discussed above. Interestingly, the EIS analysis of GF/CNTs/Ppy hybrid films (Fig. S16f and Table S1, see ESI) shows slight decrease and then increase in R_{ct} with the gradual increase of Ppy loading. Such a phenomenon could be attributed to the uniform coating of Ppy onto the GF/CNTs film that improves the conductivity between CNT/CNT junctions,⁵⁹ where the resistance of CNTs network usually comes from.⁶⁰ However, further increasing the loading amount of Ppy eventually blocks the ion diffusion and migration process, resulting in the increase of R_{ct} from 10.7 Ω for GF/CNTs/Ppy-1000 to 28.6 Ω for GF/CNTs/Ppy-2000.

3.6 Assembly of asymmetric supercapacitors

It is well known that charge balance of positive and negative electrodes is crucial to maximize the energy density of ASCs.⁴⁴ According to the areal capacitance and voltage window of the GF/CNTs/MnO₂ and GF/CNTs/Ppy hybrid films obtained in three-electrode systems as discussed above, two couples of hybrid films are selected, namely GF/CNTs/MnO₂-0.6 with GF/CNTs/Ppy-250 and GF/CNTs/MnO₂-2.1 with GF/CNTs/Ppy-1000. These two couples of electrodes exhibit close total amount of charge in a wide range of scan rates as shown in Fig. S17 (see ESI), thus maximizing the utilization of active materials when further assembled into ASCs. The weight ratio of positive electrode (MnO₂) and negative electrode (Ppy) is 1.2:1 for ASC-0.6 and 1.3:1 for ASC-2.1. Based on the above coupled electrodes, we further demonstrate the fabrication of two ASCs, namely ASC-0.6 and ASC-2.1.

Fig. 4a illustrates the schematic structure of the assembled ASC device that consists of an electrolyte-soaked separator sandwiched by positive and negative electrodes. In view of the excellent flexibility and structural integrity of both electrodes, flexible ASCs are fabricated using two poly(ethylene terephthalate) (PET) sheets as the flexible substrate. Since the operating potential windows for GF/CNTs/MnO₂ and GF/CNTs/Ppy hybrid films are 0 – 1.0 V and -0.6 – 0.2 V, respectively (Fig. 4b), the ASC device is expected to work stably with a voltage window of 0 – 1.6 V in 0.5 M Na₂SO₄. A series of CV measurements under different voltage windows are collected in Fig. 4c. It should be noted that the maximal voltage window of 1.6 V exceeds the theoretical decomposition voltage of water (1.23 V), which could be ascribed to the high overpotential of hydrogen evolution on the GF/CNTs/Ppy hybrid electrode. CV curves at different scan rates (ranging from 10 to 500 mV/s) are collected in order to evaluate the performance of ASC-2.1 (Fig. 4d) and ASC-0.6 (Fig. 4e). Similar to the results measured in three-electrode configuration, the assembled full cells exhibit quasi-rectangular CV curves at low scan rates, agreeing with a good capacitive behavior.⁶¹ Moreover, even at

a high scan rate of 500 mV/s, the CV curves still remain symmetrical, suggesting the good reversibility of electrochemical processes.

3.7 Electrochemical performance of the asymmetric supercapacitors

The typical galvanostatic charge/discharge curves with different current densities ranging from 1.0 to 3 mA/cm² are plotted in Fig. 5a and Fig. S18a (see ESI). The deviation of charge-discharge curves from the linear voltage-time relation for pure double-layer supercapacitors indicates pseudo-capacitive behavior resulting from redox reactions in the hybrid electrodes.⁶² The ASC-2.1 shows a Coulombic efficiency of 74 - 85% at current density of 1 - 3 mA/cm², while the value for ASC-0.6 is above 95%. The relatively low Coulombic efficiency is commonly observed in asymmetric supercapacitors, and it could be ascribed to the relatively large resistance in the ASC-2.1 with high mass loading, as well as some unavoidable electrolysis of water due to the high working voltage. Ragone plot of the ASCs, showing energy and power densities (based on the total weight of active materials) of the devices, is shown in Fig. 5b. Importantly, a maximum energy density of 22.8 Wh/kg at 860 W/kg and a high power density of 2.7 kW/kg at 6.2 Wh/kg are obtained for ASC-2.1. ASC-0.6 exhibits better rate performance, with a maximum energy density of 22.2 Wh/kg at a power density of 3.2 kW/kg. Even at a high power density of 10.3 kW/kg, ASC-0.6 still displays an energy density of 10.9 Wh/kg. Such performance is superior to that of many other MnO₂-based symmetric or asymmetric supercapacitors,^{50, 61, 63-69} as given in the same plot for comparison. The superior rate performance of ASC-0.6 over ASC-2.1 could be attributed to the lower resistance and fast charge transport of the former as revealed by the EIS in Fig. 5c. The Nyquist plots display a typical diffusion-controlled Warburg capacitive behavior with a diagonal line in the low frequency region and small depressed semicircle in the high frequency region.^{48, 49} The series resistance of the devices is estimated to be 17.7 Ω (R_s , 1.6 Ω ; R_{ct} , 16.1 Ω) for ASC-0.6 and 26.4 Ω for ASC-2.1 (R_s , 6.4 Ω ; R_{ct} , 20.0 Ω). The relatively small serial resistances in our

ASCs suggest the compact electrode system that ensures fast charge transfer between electrolyte and electrodes. Further, we have made some calculation for both the overall volumetric and gravimetric energy and power densities based on the full cell configuration (Table S2, see ESI).⁷⁰ The maximum volumetric energy density based on the fully packaged cell for ASC-2.1 is 8.7 Wh/L, which is more than 3 times of that of ASC-0.6 (2.7 Wh/L). The volumetric energy density reported here is quite satisfactory, and higher than reported MnO₂-based ASCs⁶⁹ and Ni(OH)₂-based ASCs.⁷¹ In addition, the assembled ASCs deliver decent volumetric power densities of 1.2 kW/L and 1.0 kW/L for ASC-0.6 and ASC-2.1, respectively. Moreover, the ASCs exhibit excellent cycling stability with a high capacitance retention of 90.2% for ASC-0.6 (Fig. S18b, see ESI) and 83.5% for ASC-2.1 (Fig. 5d), even after 10,000 charge/discharge cycles. These values are comparable with or better than those of previously reported ASCs.⁷²⁻⁷⁴

Lightweight and flexible supercapacitors that have excellent electrochemical performance even under mechanical deformation are highly desired to meet demands of future development of multifunctional flexible electronics. In order to explore the potential application of GF/CNTs/MnO₂-GF/CNTs/Ppy ASCs as flexible power source, the ASC is placed with a mechanical bending angle and its electrochemical performance is evaluated by corresponding CV curves (Fig. 5e). Owing to the flexible nature and excellent integrity of the hybrid electrodes, the ASC shows perfectly overlapped CV curves and similar specific capacitance (Fig. S19, see ESI) at different bending angles, indicating that the device could be bent to a large extent without degrading the performance.⁷⁵ We further demonstrate the practical application of our GF/CNTs/MnO₂-GF/CNTs/Ppy ASCs by powering light-emitting diodes (LEDs) or a fan with two pieces of ASC-0.6 connected in series. Connecting two ASCs in series provides the output voltage window of 3.2 V (Fig. S18c, see ESI). Due to the high power/energy density, the ASC could power three red LEDs (1.8 V, 20 mA, 5 mm diameter) after charging for only

30 s (Fig. 5f) or even drive a small rotation motor (3V, 0.45 W) after charging for only a few seconds (Fig. 5g).

The energy and power densities of our ASCs are among the best reported for ASCs with a full cell configuration, especially considering the relatively high and tunable loading density of electroactive materials which offer the opportunity to further optimize the performance. The lightweight and highly porous feature of the GF/CNTs film and additive-free design of the electrodes guarantee a high areal loading density and mass fraction of electroactive materials in the as-fabricated electrodes. Such electrodes would surely lead to a high energy density of real ASCs in practice, and show apparent advantages over those conventionally prepared with additives (e.g., carbon black and binder) and planar or 3D metallic current collectors. It is also worth pointing out that our ASCs are assembled from two electrodes with high loading of pseudocapactive materials, which commonly exhibit less cyclic stability compared to materials with pure double-layer capacitance (e.g., activated carbon). Therefore, the cycling performance presented here is considered quite remarkable. Meanwhile, the excellent mechanical flexibility and robustness of the GF/CNTs film and the direct adhesion of electroactive materials also account for the successful fabrication of high-performance flexible ASCs.

The excellent electrochemical performance of GF/CNTs/MnO₂-GF/CNTs/Ppy ASCs could be mainly attributed to the unique 3D interconnected nanostructure of the flexible electrodes. Specifically, the direct growth of substantial amount of CNTs offers good electrical and mechanical contact within the hybrid films, and also provides a high surface-to-volume ratio that allows high loading of active materials (i.e., MnO₂ and Ppy). As a result, the GF/CNTs hybrid film serves as an excellent current collector and mechanical support for the deposition of nanometer sized active materials. Thus the as-prepared hybrid electrodes provide short diffusion length for ions and facile transfer pathways for electrons, which result in high electrochemical activity and small resistance in the ASCs as discussed

above. Additionally, the proper selection of positive/negative electrode materials as well as the charge balance between the two electrodes also contributes to the remarkable performance of ASCs.

4. Conclusion

In summary, new 3D GF/CNTs hybrid films with unique architecture have been prepared via in-situ growth of CNTs on GF through catalyst assisted chemical vapor deposition. The resulting GF/CNTs hybrid films exhibit excellent flexibility, high conductivity, and high surface-to-volume ratio. The hybrid films are used as an excellent substrate for the deposition of pseudo-capacitive materials. Lightweight and flexible asymmetric supercapacitors (ASCs) with a maximum working voltage of 1.6 V have been fabricated using GF/CNTs/MnO₂ as the positive electrode and GF/CNTs/Ppy as the negative electrode with 0.5 M Na₂SO₄ aqueous electrolyte. The ASCs manifest high energy/power densities, remarkable cycling stability and excellent flexibility. The superior electrochemical performance could be attributed to the unique 3D nanostructure of the integrated electrodes, which allows high loading of electroactive materials and ensures facile charge transport. It is thus expected that such ASCs hold great promise as the high-energy density power source for flexible and lightweight electronics.

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Figures and captions

Fig. 1 (a1-a2) Representative photograph showing the large-size and flexibility of the film. (b-d) Typical FESEM images. (e,f) TEM images of CNTs in the GF/CNTs hybrid film. (g) Cross-sectional images of GF/CNTs branch. (h) Raman spectra of GF/CNTs hybrid film. (i) Comparative specific surface area (SSA) of GF/CNTs and GF. Inset of (d) suggests the tip-growth mechanism for CNTs. Arrows in the inset of (e) indicate the bamboo-like structure. The inset in (g) reveals the uniform growth of CNTs on both outer and inner surfaces of GF branches.

Fig. 2 (a, b) Representative FESEM images. (c,d) TEM images of MnO₂ nanosheets on the GF/CNTs/MnO₂ hybrid film.

Fig. 3 CV curves of GF/CNTs/MnO₂ hybrid films with different loading of MnO₂ (from 0.6 to 8.4 mg/cm²) at the scan rate of 5 mV/s (a) and 50 mV/s (b). (c) Representative CV curves of GF/CNTs/MnO₂-2.1 hybrid film at different scan rates. (d) Specific capacitance vs. scan rate for GF/CNTs/MnO₂ hybrid films with different loading of MnO₂. (e) Areal capacitance vs. mass loading for GF/CNTs/MnO₂ hybrid films at different scan rates. (f) Corresponding Nyquist plots of GF/CNTs/MnO₂ hybrid films with different loading of MnO₂. The inset of (f) shows an equivalent electrical circuit consisting of the electrolyte resistance (R_s), interface charge transfer resistance (R_{ct}), Warburg element (W) and constant phase element (CPE).

Fig. 4 (a) Schematic illustration of an ASC that consists of GF/CNTs/MnO₂ positive electrode, electrolyte-soaked separator and GF/CNTs/Ppy negative electrode. (b) CV curves of GF/CNTs/MnO₂ and GF/CNTs/Ppy half cells in 0.5 M Na₂SO₄ solution at a scan rate of 20 mV/s. (c) CV curves of ASC-2.1 measured with different potential windows (at 50 mV/s). CV curves of ASC-2.1 (d) and ASC-0.6 (e) measured between 0 and 1.6 V with different scan rates from 10 to 500 mV/s.

Fig. 5 (a) Galvanostatic charge/discharge curves of ASC-2.1 at different current densities. (b) Ragone plot of the ASCs and some other devices from previous literatures for comparison. (c) Nyquist plots for ASC-2.1 and ASC-0.6. (d) Cycling performance of ASC-2.1 at a current density of 1.5 mA/cm^2 for 10000 cycles. Inset of (d) shows the charge/discharge curves for the 1st and 10000th cycles. (e) CV curves of ASC-2.1 at different bending angles. Optical images show two ASCs connected in series powering (f) LEDs and (g) a small rotation motor.

For TOC use

Lightweight and flexible asymmetric supercapacitors (ASCs) fabricated using a new 3D graphene foam (GF)/carbon nanotubes (CNTs) hybrid film as support exhibit capacitance retention of 90.2-83.5% after 10000 cycles.