Supporting Information

Boosting Water Oxidation on $Cu_2V_2O_7$ by Atomic-Scale Frustrated Lewis Pairs

Zheng-Yi Huang,[a] Bowen Liao,[a, c] Xiaoxuan Song,[a] San Ping Jiang,[b] Xiaoxia Li,[c] Shuwang Duo,[*a] Zhong Chen,[*a] Jingwei Li[*b]

a: Jiangxi Province Key Laboratory of Surface Engineering, School of Materials and Energy, Jiangxi Science and Technology Normal University, Nanchang 330013, China

b: National Energy Key Laboratory for New Hydrogen-Ammonia Energy Technologies, Foshan Xianhu Laboratory, Foshan 528216, China

c: Institute of Functional Materials, Jiangxi University of Finance and Economics, Nanchang 330013, PR China

Structure characterization

The phase composition of the samples is detected by X-ray diffraction (XRD, Cu Kα radiation, λ = 0.154 nm). The morphology and lattice structure of the samples were examined by Field emission scanning electron microscopy (FE-SEM, EISS-SIGMA HD, 15 kV, 1nA) and Transmission electron microscopy (TEM, JEOL F200, 100kV, 2.5 nA). Spherical aberration corrected Transmission Electron Microscope (AC-TEM, Thermo Scientific Themis Z, 200kV) is used to characterize the atomic arrangements on the surface of samples (USA-FEI-Titan Cubed Themis G2 300). The sample composition was determined by X-ray Photoelectron Spectroscopy (XPS, ThermoFisher Nexsa). Raman spectra (Raman, Renishaw inVia) are used to characterize the molecular structure and chemical bonding of catalysts.

Optica characterization

UV-Visible (UV-Vis) absorption spectra were recorded by UV-Vis-NIR (Shimadzu UV 3600 Plus, 280~800 nm) spectrophotometer. The irradiative recombination of electrons and holes of all samples was evaluated by photoluminescence spectroscopy (PL, Edinburgh FLS 1000, excitation wavelength: 365 nm) and Time resolved photoluminescence spectroscopy (TRPL, Edinburgh FLS 1000, excitation wavelength: 365 nm) to investigate the charge separation process.

Computational details

Based on the XRD and TEM information, CVO (200) and crystal faces were selected to construct the model. Spin-polarized electronic structure calculations were performed using the plane-wave basis set approach as implemented in the Vienna ab initio simulation package (VASP).[1] The projector augmented wave (PAW) method was used to represent the ion–core electron interactions.[2] The valence electrons were represented with a plane wave basis set with an energy cutoff of 450 eV. Electronic exchange and correlation were described with the Perdew–Burke–Ernzerhof (PBE) functional.[3] DFT-D3 method was used to treat the van der Waals interaction.[4] A 2×2×1 Monkhorst–Pack scheme was used to generate the k-point grid for the modeled surfaces.[5] The convergence criteria for the self-consistent electronic structure and geometry were set to 10−5 eV and 0.05 eV/Å, respectively. Molecular dynamics (MD) simulations were conducted using the Forcite module with the COMPASS force field in Materials Studio.[6] Van der Waals and Coulomb interactions were considered, using atom-based and Ewald methods with a 12.5 Å cutoff. The motion equations were integrated at a 1 fs time step. Following energy

minimization, each system underwent a 500 ps relaxation period under periodic boundary conditions in the NVT ensemble, using the Nose thermostat and Berendsen barostat for stabilization of temperature, potential, and total energy.

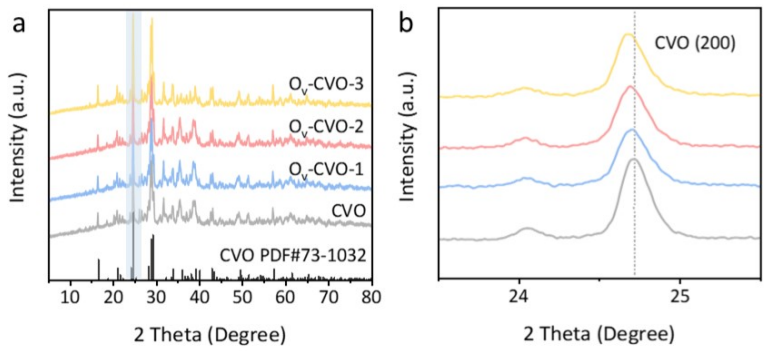

Fig. S1. XRD patterns of CVO, Vo-CVO-1, O_v-CVO-2 and O_v -CVO-3. (a) Total XRD patterns. (b) Locally amplified XRD patterns.

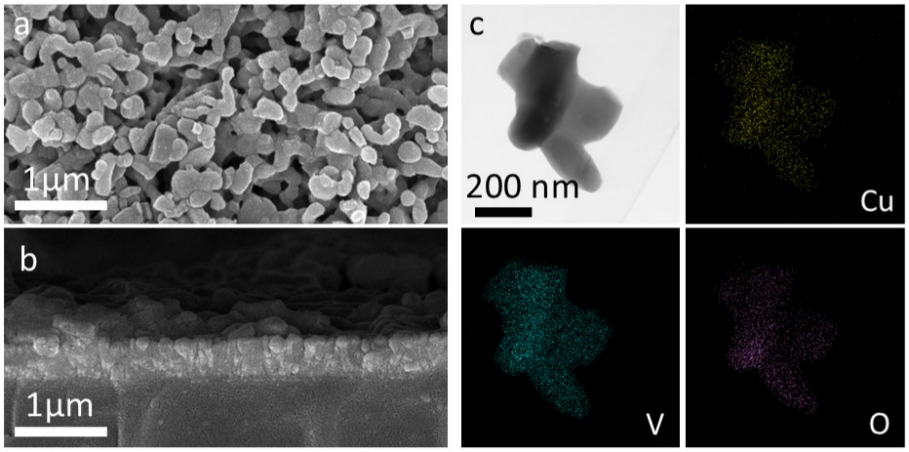

Fig. S2. (a) Longitudinal SEM images of CVO. (b) Transverse SEM images of CVO. (c) Mapping images of CVO.

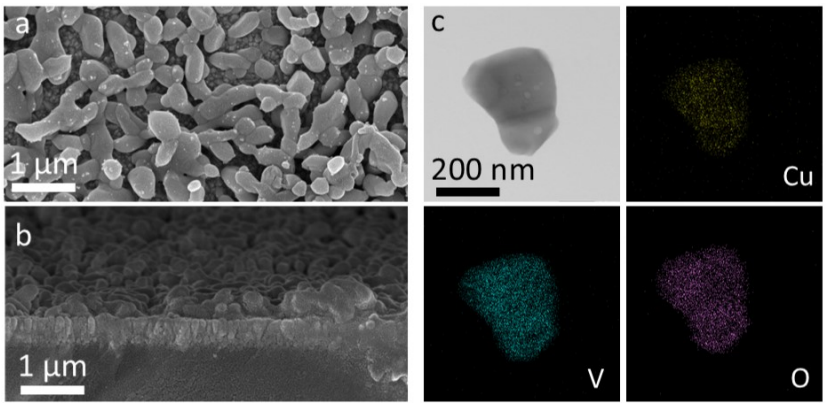

Fig. S3. (a) Longitudinal SEM images of O_v-CVO-2. (b) Transverse SEM images of O_v-CVO-2. (c) Mapping images of O_v-CVO-2

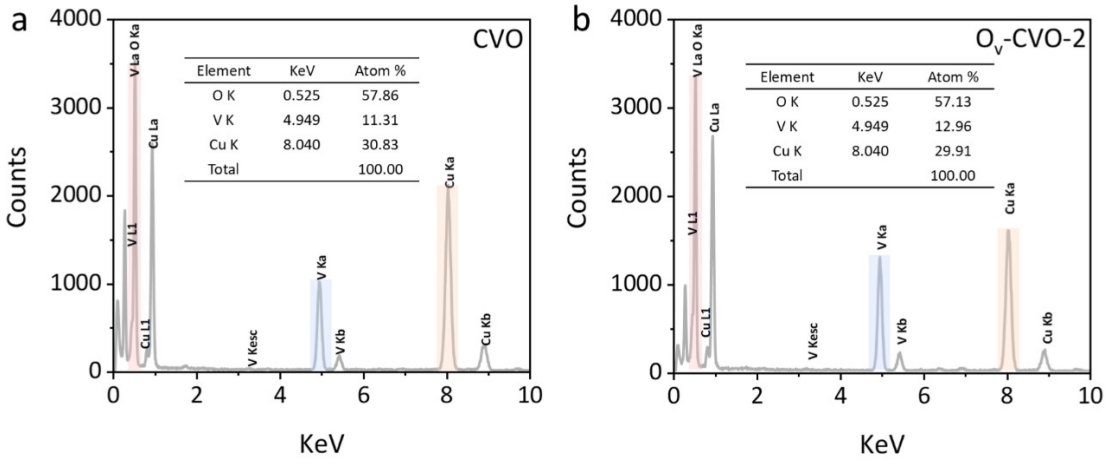

Fig. S4. (a) Energy dispersive spectrometer of CVO (b) Energy dispersive spectrometer of O_v-CVO-2.

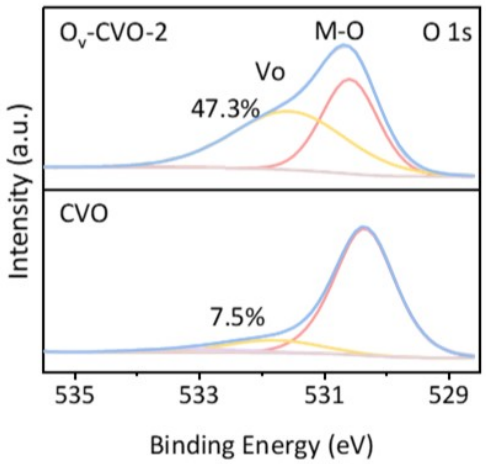

Fig. S5. O 1s curves of CVO and O_v-CVO-2.

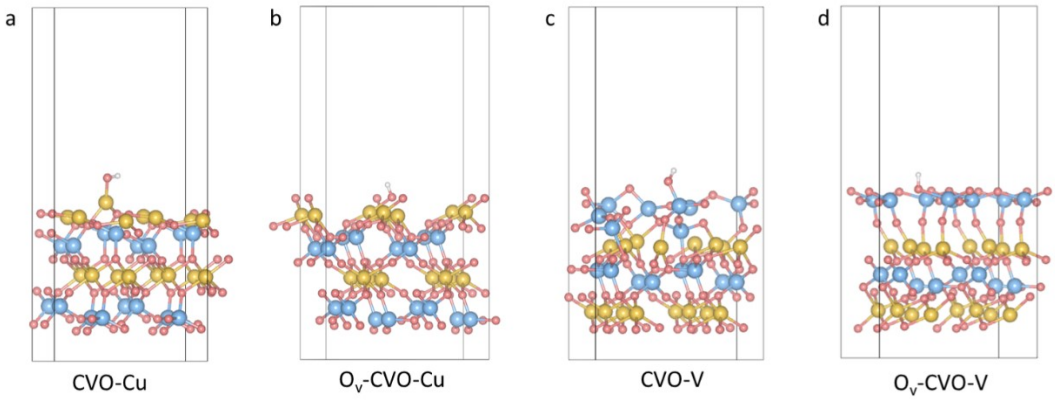

Fig. S6. The structure for calculating the adsorption energy of -OH by CVO and O_v-CVO. (a) CVO-Cu site. (b) O_v-CVO-Cu site. (c) CVO-V site. (d) O_v-CVO-V site.

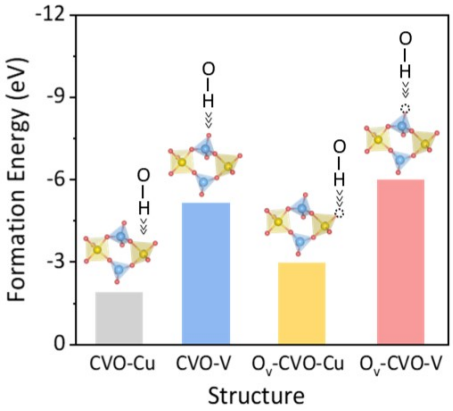

Fig. S7. Adsorption energy of CVO and O_v-CVO-2 at different sites.

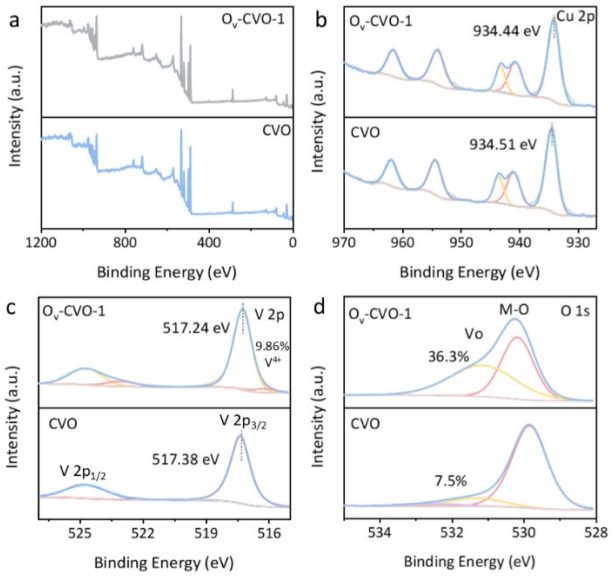

Fig. S8. XPS patterns of CVO and O_v -CVO-1. (a) Full curves. (b) Cu 2p curves. (c) V 2p curves. (d) O 1s curves.

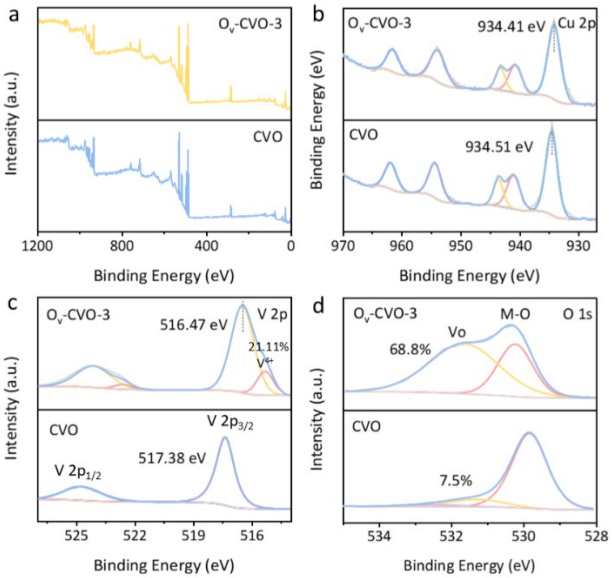

Fig. S9. XPS patterns of CVO and O_v -CVO-3. (a) Full curves. (b) Cu 2p curves. (c) V 2p curves. (d) O 1s curves.

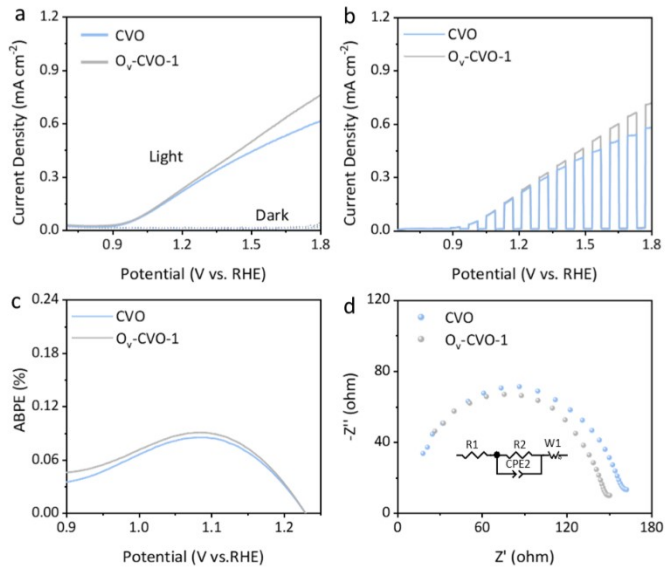

Fig. S10. The electrochemical test curve of CVO and O_v -CVO-1. (a) LSV curve. (b) LSV curve under chopping light. (c) ABPE curve; (d) EIS plots.

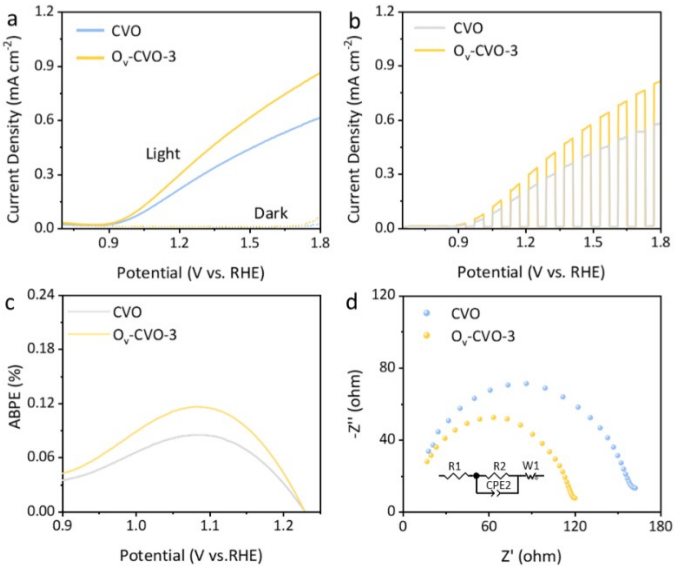

Fig. S11. The electrochemical test curve of CVO and O_v -CVO-3. (a) LSV curve. (b) LSV curve under chopping light. (c) ABPE curve; (d) EIS plots.

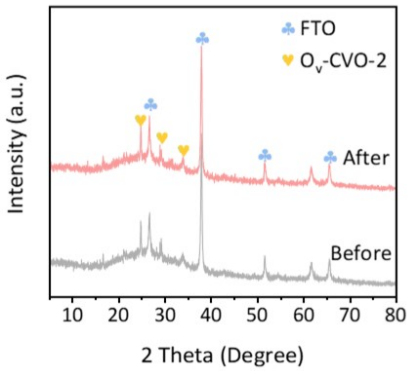

Fig. S12. XRD patterns of O_v -CVO-2 before and after stability tests.

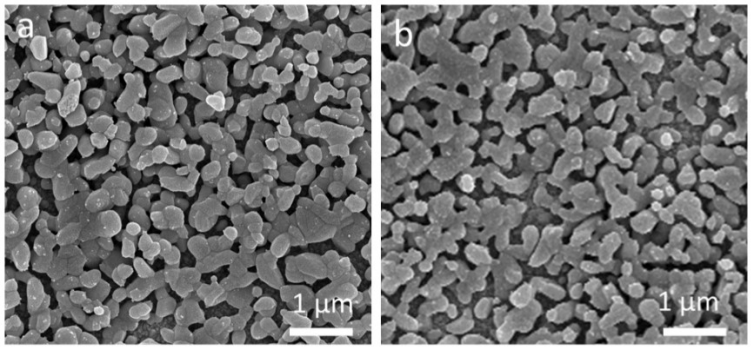

Fig. S13. SEM images before and after the stability test of O_v -CVO-2. (a) SEM image before reaction. (b) SEM image after the reaction.

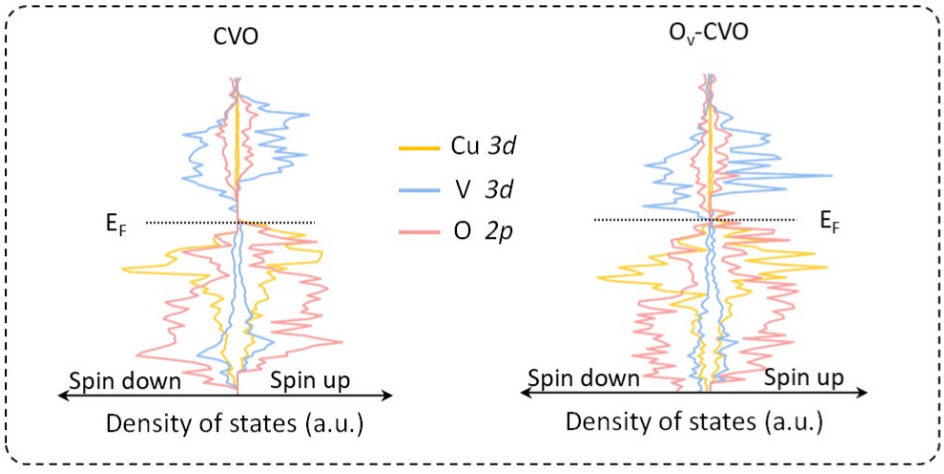

Fig. S14. PDOS of CVO and O_v -CVO.

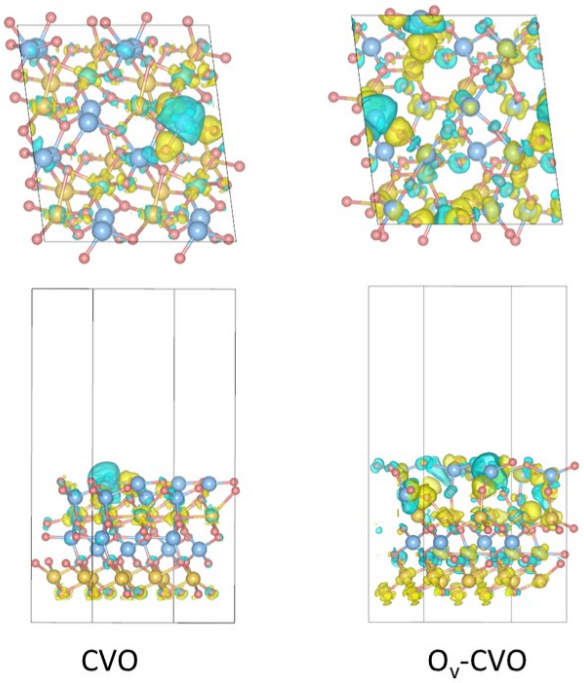

Fig. S15. The differential charge structure models of CVO and O_v-CVO.

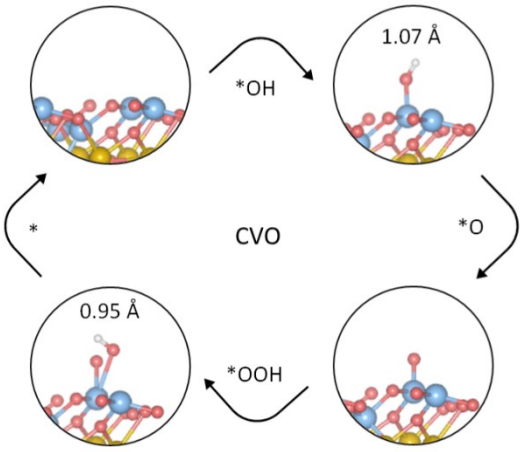

Fig. S16. Adsorption model of CVO in the OER process and O-H bond length.

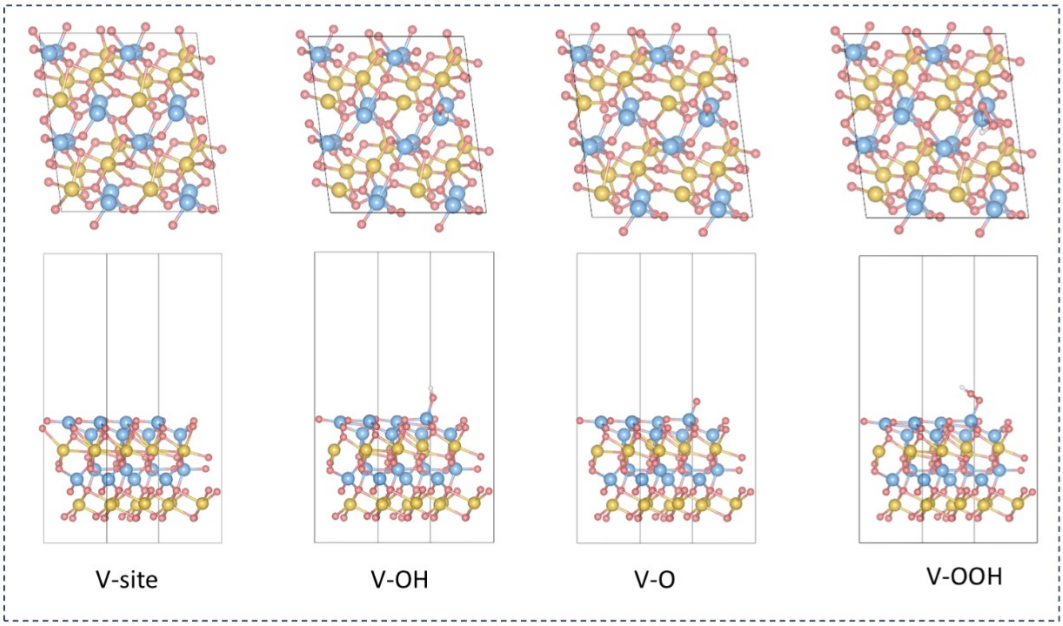

Fig. S17. The structural type of the OER intermediate on CVO.

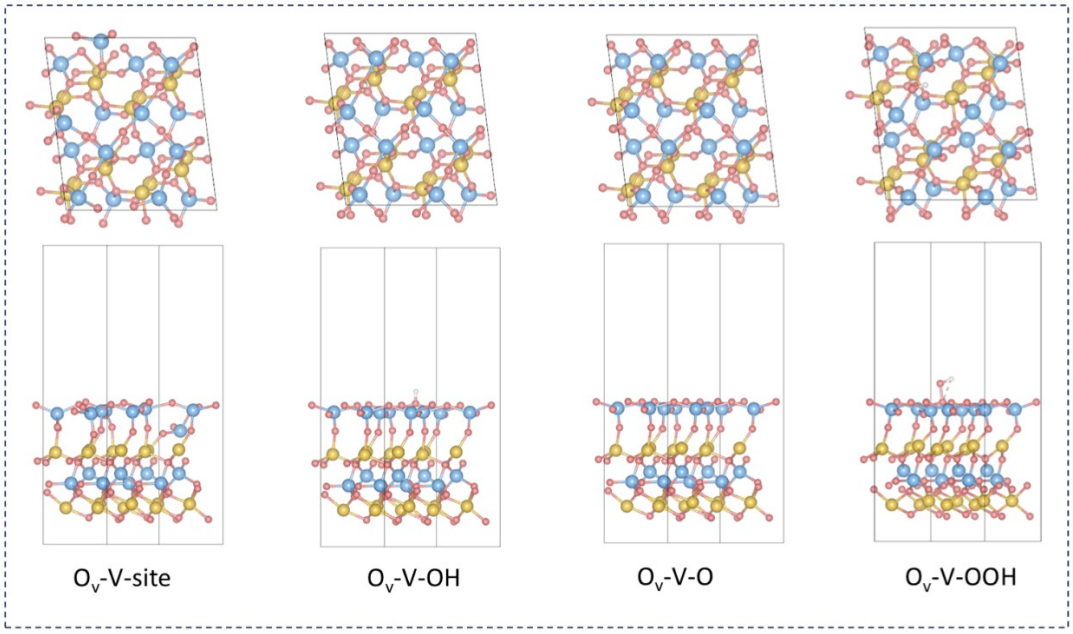

Fig. S18. The structural type of the OER intermediate on O_v-CVO.

Table S1. Equivalent circuit fitting parameters of EIS curves for CVO, O_v-CVO-1, O_v -CVO-2 and O_v -CVO-3.

	CVO	O_v -CVO-1	O_v -CVO-2	O_v -CVO-3
R_s (Ω)	11.28	7.61	6.34	6.94
R_{ct} (Ω)	94.97	73.96	51.79	52.63

Reference：

[1] G. Kresse and J. Furthmüller, *Computational materials science*, 1996, **6**, 15-50.

[2] G. Kresse and D. Joubert, *Physical review b*, 1999, **59**, 1758.

[3] J. P. Perdew, K. Burke and M. Ernzerhof, *Physical review letters*, 1996, **77**, 3865.

[4] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of chemical physics*, 2010, **132**, 154104.

[5] H. J. Monkhorst and J. D. Pack, *Physical review B*, 1976, **13**, 5188.

[6] H. Sun, *The Journal of Physical Chemistry B*, 1998, **102**, 7338-7364.