Supporting Information

$MoSe_2$ promoted PtRu catalyst for efficient methanol electrooxidation

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1. Experimental section

1.1 Materials

All the chemical reagents in the experiment were used directly without further purification. Tetrapropyl orthosilicate (TPOS), tetraethyl orthosilicate (TEOS), ethanol, methanol, resorcinol, sodium molybdenum oxide (Na_2MoO_4), selenium powder, chloroplatinic acid hexahydrate ($H_2PtCl_6·6H_2O$), ruthenium chloride ($RuCl_3$), ethylene glycol ($C_2H_6O_2$) and potassium hydroxide (KOH) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Formaldehyde solution, and ammonia solution (25 wt.%) were acquired from Sinopharm Chemical Reagent Co., Ltd. Nafion (5 wt.%) was purchased from Sigma-Aldrich. Commercial PtRu/C catalyst was purchased from Johnson Matthey company. All solutions were prepared with ultrapure water with a resistance of 18.2 MΩ (Thermo Fisher Scientific (USA) Co., Ltd).

1.2 Preparation of Mesoporous Hollow Carbon Spheres (MHCS)

In a typical synthesis of MHCS, 3.46 mL of tetrapropyl orthosilicate (TPOS) and 3.46 mL of tetraethyl orthosilicate (TEOS) were added to the solution containing ethanol (60 mL), H_2O (20 mL), and $NH_3·H_2O$ (3 mL) under stirring at room temperature for 20 min. Then, 0.4 g of resorcinol and 0.56 mL of formaldehyde were added to the solution, and the system was stirred for 20 h at room temperature. The precipitates were collected through centrifugation, washed with ultrapure water and ethanol three times, and dried in a vacuum oven at 80 °C. The dried powder was heated to 700 °C at a rate of 3 ^{o}C min in N_2 atmosphere for 5 h. Then, the carbonized materials were dispersed in NaOH solutions at room temperature under stirring for 12 h to remove the silica. Finally, the MHCS was obtained by washing the precipitates with ultrapure water and ethanol several times to remove the impurities.

1.3 Preparation of $MoSe_2$@MHCS and $MoSe_2$

In a typical synthesis process, 4 mmol of selenium powder was dissolved into 10 mL of $N_2H_4·H_2O$ solution and the solution was stirred continuously for 5 h until the color of the solution turned dark brown, which was named solution A. Then, 2 mmol of Na_2MoO_4 was dispersed in a mixed solution consisting of 20 mL of ethanol and 30 mL of H_2O under constant stirring to form solution B. Subsequently, solution A was dropped into solution B at room temperature and stirred continuously for 30 min to make the solution fully mixed. Then, 50 mg MHCS was added to the mixture, followed by a rigorous ultrasonic treatment for 2 h. After that, the mixture was transferred into a 100 mL Teflon-lined autoclave for hydrothermal treatment at 200 °C for 12 h. After cooling naturally, the precipitate was collected and washed with ultrapure water and ethanol before being dried at 60 °C in a vacuum oven overnight. Finally, the product was treated at 500 °C for 5 h with an argon atmosphere (containing 5 % H_2) to achieve highly crystalline $MoSe_2$@MHCS. For comparison, pure $MoSe_2$ nanosheets were synthesized using the same method in the absence of MHCS.

1.4 Preparation of PtRu/$MoSe_2$@MHCS, PtRu/$MoSe_2$, PtRu/MHCS

21 mg of the precursor of the $MoSe_2$@MHCS was ultrasonically dispersed evenly in 50 mL of ethylene glycol to form a uniform suspension. After that, 200 μL of H_2PtCl_6 (30 mg mL^{-1}) and 150 μL of $RuCl_3$ (20 mg mL^{-1}) solution was slowly added into the dispersion under continuous magnetic stirring for 30 min. The pH value of the mixture was adjusted to 9 by adding 1 M KOH solution. Then the beaker containing the suspension was placed in the center of a microwave oven, and the suspension was repeatedly operated at 700 W for 60 s on and 30 s off for 3 times. After cooling down to room temperature, the mixture solution was further stirred overnight. Finally, the black product was filtered and washed several times and dried at 60 ^{o}C in a vacuum oven for 10 h. The obtained catalyst was denoted as PtRu/$MoSe_2$@MHCS. The PtRu/$MoSe_2$, PtRu/MHCS catalysts were synthesized following the same procedure by replacing the $MoSe_2$@MHCS with the $MoSe_2$ and MHCS during the fabrication.

1.5 Physical characterizations

The morphology and structure of catalysts and their precursors were researched by scanning electron microscope (SEM), transmission electron microscopy (TEM) and X-ray powder diffraction (XRD). The XRD was implemented by Bruker D8 advance X-ray diffraction with Cu Kα radiation. The morphology was examined with a transmission electron microscope (TEM) operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried on an ECSALAB250Xi S3 spectrometer with an Al Kα radiation source. X-ray detector spectrum (EDS) images were obtained on a TECNAI G2 F30 transmission electron microscope (acceleration voltage: 300 kV).

1.6 Electrochemical Pre-treatment

All the electrochemical measurements were conducted in a conventional three-electrode system controlled by a Bio-Logic VSP electrochemical workstation (Bio-Logic Co., France). The graphite rod and the saturated calomel electrode (SCE, Hg/Hg_2Cl_2) worked as the counter and reference electrode and the reference electrode was positioned close to the working electrode through a double salt-bridge via luggin capillary tip. Please note the reference electrode was carefully calibrated and checked before and after the test to make sure its accuracy.

The performance of various catalysts was evaluated by coating the catalyst over the glassy carbon electrode (3 mm diameter, 0.07 cm^{-2}). The working electrode was prepared by coating the surface of the working electrode with 10 μL dispersed catalysts ink. The catalyst ink was prepared by ultrasonically dispersing a mixture containing 2.5 mg catalyst, 475 μL of ethanol and 25 μL of a 5 wt.% Nafion solution. All of the potentials were relative to the SCE electrode.

1.7 Electrochemical analysis

The activity of metal nanoparticles for methanol electro-oxidation was measured. Before electrochemical measurements, a nitrogen flow was bubbled into the test system to remove the oxygen and ad/desorption of hydrogen on metal nanoparticles surface was evaluated in 0.5 M H_2SO_4. Cyclic voltammetry was carried out at room temperature in 0.5 M H_2SO_4 + 1 M CH_3OH solution of methanol at a potential range between -0.2 and 1 V vs. SCE and at a potential scan rate of 50 mV s^{-1}.

The chronoamperometry (CA) experiments were performed in 0.5 M H_2SO_4 and 1 M CH_3OH solution at 0.6 V vs. SCE for 7200 s to estimate the stability of the catalysts for methanol oxidation.

For methanol oxidation, 99.99 % CO was subsequently bubbled in the 0.5 M H_2SO_4 for 15 min when the potential was controlled to be 0 V vs. SCE. The excess CO in the electrolyte was purged out with N_2 for 15 min. The CO stripping was performed in the potential of the range -0.2 ~ 1.0 V vs. SCE at a scan rate of 20 mV s^{-1}. The electrochemical surface areas (ECSA) and the tolerance to CO poisoning were estimated by the CO stripping test.

The Electrochemical surface areas (ECSA) values were calculated from the equation:

ECSA=Q/Sl, where Q is the coulombic charge (in mC) obtained from the CO stripping curve. l is the loading of Pt on the surface of the electrode (in mg) and S is a proportionality constant of 420 $\mu C/cm^2$.

For the Tafel equation, η= a + blog (j), where η is the overpotential and j is the current density. The electrochemical impedance spectra (EIS) were recorded at the frequency range from 1000 kHz to 30 mHz with 12 points per decade. The amplitude of the sinusoidal potential signal was 5 mV.

2. Supporting Figures and Tables

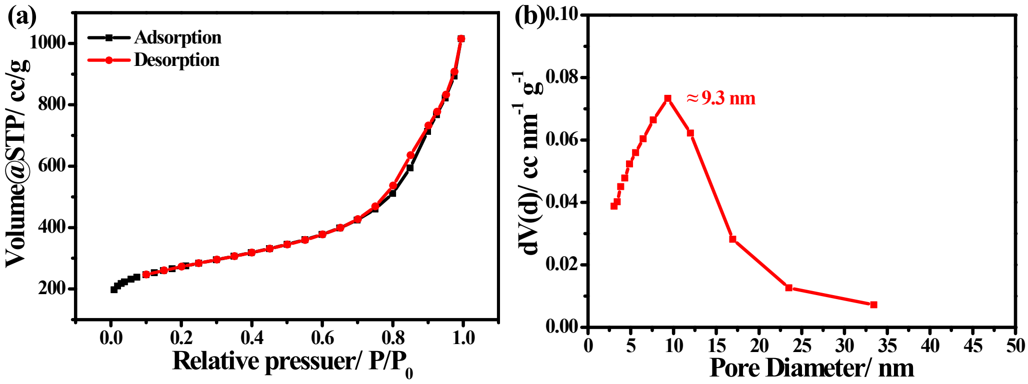

Figure S1. (a) BET nitrogen adsorption and desorption isotherms and (b) pore size distribution of the MHCS.

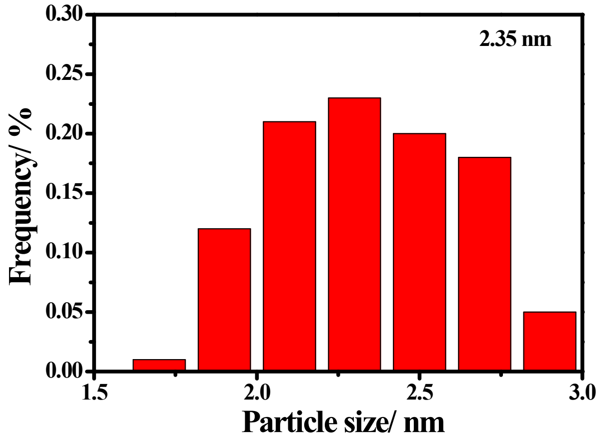

Figure S2. Particle size distribution histogram of PtRu in Pt/$MoSe_2$@MHCS catalyst.

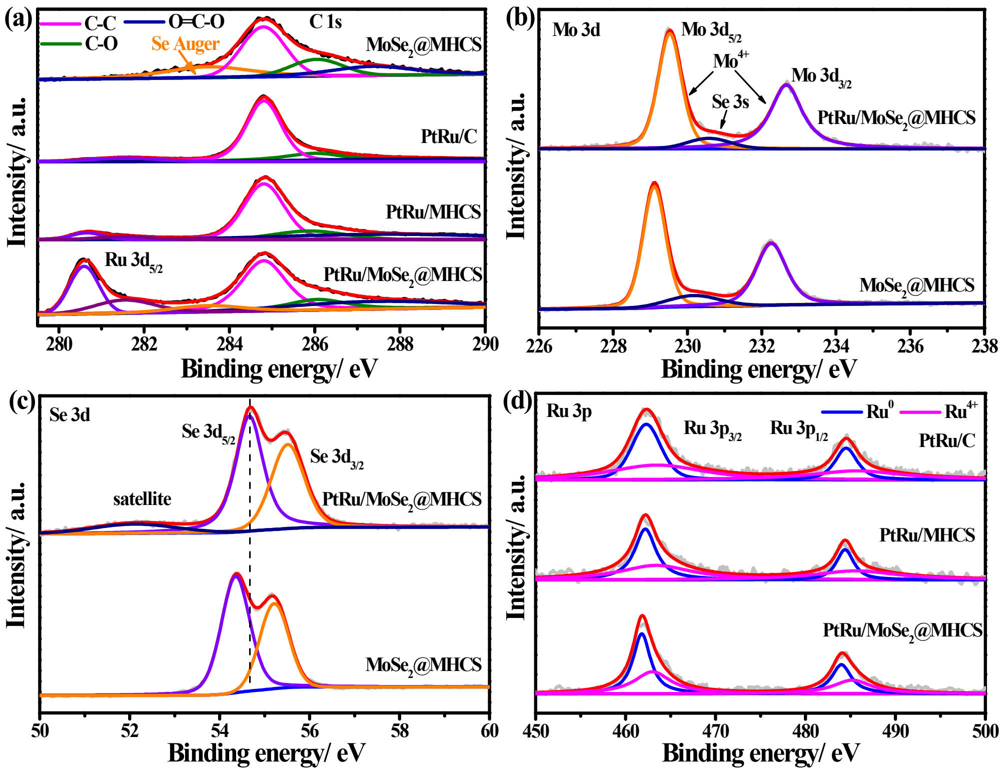

Figure S3. XPS spectra of (a) C 1s for $MoSe_2$@MHCS, PtRu/$MoSe_2$@MHCS, PtRu/MHCS and PtRu/C, (b) Mo 3d and (c) Se 3d for $MoSe_2$@MHCS and PtRu/$MoSe_2$@MHCS, (d) Ru 3p for PtRu/$MoSe_2$@MHCS, PtRu/MHCS and PtRu/C.

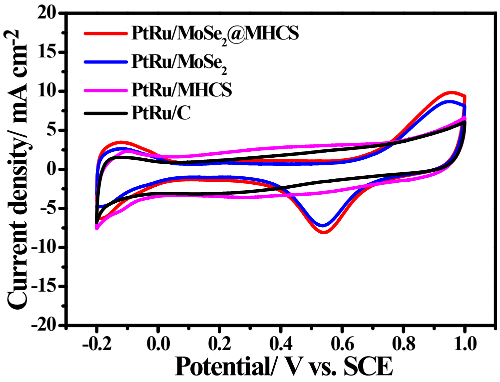

Figure S4. CV curves of the PtRu/$MoSe_2$@MHCS, PtRu/$MoSe_2$, PtRu/MHCS and PtRu/C catalysts in 0.5 M H_2SO_4 at 50 mV s^{-1}.

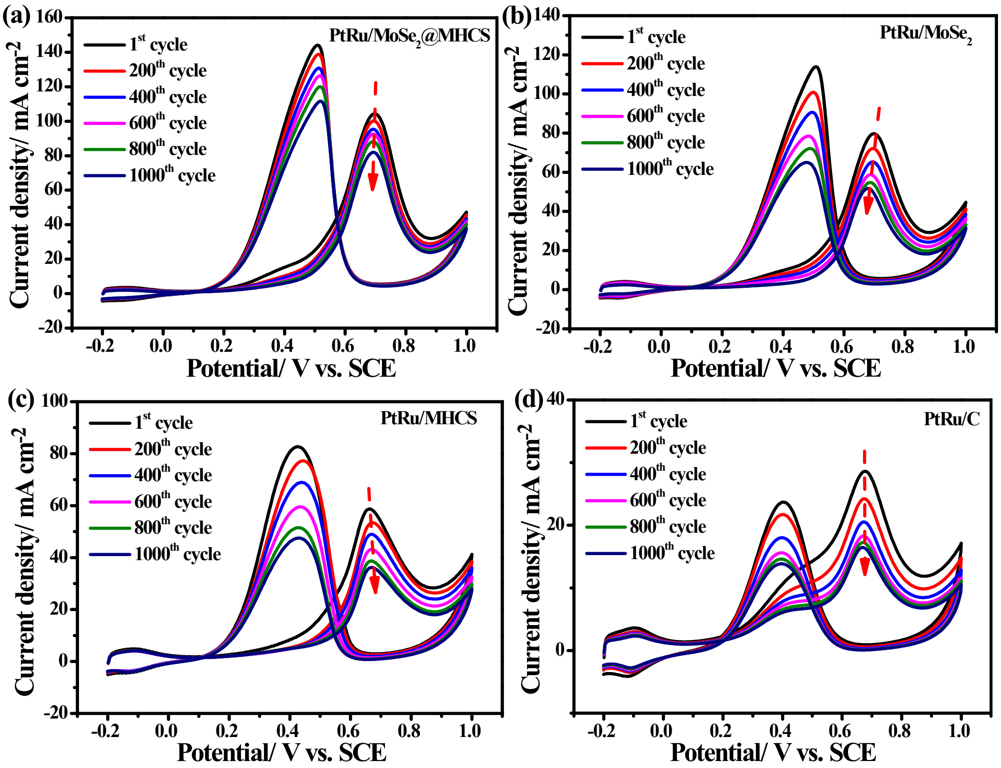

Figure S5. The accelerated durability tests for (a) PtRu/MoSe$_2$@MHCS, (b) PtRu/MoSe$_2$, (c) PtRu/MHCS and (d) PtRu/C catalysts at the 1st, 200th, 400th, 600th, 800th and 1000th cycle in 0.5 M H_2SO_4 + 1.0 M CH_3OH solution at 150 mV s^{-1}.

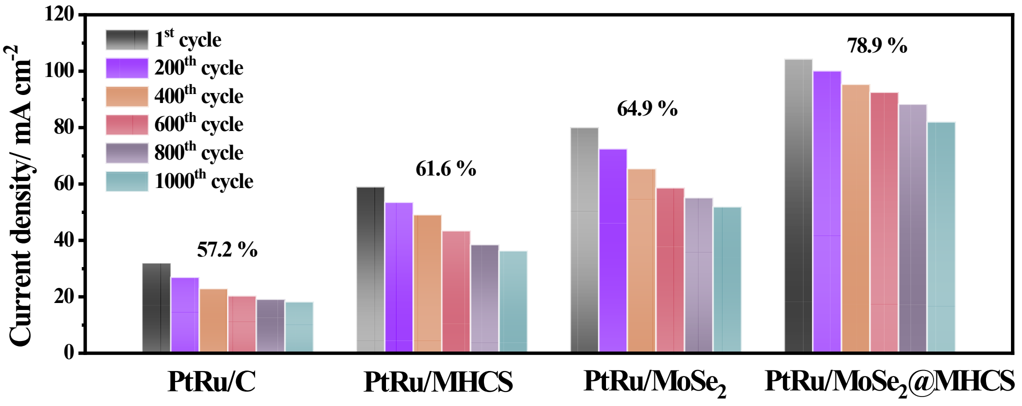

Figure S6. The graphical comparison of peak current density after different scan cycles of PtRu/MoSe$_2$@MHCS, PtRu/MoSe$_2$, PtRu/MHCS and PtRu/C catalysts.

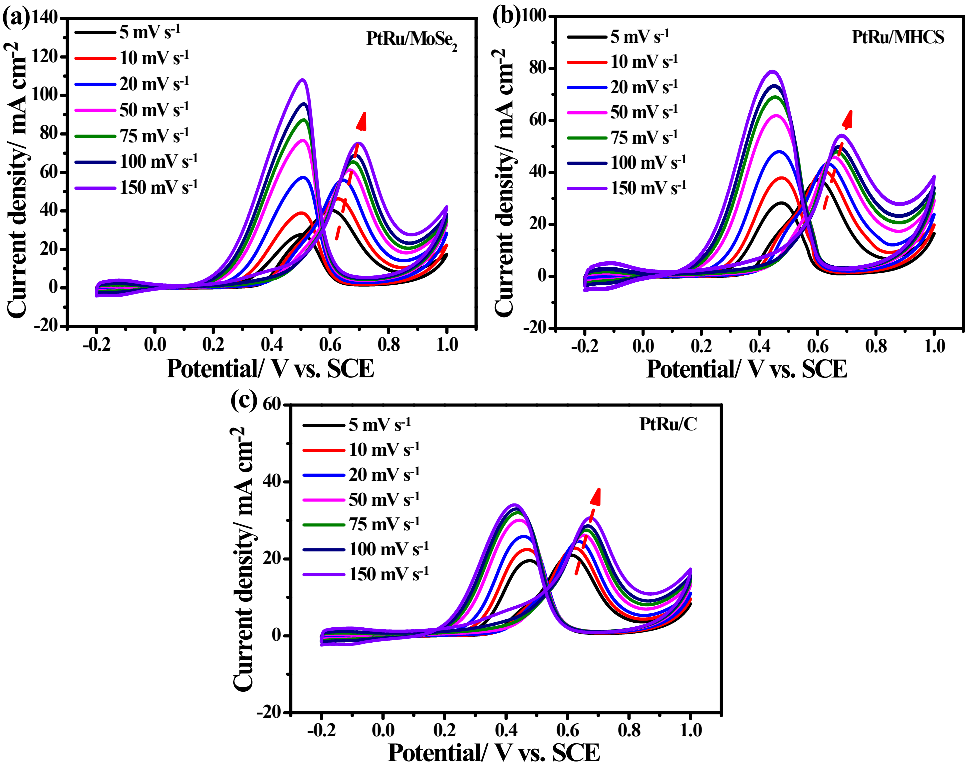

Figure S7. CV curves of the (a) PtRu/MoSe$_2$, (b) PtRu/MHCS and (c) PtRu/C catalysts in 0.5 M H_2SO_4 + 1 M CH_3OH at the scan rates of 5, 10, 20, 50, 75, 100 and 150 mV s^{-1}.

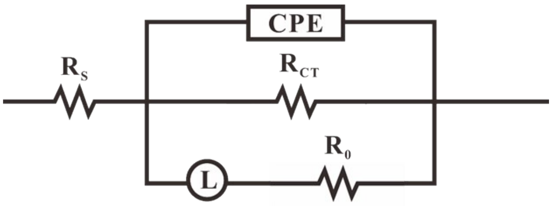

Figure S8. The equivalent circuit diagram used to fit the Nyquist plot.

Table S1. Binding energies of the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ components for the PtRu/$MoSe_2$@MHCS, PtRu/MHCS and PtRu/C catalysts.

Catalysts	**Pt $4f_{7/2}$**		**Pt $4f_{5/2}$**	
	Peak	**Binding energy/ eV**	**Peak**	**Binding energy/ eV**
PtRu/$MoSe_2$@MHCS	Pt^0	71.3	Pt^0	74.6
	Pt^{2+}	72.3	Pt^{2+}	75.6
PtRu/MHCS	Pt^0	71.6	Pt^0	74.9
	Pt^{2+}	72.6	Pt^{2+}	75.9
PtRu/C	Pt^0	71.7	Pt^0	75.0
	Pt^{2+}	72.6	Pt^{2+}	76.0

Table S2. Electrochemical surface area (ECSA) of different catalysts in 0.5 M H_2SO_4 estimated from CO stripping tests and the onset potential and CO oxidation peak potential for CO stripping.

Catalysts	**ECSA (m^2 g^{-1})**	**Onset potential (V vs. SCE)**	**Peak potential (V vs. SCE)**
PtRu/$MoSe_2$@MHCS	72.4	0.41	0.46
PtRu/$MoSe_2$	67.8	0.43	0.49
PtRu/MHCS	57.3	0.45	0.52
PtRu/C	56.6	0.47	0.54

Table S3. Mass activity and specific activity expressed as the positive peak current density of different catalysts in 0.5 M H_2SO_4 + 1 M CH_3OH solution.

Catalysts	**Mass activity/ mA mg_{Pt}^{-1}**	**Specific activity/ mA cm^{-2}**
PtRu/$MoSe_2$@MHCS	1157.8	1.6
PtRu/$MoSe_2$	814.2	1.2
PtRu/MHCS	573.1	1.0
PtRu/C	339.4	0.6

Table S4. Comparisons of activities of various electrocatalysts for methanol oxidation in acidic media. The scan rate was 50 mV s^{-1}.

Catalysts	**Mass activity/ mA mg_{Pt}^{-1}**	**Electrolyte**	**Reference**
PtRu/$MoSe_2$@MHCS	1157.8	0.5 M H_2SO_4 + 1 M CH_3OH	This work
PtRu/GA	219.78	0.5 M H_2SO_4 + 1 M CH_3OH	[1]
PtRu/C-JH-1000-50	705.9	0.1 M $HClO_4$ + 1 M CH_3OH	[2]
PtRu (2:1) MNs/C	111.77	0.5 M H_2SO_4 + 0.5 M CH_3OH	[3]
Pt_2Ru_1 NWs	1290	0.1 M $HClO_4$ + 1 M CH_3OH	[4]
$PtRu_{0.5}$@C/$NrGO_7$-$OCNTs_3$	1508	0.5 M H_2SO_4 + 0.5 M CH_3OH	[5]
Cu-$Pt_{5.2}Ru_1$	638.2	0.5 M H_2SO_4 + 1 M CH_3OH	[6]
PtRu/TiO_2/ONCNT-400	512	0.5 M H_2SO_4 + 0.75 M CH_3OH	[7]
NPTF-Pt_2Ru_1	1640	0.1 M $HClO_4$ + 1 M CH_3OH	[8]
U-PtRu/C	930	0.1 M $HClO_4$ + 1 M CH_3OH	[9]

Table S5. EIS fitting parameters from equivalent circuits for different catalysts in the 0.5 M H_2SO_4+1 M CH_3OH solution.

Catalysts	**R_s/ Ω**	**R_{ct}/ Ω**	**R_o/ Ω**	**CPE /S s^{-n}**	**L/ H**	**Chi squared**
PtRu/$MoSe_2$@MHCS	7.5	154.8	27.2	6.385E-004	3.200E+002	3.690E-003
PtRu/$MoSe_2$	7.8	389.7	35.4	3.569E-004	4.600E+002	2.540E-003
PtRu/MHCS	7.4	546.2	60.5	4.978E-004	1.320E+003	2.396E-003
PtRu/C	7.6	1400.5	245.7	5.866E-004	4.325E+003	6.231E-003

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