

Supplementary Material

Can Re cluster complexes be an efficient catalyst for hydrogen evolution reaction? Insights from experiment and computations

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Experimental Section

Reagents.

Solvents (dimethylformamide (DMF) and acetonitrile (CH₃CN)), ionic liquid Bu₄NBF₄, HCl and H₂SO₄ were purchased from Sigma Aldrich and used without further purification.

Methods

Size distribution in solution and ζ-potential were performed by Malvern Mastersize 2000 particle analyzer. The average error did not exceed 4%. All measurements were carried out in at least six repetitions at 298K.

UV-VIS spectra were recorded by spectrophotometer Specord 50 Plus (Analytik Jena AG)

Microscopy studies were carried out on an auto-emission scanning electron microscope Merlin (Carl Zeiss) equipped with an AZtec X-Max energy dispersion spectrometer (Oxford Instruments). The resolution of the spectrometer is 127 eV.

The surface morphology was photographed at an accelerating voltage of 5 keV to improve the depth of field of the image.

The elemental analysis was carried out at an accelerating voltage of 20 keV

X-ray photoelectron spectra (XPS) were recorded in an ultra-high vacuum (UHV) chamber (base pressure 5×10^{-10} mbar) equipped with an Mg K α X-ray source operated at 12.5 kV and 250 W using Phoibos 150 hemispherical energy analyzer (SPECS GmbH, Berlin, Germany). Raw experimental spectra were processed using CasaXPS software [49].

The phase composition was investigated using the X-ray diffraction (XRD) method using MD-10 desktop diffractometer, equipped with the Fe-K α X-ray tube.

DFT calculations

The DFT calculations were performed using the b3lyp hybrid functional (implemented into the Gaussian 16 program suit [50]). The double-split basis set (DZ) was employed to describe the valence orbitals of the Re atom, and the effect of internal electrons was addressed by the Hay-Wadt relativistic core potential (LanL2) [51]. The electrons of the Se, O and H atoms were treated using the standard 6-311++g (d, p) basis. Open-shell systems were addressed in terms of the non-restricted Kohn-Sham scheme. True total energy minima were identified by the absence of negative frequency values in the vibrational spectrum. The environment was treated as a pure DMFA for simplicity. Solvent effects were taken into account implicitly in the framework of Polarizable Continuum Model (PCM) [52] using values 2.046 and 37.22 for static and optical dielectric environment constants of DMFA, respectively. The effect of electrode surface on the geometry and electronic structure of reactants was neglected. The geometry, molecular orbitals and vibrations were visualized by the Chemcraft program package [51].

Synthesis of $K_4Re_6Se_8(OH)_6$

$K_4\{Re_6Se_8\}(OH)_6$ was synthesized and characterized according to a previously published work [44].

Synthesis of $\{Re_6Se_8\}$

The solution of $K_4[Re_6Se_8(OH)_6]$ (0.18 mM) was adjusted by syringe pump (100 mL/sec) with HCl to pH=4.1. Obtained acidified colloidal solution of $\{[Re_6Se_8(OH)_2(H_2O)_4]^0 + [Re_6Se_8(OH)_4(H_2O)_2]^{2-}\}$, which here and then was named as $\{Re_6Se_8\}$, was centrifugated at 13000 rpm, 25 °C and 20 minutes and dried up at 60°C. Water solution was added to the dry residue and redispersed in an ultrasonic bath at 30 °C within 10 minutes.

Paste electrodes

Paste electrode was prepared in accordance with previous published work [54]

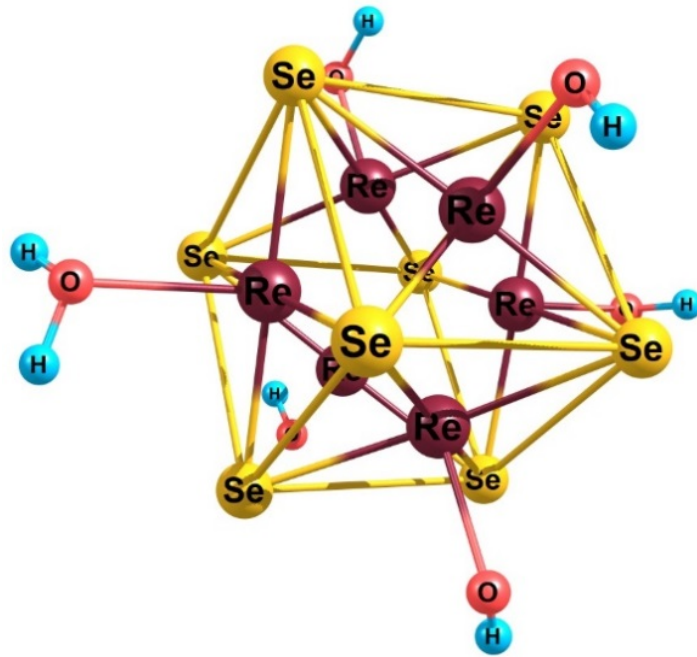


Figure S1. Structure of $K_4[Re_6Se_8(OH)_6]$ cluster.

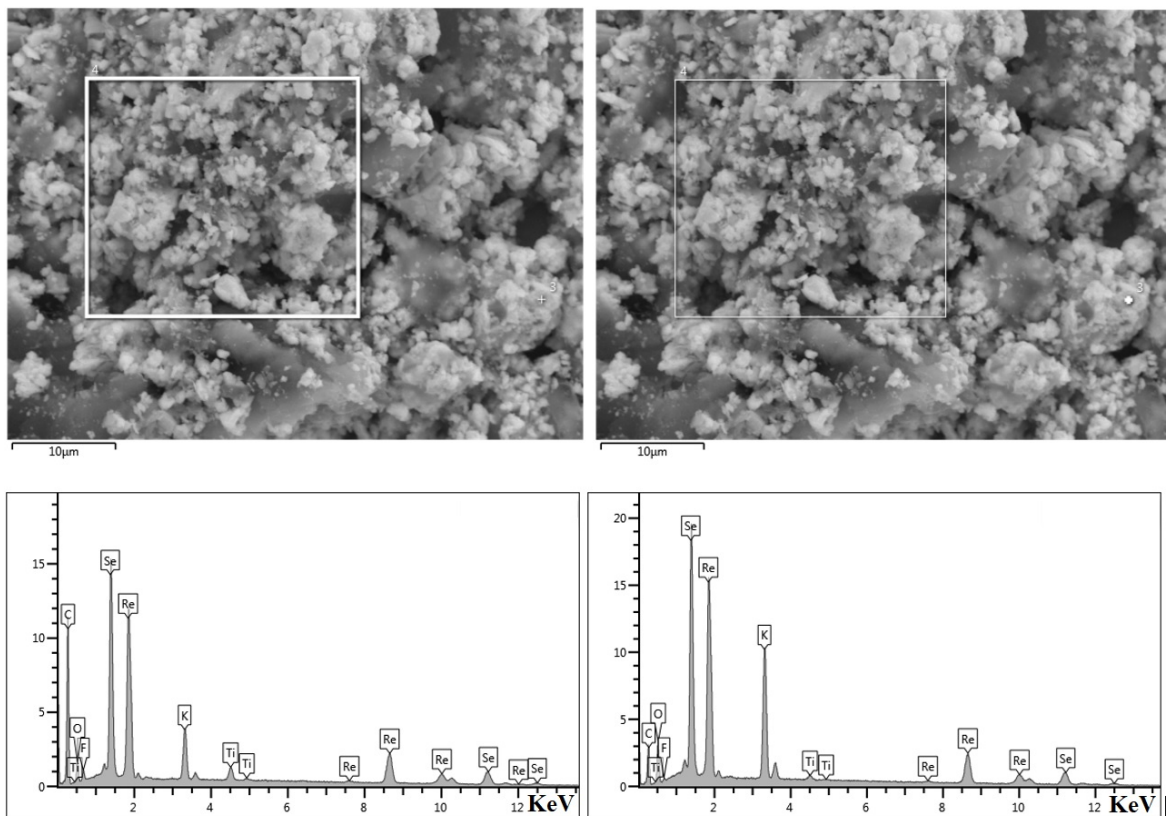


Figure S2. EDX spectrum collected from large area 4 (a) and point 3 (b) of $K_4[Re_6Se_8(OH)_6]$ cluster containing paste with corresponding elemental composition.