MICRO SUPERCAPACITORS FOR ENERGY STORAGE, ON-CHIP DEVICES BASED ON PROTOTYPING OF PATTERNED NANOPOROUS CARBON

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ABSTRACT

Micro energy storage devices have drawn increasing attention due to the importance of power supply in miniaturized multi-functional systems. This paper reviews the recent progress in micro energy storage devices, particularly the micro supercapacitors, including the design issues of device architectures, electrode materials, and fabrication technologies. The work developed in our laboratory is then demonstrated, mainly a method of direct prototyping of nanoporous carbon for batch-fabricated micro energy storage devices, like three-dimensional micro supercapacitors and silicon-based anode for Li-ion batteries.

KEYWORDS

Energy storage device, Micro supercapacitor, Electrode architecture and material, Direct prototyping, Li-ion battery.

INTRODUCTION

With the rapid growth of portable electronic equipment and wireless sensor networks, the demand for better power supply systems under various environments and conditions is increasing. Pre-charged storage devices, and self-powered systems containing harvesters, energy storage and management components at comparable scale are designed to provide the power supply. Micro energy storage devices are essential in such diagrams but stay behind the development of low power technologies and miniaturization of sensors, circuits and communication modules [1-2].

Rechargeable batteries and supercapacitors are promising energy storage devices. Batteries suffer low power capability, limited cycle life and strict operating environmental conditions, so do their miniaturized counterparts. Supercapacitors, on the other hand, have advantages of high power density, long cycle life with high capacity retention after even millions of cycles, and the capability of operating in wide temperature ranges. The properties make supercapacitors efficient to satisfy the power demand in micro systems and serve in the situations where the devices are hard to be maintained or substituted, but the energy density remains the bottleneck.

Supercapacitors store charge by electric double layer (EDL) capacitance and/or pseudocapacitance at the interface of electrode/electrolyte when voltage is applied. The former type creates double layers separated at angstrom-scale, capacitance per area is thus large as a static capacitor. Pseudocapacitance is generated by the reversible redox adsorption/desorption or intercalation/deintercalation of ions at the surface layer of electrodes. The function between charge and voltage shows capacitive behavior during the dynamic process. For both types, increasing the specific surface area and conductivity of electrodes, together with high accessibility of electrolyte improve the performance.

Efforts on micro supercapacitors have a nearly two-decade history, with remarkable growth in recent years. This paper gives a review of recent work on micro supercapacitors first, with discussions on current design issues. Then, elaboration of micro energy storage devices developed in our laboratory is presented, including micro supercapacitors and silicon-based anode for Li-ion batteries based on direct prototyping of patterned nanoporous carbon.

RECENT RESEARCH ON MICRO SUPERCAPACITORS

To power miniaturized systems, micro supercapacitors are constructed in limited area and volume. Different from conventional supercapacitors, which are generally evaluated by gravimetric capacitance (F/g), micro supercapacitors are calibrated by areal capacitance (mF/cm^2). Considering different heights of electrodes, volumetric capacitance (F/cm^3) is also used to characterize the micro devices, so do volumetric energy density and power density. The projected area or volume of electrodes is generally used in the calculation.

Architecture and electrode material are factors to achieve high-capacity micro supercapacitors while keep their power performance. The architecture of a device should enable electrode material to be efficiently loaded with considerable mass without deteriorating the intrinsic performance. Advanced electrode material has not only high gravimetric capacitance but also high density to be densely assembled in the limited space. The fabrication processes are designed according to the properties of electrode materials.

Architectures

In early 2000s, micro supercapacitors rose with two electrodes and the solid electrolyte assembled layer by layer to form a sandwich-like cell [3]. The two-dimensional (2D) structure is recognized suitable for low-cost and scalable fabrication. However, the architecture limits the amount of material loaded. Though some techniques were applied to shape the substrate of layered structure into roll-like structure [4] and achieved higher areal capacitance than flat substrate, the areal capacitance remained low.

Compared with the layered sandwich-like structure (Fig.

1(a)), planar design with two electrodes in the same plane (Fig. 1(b)) forming alternate interdigital fingers shows several advantages [5]. Distance between adjacent electrodes can be precisely controlled in small scale, shortening the diffusion length of ions and resulting in fast charge/discharge rate. Furthermore, the diffusion length and accessibility of ions will not be severely affected by increasing the thickness of electrodes. With the merits, this architecture is promising to be extended in the third dimension, building electrodes from 2D to three-dimensional (3D) ones, and making full use of the limited on-chip space. Furthermore, the architecture can be built by compatible fabrication methods. It is also well-applied in flexible micro supercapacitors with bendable substrate and electrodes.

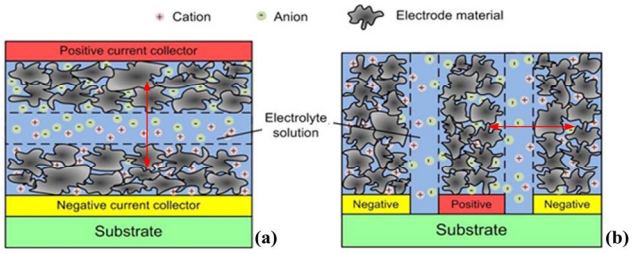

Figure 1: (a) The 2D design and (b) the planar interdigital design configuration. Red arrows: the diffusion paths of ions in the electrolyte.

Electrode Materials

Electrode material with both good electrochemical performance and fabrication feasibility is essential to high-performance micro supercapacitors. Conventional materials have been applied in micro electrodes via various designed fabrication processes, and some new materials show even higher compatibility and superior performance in micro supercapacitors. Following discussions classify electrode materials into EDL materials, pseudocapacitance materials and composites.

EDL materials are dominated by various types of porous carbon with high specific surface area. Activated carbon (AC) is the most important commercially applied one, with high specific area ranging from hundreds of m^2/g to even higher than $3000m^2/g$. However, the application of AC in micro supercapacitors is not as wide as in the conventional ones, due to the particle-type microstructure and the synthesis routes. Micro AC electrodes have been constructed by ink-jet printing method [6] and in-situ activation of carbon films on Si substrate by CO_2 [7]. The CO_2 activation created nanopores with a specific surface area of $1636m^2/g$, providing high EDL capacitance, together with an outstanding volumetric capacitance. But the loaded material is limited with only 1.5μm-thick electrodes.

Carbon nanotube (CNT) shows specific surface area of $500\text{-}1000m^2/g$. Though the capacitance is not outstanding, its high conductivity and unique one-dimensional (1D) structure as conductive highway makes it a promising material for supercapacitors. Vertically aligned CNTs make every single wire connected to the current collector directly. By designing the bottom metal layer, vertically aligned CNT arrays of 80μm were grown [8], but the CNT forest was not dense enough to provide high density and volumetric capacitance.

Graphene is attractive with its properties including high specific surface area ($2630m^2/g$), and high conductivity, providing a theoretical capacitance up to 550F/g and high power density. Besides, the mechanical stability of graphene makes it applicable in flexible devices. Graphene as supercapacitor material is generally prepared by exfoliation and reduction of graphite oxide (GO), so called reduced graphene oxide (rGO). It is demonstrated that the agglomeration of 2D graphene nanosheets restricts both specific surface area and the accessibility of electrolyte, making practical specific capacitance far lower than the theoretical value. As a result, a full use of intrinsic properties of graphene by orienting the nanosheets or adding nanostructured additives to prevent restacking of dispersed graphene flakes are commonly accepted techniques.

Graphene-based micro supercapacitor has been fabricated by direct laser reduction and patterning of GO films, with GO as solid-state electrolyte. The capacitance of such prototype was $0.51mF/cm^2$ and $3.1F/cm^3$. However, the power performance was not satisfactory with large resistance, possibly due to the inaccessibility of solid electrolyte to permeate into electrodes [9]. Direct laser writing on GO films using a standard LightScribe DVD burner was then conducted, with ionogel electrolyte, and the device showed high power density up to $200W/cm^3$ [10].

With the high power capability of graphene, efforts to design micro supercapacitors that response to 120Hz, aiming at replacing electrolytic capacitors in ac-line filter applications, were carried out. To satisfy the requirement, vertically oriented graphene nanosheets on Ni substrate was proposed. The design showed good adhesion between graphene/Ni with high conductivity, and high electrolyte accessibility because of unstacked graphene flakes. The time constant was only 0.2ms [11]. In micro devices, short diffusion length of ions also benefits the power capability. A rGO/CNT composite was designed with CNT as additives to avoid agglomeration between graphene nanosheets, the prototype showed a power density of $77W/cm^3$ and a time constant of 4.8ms [12]. The planar interdigital electrode architecture together with the in-plane orientation design of graphene nanosheets increased the accessibility and made ions transportation in the same plane, the device with ultra-thin graphene electrodes showed a power density of $495W/cm^3$ with a time constant of 28ms [13].

The prototypes show high response frequency exceeding 120Hz, but to achieve such frequency responsibility, the expected low time constant defined as $\tau=RC$ shows limitation in both resistance and capacitance. Generally, the capacitances of this type of devices are at the level of $1mF/cm^2$, but still much higher than electrolytic capacitors.

Onion-like carbon (OLC) as another particle-type carbon shows moderate specific surface area and high conductivity. Unlike AC, whose high specific-surface area comes from micropores in particles, OLC has a specific surface area comes from nanoscale particles with no internal

Table 1: A summary of EDL micro supercapacitors

Ref	Electrode material	Property and method	Areal capacitance (mF/cm^2)	Volumetric capacitance (F/cm^3)
[6]	AC	Ink-jet	2.1 (1mV/s)	1.6
[7]	AC	CO_2 activation of carbon film	N/A	250 (electrode)
[14]	OLC	Electrodeposition	1.7 (1V/s)	0.24
[16]	CDC	Chlorination	1.5 (100mV/s)	9.4
[9]	rGO	Direct laser writing (GO as electrolyte)	0.51(40mV/s)	3.1
[10]	rGO	Direct laser writing (ionogel electrolyte)	2.32 (16.8mA/cm^3)	3.05
[13]	rGO	In-plane geometry	0.081 (10mV/s)	N/A
[8]	CNT	CVD, vertically aligned array	0.428 (50mV/s)	0.054
[12]	rGO/CNT	ESD deposition	2.8 (50V/s)	3.1
[5]	AC	3D self-supporting electrodes	90.7 (50mV/s)	1.5

pore structure. Though the specific surface area is not as high as AC, the surface is fully accessible to electrolyte, facilitating fast ion transportation and thus high power density. The micro supercapacitor formed by electrodeposition of OLC on Au interdigital current collectors showed a maximum power density even up to $1kW/cm^3$ with a time constant 26ms [14].

Carbide-derived carbon (CDC), prepared by selective etching Ti element from TiC by chlorination, with controllable uniform micropores, showed $180F/cm^3$ volumetric capacitance in organic electrolyte with a thickness of 2μm. For a 100-μm-thick electrode, $50\text{-}60F/cm^3$ is also a high value for EDL capacitance [15]. The route was applied on various substrates with smooth morphology, and patterned by reactive ion etching (RIE). The prototype showed $1.5mF/cm^2$ and $9.4F/cm^3$ [16].

Silicon-based materials providing EDL capacitance for micro supercapacitors rose in recent years. The materials are rarely used in conventional supercapacitors due to relative low specific surface area. However, because of its compatibility to silicon-based fabrication technologies and high electrochemical stability with long cycle life, it has been studied in micro supercapacitors with designed micro structures to increase the surface area. Si nanowires [17], silicon carbide [18] and porous silicon coated with carbon sheath [19] showed potential as high-cycle-life materials for micro supercapacitors. However, few on-chip prototypes have been presented, and the capacitances remained low compared with carbon EDL materials.

Pseudocapacitance providing higher theoretical capacity than EDL capacitance has been adopted in micro supercapacitors. Conducting polymers (Polypyrrole (PPy), Poly(3,4-ethylenedioxythiophene) (PEDOT)) and transition metal oxides (RuO_2, MnO_2, $NiO/Ni(OH)_2$) were studied.

Deep etching of Si followed by Ni layer coating was fabricated as 3D current collectors, and PPy films were then electrochemical polymerized [20]. Though 3D electrodes were constructed, the active material remained thin films, and the capacitance was limited.

The ink-jet printing technique was applied to PEDOT, by adding additives into the composite ink to adjust its viscosity, the PEDOT:PSS could be successfully ink-jet printed and the film showing uniform and continuous morphology [21]. The thickness of electrodes is still limited, but PEDOT shows much higher volumetric capacitance than ink-jet printed AC.

Among metal oxides, RuO_2 is recognized as a promising material with high capacitance and conductivity. Direct laser writing [22] and electrodeposition [23] of RuO_2 have been presented. By optimization of the micro morphology, the electrodes showed high volumetric capacitance.

MnO_2 shows the capacitive behavior in neutral electrolyte, avoiding the acid medium for RuO_2. It has higher theoretical capacitance than RuO_2, but is strictly limited by the low conductivity (10^{-6}-$10^{-5}S/cm$). MnO_2 micro electrodes were formed by electrodeposition [24] or electrospinning [25]. A MnO_2/Au multilayer structure was designed to increase the conductivity of electrodes [26], improved power performance with a time constant of 5ms was achieved.

Pure EDL or pseudocapacitance materials show respective limitations, i.e., the low specific capacitance of EDL capacitance, and for pseudocapacitance, the limited surface area and conductivity which will also decrease the practical capacitance. By combining different mechanisms, composites with synergic effects take advantages of both components. Generally, EDL component serves as the scaffold, providing conductive path and high surface area for pseudocapacitance material active layer. As demonstrated by the nanoporous Au electrode with MnO_2 inside the nanopores [27], ultrahigh volumetric of $1160F/cm^3$ was achieved in a thin film of 100nm.

The application of composites in micro supercapacitors ameliorated the performance. $Ni(OH)_2$ embedded in vertical aligned CNT increased the capacity greatly [28]. $Co(OH)_2$ was grown on vertically oriented graphene sheets, though covered only the upper 6μm layer of the 12μm-thick electrodes [29], the capacitance was outstanding.

In our laboratory, to build efficient 3D electrode architecture for high capacity micro supercapacitors, we designed self-supporting electrodes assisted by deep etching. The high and dense electrodes allowed considerable electrode materials to be loaded [5].

Developed from the method, asymmetric supercapacitors with MnO_2-AC configuration [30] was built to increase the capacity by pseudocapacitance and extend the cell potential. Further improvement was then carried out by

Table 2: A summary of pseudocapacitance-based micro supercapacitors

Ref	Electrode material	Property and method	Areal capacitance (mF/cm^2)	Volumetric capacitance (F/cm^3)
[20]	PPy	Electrochemical polymerization	56 (20mV/s)	1.1
[21]	PEDOT	Ink-jet printing	6.4 (20mV/s)	32
[23]	RuO_2	Reactive sputtering and electrodeposition	21.4 (electrode)	N/A
[26]	MnO_2/Au	Electron beam evaporation	N/A	78.6 (electrode)
[29]	RuO_2/graphene	Electrodeposition	1094 (electrode)	N/A
[28]	$Ni(OH)_2$/CNT	Vacuum-assisted electroplating	26.7 (100mV/s)	1.26 (electrode)
[33]	PPy/CMEMS	Electrodeposition	162 (electrode)	N/A
[30]	MnO_2-AC	Asymmetric, self-supporting electrodes	30 (20mV/s)	30

incorporating Li-ion battery electrode to form the asymmetric AC-graphite micro Li-ion capacitor. By utilizing different types of mechanisms, higher capacity and wider voltage range than supercapacitors could be achieved with much higher energy density [31].

Wafer-level Fabrication

Though multiple electrode materials and corresponding routes are summarized in the above sections, the batch fabrication as a feature of microfabrication is another topic.

Photolithography is used to pattern the current collectors and electrodes in much work. However, the direct transformation of patterned photoresist into carbon can be applied as wafer-level photoresist-derived carbon. Positive photoresist films were carbonized with a two-step process consisted of Ar atmosphere carbonization followed by Ar/H_2 activation [32].

Positive photoresist has difficulty in forming high aspect-ratio structure while SU-8 negative photoresist makes it possible. 3D high carbon post arrays could be fabricated with height of tens of micrometers, but the surface area of such carbon posts was limited [33]. To increase the capacitance, growth of PPy as pseudocapacitance material was applied [33].

Summary of State-of-art Micro Supercapacitors

Micro EDL capacitors and pseudocapacitors (including composites and asymmetric supercapacitors) are summarized in *Table 1 and 2*, respectively, listing their electrode materials, fabrication methods and specific capacitances.

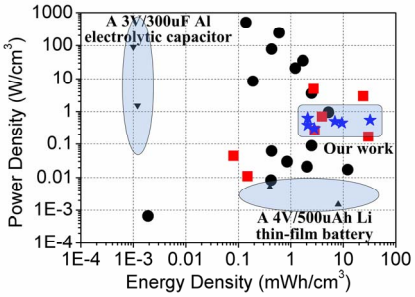

Figure 2: Ragone Plot of state-of-art micro supercapacitors (black circle: EDL capacitors; red rectangle: pseudocapacitors; blue asterisk: our laboratory's work). Data come from plots in references, or calculated by $E=0.5CV^2$ and $P_{average}=E/t$.

A Ragone Plot is shown in Fig. 2, summarizing typical volumetric energy/power density of micro supercapacitors (normalized by the volume of two electrodes). The power density centers around $1W/cm^3$, indicating a $10^{-3}cm^3$ volume for 1mW. Compared with the micro energy harvesters [34], the performance of micro supercapacitors is applicable for applications in receiving the output of harvesters and powering devices and circuits. Ability to light LED and power micro UV sensors has been demonstrated for micro supercapcacitors in some recent papers.

DIRECT PROTOTYPING OF NANOPOROUS MATERIALS

Direct Prototyping of Micro Supercapacitors

To construct porous electrodes with defined patterns by wafer-level fabrication for integration, we proposed a novel concept to synthesis nanoporous materials with 3D micro patterns, as direct prototyping of nanoporous materials. We presented the approach by incorporating templating method into photolithography technique, as shown in Fig. 3 [35]. It achieved wafer-level fabricated materials with high surface area and designable pore size distribution.

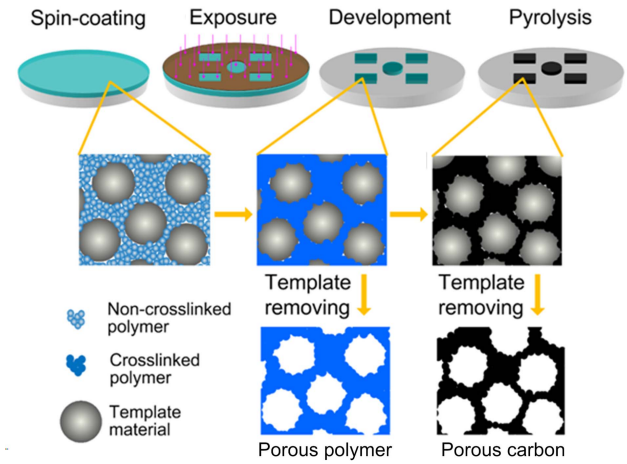

Figure 3: The concept of direct prototyping of nanoporous materials.

The whole wafer and a single cell with patterned porous carbon electrodes are shown in Fig 4(a). The areal capacitances at different scan rates are plotted in Fig. 4(b) and a calculated volumetric capacitance of $12F/cm^3$ at 20mV/s is comparable to the AC-based prototype [5].

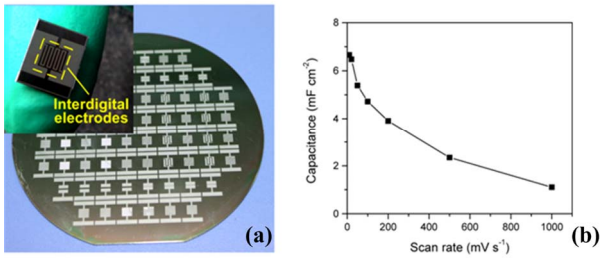

Figure 4: (a) Photographs and (b) specific capacitance of the as-fabricated micro supercapacitors.

Decoration of Pseudocapacitance

Direct prototyping of nanopours carbon established a route from material to on-chip devices, but the EDL mechanism of porous carbon provides limited capacity. Incorporating of pseudocapacitance to build composite is feasible to improve the capacity and the nanoporous carbon is a suitable scaffold for material decoration. We grew nano MnO_2 inside the carbon electrode, shown in Fig. 5(a) [36], as the composite electrodes.

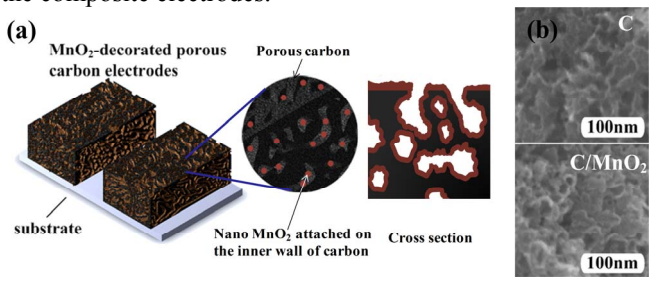

Figure 5: (a) The concept of MnO_2 decorated porous carbon. (b) SEM of porous carbon and C/MnO_2 composite.

To deposit MnO_2 uniformly with considerable mass loaded inside the disordered nanopore network, electrodeposition process was designed by controlling the deposition rate. A comparison of porous carbon and the composite is shown in Fig. 5(b). The volumetric capacitance of composite micro supercapacitor, 44F/cm^3 at 25mV/s, with nearly 90% of initial capacity retained after 10,000 cycles are shown in Fig. 6.

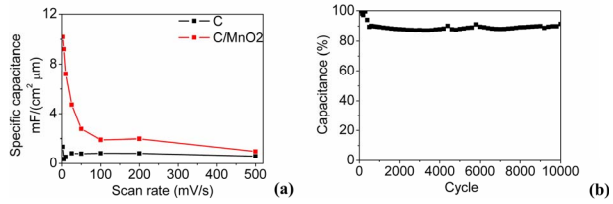

Figure 6: (a) Capacitances of micro supercapacitors with porous carbon and C/MnO_2 composite electrodes. (b) Cycle stability of the C/MnO_2 micro supercapacitor

Silicon-based Anode for Li-ion Batteries

Since Li-ion batteries provide high energy density and the integration of supercapacitor/battery is an efficient design, advanced electrodes for micro Li-ion batteries are important. Silicon as a high-capacity anode material for Li-ion battery shows 4200mAh/g theoretical capacity, however, the over 300% volume change during charge/discharge seriously deteriorates the cycle stability. To relax the stress during cycling and increase the conductivity, we developed the Si/void/C configuration with Si as active material, carbon for conductivity and void for the volume change of Si, as shown in Fig. 7 [37]. SiO_2 sacrificial layer coated Si nanoparticles (SiNPs) were incorporated in the diagram of direct prototyping. After carbonization and removal of SiO_2, the Si/void/C nanocomposite was then constructed.

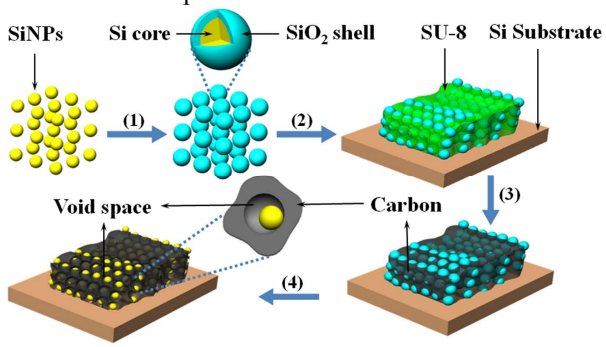

Figure 7: The concept of Si/void/C nanocomposite.

The Si/void/C nanocomposite showed high capacity retention during cycling, while SiNPs and Si/C (composite without the void) lost almost all the capacities after 20 cycles in Fig 8(a). An optimization of Si content in the composite demonstrated that the sample with 60wt% Si achieved the best overall performance, as shown in Fig 8(b).

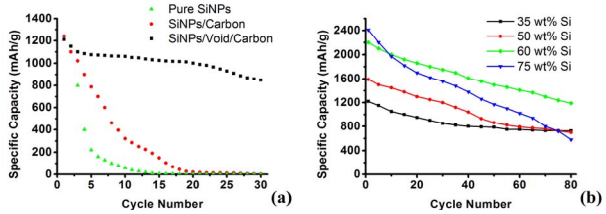

Figure 8: (a) Cycling of Si/void/C compared with SiNPs and Si/C. (b) Cycling of Si/void/C with different Si content.

CONCLUSIONS

In this paper, recent work on micro supercapacitors is reviewed, with device architectures, advanced electrode materials and fabrication technologies as issues of their performance. The direct prototyping of nanoporous materials developed in our laboratory is then demonstrated, showing facile batch fabrication capability and good performance in micro supercapacitors and micro Li-ion batteries.

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