# Controlled reverse pulse electrosynthesized spike-piece-structured Ni/Ni(OH)$_2$ interlayer nanoplates for electrochemical pseudocapacitor application

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## Experimental

All of the chemicals were commercially available and used without further purification.

### Controlled reverse pulse electrosynthesis of Ni/Ni(OH)$_2$ hybrid electrode

The pulse electrosynthesis were carried out by Pulse Reverse Power Supply (Type: pe86CB-20-5-25-S/GD) of plating electronic GmbH, Germany. The output current of the power supply is controlled with a high-voltage bipolar square pulse generator which produces both unipolar and bipolar high-powered perfect square pulses. A standard two electrode plating cell has been used for Watt's bath prepared by mixing 240 g L$^{-1}$ nickel sulphate, 30 g L$^{-1}$ nickel chloride, 30 g L$^{-1}$ boric acid in double distilled water where nickel plate has been used as anode and pure copper foil as a cathode. Prior to deposition, the copper surface was first degreased with acetone and subsequently dipped in dilute sulphuric acid to remove any oxides present on the copper surface. The loading area of all the samples was defined as 1.0 cm$^2$. A galvanostatic unit keeps the average current density ($I_A$), during the pulse duration ($t_{on}$) constant as per pulse modulation applied. The Ni films on a cleaned copper surface have been developed by a controlled reverse pulse modulated electrochemical approach at an average current density of 50 mA cm$^{-2}$ for 5 minutes. After deposition, the samples were removed carefully and washed with deionised water to remove excessive electrolyte and finally dried in a vacuum oven at 60 °C for 1 h. For *in situ* growth of well crystalline Ni/Ni(OH)$_2$ hybrid nanostructure, we have soaked the samples 24 hours in 6 M KOH solution and perform mild sonication at every 4 hour interval. The as-prepared electrodes were washed with water and ethanol several times.

### Material characterization

The size and surface morphology of as-synthesized samples were characterized by field-emission scanning electron microscopy(FE-SEM)(Model:Carl Zeiss SUPRA 55VP with accelerating voltage at 5 kV), transmission electron microscopy (TEM) (Model: TEM, Tecnai™ G2 F20, FEI) and X-ray diffraction (XRD; PW3040/60 X'pert PRO (PANalytical), Cu $K_\alpha$ radiation, $\lambda = 1.5414$ Å).The chemical state and composition of the products were analyzed by X-ray photoelectronspectroscopy (XPS) using a Thermo Scientific model MULTILAB 2000 system X-ray photoelectron spectrometer with twin anode Mg/Al (300/400W) X-ray source.

### Electrochemical measurements

Cyclic voltammetry (CV) and galvanostatic charge–discharge(GCD) measurements were conducted using a standard electrodecell with a conventional three- and two-electrode configuration, respectively onan IVIUMSTAT electrochemical workstation (Ivium Technologies BV Co., Holland).The Ag/AgCl electrode (saturated KCl) and a platinum foil (1.0 cm x 1.0 cm)were used as the reference electrode and counter electrode, respectively. Cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurements were performed in a 1.0 M KOH solution at room temperature.

### Fundamental aspects of pulse electrosynthesis[1,2]

Electrosynthesis of nanostructured materials using pulsed currents is known as pulse electrosynthesis. It is a well established technique.[1] The pulsed currents can be unipolar (on-off) or bipolar (current reversal). Pulses can be used along or be superimposed on a DC feed. In the bipolar pulse, metal deposition occurs in the cathodic pulse period whereas a limited amount of metal is being re-dissolved in the anodic period. This repeated deposition and partial re-dissolution could improve the morphology and the physical properties of the deposit. Basically two fundamental factors are responsible for a high nucleation rate (current density) and a slow grain growth (inhibiting molecules) which led to the formation of nanostructured morphology. In case of direct current (DC) plating, there is only one parameter i.e., current density (*I*) can be varied whereas pulse reverse current (PRC) method it depends on multiple factors like: cathodic current density, forward cathodic time, anodic current density and reverse anodic time. The average current density for pulse reverse current (PRC) technique can be represented by the following equation[3]

$$\overline{I_\mathrm{A}} = \frac{I_\mathrm{c} \times t_c - I_\mathrm{a} \times t_a}{t_c + t_a} \tag{2}$$

In the above mentioned equation, the terms involved having usual meaning like $I_c$, $t_c$, $I_a$ and $t_a$ are cathodic current density, forward cathodic time, anodic current density and reverse anodic time, respectively.

Fig. S1 shows a schematic diagram for square wave reverse pulse modulation approach. Basically this is a process of pulse-on-pulse reverse method where during anodic scan, partial dissolution of deposited material is taking place. Here we have to select the pulse width and pulse amplitude in such a way that we can get a desired morphology. For that, we have optimised the pulse width and amplitude of peak current in such a way that it activates the growth centres and leading to larger grain size. Finally, we have optimized and selected the ratio of cathodic to anodic pulse current amplitude as $I_c/I_a \geq 4$ and the ratio of cathodic to anodic pulse width also be $t_c/t_a \geq 4$. The as-synthesized active material is also following an anisotropic growth self-assembly mechanism, where the individual nanoplates are minimizing the extraordinarily high surface energy and forming a spike-piece-structured Ni/Ni(OH)$_2$ interlayer nanoplates at an average current density of 50 mA cm$^{-2}$.

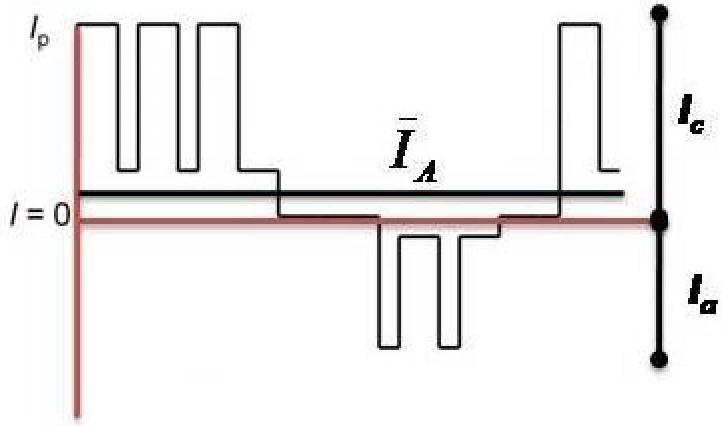

**Fig. S1** Schematic for controlled reverse pulse modulated approach for electrosynthesis of Ni/Ni(OH)$_2$ hybrid morphology.

The post-mortem XRD analysis of Ni/Ni(OH)$_2$ hybrid electrodes by DC and controlled reverse pulse modulated approach has been shown in Fig. S2. The close examination of this result reveals that there is a disappearance of peaks in the case of DC deposited electrode after 5000 cycles whereas almost all the peaks are intact except with small reduction in peak intensity for controlled reverse pulse modulated approach synthesized Ni/Ni(OH)$_2$ hybrid electrode. Also a small peak shift for controlled reverse pulse modulated approach sample has been noticed and it can be attributed to internal strain or a chemical reaction (like oxidation) which might change locally the stoichiometry and hence the peaks of Ni shifted to higher angles. The morphological modulation and phase conversion of Ni(OH)$_2$ in complex architectures of Ni/Ni(OH)$_2$ electrode materials in the controlled reverse pulse modulated approach has not changed much even after extensive 5000 cycling.

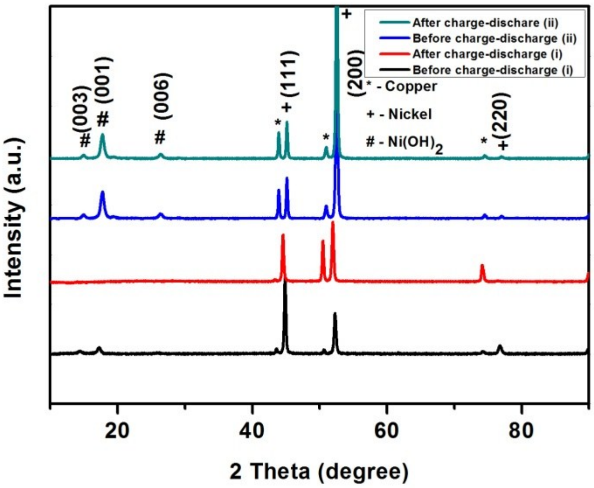

**Fig. S2** Post-mortem XRD analysis of Ni/Ni(OH)$_2$ hybrid electrodes by DC (i) and controlled reverse pulse modulated approach (ii) before and after 5000 charge–discharge cycles.

The close examination of the initial few cycles of cyclic voltammogram (Fig S3A), clearly indicates that the peak potential position changes greatly and appearance of peaks observed after few cycles (i.e., 900th cycle) along with the negative shift in peak potential. It means that the electrochemical performance is not very stable over the first few cycles and appearance of additional peak at 0.3 V is due to the phase transformation where one phase of Ni(OH)$_2$/NiOOH redox couple is transforming to another phase. The initial process will activate the electrode. Fig S3B shows the hybrid electrode materials are again restoring the same phase after 5000th cycle along with additional peak at 0.3 V. But from 900th to 5000th cycle, though the current signals related to the redox reactions of the active material change very little, the current of the oxygen evolution reaction increases at a higher positive potential which contributes to the calculated capacitance.[4] Finally, the morphological modulation and phase conversion of Ni(OH)$_2$ in complex architectures of Ni/Ni(OH)$_2$ electrode are getting saturated between 900th to 5000th cycle and reduces the strain in the interlayer structure and acts as a ion-buffering reservoir for OH$^-$ ions and giving excellent cycling performance.

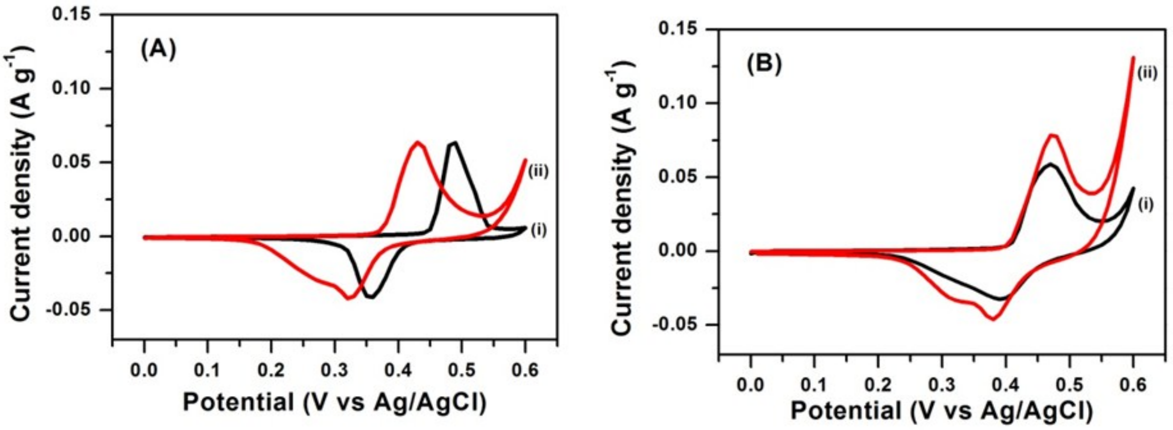

**Fig. S3** Post-mortem CV analysis of Ni/Ni(OH)$_2$ hybrid electrodes by DC (i) and controlled reverse pulse modulated approach (ii) at (A) 900th cycles and (B) 5000th cycles, respectively.

To understand the morphological changes due to phase transformations, we have performed scanning electron microscopy (SEM) analysis for Ni/Ni(OH)$_2$ hybrid electrodes for both the samples i.e., as-deposited and after 5000 electrochemical cycling and shown in Fig. S4. The change in morphology of cycled DC deposited sample is observed more than that of controlled reverse pulse modulated approach deposited sample. It indicates the recrystallization and mass transfer process in the activated material during electrochemical cycling. This could lead to the growth of particle size and crystal size; and probably the reason of decay of specific capacitance.[5]

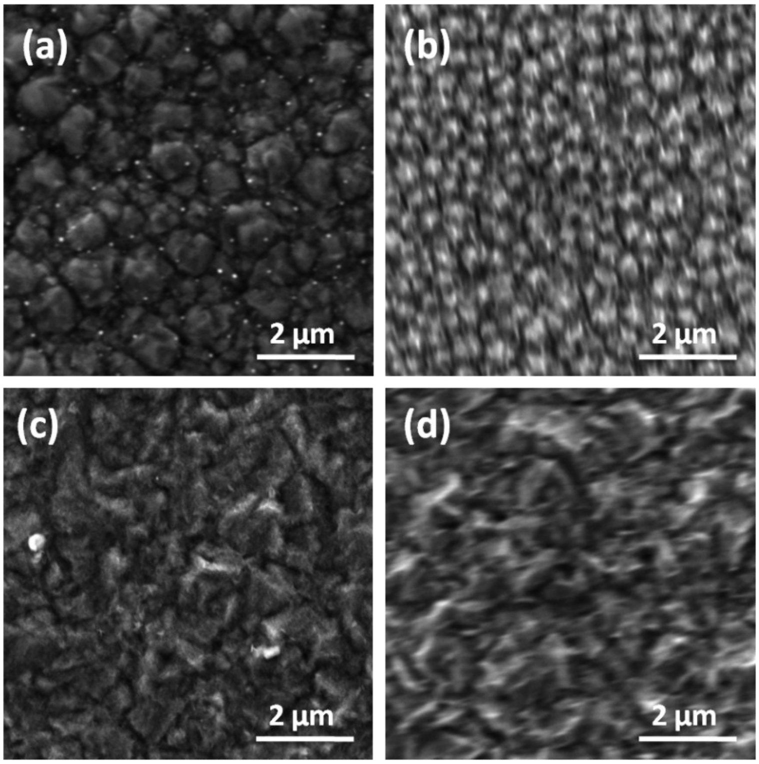

**Fig. S4** SEM images (10 kx) of Ni/Ni(OH)$_2$ hybrid electrodes by DC: (a) as-deposited, (b) after 5000 cycles; and controlled reverse pulse modulated approach (c) as-deposited, (d) after 5000 cycles.

## Notes and references

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