

Experimental

The zinc oxide template composed of hexagonal nanorod arrays was deposited directly onto the stainless steel (SS) foil by applying a cathodic potential of -0.8 V versus a saturated Ag/AgCl electrode at 60 °C for 15 min. Prior to cathodic deposition, SS foil was cut into pieces of 2 cm × 2 cm, which were then soaked in acetone and ultrasonically vibrated for 5 min to wash away any contaminants from their surface. De-ionized water was then used to rinse the SS foils in ultrasonic vibration for another 5 min. The cathodic deposition of zinc oxide template was carried out in a homemade three-compartment cell. A saturated Ag/AgCl electrode was used as the reference electrode and a platinum foil (2 cm × 2 cm) was the counter electrode. The plating solution was a mixture of 0.1 M zinc nitrate and 0.1 M potassium nitrate and was stirred using a Teflon stir bar on a magnetic plate during the deposition process. After deposition, the template was rinsed several times in de-ionized water, and then the template was dried at 150 °C for 30 min in air.

The nickel hydroxide electrode with nanotube arrays was formed by dipping the zinc oxide template in a solution of 1 M nickel chloride for 20 min, and then the electrode was rinsed in de-ionized water. Finally, the electrode was immersed in 6 M sodium hydroxide solution for 60 min to remove the remnants of zinc oxide. After deposition, the resultant electrode was rinsed several times in de-ionized water and dried at 100 °C for 30 min in air.

The surface morphology of the nickel hydroxide electrode was examined with a scanning electron microscope (SEM) with an accelerating voltage of 3 keV. The tabular structure of the nickel hydroxide was identified by a transmission electron microscope (TEM) with an accelerating voltage of 200 keV. The crystal structure of nickel hydroxide and zinc oxide was identified by an X-ray diffractometer (XRD, Rigaku D/MAX2500) with a Cu K α target (wavelength = 1.54056 Å). Samples were stripped from electrodes for XRD measurement.

The electrochemical behavior of the nickel hydroxide electrode was determined by cyclic voltammetry and galvanostatic charge-discharge test in a three-electrode cell with a 1 M KOH electrolyte. A saturated Ag/AgCl electrode was used as the reference

electrode and a platinum foil with dimensions of 2 cm × 2 cm as the counter electrode. The potential was cycled at a scan rate of 1 mV s⁻¹ using a potentiostat (CH Instruments, CHI 608) over a range of 0-0.45 V. The electrode was charged at a current density of 1 A g⁻¹ to a cut-off potential of 0.45 V. The fully charged electrode was discharged at various current densities to a cut-off potential of 0.0 V. All chemicals used were of analytical grade and were used as received without further purification.

Morphology, structure, and X-ray diffraction

Figure S1a shows the SEM micrographs of ZnO nanorod arrays. ZnO tends to grow as a hexagonal rod during cathodic deposition. As can be seen from Figure S1b, the hexagonal ZnO nanorods converted to open-ended hexagonal Ni(OH)₂ nanotubes composed of stacked nanoplatelet wall. Nickel hydroxide nanoplatelets preferentially stack along its hexagonal facet. Actually, the electrodeposited ZnO nanorods have different sizes in diameter (60-120 nm). Most of the nanoplatelets formed around large ZnO nanorods were stacked compactly as nanotubes. Some nanoplatelets formed around small ZnO nanorods could be observed on the surface of nanotubes. EDS (Energy-dispersive X-ray spectroscopy) analysis showed that the ZnO content in the nickel hydroxide nanotube arrays was approximately 15 wt.% after hydrolysis of Ni²⁺ for 20 min. The ZnO may be etched completely at prolonged hydrolysis times or by using a concentrated NaOH solution. Figure S1c shows the nickel hydroxide nanotube arrays after removal of ZnO in a 6M NaOH solution. Clearly, after etching in NaOH solution, the change in morphology is quite small compared to Figure S1b. The ZnO content in the nickel hydroxide nanotube arrays measured from EDS was less than 2 wt.% after etching process. As can be seen from TEM image shown in Figure S2, the nickel hydroxide nanotube was composed of open-ended hexagonal nanotubes with hexagonal hole. Typical dimensions of the nickel hydroxide nanotubes are a length of approximately 460 nm, a diameter of 130 nm, a wall thickness of 40 nm, and an inner diameter of 50 nm.

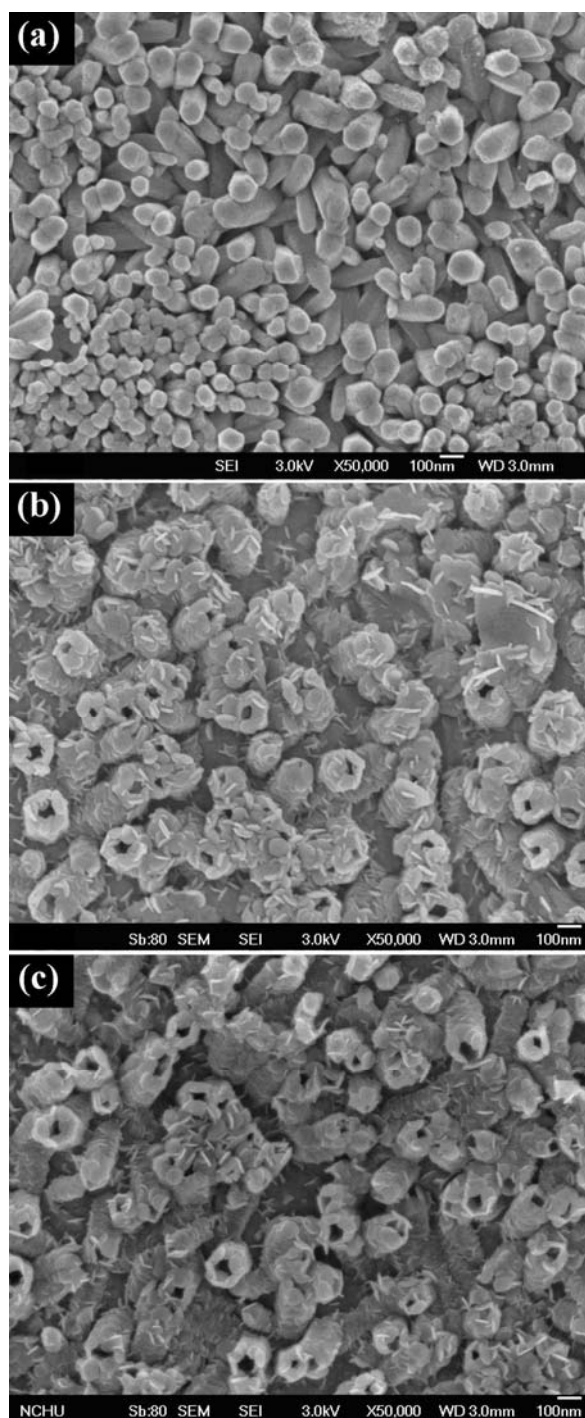


Fig. S1 SEM micrographs of the (a) zinc oxide rods, (b) nickel hydroxide nanotubes before etching, and (c) nickel hydroxide nanotubes after etching with 6 M NaOH.

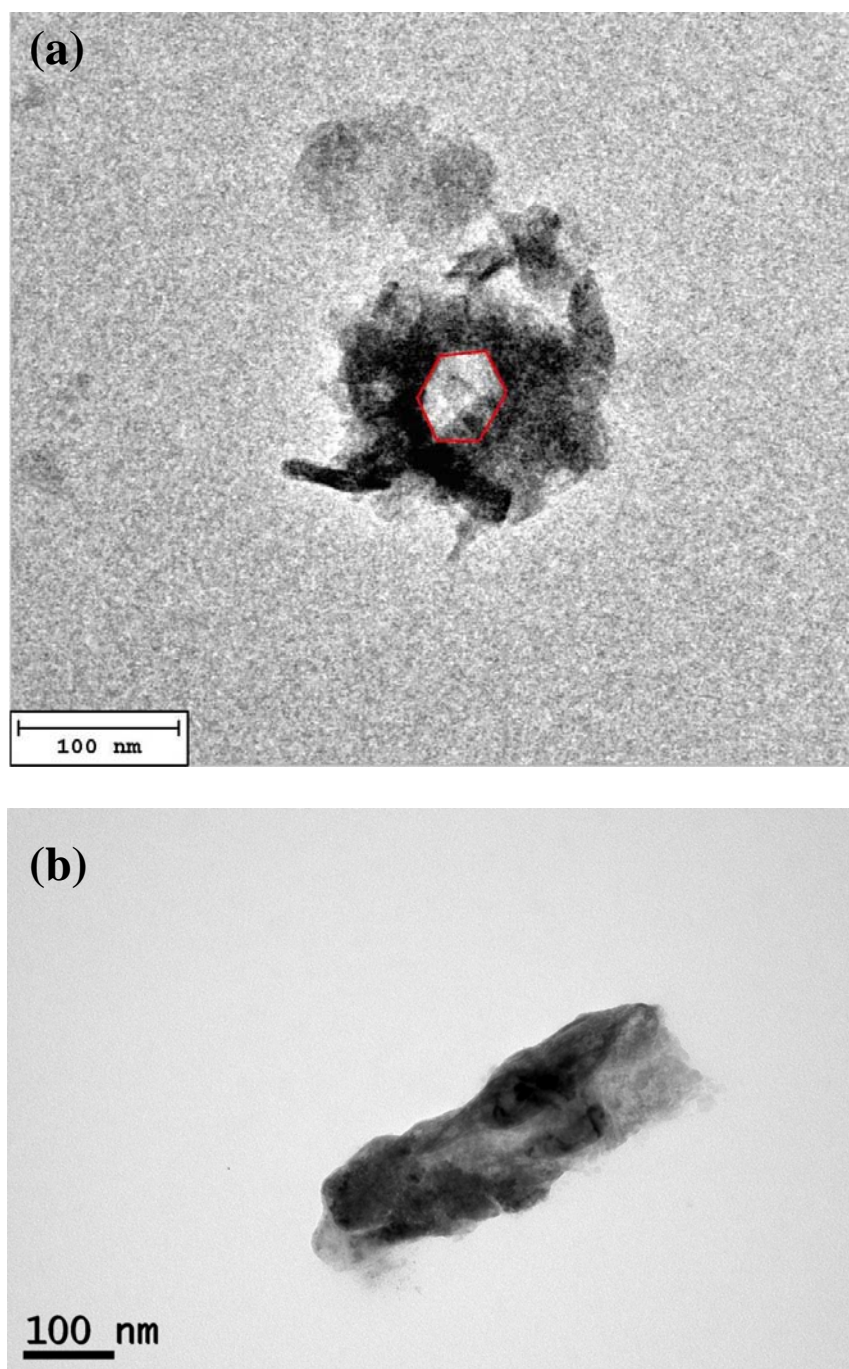


Fig. S2 (a) Top-view and (b) side-view TEM micrographs of nickel hydroxide nanotube.

Figure S3 shows the XRD patterns of the ZnO template, Ni(OH)₂ nanotubes, and Ni(OH)₂ nanotubes after etching with NaOH solution. The XRD pattern of the as-prepared zinc oxide can be assigned as hexagonal ZnO (JCPDS No. 36-1451). In addition to the characterization peaks of ZnO template, the diffraction peaks which can be characterized as α -Ni(OH)₂ (JCPDS No. 22-0444) appear after the hydrolysis of Ni²⁺. Only the diffraction peaks of α -Ni(OH)₂ can be detected after etching with NaOH solution, meaning that most of the unreacted ZnO has been removed from the Ni(OH)₂ nanotube arrays.

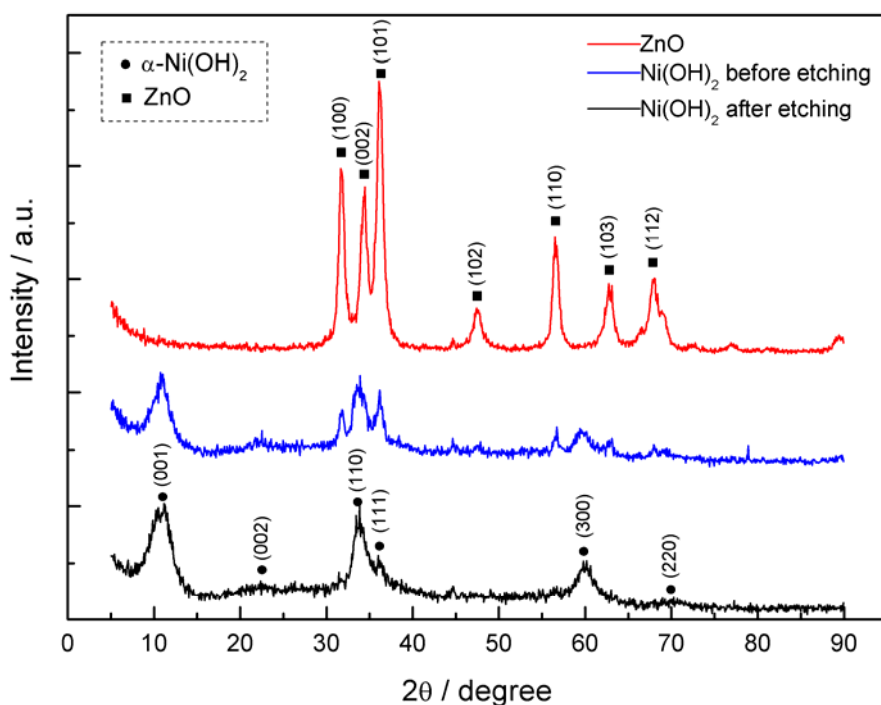


Fig. S3 XRD diffraction patterns of the zinc oxide rods, nickel hydroxide nanotubes before etching, and nickel hydroxide nanotubes after etching.

Cycle-life stability and capacitance retention

The electrode materials used in electrochemical capacitors and batteries are expected to have long cycle lives. In this study, the cycle-life stability of nickel hydroxide electrodes was carried out by galvanostatic charging/discharging at 4 A g⁻¹ for 1000 cycles. Figure S4 shows the relationship between specific capacitance and

cycle number for nickel hydroxide electrodes. The specific capacitance of the electrode decreases with increasing numbers of charging/discharging cycles, it decreases to approximately 570 F g^{-1} after 1000 cycling tests. Therefore, the cycle performance of the nickel hydroxide electrode needs to be improved in the future. Probably, the capacitance loss of nickel hydroxide during successive charging and discharging cycles is attributed to the oxygen evolution reaction, which can be mitigated by modifying the surface of the nickel hydroxide electrode with cobalt or cobalt oxide.^{1,2}

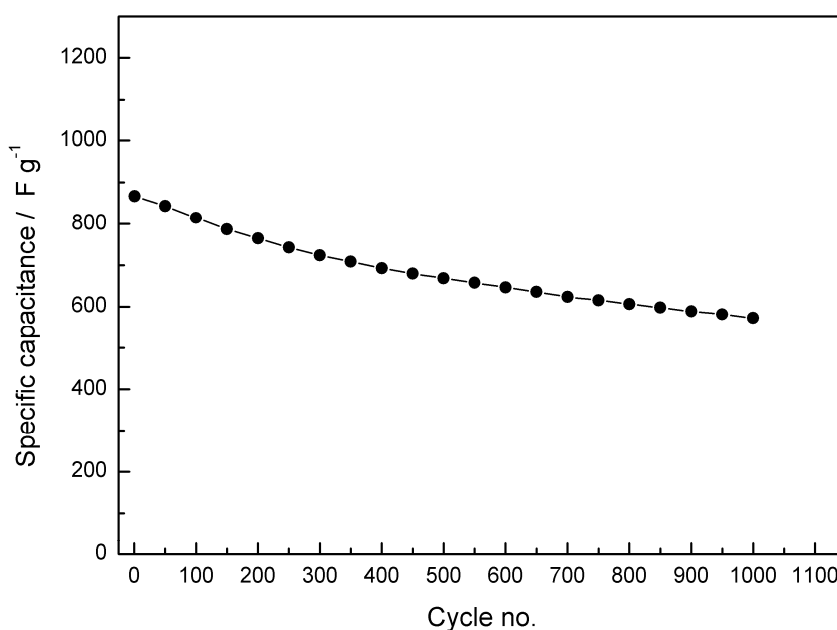


Fig. S4 Relationship between capacitance retention and cycle number of nickel hydroxide electrode with nanotube arrays.

In comparison with Ni(OH)_2 nanotube electrode, the solid Ni(OH)_2 electrode (compact film electrode) was prepared by cathodic deposition in a bath consisted of 0.1 M nickel nitrate and 0.1 M potassium nitrate. Figure S5 shows the specific capacitances of the nickel hydroxide electrodes at various discharge current densities. These two electrodes showed higher specific capacitances at low current density than those at high current density. A nickel hydroxide electrode with open-ended hollow nanotubes exhibited superior capacitance at all discharging rates compared with solid nickel hydroxide electrode. The specific capacitance of the nickel hydroxide electrode with open-ended hollow nanotubes reaches 767 F g^{-1} , which is much higher than that of the

solid nickel hydroxide electrode (426 F g^{-1}) at a high discharging current density of 10 A g^{-1} . The open-ended hollow nanotubes allow electrolyte ions to readily penetrate into the nanotube array electrode and access their internal surfaces, while porous wall composed of nanoplatelets provides short diffusion distance to facilitate the ion transport in the solid phase. Thus, the capacitive behavior of a nickel hydroxide electrode with open-ended hollow nanotubes is significantly improved.

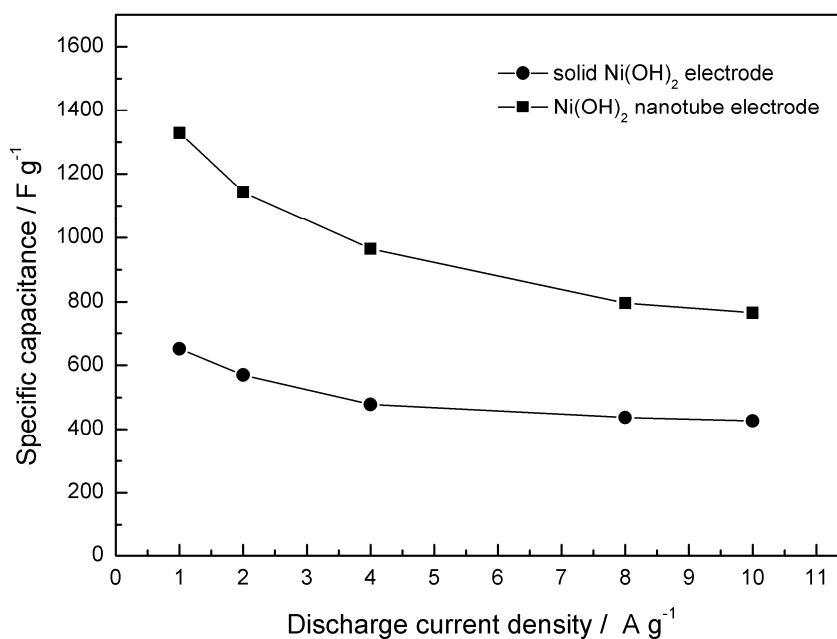


Fig. S5 Specific capacitances of the nickel hydroxide electrodes at various discharge current densities.

References

1. X. Wang, H. Luo, H. Yang, P. J. Sebastian and S. A. Gamboa, *Int. J. Hydrogen Energy*, 2004, **29**, 967.
2. Z. Chang, H. Li, H. Tang, X. Z. Yuan and H. Wang, *Int. J. Hydrogen Energy*, 2009, **34**, 2435.