

## **Supplementary Information**

### **Self-recoverable Pd-Ru/TiO<sub>2</sub> nanocatalysts with ultrastability for ethanol electrooxidation**

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## 1. Experimental

### 1.1. Chemicals.

Palladium chloride ( $\text{PdCl}_2$ ), ruthenium chloride ( $\text{RuCl}_3$ ), ethylene glycol (EG) and sodium borohydride ( $\text{NaBH}_4$ ) were analytical grade and purchased from Sinapharm Chemical Reagent Co. Ltd. 3-Aminopropyltrimethoxysilane (APTMS) was purchased from J&K. Nafion (perfluorinated ion-exchange resin, a 0.5 wt% solution in a mixture of ethanol and water) was purchased from Aldrich. The chemicals were used as received without any further purification. All solutions were prepared using ultrapure water with resistivity greater than  $18.2 \text{ M}\Omega \text{ cm}$ .

### 1.2. Synthesis of Pd-Ru/ $\text{TiO}_2$ nanocatalysts.

$\text{NH}_2$ -functionalized  $\text{TiO}_2$  precursor spheres (f- $\text{TiO}_2$ ) were synthesized according to the reported procedures.<sup>1</sup> Pd-Ru/ $\text{TiO}_2$  precursors with different proportion of Pd and Ru are prepared by chemical reduction of  $\text{PdCl}_2$  and  $\text{RuCl}_3$  on the surface of  $\text{TiO}_2$ . The procedure for preparation of Pd-Ru/ $\text{TiO}_2$  precursors is as follow: 10 mg of f- $\text{TiO}_2$  was dispersed in 10 mL of ethylene glycol (EG) by sonication for 30 min, and then a 0.09 M  $\text{PdCl}_2$  solution and a 0.0303 M  $\text{RuCl}_3$  solution were added simultaneously. The pH of the solution was adjusted to 10 by adding a 0.5 M NaOH/EG solution, followed by slow injecting an aqueous sodium borohydride ( $\text{NaBH}_4$ ) solution with a concentration of  $2.0 \text{ mg mL}^{-1}$ . The solution was stirred for 6 h at room temperature.<sup>2</sup> The procedure for preparation of Pd/ $\text{TiO}_2$  nanocomposites is the same as the preparation of Pd-Ru/ $\text{TiO}_2$  precursors without adding a  $\text{RuCl}_3$  solution. The mixture was centrifuged and washed repeatedly with ultrapure water. The resulting product was collected and dissolved in 3.0 mL of ultrapure water.

Then, Pd-Ru/ $\text{TiO}_2$  nanocatalysts with different proportion of Pd and Ru are synthesized by

electrochemical stripping Pd-Ru/TiO<sub>2</sub> precursors in the potential range of -0.80 to 0.60 V, to preferentially dissolve Ru inside the nanocomposites and reach electrochemical stripping equilibrium.

During the cycling of the as-prepared Pd-Ru/TiO<sub>2</sub> precursors in a 1.0 M NaOH solution in the potential range of -0.80 to 0.60 V, some yellow substances form on the surface of the electrode and dispersed in the NaOH solution. While the as-prepared Pd-Ru/TiO<sub>2</sub> precursors are cycled in the potential range of -0.80 to 0.20 V, yellow substances don't form. The yellow substance dispersed in the NaOH solution is verified by inductively coupled plasma mass spectrometry (ICP), and the concentration of Pd and Ru in the NaOH solution is confirmed by the ICP data (Table S1). The concentration of Ru elements in the NaOH solution is higher after cycling in the potential range of -0.80 to 0.60 V compared with cycling in the potential range of -0.80 to 0.20 V, therefore it must be the successful preferential dissolution of Ru substances inside the Pd-Ru/TiO<sub>2</sub> precursors. The catalysts of Pd<sub>1</sub>Ru<sub>0.76</sub>/TiO<sub>2</sub>, Pd<sub>1</sub>Ru<sub>0.69</sub>/TiO<sub>2</sub> and Pd<sub>1</sub>Ru<sub>0.54</sub>/TiO<sub>2</sub> (Table S2) are prepared and used in the catalytic experiments.

### **1.3. Preparation of Modified Electrodes.**

The glassy carbon (GC) electrode was polished with 1, 0.5 and 0.3 μm alumina slurry sequentially to mirror and then ultrasonically washed in ultrapure water for 20 min. The cleaned GC electrode was dried at room temperature for further modification. Catalyst ink was prepared by diluting catalyst (Pd-Ru/TiO<sub>2</sub>, Pd/TiO<sub>2</sub>, Pd/C (JM) (20 wt%)) with ultrapure water to a given volume. 10 μL of this slurry was pipetted out on the surface of the GC electrode and dried at room temperature. Then, 10 μL of Nafion (0.5 wt %) was dropped on the surface of the modified electrode.

#### 1.4. Characterization.

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku (miniflex) using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) at 35 kV and 15 mA to analyze the crystal structure, at a scanning rate of  $0.5^\circ \text{ min}^{-1}$  in a  $2\theta$  angle range from  $10^\circ$  to  $90^\circ$ . The energy dispersive X-Ray spectroscopy (EDX) attached to a Zeiss Sigma scanning electron microscope (SEM) operated at 15 kV was used for estimating the bulk composition of the catalysts and analyzing the morphology of the catalysts. A JEM-1400 electron microscope was operated at 120 kV to observe the nano-morphological structure and to determine the particle size of the catalysts. The surface morphologies and microstructures of the prepared catalysts were analyzed using a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical state on a PHI Quantum 2000 XPS system with a monochromatic Al K $\alpha$  source and charge neutralizer. The content of Pd and Ru of the catalysts was analyzed using an inductively coupled plasma-optical emission spectrophotometer (ICP-OES, Thermo Electron IRIS Intrepid II XSP, USA). An in situ Fourier transform infrared (FTIR) spectrometer (Nicolet, Nexus 870) equipped with a liquid-nitrogen-cooled MCT-A detector) was used to gain insight into the mechanism of the EOR in an alkaline medium on the Pd-Ru/TiO<sub>2</sub> nanocatalysts.

Electrochemical measurements were performed using a CHI 660E electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China). A conventional three-electrode system was used for the electrochemical activity studies via cyclic voltammetry (CV) and chronoamperometry, including Ag/AgCl ( $E_0 = 0.22$  V vs. RHE) as the reference electrode, GC electrode (geometric area  $0.07 \text{ cm}^2$ ) as the working electrode and platinum wire as the counter

electrode. For the sake of cleaning and activating the electrode surface, a series of CV experiments were carried out in a nitrogen-purged 1.0 M NaOH solution until a steady cyclic voltammogram was achieved. Then, electrode was cycled between -0.8 and 0.6 V vs. Ag/AgCl in a 1.0 M NaOH + 1.0 M C<sub>2</sub>H<sub>5</sub>OH solution at a scan rate of 0.05 V s<sup>-1</sup>. Chronoamperometry was used to investigate the activity and stability of the catalyst towards EOR after a steady cyclic voltammogram was achieved in a 1.0 M NaOH + 1.0 M C<sub>2</sub>H<sub>5</sub>OH solution. CO anti-poisoning tests were carried out at room temperature in a 1.0 M NaOH solution purged with nitrogen for 30 min and then bubbled with CO gas (99.9%) for 15 min. The residual CO in the solution was expelled by N<sub>2</sub> for 30 min.

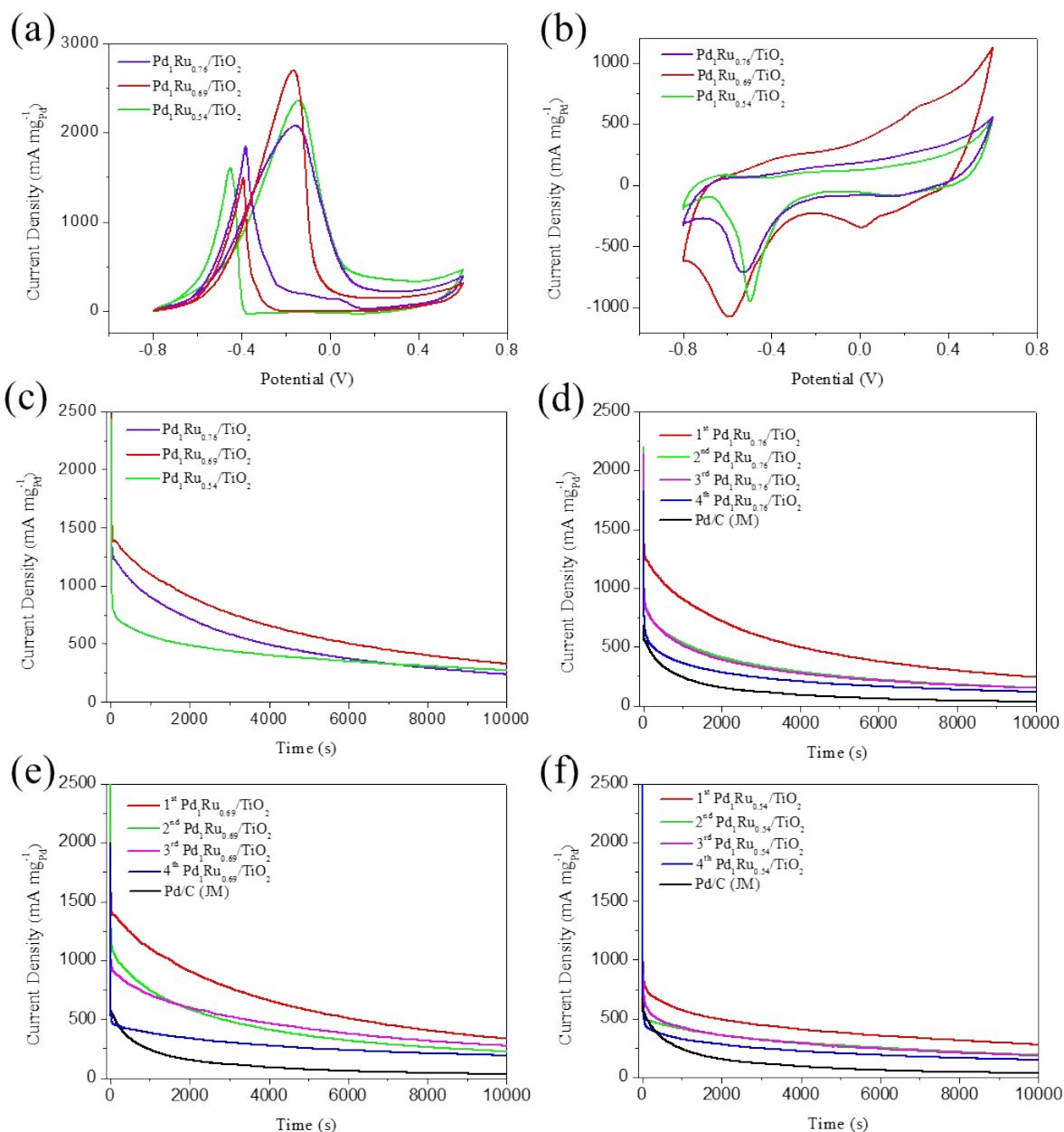
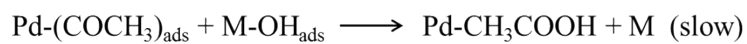
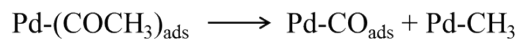


Fig. S1. Cyclic voltammograms of Pd<sub>1</sub>-Ru<sub>x</sub>/TiO<sub>2</sub> nanocatalysts in a 1.0 M NaOH solution (a) and in a 1.0 M NaOH + 1.0 M C<sub>2</sub>H<sub>5</sub>OH solution (b) at a scan rate of 50 mV s<sup>-1</sup>. Chronoamperogram of Pd<sub>1</sub>-Ru<sub>x</sub>/TiO<sub>2</sub> nanocatalysts in a 1.0 M NaOH + 1.0 M C<sub>2</sub>H<sub>5</sub>OH solution (c) at -0.2 V vs. Ag/AgCl. Chronoamperograms of Pd<sub>1</sub>Ru<sub>0.76</sub>/TiO<sub>2</sub>, Pd<sub>1</sub>Ru<sub>0.69</sub>/TiO<sub>2</sub>, Pd<sub>1</sub>Ru<sub>0.54</sub>/TiO<sub>2</sub>, Pd/C (JM) in a 1.0 M NaOH + 1.0 M C<sub>2</sub>H<sub>5</sub>OH solution (d, e, f) at -0.2 V vs. Ag/AgCl.

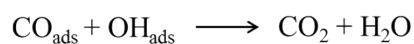
### Rate-determining step for EOR



### Poisoning intermediate (CO) pathway



### $\text{CO}_{\text{ads}}$ oxidation pathway



Scheme S1. Scheme for ethanol electrooxidation reaction in alkaline media.

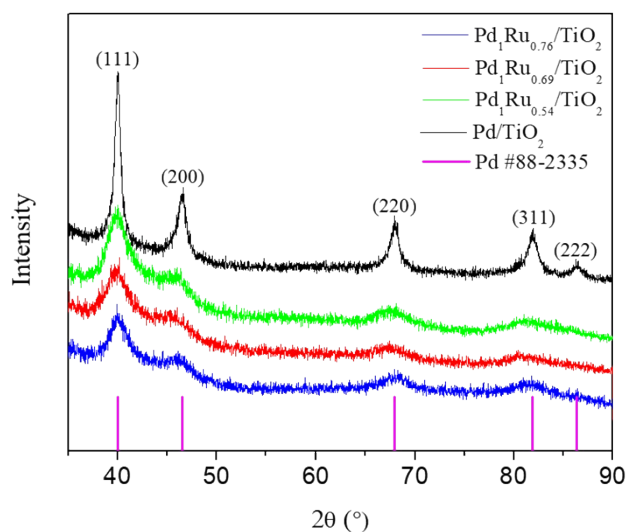


Fig. S2. XRD patterns of Pd/TiO<sub>2</sub>, Pd<sub>1</sub>Ru<sub>0.76</sub>/TiO<sub>2</sub>, Pd<sub>1</sub>Ru<sub>0.69</sub>/TiO<sub>2</sub> and Pd<sub>1</sub>Ru<sub>0.54</sub>/TiO<sub>2</sub>.

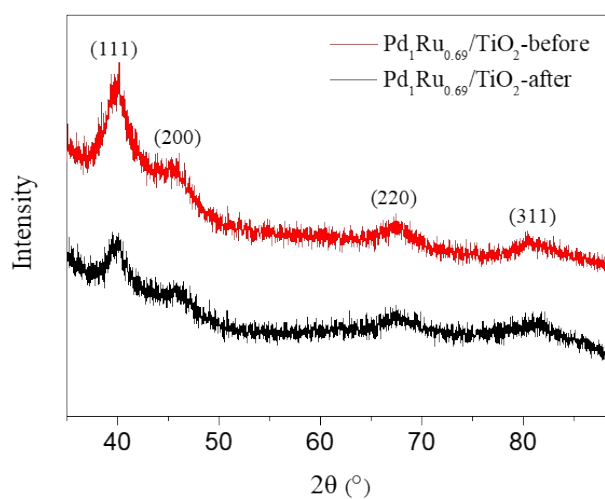


Fig. S3. XRD patterns of Pd<sub>1</sub>Ru<sub>0.69</sub>/TiO<sub>2</sub> nanocatalysts before and after 40000 s stability test.

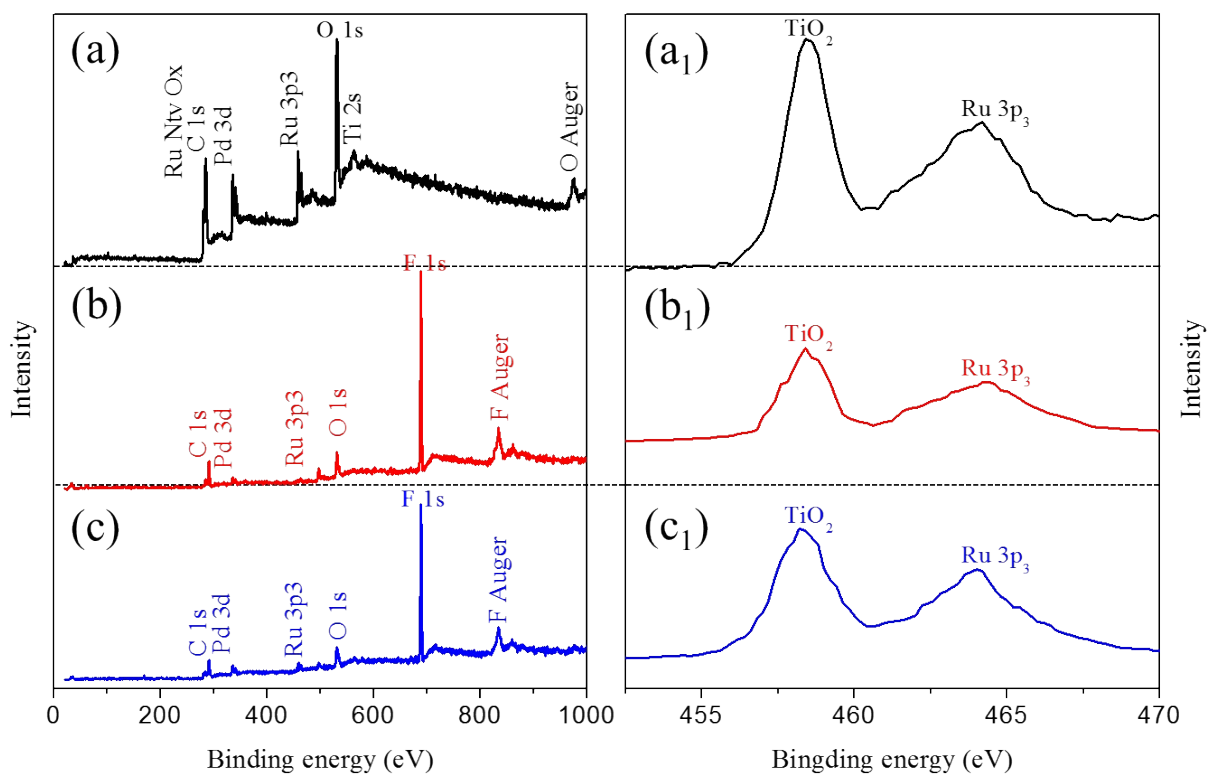


Fig. S4. XPS spectra and Ru 3p high-resolution region of Pd<sub>1</sub>Ru<sub>x</sub>/TiO<sub>2</sub> precursors (a, a<sub>1</sub>), Pd<sub>1</sub>Ru<sub>x</sub>/TiO<sub>2</sub> nanocatalysts (b, b<sub>1</sub>), Pd<sub>1</sub>Ru<sub>x</sub>/TiO<sub>2</sub> nanocatalysts after 40000 s stability test (c, c<sub>1</sub>). All of the spectra were calibrated by C 1s peak located at 284.8 eV.



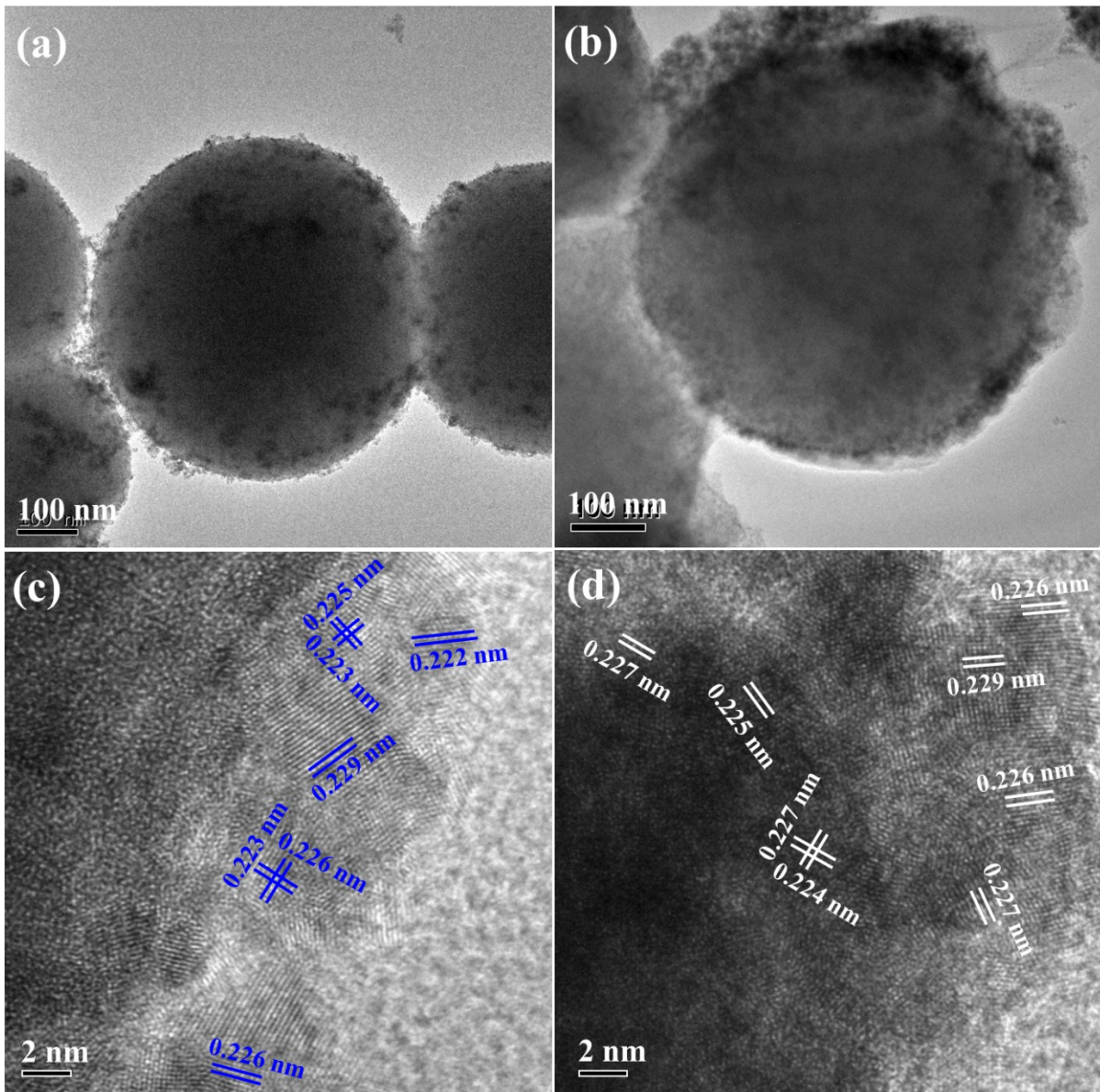


Fig. S5. HRTEM images of Pd-Ru/TiO<sub>2</sub> nanocatalysts (a) and Pd-Ru/TiO<sub>2</sub> after 40000 s stability test (b). The magnified HRTEM images of Pd-Ru/TiO<sub>2</sub> nanocatalysts (c) and Pd-Ru/TiO<sub>2</sub> after 40000 s stability test (d).

Table S1. The concentration of Pd and Ru elements in NaOH solution after cycling in a 1.0 M NaOH solution in the potential range of -0.80 to 0.20 V (sample a) and in the potential range of -0.80 to 0.60 V (sample b).

Sample	Pd (mg L <sup>-1</sup> )	Ru (mg L <sup>-1</sup> )
<b>a</b>	0.26	0.19
<b>b</b>	0.22	15.43

Table S2. The concentration of Pd and Ru elements in as-prepared Pd-Ru/TiO<sub>2</sub> catalysts.

Sample	Pd (mg L <sup>-1</sup> )	Ru (mg L <sup>-1</sup> )
<b>Pd<sub>1</sub>Ru<sub>0.76</sub>/TiO<sub>2</sub></b>	75.67	57.43
<b>Pd<sub>1</sub>Ru<sub>0.69</sub>/TiO<sub>2</sub></b>	75.91	52.28
<b>Pd<sub>1</sub>Ru<sub>0.54</sub>/TiO<sub>2</sub></b>	74.85	40.42

## References

1. X.C. Jiang, T. Herricks and Y.N. Xia, *Adv. Mater.*, 2003, **15**, 1205-1209.
2. J.L. Tan, A.M. De Jesus, S.L. Chua, J. Sanetuntikul, S. Shanmugam, B.J.V. Tongol and H. Kim, *Appl. Catal. A*, 2017, **531**, 29-35.