Supporting Information

Engineering High Reversibility and Fast Kinetics of Bi Nanoflakes by Surface Modulation for Ultrastable Nickel-Bismuth Batteries

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Experimental details

Synthesis of Bi and BiO\(_x\) sample on carbon cloth: Bi was prepared by electrodeposition at -0.8 V for 20 min at room temperature. The electrolyte for electrodeposition was a mixed solution by dissolving 1 mmol Bi(NO\(_3\))\(_3\)·5H\(_2\)O, 4 mmol ETDA and 1 mmol hexadecyltrimethylammonium bromide (CTMAB) into 20 mL distilled water. After electrodeposition, the obtained sample was washed with distilled water and dried in a vacuum oven at 60 °C. To realize the surface oxidation of Bi (BiO\(_x\)), the as-prepared Bi sample was further undergoing controllable successive water oxidation process by atomic layer deposition (ALD) technology (ALD-SC6-PE, Syskey Technology Co., Ltd.). Additionally, the as-prepared Bi sample was also calcined at 200 °C for 5 min in air to complete the surface oxidation of Bi.

Synthesis of Ni-NiO on carbon cloth: Ni-NiO was prepared by electrodeposition of Ni and followed by oxidation. The electrodeposition of Ni was conducted at -1.4 V for 15 min at room temperature. Electrolyte for electrodeposition (20 mL) contain 5 mmol Ni(NO\(_3\))\(_2\)·6H\(_2\)O, 5 mmol NiCl\(_2\), 25 mmol H\(_3\)BO\(_3\) and 1.735 mmol sodium lauryl sulfate. After electrodeposition, the as-prepared sample was washed with distilled water and then oxidized by sonicating in the solution containing 35 mL 4 M HCl and 15 mL ethanol for 5 min. The as-obtained sample was placed under ambient conditions for 15 min to derive Ni-NiO electrode at room temperature.

Structural Characterization: the microstructures and compositions of the electrode materials were analyzed using field-emission SEM (FE-SEM, JSM-6330F), transmission electron microscopy (TEM, FEI Tecnai G2 F30), Raman spectroscopy (Renishaw inVia), and X-ray diffractometry (XRD, D8 ADVANCE). XPS was carried out at BL10B and BL12B beamlines in NSRL, Hefei. Thermogravimetric analysis (TGA) curves were conducted by using a Netzsch TG209F1 analyzer. The thickness and the morphology of the BiO\(_x\) nanoflakes were measured in air using Digital Instrument Shimadzu AFM (SPM-9500J3) with a silicon microcantilever (spring constant of 30 N m\(^{-1}\) and resonance frequency of ~270 kHz). The ultrasounding was carried out using a Shumei ultrasound cleaner (KQ-400DE) with power of 400 W and frequency of 40 kHz. The in situ Raman test was run on a laser micro-Raman spectrometer (Renishaw inVia) equipped with a He-Ne laser (wavelength = 514.5 nm) and a long working distance 50× objective lens. Raman spectra of the sample were captured with exploration time of 30 s after certain cycles of CV test in a three electrode cell at a scan rate of 100 mV s\(^{-1}\).

Electrochemical Measurement: cyclic voltammetry (CV), galvanostatic charge/discharge measurements and electrochemical impedance spectroscopy were conducted employing an electrochemical workstation (CHI 760E). The electrochemical studies of the individual electrode were performed in a three-electrode cell, with a carbon rod auxiliary electrode and a saturated calomel electrode (SCE) reference electrode. All the electrochemical characterizations for electrodes and aqueous Ni//Bi battery were performed in 1 M KOH aqueous solution.
Calculations:

1. Single Electrode:

The areal capacities of the Bi, BiOₓ and NiO electrodes were measured by galvanostatic charge/discharge method based on the following equation:

\[ C_s = \frac{\int_0^{\Delta t} I \times dt}{S} \]  \hspace{1cm} (1)

where \( C_s \) (mA h cm\(^{-2}\)) is the areal capacity, \( I \) (mA) is the constant discharging current, \( \Delta t \) (h) is the discharging time and \( S \) (cm\(^2\)) is the area of electrode.

2. Ni//Bi battery:

The areal capacities of the Ni//Bi battery (\( C_{cell-a} \)) were measured by galvanostatic charge/discharge method based on the following equation:

\[ C_{cell-a} = \frac{\int_0^{\Delta t} I \times dt}{S} \]  \hspace{1cm} (2)

where \( C_{cell-a} \) (mA h cm\(^{-2}\)) is the areal capacity of the Ni//Bi battery, \( I \) (mA) is the constant discharging current, \( \Delta t \) (h) is the discharging time and \( S \) (cm\(^2\)) is the area of the Ni//Bi battery.

The energy density \( E \) and specific power density \( P \) of the Ni//Bi battery were obtained from the following equations:

\[ E = \frac{\int_{V_1}^{V_2} C_{cell} \times dV}{d} \]  \hspace{1cm} (3)

\[ P = \frac{E}{1000 \times \Delta t} \]  \hspace{1cm} (4)

where \( E \) (mWh cm\(^{-3}\)) is the energy density of the Ni//Bi battery, \( C_{cell} \) is the specific areal capacity obtained from Equation (4), \( V \) (V) is the voltage window and \( d \) is the thickness of the Ni//Bi battery (0.08 cm). \( P \) (W cm\(^{-3}\)) is the specific power density of the Ni//Bi battery and \( \Delta t \) (h) is the discharging time.

DFT Calculations:

All the calculations were performed based on density functional theory (DFT) implemented in The Vienna Ab-initio Software Package (VASP). The generalized
gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE) function was used to calculate the electron exchange-correlation interactions. All atomic positions and lattice vectors were fully optimized using a conjugate gradient algorithm to obtain the unstrained configuration. The plane wave is set to an energy of 600 eV. To model the surface of Bi and O doping in Bi solid solution, we use a (2×2) periodic slab models with four atomic layers combined with a 15 Å vacuum layer along the Z axis to eliminate the interaction between the slabs. The Brillouin zone integrations were performed using a 5×5×1 Monkhorst–Pack grid for (012) surfaces. In the slab calculations, the atoms in the bottom layer of the slab are fixed and other bottom atoms are allowed to relax. The atomic relaxation will be stop as soon as the energies within $1.0 \times 10^{-5}$ eV/atom for total energy and the same the force on each atom is smaller than 0.01 eV/Å for force on every atom. The adsorption energies ($E_{ads}$) are calculated using following Equation:

$$E_{ads} = E_{ads} - (E_{slab} + E_{OH^-})$$  \hspace{1cm} (5)

where $E_{ads}$, $E_{slab}$, and $E_{OH^-}$ correspond to the total energy of an adsorbate bound to the Bi or Bi with O doping (012) surface, a bare Bi or Bi with O doping (012) surface and an isolated OH$^-$ group, respectively. By this definition, a negative value, corresponding to an exothermic process, indicates a stable adsorption.
Fig. S1 SEM image of the pristine Bi sample.

Fig. S2 TEM image of the pristine Bi sample.
Fig. S3 Raman spectra of the pristine Bi and BiO$_x$ electrodes.

Fig. S4 CV curves of the (a) pristine Bi and (b) BiO$_x$ electrodes at various scan rates.
Fig. S5 Determination of the b-value using the relationship between anode and cathode peak currents and scan rates. (a) is pristine Bi and (b) is BiO\textsubscript{x} electrodes.

Fig. S6 Discharge curves of the (a) pristine Bi and (b) BiO\textsubscript{x} electrodes at various current densities.
Fig. S7 Nyquist plots of the pristine Bi and BiO$_x$ electrodes.

Fig. S8 SEM images of the pristine Bi electrode after certain cycles test.
Fig. S9. SEM images of the BiOₓ electrode after certain cycles test.

Fig. S10 Concentration of Bi in electrolyte for the pristine Bi and BiOₓ electrodes after 20000 cycles test.
Fig. S11  (a) Ratio of O/Bi for the pristine Bi and BiOₓ electrodes with different oxidation degree. (b) TGA results for the BiOₓ electrodes with different oxidation degree.

Fig. S12 Cycling performance of the pristine Bi and BiOₓ electrodes with different oxidation degree for 20000 cycles tested at 100 mV s⁻¹.
Fig. S13 Discharge curves of the pristine Bi and BiOₓ electrodes with different oxidation degree at (a) 40 mA cm⁻² and (b) 6 mA cm⁻².

Fig. S14 Raman spectra of the pristine Bi and BiOₓ electrodes after 20000 cycles test.

Table S1 The ratios of O/Bi for the pristine Bi and BiOₓ electrodes after certain cycles.

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>10</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>500</th>
<th>1000</th>
<th>5000</th>
<th>1000</th>
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</thead>
<tbody>
<tr>
<td>Pristine Bi</td>
<td>0.23</td>
<td>0.59</td>
<td>0.74</td>
<td>0.89</td>
<td>0.95</td>
<td>1.02</td>
<td>1.07</td>
<td>1.14</td>
<td>1.21</td>
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<tr>
<td>BiOₓ</td>
<td>0.52</td>
<td>0.54</td>
<td>0.53</td>
<td>0.55</td>
<td>0.55</td>
<td>0.56</td>
<td>0.58</td>
<td>0.63</td>
<td>0.69</td>
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</table>
Fig. S15. SEM images of BiO$_x$ electrode after ultrasounding for 1h.

Fig. S16 Cycling performance of the Bi electrode annealed at 200 °C for 5 min in air tested at 100 mV s$^{-1}$ for 20000 cycles.

Fig. S17 (a) SEM image (b) XRD pattern of the as-prepared Ni-NiO electrode.
Fig. S18 (a) CV curves (b) Areal capacity and capacity retention as a function of current density obtained from discharge curves. (c) Nyquist plots of the Ni-NiO electrode.

Fig. S19 (a) CV curves collected for Ni-NiO cathode and BiO$_x$ anode at a scan rate of 40 mV s$^{-1}$. (b) CV curves collected for the Ni//Bi battery at various voltage windows at a scan rate of 100 mV s$^{-1}$. (c) CV curves collected for the Ni//Bi battery.

Fig. S20 Cycling performance and Coulombic efficiency of the Ni//Bi battery tested at 40 mA cm$^{-2}$ for 5000 cycles.
Table S2 Comparison of the cycling performance of the Ni/Bi battery with recently reported aqueous rechargeable batteries.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Cathode</th>
<th>Cycling performance</th>
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<tbody>
<tr>
<td>BiO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Ni-NiO</td>
<td>96% after 5000 cycles (This work)</td>
</tr>
<tr>
<td>Bi</td>
<td>NiCO&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>89% after 1000 cycles&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Bi/C</td>
<td>Ni-NiO</td>
<td>94% after 5000 cycles&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>FeO&lt;sub&gt;x&lt;/sub&gt;/graphene</td>
<td>Ni(OH)&lt;sub&gt;2&lt;/sub&gt;/MWNT</td>
<td>~80% after 800 cycles&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>CNTs/Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>CNTs/Ni(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>89.1% after 1000 cycles&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>CC–CF@Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>CC–CF@NiO</td>
<td>70.5% after 2000 cycles&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>Zn nanoflakes</td>
<td>nickel cobalt hydroxide</td>
<td>60% after 1000 cycles&lt;sup&gt;6&lt;/sup&gt;</td>
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<tr>
<td>CC-CF@ZnO</td>
<td>CC-CF@NiO</td>
<td>72.9% after 2400 cycles&lt;sup&gt;7&lt;/sup&gt;</td>
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<td>Zn</td>
<td>P–NiCo&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;x</td>
<td>73.8% after 5000 cycles&lt;sup&gt;8&lt;/sup&gt;</td>
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<tr>
<td>Zn</td>
<td>Co-doped-Ni(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>88% after 5000 cycles&lt;sup&gt;9&lt;/sup&gt;</td>
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<tr>
<td>Zn@CF</td>
<td>Co&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>80% after 2000 cycles&lt;sup&gt;10&lt;/sup&gt;</td>
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<tr>
<td>CC-ZnO@C-Zn</td>
<td>Co(CO)&lt;sub&gt;3&lt;/sub&gt;·0.5(OH)&lt;sub&gt;x&lt;/sub&gt;·0.11H&lt;sub&gt;2&lt;/sub&gt;O@CoMoO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>71.1% after 5000 cycles&lt;sup&gt;11&lt;/sup&gt;</td>
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<tr>
<td>Zn</td>
<td>Co(III) rich-Co&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>92% after 5000 cycles&lt;sup&gt;12&lt;/sup&gt;</td>
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<tr>
<td>Zn</td>
<td>V&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;·H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>60% after 200 cycles&lt;sup&gt;13&lt;/sup&gt;</td>
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<tr>
<td>Zn</td>
<td>Zn&lt;sub&gt;3&lt;/sub&gt;V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;(OH)&lt;sub&gt;2&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>68% after 300 cycles&lt;sup&gt;14&lt;/sup&gt;</td>
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<tr>
<td>Zn</td>
<td>VO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>91.2% after 300 cycles&lt;sup&gt;15&lt;/sup&gt;</td>
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<td>Zn</td>
<td>V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;·nH&lt;sub&gt;2&lt;/sub&gt;O/graphene</td>
<td>71% after 900 cycles&lt;sup&gt;16&lt;/sup&gt;</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn&lt;sub&gt;n&lt;/sub&gt;0.25V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;·nH&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>~80% after 1000 cycles&lt;sup&gt;17&lt;/sup&gt;</td>
</tr>
<tr>
<td>Zn</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;V&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;16&lt;/sub&gt;·3H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>~80% after 1000 cycles&lt;sup&gt;18&lt;/sup&gt;</td>
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<tr>
<td>Zn</td>
<td>Na&lt;sub&gt;0.33&lt;/sub&gt;V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>93% after 1000 cycles&lt;sup&gt;19&lt;/sup&gt;</td>
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<tr>
<td>Zn</td>
<td>Zn&lt;sub&gt;2&lt;/sub&gt;(OH)VO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>89% after 2000 cycles&lt;sup&gt;20&lt;/sup&gt;</td>
</tr>
<tr>
<td>Zn</td>
<td>Ca&lt;sub&gt;0.25&lt;/sub&gt;V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;·nH&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>78% after 5000 cycles&lt;sup&gt;21&lt;/sup&gt;</td>
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<tr>
<td>Zn</td>
<td>ZnMn&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;/C</td>
<td>94% after 500 cycles&lt;sup&gt;22&lt;/sup&gt;</td>
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<td>Zn</td>
<td>MnO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>94% after 2000 cycles&lt;sup&gt;23&lt;/sup&gt;</td>
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<tr>
<td>Zn</td>
<td>MnO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>92% after 5000 cycles&lt;sup&gt;24&lt;/sup&gt;</td>
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References: