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Nanoscale

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Encapsulation of Nanoscale Metal Oxides into Ultra-thin Ni Matrix for Superior Li-Ion Batteries: A Versatile Strategy

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1. Experimental Details:

1.1 Preparation of $Ni(OH)_2$ film: 0.3g $Ni(NO_3)_2{\cdot}6H_2O$ and 0.7g hexamethylenetetramine (HMT) were dissolved in 50 mL distilled water. After 30 min ultrasonication treatment, the transparent suspension was then transferred into a sealed container (80 mL) and held at 95 ^oC for 6 h. The pure $Ni(OH)_2$ films can be harvested after wash for several times.

1.2 Preparation of Fe_3O_4@Ni hybrids: Single-crystalline Fe_3O_4 hexagonal nanoplates were synthesized by referring to the previous work.[17] In brief, a green mixture of $FeSO_4{\cdot}7H_2O$ (0.4 g), NaOH (0.53 g), ethylene glycol (45 mL) and distilled water (15 mL) was treated by ultrasonication for 30 min, transferred into a Teflon-lined stainless steel autoclave and held at 95 ^oC for 20 h. The as-formed Fe_3O_4 precipitation was then washed, dried and collected as raw materials for later fabrication. In typical synthesis of Fe_3O_4@Ni hybrids, 0.15 g Fe_3O_4 nanoplates, 0.7 g HMT, 0.3 g $Ni(NO_3)_2{\cdot}6H_2O$ and 50 mL distilled water were mixed and dissolved by ultrasonication for 15 min. The obtained suspension was then transferred into a sealed container (80 mL) and held at 95 ^oC for 6 h. Later, the Fe_3O_4@$Ni(OH)_2$ intermediate was collected and washed by distilled water several times. The reduction procedure was performed in a horizontal, quartz tube-furnace system. 0.3 g Fe_3O_4@$Ni(OH)_2$ (pre-dispersed into 10 ml distilled water, dropped onto a ceramic wafer and dried at 60 ^oC) were placed into the centre of a quartz tube (tube diameter: 2 inch). 1.5 mL of ethylene glycol (EG) loaded in an alumina boat was put at the upstream zone of quartz tube. Before heating, the tube reactor was sealed and flushed by Ar gas (200 sccm) for 10 min. The furnace was then heated to 610±10K at a heating rate of ~10 K min^{-1} under a constant Ar flow of 80 sccm, kept for 15 min and allowed to cool down to room temperature naturally.

1.3 Preparation of C/CoFeO$_x$@Ni NWAs: The C/CoFeO$_x$ NWAs were applied directly as raw materials and synthesized according to our previous work.[20] In brief, one piece of Fe-Co-Ni alloy substrate with C/CoFeO$_x$ NWAs (area: 2.5×3.5 cm^2) grown on was immersed into a 80 mL container wherein there was a 50 mL homogeneous aqueous solution containing 0.15 g $Ni(NO_3)_2 \cdot 6H_2O$ and 0.3 g HMT. The container was then sealed and held at 95 ^oC for 6 h. The obtained C/CoFeO$_x$ NWAs were fetched out, rinsed and dried at 60 ^oC. The next reduction treatment was exactly the same with that of Fe_3O_4@Ni hybrids except that the C/CoFeO$_x$@$Ni(OH)_2$ NWAs replaced the above Fe_3O_4@$Ni(OH)_2$.

2. Figures

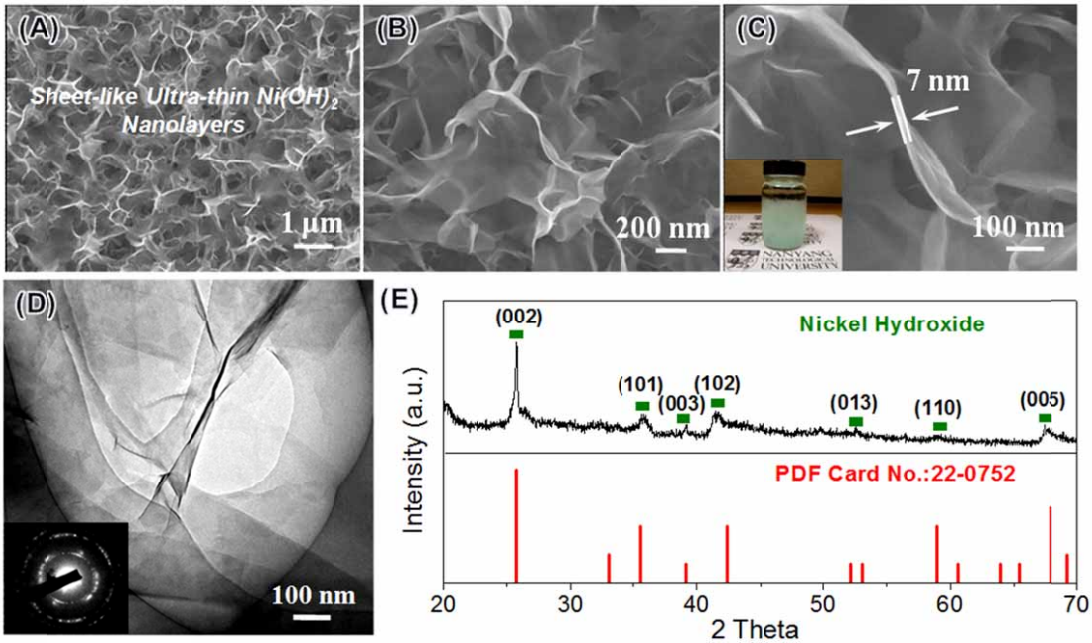

Fig. S1 (A-C) SEM and (D) TEM observations on sheet-like ultra-thin $Ni(OH)_2$ nanofilms. (E) XRD pattern of as-formed $Ni(OH)_2$ products. Inset in Fig. S1(D) shows their SAED spectrum.

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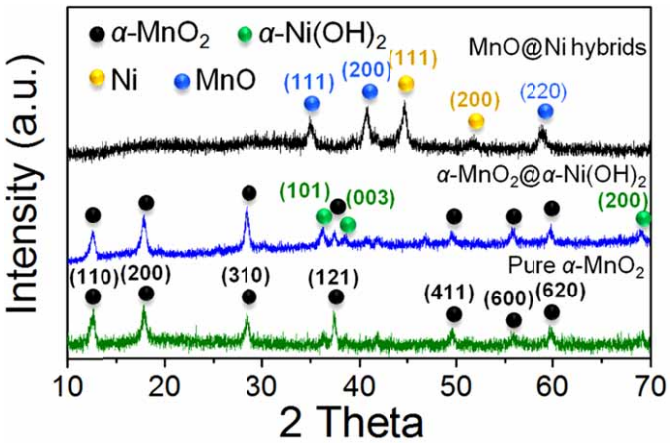

Fig. S2 XRD patterns showing the evolution process of MnO@Ni core-shell hybrid nanowires.

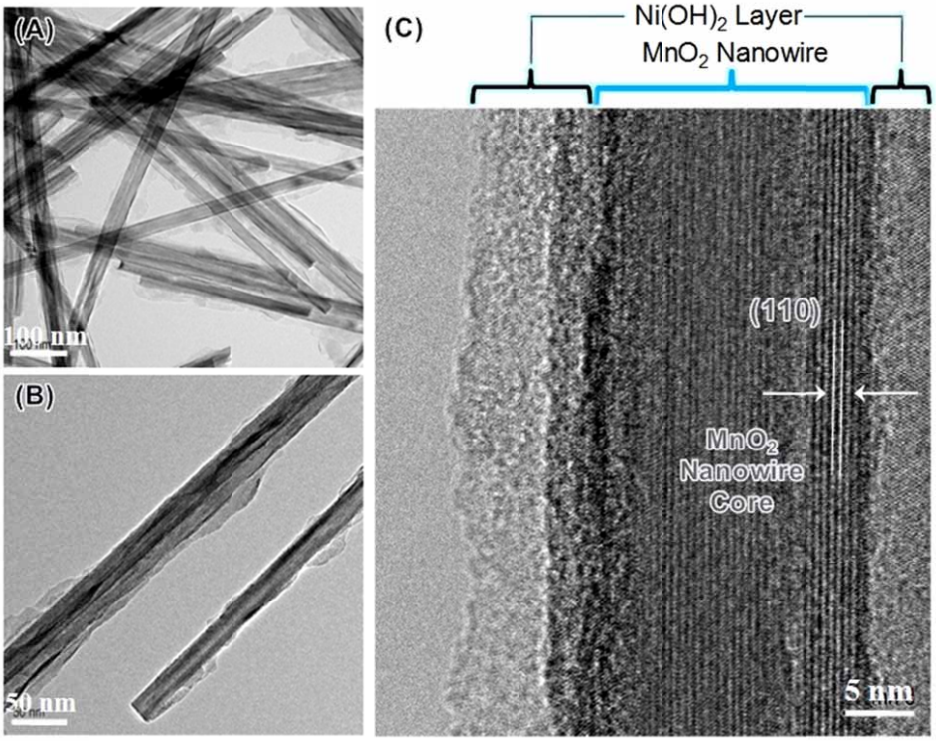

Fig. S3 (A-B) TEM and (C) HRTEM images of the MnO_2@$Ni(OH)_2$ intermediate.

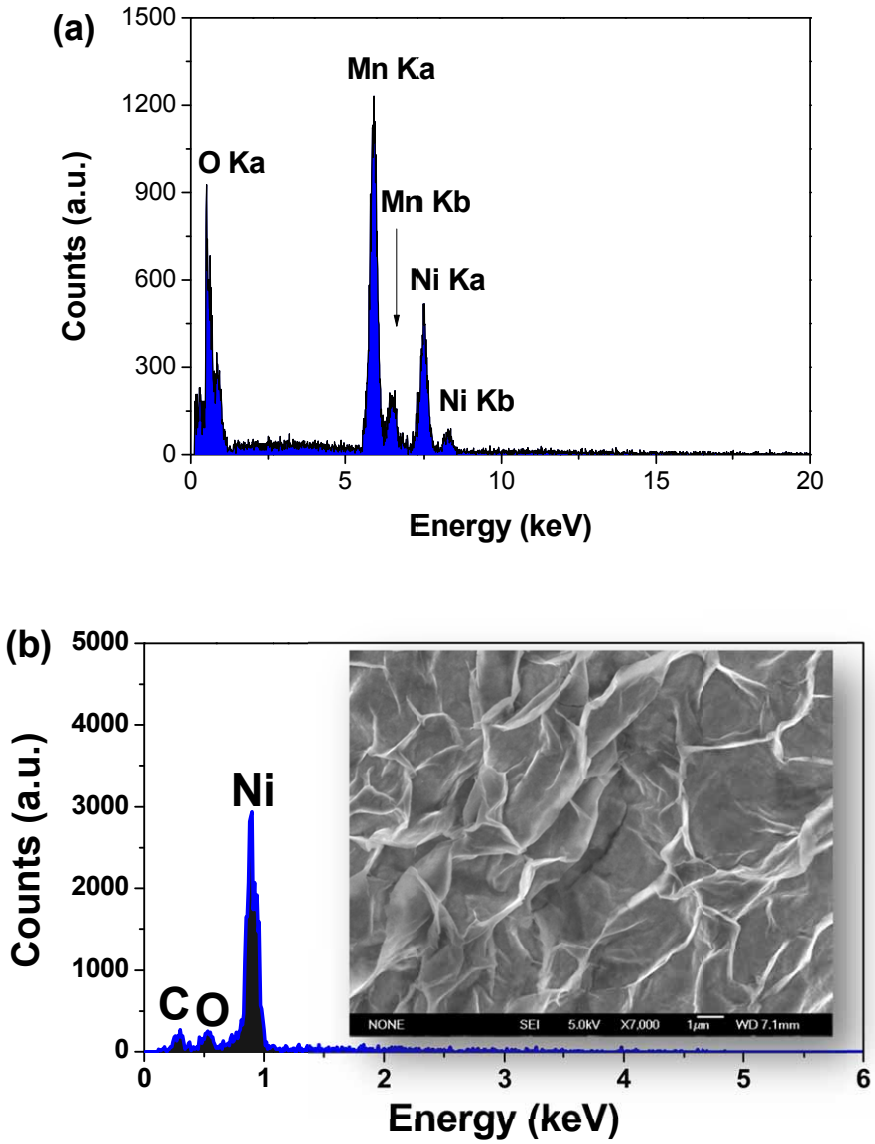

Fig.S4 (a) EDS spectrum of MnO@Ni core-shell hybrid NWs; (b) EDS spectrum and SEM image (inset) of Ni products evolved from pure $Ni(OH)_2$ thin films.

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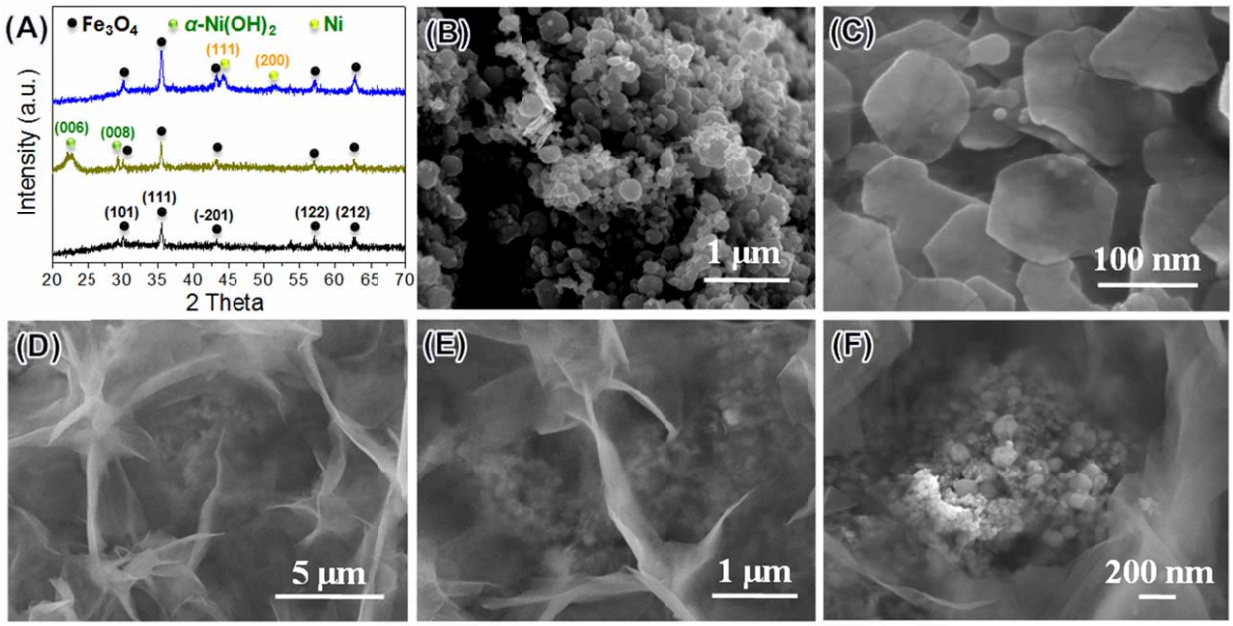

Fig. S5 (A) XRD patterns monitoring the evolution process of Fe_3O_4@Ni hybrid. SEM observations toward samples within different evolution stages: (B-C) the pristine Fe_3O_4 nanoplates, (D-E) the intermediate Fe_3O_4@$Ni(OH)_2$ and (F) the final products of Fe_3O_4@Ni hybrid.

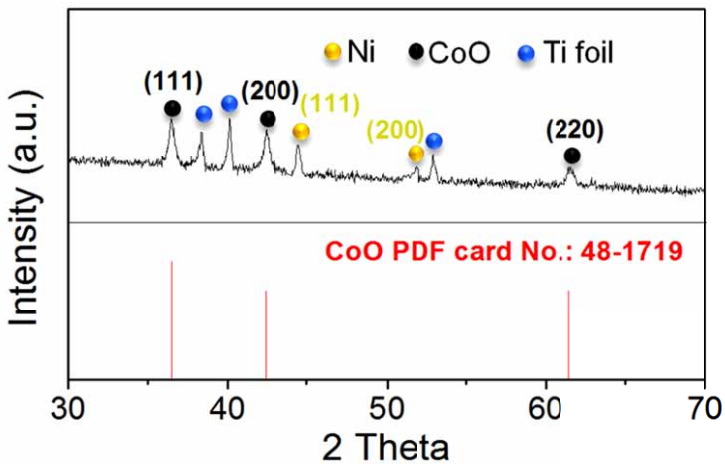

Fig.S6 XRD pattern of CoO@Ni core-shell hybrid NWs.

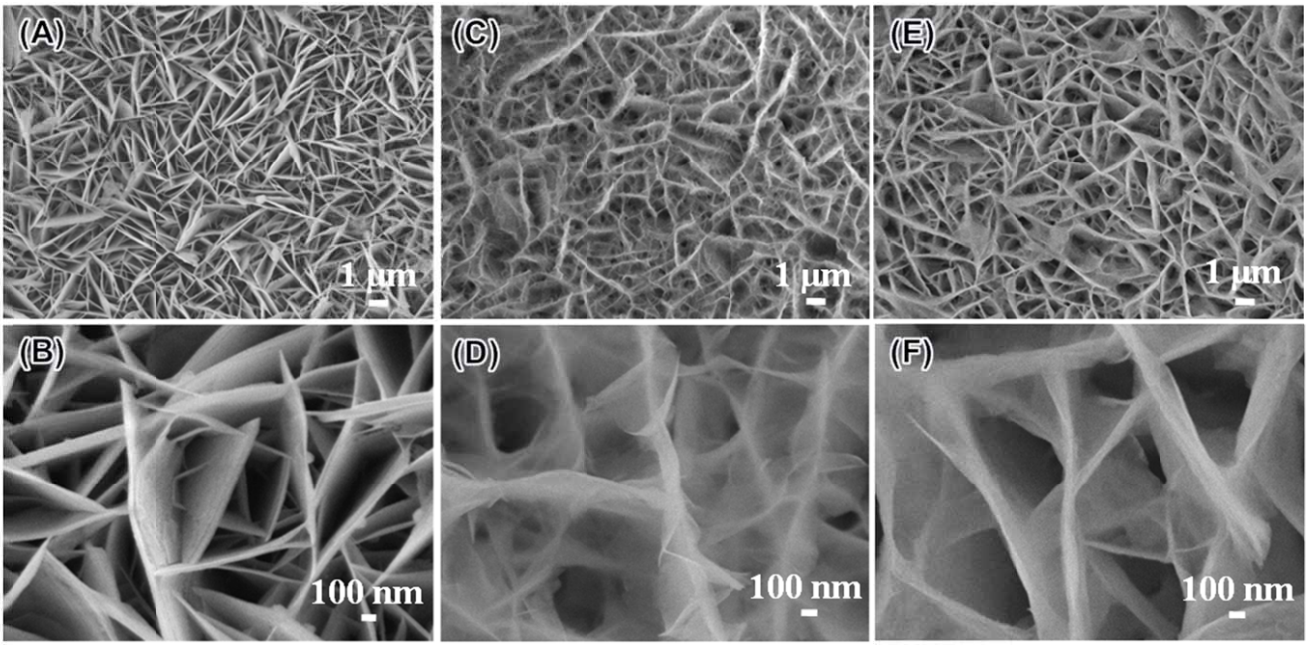

Fig. S7 SEM observations monitoring the overall evolution of C/$CoFeO_x$@Ni NWAs: (A-B) the pristine C/$CoFeO_x$ NWAs, (C-D) the intermediate C/$CoFeO_x$@$Ni(OH)_2$ NWAs and (E-F) the final products of C/$CoFeO_x$@Ni NWAs.

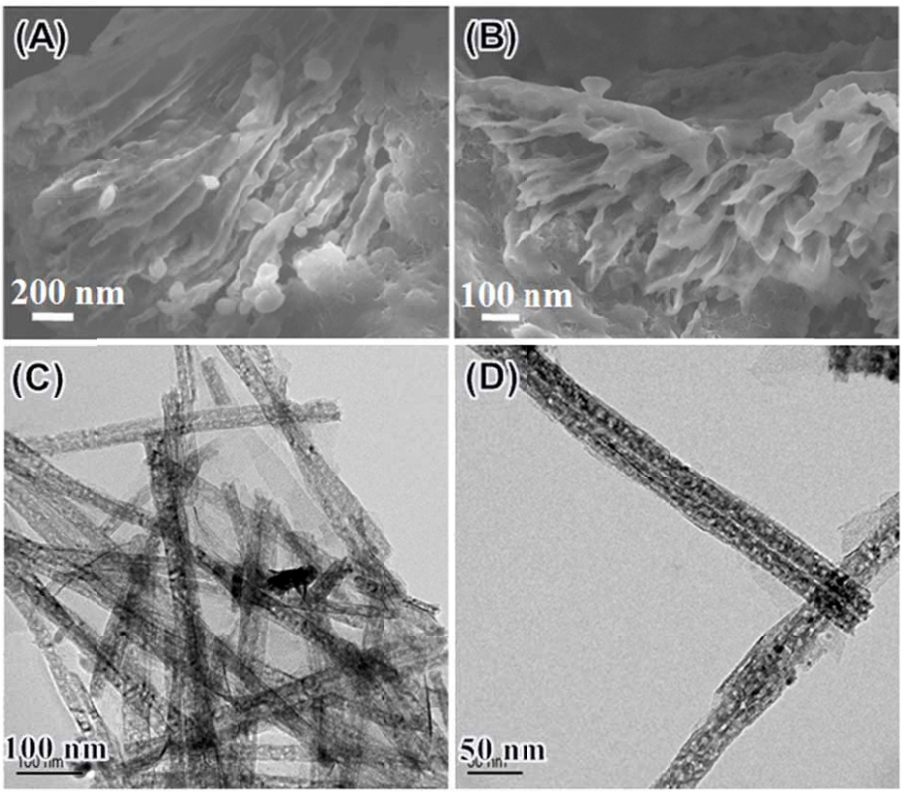

Fig. S8 (A-B) SEM and (C-D) TEM images of MnO@Ni hybrids after 250 charge-discharge cycles.

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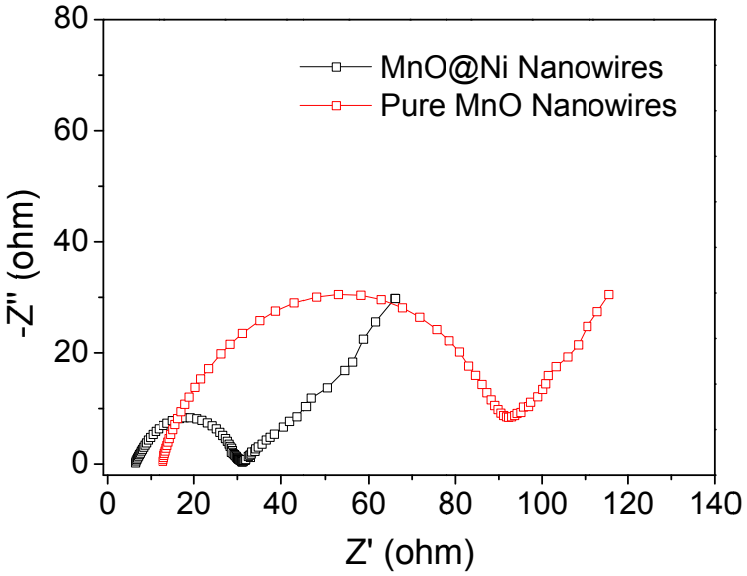

Fig.S9 EIS spectra of pure MnO and MnO@Ni hybrid nanowires.

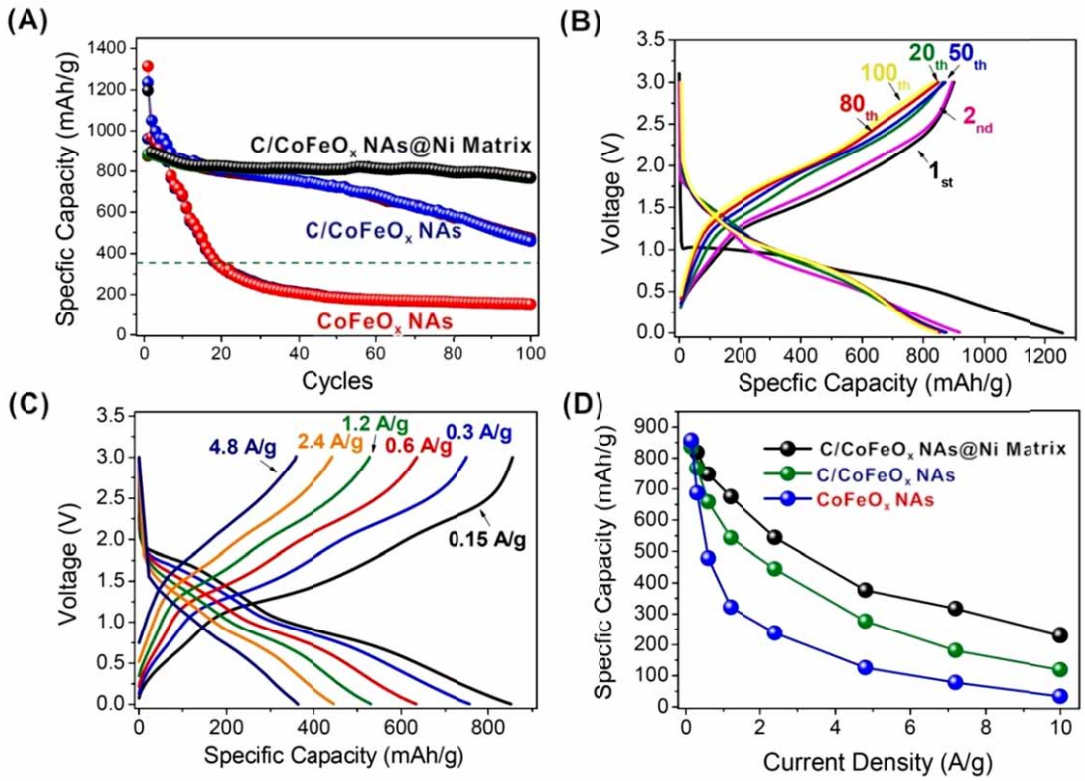

Fig. S10 (A) Cyclic comparison of pure $CoFeO_x$ NWAs, C/$CoFeO_x$ NWAs and C/$CoFeO_x$@Ni NWAs at a constant current density of ~350 mA/g; (B) Charge/discharge profiles of C/$CoFeO_x$@Ni NWAs in a voltage window of 0.005-3V at ~350 mA/g; (C) Charge/discharge profiles of C/$CoFeO_x$@Ni NWAs performed under varied current densities; (D) Comparison of rate capabilities on bare $CoFeO_x$ NWAs, C/$CoFeO_x$ NWAs and C/$CoFeO_x$@Ni NWAs.