Supporting Information

Microwave quasi-solid state constructed low-content Pt on CeO₂ with strong electronic interaction for efficient electrocatalytic acidic overall water splitting

Jing Li^a, Qihao Wang^a, Ruotong Guo^a, Yingxia Zong^a, Jun Xing^a, Weiping Xiao^b, Guangrui Xu^c, Dehong Chen^{c, *}, Lei Wang^{a, *}, Zexing Wu^{a, *}

a) Key Laboratory of Eco-chemical Engineering, Ministry of Education, International Science and Technology Cooperation Base of Eco-chemical Engineering and Green Manufacturing, College of Chemistry and Molecular Engineering, Qingdao University of Science & Technology 53 Zhengzhou Road, 266042, Qingdao, P. R. China E-mail: splswzx@qust.edu.cn; inorchemwl@126.com

b) College of Science, Nanjing Forestry University, Nanjing, 210037, P. R. China.

c) College of Materials Science and Engineering, Qingdao University of Science & Technology

53 Zhengzhou Road, 266042, Qingdao, P. R. China. E-mail: dhchen@qust.edu.cn

1. Experimental Section

Chemicals and Materials

Cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O) was purchased from Aladdin. Potassium tetrachloroplatinate (II) (K₂PtCl₄ 98%) was obtained from Macklin. Ethylene glycol (C₂H₄(OH)₂) was purchased from Sinopharm. Potassium thiocyanate (KSCN) was purchased from Aladdin. Urea was purchased from Aladdin. Sulfuric acid (H₂SO₄98%) was purchased from Sinopharm. Commercial Pt/C catalyst (20 *wt*% Pt on carbon black) purchased from Alfa Aesar. Vulcan XC-72R carbon black was purchased from Cabot Corp. Commercial ruthenium (IV) oxide (RuO₂ 99.9%) catalyst was purchased from Sigma-Aldrich. Conductive carbon paper was purchased from TORAY (TGP-H-060). **Synthesis of CeO₂**

5.699 g Ce(NO₃)₃·6H₂O and 3.940 g urea were dissolved in 30 mL deionized water and stirred for 30 min. Subsequently, the solution was stirred at 140 °C in an oil bath for 240 min. The obtained products were washed with deionized water. The products were dried at 105 °C for 2 h. Finally, the powder, placed in a tube furnace, was heated to 500 °C for 180 min with a heating rate of 10 °C min⁻¹ in air atmosphere and then naturally cooled to room temperature. The yellow CeO₂ powder was obtained.

Synthesis of Pt/CeO₂-O_V

10 mg of K_2PtCl_4 and 100 mg CeO₂ were fully ground to obtain the yellow powder, which was put into the porcelain boat and added 30 µL ethylene glycol. Then, it is placed in the microwave for 60 s. The yellow powder changed into black. Then, 20 mL deionized water was added and evaporated at 80 °C with stirring to obtain black Pt/CeO_2-O_V .

2. Physical Characterization

Physical characterizations of the catalysts were performed by scanning electron microscopy (SEM) (Regulus 8100) and transmission electron microscopy (TEM) (JEM-F200). X-ray diffraction (XRD) (Japan Rigaku Ultima IV) and X-ray photoelectron spectroscopy (XPS) (America Thermo Scientific K-Alpha) were used to determine the crystal structure and chemical composition. Electron paramagnetic resonance (EPR) (BRUKE EMXPLUS) can be used to qualitatively and quantitatively

detect oxygen vacancies in catalysts. Raman spectroscopy (D-MAX 2500/PC) can analyze the structural information of the catalysts. Inductively coupled plasma optical emission spectrometer (ICP-OES) (Hitachi U4150) analyzes the amount of Ru in the catalyst.

3. Electrochemical Measurements

All electrochemical measurements were conducted using a typical three-electrode setup in 0.5 M H₂SO₄ with a reversible hydrogen electrode (RHE), glassy carbon electrode and carbon rod as the reference electrode, working electrode, and counter electrode, respectively, at room temperature. For ink preparation, 5 mg of catalyst and 1mg of carbon black were added to 1 mL Nafion solution and sonicated for 30 min. Then, the 10 µL prepared ink was decorated onto the glassy carbon electrode for testing. Linear sweep voltammetry (LSV) was collected with scanning rate of 5 mV s⁻¹ with 95% IR compensation. Electrochemical impedance spectroscopy (EIS) measurements were carried out in frequency ranges from 100 kHz to 0.01 Hz with an amplitude of 5 mV. Multi-step chronopotentiometry, multi-step chronoamperometry and chronoamperometry were performed to study the stability of the prepared catalysts. Overall water splitting tests are measured by two electrodes with carbon paper as a substrate to load the catalyst. The size of the carbon paper is 1×1 cm² with 2 mg of catalysts.

CV Measurements

Cyclic voltammetry was performed with different scan rates (20-120 mV s⁻¹) in the non-Faraday interval.

ECSA (electrochemically active surface area) measurements

$$ECSA = \frac{C_{dl} \times S}{C_s}$$

S is the area of the working electrode (0.19625 cm²). And C_s is the constant (0.5 M H₂SO₄) that converts the capacitance to ECSA with a value of 0.02 mF cm⁻².¹

Mass activity computation

Mass activity = Current (mA) / m (Pt)

Current is taken from linear sweep voltammetry curves at an overpotential of 100 mV, and $m_{(Pt)}$ is the mass of Pt on the working electrode.

Turnover frequency calculation (TOF)

Turnover frequency (TOF) is a familiar evaluation criterion of catalysts, which is identified as the number of reactants of the electrocatalytic active sites per area to convert to the expected product per time².

Total hydrogen turnovers

$$= (|j|\frac{mA}{cm^2})(\frac{\frac{1C}{s}}{1000 mA})(\frac{1 \text{ mol } e^-}{96485.3 C})(\frac{1 \text{ mol}}{2 \text{ mol } e^-})(\frac{6.022 \times 10^{23} \text{ molecules } H_2}{1 \text{ mol } H_2})$$
$$= 3.12 \times 10^{15} \frac{H_2/s}{cm^2} \text{per}\frac{mA}{cm^2}$$

Pt/CeO₂ - O_V (active sites) 10 mV

$$= \left(\frac{\left(\operatorname{catalyst loading per geometric area \times \left(\frac{g}{\operatorname{cm}^2}\right) \times Pt wt^{9/6}}{Pt \operatorname{M}_{W}\left(\frac{g}{\operatorname{mol}}\right)}\right) \left(\frac{6.022 \times 10^{23} Pt \text{ atomes}}{1 \operatorname{mol} Pt}\right)$$
$$= \left(\frac{0.255 \times \frac{10^{-3} g}{\operatorname{cm}^2} \times 3.85 \operatorname{wt^{9/6}}}{195.1}\right) \left(\frac{6.022 \times 10^{23} Pt \operatorname{atomes}}{1 \operatorname{mol} Pt}\right)$$
$$= 3.03 \times 10^{16} Pt \text{ sites per cm}^{2}$$

TOF =
$$\left(\frac{3.12 \times 10^{15}}{3.03 \times 10^{16}} \times |\mathbf{j}|\right) = 0.10 \times |-11.07| = 1.14 \text{ Pt sites per cm}^2$$

 $Pt/CeO_2 - O_V$ (active sites) 30 mV

TOF =
$$\left(\frac{3.12 \times 10^{15}}{3.03 \times 10^{16}} \times |\mathbf{j}|\right) = 0.10 \times |-56.25| = 5.63 \text{ Pt sites per cm}^2$$

Pt/CeO₂ - O_V (active sites) 50 mV

TOF =
$$\left(\frac{3.12 \times 10^{15}}{3.03 \times 10^{16}} \times |j|\right) = 0.10 \times |-106.80| = 10.68 \text{ Pt sites per cm}^2$$

Pt/C (active sites)10 mV

$$= (|j|\frac{mA}{cm^{2}})(\frac{\frac{11}{1000}}{1000}mA})(\frac{1}{96485.3} \frac{mol}{2} c)(\frac{1}{2} \frac{mol}{mol} e^{-})(\frac{6.022 \times 10^{23} \text{ molecules H}_{2}}{1 \text{ mol H}_{2}})$$

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

$$= \left(\frac{\text{catalyst loading per geometric area } \times \left(\frac{g}{cm^{2}}\right) \times \text{Pt wt}^{6}}{1 \text{ mol Pt}}\right) \left(\frac{6.022 \times 10^{23} \text{Pt atomes}}{1 \text{ mol Pt}}\right)$$

$$= \left(\frac{0.255 \times \frac{10^{-3}g}{cm^{2}} \times 20 \text{ wt}^{6}}{195.1}\right) \left(\frac{6.022 \times 10^{23} \text{Pt atomes}}{1 \text{ mol Pt}}\right)$$

$$= 1.57 \times 10^{17} \text{ Pt sites per cm}^{2}$$

TOF =
$$\left(\frac{3.12 \times 10^{15}}{1.57 \times 10^{17}} \times |\mathbf{j}|\right) = 0.020 \times |-20.06| = 0.40 \text{ Pt sites per cm}^2$$

Pt/C (active sites) 30 mV

TOF =
$$\left(\frac{3.12 \times 10^{15}}{1.57 \times 10^{17}} \times |j|\right) = 0.020 \times |-143.13| = 2.86 \text{ Pt sites per cm}^2$$

Pt/C (active sites) 50 mV

$$\text{TOF} = \left(\frac{3.12 \times 10^{15}}{1.57 \times 10^{17}} \times |\mathbf{j}|\right) = 0.020 \times |-233.22| = 4.66 \text{ Pt sites per cm}^2$$

 Pt/CeO_2 - O_V (active sites) 10 mV = 1.14 Pt sites per cm²

 $Pt/CeO_2 - O_V$ (active sites) 30 mV = 5.63 Pt sites per cm²

 $Pt/CeO_2 - O_V$ (active sites) 50 mV = 10.68 Pt sites per cm²

Pt/C (active sites) 10 mV= 0.40 Pt sites per cm²

Pt/C (active sites) 30 mV = 2.86 Pt sites per cm²

Pt/C (active sites) 50 mV = 4.66 Pt sites per cm²

0.5 M H₂SO₄: When the overpotential is 10 mV, 30 mV and 50 mV, the current density of $^{Pt/CeO_2 - O_V}$ are 11.07 mA cm⁻², 56.25 mA cm⁻² and 106.80 mA cm⁻², TOF=1.14 H₂ s⁻¹, 5.63 H₂ s⁻¹ and 10.68 H₂ s⁻¹. Similarly, the current density of $^{Pt/C}$ at 10 mV, 30 mV

and 50 mV are 20.06 mA cm⁻², 143.13 mA cm⁻² and 233.22 mA cm⁻² and TOF = 0.40 H₂ s⁻¹, 2.86 H₂ s⁻¹ and 4.66 H₂ s⁻¹.



Figure S1. The cyclic voltammetry (CV) plots with different scan rates of (a) CeO₂ and (b) Pt/CeO₂-O_v in 0.5 M H₂SO₄.



Figure S2. LSV curves before and after poisoning tests with 5 mM KSCN in 0.5 M H_2SO_4 .



Figure S3. CV curves of (a) Pt/CeO_2-O_v , (b) CeO_2 and (c) Pt/C at the potential 0.05 to 1.20 V under Ar.



Figure S4. Dry cell simulation derived overall water splitting in $0.5 \text{ M H}_2\text{SO}_4$.



Figure S5. Wind energy derived overall water splitting in 0.5 M H_2SO_4 .



Figure S6. Solar energy derived overall water splitting in $0.5 \text{ M H}_2\text{SO}_4$.

catalysts	wt %
CeO ₂	43.86 %
Pt/CeO ₂ -O _v	48.44 %

Table S1. The variation of oxygen vacancies is illustrated through XPS spectra of O 1s

Catalysts	Overpotential (mV)@ 10 mA cm ⁻²	Tafel slope (mV dec ⁻¹)	References
Pt/CeO ₂ -O _v	10	25.6	This work
PtCo@PtSn	21	19	3
Pt ₂ Ir/G	29	26	4
Pt/CP	30	68	5
Pt NC	38	31	6
Pt _{NPs} @MXene/PPy	40	44	7
Pt/RuO _x -PA	41	31	8
Pt/CNT	44	27	9
Pt/GNPs	54	37	10
Pt_1/Fe_2O_3	60	40	11
Pt VN	82	59	12

Table S2. Comparison of the hydrogen evolution reaction (HER) activity of the Pt/CeO_2-O_v with other previously reported electrocatalysts in 0.5 M H₂SO₄.

Catalysts	Cell voltage (V)@ 10 mA cm ⁻²	References
RuO ₂ Pt/CeO ₂ -O _V	1.57	This work
Ir-doped WO ₃ Ir-doped WO ₃	1.56	13
RhCu NTs/CP RhCu NTs/CP	1.64	14
NC-CNT/CoP NC-CNT/CoP	1.66	15
Mo-Co ₉ S ₈ @C Mo-Co ₉ S ₈ @C	1.68	16
Pt/C Ir/C	1.69	17
Co-MoS ₂ Co-MoS ₂	1.90	18

Table S3. Comparison of the overall water splitting activity of the $RuO_2 ||Pt/CeO_2-O_V$ with other previously reported electrocatalysts in 0.5 M H₂SO₄.

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