Supplementary Information for

Atomically ordered Rh_2P catalysts anchored within hollow mesoporous carbon for efficient hydrogen production

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Materials and Methods

Materials and Chemicals

Ammonium hexachlororhodate ($(NH_4)_2RhCl_6$), commercial Rh/C, *p*-nitrophenol, and deuterium water (D_2O) were obtained from Alfa Aesar. Tetrapropyl orthosilicate (TPOS), resorcinol, ammonia borane (AB), and formaldehyde were purchased from Shanghai Macklin Biochemical Co., Ltd. Ethanol, $NH_3 \cdot H_2O$ (25%), sodium hypophosphite (NaH_2PO_2), sodium borohydride ($NaBH_4$), sodium hydroxide (NaOH), hydrofluoric (HF), and urea were obtained from Sinopharm Chemical Reagent Co. Ltd. All the reagents are of analytical reagent grade and used without further purification. Deionized H_2O with the resistivity of 18.25 mΩ was used in all experiments.

Synthesis of nitrogen-functionalized Hollow mesoporous carbon (HMC)

Nitrogen-functionalized hollow mesoporous carbon (HMC) was synthesized through a template-free route according to the reported method with a modification (*ACS Nano* **2016**, *10*, 4579). In a typical synthesis, 17.3 mL of TPOS was injected in the mixed solution containing 350 mL of ethanol, 30 mL of H_2O, and 15 mL of $NH_3 \cdot H_2O$ (25%). After stirring for 15 min, 2 g of resorcinol, 200 mg of urea, and 2.8 mL of formaldehyde were added. After stirring for another 24 h, the powder was collected by centrifugation and further washed with water/ethanol for several times. The samples were then carbonized at 700 ^oC for 5 h under N_2 and washed with HF to remove silica. The HMCs were finally dried at 50 ^oC before use.

Synthesis of Rh@HMC and Rh_2P@HMC

In a typical synthesis of Rh@HMC, 0.30 g of as-made HMC was slowly dipped in 4.0 mL of 10.0 mM $(NH_4)_2RhCl_6$ and further stirred for 12 h. After that, the powder was washed several times with water/ethanol and dried at 50 ^oC overnight. Then, obtained powder was moved into a tube furnace and calcined at 700 ^oC for 5 h under a H_2/N_2 atmosphere (5:95). After be washed with HF to remove silica, Rh@HMC was accordingly obtained by drying at 50 ^oC for 12 h. By contrast, Rh_2P@HMC was synthesized by direct solid-phase phosphation of Rh@HMC with NaH_2PO_2. Typically, 0.30 g of Rh@HMC was physically mixed with 0.60 g of NaH_2PO_2 and further calcined in a tube furnace under 350 ^oC for 3 h under a H_2/N_2 atmosphere (5:95). After be washed by diluted HCl and water/ethanol for 3 times, Rh_2P@HMC was obtained finally.

Electrocatalytic hydrogen evolution reaction (HER)

Electrocatalytic studies were carried out on a CHI 660E electrochemical analyser at 25 ^oC according to our previous works (*Inorg. Chem.* **2021**, *60*, 4380; *Appl. Catal. B Environ.* **2018**, *238*, 525). Typically, a nanocatalyst ink was prepared by adding 5.0 mg of nanocatalysts to 1.0 mL of ethanol/DI H_2O (8:2 by volume). After sonicating for > 30 min, 50 µL of Nafion solution was mixed and further sonicated for an additional 30 min. Then, 6.0 µL of the ink solution (~6.0 µg of the catalyst) was casted on GCE and dried at 40 ^oC before test. Linear sweep voltammetry (LSV) curves were obtained at 0.5 M H_2SO_4 with a scan rate of 5 mV s^{-1}, while cyclic voltammetry (CV) curves were collected at 0.5 M H_2SO_4 with a scan rate of 50 mV s^{-1}. All results were obtained by IR compensation and all reported potentials in this work were referenced to the reversible hydrogen electrode (RHE).

Catalytic dehydrogenation of AB

Catalytic dehydrogenation of AB was carried out at ambient conditions (298 K) according to our previous works (*J. Phys. Chem. Lett.* **2019**, *10*, 7374; *J. Phys. Chem. Lett.* **2021**, *12*, 696). Typically, 10.0 mg of catalyst was first dispersed in 3.0 mL of H_2O and further sonicated for 10 min. Then, dehydrogenation reaction of AB was started rapidly when injected 4.0 mL of 5.0 mg mL^{-1} AB into above solution at 298 K. The volume of the generated H_2 was monitored by recording the displacement of water in the gas burette.

Tandem reaction coupled AB dehydrogenation and *p*-nitrophenol hydrogenation

Typically, 1.0 mL of 0.10 mM *p*-nitrophenol and 1.0 mL of 30 mM AB were successively mixed in a quartz cuvette. Then, 0.05 mL of 0.20 mg mL^{-1} Rh_2P@HMC was injected above solution to start AB dehydrogenation and *p*-nitrophenol hydrogenation reactions simultaneously. Hydrogenation kinetics was collected by *in situ* Ultraviolet-visible (UV-vis) spectroscopy.

Characterizations

SEM images were collected using a JEOL JSM-7610F field emission scanning electron microscope. TEM and STEM studies were carried out using a field emission transmission electron microscope (JEM-F200, JEOL Ltd., Japan) with an accelerating voltage of 200 kV. PXRD patterns were recorded on powder samples using a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite-monochromatized Cu Kα radiation in 2ϑ ranging from 30^o to 90^o. XPS was performed on a scanning X-ray microprobe (Thermo ESCALAB 250Xi) that uses Al Kα radiation. ICP-MS was recorded on a NexION 350D. N_2 adsorption/desorption isotherms were measured at 77 K using an ASAP 2010 M+C analyzer.

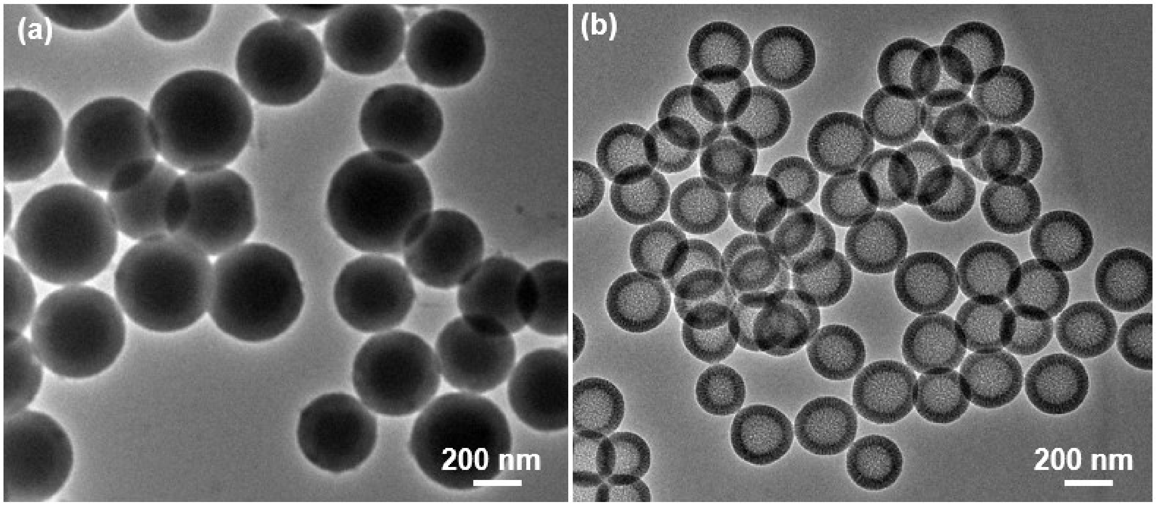

Fig. S1 (a) TEM image of as-made nitrogen-functional HMC, indicating it composed of a silica core surrounded by a carbon shell. (b) TEM image of nitrogen-functional HMC, suggesting highly uniform and homogeneously dispersed nanostructure.

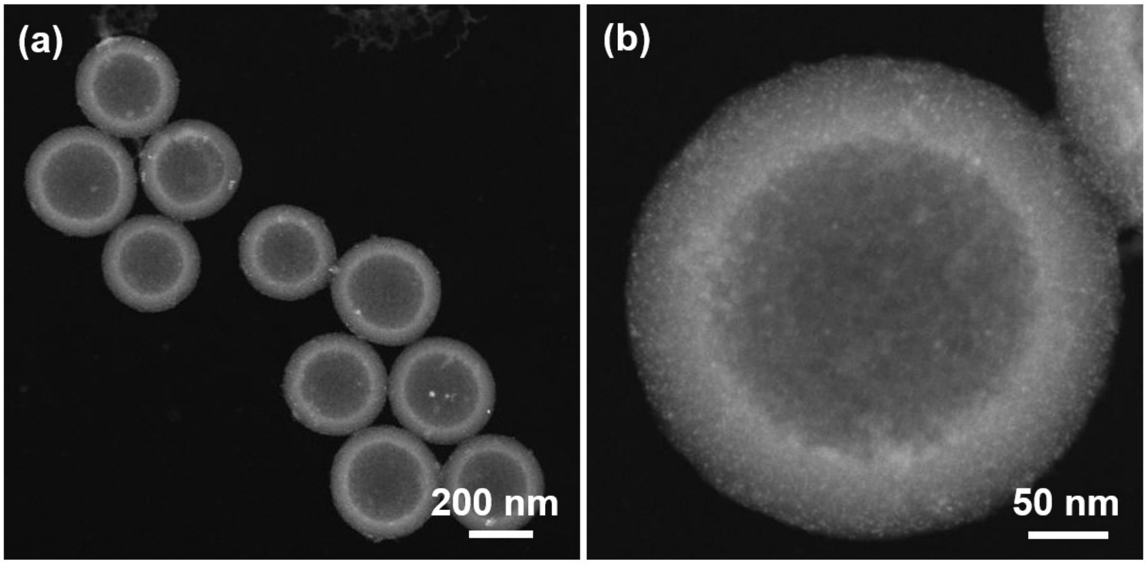

Fig. S2 (a) Low-magnification and (b) high-magnification STEM images of Rh@HMC, confirming uniform Rh nanoclusters dispersed within mesoporous channels of HMCs.

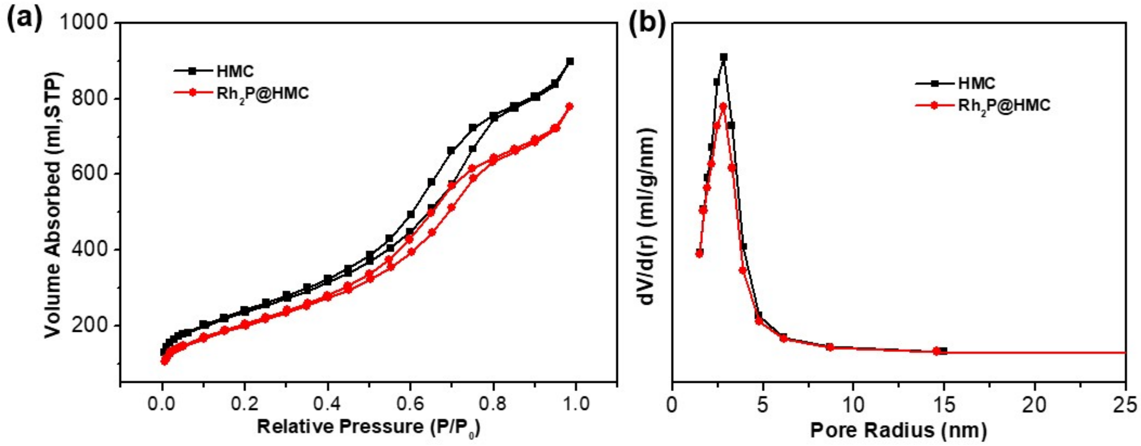

Fig. S3 (a) N_2 adsorption/desorption isotherms and (b) corresponding pore size distributions of HMC and Rh_2PHMC.

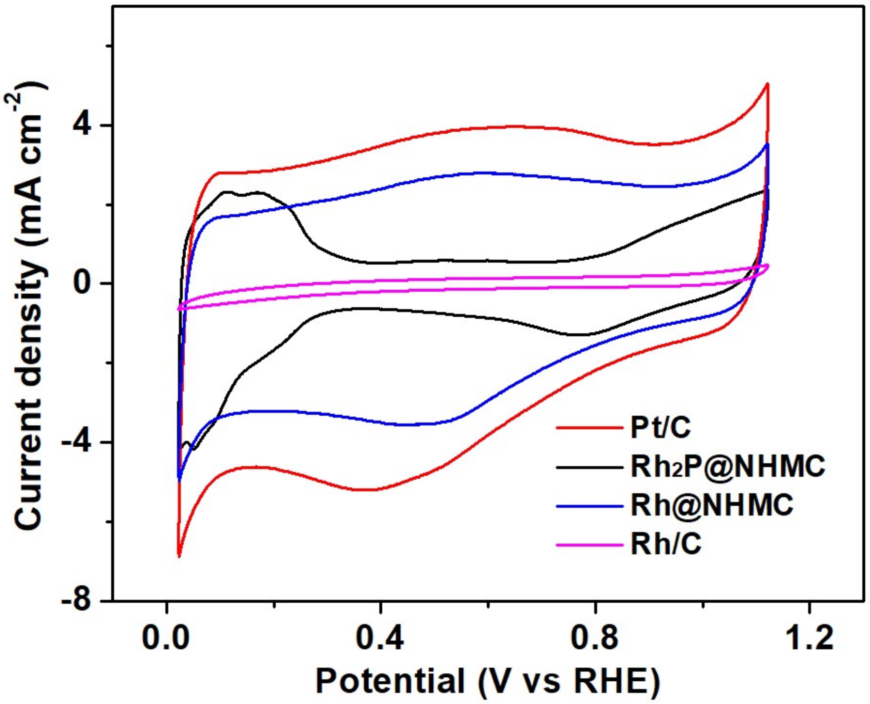

Fig. S4 CV curves of Rh_2P@HMC, Rh@HMC, commercial Rh/C and Pt/C, indicating they are electrocatalytically active for HER.

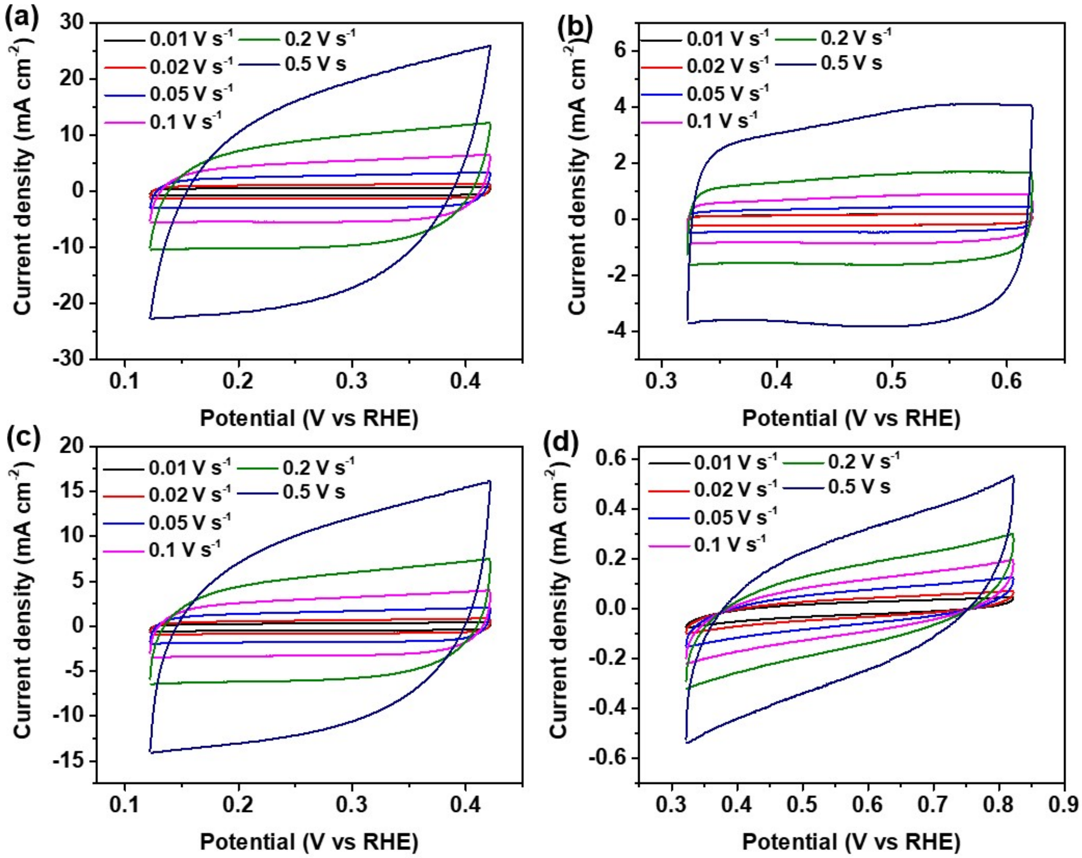

Fig. S5 CV curves of (a) Rh_2P@HMC, (b) Pt/C, (c) Rh@HMC, and (d) Rh/C with different scan rates.

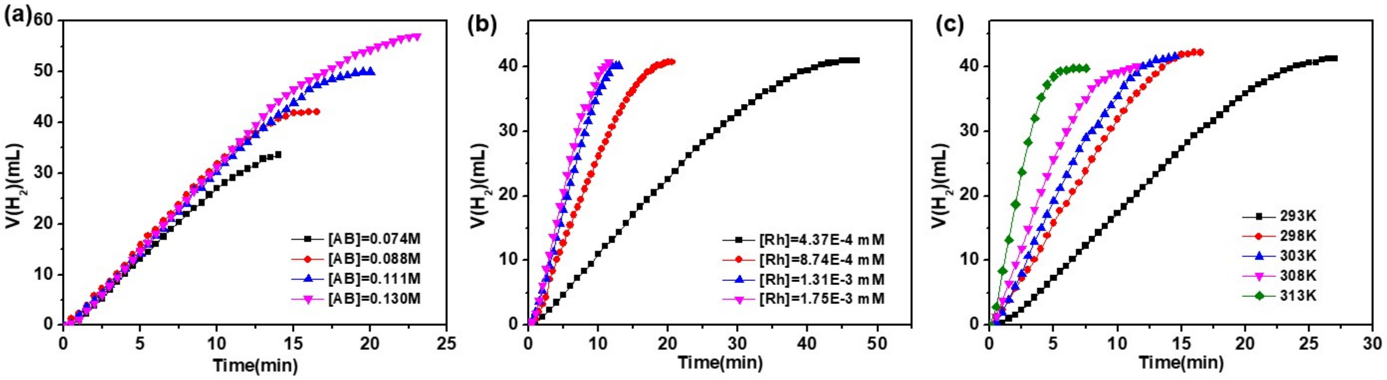

Fig. S6 AB dehydrogenation dependance over Rh/C by (b) AB concentrations, (c) Rh concentrations, and (d) test temperatures.

Table S1. Comparisons of catalytic activities of previously reported nanocatalysts and Rh_2P@HMC in room-temperature AB dehydrogenation.

No.	Catalyst	Temperature (°C)	TOF (mol_{H2} mol^{-1} min^{-1})	References
1	**RuP@NHMC**	**25**	**939** **1663 (0.4 M NaOH)**	**This work**
2	**Rh@ZSM-5-H**	25	432	*Angew. Chem. Int. Ed.* **2019**, *58*, 18570
3	**Rh/WO_{3-x}**	25	535.7	*Nanoscale Adv.* **2019**, *1*, 3941
4	**Rh/ATP-C**	25	566	*Nanoscale Adv.* **2020**, *2*, 1685
5	**Ru/CB**	25	429.5	*Int. J. Hydrogen Energy* **2012**, *37*, 17921
6	**Ru/graphene**	25	325	*Int. J. Hydrogen Energy* **2015**, *40*, 6180
7	**Ru/CeO_2**	25	361	*Dalton Trans.* **2016**, *45*, 10969
8	**Ru NPs@PCC**	25	215	*Chem* **2018**, *4*, 555
9	**RuNi/p-g-C_3N_4**	30	840.3	*ACS Sustainable Chem. Eng.* **2020**, *8*, 8458
10	**Pt25@TiO_2**	25	311	*Angew. Chem. Int. Ed.* 2016, *55*, 12257
11	**Ni_2Pt@ZIF-8**	rt	600	*J. Am. Chem. Soc.* 2018, *140*, 10034
12	**Pt_1Co_1 (Dendrimer)**	20	606	*ACS Catal.* **2019**, *9*, 1110
13	**PdCu/NAs215**	25	72.9	*Int. J. Hydrogen Energy* **2019**, *44*, 30226