

Manganese Oxides Micro-Supercapacitors with Ultra-high Areal Capacitance

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Experimental Section

Micro electrode fabrication: The fabrication process of a symmetric manganese oxide micro supercapacitor is illustrated in Scheme 1. The electrode pad patterns for contact purpose were fabricated by photolithography and the micro electrode arrays (finger patterns) were fabricated by electron beam lithography.

The photolithography was carried out in a Quintel Q-4000 mask aligner. Briefly, AZ-5214E photo resist was spin-coated on a SiO₂/Si wafer under 3000 rpm for 45 s. After baking on a hot plate at 90 °C for 1 min, it was exposed for 60s (exposure power approximately 14.2 mW cm⁻²) and developed (develop solution: DI water: AZ 400K=3:1) for 40 s. After cleaning and drying, metal electrodes with 10 nm Ti and 120 nm Au were deposited using a Lesker Nano38 thermal evaporator. Electrical contact pads can be retrieved after lift-off processing in acetone. The wafer was cut into small pieces (1 cm × 1.5 cm) for eBL.

To create the micro electrode pattern arrays, PMMA (495 PMMA A4, MicroChem Corp., USA) and PMMA (950 PMMA A3, MicroChem Corp., USA) bilayer resist was spin coated followed by baking at 175 °C for 1 min on a hotplate. The bilayer resist was patterned using a Quanta 600F (FEI Company, USA) equipped with an NPGS lithography system at 30 kV with an area dose of 325 μC cm⁻². The metallization and lift off processes were the same with PL process. The specific parameters of micro electrodes are described in support information Figure S1.

Manganese oxide was electrochemically deposited on micro electrode arrays. Briefly, the electrochemical deposition was carried out in 20 mM Mn(CH₃COO)₂ and 0.1 M NaNO₃ electrolyte. A small anodic current of + 0.5 mA cm⁻² was applied on micro electrode patterns with different time. The samples with different quantity of electrons (Q) of 0.3 C cm⁻², 0.6 C cm⁻² and 0.9 C cm⁻² were labeled as M-0.3C, M-0.6C and M-0.9C respectively.

Structural characterization: X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Scientific ESCALAB 250 Xi spectrometer with a monochromatized Al Kα X-ray source (1486.6 eV) at a constant dwell time of 50 ms and a pass-energy of 50 eV. The X-ray source was run at a power of 300 W. The pressure in the analysis chamber was maintained at 2×10⁻⁸ mbar or lower during each measurement. All the binding energies were referenced to the C 1s hydrocarbon peak at 284.5 eV. Scanning electron microscopy (SEM) was carried out in Quanta 600F system (FEI Company, USA). Atomic force microscopy (AFM) was carried out using tapping mode in a Bruker Dimension Fast Scan AFM in ambient environment.

Electrochemical characterization: The electrochemical tests were conducted in 1M Na₂SO₄ using Autolab PGSTAT 30 potentiostat.

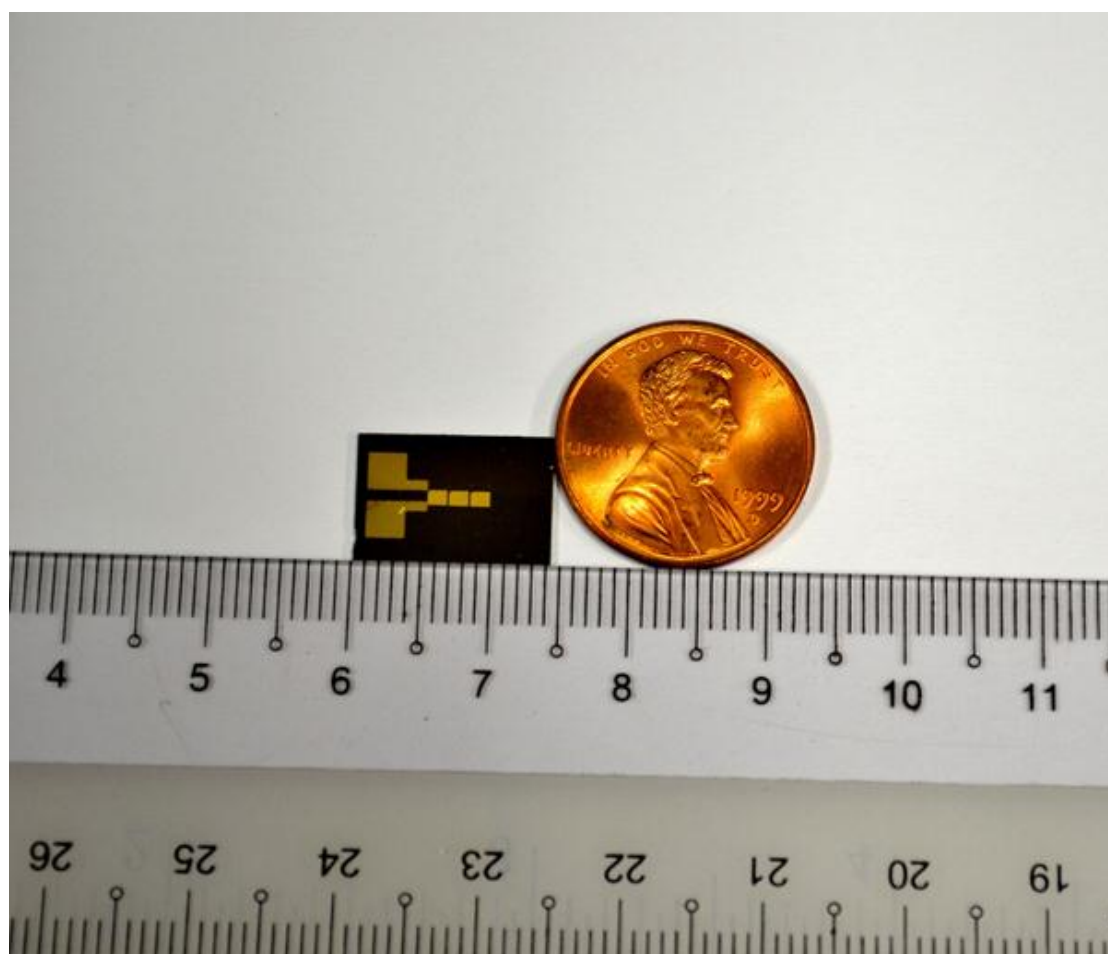


Figure S1. Optical image of electrode pads created by photolithography.

Table S1. Areal capacitance of different samples at a scan rate of 5 mV s⁻¹

Smagle	Areal capacitance mF cm ⁻²
M-0.3C	30.6
M-0.6C	40.7
M-0.9C	47.3

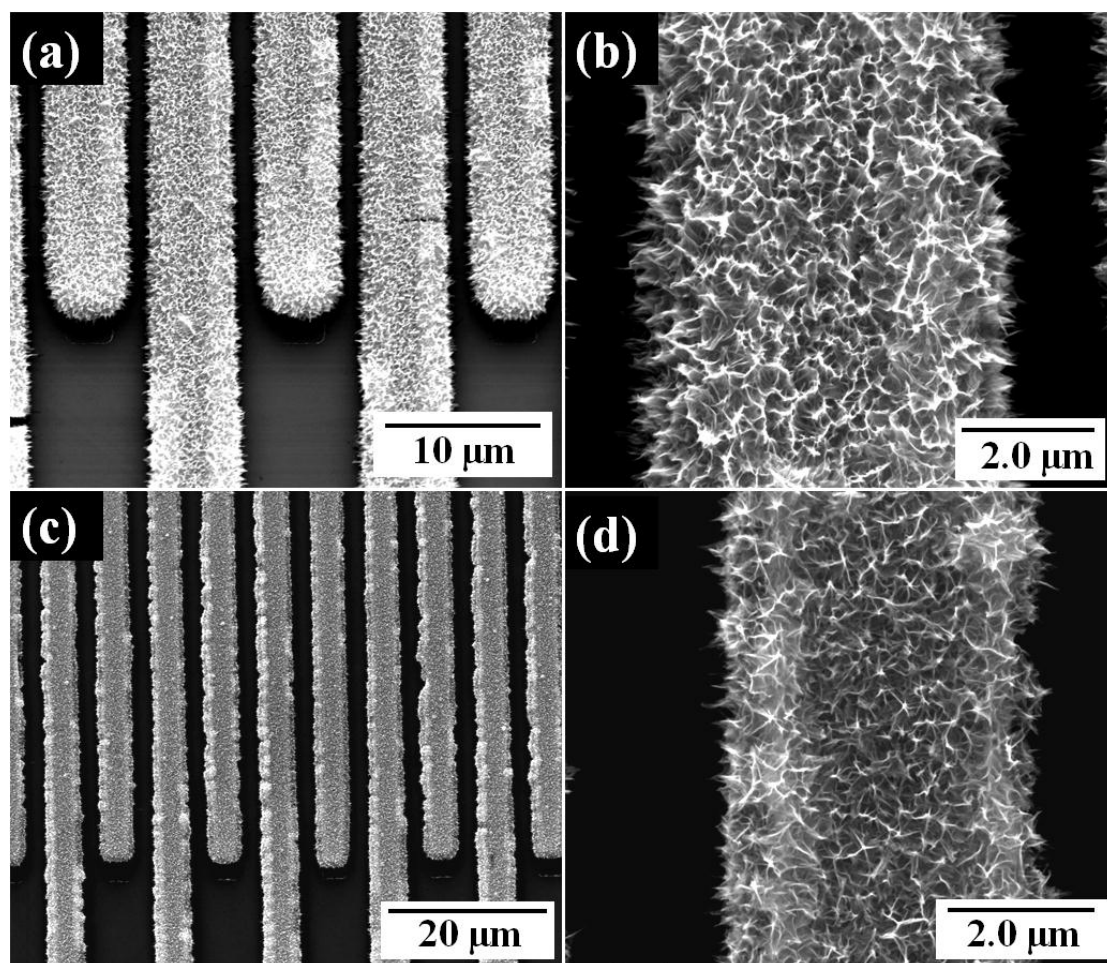
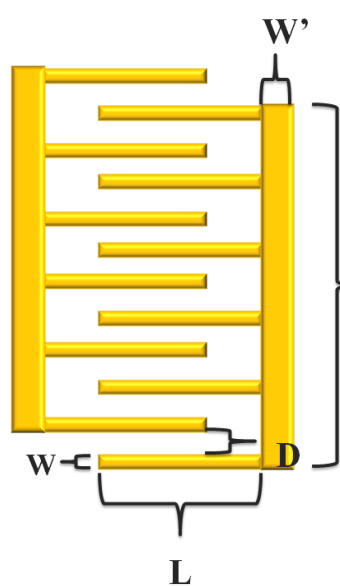


Figure S2. SEM images of (a) and (b) sample MC-0.6C; (c) and (d) sample MC-0.9C.



For Micro supercapacitor Unit:

300 fins

$W = 3 \mu\text{m}$

$W' = 5 \mu\text{m}$

$L = 1000 \mu\text{m}$,

$D = 4 \mu\text{m}$,

Thickness = 130 nm

(10 nm Ti + 120 nm Au)

Area = $1.87 \times 10^{-2} \text{ cm}^2$

Figure S3. Illustration of interdigital structures and their designed parameters.

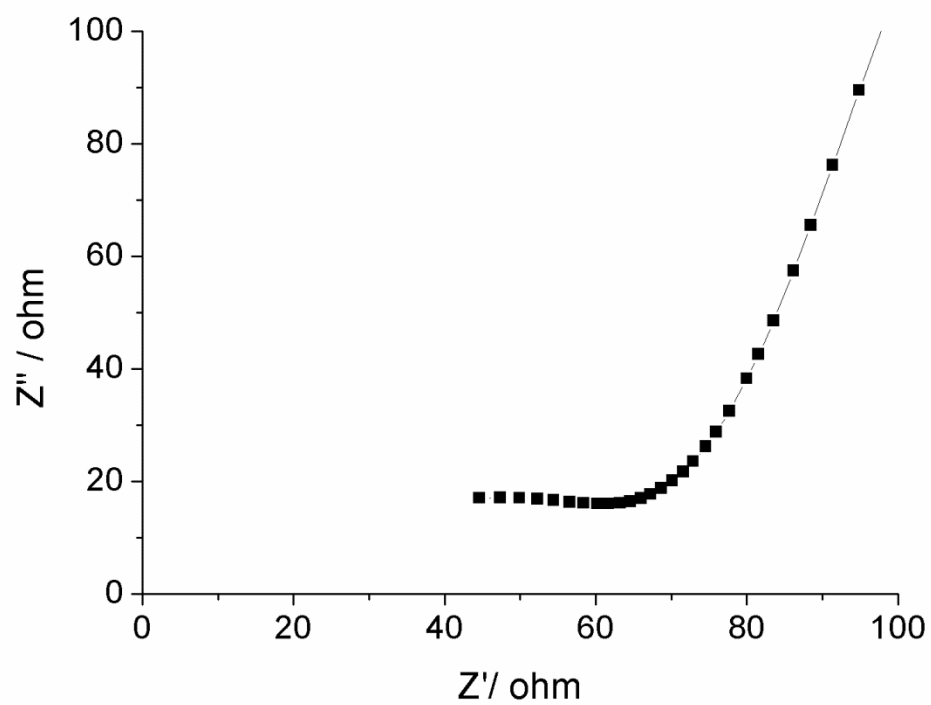


Figure S4. Nyquist plot of electrochemically deposited $\text{Co}(\text{OH})_2$ on micro electrodes.