

Fig. S1 FESEM image of  $\text{TiO}_2$  NRs on a carbon paper

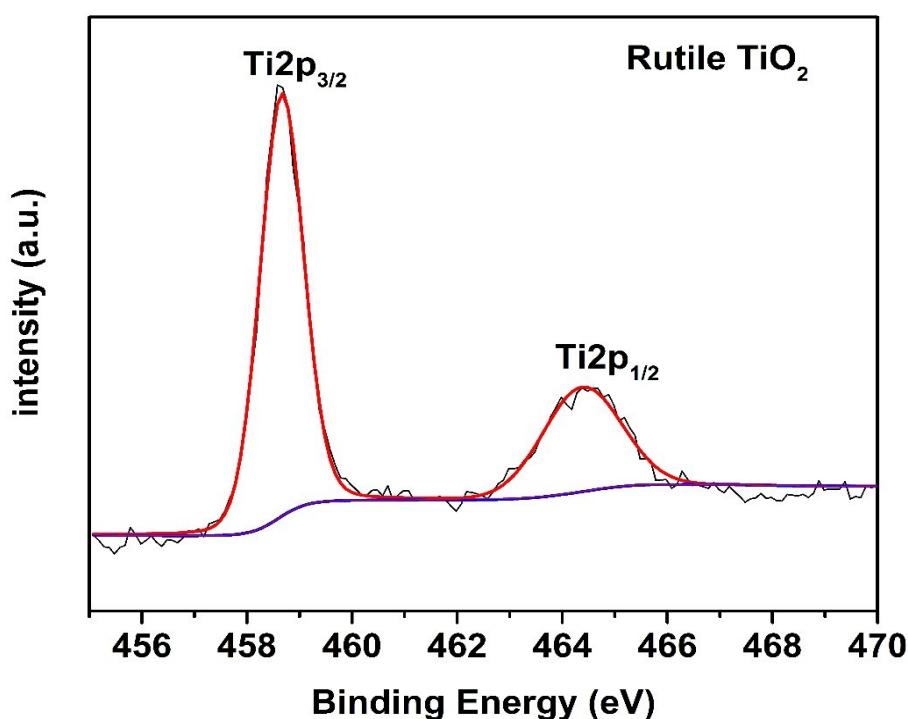


Fig. S2 Ti 2p XPS spectrum of rutile  $\text{TiO}_2$ .

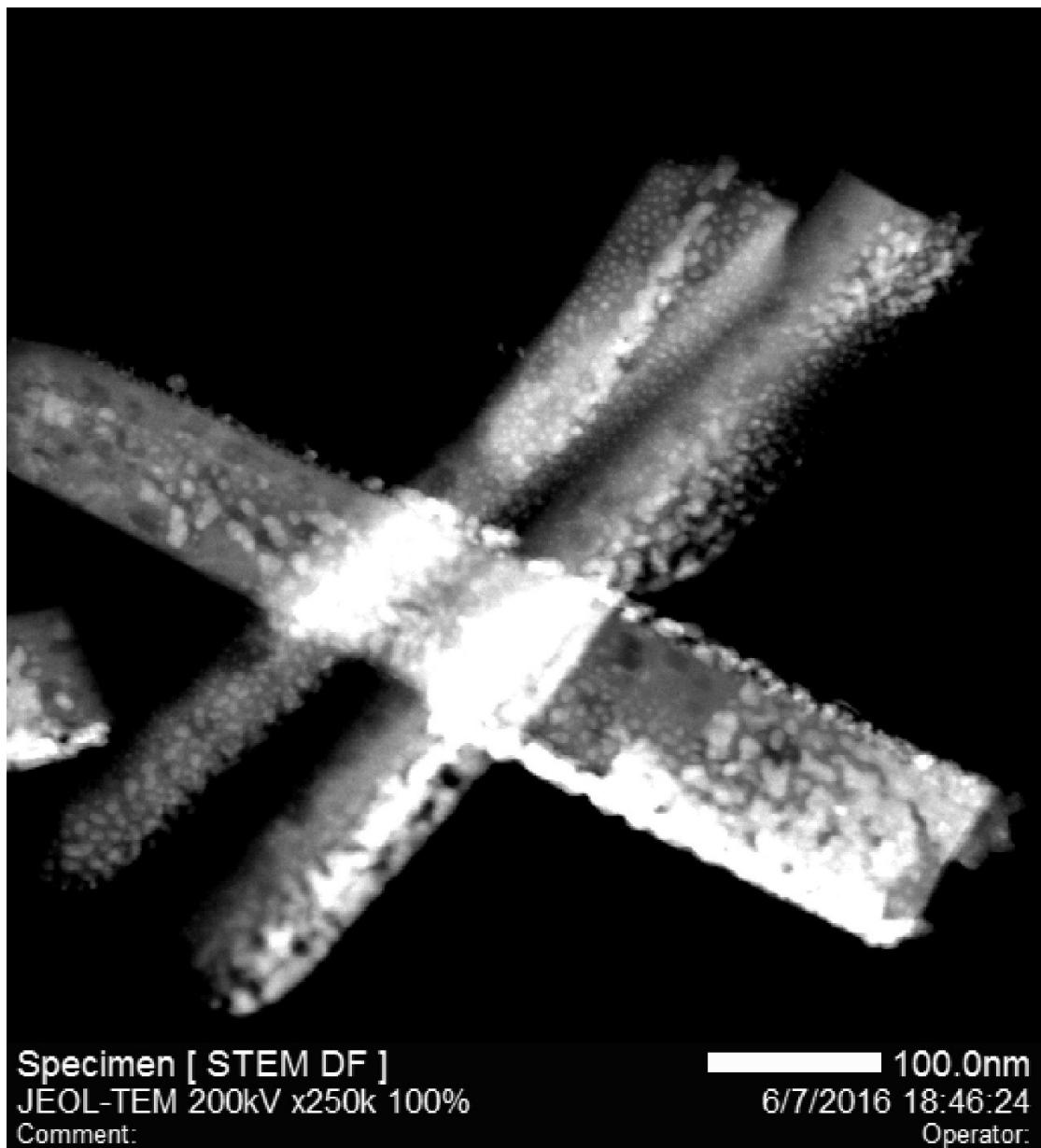


Fig. S3 STEM of PdNi nanoparticles on a  $\text{TiO}_2$  nanorods

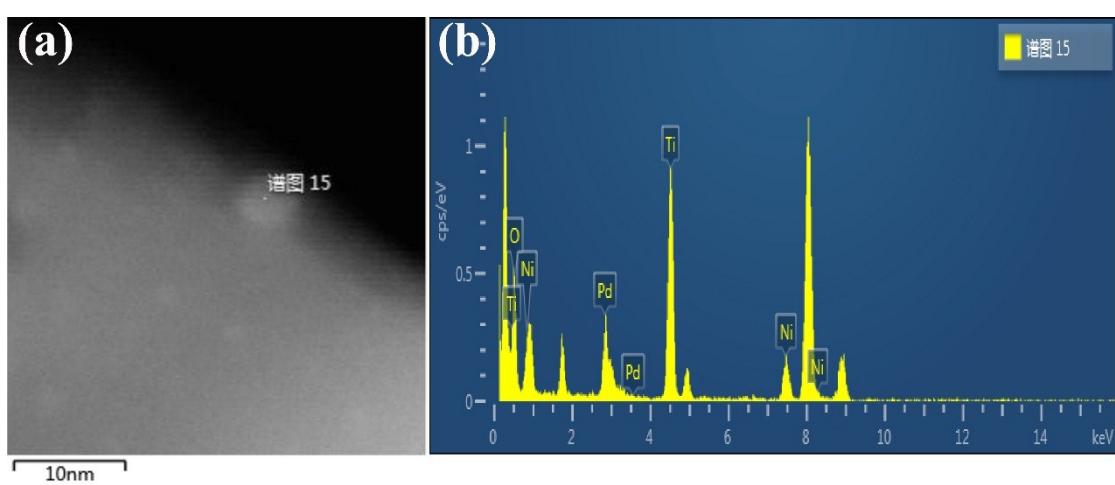


Fig. S4 STEM image (a), and EDX spectrum (b) of the  $\text{PdNi}-\text{TiO}_2$  NRs

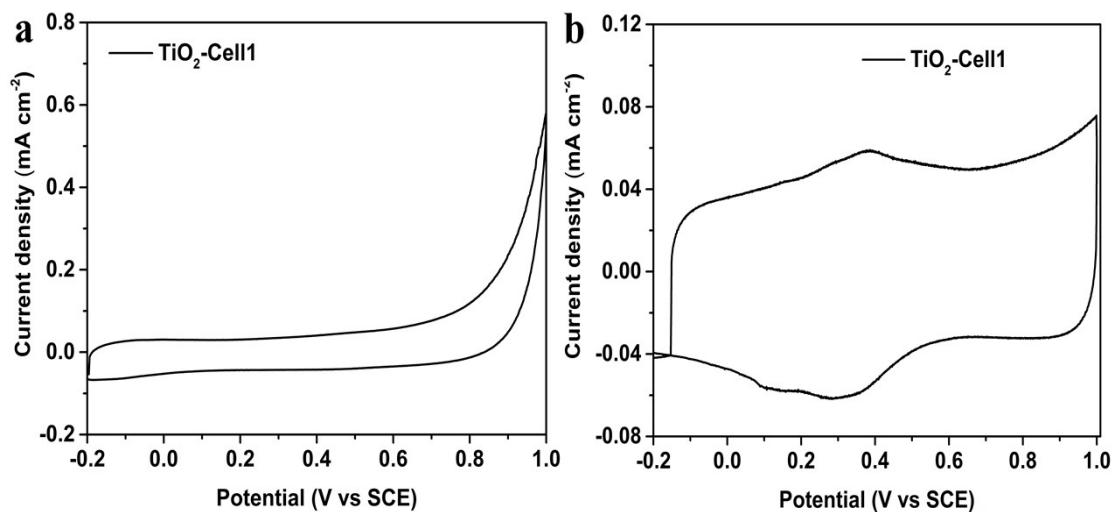


Fig. S5 CVs of  $\text{TiO}_2$  sample in  $0.5 \text{ M H}_2\text{SO}_4$  (a) and  $0.5 \text{ M H}_2\text{SO}_4$  containing  $0.5 \text{ M HCOOH}$  at the scan rate of  $50 \text{ mV s}^{-1}$ .

Table S1 Comparison of the mass activity of the Pd<sub>2</sub>Ni<sub>3</sub>-TiO<sub>2</sub> with previous reported Pd-based catalysts.

| Samples   | Test conditions   | ECSA<br>(m <sup>2</sup> g <sup>-1</sup> <sub>Pd</sub> ) | Mass activity<br>(mA mg <sup>-1</sup> <sub>Pd</sub> ) | Ref.              |
|---|---|---|---|-------------------|
| Pd <sub>2</sub> Ni <sub>3</sub> -TiO <sub>2</sub> | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>50 mV s <sup>-1</sup> | 43.6  | 753.1   | This work         |
| Pd/NS-G   | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>50 mV s <sup>-1</sup> | 83.4  | 501.8   | S1 <sup>1</sup>   |
| Pd <sub>6</sub> Co/3DG                            | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>50 mV s <sup>-1</sup> | 51.0  | 430.8   | S2 <sup>2</sup>   |
| PdNi/C  | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>50 mV s <sup>-1</sup> | ---   | 556.7   | S3 <sup>3</sup>   |
| PdNi/C  | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>50 mV s <sup>-1</sup> | ---   | 396   | S4 <sup>4</sup>   |
| PdCu/C  | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>50 mV s <sup>-1</sup> | ---   | 654   | S4 <sup>4</sup>   |
| Pd@graphene                                       | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>50 mV s <sup>-1</sup> | 56.0  | 89.5  | S5 <sup>5</sup>   |
| Porous Pd <sub>57</sub> Ni <sub>43</sub>          | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>50 mV s <sup>-1</sup> | 58.4 mC mg <sup>-1</sup>                                | ~800  | S6 <sup>6</sup>   |
| Pd-NF/C   | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>20 mV s <sup>-1</sup> | 2.47  | 16.4  | S7 <sup>7</sup>   |
| Pd <sub>1</sub> Ni <sub>1</sub> NNs/RGO           | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>50 mV s <sup>-1</sup> | 98.2  | 604.3   | S8 <sup>8</sup>   |
| AP - Pd/GN  | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>50 mV s <sup>-1</sup> | 72.72   | 446.3   | S9 <sup>9</sup>   |
| Pd-DNA@Graphene                                   | 0.5 M H <sub>2</sub> SO <sub>4</sub><br>+ 0.5 M HCOOH;<br>50 mV s <sup>-1</sup> | 147.1   | 140.1   | S10 <sup>10</sup> |

## References:

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