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Pt-like electrocatalytic behavior of Ru-MoO_2 nanocomposites for hydrogen evolution reaction

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Calculation details:

Computations of free-energy for the hydrogen evolution reaction (HER) were carried out using density-functional theory as implemented in VASP 5.2. The PW91 GGA functional and the projector augmented wave (PAW) technique were used to treat the exchange-correlation energy and the ion-electron interaction. For geometric optimization, both lattice constants and atomic positions were relaxed until the forces on atoms were less than 0.02 eV $Å^{-1}$ and the total energy change was less than 1.0×10^{-5} eV. The Brillouin zone was sampled using k-points with 5*5*1 grid in the Monkhorst-Pack scheme for geometry optimization.

During the optimization, the bottom layer of model was fixed and the cut-off energy for plane waves is 400 eV. The hydrogen binding energy ΔE_H was calculated by $\Delta E_H = E_{H\text{-}slab} - E_{slab} - 1/2$

E_{H2}. The free energies at 298.15 K were obtained using $\Delta G=\Delta E_H+\Delta ZPE-T\Delta S$ according to previous work where $\Delta ZPE-T\Delta S= 0.24eV$ for model of metal and metal oxide surface. ΔE_H is the hydrogen binding energy, ΔZPE, ΔS and U are the zero point energy changes, entropy changes, respectively.

Results and Discussion

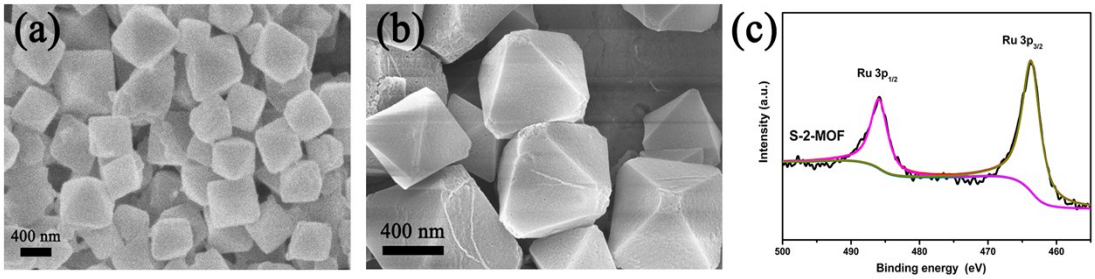

Figure S1 (a) SEM image of $Mo_3(btc)_2$, (b) SEM image of S-2-MOF, (c) Ru 3p XPS spectra of S-2-MOF.

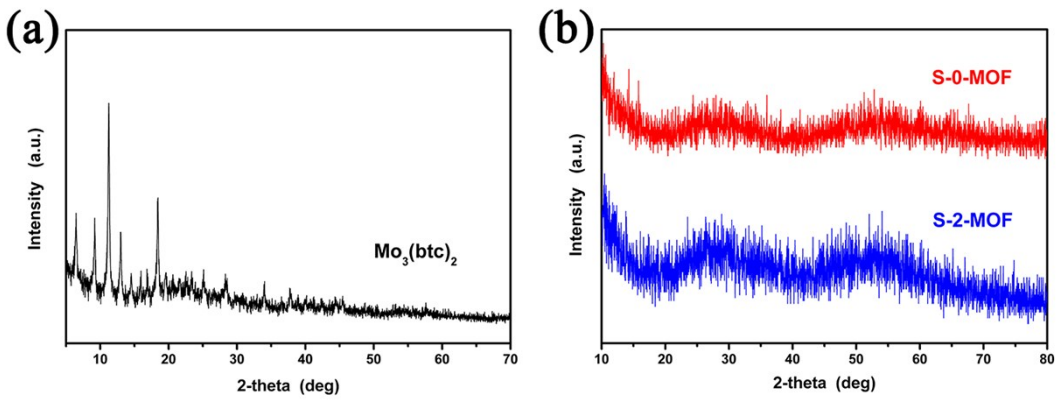

Figure S2 XRD patterns of Mo-btc (a), S-0-MOF (b, red line) and S-2-MOF (b, blue line).

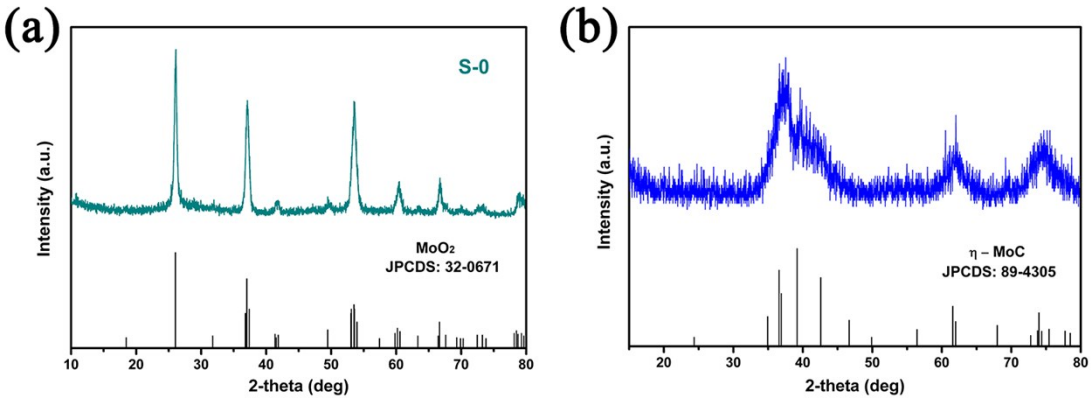

Figure S3 XRD diffraction patterns of S-0 (a) and MoC@GS (b).

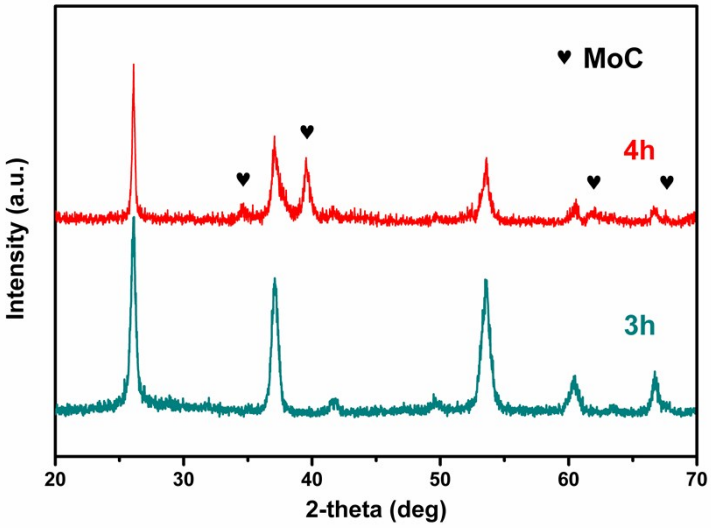

Figure S4 XRD patterns of the S-0-MOF after annealing at 700°C for 3h and 4h in nitrogen atmosphere.

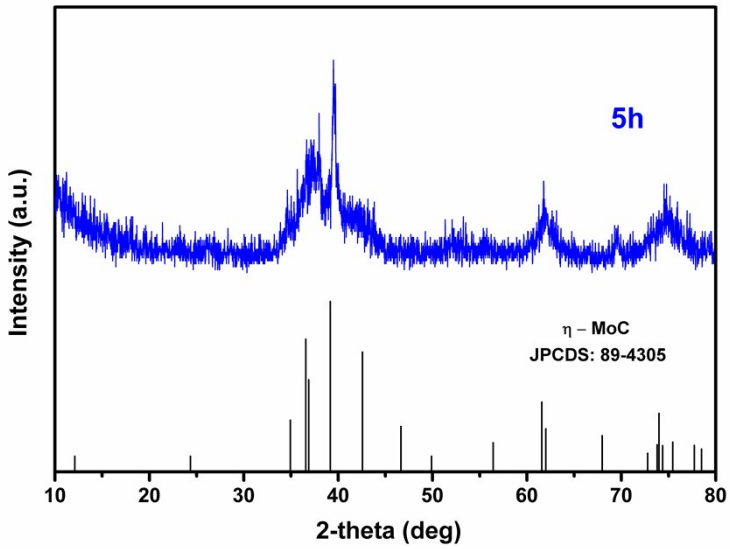

Figure S5 XRD pattern of the S-0-MOF after annealing at 700°C for 5h in nitrogen atmosphere.

The formation mechanism of MoO_x/MoC_x by carburization of polyoxometalate-based metal-organic frameworks (POMOFs, NENU-5) has been explained by previous studies.[1-3] Actually, the decomposition of phosphomolybdic acid (PMo_{12}) occurs at the temperature below 500°C, meanwhile, MoO_3 is formed. As the temperature increase, oxygen molecules were removed by combining with the pyrolysis carbon to form carbon dioxide (CO_2). At the same time, Mo (Ⅵ) turns into Mo (Ⅳ) and MoO_3 is reduced to MoO_2 which is relatively stable at the high temperature. However, with the carbonizing temperature as well as time increased, Mo_2C could be formed. Similarly, in this work, during the carburization process, the organic ligands (btc^{3-}) of precursor played two important roles: a) combining with the oxygen in the mixtures to form CO_2 gas and b) acting as carbon source to form MoO_x and MoC_x.[4] As illustrated in Figure S4, MoO_2 could be obtained at 700 °C for 3 h. While increasing the carbonizing time to 4h, the main diffrraction peaks can be indexed to MoO_2 and MoC (JCPDS no. 89-4305). Besides, we can only get MoC if the carbonizing time increased to 5h (Figure S5). Therefore, the carburizing time is an important factor

that would affect the formation of final product.

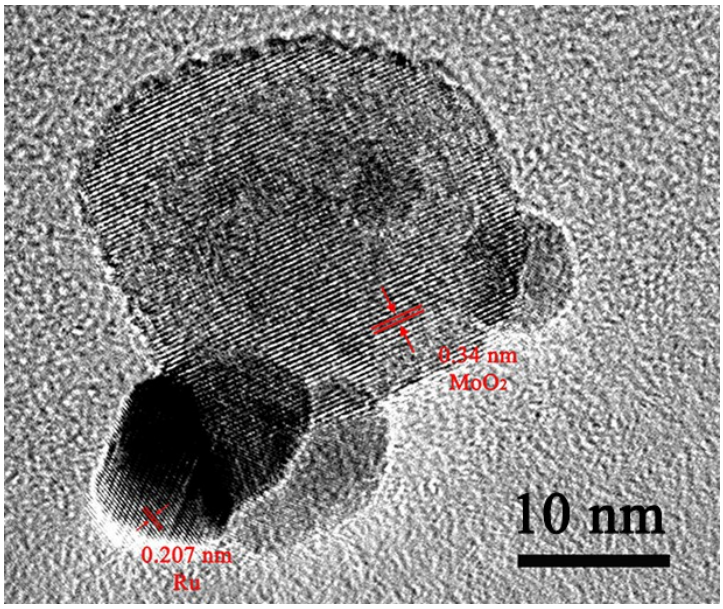

Figure S6 HRTEM image of S-1.

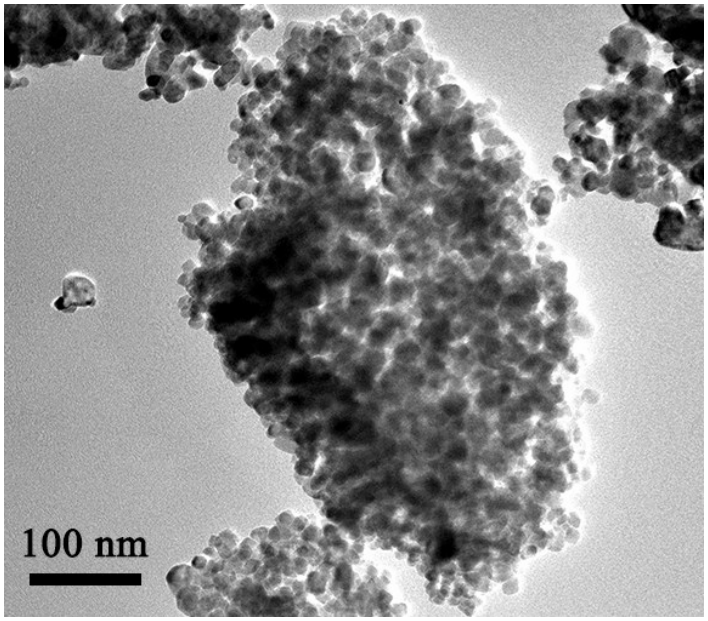

Figure S7 TEM image of S-1.

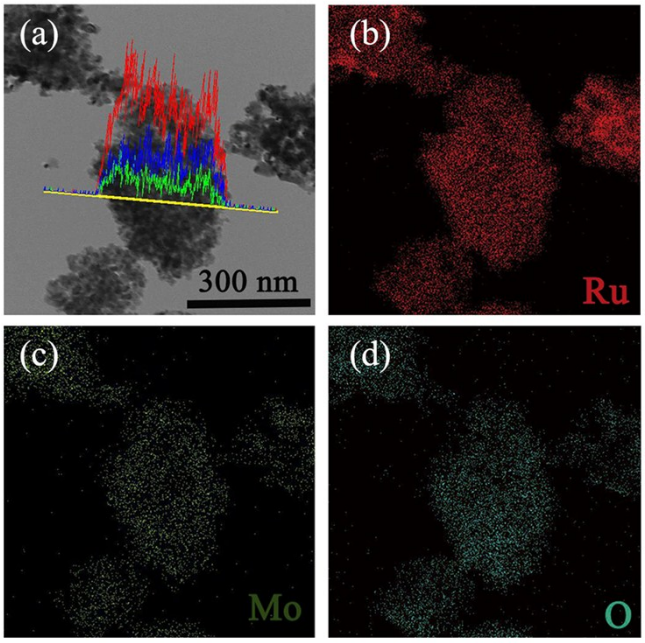

Figure S8 (a) TEM image and EDX line-scanning analysis of S-1, (b-d) Elemental mapping of Mo, Ru and O.

Table S1 Comparision of Ru concentration from ICP-OES results for S-1, S-2 and S-4.

Samples	S-1	S-2	S-4
Ru:Mo (molar ratio)	0.105	0.244	0.682

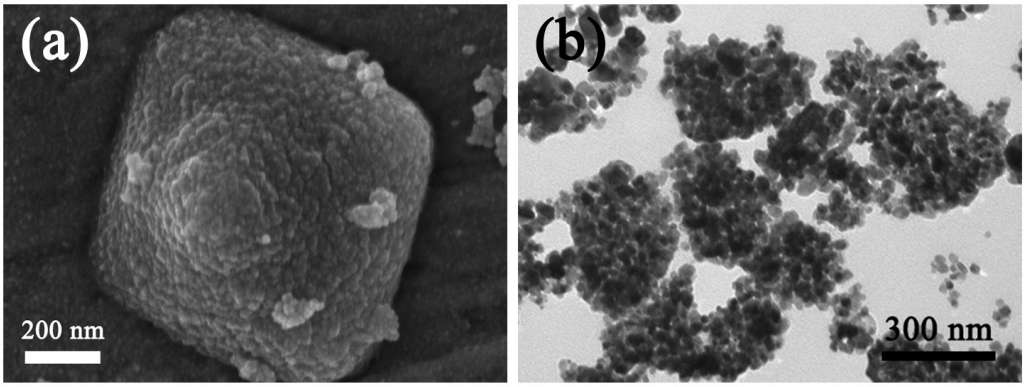

Figure S9 SEM (a) and TEM (b) images of S-2 electrocatalyst after 1000 cycles in acid solution.

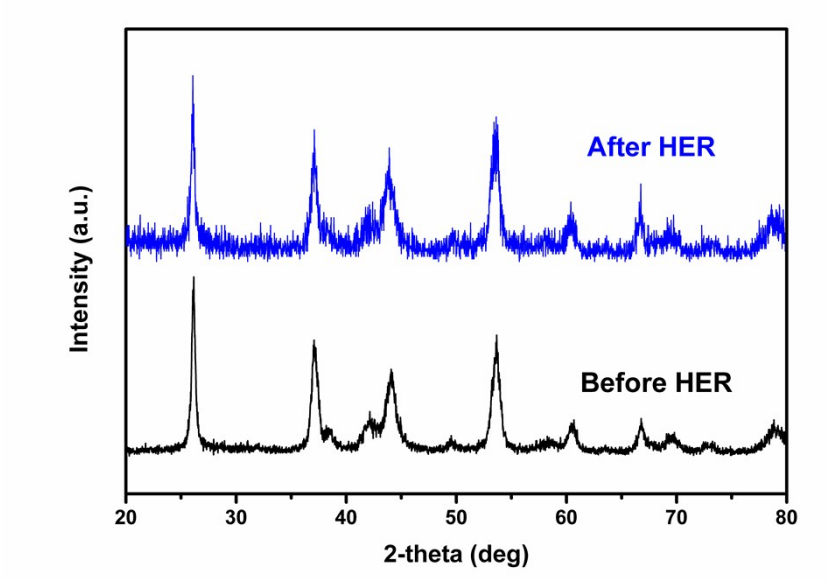

Figure S10 XRD patterns of S-2 catalyst before and after 1000 cycles in N_2-saturated 0.5 M H_2SO_4.

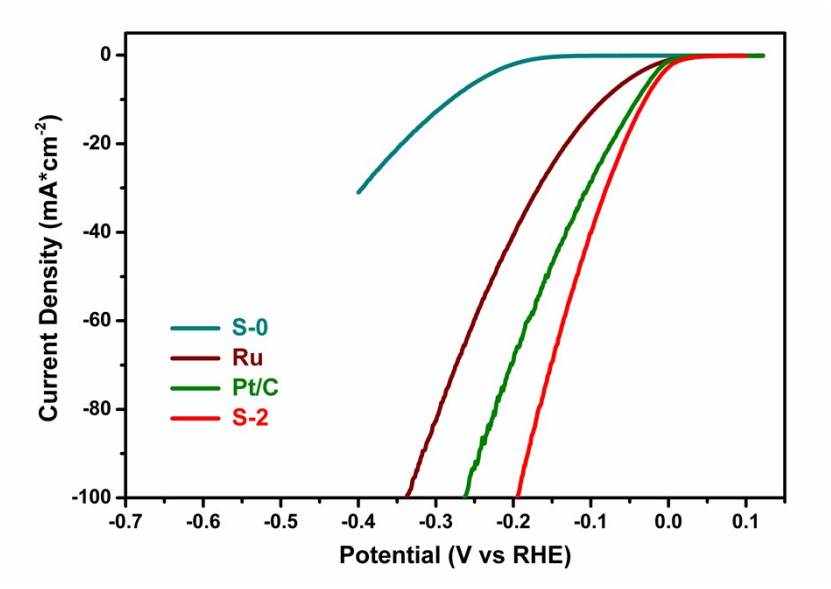

Figure S11 HER polarization curves of catalysts in 1 M KOH solution.

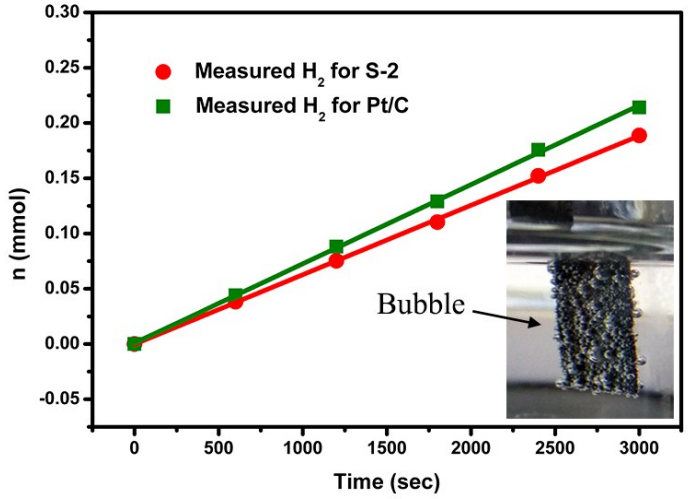

Figure S12 Hydrogen production efficiency of Pt/C and S-2 in 1M KOH under the same conditions.

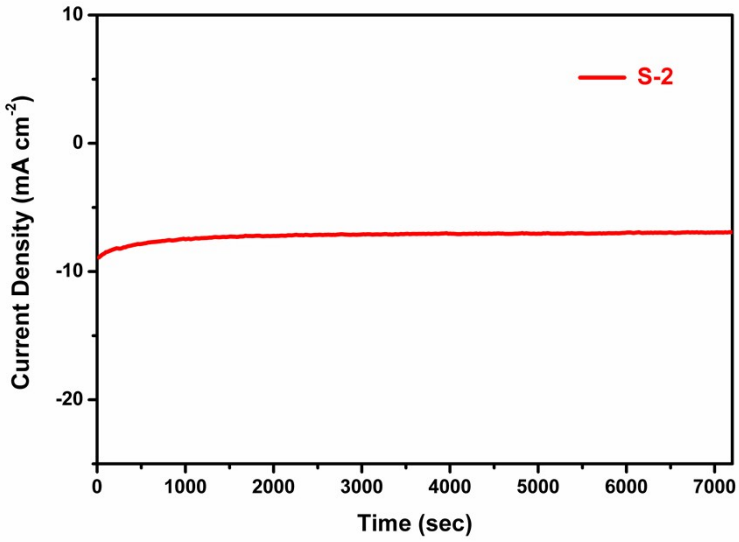

Figure S13 Current–time plots of S-2 electrode.

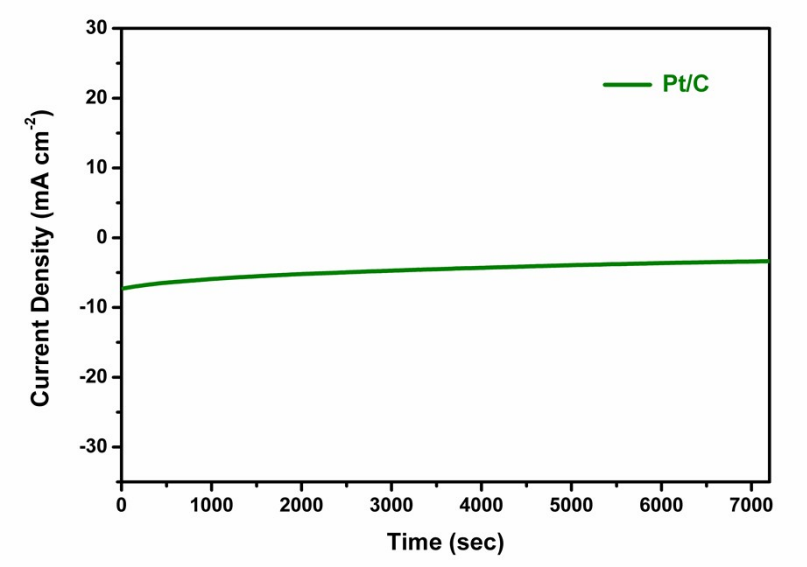

Figure S14 Current–time plots of the commercial 20 wt. % Pt/C electrode.

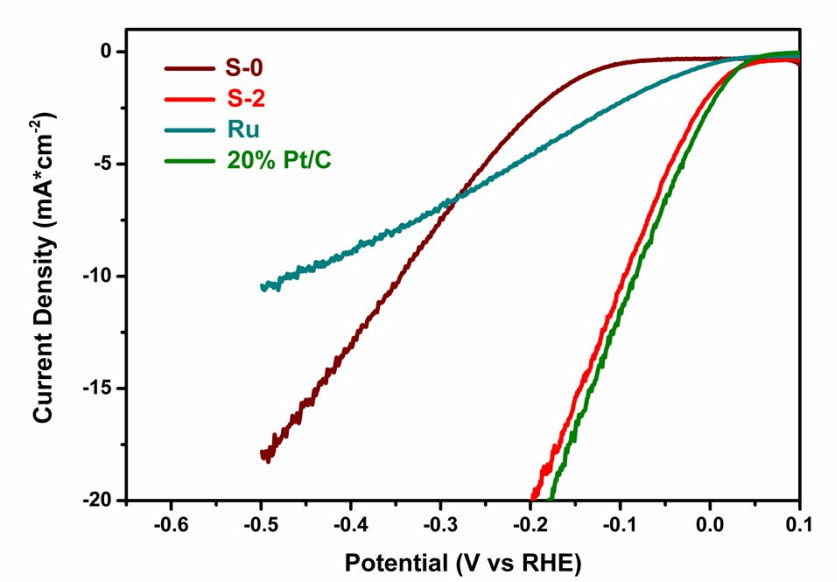

Figure S15 HER polarization curves of catalysts in 0.5 M phosphate buffer (pH=7).

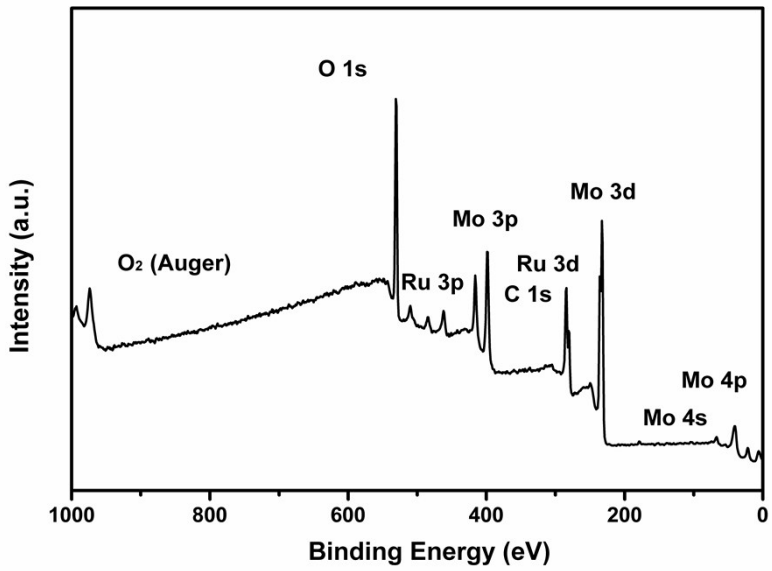

Figure S16 XPS survey scan of obtained S-2 sample.

Table S2 Atomic ratios of different elements in obtained S-2 sample estimated from XPS analysis.

Element	Mo 3d	Ru 3d	O 1s	C 1s
Ratio (%)	15.74	8.09	49.06	27.11

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