Electronic Supplementary Information (ESI)

Ultrathin nickel hydroxidenitrate nanoflakes branched on nanowire arrays for high-rate pseudocapacitive energy storage†

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I. Experimental Details:

Synthesis. All of the reagents used in the experiments were of analytical grade and utilized without further purification. ZnO nanowire array on stainless steel (SS) substrate was first fabricated by a simple solution-based route as described in our previous report [1]. The growth time was 5 hours. After this, the array was subjected to an annealing process at 450 ^{o}C for 3 h in Ar gas to improve the adhesion of the nanowires to SS substrate. To grow nickel hydroxidenitrate-ZnO hybrid nanowire array, a piece of obtained ZnO nanowire array was immersed into a 0.085 M $Ni(NO_3)_2$ aqueous solution, sealed in a Teflon-lined stainless steel autoclave, and maintained at 85 ^{o}C for desired time period. After the reaction, the SS substrate was taken out, washed several times with deionized water and finally dried at 60 ^{o}C in an electric oven. For nickel hydroxidenitrate powder synthesis, 0.25 M green and transparent $Ni(NO_3)_2$ *ethanol* solution was first prepared, and then transferred to a Teflon-lined stainless steel autoclave with a filling degree of 75%, which was allowed to react at 130 ^{o}C for 3 h. After cooling to room temperature, the green precipitation was washed with deionized water and dried at 60 ^{o}C in air to obtain the final sample.

Characterizations. Products were characterized by powder X-ray diffraction (XRD) (Bruker D-8 Avance) measurement, transmission electron microscopy(TEM) (JEM-2010FEF, 200 kV) observation, and scanning electron microscopy (SEM) (JSM-6700F, 5.0 kV) equipped with an Energy dispersive X-ray spectrometry (EDS). Infrared (IR) spectrum was recorded on a NICOLET NEXUS470 Fourier transform infrared (FT-IR) spectrometer. The mass of electrode materials was measured on an

AX/MX/UMX Balance (METTLER TOLEDO, Maximum=5.1 g; d= 0.001 mg).

Electrochemical testing. CV experiments and charge-discharge tests (CHI660C, CH Instruments Inc.) were all conducted using a three-electrode mode in a 1M NaOH solution. The hybrid nanowire array (~2 cm^2 area; ZnO mass: 0.65 mg, nickel hydroxidenitrate mass: 0.554 mg) was directly used as the working electrode. The reference electrode and counter electrode were Ag/AgCl and platinum plate, respectively. Typical CV curves were measured between 0~0.55 V. For comparison purpose, nickel hydroxidenitrate powder-based electrode were obtained by conventional method: Briefly, the as-prepared nickel hydroxidenitrate, carbon black and poly(tetrafluoroethylene) (PTFE) were mixed in a mass ratio of 80:15:5 and dispersed in ethanol. Then the resulting mixture was coated onto a Ti foil via the doctor blade technique to form a thin film, which was followed by drying at 80 ^oC for 12h in a vacuum oven.

II. Figures:

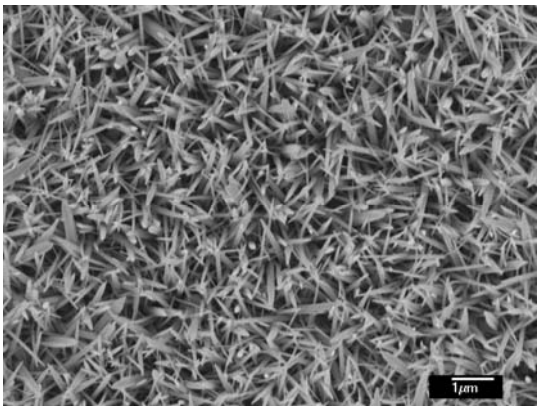

Fig.S1. Typical SEM image of ZnO nanowire array grown on stainless steel (SS) substrate.

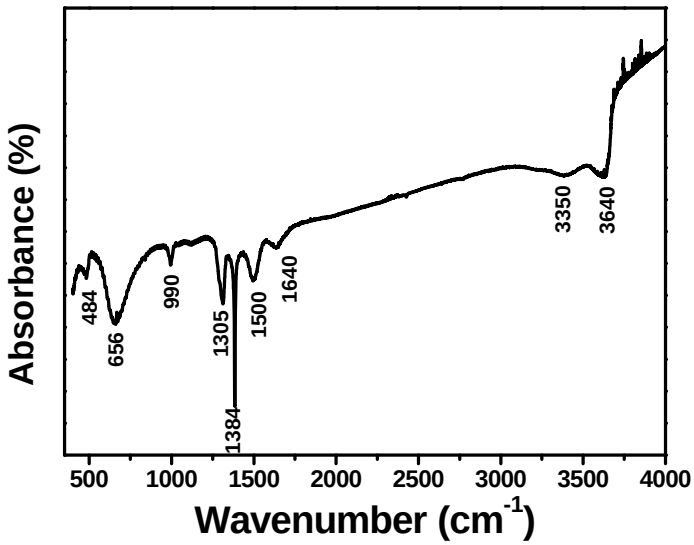

Fig.S2. FTIR spectrum of the hybrid structure. Three peaks observed at 484, 656, and 3640 cm^{-1} are associated with the ν-Ni–O vibration, σ-OH vibrations and ν-OH stretching, respectively. The interlayer nitrate anion manifests itself by a set of strong peaks in the range of 990 to 1500 cm^{-1}. Two peaks at 1640 and 3350 cm^{-1} are associated with the vibrations of H_2O [2].

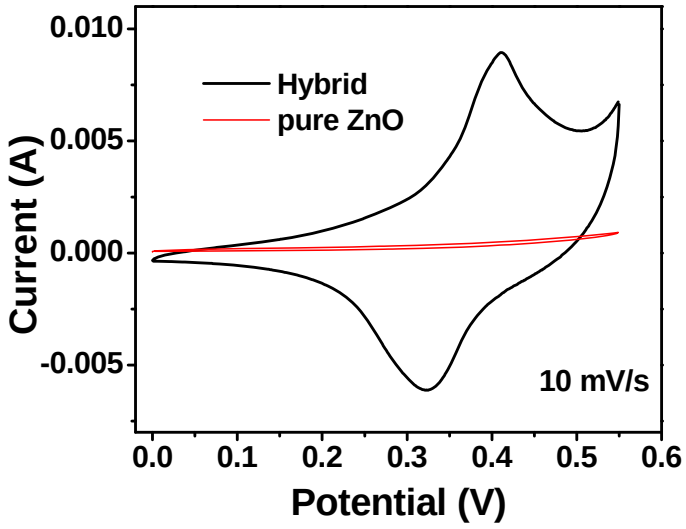

Fig.S3. The CV of pure ZnO nanowire array electrode in 1 M NaOH solution at 10 mV/s. The CV of hybrid array electrode is also shown for comparison.

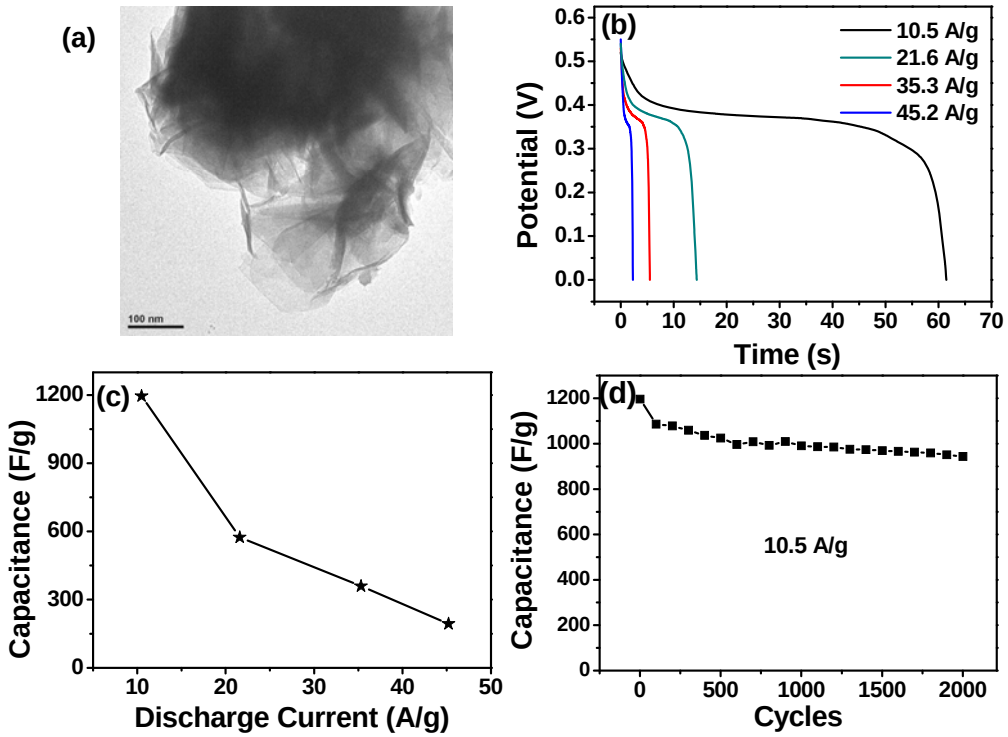

Fig.S4. (a) TEM image showing that the powder sample has similar size and shape to the nickel hydroxidenitrate flakes grown on ZnO nanowire. (b) Discharge curves (at various current densities), (c) Specific capacitance versus current density plots, and (d) cycling performance of nickel hydroxidenitrate powder-based electrode. It can be seen that the electrode is not suitable to cycle at high current densities; specific capacitance of lower than 200 F/g is obtained at 45.2 A/g. In addition, the SC decreases continuously from 1196 F/g to 943 F/g when discharged to 2000 cycle at 10.5 A/g.

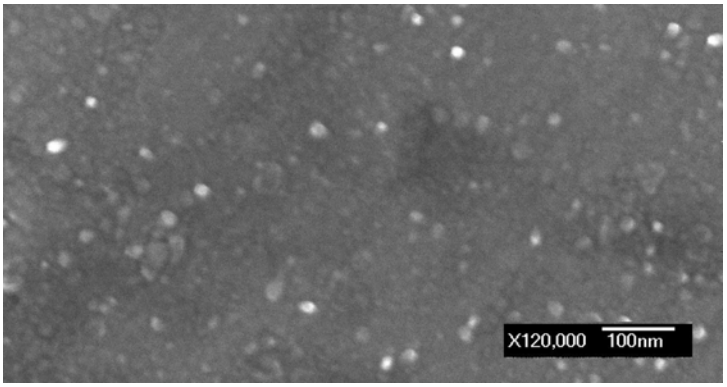

Fig.S5. SEM image of a SS substrate surface after the reaction in the same solution to that for nickel hydroxidenitrate -ZnO array growth. It is clearly demonstrated that without ZnO nanowire array, the nickel hydroxidenitrate nanoflakes can not grow on SS through heteronucleation. Only a nanosized rough surface of the substrate can be seen [1].

References:

[1] J. P. Liu, X. T. Huang, Y. Y. Li, X.X. Ji, Z.K. Li, X. He and F. L. Sun, *J. Phys. Chem. C*, 2007, **111**, 4990.

[2] M. Taibi, S. Ammar, N. Jouini, F. Fiévet, P. Molinié and M. Drillon, *J. Mater. Chem.*, 2002, **12**, 3238.