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Supporting information

Salt template-assisted in situ construction of Ru nanoclusters and porous carbon: Excellent catalysts toward hydrogen evolution, ammonia-borane hydrolysis, and 4-nitrophenol reduction

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This file includes Experimental Section, Figs. S1-S14 and Tables S1-S5.

Experimental Section

Chemicals and Materials

Potassium oleate, $RuCl_3 \cdot xH_2O$ (35.0-42.0% Ru basis), sodium sulfate anhydrous, $NaBH_4$, 4-nitrophenol were obtained from Aladdin Reagent (Shanghai) Co. KOH was purchased from Alfa Aesar Co., Inc. AB complex (90%), Nafion, and commercial Pt/C (20 wt%) were purchased from Sigma-Aldrich Co., Inc. Conductive carbon (Vulcan XC-72R) was obtained from Carbot Co., Inc. Absolute ethanol, hydrochloric acid, and methanol were provided by Kelong Co., Inc. All reagents were used without any purification and deionized water was used in all reactions.

Synthesis of Ru/PC

Briefly, 0.05 g of $RuCl_3 \cdot xH_2O$ was dissolved in 3 mL of deionized water and then 1.22 g of potassium oleate was slowly added into the solution. Until it was completely dissolved, the suspension was heated at 90 °C for 2 h. Afterward, 10 g of Na_2SO_4 was slowly added with vigorous stirring. The mixture was allowed for another 2 h at the same temperature. The obtained solid was grounded into powder and was transformed in a porcelain boat, then pyrolyzing at 500 ℃ for 3 h under Ar atmosphere. To remove the salt template, the resultant product was rinsed with hot water for several times. Then, the collect solid was treated by hydrochloric acid (1.0 M) for 24 h, followed by drying at 60 °C under vacuum overnight.

Synthesis of Ru/C

The control sample of Ru/C was synthesized in parallel by the same approach as that

for Ru/PC except for no addition of sodium sulfate.

Synthesis of Ru/PC-IM

In a typical synthesis, 100 mg of potassium oleate was mixed with Na_2SO_4, then pyrolyzing at 500 ℃ for 3 h under Ar atmosphere. To remove the salt template, the resultant product was rinsed with hot water for several times. Then, the collect solid was treated by hydrochloric acid (1.0 M) for 24 h, followed by drying at 60 °C under vacuum overnight, getting the product of carbon. The product was dissolved in 15 mL H_2O, and then a certain concentration of $RuCl_3 \cdot xH_2O$ was subsequently added. After that, the resulted mixture was stirred at 80 ℃ to evaporate all waters. The achieved powder was then annealed at 500 ℃ for 3 h under Ar atmosphere for producing the carbon supported Ru nanoparticles (Ru/PC-IM).

Characterization

X-ray diffraction (XRD) measurements were carried out on a Regaku D/Max-2500 diffractometer. Transmission electron microscopy (TEM, JEM-2100F, JEOL) was used to test the morphology and microstructure of samples at 200 kV. Energy dispersive X-ray spectroscopy (EDX) was conducted on Oxford instrument operating at 200 kV. The surface elements and chemical valence of samples were detected by X-ray photoelectron spectroscopy on a Thermo ESCALAB 250 Axis Ultra spectrometer. Thermal gravimetric analysis (TGA) was operated on a Netzsch DSC214 apparatus. N_2 sorption measurements were performed on an Automated Gas Sorption Analyzer (Quanta Autosorb-IQ). Inductively coupled plasma-atomic emission spectrometry

(ICP-AES) analysis was carried out on SPECTRO ARCOS spectrometer.

Electrochemical measurements

The electrochemical measurements were measured on an electrochemical workstation (CHI 760E). All measurements were carried out on a three-electrode system which consists of a carbon cloth (0.25 cm^2) loading with catalyst as the working electrode, a Hg/HgO as the reference electrode, and a graphite rod as the counter electrode. Preparation of working electrode: 2.0 mg of catalyst was added into the solution containing 800 μL of ethanol and 8 μL of 5% Nafion. After ultrasonication for 30 min, the catalyst ink was achieved. Then, 50 μL of ink was loaded as uniformly as possible on the carbon cloth. The catalyst loading on the working electrode is about 495 μg cm^{-2}. The linear sweep voltammetry curves were performed in 1.0 M KOH solution and corrected with iR-compensation. The potential was converted to the reversible hydrogen electrode (RHE) according to the following Nernst equation: E (RHE) = E (vs Hg/HgO) + 0.059×pH. The overpotential was calculated as follows:

η= E (vs. RHE) –E^0 (vs. RHE)

Where η, E, and E^0 denote the overpotential, actual applied potential, and reversible potential of the reaction, respectively. E^0 is 0 V for the HER [1].

Catalytic hydrolysis of AB

Briefly, 10 mg of catalyst was added into a two-necked round-bottom flask containing 4.0 mL of water. The mixture was ultrasonicated for 30 min to uniformly disperse the catalyst. To trigger the hydrogen generation reaction, AB aqueous solution (1.0 mL, 1.0

mmol) was quickly injected into the mixture under stirring. The reaction temperature was kept at 25 ℃ through a water bath during the catalytic hydrolysis of AB. The hydrogen produced was measured by recording the drained water. The reusability of Ru/PC was determined as the following: When the previous cycle was finished, the fresh AB aqueous solution was directly injected to start the next recycling. Recycling tests were repeated for six times.

Catalytic 4-NP reduction

For reduction of 4-nitrophenol, all experiments were measured by UV-vis absorption spectrum at room temperature. 1.0 mL of $NaBH_4$ solution (0.125 M) was mixed with 2.0 mL of 4-NP aqueous solution (0.080 mM) to form a yellow solution. Subsequently, an aqueous suspension of Ru/PC catalyst (300 μL, 0.30 mg/mL) was added rapidly. At the end of the reaction, the color of solution disappeared (Fig. S13). After the reduction of 4-NP was completed, the $NaBH_4$ solid and fresh concentration of 4-NP were added for the next recycle.

<u>Turnover Frequency Calculation</u> [2]

The following formula was used to calculate the TOF per metal active site:

$$\mathrm{TOF} = \frac{\#\text{number of total hydrogen turnover per cm}^2}{\#\text{number of active sites per cm}^2} = \frac{\#\mathrm{H_2} \times |j|}{\text{active sites}}$$

The number of total hydrogen turnovers ($\#H_2$) was calculated from the current density according to the formula:

$$\#\mathrm{H_2} = |j| \frac{\mathrm{mA}}{\mathrm{cm}^2} \cdot \frac{1\mathrm{C/s}}{1000\ \mathrm{mA}} \cdot \frac{1\ \mathrm{mol\ e^-}}{96485.3\ \mathrm{C}} \cdot \frac{1\ \mathrm{mol\ H_2}}{2\ \mathrm{mol\ e^-}} \cdot \frac{6.02 \times 10^{23}}{1\ \mathrm{mol\ H_2}}$$

$$= 3.12 \times 10^{15} \frac{\mathrm{H_2/s}}{\mathrm{cm^2}} \mathrm{per} \frac{\mathrm{mA}}{\mathrm{cm^2}}$$

The upper-limit number of active sites was calculated on the hypothesis: surface metal atoms on the sample are considered as the active centers and all are accessible to the electrolyte.

Surface metal atoms on three samples were measured from XPS data (atomic percentage):

Ru/PC: Ru: 0.88%, C: 92.89%, O: 6.23%,

Ru/C: Ru: 0.49%, C: 88.36%, O: 11.15%,

Ru/PC-IM: Ru: 1.19%, C: 89.18%, O: 9.63%

Specific Ru sites for Ru/PC:

Ru/PC:

$$101g/molRu + 12g/mol\frac{92.89\ \%}{0.88\%}Ru + 16g/mol\frac{6.23\ \%}{0.88\ \%}Ru = 4.9 \times 10^{-4} g/cm^2$$

$$Ru \times 6.02 \times \frac{10^{23} sites}{mol} = 2.398 \times 10^{17} sites\ cm^{-2}$$

The HER current density at the overpotential of 30 mV is 15 mA cm^{-2} for Ru/PC. The TOF per Ru site was calculated as:

$$TOF = \frac{3.12 \times 10^{15} \frac{H_2/s}{cm^2} per \frac{mA}{cm^2} \times 15 \frac{mA}{cm^2}}{2.398 \times 10^{17} sites\ cm^{-2}} = 0.2\ s^{-1}$$

Ru/C:

$$101g/molRu + 12g/mol\frac{88.36\ \%}{0.49\%}Ru + 16g/mol\frac{11.15\ \%}{0.49\ \%}Ru = 4.9 \times 10^{-4} g/cm^2$$

$$Ru \times 6.02 \times \frac{10^{23} sites}{mol} = 1.289 \times 10^{17} sites\ cm^{-2}$$

The HER current density at the overpotential of 30 mV is 4.1 mA cm^{-2} for Ru/C. The TOF per Ru site was calculated as:

$$TOF = \frac{3.12 \times 10^{15} \frac{H_2/s}{cm^2} per \frac{mA}{cm^2} \times 4.1 \frac{mA}{cm^2}}{1.289 \times 10^{17} sites\ cm^{-2}} = 0.09\ s^{-1}$$

Ru/PC-IM:

$$101 g/mol Ru + 12 g/mol \frac{89.18\%}{1.19\%} Ru + 16 g/mol \frac{9.63\ \%}{1.19\ \%} Ru = 4.9 \times 10^{-4} g/cm^2$$

$$Ru \times 6.02 \times \frac{10^{23} sites}{mol} = 2.610 \times 10^{17} sites\ cm^{-2}$$

The HER current density at the overpotential of 30 mV is 1.67 mA cm^{-2} for Ru/PC-IM. The TOF per Ru site was calculated as:

$$TOF = \frac{3.12 \times 10^{15} \frac{H_2/s}{cm^2} per \frac{mA}{cm^2} \times 1.67 \frac{mA}{cm^2}}{2.610 \times 10^{17} sites\ cm^{-2}} = 0.019\ s^{-1}$$

Calculation Methods: The turnover frequency (TOF) values of the catalysts for hydrolysis of AB were calculated according to the following equation [3]:

$$TOF = \frac{P_{atm} V_{H_2} / RT}{n_{Ru} t}$$

where P_{atm} is the atmospheric pressure (101325 Pa), V_{H_2} is the volume of at the time of half-completion of H_2, R is the universal gas constant (8.3145 m^3 Pa mol^{-1} K^{-1}), T is the reaction temperature (K), n is the mole number of Ru atoms in catalyst (mol) and t is the time for half-completion of gas evolution (min).

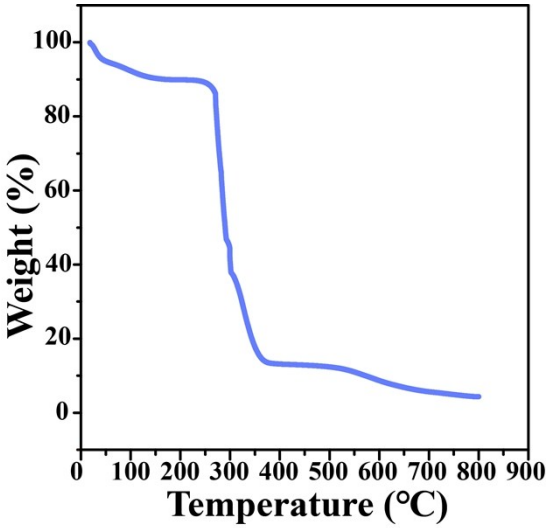

Fig. S1 TGA curve of Ru/PC.

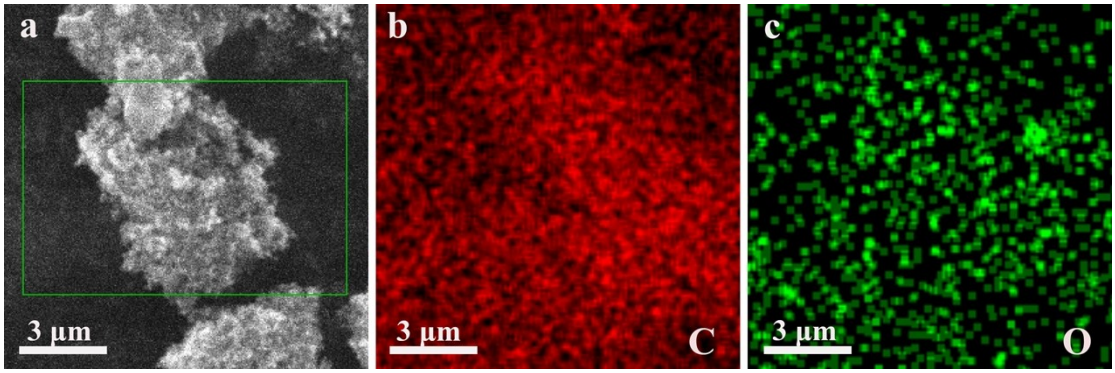

Fig. S2 (a-c) SEM-EDX mapping images for the sample prepared through direct pyrolysis of conductive carbon black and Na_2SO_4.

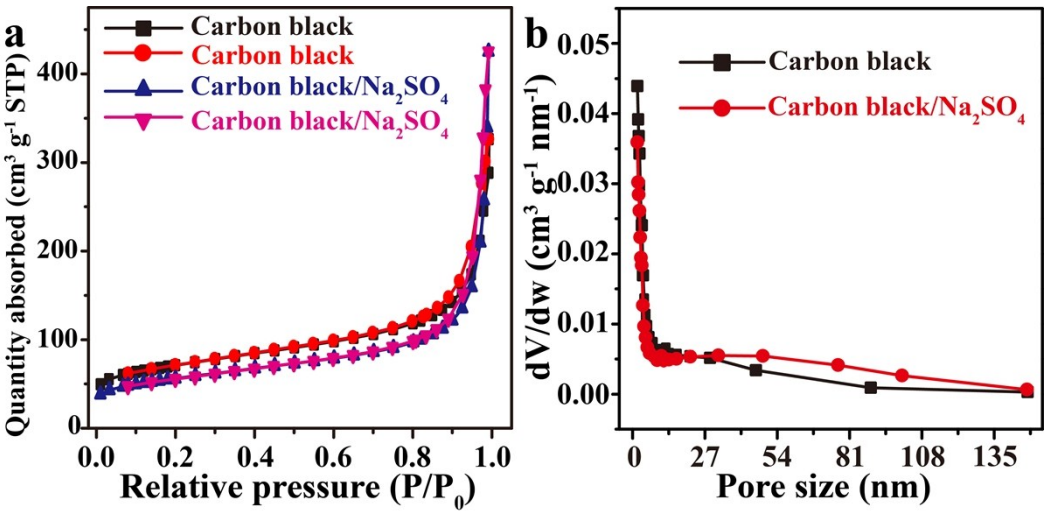

Fig. S3 (a) N_2 sorption isotherm curves of carbon black and the sample prepared through direct pyrolysis of carbon black/Na_2SO_4, (b) pore size distribution curves.

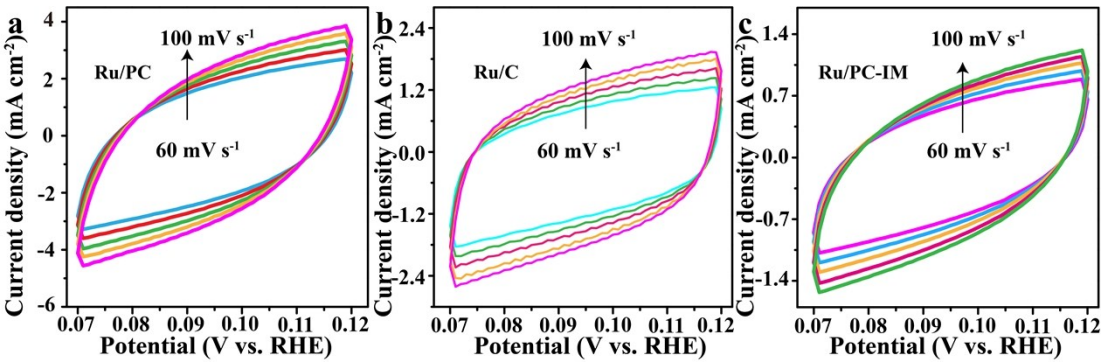

Fig. S4 CV curves measured at different scan rates from 60 to 100 mV s^{-1} in 1.0 M KOH for (a) Ru/PC, (b) Ru/C, and (c) Ru/PC-IM.

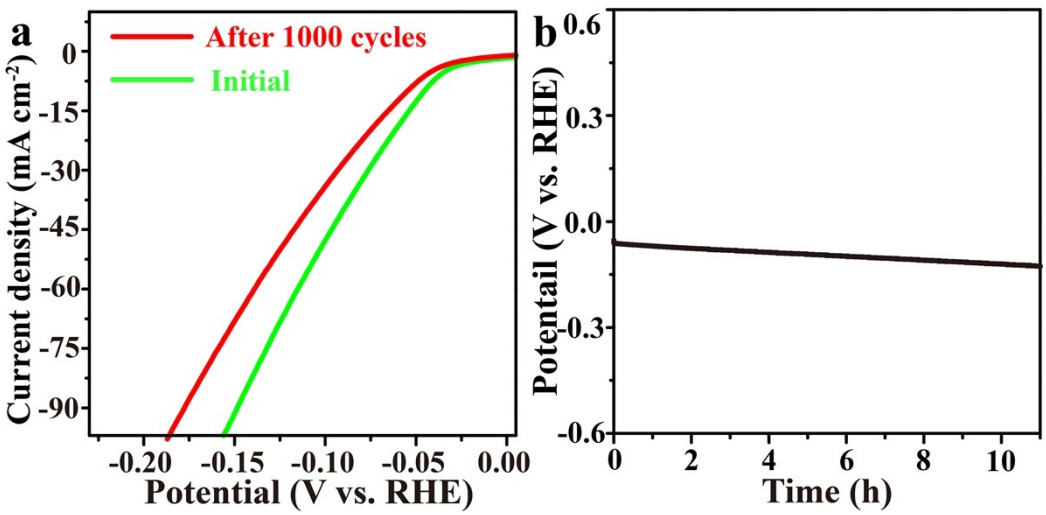

Fig. S5 (a) HER polarization curves before and after 1000 cycles and (b) V-t curve at 10 mA cm^{-2} for Ru/C.

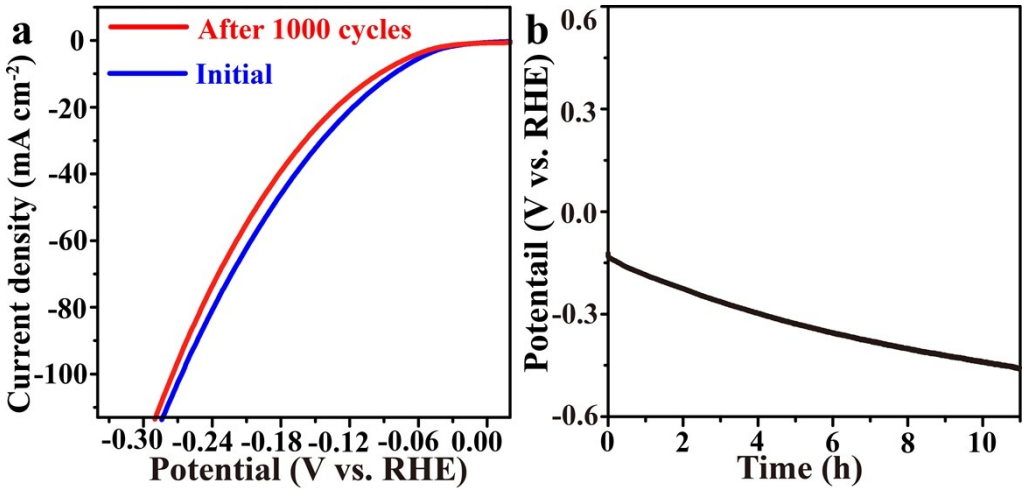

Fig. S6 (a) HER polarization curves before and after 1000 cycles and (b) V-t curve at 10 mA cm^{-2} for Ru/PC-IM.

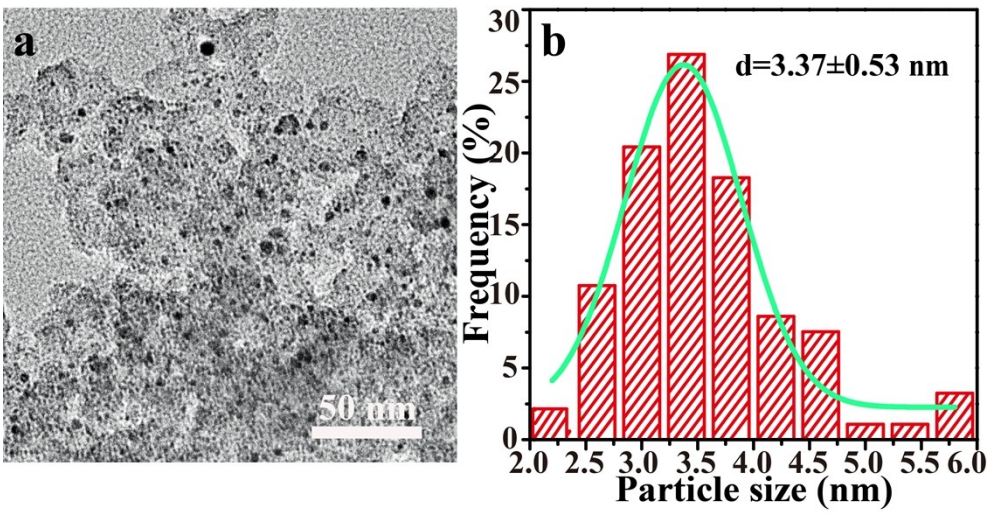

Fig. S7 (a) TEM image of Ru/PC after stability test, and (b) corresponding size distribution of Ru NPs.

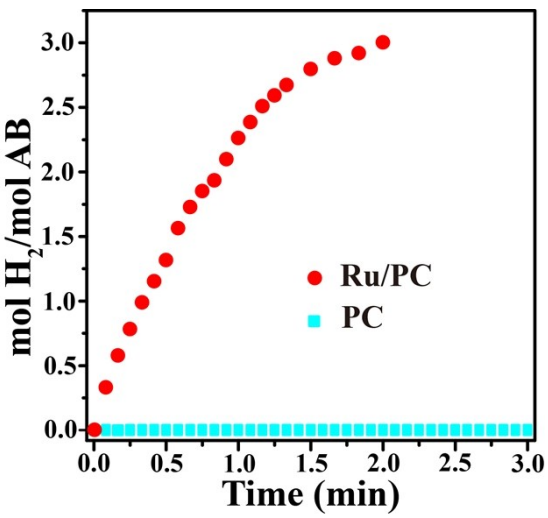

Fig. S8 Hydrolytic decomposition of AB catalyzed by PC and Ru/PC.

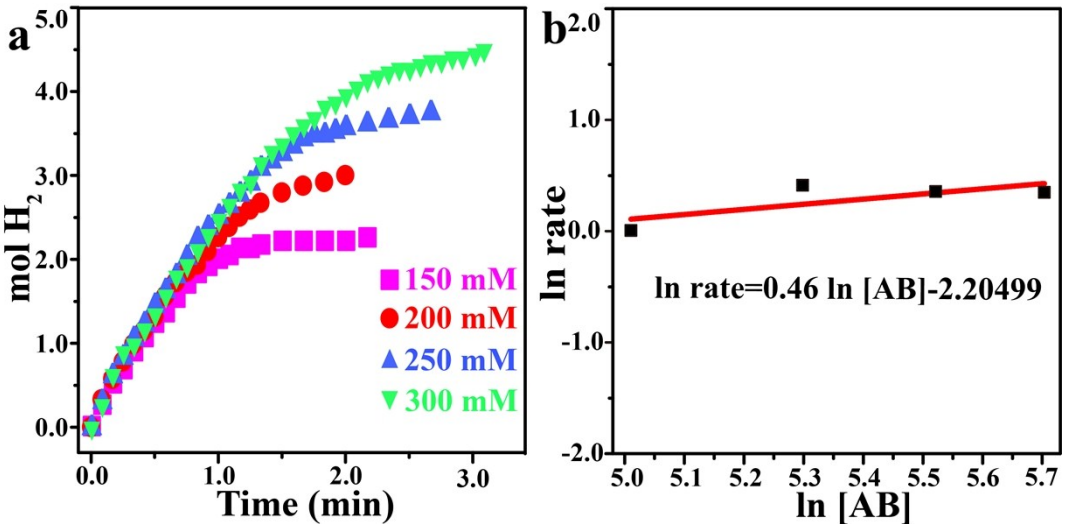

Fig. S9 (a) The plots of hydrogen generation rate versus the concentration of AB. (b) The natural logarithmic plots of hydrogen evolution rates versus AB concentration.

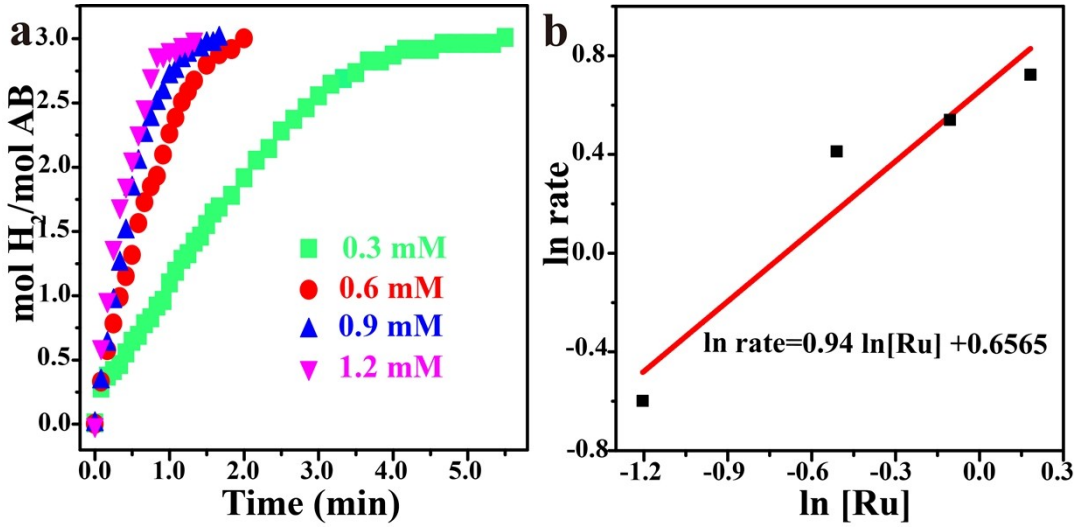

Fig. S10 (a) Plots of hydrogen generation rate versus Ru concentration. (b) The natural logarithmic plots of hydrogen evolution rates versus Ru concentrations.

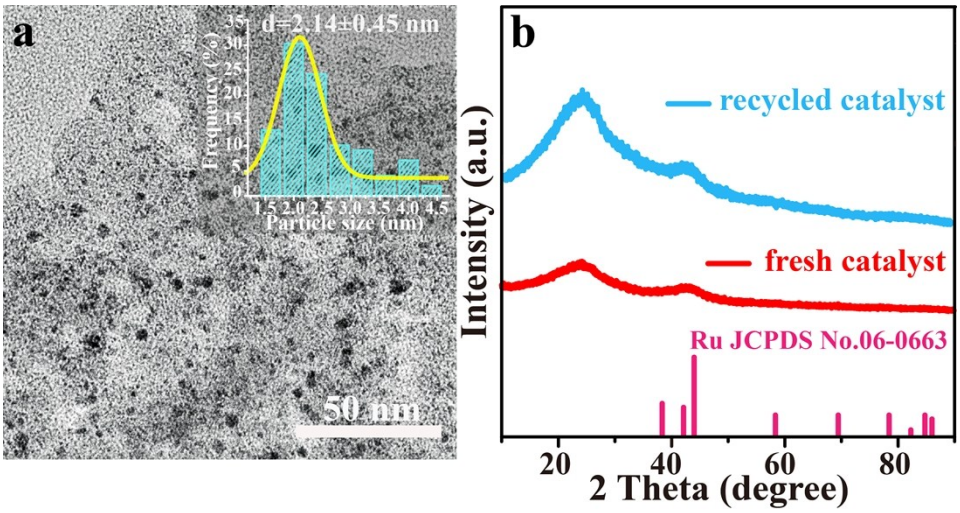

Fig. S11 (a) TEM image of Ru/PC after six runs toward AB hydrolysis. (b) XRD patterns of the fresh Ru/PC and the Ru/PC after six runs toward AB hydrolysis. Inset in (a) is the size distribution of Ru NPs.

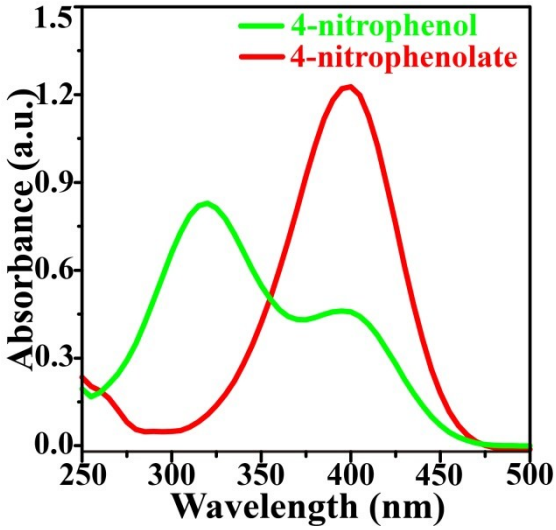

Fig. S12 UV-vis absorption spectra of 4-NP with (red) and without (green) $NaBH_4$.

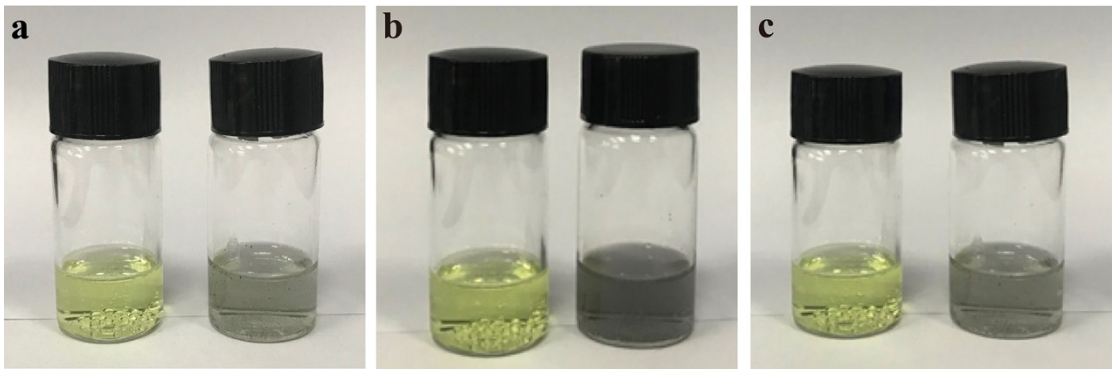

Fig. S13 Photos of 4-NP before (left) and after (right) addition of (a) Ru/PC, (b) Ru/C, and (c) Ru/PC-IM into the aqueous solution of 4-nitrophenol and $NaBH_4$.

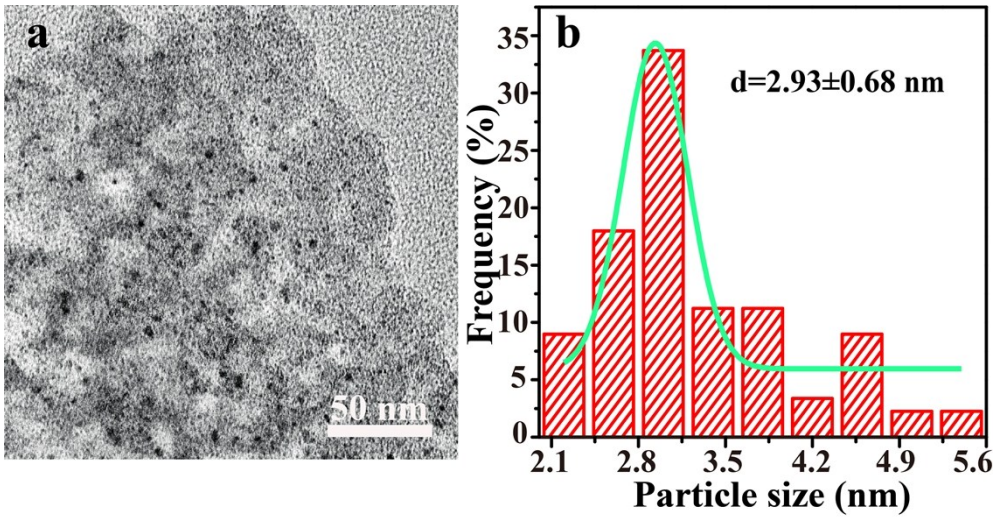

Fig. S14 (a) TEM image of Ru/PC after seven runs toward 4-NP reduction, and (b) corresponding size distribution of Ru NPs.

Table S1. XPS analyses for Ru/PC.

Catalyst	Ru (wt%)	C (wt%)	O (wt%)
Ru/PC	6.82	85.53	7.65

Table S2. BET surface areas, pore volumes and pore diameters for the carbon and the carbon treated with Na_2SO_4.

Samples	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)
Carbon	238	0.48857	9.9
Carbon/Na_2SO_4	199	0.65508	15.5

Table S3. BET surface areas, pore volumes and pore diameters for the Ru/PC, Ru/C and Ru/PC-IM.

Catalysts	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)
Ru/PC	575.2	0.726	7.39
Ru/C	486.7	0.382	8.60
Ru/PC-IM	225.3	0.145	9.40

Table S4. Comparison of HER activities of previous catalysts.

Electrocatalysts	Overpotential (mV) at 10 mA cm^{-2}	Electrolyte	Refs.
RuP_2@NPC	52	1.0 M KOH	4
RuCo@NC	28	1.0 M KOH	5
Ru/C_3N_4/C	79	1.0 M KOH	6
$MoRu_3$	30.5	1.0 M KOH	7
Ni@Ni_2P-Ru HNRs	31	1.0 M KOH	8
Ru@GnP	22	1.0 M KOH	9
4H/fcc Au-Ru	27	1.0 M KOH	10
HCP-PPh_3-Ru	61	1.0 M KOH	11
Ru–MoO_2	29	1.0 M KOH	12
Ru/PC	21	1.0 M KOH	This work

Table S5. Catalytic activity of the reported Ru-based catalysts for AB hydrolysis.

Catalysts	TOF (min^{-1})	*E*a (kJ/mol)	Particle size (nm)	Recyclability		Refs.
				Run times	% of retaining initial activity	
Ru/NC-Fes.	102.9	47.42	3~4	5	-	13
Ru/PPC	413	35.2	1.13	4	-	14
Ru/Al_2O_3-NFs	327	36.1	2.90	5	-	15
HCP-PPh_3-Ru	402	25.5	3.80	5	50%	11
Ru/HPCM	440	43	1.41	8	50%	16
Ru/3DNPC	584	31	1.32	7	50%	17
Ru/NPC	813	24.95	-	5	67.30%	18
Ru/C	429.5	34.8	~1.70	5	43.10%	19
Ru/PC	744	39.11	1.50	6	53.90%	This work

References:

1. Y. Zhao, T. Ling, S. Chen, B. Jin, A. Vasileff, Y. Jiao, L. Song, J. Luo and S.-Z. Qiao, *Angew. Chem., Int. Ed.*, 2019, **58**, 12252-12257.
2. T. Zhu, J. Ding, Q. Shao, Y. Qian and X. Huang, *ChemCatChem*, 2019, **11**, 689-692.
3. P. Pachfule, X. Yang, Q.-L. Zhu, N. Tsumori, T. Uchida and Q. Xu, *J. Mater. Chem. A.*, 2017, **5**, 4835-4841.
4. Z. Pu, I. S. Amiinu, Z. Kou, W. Li and S. Mu, *Angew. Chem., Int. Ed.*, 2017, **56**, 11559-11564.
5. J. Su, Y. Yang, G. Xia, J. Chen, P. Jiang and Q. Chen, *Nat. Commun.*, 2017, **8**, 14969.
6. Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, M. Jaroniec and S.-Z. Qiao, *J. Am. Chem. Soc.*, 2016, **138**, 16174-16181.
7. Z. Zhang, P. Li, Q. Wang, Q. Feng, Y. Tao, J. Xu, C. Jiang, X. Lu, J. Fan, M. Gu, H. Li and H. Wang, *J. Mater. Chem. A.*, 2019, **7**, 2780-2786.
8. Y. Liu, S. Liu, Y. Wang, Q. Zhang, L. Gu, S. Zhao, D. Xu, Y. Li, J. Bao and Z. Dai, *J. Am. Chem. Soc.*, 2018, **140**, 2731-2734.
9. F. Li, G.-F. Han, H.-J. Noh, I. Ahmad, I.-Y. Jeon and J.-B. Baek, *Adv. Mater.*, 2018, **30**, 1803676.
10. Q. Lu, A.-L. Wang, H. Cheng, Y. Gong, Q. Yun, N. Yang, B. Li, B. Chen, Q. Zhang, Y. Zong, L. Gu and H. Zhang, *Small*, 2018, **14**, 1801090.
11. C. Xu, H. Wang, Q. Wang, Y. Wang, Y. Zhang and G. Fan, *Appl. Surf. Sci.*, 2019, **466**, 193-201.
12. P. Jiang, Y. Yang, R. Shi, G. Xia, J. Chen, J. Su and Q. Chen, *J. Mater. Chem. A.*, 2017, **5**, 5475-5485.
13. Z. Cui, Y. Guo, Z. Feng, D. Xu and J. Ma, *New J. Chem.*, 2019, **43**, 4377-4384.
14. R. Lu, C. Xu, Q. Wang, Y. Wang, Y. Zhang, D. Gao, J. Bi and G. Fan, *Int. J. Hydrogen Energy.*, 2018, **43**, 18253-18260.
15. M. Hu, H. Wang, Y. Wang, Y. Zhang, J. Wu, B. Xu, D. Gao, J. Bi and G. Fan, *Int. J. Hydrogen Energy.*, 2017, **42**, 24142-24149.
16. F. Zhong, Q. Wang, C. Xu, Y. Yang, Y. Wang, Y. Zhang, D. Gao, J. Bi and G. Fan, *Appl. Surf. Sci.*, 2018, **455**, 326-332.
17. H. Wang, C. Xu, Q. Chen, M. Ming, Y. Wang, T. Sun, Y. Zhang, D. Gao, J. Bi and G. Fan, *ACS Sustainable Chem. Eng.*, 2019, **7**, 1178-1184.
18. H. Chu, N. Li, S. Qiu, Y. Zou, C. Xiang, F. Xu and L. Sun, *Int. J. Hydrogen Energy.*, 2019, **44**, 1774-1781.
19. H. Liang, G. Chen, S. Desinan, R. Rosei, F. Rosei and D. Ma, *Int. J. Hydrogen Energy.*, 2012, **37**, 17921-17927.