Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Stackable, Three Dimensional Carbon-Metal Oxide Composite for High Performance Supercapacitors

Joo Hyun Kim [a,§], Sangkyu Lee [b,§], Junghyun Choi [a], Taeseup Song [c], and Ungyu Paik [a*]

[a]*Department of Energy Engineering, Hanyang University, Seoul 133-791, Korea*

[b]*Department of Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea*

[c]*School of Materials Science and Engineering, Yeungnam University, Gyeongsan 712-749, Korea*

[§]Both authors contributed equally to this work.

[*]Corresponding Authors

Prof. Ungyu Paik (U. Paik)

E-mail: upaik@hanyang.ac.kr, Tel: +82-2-2220-0502

Experimental Section

Preparation of GO-CNT film: GOs were prepared from natural graphite (APS 7-11 μm, 99%, Alfa Aesar) using modified Hummer's method. An adequate amount of sodium dodecyl sulphate (SDS, ACS reagent, 99.0 %, Sigma-Aldrich) was dissolved in the de-ionized water (DI water) to prepare 5 wt% of stock solution. 3 mg of GO and 3 mg of CNTs (Single-walled carbon nanotube, Cheaptube Inc.) were dispersed in the SDS stock solution using a direct tip sonication for 30 min. In order to remove any bundled CNTs and agglomerates, the suspension of GO and CNT was centrifuged at 2,000 rpm for 15 min and the resulting supernatant was filtered through a poly(tetrafluoroethylene) membrane (pore size : 0.2 μm, Hyundai Micro). The filter cake consisted of GO and CNT was rinsed with a copious of DI water to remove residual SDS thoroughly. Finally, the film was dried in a fume hood for at least 6 hr to produce a freestanding film of GO-CNT.

Synthesis of NiO nanowalls on RGO-CNT film: 1.24 g of nickel acetate tetrahydrate (99.998 % trace metals basis, Sigma-Aldrich), 0.37 g of ammonium fluoride (ACS reagent, ≥ 98.0 %, Sigma-Aldrich), and 1.5 g of urea (ACS reagent, 99.0-100.5 %, Sigma-Aldrich) were dissolved in 46.9 ml of DI water to prepare the precursor solution for NiO nanowalls. The freestanding film of GO-CNT was cut into 1.2 cm by 3 cm pieces and then transferred into 100 mL Teflon-lined stainless steel autoclave containing the precursor solution. Hydrothermal reaction was conducted at 130 ^{o}C for 4 hr to prepare $Ni_2(OH)_2CO_3$ nullaginite nanowalls. After cooling down to room temperature, the film was washed with DI water and then dried in the hume hood. Nullaginite nanowalls were annealed at 500 ^{o}C for 2 hr in a nitrogen atmosphere to form NiO crystal phase.

Coating of NiO nanowalls with PPy: 0.4 mL of pyrrole monomer was dissolved in 66 mL of DI water. The RGO-CNT film containing NiO nanowalls was dipped into the pyrrole solution for 30 min. 0.26 g of ammonium persulfate was dissolved in 50 mL of DI water. The aqueous solution of ammonium persulfate was slowly dropped into the pyrrole solution with a magnetic stirring. The reaction between pyrrole monomer and ammonium persulfate was allowed to maintain for 4 hr, followed by washing process with DI water. Finally, a layer of PPy was successfully coated on the surface of NiO nanowalls. The photo images of each electrodes (GO, $Ni_2(OH_2)CO_3$, NiO, Ppy-coated NiO) were shown in Fig. S10(a).

Fabrication of all-solid-state electrochemical capacitors: 6 g of poly(vinyl alcohol) (PVA, Mw 89,000 - 98,000, 99+ % hydrolyzed, Sigma-Aldrich) and 4.5 g of potassium hydroxide (KOH, pellet 93%, Daejung Chemicals & Metals) were dissolved in 60 mL of DI water at 90 ^oC for 1 hr. PPy-coated NiO nanowalls on RGO-CNT film was dipped into the PVA-KOH gel electrolyte solution leaving a small part of the film which acts as a current collector. The region, which is covered by active materials, of electrodes was overlapped and then pressed with a uniaxial pressing machine to provide uniform contact. Silver paste was applied on the exposed RGO-CNT part of the electrode film for the electrical contact between electrochemical capacitors. The photo image of triple stacked all-solid-state supercapcitor was shown in Fig. S10(b).

Characterization: The morphology and microstructure of materials were observed using a JSM 4700F field emission scanning electron microscope (FE-SEM, JEOL) and a JEM 2100F transmission electron microscope (FE-TEM, JEOL). The crystallographic information was obtained using a Bruker Miller diffractometer using Cu-Kα radiation.

Chemical analysis on the surface of nanocomposite was carried out using a Nicolet Nexus 470 Fourier transform-infrared (FT-IR) spectrometer (Thermo). Electrochemical performances of electrodes including cyclic voltammetry (CV), galvanostatic charge-discharge test, and electrochemical impedance spectroscopy (EIS) were evaluated using an Autolab PGSTAT 302N potentiostat/galvanostat apparatus (Metrohm AG) with a 3 electrode configuration. Two electrode configuration was also employed to investigate the electrochemical performances of all-solid-state electrochemical capacitors. The areal capacitance (C_a) of the cells was calculated from the results of CV and galvanostatic charge-discharge tests using the following equations:

$$C_a\,(CV) = Q/(\Delta V \times S) \quad (1)$$

$$C_a\,(gavanostatic) = (I \times \Delta t)/(\Delta V \times S) \quad (2)$$

where Q is the enclosed area of CV curve, ΔV is the potential window (three electrode configuration: - 0.2 to 0.55 V, two electrode configuration: 0 to 0.4 V), S is the active area of the electrode, I is the discharge current, and Δt is the discharge time. The cycle performance was measured up to 5,000 cycles at a current density of 2 mA cm^{-2}. EIS was conducted in the freqeuncy range 0.1 Hz to 100 kHz with an AC amplitude of 5 mV.

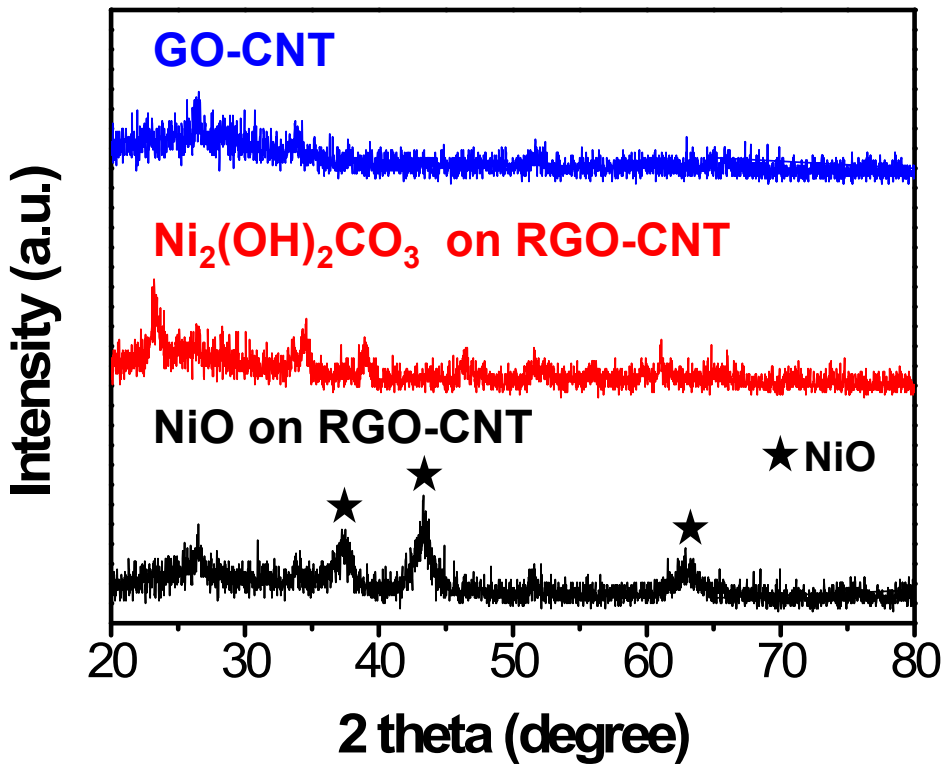

Fig. S1 XRD patterns of GO-CNT, $Ni_2(OH)_2CO_3$ nullaginite nanowalls on RGO-CNT, and NiO nanowalls on RGO-CNT.

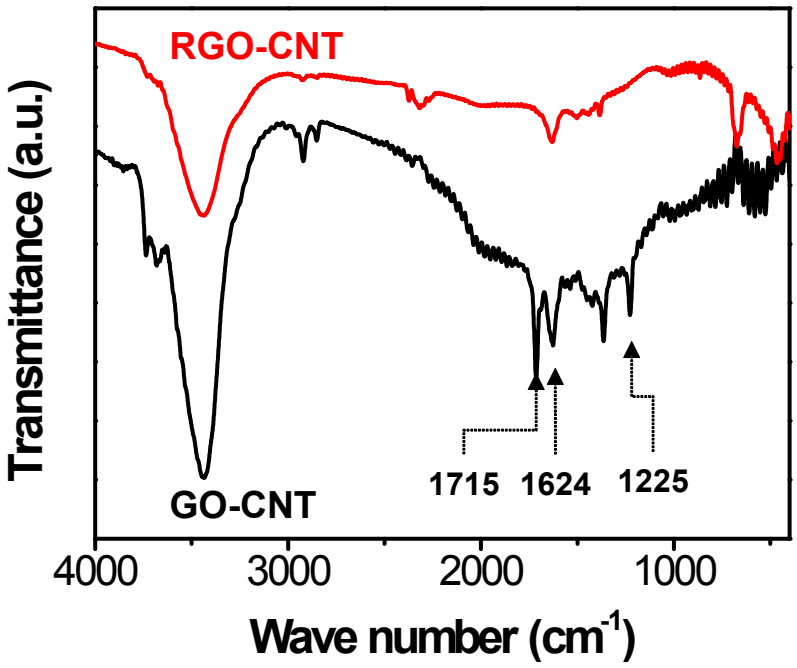

Fig. S2 FT-IR spectra of GO-CNT and RGO-CNT.

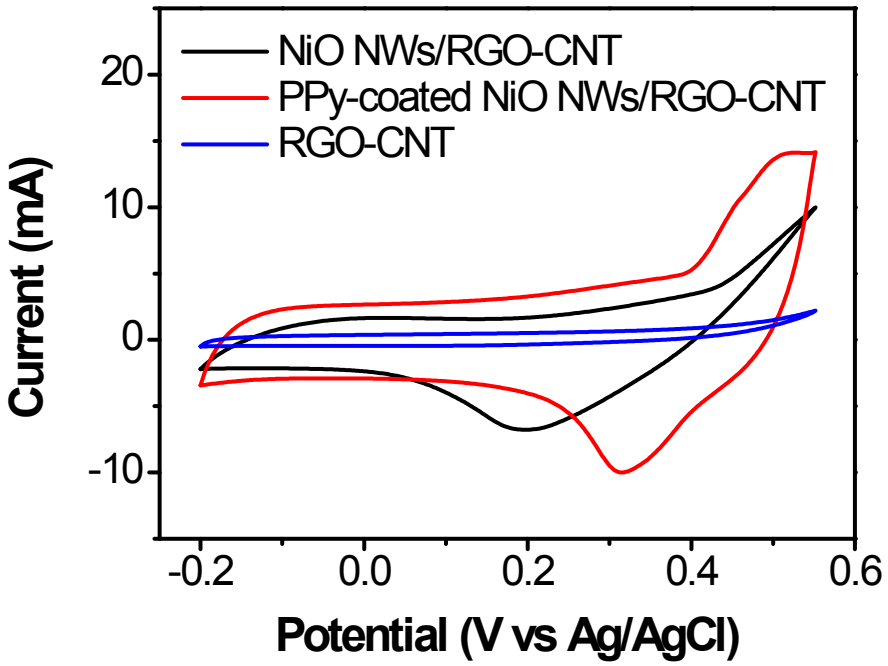

Fig. S3 CV curves of RGO-CNT, and NiO and PPy-coated NiO nanowalls electrodes obtained at a scan rate of 20 mV s^{-1} (CV curves of NiO and PPy-coated NiO nanowalls electrodes are shown in Fig. 4a).

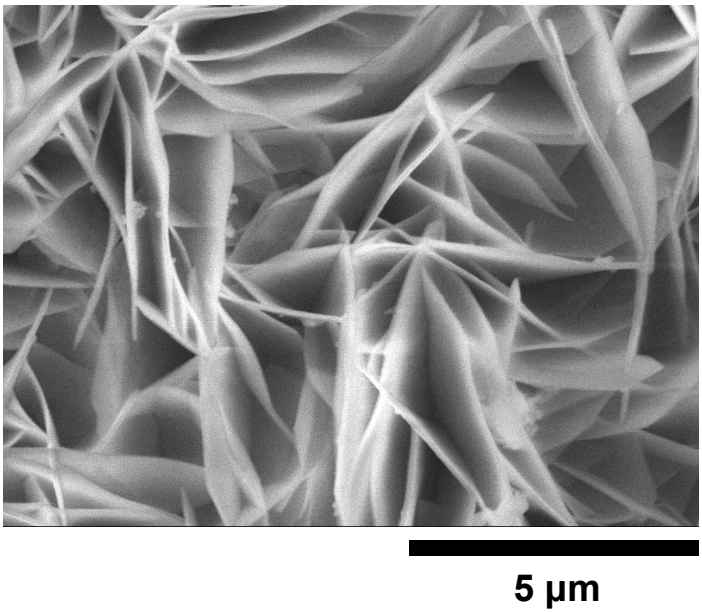

Fig. S4 SEM image of Ppy-coated NiO NWs on RGO-CNT electrode after 3000 cycles

<Table>

Metal oxide–carbon composite	Specific capacitance	References
GO/MnO_2 paper	454 mF/cm^2 at 0.5 mA/cm^2	30
Vanadium nitride/ CNT hybrid film	178 mF/cm^2 at 1.1 mA/cm^2	31
Porous NiO-carbon cloth	1054 mF/cm^2 at 0.5 mA/cm^2	32
Mo_2N nanobelts/rGO film	142 mF/cm^2 at 1 mA/cm^2	33
MnOOH/nitrogen-doped graphene film	173.2 mF/cm^2 at 1 mA/cm^2	34
$Ni_xCo_{2x}(OH)_{6x}$/rGO foam	703.6 mF/cm^2 at 1 mA/cm^2	35
PANI@MnO_2@carbon cloth	421.6 mF/cm^2 at 0.2 mA/cm^2	36
Co_3O_4 on carbon nanotubes/carbon cloth	416.7 mF/cm^2 at 1 mA/cm^2	37
Our sample	622 mF/cm^2 at 2 mA/cm^2	

Fig. S5 Electrochemical performance of the supercapacitors based on transition metal oxide materials.

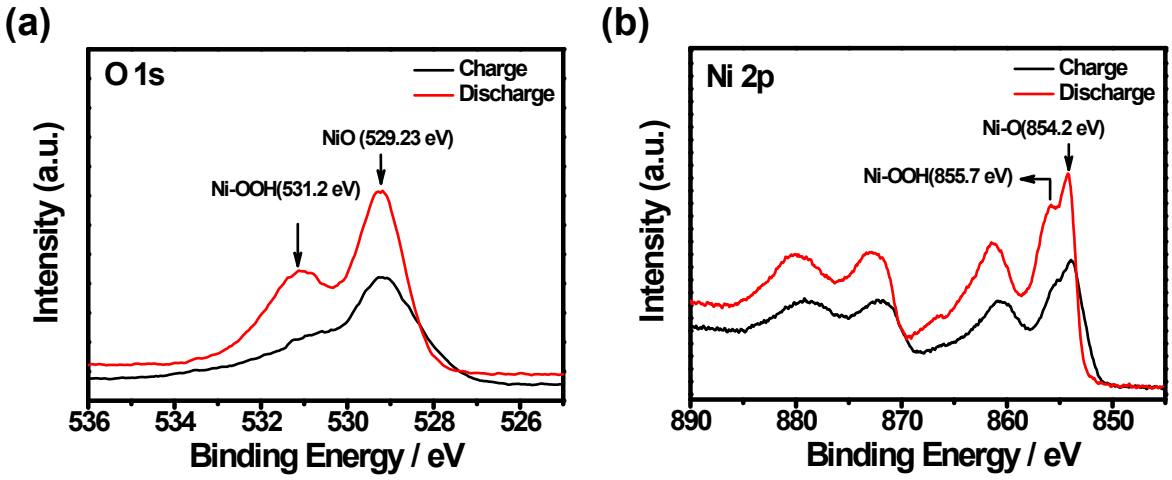

Fig. S6 (a) O 1s XPS spectrum and (b) Ni 2p XPS spectrum of Ppy-coated NiO NWs on RGO-CNT electrode after discharging and charging

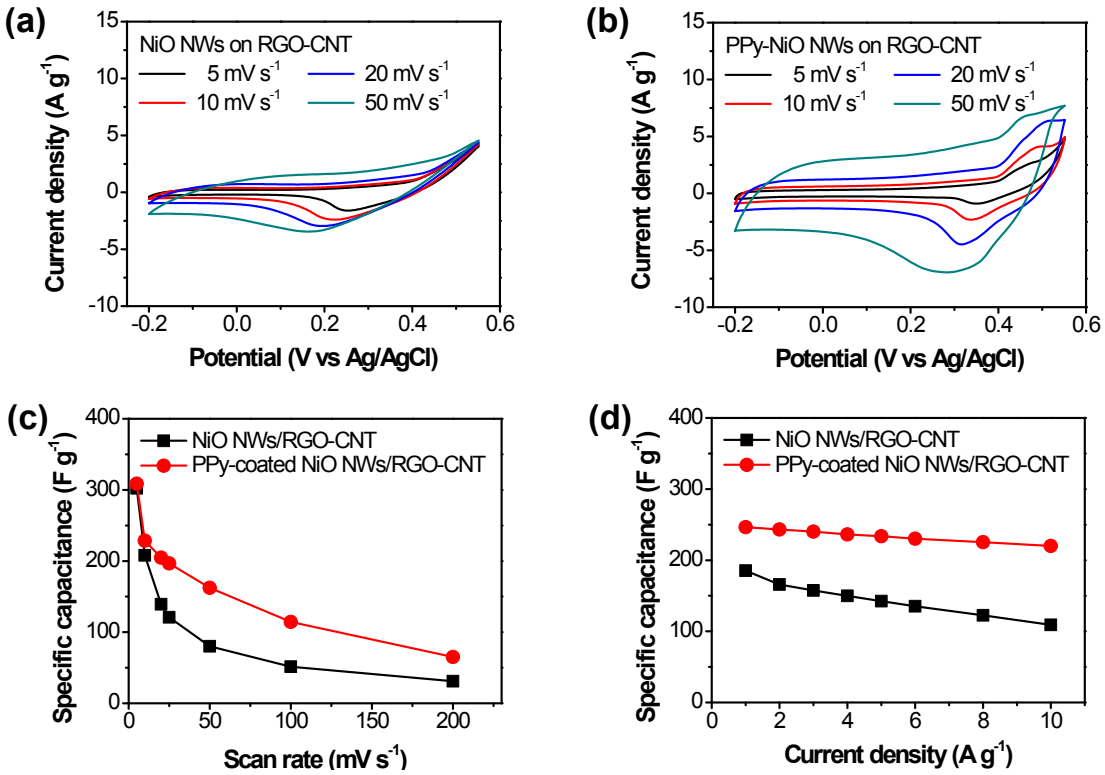

Fig. S7 CV curves of (a) NiO and (b) PPy-coated NiO nanowalls electrodes obtained at different scan rates. Specific capacitance of NiO and PPy-coated NiO nanowalls electrodes obtained at different (c) scan rates and (d) current densities.

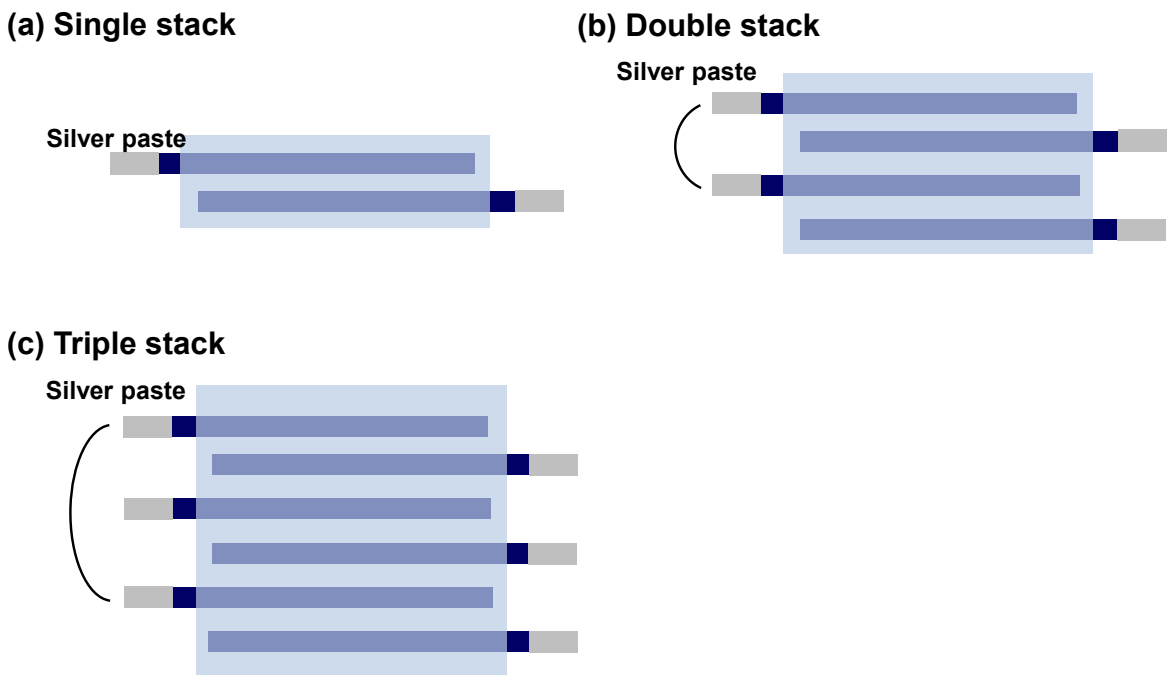

Fig. S8 Stacked electrochemical capacitors. (a) Single stack, (b) double stack, and (c) triple stack.

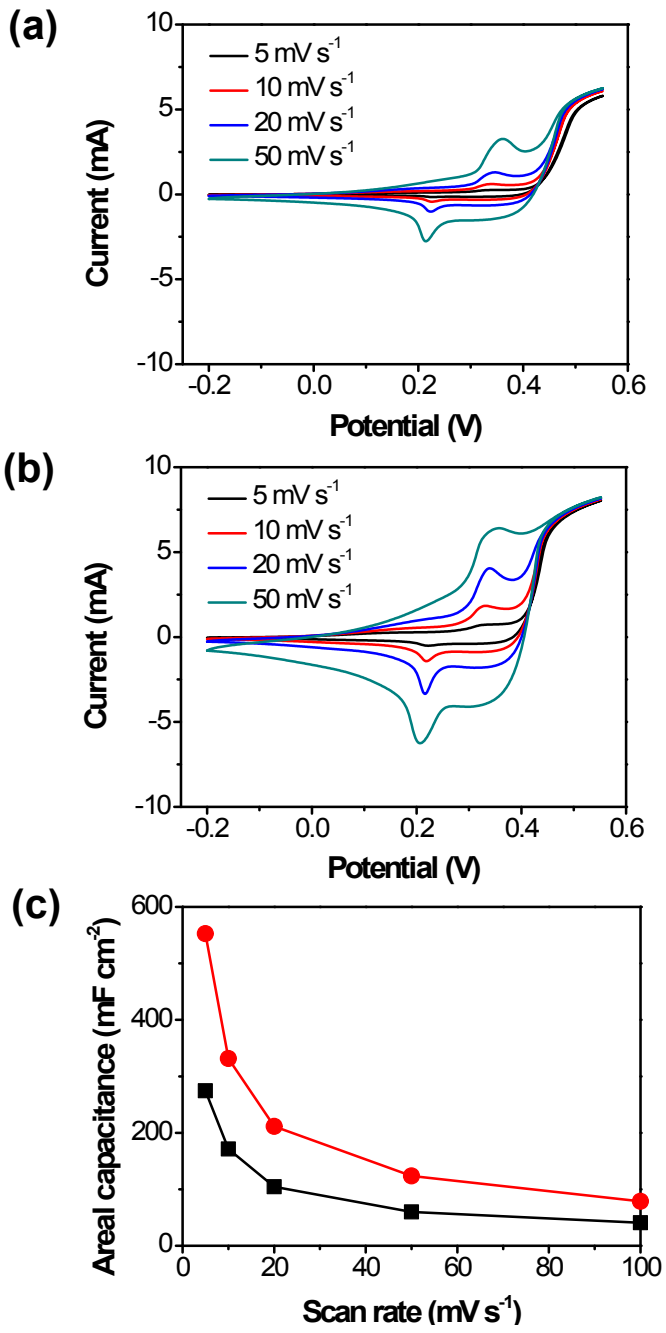

Fig. S9 (a) CV curves of single-sided and (b) double-sided NiO nanowalls on stainless steel substrate. (c) Areal capacitance of both electrodes with increasing scan rate.

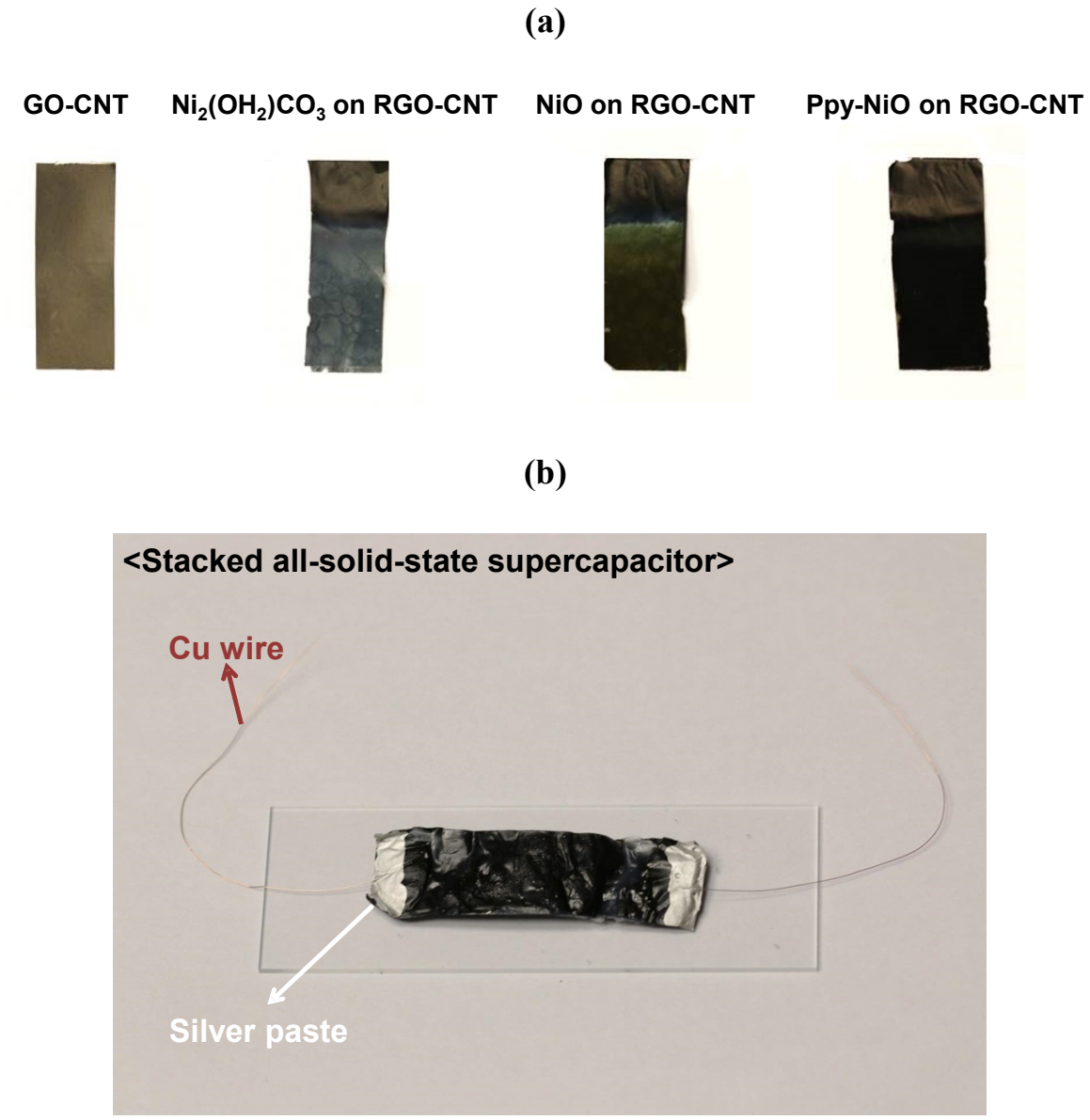

Fig. S10 Photo images of (a) each electrodes and (b) triple stacked all-solid-state capacitor