### **Supporting Information**

# Pore structure dependent activity and durability of mesoporous rhodium nanoparticles towards methanol oxidation reaction

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#### **Experimental Section**

*Chemicals.* Rhodium (III) chloride hydrate (RhCl<sub>3</sub>·nH<sub>2</sub>O, Rh≥39.5%) was obtained from Energy Chemicals. Cetyltrimethylammonium chlorine (CTAC, 99.0%), Cetyltrimethylammonium bromide (CTAB, 99.0%), 1,3,5-trimethylbenzene (TMB, 99.0%), Poly (vinyl pyrrolidone) (PVP, MW≈40000) and sodium borohydride (NaBH<sub>4</sub>, 99.9%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hexadecylpyridinium chloride monohydrate (HDPC, 99.0-102%) and ascorbic acid (AA, reagent grade) were purchased from Sigma-Aldrich. Commercial Pt/C was purchased from Aladdin. Carbon black was purchased from Kabote (china) Investment Co., Ltd. Ultrapure water (18 MΩ\*cm) was used in all experiments and all regents were utilized as received.

## Synthesis of mesoporous Rhodium nanoparticles (MRhS) with tunable mesoporous structures

In a typical synthesis, 100 mg of desired surfactant dissolved in a mixture of RhCl<sub>3</sub> (19 mM, 5 mL) and H<sub>2</sub>O (4 mL) at room temperature to form a homogeneous red solution. Then a freshly prepared AA aqueous solution (0.1 M, 1.0 mL) was added to the above mixed solution, and the resulting mixture was aged at 80 °C for 12 hours. The obtained black colloidal product was separated by centrifugation, followed by washing thoroughly with abundant water and ethanol. Then the black colloidal was refluxing in an acidic ethanol solution for 12 hours twice to remove the surfactant. Finally, MRhS with clean mesoporous surfaces were obtained and dried at 60 °C for 6 h in an oven. Typically, using CTAC, CTAB + TMB and HDPC, as the structure-directing agents leads to the formation of MRhS with stacking, radial and net-like mesoporous structure, respectively.

#### Synthesis of Rhodium nanoparticles (Rh NPs)

Typically, 100 mg of PVP, 5 mL of RhCl<sub>3</sub> (19 mM) and 4.0 mL of  $H_2O$  were mixed at room temperature to form a clear red solution. After addition of a freshly prepared NaBH<sub>4</sub> aqueous solution (0.1 M, 1.0 mL), the obtained mixture was aged at room temperature for 12 hours. The PVP-capped Rh NPs were obtained via high-speed centrifugation.

S2

#### **Materials Characterization**

Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on an FEI Tecnai G2 F20s-twin D573 field emission transmission electron microscope with an accelerating voltage of 200 kV. The crystal structures were acquired by powder X-ray diffraction (XRD) on a D8 Advance (Bruker AXS) diffractometer with Cu Kα radiation in a 2θ range from 30° to 90° with a scan rate of 5° min<sup>-1</sup>. N<sub>2</sub> adsorption-desorption isotherms were obtained at 196 °C on a Micromeritics ASAP 2020 sorptometer. Samples were degassed at 120 °C for 12 h prior to analysis. Brunauer-Emmett-Teller (BET) surface areas were calculated from the linear part of the BET plot. X-ray photoelectron spectroscopy (XPS) measurements were investigated on a Kratos Axis Ultra DLD spectrometer with an AI Kα X-ray source. The Rh loading of all samples was accurately confirmed with a NexION 350 ICP-MS instrument.

#### **Electrochemical Measurements**

All Rh-based catalysts were supported on the carbon black via a simple impregnation method for electrochemical measurements. The Rh loading was identified to be 20 wt% measured by ICP-MS instrument. Electrochemical measurements were conducted in a standard three-electrode system by a CHI760E electrochemical work station (CH Instruments) at room temperature. EIS analysis was performed on a Zahner work station at 0.5 V in the frequency range of 100 kHz-0.01 Hz with the amplitude of 5mV. The catalyst-modified glassy carbon electrode (GCE) with 5 mm diameter was used as the working electrode. A 1.5 cm\*1.5 cm Pt plane and a saturated calomel electrode (SCE) were acted as the counter andthe reference electrode, respectively. In order to obtain uniform catalyst inks, 4 mg of each catalyst powder was dispersed in a mixture containing 500  $\mu$ L of deionized water, 500  $\mu$ L of suspension was dropped on the GCE surface and dried at room temperature.As a result, the Rh loading on GCE was 0.020 mg

cm<sup>-2</sup>. All of the potentials in this work were converted into the reversible hydrogen electrode (RHE) according to the equation1:

E (vs RHE) = E (vs SCE) + 
$$E_{SCE}^{B}$$
 (0.242 V) + 0.059 \* pH (1)

The electrochemically active surfacearea (ECSA) of Rh samples was measured by integrating the charges associated with hydrogen adsorption ( $Q_H$ ) between 0.10 V and 0.36 V and calculated by the following equation:

$$ECSA = Q_{\rm H} / (Cm) \tag{2}$$

Where,  $Q_H$  is the charge forhydrogen desorption, m isthe mass of Rh loading on the electrode surface, and C is the hydrogen adsorption constants ( $C_{Rh}$  = 220 µC cm<sup>-2</sup>).<sup>1-2</sup> The ECSA and CO-stripping voltammograms were carried out in 1 M KOH electrolyte at a scan rate of 0.05 V s<sup>-1</sup> ranging from 0.1 to 1.1 V vs. RHE. Methanol oxidation was evaluated in 1 M KOH +1 M CH<sub>3</sub>OH electrolyte with a scan rate of 0.05 V s<sup>-1</sup>. The current-time (i-t) tests were performed at 0.6 V vs.RHE for 7200 s.

#### **Supplementary Figures and Legends**



**Scheme S1**. Schematic illustration of the synthetic route to MRhS with tunable porous structures.

**NOTING:** Soft template is emerging as one of the most popular methods for preparing mesoporous metal nanoparticles (MMNs).<sup>3-4</sup> Using different surfactants as the structure-directing agents can result in the formation of MMNs with various pore constructions. Generally, the structures of mesoporous materials are highly dependent on the surfactant packing parameter,  $g = V / Ia_0$ , where V is the volume of the hydrophobic surfactant chains, l is the surfactant chain length, and  $a_0$  is the effective area of the hydrophilic head group of surfactant.<sup>5</sup> A larger surfactant packing parameter means the formed micelle having a smaller surface mean curvature, with the mesophase transiting gradually from globular to columnar and lamellar.<sup>6</sup> Moreover, the interaction between the head groups of surfactants and the metal precursors is another critical role in modulating the mesoporous structures of MMNs.<sup>7</sup> Based-on these considerations, thereby, we selected CTAC, CTAB and HDPC as the surfactants and TMB as the additive to prepare mesoporous Rh NPs (MRhS) with tunable mesoporous structures by a hydrothermal co-assembly process (Scheme S1).



**Figure S1**. (a) TEM and (b) HRTEM inages of Rh NPs. (c) The particle size distribution of RhNPs. (d) Rh 3d XPS spectrum of Rh NPs.



**Figure S2**. XRD patterns (a), Rh 3d XPS spectra (b),  $N_2$  adsorption-desorption isotherms (c), BET surface area (d) and pore size distributions (e) of three MRhS samples.

**NOTING:** According to the XRD patterns of three MRhS samples (based-on the Scherrer formula), their average crystallite sizes were calculated to be 4.2 nm (N-MRhS), 4.9 nm (R-MRhS) and 5.7 nm (S-MRhS), respectively. This result was in good agreement with the TEM results. From the pore size distributions of three MRhS samples, we can see that R-MRhS shows two pore sizes centered at 5.0 nm and 12.0 nm while N-MRhS and S-MRhS present only one pore size centered at 20.0 nm. The pore size of  $\geq 10.0$  nm should be attributed the irregular intercrystalline mesopores. The uniform mesochannel of 5.0 nm should be assigned to the ordered radial mesoporous structure of R-MRhS. It is noting that although N-MRhS has a higher porosity than R-MRhS, as evidenced by the TEM images in Fig.1, the unordered mesoporous structure of N-MRhS may result in a lower BET surface area.



**Figure S3**. CV curves (a) and calculated ECSA values (b) of different catalysts: N-MRhS, R-MRhS, S-MRhS and Rh NPs in 1 M KOH electrolyte.



**Figure S4**. Multiple CVs of (a) N-MRhS, (b) R-MRhS (c) S-MRhS, and (d) Rh NPs measured 500 cycles in 1 M KOH + 1 M CH<sub>3</sub>OH electrolyte at a scan rate of 0.05 Vs<sup>-1</sup>, respectively.



**Figure S5**. HRTEM images of single particle for the sample S-MRhS (a), R-MRhS (b) and N-MRhS (c). (d) HRTEM imgaes of the sample N-MRhS in the zone highlighted in *c*, which indicates that there are some step atoms on the pore surfaces.



**Figure S6**. The particle size distributions of the branches of three MRhS: (a) N-MRhS; (b) R-MRhS and (c) S-MRhS.



Figure S7. CV plots of (a) N-MRhS, (b) R-MRhS, (c) S-MRhS and (d) Rh NPs measured in 1 M KOH +1 M CH<sub>3</sub>OH electrolyte at different scan rates.



Figure S8. The Nyquist plot of EIS spectra of Rh NPs toward methanol oxidation in 1 M  $CH_3OH + 1$  M KOH electrolyte at 0.5 V vs.RHE.



**Figure S9**. The possible path of electron transfer on the pore surfaces of different MRhS catalysts: (a) N-MRhS; (b) R-MRhS and (c) S-MRhS.



**Figure S10**. TEM images of the recovered sample N-MRhS after 500 CVs. Compared with the TEM images of fresh N-MRhS, the branch size has aggregated and grown up from 3.1 nm to 5-8 nm. However, in spite of the serious aggregation, the nanoporous structure still remained good.



**Figure S11**. CO-stripping voltammograms of recovered MRhS catalysts in Arsaturated 1 M KOH electrolyte.

Catalysts	Peak potential (V vs. RHE)	Mass activity (mA mg <sup>-1</sup> <sub>metal</sub> )	ECSA (m² g⁻¹)	Reference
N-MRhS	0.63	722	110.9	This work
R-MRhS	0.64	425	84.5	This work
S-MRhS	0.63	270	51.0	This work
Rh nanodendrites	0.60	255.6	43.35	S8
Rh aggregates	0.77	27.5	23.09	S8
Rh-NSs/RGO	0.61	264	48.66	S9
Rh-NPs/RGO	0.61	171	40.09	S9
Mesoporous Rh	0.64	288	50	S10
Rh hollow nanospheres	0.60	292	50.66	S11
Mesoporous Rh film	0.62	277	162	S12
Rh wave nanowire	0.61	722	105	S13
3D net-like PdRh ( $Pd_1Rh_3$ )	0.85	257	-	S14
PtRh nanosponges	0.71	404.9	60.7	S15
Pt/C@SiC	0.85	647.4	81.2	S2
Pt/CeO2/PANI	0.85	361.33	43.3	S16
PtRu nanowire	0.7	820	72.1	S17
PtNi Nanocrystal Clusters	0.64	696	51	S18

**Table S1.** The electrocatalytic activity of different Rh-based catalysts for MOR in alkaline media.

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