On-Chip Micro-Pseudocapacitors for Ultrahigh Energy and Power Delivery

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The demands of continuous miniaturization of micro-electromechanical systems (MEMS) and portable electronic devices have motivated the efforts on integrating power sources with electronic circuits.\[1\] This calls for the electrochemical energy storage devices, such as batteries and supercapacitors, not only to scale down in dimensions to fit on-chip geometries of integrated circuits but also to be compatible in fabrication methods with current MEMS and semiconductor techniques. In contrast to thin film batteries whose properties drop dramatically with the decrease of sizes, micro-supercapacitors often have better performance in comparison with their bulk counterparts as the result of reduced transport length of charge and electrolytes.\[1,2\] Interdigital planar form micro-supercapacitors (MSCs) with active carbon,\[3\] carbide-derived carbon,\[4\] carbon nanoparticles/nanotubes\[5-7\] and multilayer graphene\[7-13\] as electrode materials have been developed and are capable of delivering high power density by electrochemical double layer charge storage. However, their energy densities, typically, 0.1–1.0 mW h cm\(^{-2}\), are insufficient to meet the requirements of the reasonable operational time of microdevices. Pseudocapacitive materials, such as transition metal oxides (MnO\(_2\), RuO\(_2\), etc.) and conductive polymers (polyaniline, polypyrrole, etc.), represent an important branch of electrode materials for supercapacitor applications.\[14\] As the charge storage is based on the fast surface redox (faradic) reactions, they have very high theoretical capacitance, for instance, 1370 F g\(^{-1}\) for MnO\(_2\).\[15,16\] Indeed, MSCs with pseudocapacitive electrode materials have been reported to have respectable gravimetric and volumetric capacitance.\[17-25\] Nevertheless, the pseudocapacitive materials usually suffer from low electrical conductivity and, as a result, their achievable capacitances and power performance are far from the theoretical expectation and device requirements. In addition to the demands of an increased conductivity, porous structure design is also important for supercapacitor electrodes because it can provide/allow a large surface area, good accessibility of the ions to the electrochemically active surface and excellent capacitive behaviors even in quick charge-discharge operations.\[26-30\] Despite many efforts made in recent years, it is still the most challenging task to concurrently realize high energy and high power densities in MSCs. Moreover, although many new methods have recently been developed to fabricate MSCs,\[6,8,9,13,22\] most of them are incompatible or not fully compatible with current MEMS and semiconductor techniques and, hence, cannot be employed directly to integrate the MSCs into electronic circuits. Here we report a hierarchical nanoporous gold (NPG)/manganese oxide (MnO\(_2\)) hybrid micro-pseudocapacitor (MPC), fabricated by the standard MEMS technique, with the high power densities comparable to carbon/graphene-based MSCs and, remarkably, ultrahigh specific energy which is even better than that of commercial thin film Li ion batteries and more than an order of magnitude higher than that of carbon/graphene-based MSCs.

**Figure 1a** schematically illustrates the structure of the NPG/MnO\(_2\) based MPCs. The entire device, with dimensions of 3.95 × 5.45 mm (Table S1, Supporting Information), is settled on a glass substrate and consists of 16 microelectrodes organized in an interdigital planar geometry. Every eight out of the 16 electrodes, made of NPG and MnO\(_2\), form either the cathode or anode and the gap between two electrodes is 50 µm (Figure 1b,c). The fully integrated on-chip NPG/MnO\(_2\) MPCs were fabricated by the standard MEMS technique and the complete fabrication process is schematically illustrated in Figure S1, Supporting Information. The hierarchical NPG was prepared by two-step dealloying of a electrochemically plated Au\(_{17.7}\)Ag\(_{82.3}\) (at%) precursor (Figure S2, Supporting Information).\[31\] In the first step, electrochemical dealloying only partly removed the Ag (≈49% of the entire Ag) and formed a nanoporous AuAg alloy (np-AuAg) with a nanopore size of ≈10–20 nm. After annealed at 300 °C for 1 h, the coarsened nanoporous alloy

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was subjected to the second step dealloying to generate small pores in the coarsened AuAg ligaments by further selectively leaching away Ag. As shown in Figure 2a,b and Figure S3, Supporting Information, the hierarchical NPG is uniform in pore distribution and film thickness, and more importantly, crack-free. The large pores have a size of 200–300 nm and the second-level small pores are of 20–40 nm. Different from free-standing AuAg thin films that the volume changes during the removal of Ag can be compensated by the macroscopic shrinkage of the film, the on-chip AuAg alloy films are horizontally constrained by the solid substrates and hence cracks are easy to form during dealloying, especially when the precursors contain a high concentration of Ag. The flaw-free porous structure benefits from the two-step dealloying, which gives rise to a small film thickness shrinkage from precursor 840 ± 30 nm to dealloyed 800 ± 30 nm (Figure S4, Supporting Information) and a limited volume reduction of ≈5%, much lower than the ≈30% volume shrinkage in conventionally dealloyed samples. On the basis of the composition evolution and the volume contraction of the NPG films, a high porosity of ≈79 vol% can be achieved in the on-chip hierarchical NPG (Figure 2c).

Figure 2d,e show the microstructure of the hierarchical NPG electrodes after MnO₂ deposition (see also Figure S5, Supporting Information). Chemical composition of MnO₂ is verified by X-ray energy-dispersive spectroscopy (EDS) (Figure 2e, inset) and has been demonstrated by detailed XPS and TEM characterizations in our previous studies. It is clear that the flocculent MnO₂ has been successfully plated into the nano-pore channels of NPG. For the sample with MnO₂ plating time up to 11 min (corresponding to an areal density of 74.5 ± 2.1 µg cm⁻²), no accumulation of MnO₂ can be seen from the top surface of NPG films. This is in obvious contrast to the MnO₂ growth on regular monolithic NPG. With the same MnO₂ plating amount, a very thick MnO₂ film (520 ± 30 nm, Figure S6, Supporting Information) usually forms on the NPG top surface. The exceptional plating performance of hierarchical NPG is due to the large porosity as well as enhanced mass transport by the novel hierarchical porous structure. Cross-sectional SEM image of the NPG/MnO₂ composite reveals a conformal electrodeposition of MnO₂ across the entire 800 nm porous film (Figure 2f), which has also been confirmed by EDS mapping and line sweep (Figures S7,S8, Supporting Information). It is worth noting that after the deposition of MnO₂, the hybrid film remains the open porosity, even for the 15 min plated NPG/MnO₂ (MnO₂ areal density 95.4 ± 4.2 µg cm⁻²) in which a ≈200 nm MnO₂ film was formed on the NPG top surface (Figure 2e,f). The open pores in the electrode are filled upon the casting of electrolytes. Finally, the microelectrodes are functionalized with interconnected current collector, active material and electrolyte together with minimized lengths for ionic and electric transport in the 3D nanoporous structure.

Electrochemical performance of the hierarchical NPG/MnO₂ MPCs was firstly evaluated in a 5.0 M LiCl aqueous solution. Cyclic voltammograms (CVs) of the supercapacitors retain a perfectly symmetrical rectangular shape over 0.7 V potential window at scan rates varying from 5 to 100 mV s⁻¹ (Figure 3a and Figure S9, Supporting Information). This double-layer capacitor-like CV behavior actually originates from the fast, reversible successive surface redox reactions of MnO₂ by means of proton incorporation, as well as surface electroadsorption of Li⁺ cations according to the reaction:
MnO$_2$ + xH$^+$ + yLi$^+$ + (x + y)e$^-$ ⇌ MnOOH$_x$Li$_y$.

The absence of redox peaks indicates that the supercapacitors are charged and discharged at a pseudocapacitive rate over the entire voltammetric cycles. Even though the NPG network may also contribute some double-layer capacitance, the contribution is very small, especially for samples with a high MnO$_2$ loading amount (~3.5% of the overall capacitance for 5 min plating, and ~2% for 15 min plating). Therefore, the hierarchical NPG mainly acts as the current collector and support of the active MnO$_2$.

The MPCs were also tested by galvanostatic charging/discharging (Figure 3b and Figure S10, Supporting Information). Regardless of MnO$_2$ loading amounts, the MPCs show near triangular charge/discharge profiles, in accordance with the CV curves as in Figure 3a. The areal capacitance of the MPCs dramatically increases with the plating time from 5 to 15 min (Figure 3c). More importantly, a linear relationship can be found between the areal capacitance and the MnO$_2$ plating time/amounts (Figure S11, Supporting Information), indicating insignificant capacity trade-off with increasing MnO$_2$ loading amounts. The specific capacitance, normalized to the mass of MnO$_2$, shows a small divergence of no more than 50 F g$^{-1}$MnO$_2$ (Figure S11, Supporting Information), suggesting an efficient utilization of the active material. For comparison, MSCs constructed by MnO$_2$ directly grown on bare Au templates (bare Au/MnO$_2$ MPCs, Figure S12, Supporting Information) were also tested. With the same plating time, the areal capacitance of bare Au/MnO$_2$ MPCs is much lower than that of the hierarchical NPG/MnO$_2$ MPCs (Figure 3c). The gravimetric capacitance of MnO$_2$ in the bare Au/MnO$_2$ MPCs is also lower, and decreases significantly when the MnO$_2$ plating time increases from 5 to 11 min (Figure S11, Supporting Information). An areal capacitance up to 7.1 F cm$^{-2}$ can be obtained from the hierarchical NPG/MnO$_2$ MPCs, which is much higher than those of electrochemical double-layer microcapacitors (0.4–2 F cm$^{-2}$, [2] carbon/graphene based MSCs (1.7 F cm$^{-2}$ for onion-like carbon based MSCs, [2] 0.51 F cm$^{-2}$ for laser-written reduced graphene oxide MSCs [8]) and is also superior to other MnO$_2$ based MPCs with a similar electrode thickness (0.2–1.2 F cm$^{-2}$) [37,38] (Table S2, Supporting Information).

The hierarchical NPG/MnO$_2$ MPCs were also fabricated as all-solid-state microdevices using a hydrogel-polymer PVA-LiCl electrolyte. The CVs and galvanostatic charging/discharging profiles of the all-solid-state microdevices are similar to those of the MPCs with the liquid electrolyte (Figure 4a and Figures S13 and S14, Supporting Information). In the all solid configuration, the specific capacitance of MnO$_2$ is ~10–30 F g$^{-1}$MnO$_2$ higher than that in liquid electrolyte MPCs at the same current density. This is probably due to a higher salt concentration in the electrolyte as the result of gel drying. A stack capacitance up to 99.1 F cm$^{-3}$, corresponding to an energy density of 6.74 mW h cm$^{-3}$, has been obtained from the solid-state hierarchical NPG/MnO$_2$ MPCs with a MnO$_2$ plating time of 11 min (Figure 4b), which is much higher than the literature values of the best carbon/graphene-based MSCs (1.3 F cm$^{-3}$ for onion-like carbon based MSCs, [2] 3.1 F cm$^{-3}$ for laser-written reduced graphene oxide MSCs, [8] 3.05 F cm$^{-3}$ for laser-scribed graphene MSCs, [9] 17.9 F cm$^{-3}$ for reduced graphene MSCs [10] and 6.1 F cm$^{-3}$ for reduced graphene oxide/carbon nanotube MSCs [11] and pseudocapacitive microdevices (16.4–39.3 F cm$^{-3}$ for MnO$_2$/Au multilayer MSCs, [12] 26.5–66.0 F cm$^{-3}$ for polyaniline nanowire array MSCs, [13] 8–25 F cm$^{-3}$ for CoO/carbon nanotube MSCs, [14] 4.42 F cm$^{-3}$ for graphene/MnO$_2$/Ag nanowire MSCs [15] and...
30–50 F cm\(^{-3}\) for MWCNT/MnO\(_x\) MSCs\(^{41}\) (Table S2, Supporting Information). Even at a high current density of 0.5 mA cm\(^{-2}\), the MPC shows a pure capacitive behavior at frequencies lower than 3 Hz and is characterized by a small relaxation time constant \(t_0\) of 200 ms which is much lower than that of other MnO\(_2\) based supercapacitors (500 ms for carbon nanoparticles/MnO\(_2\) nanorods hybrid structure,\(^{42}\) 3.2–8.0 s for MnO\(_2\)/carbon composites\(^{43}\)). The high rate capability and excellent frequency response of the MPCs originate from the highly accessible surface of MnO\(_2\) from the open nanoporous structure of the hybrid electrodes. The hierarchical NPG/MnO\(_2\) MPCs are also very stable, showing 90% capacitance retention over 1000 repeated cycles and 87% over 1500 cycles (Figure S15, Supporting Information).

Because of the microscale volume, a single device can only provide a limited power, which cannot meet the demand of most practical applications. Therefore, the microdevices need to be assembled together in series or/and parallel combinations to come up with a specific voltage and capacitance rating. Figure 4e,f demonstrates the feasibility of connecting the hierarchical NPG/MnO\(_2\) MPCs in series and parallel configurations (see also Figure S16, Supporting Information). By connecting three solid-state MPCs in series, the output voltage can be amplified by three times while the charging/discharging time is identical to that of a single device (Figure 4e), verifying a very good control over the operating voltage window. As the voltage meets that of a red light-emitting diode (LED), the LED can be powered by such a MPC combination (Figure 4e, inset). On the other hand, by connecting three MPCs in parallel, the powering life of the MPCs can be extended for three times (Figure 4f).

The hierarchical NPG/MnO\(_2\) MPCs with either liquid- or solid-state electrolytes described above are all based upon aqueous electrolytes which have a narrow operating voltage window, barely exceeds 1.0 V. As the energy density is proportional to the square of the potential window according to \(E = \frac{1}{2} CV^2\), enlarging the potential window will quadratically increase the energy density.\(^{14,44}\) Organic electrolytes and ionic liquids have been used in supercapacitors due to their large stability voltage window. In this study, an ionogel, prepared by mixing 1-ethyl-3-methylimidazolium dicyanamide (EMI-DCA) ionic liquid (Table S3, Supporting Information) with fumed silica nano-powders, was used for preparing the nonaqueous solid-state NPG/MnO\(_2\) MPCs. Electrochemical performance of the ionogel-based solid-state MPCs is shown in Figure 5.

It can be seen that the change from aqueous to ionic liquid electrolyte increases the operable cell voltage from 0.7 to 2.1 V. Although the microdevices exhibit resistive behavior, the CVs retain a rectangular shape over scan rates from 10 to 800 mV s\(^{-1}\), indicating a good high-rate performance (Figure 5a). The galvanostatic discharge curves of the microdevices with EMI-DCA ionogels show a relatively quick voltage drop at the initial stage of the discharge process (Figure 5b, inset), which is mainly due to the large resistance of the ionic liquid. Stack capacitance of the microdevice was calculated according to the formula:\(^{45}\)

\[
C_s = \frac{C_{MPC}}{V} = \frac{2i \int E \, dt}{V(\Delta E)^2}
\]
where \(i\) is the applied current (in A), \(E\) is the potential (in V), \(\Delta E\) is the operating voltage window (in V) and \(V\) is the stack volume of the microdevice (in cm\(^3\)). A capacitance of 20.8 F cm\(^{-3}\) can be obtained from the ionogel-based MPCs at 0.25 mA cm\(^{-2}\) (Figure 5b), which is only 1/3 of that for PVA-LiCl based micro-devices (64.7 F cm\(^{-3}\)) at the same current density (Table S4, Supporting Information). However, the stack capacitance of the hierarchical NPG/MnO\(_2\) MPCs is still one order of magnitude higher than that of the reported graphene-based MSCs, 1.40–2.35 F cm\(^{-3}\), with an ionogel electrolyte. In addition, because of the threefold increase in the operating voltage, the ionogel-based MPCs possess a high energy density of 12.7 mW h cm\(^{-3}\) at 0.25 mA cm\(^{-2}\), which is about three times higher than that of PVA-LiCl based MPCs (4.4 mW h cm\(^{-3}\) at 0.25 mA cm\(^{-2}\)). Moreover, the high capacitances of 16.0 F cm\(^{-3}\) and 9.1 F cm\(^{-3}\) can be maintained at 1.25 mA cm\(^{-2}\) and 10.0 mA cm\(^{-2}\), respectively (Figure 5b), indicating that the MPCs can work well at ultrahigh current densities.

Figure 5c shows the Ragone plot in which the stack energy and power densities of the hierarchical NPG/MnO\(_2\) MPCs are compared with those of commercially available energy-storage systems and other best MSCs reported in the literature. Remarkably, the hierarchical NPG/MnO\(_2\) MPCs show a comparable power density as the commercial electrolytic capacitors and conventional carbon based supercapacitors, but can deliver two orders of magnitude higher energy density. The high energy density is even better than the commercial Li thin film batteries.
The outstanding supercapacitor performance for the hierarchical NPG/MnO$_2$ MPCs originates from the full utilization of the pseudocapacitive MnO$_2$ in an interdigital 3D configuration, which highlights the key merits of the hierarchical nanoporous hybrid electrodes. First, the large porosity of hierarchical NPG together with an efficient mass transport can accommodate a large amount of active materials within the NPG framework for high specific and areal capacitance. Second, the bicontinuous and highly conductive porous structure with interconnected open pores allows an easy access of the ions, and thus facilitates the efficient utilization of the active material and a high power delivery. Third, the high surface area of the hierarchical NPG helps maximize the area of contact junctions for both electrolytes and active materials.

All the techniques involved in the fabrication of hierarchical NPG/MnO$_2$ MPCs, including the electrochemical plating of precursor alloys, dealloying and microfabrication for patterning, are adopted from existing MEMS techniques. Hence, the MPCs can be directly integrated into the electric circuits of MEMS as on-chip power supply without additional assembly and integration and is ready to scale up to industry level for mass production at a lower cost in processing. Together with unprecedented capacitive properties of concurrently realized high energy and power delivery, the hierarchical NPG/MnO$_2$ MPCs are very promising candidates as on-chip micro power supply for miniaturized MEMS and electronic devices.

In summary, we have successfully developed an on-chip micro-pseudocapacitor based on hierarchical nanoporous hybrid electrodes consisting of 3D bicontinuous PEG and pseudocapacitive MnO$_2$. The novel structure design offers the hierarchical NPG/MnO$_2$ micro-pseudocapacitors an ultrahigh specific energy of 12.7 mW h cm$^3$, better than the state-of-the-art thin film Li ion batteries, and a high power density of 46.6 W cm$^3$, comparable to carbon/graphene-based micro-supercapacitors. Importantly, the hierarchical NPG/MnO$_2$ micro-pseudocapacitors are fabricated by a standard MEMS method and can be directly integrated into the electric circuits of MEMS as on-chip power supply without additional assembly and integration. This study shines a light on the realization of a high-performance micro-supercapacitor towards practical applications and may have an important implication in developing high performance microdevices by designing hierarchical porous structure.

**Experimental Section**

**Fabrication of Hierarchical NPG and Assembly of the MPCs:** The fabrication process of the hierarchical NPG/MnO$_2$ MPCs is schematically illustrated in Figure S1, Supporting Information. A thin film of Au/Cr was first sputtered onto a 1-mm thick soda lime glass slide and then machined, by the microfabrication technique, into an interdigital configuration (gold template) that consists of 16 fingers, every eight out of which were electrically connected. Hierarchical NPG microelectrodes were prepared by multistep dealloying AuAg alloy precursors beforehand deposited on the gold templates. The AuAg alloy was electrochemically plated from a magnetic stirred KAu(CN)$_2$ /KAg(CN)$_2$ (6 x 10$^{-3}$/23.5 x 10$^{-3}$ m) mixture solution by applying a constant potential of −1.15 V versus Ag/AgCl on the gold templates for a duration of 2 min. NPG with hierarchical porosity was then created by subjecting the alloy precursor to a preliminary dealloying which partly removed the Ag from the alloy, followed by coarsening at high temperature and a final extraction of Ag. Electrochemical dealloying at 0.805 V versus Ag/AgCl...
in 1.0 μl HNO₃ for 900 s and chemical dealloying in concentrated HNO₃ (69 wt%) for 5 h were used for the first and second step dealloyings, respectively. The coarsening was carried out inside a 300 °C tube furnace with Ar protection (500 sccm) for 1 h. MnO₂ was plated from a solution containing 0.2 M Mn(CH₃COO)₂ 4H₂O and 0.2 M Na₂SO₄ by running a potential sequence of 0.40 V–5 s/0.45 V–10 s versus Ag/AgCl on the NPG electrodes. The hydrogen-polymer electrolyte, PVA-LiCl, was prepared by mixing 4 g PVA with 40 mL 5.0 m LiCl aqueous solution. The mixture was heated at ≈90 °C under constant stirring until a clear and transparent gel-like solution was obtained. The EM1-DC0 ionogel was prepared by mixing fumed silica nano-powders with the ionic liquid EM1-DC0 at a mass ratio of 0.4:5.7 g, and was left stirring for 5 h in an Ar-filled glove box to produce a clear viscous solution.

**Characterization and Electrochemical Measurement:** The microstructure and chemical composition of hierarchical NPG, NPG/MnO₂ and the microdevices were investigated using a field-emission scanning electron microscope (JEOL JIB-4600F, 15 keV) equipped with an X-ray energy-dispersive spectroscopy (EDS). The electrochemical performance of the MPCs was investigated by cyclic voltammetry, galvanostatic charge/discharge tests and electrochemical impedance spectroscopy using a VersaSTAT3 electrochemical workstation (Princeton Applied Research, USA) at room temperature.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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