Supporting Information

PEDOT Engineered Bi_2O_3 Nanosheet Arrays for Flexible Asymmetric Supercapacitors with Boosted Energy Density

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Summary

Experimental Section

Synthesis of CC/Bi_2O_3@PEDOT negative electrode

Specifically, prior to the growth of Bi_2O_3, CC was activated in concentrated H_2SO_4 and HNO_3 mixture (V_{H2SO4}: V_{HNO3}= 3:1) for 6 hours, and then washed with de-ionized water, acetone and alcohol to remove the acid and organic impurities. Subsequently, a piece of activated CC (3*2 cm) was immersed into the solution consist of 0.97 g $Bi(NO_3)_3$, 24 mL alcohol and 12 mL ethylene glycol, stirring for 30 min. Then, the mixture was transferred into the stainless autoclave and heated at 160 ℃ for 5 h. Finally, the CC/Bi_2O_3 NAs were obtained after thoroughly washing in alcohol and de-ionized water and finally drying in 60℃ oven. The mass loading of Bi_2O_3 is calculated around 1.55 mg cm^{-2}. To construct CC/Bi_2O_3@PEDOT NAs, a piece of CC/Bi_2O_3 (1*1.2 cm) was immersed in a cell containing 0.01 M EDOT, 0.03 M SDS and 0.07 M $LiClO_4$. Then, electrodepositions were further conducted at 1 V potentiostatic mode with Ag/AgCl as reference electrode for various durations (300 s, 500 s and 800 s). As contrast, CC/Bi_2O_3 that handled with 1 V potentiostatic deposition in the electrolyte of 0.03 M SDS and 0.07 M $LiClO_4$ was conducted. Additionally, CC/Bi_2O_3@rGO electrode was fabricated by immersing CC/Bi_2O_3 in 0.5 mg mL^{-1} GO aqueous for 5 min and subsequently reduced by N_2H_4 vapor.

Synthesis of $NiMoO_4$/CC positive electrode

A piece of activated CC was immersed into a mixture containing 0.24 g $NiCl_2$, 0.24 g $NaMoO_4$ and 0.3 g urea, continuously stirring for 30 min. Then the solution was transfer to a 50 mL stainless autoclave and heated at 150 ℃ for 8 h. After naturally cooling to room temperature, the CC was washed with de-ionized water and alcohol to remove remaining impurities, and then dried in air. Finally, $NiMoO_4$/CC electrode was obtained after vacuum annealing at 450℃ for 2h.

Materials characterization

As-prepared samples were characterized by X-ray diffraction (XRD) with Cu Kα radiation source (λ = 1.5406 Å), field-emission scanning electron microscopy (FE-SEM,

JEOL-6701F) with energy dispersive X-ray spectroscopy (EDS, Oxford), transmission electron microscopy (TEM, JEOL-2010), high resolution TEM (HRTEM, JEOL-2010), Raman spectroscopy (RTS-HiR-AM, λ= 532 nm) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi).

Electrochemical evaluations

For the capacitance evaluations, all electrochemical measurements were performed in 1 M KOH solution with platinum foils as the counter electrode and Hg/HgO as the reference electrode, respectively. CC/Bi_2O_3 and CC/Bi_2O_3@PEDOT (300 s, 500 s and 800 s) NAs with operational area of 1 cm^2 were directly utilized as the working electrodes. Electrochemical workstation (CH Instruments, CHI760e) was utilized for cyclic-voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge tests. EIS was recorded with AC voltage amplitude of 5 mV and a frequency range from 100 kHz to 0.01 Hz. Investigations on galvanostatic charge/discharge were carried out from -1.1 V to -0.2 V at 1, 2, 4, 8 and 16 mA cm^{-2}, respectively.

Capacitance(Cs), energy density (E) and power density (P) were calculated according to the following equations:

$$Cs=\frac{\int I\,dV}{vm\Delta V} \qquad or \qquad Cs=\frac{\int I\,dV}{vS\Delta V}$$

where I (A), v (V s^{-1}), ΔV (V), m (g) and S (cm^2) are corresponding to response current, scan rate, potential window, the mass of active material and the effective electrode area, respectively.

$$Cs=\frac{I\Delta t}{S\Delta V}$$

where I is the discharge current, Δt is the discharge time, ΔE is the potential window during the discharge process and S is the effective electrode area.

$$E=\frac{CV^2}{2U}$$

$$P=\frac{E}{t}$$

Where C is total capacitance of the device, V is the cell voltage, U is the device volume, and t is the dischargetime.

ASC device assembly

CC/$NiMoO_4$ and CC/Bi_2O_3@PEDOT (500 s) were selected as the positive and negative electrodes respectively to assemble the asymmetric device. PVA/KOH electrolyte was prepared with 6 g PVA, 6g KOH and 60 mL de-ionized water and kept on stirring at 85℃ for 3 h. As-prepared PVA/KOH electrolyte was evenly pasted onto the CC/$NiMoO_4$ and CC/Bi_2O_3@PEDOT NAs electrodes respectively and dried at room temperature. Finally, the two dried electrodes were stacked together with a piece of filter in-between

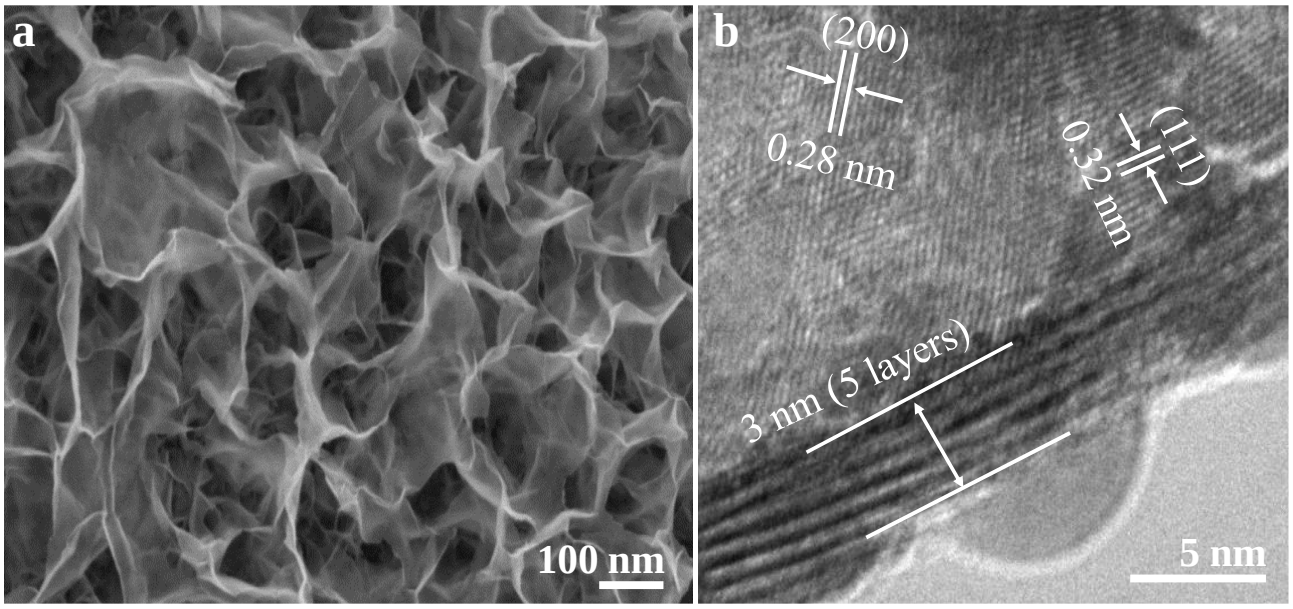

Fig. S1 (a) Amplified SEM image of ultrathin CC/Bi_2O_3 nanosheets with vertical orientation and interconnected network structure. (b) HRTEM image of CC/Bi_2O_3 with lattice fringes of 0.28 nm and 0.32 nm, corresponding to the facets of (200) and (111), respectively.

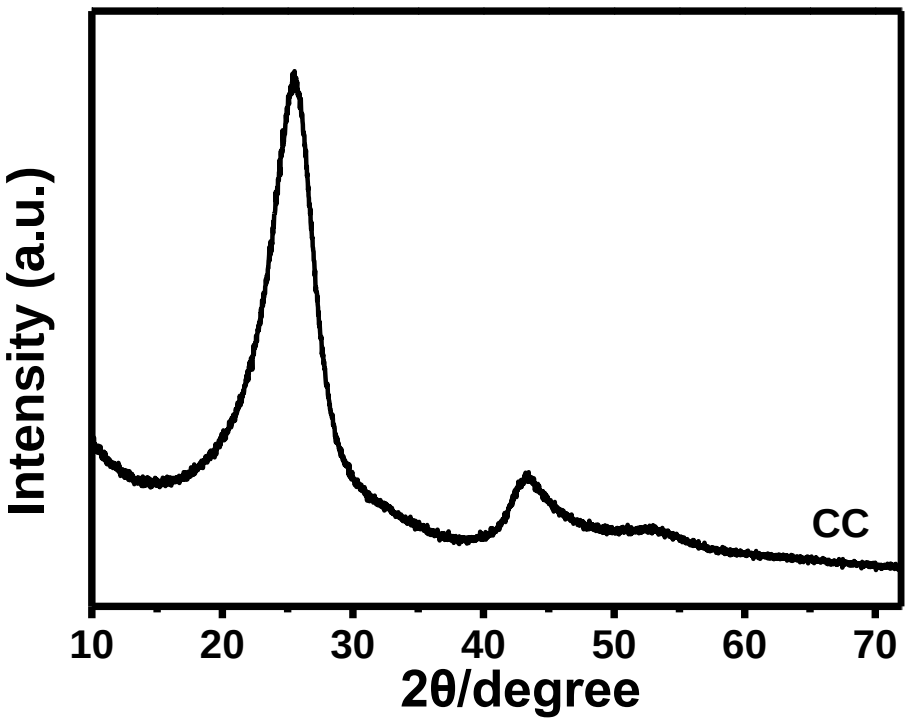

Fig. S2 XRD pattern of pristine carbon cloth (CC) with two diffraction peaks located at 25° and 43°, respectively.

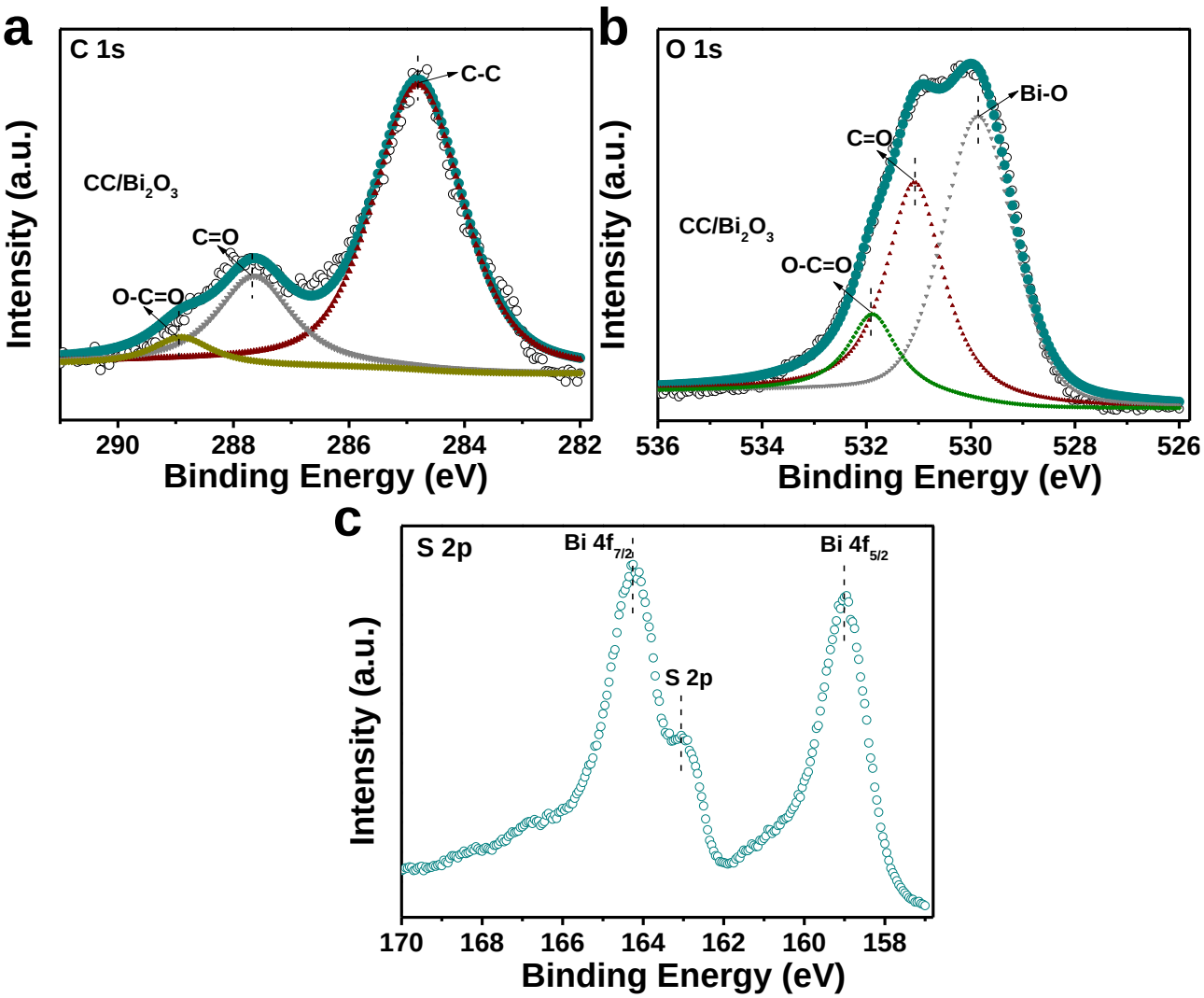

Fig. S3 (a)C 1s high –resolution spectra of CC/Bi_2O_3 with three fitting peaks (O-C=O, C=O and C-C). (b) O 1s high –resolution spectra of CC/Bi_2O_3 with three fitting peaks (O-C=O, C=O and Bi-O). (c) S 2p high –resolution spectrum of CC/Bi_2O_3@PEDOT (500 s) with two Bi 4f peaks and S 2p peak.

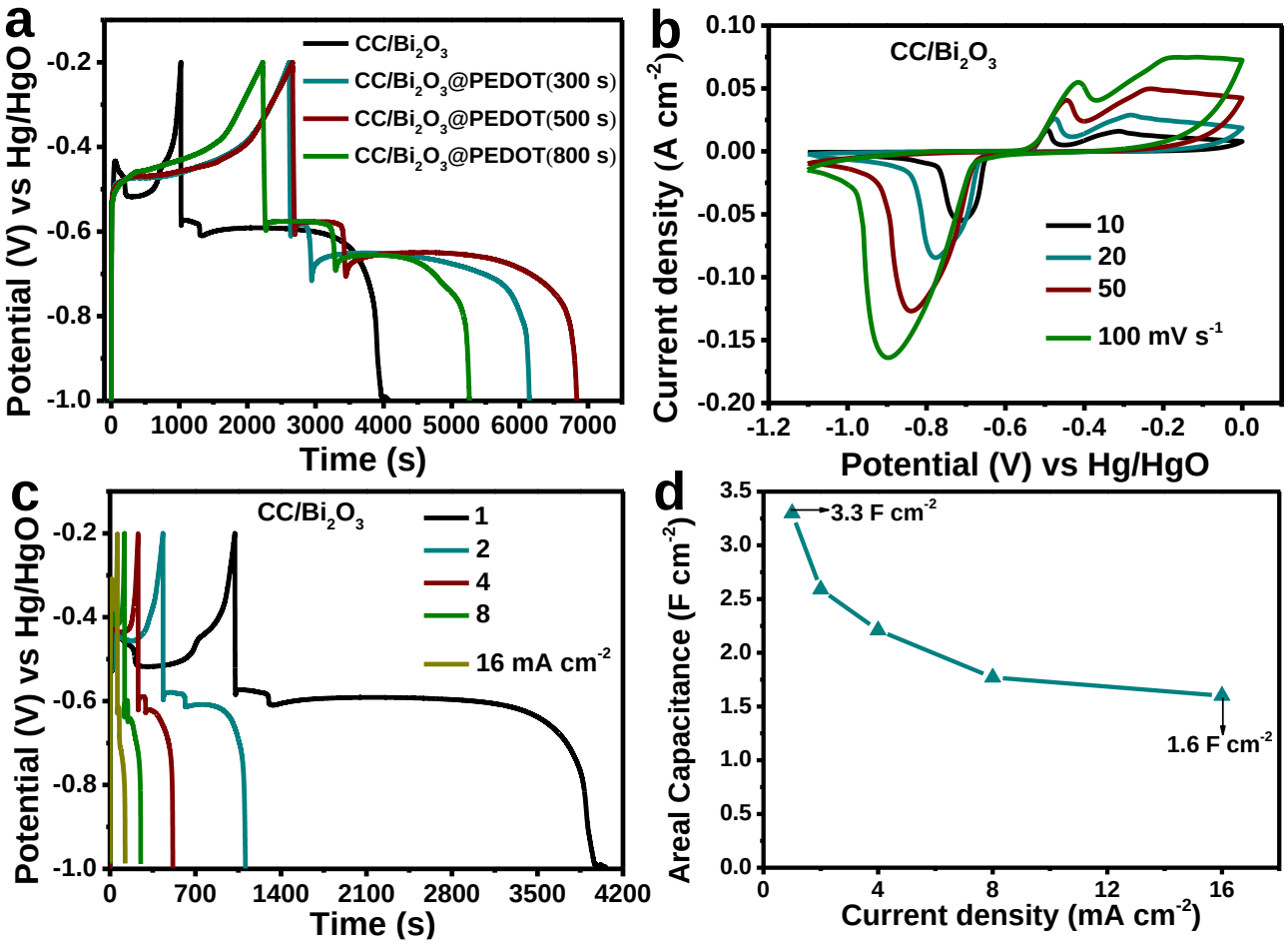

Fig. S4 (a) Galvanostatic charge/discharge of CC/Bi_2O_3 and CC/Bi_2O_3@PEDOT (300 s, 500 s, 800 s) at current density of 1 mA cm^{-2}. (b) CV curves of CC/Bi_2O_3 at various scanning rate (from 10 to 100 mV s^{-1}) at voltage window of-1.1 V -0 V. (c) GCD of CC/Bi_2O_3 at various current densities (from 1 to 16 mA cm^{-2}) at voltage window of -1.1 V to -0 .2 V. (d) Rate performance of CC/Bi_2O_3@PEDOT (500 s) with various current densities (from 1 to 16 mA cm^{-2}).

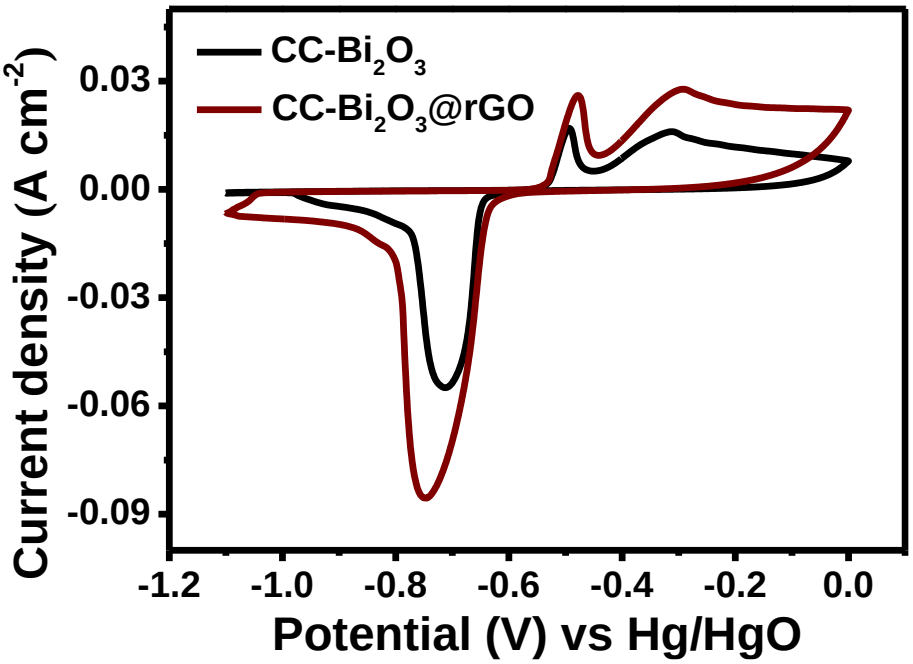

Fig. S5 CV curves comparison between CC/Bi_2O_3 and CC/Bi_2O_3@rGO at scanning rate of 10 mV s^{-1}.

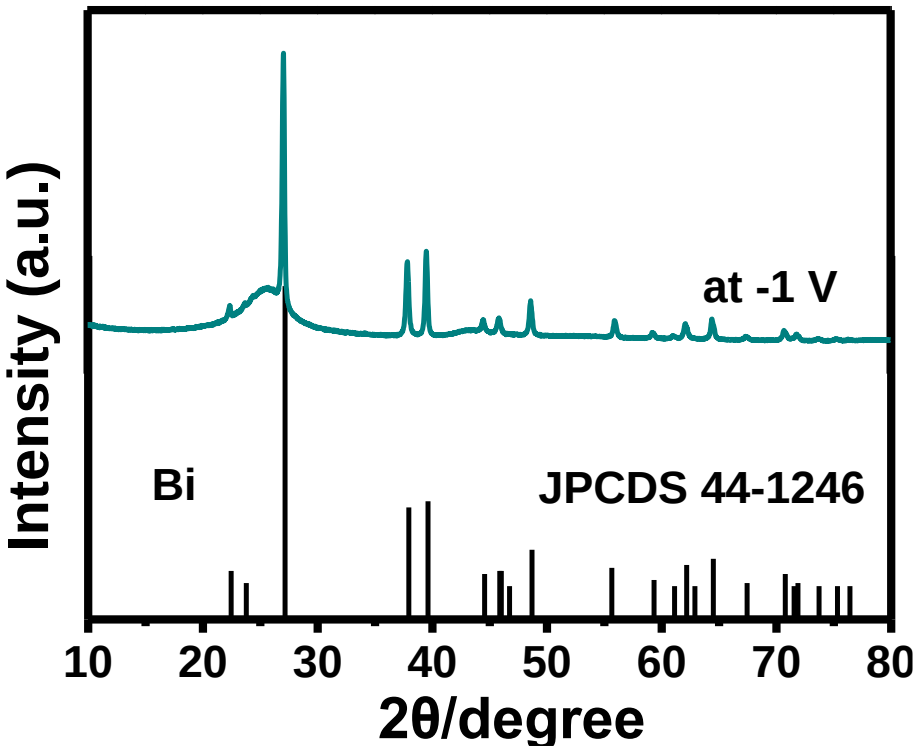

Fig. S6 XRD patterns of CC/Bi_2O_3@PEDOT (500 s) measured at -1 V and 0 V after 100 CV cycles.

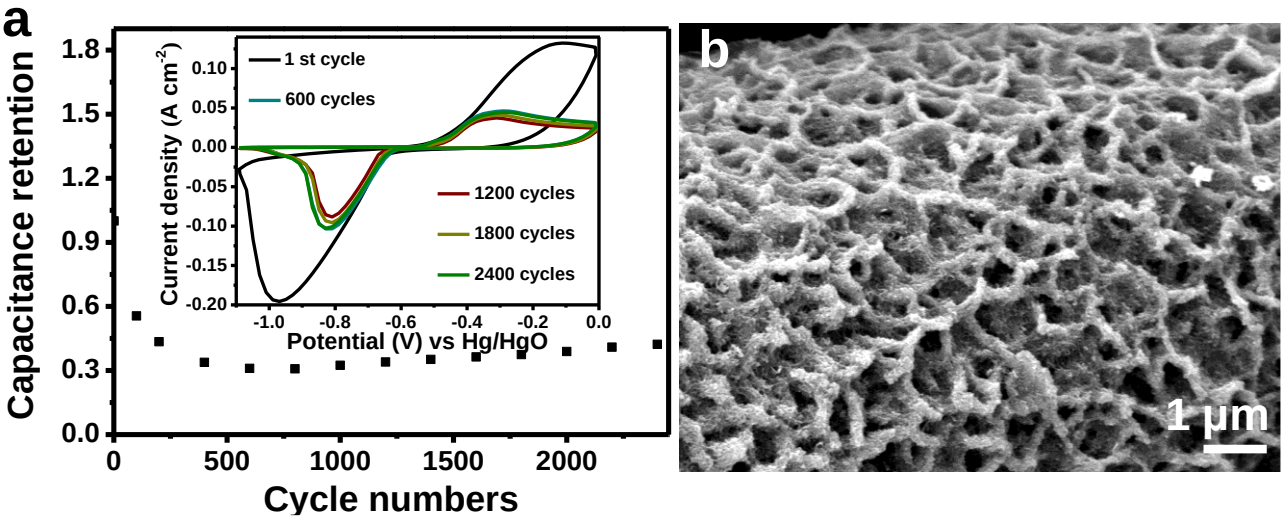

Fig. S7 (a) 2400 cycles stability of CC/Bi_2O_3@PEDOT (500 s) scanned at rate of 100 mV s^{-1}. The inset is the CV curves that scanned at cycles of 1, 600, 1200, 1800 and 2400, respectively. (b) SEM image of CC/Bi_2O_3@PEDOT (500 s) NAs after 2400 CV cycles that scanned at 100 mV s^{-1}.

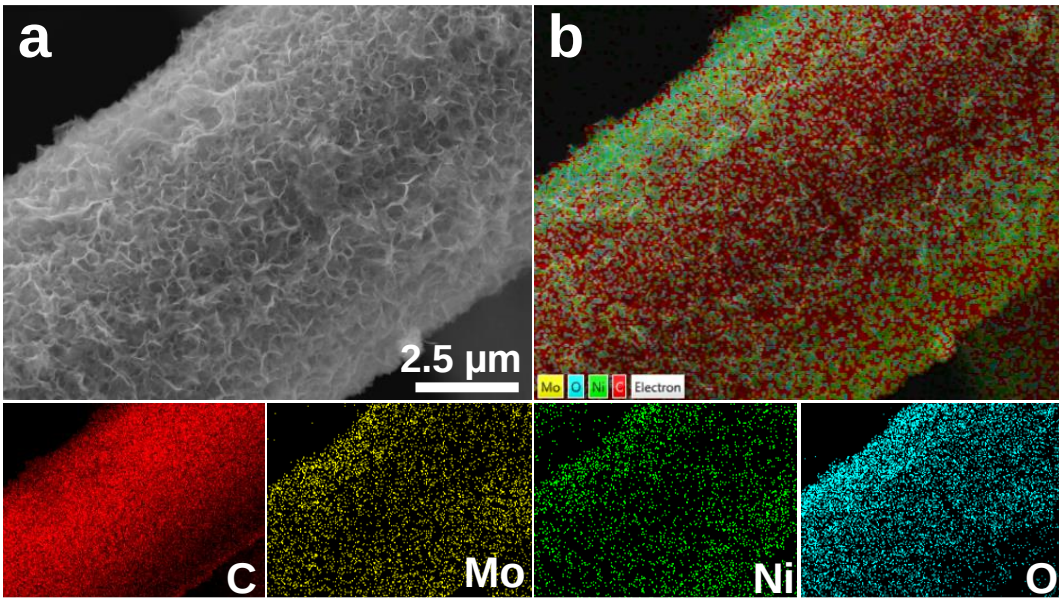

Fig. S8 (a) SEM image and the corresponding EDS mapping (b) of $NiMoO_4$ vertical on CC.

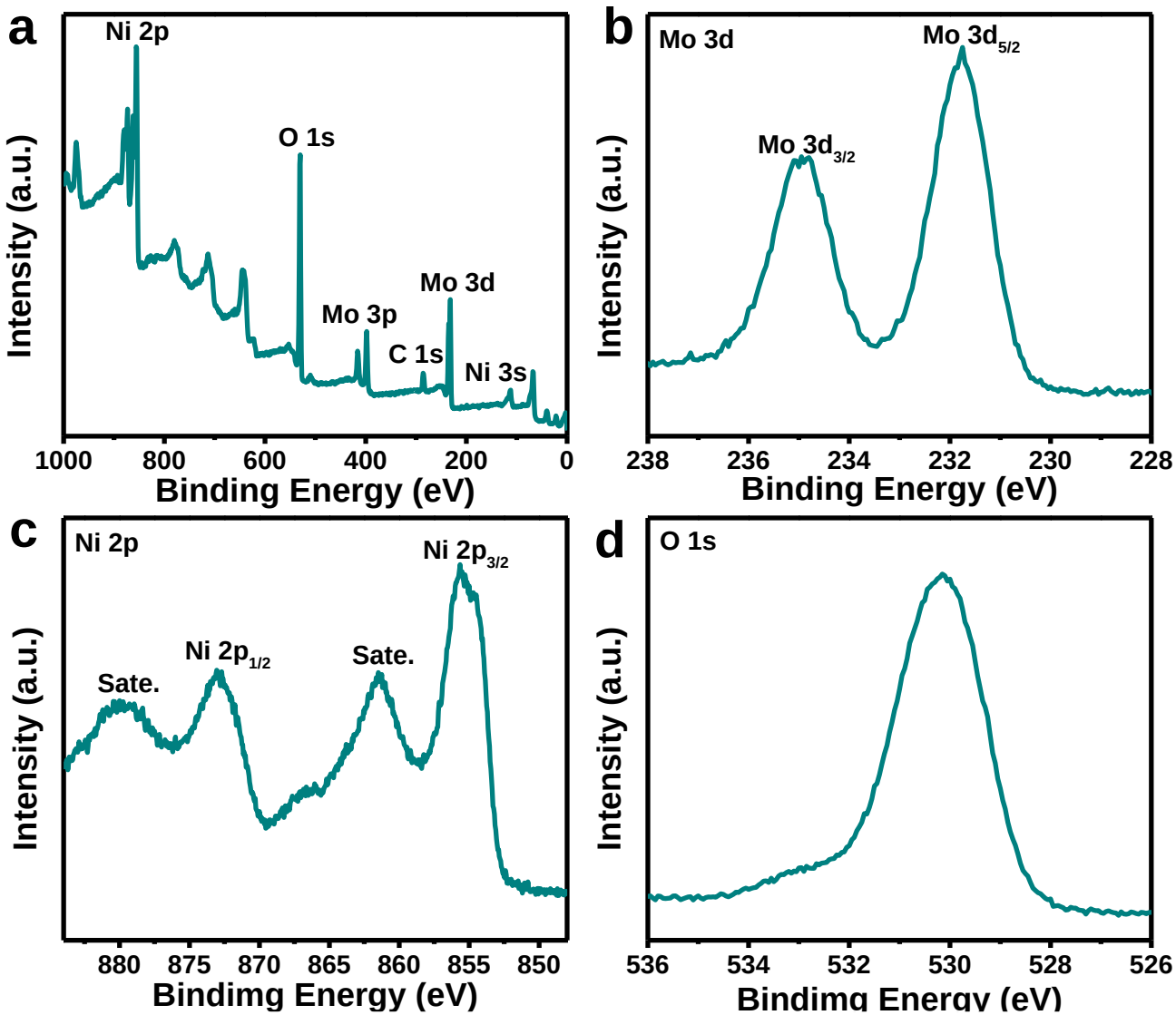

Fig. S9 XPS of CC/$NiMoO_4$ NAs positive electrode, (a) survey spectrum, (b) Mo 3d high-revolution spectrum, (c) Ni 2p high-revolution spectrum, (d) O 1s high-revolution spectrum.

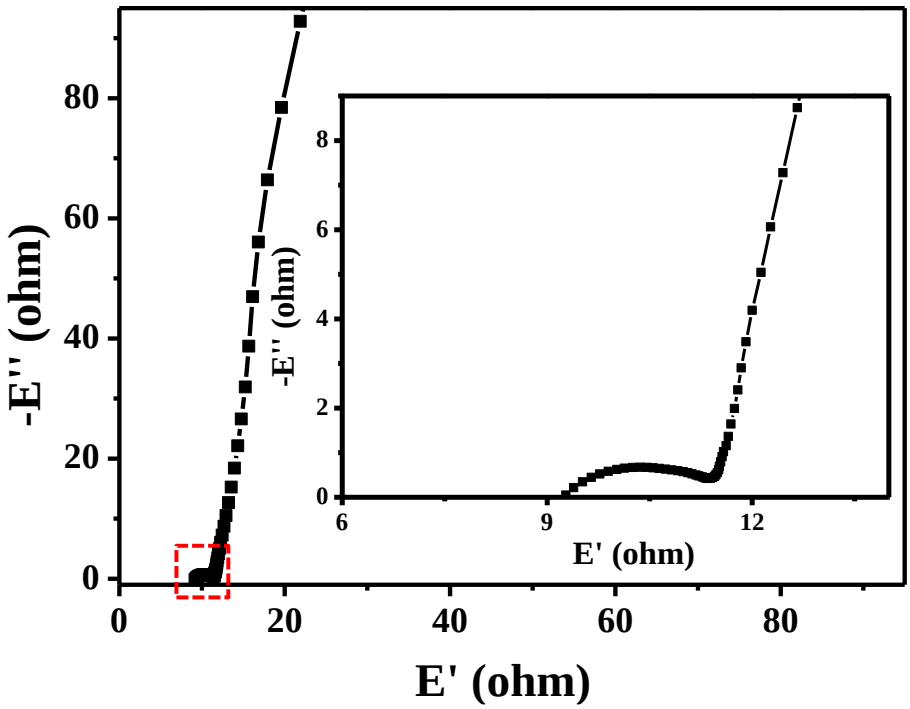

Fig. S10 EIS plots of as-assembled CC/$NiMoO_4$ and CC/Bi_2O_3@PEDOT (500 s) ASC device with frequency ranged from 0.01Hz to 100000 Hz. The inset is the corresponding amplified portion that marked in red.

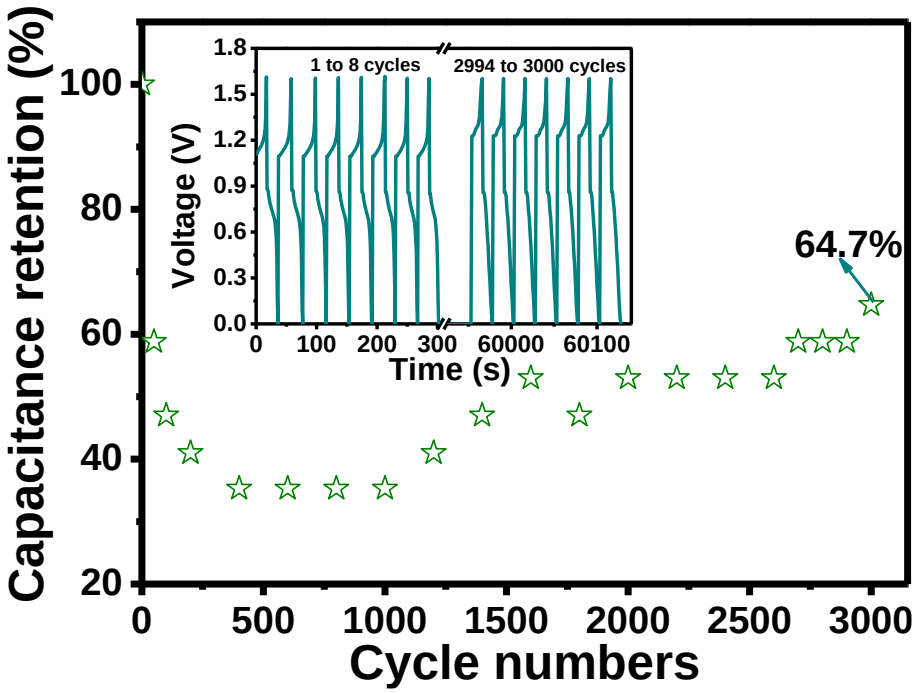

Fig. S11 GCD stability (3000 cycles) of as-assembled ASC device measured at current density of 8 mA cm^{-2}. The inset is the corresponding GCD curve of the 1 to 8 cycles and 2994 to 3000 cycles, respectively.

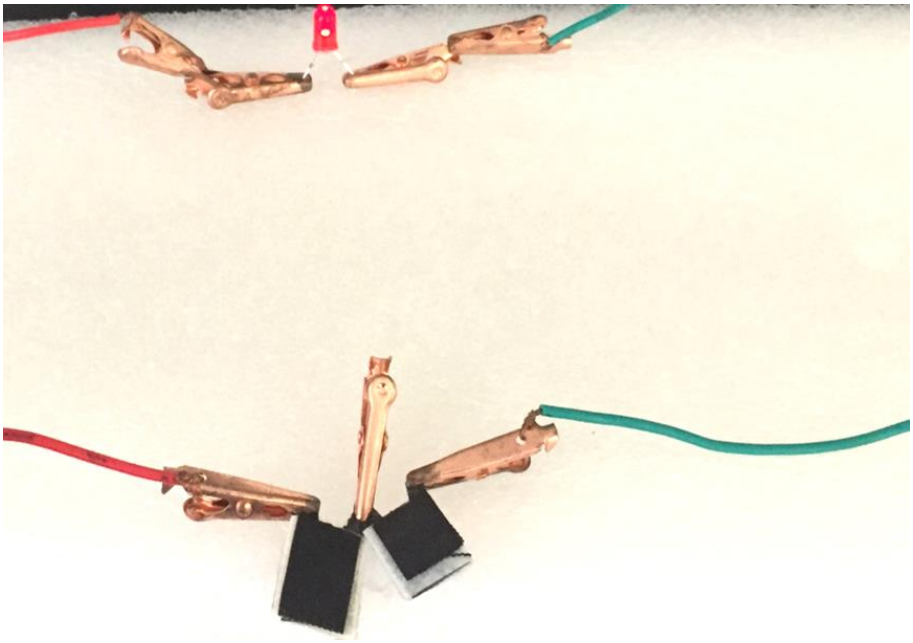

Fig. S12 Practical application of two assembled ASC device in series to power a red LED light.

Table 1 Recent Bi_2O_3-based negative electrodes and their specific or areal capacitance under various current densities.

Electrode materials	Specific/areal capacitence	Current density	Ref.
Bi_2O_3 on Ni foam	557 F g^{-1}	1 Ag^{-1}	[1]
Bi_2O_3 on ESCNF	783 mF cm^{-2}	5 mV s^{-1}	[2]
Bi_2O_3/AC	466 Fg^{-1}	1 Ag^{-1}	[3]
Bi_2O_3/AC	332.6 F g^{-1}	1 A g^{-1}	[4]
Bi_2O_3 NTs- graphene	69.3 mF cm^{-2}	0.1 mA cm^{-2}	[5]
Bi_2O_3 nanorods	1350 F g^{-1}	0.1 A g^{-1}	[6]
3D hierarchical Bi_2O_3	832 F g^{-1}	1 A g^{-1}	[7]
Rod-like Bi_2O_3 nanoparticles	528 F g^{-1}	5 mV s^{-1}	[8]
Flower-like Bi_2O_3	545 mF cm^{-2}	3 mA cm^{-2}	[9]
CC/Bi_2O_3/PEDOT	1700 mF cm^{-2}	10 mV s^{-1}	This work
CC/Bi_2O_3/PEDOT	1096 F g^{-1}	10 mV s^{-1}	This work

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