**Supporting Information**

**Electrosynthesis of NiPₓ nanospheres for electrocatalytic hydrogen evolution from a neutral aqueous solution**

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General Materials and Instruments:

All chemical reagents were purchased from commercial suppliers and used as received without further purification. Milli-Q water of 18 MΩ cm was used in all experiments. SEM images were observed on a Hitachi SU8020 cold-emission field emission scanning electron microscope (FE-SEM) with an accelerating voltage of 5 kV. The morphology was also examined by TEM (FEI, Tecnai G2 F20). The EDX spectra of the catalyst coated on carbon cloth and blank carbon cloth were obtained by a FEI Quanta 200. XPS was performed on a Kratos AXIS ULTRA using monochromatic Al Kα X-ray (hν = 1486.6 eV) with photoelectron take-off angle of 90° with respect to surface plane. The C 1s peak at 284.6 eV from the adventitious carbon was used for binding energy calibration. The amount of Ni loaded on the CC electrode was detected by aurora M90 of Bruker. Bruker D8 ADVANCE (Cu Kα radiation) in the grazing incidence measurement mode was used to record XRD patterns of the catalyst coated on an ITO electrode.

Electrochemical studies:

All electrochemical experiments were carried out at 25 °C using CH Instruments (model CHI 660D Electrochemical Analyzer). Prior to the electrosynthesis of the NiP₃ nanospheres, ITO or carbon cloth was ultrasonically washed with water and acetone to remove residual organic species. The ITO or CC (S = 0.25 cm²) working electrode was immersed into a 10 mL 0.1 M acetate buffer solution (pH = 7) containing 0.05 M Ni(CH₃COO)₂ and 0.1 M NaH₂PO₂. A saturated Ag/AgCl was used as the reference
electrode, and a Pt wire was used as the counter electrode. After 5-cycle CVs between 0.2 V and −0.7 V vs NHE at a scan rate of 50 mV s⁻¹, NiP₃ nanospheres were uniformly generated. All potentials reported in this work were versus NHE unless otherwise stated. Compensation for iR drop was used for all CVs. CPE and polarization curves were recorded in a 15 mL 1 M phosphate buffer solution.
Figure S1. (a) CVs with multiple scan cycles of ITO electrodes in a 0.1 M acetate buffer solution (pH = 7.0) containing different electrolytes and (b) the corresponding enlarged view.
Figure S2. SEM images of an ITO electrode electrodeposited from 5 CV cycles in a 0.1 M acetate buffer solution (pH = 7) with 50 mM Ni(OAc)$_2$ and without NaH$_2$PO$_2$. 
Figure S3. SEM images of ITO electrodes electrodeposited from 5 CV cycles in a 0.1 M acetate buffer solution (pH = 7, Ni-free) (a, b) with only 100 mM NaH$_2$PO$_2$ and (c, d) without NaH$_2$PO$_2$. 
Figure S4. CVs of an ITO electrode electrodeposited from 50 cycles between 0.2 V and \(-0.5\) V vs NHE in a 0.1 M acetate buffer solution (pH = 7.0) containing 50 mM Ni(OAc)$_2$ and 100 mM NaH$_2$PO$_2$. 
Figure S5. SEM images of an ITO electrode electrodeposited from 50 CV cycles between 0.2 V and −0.5 V vs NHE in 0.1 M acetate buffer solution (pH = 7.0) containing 50 mM Ni(OAc)$_2$ and 100 mM NaH$_2$PO$_2$. 

Figure S6. SEM images of the NiPₓ materials synthesized under the potentiostatic mode with the potential at −0.62 V vs NHE from different deposition time.
**Figure S7.** XPS spectrum of the NiPₓ nanospheres electrodeposited on an ITO electrode.
**Figure S8.** Electrodeposition CV of a CC electrode (5 cycles) between 0.2 V and −0.7 V vs NHE in a 0.1 M acetate buffer solution (pH = 7.0) containing 50 mM Ni(OAc)$_2$ and 100 mM NaH$_2$PO$_2$. 
Figure S9. SEM images of a CC electrode electrodeposited from 5 CV cycles between 0.2 V and −0.7 V vs NHE in a 0.1 M acetate buffer solution (pH = 7.0) containing 50 mM Ni(OAc)_2 and 100 mM NaH_2PO_2.
Figure S10. The EDX spectrum of the NiP₅ nanospheres electrodeposited on a CC electrode.
Figure S11. The EDX spectrum of a blank CC electrode.
Figure S12. (left) The XRD patterns of the NiPₓ/CC and blank CC electrodes and (right) the HRTEM image of the NiPₓ on CC.
Figure S13. The SEM image of the NiPₓ/CC electrode after long-term electrolysis.
Figure S14. The SEM images of the NiPₓ/CC electrodes prepared from different CV cycle numbers.
**Figure S15.** The HER activities of the NiP_3/CC electrodes prepared from different CV cycle numbers (left) and the corresponding normalized activities by electrochemical surface areas (right).
Figure S16. (left) The charging currents of NiPₓ/CC electrode recorded in the non-Faradaic potential region at different scan rates and (right) the anodic charging currents at −0.45 V plotted against the scan rates. (a, b) 1-cycle CC; (c, d) 5-cycle CC; (e, f) 10-cycle CC; and (g, h) 15-cycle CC.
Figure S17. (left) The HER activity comparison between the NiPₓ/ITO and NiPₓ/CC electrodes; (right) The normalized activities of the two electrodes by electrochemical surface areas.
Figure S18. (a) The charging currents of NiP$_x$/ITO electrode recorded in the non-Faradaic potential region at different scan rates and (b) the anodic charging currents at $-0.45$ V plotted against the scan rates.
Table S1. Comparison of electrocatalytic HER performances in neutral solution between the NiPₓ nanospheres and published results.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte (PBS)</th>
<th>η_{onset} (mV)</th>
<th>η (mV)@ 10 mA cm⁻²</th>
<th>Loading (mg cm⁻²)</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>NiPₓ</td>
<td>1 M</td>
<td>150@2 mA cm⁻²</td>
<td>230</td>
<td>0.235</td>
<td>This work</td>
</tr>
<tr>
<td>FeP@NPC</td>
<td>1 M</td>
<td>163@2 mA cm⁻²</td>
<td>386</td>
<td>1.4</td>
<td>Nanoscale, 2017, 9, 3555</td>
</tr>
<tr>
<td>FeP/Ti</td>
<td>1 M</td>
<td>122@2 mA cm⁻²</td>
<td>200</td>
<td>1.5</td>
<td>Int. J. Hydrogen Energy, 2015, 40, 5092</td>
</tr>
<tr>
<td>FeP/CC</td>
<td>1 M</td>
<td>112@1 mA cm⁻²</td>
<td>202</td>
<td>1.5</td>
<td>ACS Catal., 2014, 4, 4065</td>
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<tr>
<td>Ni_{3}S_{2}/Ni</td>
<td>1 M</td>
<td>180@2 mA cm⁻²</td>
<td>220</td>
<td>1.5</td>
<td>Int. J. Hydrogen Energy, 2015, 40, 4727</td>
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<tr>
<td>WP₂ NRs</td>
<td>1 M</td>
<td>172@2 mA cm⁻²</td>
<td>298</td>
<td>–</td>
<td>J. Power Sources, 2015, 278, 540</td>
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<tr>
<td>Co-NRCNT</td>
<td>0.1 M</td>
<td>380@2 mA cm⁻²</td>
<td>540</td>
<td>0.28</td>
<td>Angew. Chem. Int. Ed., 2014, 53, 4372</td>
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<td>WP₂ SMPs</td>
<td>0.1 M</td>
<td>143@2 mA cm⁻²</td>
<td>244</td>
<td>0.5</td>
<td>ACS Catal., 2015, 5, 145</td>
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<tr>
<td>WP/CC</td>
<td>1 M</td>
<td>95@2 mA cm⁻²</td>
<td>200</td>
<td>2</td>
<td>ACS Appl. Mater. Interfaces, 2014, 6, 21874</td>
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<tr>
<td>Co-C-N</td>
<td>1 M</td>
<td>186@2 mA cm⁻²</td>
<td>273</td>
<td>–</td>
<td>J. Am. Chem. Soc., 2015, 137, 15070</td>
</tr>
</tbody>
</table>
| MoS₂₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋个百分ツ一 Prisoned carbon nanotubes; SMPs: submicroparticles; Co-C-N: cobalt bonded on carbon materials from carbon and nitrogen hybrid coordination; NPG: nanoporous gold; PBS: phosphate buffer saline; η: overpotential; –: data not available.