Supporting Information

for

Ultrafast Carbothermal Shocking Fabrication of Cation Vacancies-Rich Mo Doped Ru Nanoparticles on Carbon Nanotubes for High-Performance Water/Seawater Electrolysis

Jianpeng Sun¹, Zhan Zhao¹, Zizhen Li¹, Zisheng Zhang³, Rufan Zhang^{2*} and Xiangchao Meng^{1*}

¹Key Laboratory of Marine Chemistry Theory and Technology (Ministry of Education), College of Chemistry & Chemical Engineering, Ocean University of China, Qingdao, 266100, China

²Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

³Department of Chemical and Biological Engineering, Faculty of Engineering, University of Ottawa, Ottawa, Ontario, K1N6N5, Canada.

*Corresponding authors.

Email address: <u>zhangrufan@tsinghua.edu.cn</u> (R. Z.) <u>mengxiangchao@ouc.edu.cn</u> (X.M.)

S1 Experimental section

S1.1 Preparation of Mo-RuO₂/CNTs

In a typical synthesis method, sodium molybdate (VI) dihydrate (420 mg) and carbon nanotubes (20 mg) were separately dispersed in deionized (DI) water (7.5 mL) and ethanol (7.5 mL) under sonication. Among them, the CNTs were immersed in 0.5 M H_2SO_4 at 100 ° reflux for 5 h. And then, RuO₂ (5 mg/mL, 0.9 mL) was dissolved in the above solution. Afterwards, the autoclave was kept at 150°C for 6 h. Finally, Mo-RuO₂/CNTs was collected after washing. As-synthesized product was dried at 70°C under vacuum for 12 h. Moreover, the amount of RuO₂ was also changed to 0.6 mL and 1.2 mL to synthesize Mo-RuO₂/CNTs-1 and Mo-RuO₂/CNTs-2.

S1.2 Preparation of Mo-Ru/CNTs

Carbothermal shocking process were used to synthesize Mo-Ru/CNT. Mo-RuO₂/CNT (10 mg) was placed on a graphite heating plate and was heated at 800°C for 40 seconds under Ar-H₂ flow (Joule-heat equipment: Hefei in situ technology Co., Ltd. China). And then, Mo-Ru/CNT were collected. Meanwhile, MoO₂/CNT were also prepared via carbothermal shocking process. For comparison, Mo-Ru/RuO₂/CNTs (10 mg) was placed on tube furnace and heated for 2h at 800°C under Ar-H₂ flow. And then, Mo-Ru/RuO₂/CNTs were collected.

Other samples with different reaction ratios and reaction times were also synthesizned in a simlar method. Mo-Ru/CNTs-1 and Mo-Ru/CNTs-2 were prepared using Mo-RuO₂/CNTs-1 and Mo-RuO₂/CNTs-2 as a precursor. And Mo-Ru/CNTs-J1 and Mo-Ru/CNTs-J2 were prepared via adjusting its rapid heating time to 30 s and 60 s.

S1.3 Characterization

Scanning electron microscope (SEM) and high-resolution transmission electron microscopy (HRTEM) was characterized by Zeiss Gemini 300 and JEOL JEM 2100,

respectively. X-ray diffraction (XRD) were collected on the Rigaku Miniflex 600. The energy dispersive X-ray (EDX) element mapping images were tested on the SEM. The X-ray photoelectron spectroscopy (XPS) spectra were collected on Thermo Scientific K-Alpha. The Brunauer-Emmett-Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) model were collected on the Micromeritics ASAP 2460. ICP-OES were collected on Aglient 7850.

S1.4 Electrochemical measurements

Electrocatalytic performance was tested on the CHI660E electrochemical workstation with a typical three-electrode system. Graphite rod and a Hg/HgO electrode (SCE) were applied as the counter electrode and the reference electrode, respectively. The applied potentials were converted by the equation ($E_{RHE} = E_{SCE} + 0.0592pH + 0.098$ V) and the polarization curves were recorded with *iR*-compensation. Natural seawater was used from Yellow Sea (35°56'N, 120°56'E). Linear sweep voltammetry (LSV) were tested at a scan rate of 5 mV s⁻¹. The double layer capacitance (C_{dl}) values were studied from the CV curves to study the electrochemically active surface areas (ECSA). The electrochemical impedance spectroscopy (EIS) measurements were used with frequencies ranging from 10⁻⁵ Hz to 10⁻² Hz. The stability tests were tested under a current density of 10/20/100 mA·cm⁻². The cell voltage of alkaline exchange membrane (AEM) electrolyzers without *iR* compensation were performed on a CHI660E electrochemical workstation at a scan rate of 100 mV s⁻¹.

The solar-driven electrolysis system was tested out by the CHI660 and KEITHLET 2400, solar simulator was used via a 300-W xenon lamp (Microsolar300, Beijing Perfectlight) with AM 1.5G optical filter (100 mW cm⁻²). The solar to hydrogen efficiency of solar-driven electrolysis system was converted by the equation (

S3

 $STH(\%) = I(mA cm^{-2}) \times 1.23(V) \times 100/P_{sun}$, where I was the current density of the solardriven electrolysis system and P_{sun} was incident simulated solar energy.

S1.5 DFT computations

The Vienna ab initio software package (VASP) were applied in. The gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) parameterization was used to express the exchange correlation energy. The cutoff energy of employed planewave basis set was 300 eV and the energy convergence criterion of 10^{-5} eV was studied for structure relaxation. A 15 Å vacuum layer along c-axis direction was designed to know the interactions between adjacent layers. Mo-Ru/CNT was studied via a 3 × 3 × 1 k-point mesh in the Brillouin zone.

S2 Figures



Figure S1. Real time reaction temperature of (b) Carbothermal shocking process and

(c) CVD process.



Figure S2. The corresponding lattice fringe distance images of Ru-Mo/CNTs.



Figure S3. The corresponding lattice fringe distance images of Mo-Ru/RuO₂/CNTs.



Figure S4. The EDS mapping image of Ru-Mo/CNTs.



Figure S5. The XRD patterns of CNTs and Mo/CNTs and $MoO_2/CNTs$.



Figure S6. The SEM images of Mo/CNTs.



Figure S7. The SEM images of MoO₂/CNTs.



Figure S8. XPS survey spectrum.



Figure S9. Phase models of (a) Ru, (b) Ru with vacancies, (c) Ru with Mo doping.



Figure S10. EIS of Mo-Ru/CNTs and Mo-Ru/RuO₂/CNTs.



Figure S11. Alkaline solution: (a) HER polarization curves. (b) Tafel plots and (c) EIS of Mo-Ru/CNTs-1, Mo-Ru/CNTs and Mo-Ru/CNTs-2.



Figure S12. Alkaline solution: CV curves of (a) Mo-Ru/CNT-1, (b) Mo-Ru/CNT-2 and (c) Mo-Ru/CNT-3 with different Ru and Mo content. (d) Electrochemical double layer capacitance (C_{dl}).



Figure S13. Alkaline solution: HER polarization curves with different heating

temperature.



Figure S14. Alkaline solution: CV curves of (a) CNTs, (b) Mo/CNTs and (c) MoO₂/CNTs, (d) Mo-RuO₂/CNTs and (e) Mo-Ru/CNTs.



Figure S15. Alkaline seawater solution: CV curves of (a) CNTs, (b) Mo/CNTs and (c) MoO₂/CNTs, (d) Mo-RuO₂/CNTs and (e) Mo-Ru/CNTs.



Figure S16. Alkaline seawater solution: (a) HER polarization curves. (b) Tafel plots and (c) EIS of Mo-Ru/CNTs-1, Mo-Ru/CNTs and Mo-Ru/CNTs-2.



Figure S17. Alkaline seawater solution: CV curves of (a) Mo-Ru/CNTs-1, (b) Mo-

Ru/CNTs and (c) Mo-Ru/CNTs-2. (d) Electrochemical double layer capacitance (C_{dl}).



Figure S18. Long-term stability measurements of 20% Pt/C//RuO₂.