High-performance supercapacitor material based on $Ni(OH)_2$ nanowire-MnO_2 nanoflakes core/shell nanostructures

Hao Jiang,[a] Chunzhong Li,*,[a] Ting Sun,[b] Jan Ma[b]

[a] Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science & Technology, Shanghai 200237, China

[b] School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

* Electronic mail: czli@ecust.edu.cn (Prof. Chunzhong Li)

Part I: Experimental

Synthesis of $Ni(OH)_2$ nanowire-MnO_2 nanoflakes core/shell nanostructures: All the reagents were analytical grade (Sigma-Aldrich) and used without further purification. $Ni(OH)_2$ nanowires have first been synthesized according to the method reported by Chu et al. (*Chem.–Eur. J.*, 2008, **14**, 5064). In a typical procedure of the synthesis of $Ni(OH)_2$ nanowire-MnO_2 nanoflakes core/shell nanostructures, 50 mg of the as-synthesized $Ni(OH)_2$ nanowires were firstly dispersed in 30 mL of deionized water. Then, 10 mL of 0.08 M $KMnO_4$ aqueous solution was added into the above suspension and the mixed solution was stirred by magnetic bar for about 3 h. After that, the mixed solution was transferred to a 50 mL Teflon-lined stainless autoclave. The autoclave was sealed and put in an electronic oven at 160 °C for 3 h and then naturally cooled down to room temperature. The precipitates were collected by filtration, washed with deionized water and absolute ethanol, and

finally dried at 60 ^{o}C for 6 h. Furthermore, the content of MnO_2 in hybrid can easily be tuned only by changing the $KMnO_4$ concentration.

Synthesis of MnO_2 nanowires: The MnO_2 nanowires with diameters of ~ 25 nm have been synthesized according to our previous work (*Energy Environ. Sci.*, 2011, **4**, 1813). In a typical process, $Mn(NO_3)_2{\cdot}4H_2O$ (0.2685 g) and sodium dodecyl benzene sulfonate (SDBS, 0.3845 g) were first dissolved in 30 mL of deionized water. When the solution turned clear, $KMnO_4$ (0.2 M, 5 mL) was added to the above solution with continuous stirring for about 30 min. The resulting cloudy solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, then heated at 180 °C for 4~6 h, and followed by natural cooling to room temperature. The precipitates, i.e. MnO_2 nanowires, were collected by filtration, washed with deionized water and absolute ethanol, and finally dried at 60 °C for 6 h.

Characterization: The as-prepared products were characterized with X-ray powder diffractometer (XRD; Shimadzu XRD-6000, Cu Kα radiation) at a scan rate of 1 °C min^{-1}, scanning electron microscopy (FESEM; JEOL, JSM-7600F) equipped with an energy dispersive X-ray spectrometer (EDS), and transmission electron microscopy (TEM; JEOL, JEM-2100F) operated at 200 kV. N_2 adsorption/desorption was determined by Brunauer-Emmett-Teller (BET) measurements using a Tristar-3000 surface area analyzer.

Electrochemical measurements: The electrochemical measurements (Autolab PGSTAT30 potentiostat) were conducted using a three-electrode mode in a 1 M Na_2SO_4 aqueous solution. The working electrodes were prepared by mixing the active materials (80 wt%), acetylene black (15 wt%) and polyvinylidene fluoride (PVDF, 5 wt%) in NMP (N-methyl-2-pyrrolidone). A small amount of absolute ethanol was then added to the mixture to promote homogeneity. After that, the

mixture was coated onto the graphite paper (1 cm^2) to form the electrode layer by drying at 120 °C for around two hours. The reference electrode and counter electrode were Ag/AgCl electrode and platinum foil, respectively. Typical CV curves were measured between −0.1 and 0.9 V.

Part II: Supplementary Figures

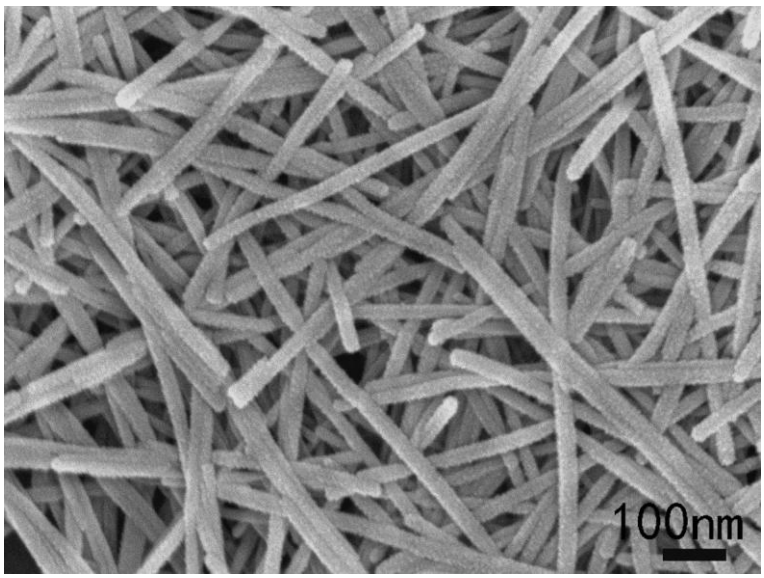

Fig. S1 SEM image of the as-synthesized $Ni(OH)_2$ nanowires

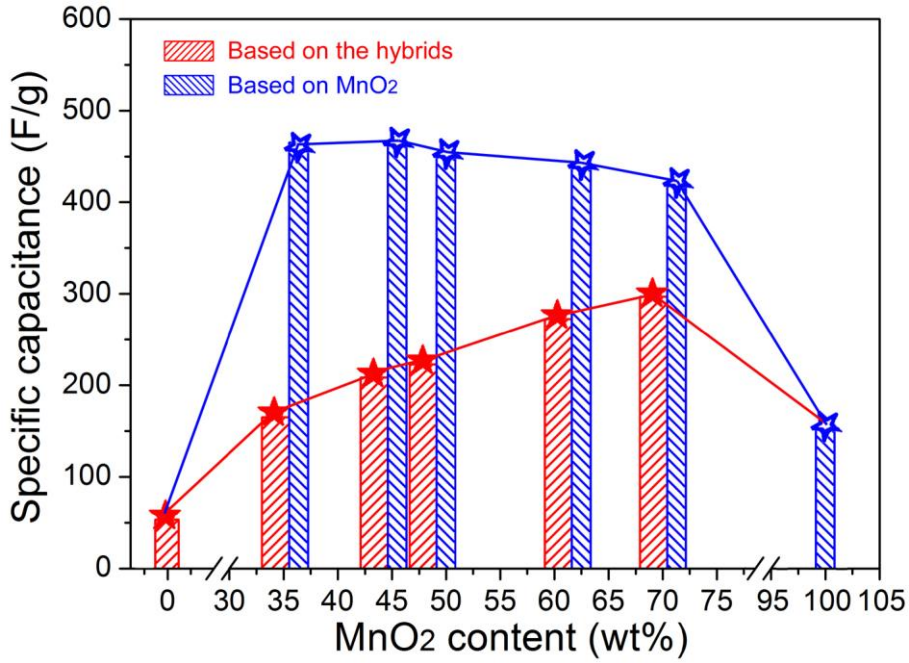

Fig. S2 The specific capacitance calculated based on MnO_2 content and the hybrid nanostructures,

respectively.

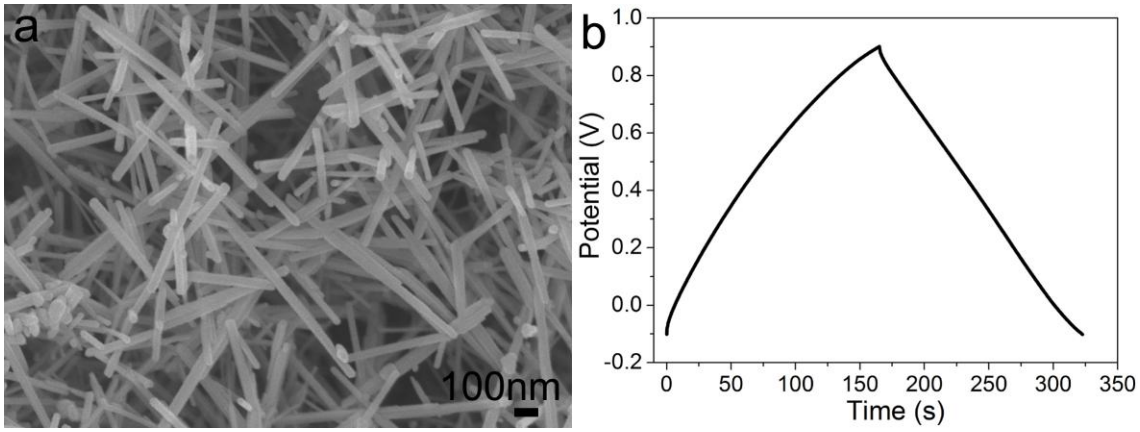

Fig. S3 (a) SEM image of MnO_2 nanowires, (b) the corresponding charge-discharge curve at a current density of 1 A g^{-1}.

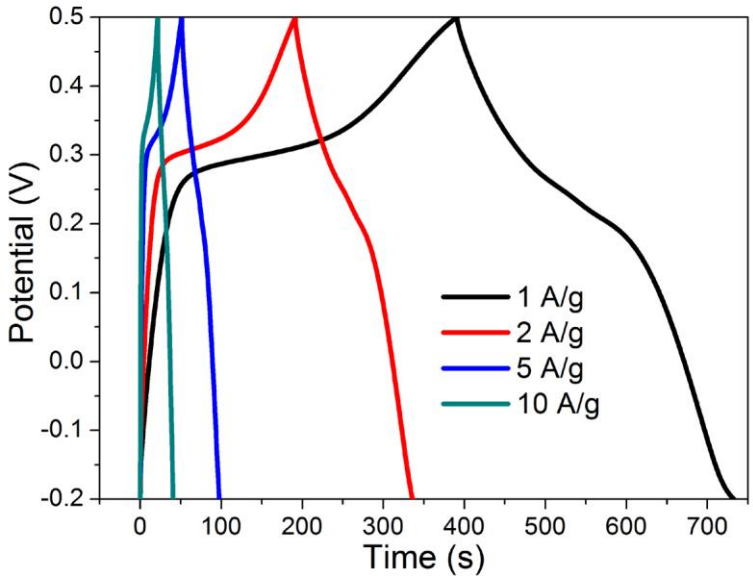

Fig. S4 Charge-discharge curves of the hybrids at 1-10 A g^{-1} in 1 M KOH aqueous solution. The hybrids show a high specific capacitance of 487.4 F g–1 at 1 A g^{-1}. Even at 10 g^{-1}, a specific capacitance of 269 F g^{-1} still can be reached.