

Supporting Information

Janus Gold Nanowire Electrode for Stretchable Micro-Supercapacitors with Discriminative Capacitances

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Experimental Section

Materials: Gold (III) chloride hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$), 4-Mercaptobenzoic acid (MBA, 99%), (3-Aminopropyl)trimethoxysilane (APTMS, 97%), sodium citrate dihydrate (99.0%), Sodium borohydride (NaBH_4 , 99.99%), L-ascorbic acid (L-AA, $\geq 99\%$), aniline ($\geq 99.5\%$) were purchased from Sigma Aldrich and used as received without further purification. Gel electrolyte was prepared by mixing PVA (1.0 g, Mw 31000-50000) and H_3PO_4 (1.0 g) in 10 ml of Millipore Milli-Q water and stirring for 6 h at 85 °C to obtain clear gel solution.

Polydimethylsiloxane (PDMS) elastomer base and curing agent (Sylgard 184) were received from Dow Corning. Poly(methyl methacrylate) (PMMA), 950 A6, was purchased from MicroChem Corp. Positive photoresist AZ 1512 and developer AZ 726 MIF were received from Microchemicals GmbH. Bare silicon wafer <100> was purchased from ELECTRONICS AND MATERIALS CORPORATION LIMITED, Japan.

Fabrication of H-MSC and T-MSC: First, a thin PMMA layer was spin-coated on bare silicon wafer at 3000 rpm for 60 s and baked at 180 °C for 3 minutes. For H-MSC, the v-AuNWs were directly grown on PMMA according to previous works with slight modification.^{1,2} In brief, the substrates were treated by air plasma for 5 minutes, immersed in APTMS ethanol solution for two hours and then in gold seeds solution for another two hours. Next, the substrates were attached with an interdigital mask (made by laser-cutting machine) and put into AuNWs growth solution (ethanol/water (v/v = 1:1.2), HAuCl_4 (12 mM), ligand MBA (1.1 mM) and L-AA (30 mM)) for 3.5 minutes. The as-prepared H-MSC was rinsed with ethanol and dried with N_2 .

The synthesis procedure for T-MSC was based on the photolithography and PDMS transfer processes from our previous work.³ AZ 1512 photoresist was spin-coated on the wafer/PMMA at 3000 rpm for 45 s with SUSS Delta 90 spinner, and electrodes patterns were formed via conventional photolithography process (MA6, SUSS). After spin-coating, the resist was prebaked at 110 °C for 2 minutes. Then the resist was exposed under 350 W UV for 5 s. After exposure, the substrate was immersed in developer solution (MIF 726) for 60 s and then rinsed by DI water and dried by N_2 flow. After the photolithography process, the substrates were bake at 160 °C for 10 minutes and followed the same v-AuNWs growth process as described above. Finally, PDMS base and curing agent were mixed (w/w = 10:1) and spin-coated on the substrates with AuNWs at 500 rpm for 60 s. After curing at 60 °C for 4 h, the PDMS was sectioned with scalpel and peeled off. Thus the patterned v-AuNWs were transferred to PDMS film and worked as stretchable T-MSC.

Polyaniline (PANI) networks deposition was conducted through an electro-polymerization of aniline at potential of 0.8 V for 20 minutes in an aqueous solution of aniline (0.1 M) and H_2SO_4

(1 M) where KCl-saturated Ag/AgCl served as reference electrode and platinum wire as the counter electrode.

Characterization: SEM images were obtained using a FEI Helios Nanolab 600 FIB (focus-ion beam)-SEM. The plasma treatment was conducted in a Harrick plasma cleaner at pressure of 500 Pa. Stretching tests were performed using a motorized moving stages (Thorlabs Model LTS150/M). The electrochemical performances of supercapacitors were recorded by the Parstat 2273 electrochemical system (Princeton Applied Research).

The areal specific capacitances C_s were calculated from CV curves by equations as below:

$$C_s = \frac{\int idV}{2v\Delta VS}$$

where v is the scan rate, S is the electrode area, ΔV is the potential window (i.e., 0.8V), I is the discharging current.

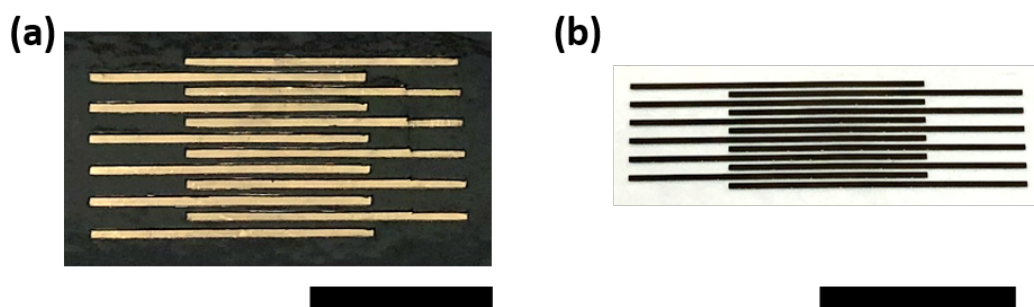


Figure S1. (a) Digital photograph of as-prepared H-MSC (active electrode area 0.48 cm^2); (b) Digital photograph of as-prepared T-MSC (active electrode area 0.36 cm^2). The scale bars in the photographs are 1 cm.

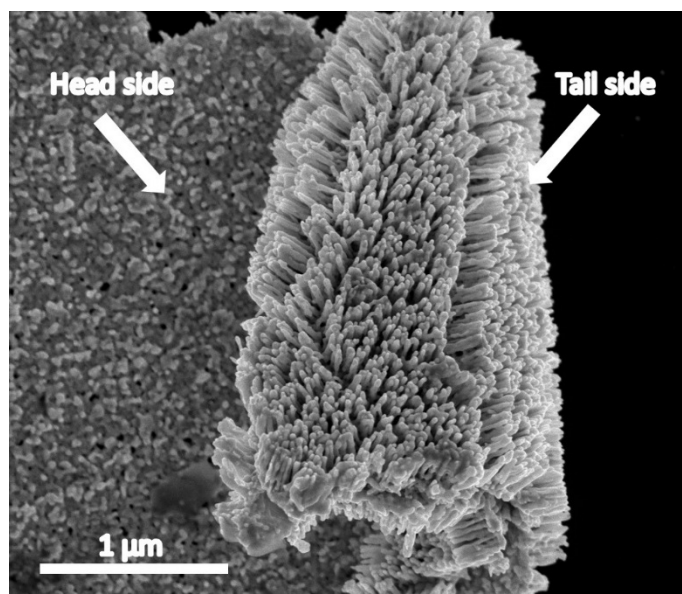


Figure S2. Overall SEM image of soft Janus v-AuNW film with both head and tail sides exposed.

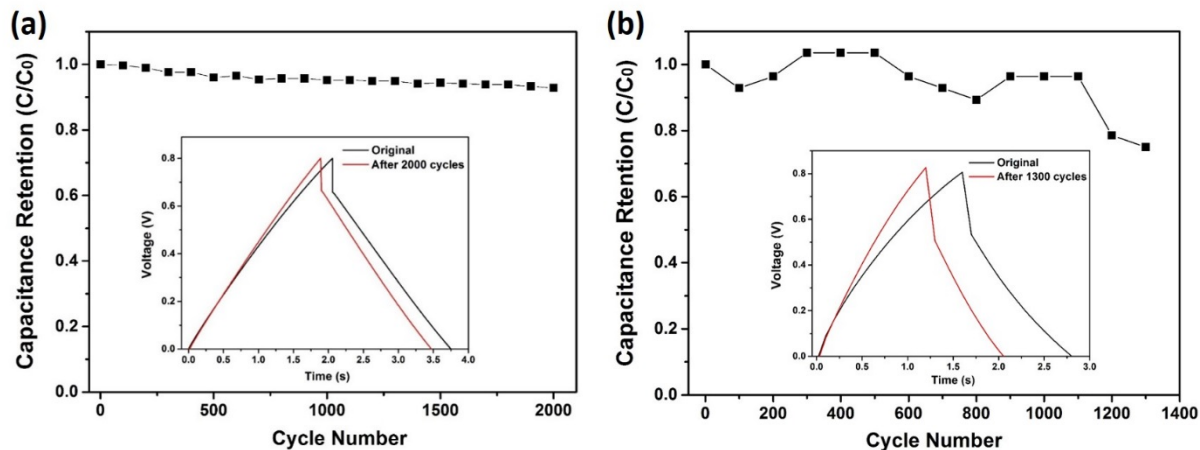


Figure S3. Cycling stability of H-MSC and T-MSC with GCD tests at current density of $13.89 \mu\text{A}/\text{cm}^2$. (a) T-MSC: capacitance retention of 92.8% after 2000 cycles of charge-discharge cycles; (b) H-MSC: capacitance retention of less than 80% after 1200 cycles of charge-discharge cycles.

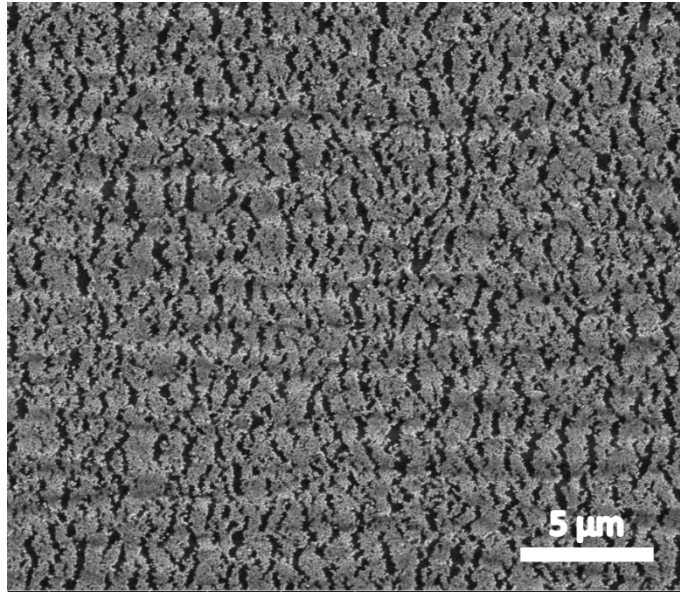


Figure S4. SEM image of the uniform crack structures of v-AuNWs film under 100% of stretching strain.

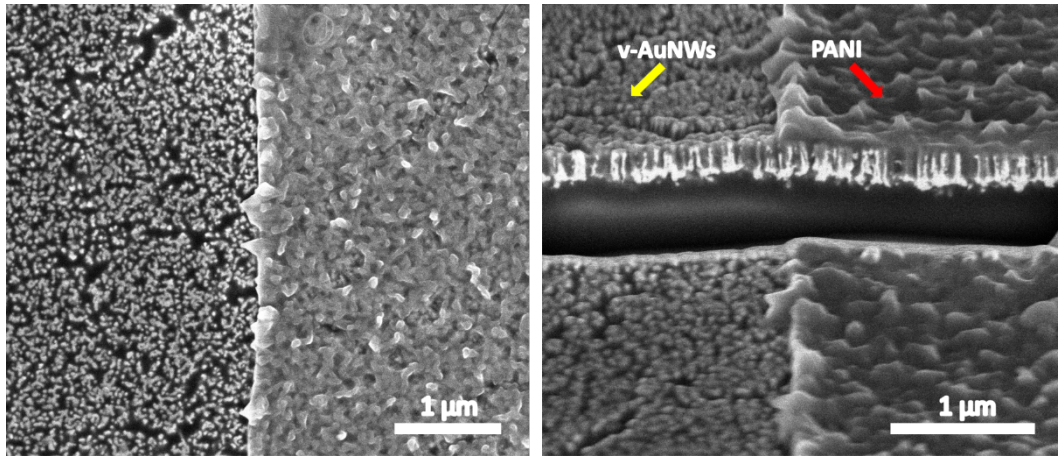


Figure S5. SEM images of v-AuNW@PANI film with 20 min of electrodeposition (left: top view; right: cross-sectional view), the yellow and red arrows indicate the v-AuNWs and PANI respectively.

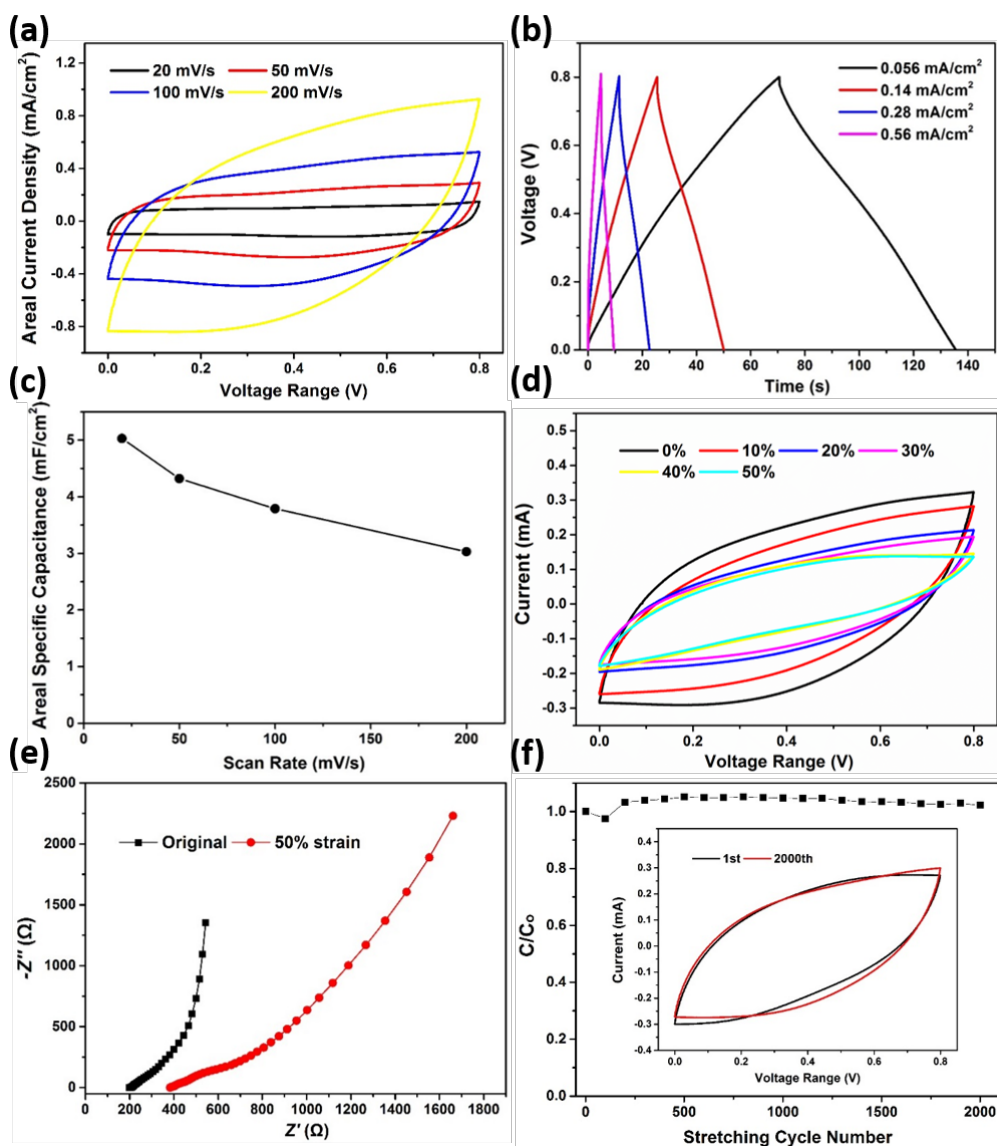


Figure S6. Electrochemical performances of T-MSC with 20 mins of PANI electrodeposition. (a) CV curves; (b) GCD curves; (c) Areal specific capacitances calculated from CV curves; (d) CV curves under different stretching strain from 0% to 50%; (e) EIS spectrum under stretching strain of 0% and 50%; (f) The capacitance retention under repeated stretching cycles (50% strain). The inset shows CV curves before and after 2000 stretching cycles.

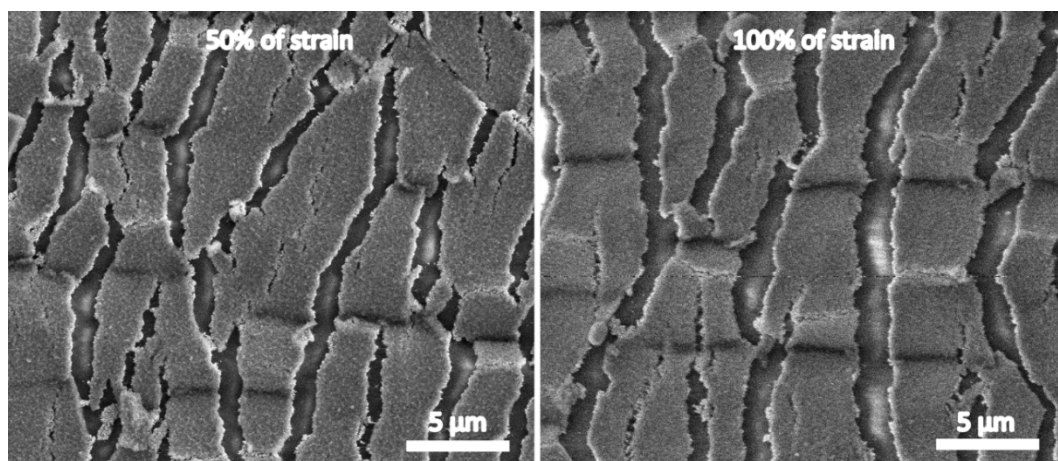


Figure S7. SEM images of v-AuNW/PANI film under 50% (left) and 100% (right) of stretching strain with large cracks.

Table 1. Stretchable Micro-supercapacitor Comparison

Materials	Design	Stretchability	Reference
Au/SWCNT	Serpentine interconnections	30%	4
Liquid metal MWNT/Mn ₃ O ₄	Island-bridge heterogeneous structure	40%	5
Liquid metal/MWNT	Island-bridge	100%	6
Liquid metal/Graphene	Suspended wavy designs	100%	7
v-AuNWs	Intrinsically stretchable	110%	Our work

References

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