

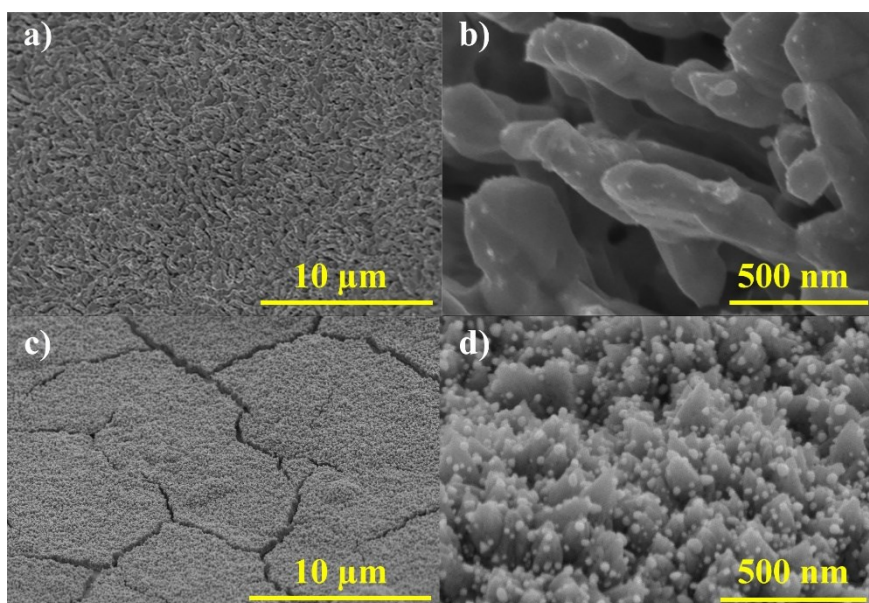
## **Host dependent electrocatalytic hydrogen evolution of Ni/TiO<sub>2</sub> composite**

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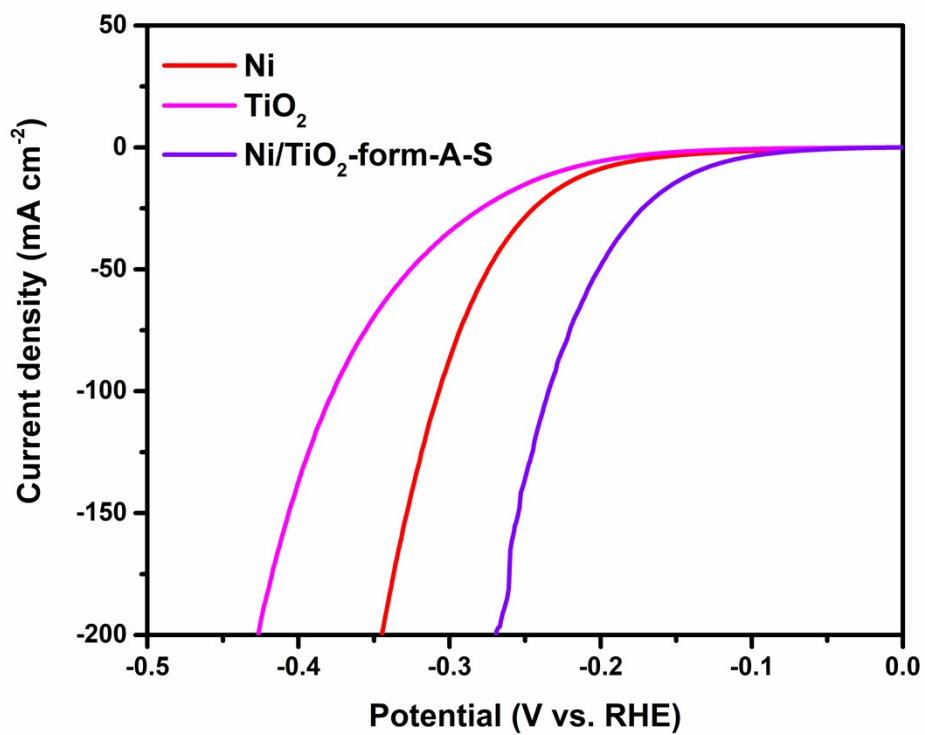
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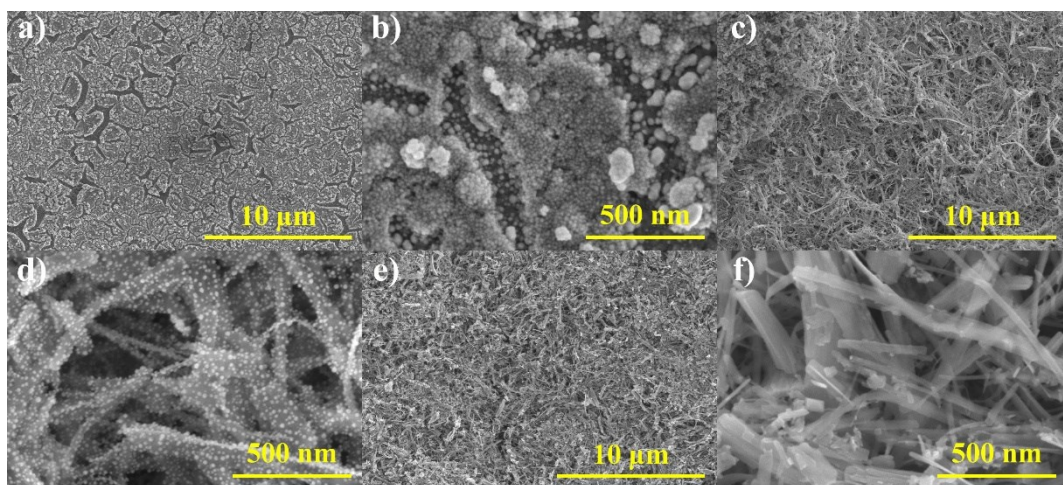
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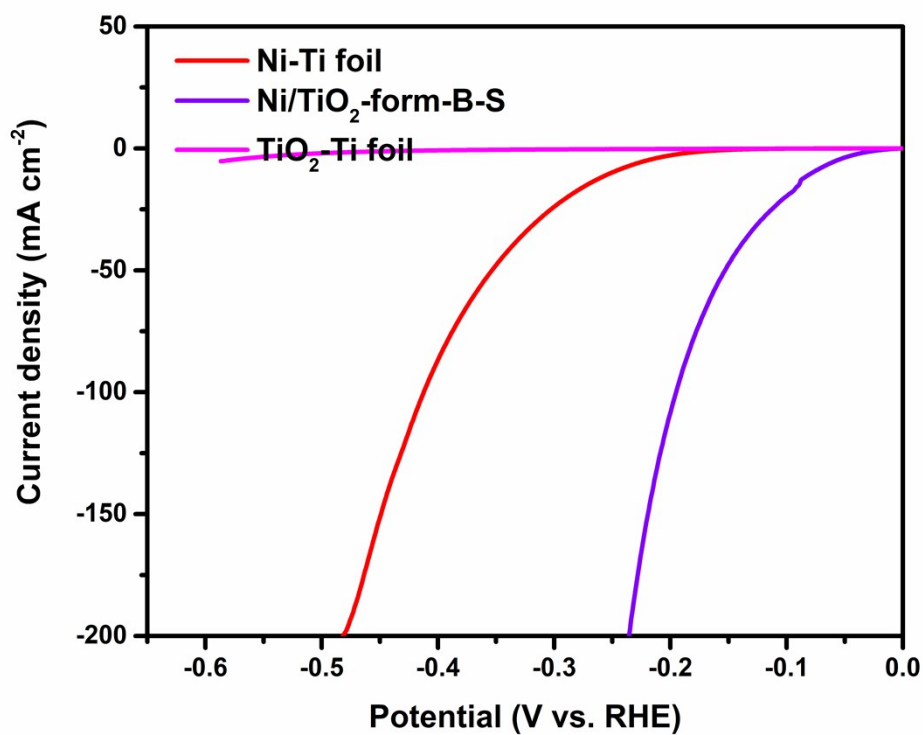
**Figure S1.** The SEM images of Ni (a, b) and Ni/TiO<sub>2</sub>-form-A-S (c, d) samples.



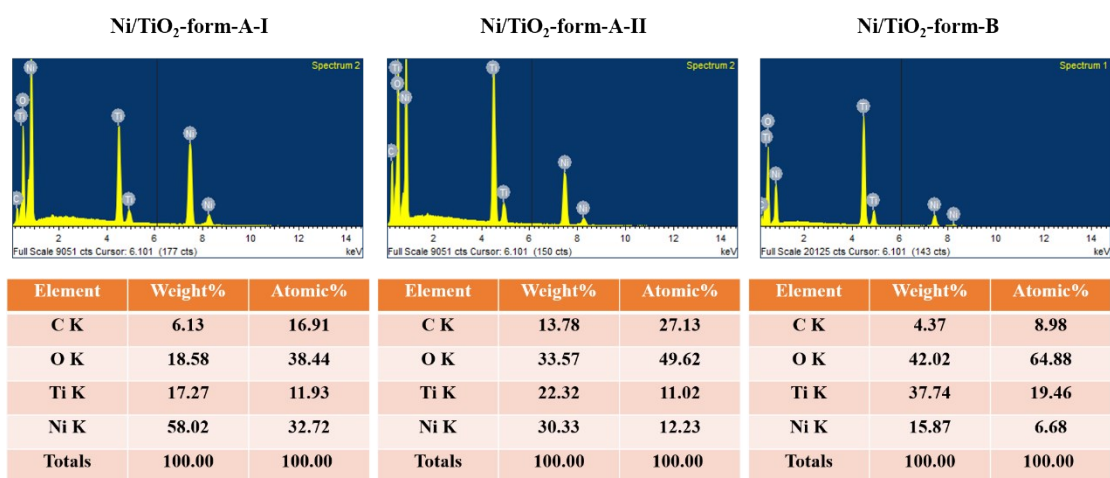
**Figure S2.** The LSV curves of Ni, Ni/TiO<sub>2</sub>-form-A-S and TiO<sub>2</sub> samples.



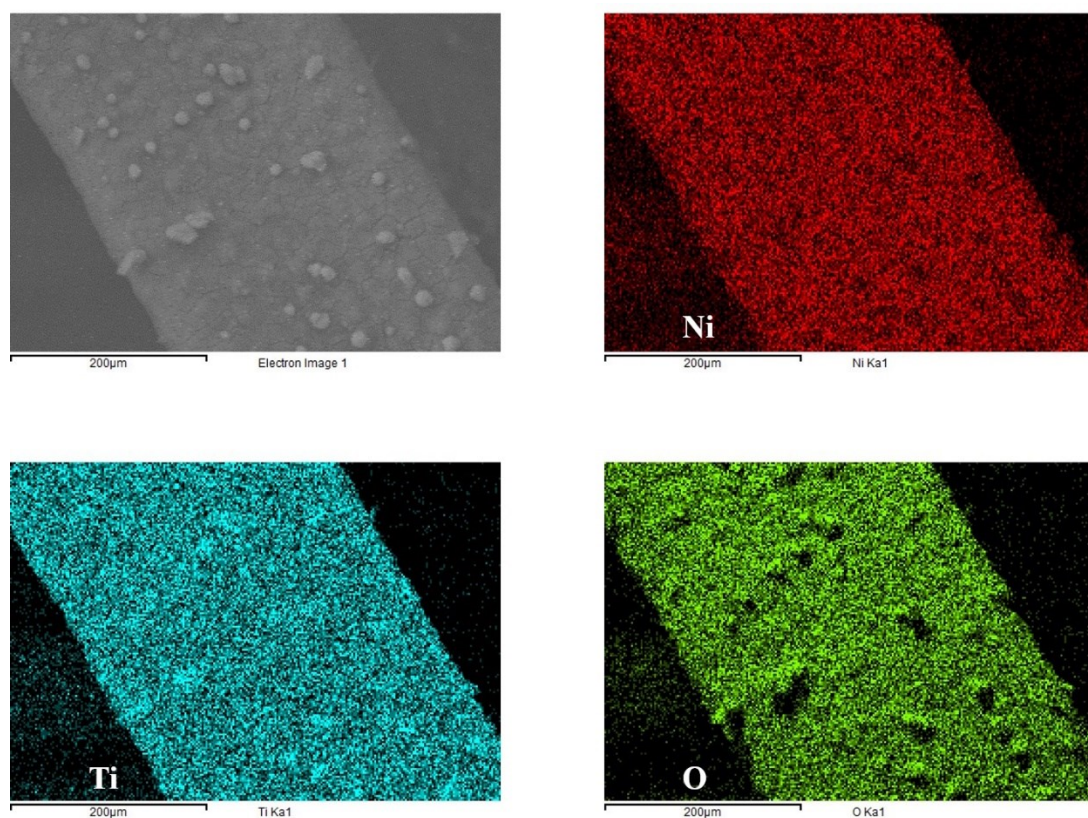
**Figure S3.** The SEM images of Ni-Ti foil (a, b), Ni/TiO<sub>2</sub>-form-B-S (c, d) and TiO<sub>2</sub>-Ti foil (e, f) samples.



**Figure S4.** The LSV curves of Ni-Ti foil, Ni/TiO<sub>2</sub>-form-B-S and TiO<sub>2</sub>-Ti foil samples.

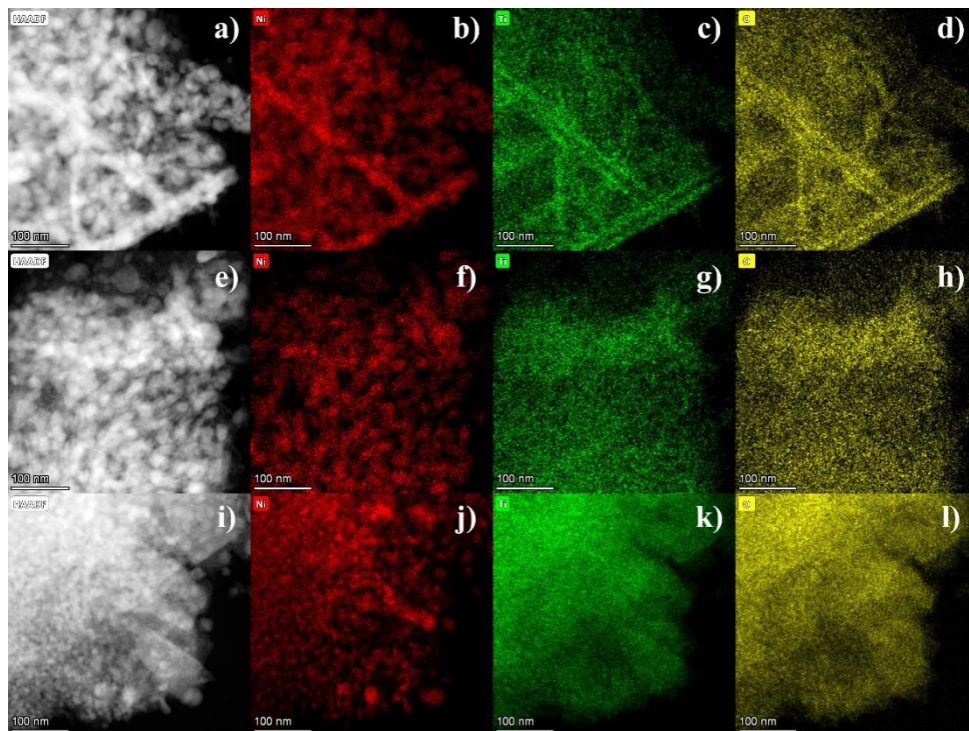


**Figure S5.** The EDS spectra of different Ni/TiO<sub>2</sub> samples.

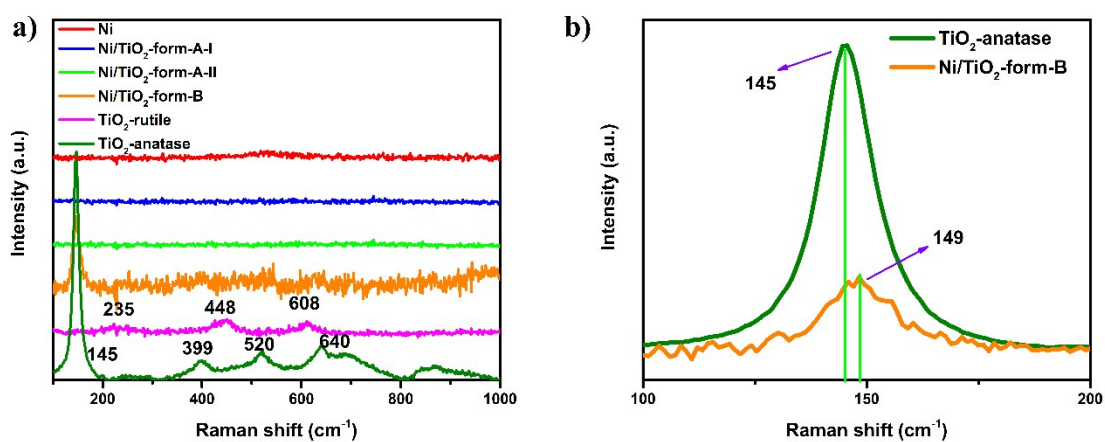


**Figure S6.** SEM-EDS Mapping images of Ni, Ti and O elements in Ni/TiO<sub>2</sub>-form-A-II sample.

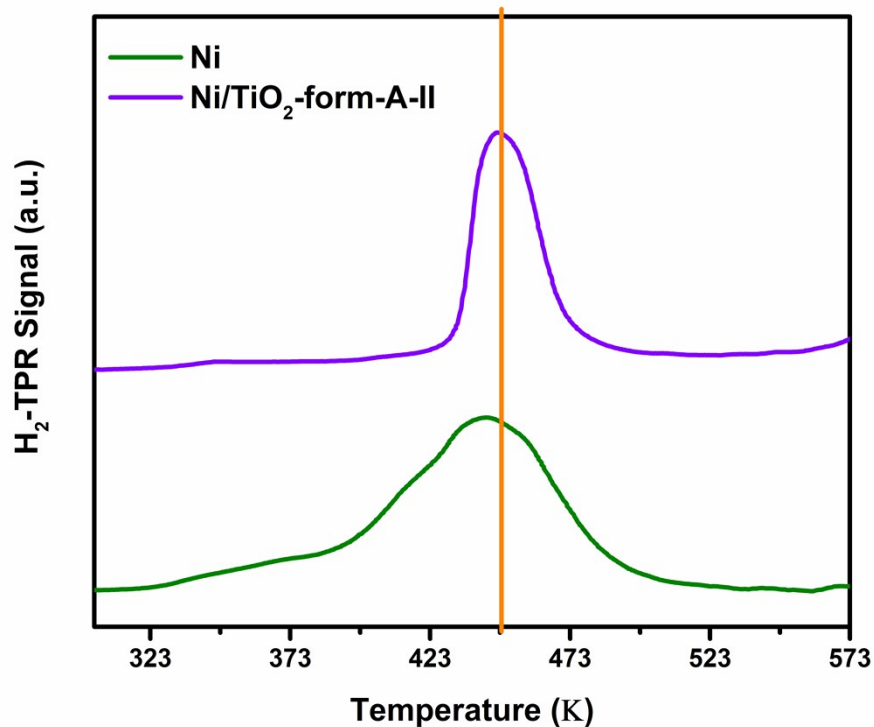




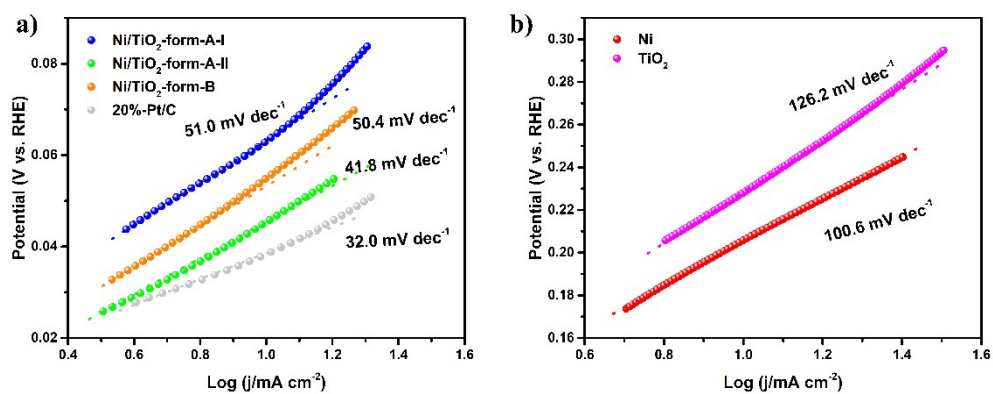
**Figure S7.** TEM-EDS Mapping images of Ni/TiO<sub>2</sub>-form-A-I (a-d), Ni/TiO<sub>2</sub>-form-A-II (e-h) and Ni/TiO<sub>2</sub>-form-B (i-l).



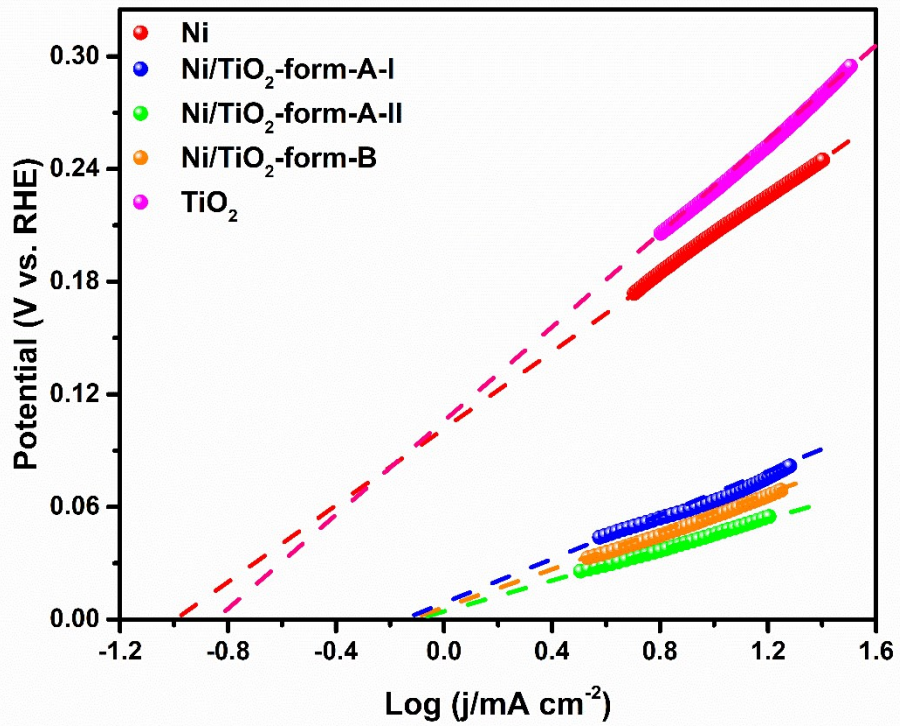
**Figure S8.** Raman spectra of Ni, TiO<sub>2</sub> with different crystal forms and Ni/TiO<sub>2</sub> samples with different combination forms.



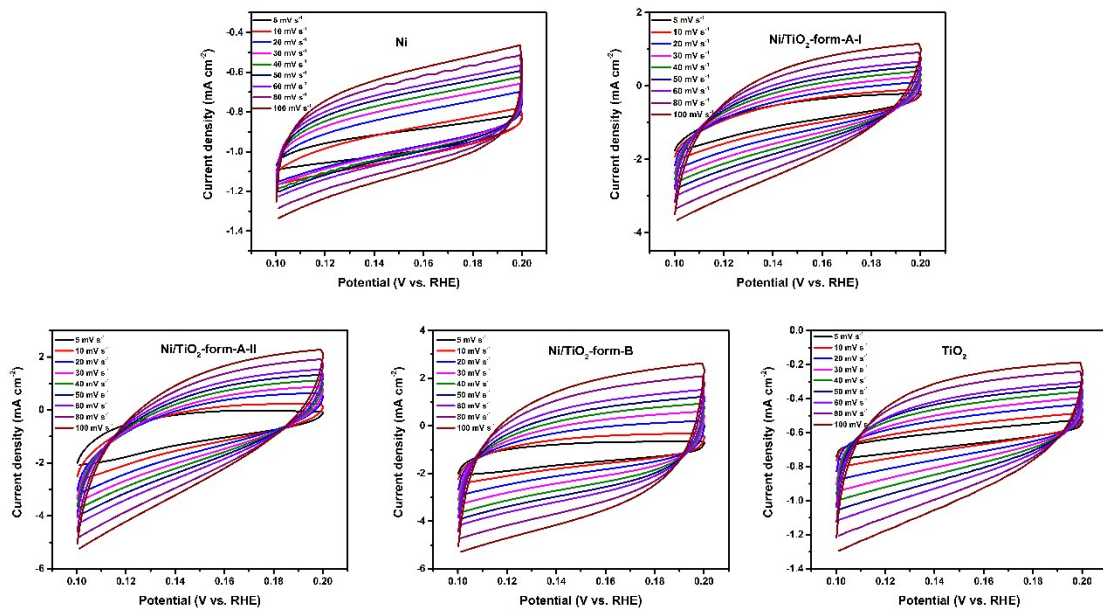
**Figure S9.** The H<sub>2</sub>-TPR spectrum of Ni and Ni/TiO<sub>2</sub>-form-A-II samples.



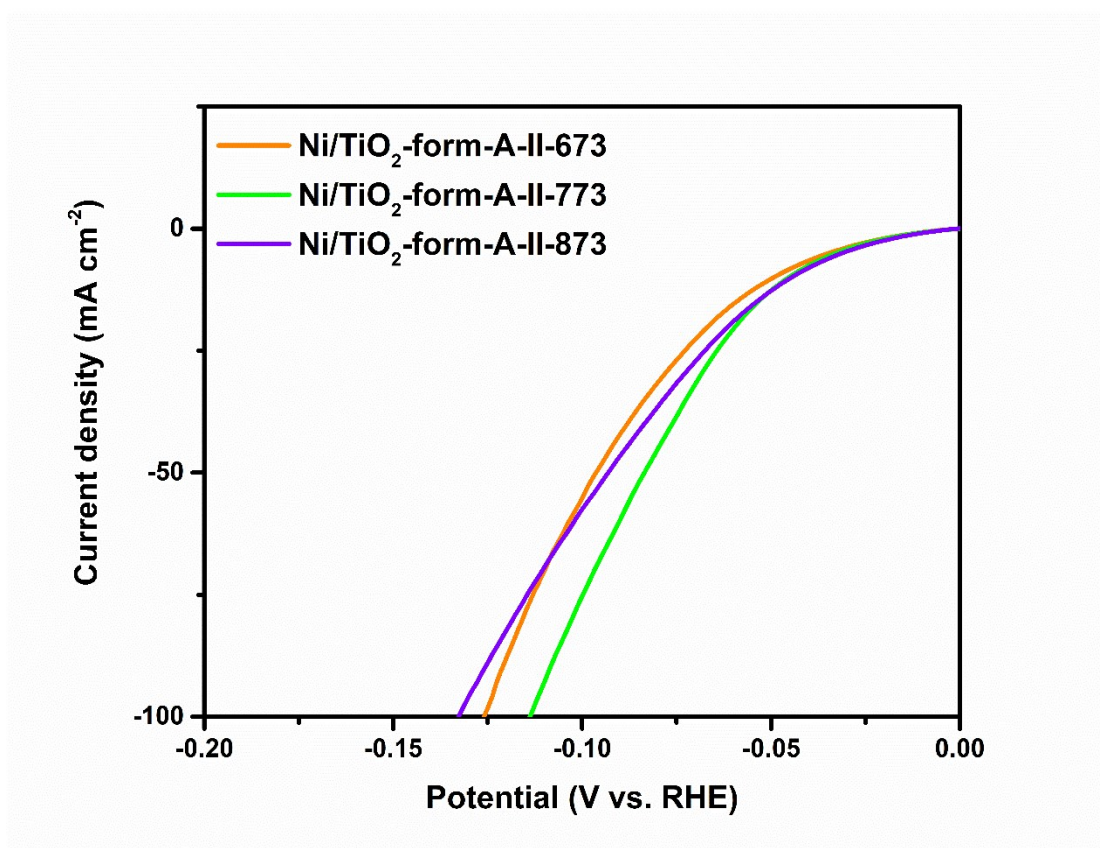
**Figure S10.** Tafel slope values of Pt/C, Ni, TiO<sub>2</sub> and Ni/TiO<sub>2</sub> samples with different forms in 1M KOH solution.



**Figure S11.** The exchange current density spectrum of Ni, different Ni/TiO<sub>2</sub> and TiO<sub>2</sub> samples derived from Tafel curves.

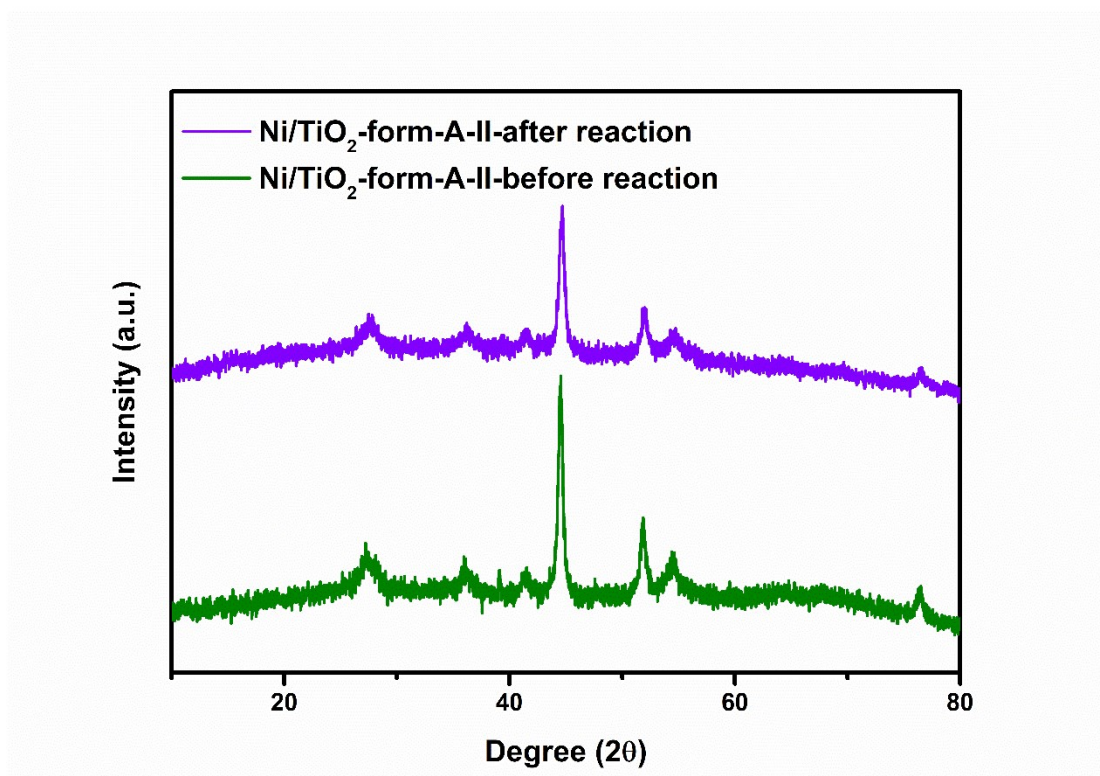


**Figure S12.** The electrical double-layer capacitance curves (which is proportion to electrochemical surface area (ECSA), vs. RHE) of Ni, different Ni/TiO<sub>2</sub> and TiO<sub>2</sub> samples.

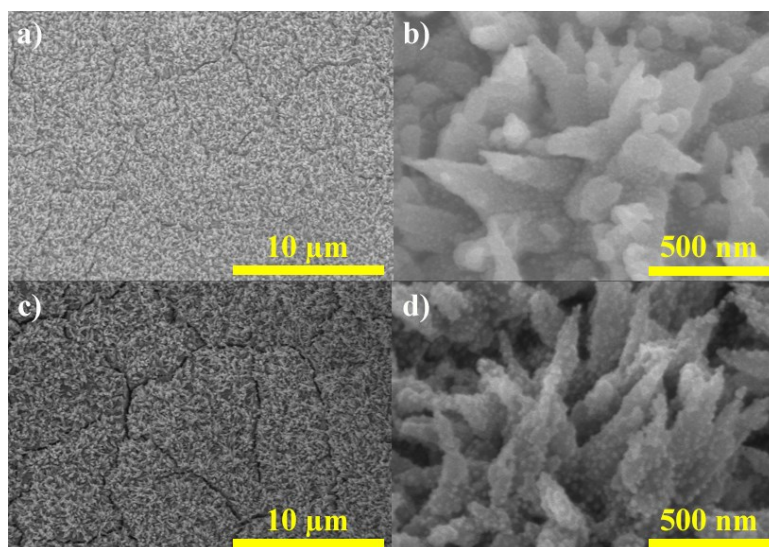


**Figure S13.** The LSV curves of Ni/TiO<sub>2</sub>-form-A-II samples with different synthesized temperatures.

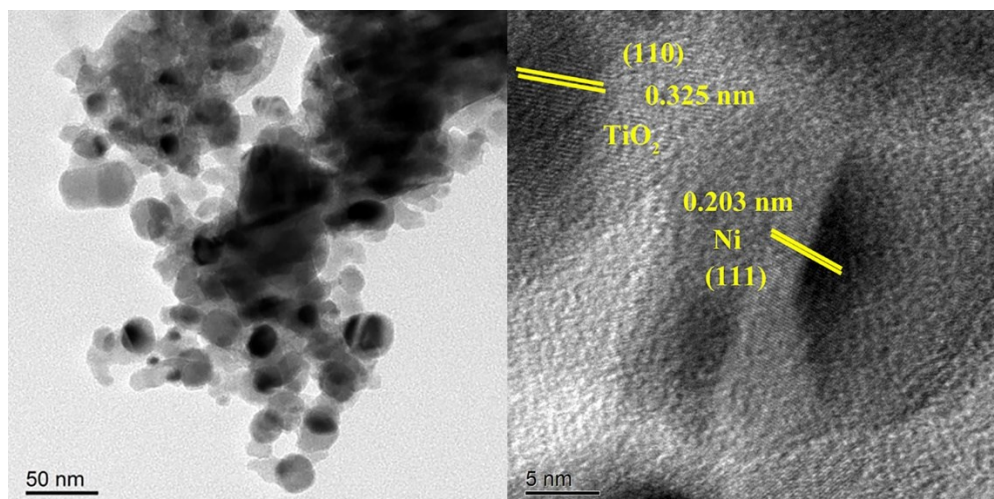




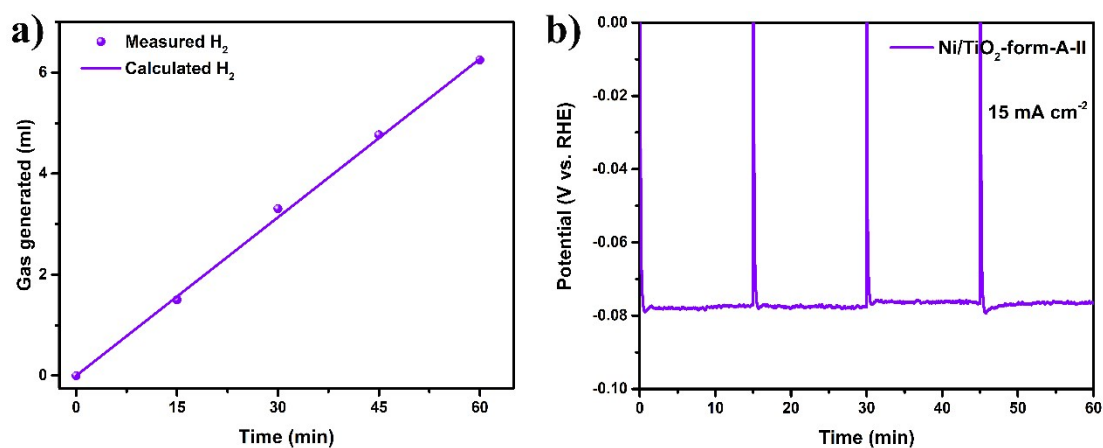
**Figure S14.** The XRD spectra of Ni/TiO<sub>2</sub>-form-A-II samples before and after reaction.



**Figure S15.** The SEM images of Ni/TiO<sub>2</sub>-form-A-II samples before and after reaction.



**Figure S16.** The TEM and HRTEM images of Ni/TiO<sub>2</sub>-form-A-II sample after reaction.



**Figure S17.** The amount of H<sub>2</sub> generated during the reaction of Ni/TiO<sub>2</sub>-form-A-II sample and the potential-time curve (without iR correction) at the current density of 15 mA cm<sup>-2</sup> over a sampling period of 1 hour.

**Table S1.** The performance comparison of Ni/TiO<sub>2</sub>-form-A-II electrode with other HER materials

Catalyst	Overpotential at 10 mA cm <sup>-2</sup> (mV)	Tafel slope (mV dec <sup>-1</sup> )	Electrolyte	Source
Ni/TiO <sub>2</sub> -form-A-II	46	41.8	1M KOH	This work
Mo <sub>2</sub> C-MoOx	60	53	1M HClO <sub>4</sub>	[1]
NiMoOP	91	55.9	1M KOH	[2]
Co-NC	157	109	1M KOH	[3]
Ni-NiO-CNT	≈90	82	1M KOH	[4]
Co-Co <sub>3</sub> O <sub>4</sub>	90	90	1M KOH	[5]
Ni-V <sub>2</sub> O <sub>3</sub>	61	79.7	1M KOH	[6]
N-CoP <sub>2</sub>	38	46	0.5M H <sub>2</sub> SO <sub>4</sub>	[7]
Ni-VC	138	62	0.5M H <sub>2</sub> SO <sub>4</sub>	[8]
CoP	122	54.8	0.5M H <sub>2</sub> SO <sub>4</sub>	[9]
MOF derived Ni	61	71	1M KOH	[10]
Ni <sub>3</sub> N-C	115	52.1	1M KOH	[11]
Ni <sub>2</sub> P-NiP <sub>2</sub>	59.7	58.8	1M KOH	[12]
MoS <sub>2</sub> -CoNi <sub>2</sub> S <sub>4</sub>	78	67	1M KOH	[13]
Al-CoS <sub>2</sub>	86	62.47	0.5M H <sub>2</sub> SO <sub>4</sub>	[14]
Ni-C	37	42	1M KOH	[15]
Co-NiS <sub>2</sub>	80	43	1M KOH	[16]

**Table S2.** Comparison of HER performance between our sample and the non-precious metal Ni materials reported in literatures in alkaline solution

<b>Catalyst</b>	<b><math>\eta_{10}</math>(mV)</b>	<b>Tafel slope (mV decade<sup>-1</sup>)</b>	<b>Electrolyte</b>	<b>Source</b>
<b>Ni/TiO<sub>2</sub>-form-A-II</b>	<b>46</b>	<b>41.8</b>	<b>1 M KOH</b>	<b>This work</b>
<b>Ni@CeO<sub>2</sub></b>	<b>91</b>	<b>51</b>	<b>1 M KOH</b>	<b>[17]</b>
<b>Ni/NiO/CNT</b>	<b>80</b>	<b>82</b>	<b>1 M KOH</b>	<b>[4]</b>
<b>Ni-Mo</b>	<b>92</b>	<b>76</b>	<b>1 M KOH</b>	<b>[18]</b>
<b>Ni@C</b>	<b>37</b>	<b>57</b>	<b>1 M KOH</b>	<b>[15]</b>
<b>Ni@NiO</b>	<b>79</b>	<b>119</b>	<b>1 M KOH</b>	<b>[19]</b>
<b>Ni@Ni(OH)<sub>2</sub></b>	<b>68</b>	<b>97</b>	<b>1 M KOH</b>	<b>[20]</b>
<b>Ni/V<sub>2</sub>O<sub>3</sub></b>	<b>61</b>	<b>79.7</b>	<b>1 M KOH</b>	<b>[6]</b>
<b>Ni@MoS<sub>2</sub></b>	<b>98</b>	<b>75</b>	<b>1 M KOH</b>	<b>[21]</b>
<b>Ni@Mo<sub>2</sub>C</b>	<b>179</b>	<b>101</b>	<b>1 M KOH</b>	<b>[22]</b>
<b>Ni-Ni(OH)<sub>2</sub></b>	<b>57</b>	<b>44.8</b>	<b>1 M KOH</b>	<b>[23]</b>
<b>NiCu</b>	<b>184</b>	<b>84</b>	<b>1 M KOH</b>	<b>[24]</b>
<b>Ni-NiMoN</b>	<b>37</b>	<b>51</b>	<b>1 M KOH</b>	<b>[25]</b>
<b>NiW-W</b>	<b>59</b>	<b>52</b>	<b>1 M KOH</b>	<b>[26]</b>
<b>Ni-Ni<sub>3</sub>C</b>	<b>98</b>	<b>88.5</b>	<b>1 M KOH</b>	<b>[27]</b>
<b>Ni-Fe<sub>3</sub>C</b>	<b>93</b>	<b>97</b>	<b>1 M KOH</b>	<b>[28]</b>
<b>NiCo</b>	<b>72</b>	<b>57</b>	<b>1 M KOH</b>	<b>[29]</b>



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