Selective deposition of metal oxide nanoflakes on graphene electrodes to obtain high-performance asymmetric micro-supercapacitors

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Introduction

Nowadays, electrical energy storage technology has revolutionized the whole world and changed our daily life with numerous portable electronic devices such as smartphones, digital watches, wireless earbuds and other wearable devices.\(^1,^2\) Due to the importance of energy storage devices, the 2019 Nobel Prize in Chemistry was awarded for the pioneering work on the rechargeable Li-ion battery. Meanwhile, supercapacitors, as another leading electrochemical energy storage technology, have also attracted intensive interest in both academia and industry in the last decade.\(^3\) In particular, planar micro-supercapacitors (MSCs) possessing a thin-layer structure, high power density, rapid charging/discharging capabilities and long cycle life are considered to be promising microscale power sources for on-chip electronic systems.\(^4,^6\) Carbon-based MSCs are excellent candidates for microscale power sources compared with conventional stacked-geometry supercapacitors, as they possess integrated thin-film electrodes with short ionic diffusion distances and separator-free structures. Besides this, the fabrication of MSCs with a wide working voltage window is a promising approach for achieving both high energy density and power density.\(^7\)

Asymmetric supercapacitors (ASCs), consisting of two different electroactive materials as positive and negative electrodes, could make full use of two different potential windows in the same cell and significantly increase the overall energy density of devices. To date, transition metal oxides have been intensively studied in ASCs since they could offer high specific capacitance by taking advantage of ultrafast surface redox reactions of transition metal cations.\(^7,^8\) According to the working potential windows of various transition metal oxides in aqueous electrolytes, most of the oxides are used as positive electrode materials with a stable potential range of around 0–1 V (vs. SCE), such as pseudocapacitive oxides MnO\(_2\), ZnO and battery-type oxides Co\(_3\)O\(_4\), V\(_2\)O\(_5\), SnO\(_2\), NiO, etc.\(^9–15\) On the other hand, there are few studies reporting negative electrode materials with a working potential range below 0 V (vs. SCE), which includes Fe\(_2\)O\(_3\), MoO\(_3\), and metal nitrides (VN), etc.\(^16–19\) Among these oxides, MnO\(_2\) and Fe\(_2\)O\(_3\) as positive and negative electrode materials, respectively, are the most promising candi-
dates for ASC devices because of their high theoretical capacitance, low cost, abundance and environmental friendliness. Moreover, the well-separated potential windows of MnO₂ (−0.1 to 0.8 V vs. SCE) and Fe₂O₃ (−0.9 to 0 V vs. SCE) could significantly increase the operating voltage of ASCs in aqueous electrolytes.

In order to assemble planar ASCs for on-chip integration, various fabrication strategies, such as photolithography, laser scribing, screen/inkjet printing, and electrodeposition have been developed to pattern carbon and other electro-active materials into interdigital electrodes to form asymmetric microsupercapacitors (A-MSCs). Among these approaches, printing is a cost-effective, cheap, fast and scalable approach for facile fabrication of micropattern electrodes. Conductive materials (e.g., active carbon, carbon nanotubes, nanofibers, and graphene) can also be printed to give interdigitated electrodes. In comparison with screen printing, inkjet printing is a flexible and non-contact method that allows precise control of high-resolution patterning without the need for prepatterned masks. However, direct inkjet printing has some limitations: unlike screen printing, which could easily pattern carbon materials and pseudo-capacitive metal oxide mixtures with sufficient thickness, inkjet printing is not suitable for thick patterns. More importantly, micro-printing asymmetric electrodes composed of two different materials would require two printing nozzles and a precise alignment of the two printing patterns, to avoid shortcuts or defects.

Unlike the inkjet printing technique, electrodeposition has its unique advantages in thin film fabrication of transition metal oxide materials. Electrodeposition is a mature and scalable technique for nanocrystalline metal plating or metal oxide functional coating in industry. It allows electrosynthesis of metal oxides from solution of metal salts and the subsequent deposition onto any complex-shape substrates through a one-step process. In addition, by tuning the electrochemical conditions (e.g. pulse or direct current output, deposition time, electrolytes), we can spatially control the loading amount and surface morphology of metal oxide on selected electrodes. Although electrodeposition has been intensively employed in the fabrication of nanostructured metal oxide films for bulk supercapacitors, there are still some challenges in this thin film formation process. For example, conventional anodic or cathodic direct current deposition of metal oxides will result in internal stresses on the substrates with the formation of delamination layers after coating, which is unfavorable for stable MSC electrodes. Besides, metal oxide materials usually suffer from poor electronic and ionic conductivity, affecting the rate capability and cycling stability of the ASC devices.

These challenges can be overcome by the introduction of new electrochemical deposition techniques and the combination of advanced current collectors with metal oxides. Herein, we used pulse current deposition (PCD) as an alternative cost-effective and simple technique for the fabrication of A-MSCs based on pseudo-active metal oxide (MO₃) nanomaterials and graphene-based current collectors. Generally, electrochemically exfoliated graphene (EG) was inkjet printed on a Kapton film to form interdigitated patterns, which served as reliable conductive deposition substrates, thanks to the high electrical conductivity, excellent electrochemical stability, large specific surface area and low cost of graphene. In our exfoliation process, the total cost including those of starting material graphite foil (ca. 0.5 € per g), electrolyte 0.1 M (NH₄)₂SO₄ (ca. 1 € per 100 mL), and power consumption (ca. 1 € per kW h) is less than 5 € per g on the lab scale. Then, MnO₂ and Fe₂O₃ were selected as positive and negative electrode materials, respectively, with well-separated potential windows and matchable capacitances. Crack-free and mesoporous MnO₂ and Fe₂O₃ thin films were fabricated by selective PCD coating on the EG layer and subsequent annealing treatment. To the best of our knowledge, there is no previous research using pulse electrodeposition in micro-scale supercapacitor applications. Our results indicated that the PCD method could significantly improve the coating uniformity, boosting the cycling stability of our prepared A-MSC devices, as compared with the conventional direct current deposition approach. The current technique described here is promising for the rapid fabrication of high-performance A-MSCs with high versatility of pseudo-capacitive metal oxide materials.

Results and discussion

Fig. 1 shows the fabrication process of Fe₂O₃/MnO₂-based A-MSCs. Generally, it was divided into the following steps. First, conductive EG inks were printed on a Kapton substrate to obtain planar interdigitated micropatterns. After annealing treatment of the EG layer, either MnO₂ or FeOOH nanoflakes were electrodeposited on the EG pattern with a two-electrode configuration (EG as the working electrode and a Pt wire as the counter electrode). Then, the obtained samples were annealed at 300 °C to convert the deposited precursors into either Fe₂O₃ or MnO₂. For the single metal oxide based MSCs, 1 M LiCl was used as the aqueous electrolyte for either Fe₂O₃ or MnO₂ based electrodes. For A-MSCs, solid electrolyte of LiCl/PVA gels was used to fabricate the all-solid-state Fe₂O₃/MnO₂ A-MSCs (named Fe-Mn).

The electrosynthesis and deposition process of MO₃ by the anodic approach can be described by the following equations:

Step 1:

\[ \text{M}^{2+}_{(aq)} \rightarrow \text{M}^{3+}_{(ads)} + e^- \]

Step 2:

\[ \text{M}^{3+}_{(ads)} + 2\text{H}_2\text{O} \rightarrow \text{MO(OH)}_{(ads)} + 3\text{H}^+ \]

Step 3:

\[ \text{MO(OH)}_{(ads)} \rightarrow \text{MO}_2 + \text{H}^+ + e^- \]

The proposed mechanism for anodic deposition of manganese oxide involves three steps: (1) oxidation of cationic Mn²⁺ precursors in the solution near the anode electrodes; (2) and the subsequent hydrolysis of Mn³⁺ to form the MnO(OH) inter-
mediate which precipitates on the anode electrode; (3) in the last step, the adsorbed manganese hydroxide is further oxidized to MnO₂ with the release of a proton. Manganese acetate (MnAc) was selected as the precursor material for electrodeposition of MnO₂, because acetate counterions could reduce the potential at which film deposition occurs and results in a high deposition rate.\textsuperscript{46,47} As for iron oxide, the deposition mechanism is similar to that of manganese oxide, starting from the oxidation of Fe²⁺ cations to Fe³⁺ and precipitation of the obtained iron hydroxide on the anode surface, but without the last oxidation step.\textsuperscript{17} Ammonium iron(II) sulfate was used as the common source material for Fe₂O₃ anodic deposition.

Unlike the conventional direct current (galvanostatic) deposition (DCD), in this work, we used pulse current deposition for the efficient coating of MOₓ functional layers. Pulse deposition has been widely used in the industrial plating of nanocrystalline metals to improve deposits for several decades, while it is scarcely studied in the field of nanostructured metal oxides. Thus, the two electrodeposition techniques for optimizing the coating qualities in energy storage devices are worth comparing. The deposition conditions for DCD and PCD methods are similar, in both cases, the applied current density for the target electrodes was a fixed value of 47 \( \mu \text{A cm}^{-2} \) (5 \( \mu \text{A per 0.105 cm}^{-2} \) for the single electrode). The deposition time for MnO₂ in the DCD mode was 5 min, 10 min, 20 min, and 40 min; whereas the deposition time for Fe₂O₃ in the DCD mode was 10 min, 20 min, 40 min, and 80 min, separately. For pulse current deposition (PCD), a square-wave pulse signal was generated with a period of 5 ms and a duty ratio of 0.5 (5 ms ‘on time’ and 5 ms ‘off time’ for one duty cycle, as shown in Fig. S1\textsuperscript{†}). Accordingly, the efficient deposition time for both MnO₂ and Fe₂O₃ in the PCD mode was the same as those of the samples obtained in the DCD mode, while the total deposition time was double due to the extra ‘off time’.

Fig. 2 and S2, 3\textsuperscript{†} show SEM images of MnO₂ and Fe₂O₃ prepared by the DCD or PCD method at different coating times with post-treatment annealing. As shown in Fig. 2a and S2c,\textsuperscript{†} MnO₂ deposited by the galvanostatic approach exhibited a considerable number of cracks after coating for 20 minutes. Spalling and warping of the coated layers were clearly observed on a scale of hundreds of micrometers. The density of cracks and defects was even higher for a longer deposition time (\( t = 40 \) min Fig. S2d\textsuperscript{†}), and the cracked films tended to peel off from the substrate, probably due to shrinkage stress of the thick layer.\textsuperscript{40} Similar issues of cracking and delamination were observed on the Fe₂O₃ film deposited by the galvanostatic method after 40 minutes of coating time (Fig. 2d and S3a-d\textsuperscript{†}), with smaller warping cracks of around 2–5 micrometer long. In contrast, both MnO₂ and Fe₂O₃ films prepared by PCD, using the same current density, revealed a uniform coating layer well adhering to the EG sublayer even after 40 minutes of deposition for MnO₂ and 80 minutes of deposition for Fe₂O₃ (Fig. 2e, f and S3e-h\textsuperscript{†}). The better film quality obtained by PCD with respect to the DCD current could be attributed to more efficient transport of ions achievable in the former tech-
MnO$_2$ layer thickness was tunable according to the deposition to the EG surface.\textsuperscript{9,50} The periodic pulse deposition gives manganese or iron ions as estimated from SEM cross-section images (Fig. S4b†). The MnO$_2$ layer thickness was tunable according to the deposition time: it increased from 150 nm to 300 nm by increasing deposition time from 20 to 80 minutes (Fig. S4d†). The Fe$_2$O$_3$ layer thickness of around 150 nm was observed (Fig. 2c–f†). In the case of Fe$_2$O$_3$, a more compact porous structure with closely packed small nanoflakes (average pore size of 50 nm) and average film thickness of around 150 nm was observed ($t = 40$ min, Fig. 2f and S4e†). The layer thickness of Fe$_2$O$_3$ increased from 90 nm to 230 nm by increasing deposition time from 20 to 80 minutes (Fig. S4d–f†). These mesoporous structures from pulse current deposition methods (PCD mode, $t = 40$ min) and (e and f) pulse current deposition methods (PCD mode, $t = 80$ min).

MnO$_2$ and 35.6° for Fe$_2$O$_3$ also reveal the presence of very small oxide crystallites, possibly corresponding to pyrolusite $\beta$-MnO$_2$ (110) and maghemite $\gamma$-Fe$_2$O$_3$ (311).\textsuperscript{53,54} We used Raman spectroscopy to compare bare EG, MnO$_2$-EG and Fe$_2$O$_3$-EG (Fig. 3a). The Raman spectra showed two distinct peaks at 1352 cm$^{-1}$ and 1580 cm$^{-1}$ for all three samples, attributed to the D peak (intervalley double resonance, usually from defect-related scattering) and the G peak (in-plane $E_{2g}$ optical phonon mode) from the defective EG layer.\textsuperscript{55,56} Another weak peak at $\sim$2700 cm$^{-1}$ was due to the 2D peak of graphene (the second order of the D peak). The Raman spectrum at low wavenumbers revealed the scattering peaks of MnO$_2$ or Fe$_2$O$_3$ nanoflakes. The dominant peaks of Fe$_2$O$_3$ were at around 350 (T$_{2g}$ mode), 511 (E$_g$ mode), and 700 cm$^{-1}$ (A$_{1g}$ modes), ascribed to the maghemite phase of $\gamma$-Fe$_2$O$_3$.\textsuperscript{57} The Raman spectrum of the MnO$_2$ film showed one main peak at 643 cm$^{-1}$, which could be identified as Mn–O stretching vibrations from the tetragonal $\beta$-MnO$_2$ structure.\textsuperscript{58} The chemical composition of bare EG, MnO$_2$-EG and Fe$_2$O$_3$-EG layers was confirmed by XPS analysis, showing C 1s, Mn 2p, Fe 2p and O 1s core levels (see in Fig. 3b–d and S6†). The C 1s spectra were measured for the bare EG sample; a sharp peak was observed at 284.6 eV (Fig. 3b) due to the sp$^3$ C–C bond and sp$^3$ C–C bond, and other peaks at 286.2, 288.2, and 288.9 eV were assigned to the C–OH/C–O–C, C=O and O=C=O components, respectively. The existence of these oxygen functional groups was due to the printed EG ink, which can be attributed to the unavoidable oxidation of graphite during the anodic exfoliation process of EG sheets. Fig. 3c shows the Mn 2p spectrum from MnO$_2$, which consists of two main peaks at 641.6 and 644.3 eV for Mn 2p$_{3/2}$, and one peak at 653.2 eV for Mn 2p$_{1/2}$. The energy separation between the Mn 2p$_{3/2}$ and Mn
2p1/2 is 11.6 eV, in agreement with previous reports on MnO2 materials. The O 1s peak was deconvoluted in two main components: Mn–O–Mn component at 529.8 eV and Mn–OH component at 531.1 eV (Fig. S6a†). The –OH bond might come from the adsorption of O2 and water molecules on the MnO2 surface. Meanwhile, Fig. 3d shows the chemical state of Fe 2p, which was used to detect the presence of iron oxide. There were one main peak and a shoulder peak at 710.4 and 718.8 eV for Fe 2p3/2, and one peak at 724.2 eV for Fe 2p1/2. The Fe 2p3/2 was also associated with a shake-up satellite around 7 eV higher than the main peak, which is close to the experimental iron(III) oxide data reported in the literature. The O 1s peak (see in Fig. S6b†) was fitted using two main components: Fe–O–Fe component at 529.7 eV and Fe–OH component at 531.3 eV, similar to the MnO2 O 1s result.

The detailed morphology and composition of Fe2O3 and MnO2 were further examined by TEM and EDS analysis at the nanoscale level. Fig. 4a and S7a† show the representative TEM images of crumpled MnO2 nanoflakes. High resolution TEM (HRTEM) image (Fig. 4a) revealed the relative lattice fringes with d spacings of 0.31 nm and 0.16 nm, which were corresponding to the (110) and (211) lattice plane of pyrolusite MnO2. In most cases, the orientation of MnO2 nanoflakes was random with no preferred direction, as evidenced by the broad diffraction rings from the fast Fourier transform (FFT) pattern (Fig. S7c†). Furthermore, the elemental composition of Mn, O and Cu was confirmed by energy dispersive X-ray spectroscopy analysis (EDS) of the TEM copper grid of MnO2 flakes (Fig. S8a†). In the case of Fe2O3, a needle-like Fe2O3 nanoflake agglomerate was observed in TEM image (Fig. S7b†) with an average thickness of 5–10 nm and a length of around 100 nm, which is consistent with the SEM results. HRTEM images in Fig. 4b and S7b† show Fe2O3 nanoflakes randomly distributed on the TEM grid, which also explains the partial amorphous nature of the Fe2O3 film by XRD. The crystalline lattice of Fe2O3 sheets showed d spacings of 0.30 nm, 0.25 nm and 0.17 nm corresponding to the (220) (311) and (422) lattice planes of the maghemite structure (Fig. S7d†), which is consistent with the Raman and XRD results. The presence of Fe and O elements were confirmed by EDS analysis (Fig. S8b†).

The electrochemical behaviour of Fe2O3 and MnO2 on EG MSCs were studied in a two-electrode configuration with a 1 M LiCl aqueous electrolyte. We first used cyclic voltammetry (CV) to study what happens by coating only one of the two EG electrodes with MnO2 or Fe2O3. MnO2 was coated by 10 minutes of PCD on the positive electrode, to obtain asymmetric MnO2/EG electrodes. On the other hand, Fe2O3 was coated by 40 minutes of pulse deposition on the negative electrode to obtain asymmetric EG/Fe2O3 electrodes. To clarify, we refer to the different electrode couples as: positive electrode material/negative electrode material, in this order. These asymmetric samples were compared with pristine, symmetric EG electrodes.

There was no significant difference in the capacitance of MnO2/EG EG/Fe2O3 as compared to symmetric EG/EG devices,
The pseudocapacitive behaviour of Fe$_2$O$_3$ could be explained by the redox transitions of interfacial oxidation species at various Mn oxidation states (e.g., Mn$^{3+}$/Mn$^{4+}$). The areal capacitances of Fe-2 and Mn-2 were 253 and 244 μF cm$^{-2}$ at a scan rate of 100 mV s$^{-1}$, respectively, which is almost 15 times higher than that of the bare EG device. Moreover, the galvanostatic charge-discharge (GCD) measurements under different current densities from 5 to 50 μA cm$^{-2}$ (Fig. 6b) shows a small deviation from the triangular shape and relatively symmetric shape of GCD curves, indicating good electrochemical performance of our metal oxide electrodes, in agreement with previous CV results. Fig. 6c presents the rate performance of the Fe–Mn device at different current densities. A high stack capacitance of 110.6 F cm$^{-2}$ was achieved at a current density of 5 μA cm$^{-2}$, which significantly exceeds that of the previously reported graphene-based devices.
Fig. 5 Electrochemical performance of symmetric MSCs. CV curves of (a) Fe-MSC-2 and (b) Mn-MSC-2 symmetric devices at different scan rates; specific areal capacitances of (c) Fe-MSCs and (d) Mn-MSCs with different loading amounts at different scan rates.

Fig. 6 Electrochemical performance of asymmetric Fe–Mn A-MSC prepared by PCD in LiCl/PVA electrodes. (a) CV curves of Fe–Mn at different scan rates; (b) charge–discharge curves of Fe–Mn at different current densities; (c) rate capability of Fe–Mn at different current densities; (d) long-term cycling stability of Fe–Mn at a current density of 100 µA cm$^{-2}$; (e) Ragone plot of specific volumetric energy density and power density for Fe–Mn compared with other microscale energy-storage devices.
1.3 F cm$^{-3}$ for onion-like graphene based MSCs and 3.1 F cm$^{-3}$ for laser-written graphene oxide MSCs,
62,63 and also superior to others state-of-the-art transition metal oxide based A-MSCs, e.g., MnO$_2$/Fe$_2$O$_3$ A-MSCs on Cr/Ni patterns (60 F cm$^{-3}$), PNG-MnO$_2$/PNG on a plasma reduced and nitrogen-doped graphene oxide substrate (38.1 F cm$^{-3}$), and NPG-MnO$_2$/NPG-Ppy on a nano-porous gold substrate (45.3 F cm$^{-3}$).15,32,38 To demonstrate the device stability of our asymmetric supercapacitor, we also performed long-term cycling of Fe–Mn A-MSC by GCD at 100 μA cm$^{-2}$. Interestingly, our device retained about 95.7% of the initial value with a high coulomb efficacy (99.3%) after 10,000 cycles, as shown in Fig. 6d. Furthermore, the bending test was performed under different angles with CV scan at 100 mV s$^{-1}$ (see in Fig. S14†). The capacitance of the Fe–Mn device maintained almost the same value after bending at ca. 90° and 180°, showing the potential applicability of this A-MSC as a flexible supercapacitor device.

Finally, the volumetric energy and power density of Fe–Mn were compared with the state-of-the-art performance metrics obtained from the literature (Fig. 6e). The Fe–Mn A-MSC device delivers a maximum energy density of 39 mW h cm$^{-3}$ (corresponding power density of 259 mW cm$^{-2}$) and a maximum power density 12.9 W cm$^{-3}$ (corresponding energy density of 7.6 mW h cm$^{-3}$). The energy density value is much higher than those of typical carbon-based micro-supercapacitors, and comparable with those of a Li thin-film battery (≤10 mW h cm$^{-3}$) and other reported pseudocapacitive hybrid A-MSCs (Table S1†) such as LiG–MnO$_2$/LiG–FeOOH (2.4 mW h cm$^{-3}$), MnO$_2$/Fe$_2$O$_3$ (12 mW h cm$^{-3}$), Co(OH)$_2$/EG/VN-EG (12.4 mW h cm$^{-3}$), and PNG/PNG-MnO$_2$ (38.1 mW h cm$^{-3}$) micro-supercapacitors.15,19,30,38,64

**Conclusions**

In summary, pulse current deposition has been demonstrated as a facile and highly efficient electrochemical approach for the fabrication of high-performance planar asymmetric MSCs. Crack-free MnO$_2$ and Fe$_2$O$_3$ mesoporous nanofoils were uniformly electrodeposited on inkjet-printed graphene micropatterns as positive and negative A-MSC electrodes respectively. The fabricated A-MSCs exhibit simultaneously increased volumetric capacitance and working voltage window, thus leading to significantly higher energy density than other MSCs previously reported in the literature. The low-cost of electrodeposition techniques facilitate upscaling Mo$_2$ coating from the laboratory level to large scale industrial production. The versatility of such an electrodeposition approach paves the way towards the fabrication of other metal oxide structures, in search for synergies between metal cations and enhanced electrochemical properties.

**Experimental section**

**Electrochemical exfoliation of graphene**

The EG was produced according to the procedure described in our previous publication.24 Briefly, two pieces of graphite foil (Alfa Aesar, 0.13 mm thick, product number: 43078) were inserted into 0.1 M (NH$_4$)$_2$SO$_4$ aqueous electrolyte solution as the cathode and anode (at a distance of 2 cm), respectively, and biased at a DC voltage of 10 V for exfoliation. The obtained graphite powder was collected and the rinsed powder was dispersed in DMF at a concentration of about 2 mg mL$^{-1}$ by ultrasonication for 10 min.

**Graphene ink formulation**

The centrifugation-assisted solvent exchange technique was used to formulate EG ink. First, ~40 mL EG/DMF dispersion was centrifuged at 3000 rpm for 15 min to remove the largest particles. Then the supernatant was harvested and centrifuged again at 10 500 rpm for 15 min to separate EG from DMF. After DMF was removed, 16 mL of the mixed solvent of cyclohexanone and terpineol (with a volume ratio of 3:1) and 320 mg of ethyl cellulose (viscosity 4 cP for 5 w/v% in 80:20 toluene:ethanol, Sigma-Aldrich, product number: 200646) were added to disperse the sedimented EG and sonicated for 30 min. Finally, the EG ink was centrifuged at 2000 rpm for 3 min to further remove big particles. The final ink concentration was about 2.3 mg mL$^{-1}$.

**Fabrication of planar EG-MSCs**

EG ink was printed using a commercial piezoelectric Dimatix Materials Printer (DMP 2800, Dimatix-Fujifilm Inc.) equipped with a 10 PL cartridge (DMC-11610). First, EG inks are printed at the drop spacing of 25 μm and substrate temperature of 45 °C on different substrates to form the electrodes for MSCs. Afterward, the samples were annealed on a hot plate in air for 1–2 h at temperatures of around 380 °C for the Kapton substrate.

**Selective deposition of the MnO$_2$ or Fe$_2$O$_3$ thin film on EG electrodes**

A polydimethylsiloxane (PDMS) mask was fixed on the top of MSC along with an electrochemical setup composed of a two-electrode cell: a Pt wire as the counter electrode and the target substrate as the working electrode. For MnO$_2$ coating, few droplets of 10 mM Mn(COOCH$_3$)$_2$ and 40 mM NaCOOCH$_3$ solution in water were deposited inside the mask as the electrolyte for MnO$_2$ deposition. For Fe$_2$O$_3$ coating, few droplets of 10 mM (NH$_4$)$_2$Fe(SO$_4$)$_2$ and 40 mM NaCOOCH$_3$ solution were used as the electrolyte. Galvanostatic direct current electrodeposition was performed under a positive bias to the target electrode, maintaining a current density of 47 μA cm$^{-2}$ to coat MnO$_2$ or FeOOH films on EG-based MSC electrodes with time from 5 to 80 min. Pulse current deposition was conducted using a square-wave pulse current of 47 μA cm$^{-2}$ (5 μA current on the 0.105 cm$^{-2}$ single electrode area, as shown in Fig. S1b†) with a period of 5 ms and a duty ratio of 0.5 with the time from 5 to 80 min. A function generator (Tenma 72-14111) was used for the generation of the wave function signal, and Keithley 2450 was connected with the wave generator as the power source. After electrochemical deposition, the composites were sequentially washed with DI water and dried under a gentle flow of nitrogen gas. Then, the MSCs were annealed at 300 °C under ambient air conditions.
Electrochemical characterization

All the electrochemical properties of the fully printed MSCs were characterized using a two-electrode configuration. Biologic SP-300 potentiostat (for CV profiles). The areal capacitance \( C_A \) was calculated either from the CV profiles or the GCD curves. For the CV profiles, \( C_A = \frac{\int_{E_1}^{E_2} \Delta I \, dE}{2(\Delta E \Delta V)} \), where \( \Delta E \) and \( \Delta I \) are the charging and discharging currents, respectively, \( \Delta V \) is the voltage window, \( A \) is the active area of the metal oxide film, and \( \nu \) is the scan rate. The total device area was calculated according to the pattern size of active materials (\( A = (2.3 \times 0.7 \times 4 + 6 \times 0.7) \times 2 = 21 \, mm^2 = 0.21 \, cm^2 \), see in Fig. S1b). For the GCD curves, \( C_A,GDC = \frac{1}{\Delta I \Delta V} \) where \( I \) is the discharging current and \( \Delta I \) is the discharging time. All the areal energy density is calculated as \( E_A = \frac{0.5C_{A,CV} \Delta I^2}{\Delta \nu} \), and the areal power density is \( P_A = \frac{\Delta I}{\Delta \nu} \) with \( \Delta I = \Delta V/\nu \) being the discharging time. The volumetric energy (power) density is calculated by dividing \( E_A \) (PA) by the average MoX layer thickness (\( T \)) measured from our SEM cross-sections (\( T = (151 + 197)/2 = 174 \, nm \)).

Materials characterization

The surface morphology of the MnO\(_2\) or Fe2O\(_3\) thin film was monitored by field emission scanning electron microscopy (JEOL JSM-7800F Prime), under an accelerating voltage of 8 kV. Transmission electron microscopy (FEI Tecnai T20, 200 kV) was used to characterize the metal oxide crystalline structures. Raman spectroscopy was performed using a WITec alpha300 R, with a 532 nm laser line and a laser spot size of 300 nm. Transmission electron microscopy (FEI Tecnai T20, 200 kV) was used to characterize the metal oxide crystalline structures.

Conflicts of interest

The authors declare no competing financial interest.

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