Supporting Information

Computational Screening of Transition Metal Atom Doped ZnS and ZnSe Nanostructures as Promising Bifunctional Oxygen Electrocatalysts

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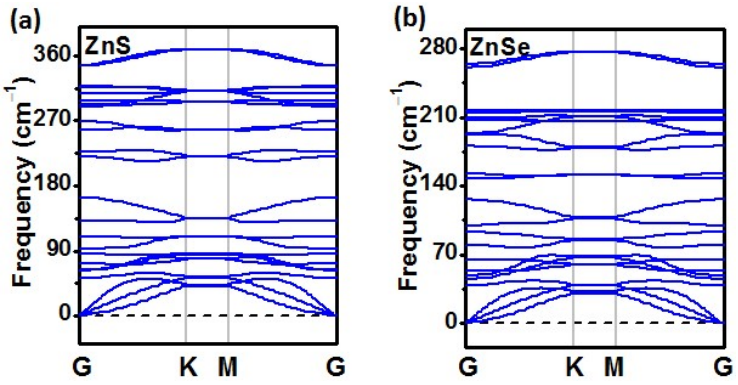


Figure S1. The phonon spectra of the optimized surface structure of (a) ZnS and (b) ZnSe nanostrucutres.

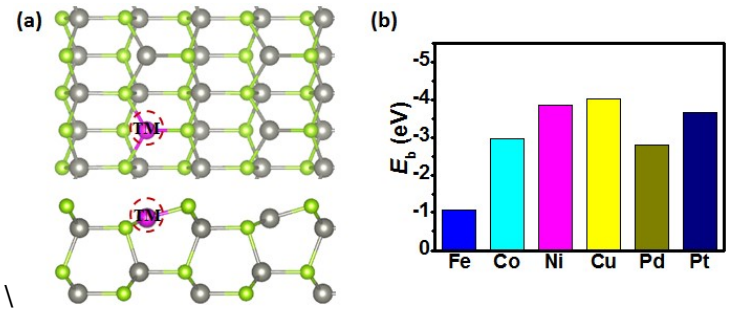


Figure S2. (a) Top and side views of the TM (TM = Fe, Co, Ni, Cu, Pd and Pt) doped ZnSe nanostructures, and the pink, gray and green represent TM, Zn and Se atoms. (b) The formation energies of Fe, Co, Ni, Cu, Pd and Pt doped ZnSe nanostructures.

Table S1. Free Energy Changes of Each Elementary Step and Overpotentials of ZnS Nanostructures for OER and ORR at U = 0 V and pH = 0

Systems	OER				ORR				η^{OER}/V	η^{OER}/V
	ΔG_1/eV	ΔG_2/eV	ΔG_3/eV	ΔG_4/eV	ΔG_1/eV	ΔG_2/eV	ΔG_3/eV	ΔG_4/eV		
pristine	1.71	0.56	2.40	0.25	-0.25	-2.40	-0.56	-1.71	1.17	0.98
Fe-doped	0.02	1.40	1.93	1.56	-1.56	-1.93	-1.40	-0.02	0.70	1.21
Co-doped	0.46	1.16	2.06	1.25	-1.25	-2.06	-1.16	-0.46	0.83	0.77
Ni-doped	0.92	1.52	1.54	0.94	-0.94	-1.54	-1.52	-0.92	0.31	0.31
Cu-doped	1.82	0.65	2.28	0.17	-0.17	-2.28	-0.65	-1.82	1.05	1.06
Pd-doped	1.14	1.77	1.34	0.67	-0.67	-1.34	-1.77	-1.14	0.54	0.56
Pt-doped	0.85	1.54	1.73	0.80	-0.80	-1.73	-1.54	-0.85	0.50	0.43

Table S2. Free Energy Changes of Each Elementary Step and Overpotentials of ZnSe Nanostructures for OER and ORR at U = 0 V and pH = 0

Systems	OER				ORR				η^{OER}/ V	η^{ORR}/ V
	ΔG_1/eV	ΔG_2/eV	ΔG_3/eV	ΔG_4/eV	ΔG_1/eV	ΔG_2/eV	ΔG_3/eV	ΔG_4/eV		
pristine	1.89	2.28	0.55	0.19	-0.19	-0.55	-2.28	-1.89	1.05	1.04
Fe-doped	0.01	1.42	1.86	1.63	-1.63	-1.86	-1.42	-0.01	0.63	1.22
Co-doped	0.50	1.25	1.94	1.23	-1.23	-1.94	-1.25	-0.50	0.71	0.73
Ni-doped	0.61	1.46	1.51	0.93	-0.93	-1.51	-1.46	-1.02	0.28	0.30
Cu-doped	1.72	2.03	0.99	0.19	-0.19	-0.99	-2.03	-1.72	0.80	1.04
Pd-doped	1.80	1.13	1.22	0.76	-0.76	-1.22	-1.13	-1.80	0.57	0.47
Pt-doped	1.24	1.32	1.50	0.86	-0.86	-1.50	-1.32	-1.24	0.27	0.37

Table S3. Zero Point Energy Corrections (ZPE) and Entropy Contributions (TS) of *OH, *O and *OOH on the Surface of ZnS Nanostructures at 298.15 K by DFT Calculations

systems	intermediates	E_{DFT}/eV	ZPE/eV	TS/eV
	*OH	-117.70	0.32	0.11
pristine	*O	-111.75	0.04	0.09
	*OOH	-122.35	0.42	0.18
	*OH	-125.05	0.33	0.12
Fe-doped	*O	-120.00	0.08	0.06
	*OOH	-129.24	0.43	0.20
	*OH	-122.95	0.33	0.14
Co-doped	*O	-118.07	0.07	0.07
	*OOH	-127.25	0.42	0.18
	*OH	-121.13	0.33	0.13
Ni-doped	*O	-116.03	0.06	0.08
	*OOH	-125.64	0.42	0.20
	*OH	-119.00	0.33	0.11
Cu-doped	*O	-113.26	0.04	0.11
	*OOH	-123.45	0.43	0.19
	*OH	-119.93	0.32	0.08
Pd-doped	*O	-115.13	0.05	0.09
	*OOH	-125.08	0.44	0.17
	*OH	-121.30	0.34	0.09
Pt-doped	*O	-116.30	0.06	0.08
	*OOH	-125.95	0.44	0.19

Table S4. Zero Point Energy Corrections (ZPE) and Entropy Contributions (TS) of *OH, *O and *OOH on the Surface of ZnSe Nanostructures at 298.15 K by DFT Calculations

systems	intermediates	E_{DFT}/eV	ZPE/eV	TS/eV
	*OH	-105.70	0.32	0.11
pristine	*O	-101.53	0.07	0.06
	*OOH	-110.21	0.42	0.19
	*OH	-112.77	0.33	0.13
Fe-doped	*O	-107.74	0.07	0.07
	*OOH	-116.92	0.42	0.17
	*OH	-110.73	0.33	0.13
Co-doped	*O	-105.94	0.06	0.08
	*OOH	-115.02	0.43	0.16
	*OH	-108.98	0.33	0.14
Ni-doped	*O	-103.82	0.06	0.09
	*OOH	-113.41	0.42	0.18
	*OH	-106.82	0.32	0.08
Cu-doped	*O	-102.53	0.07	0.06
	*OOH	-111.34	0.41	0.19
	*OH	-108.67	0.36	0.07
Pd-doped	*O	-103.17	0.05	0.09
	*OOH	-113.01	0.44	0.14
	*OH	-109.52	0.37	0.07
Pt-doped	*O	-104.26	0.06	0.08
	*OOH	-113.67	0.44	0.20

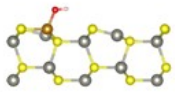
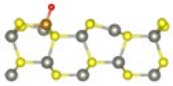
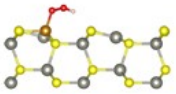
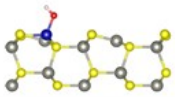
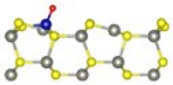
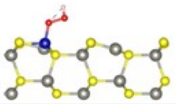
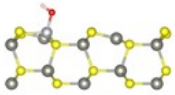
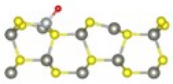
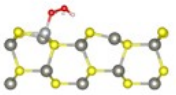
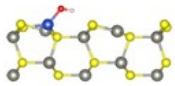
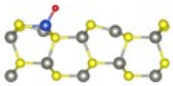
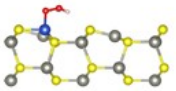
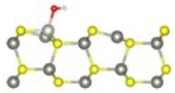
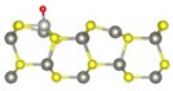
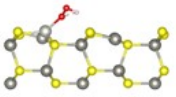
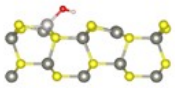
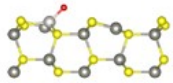
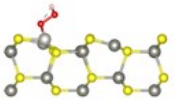
Systems	*OH	*O	*OOH
Fe-doped ZnS			
Co-doped ZnS			
Ni-doped ZnS			
Cu-doped ZnS			
Pd-doped ZnS			
Pt-doped ZnS			

Figure S3. Side views of the optimized *OH, *O and *OOH adsorption configurations of Fe, Co, Ni, Cu, Pd and Pt doped ZnS nanostructures for OER/ORR.

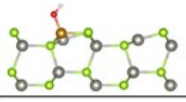
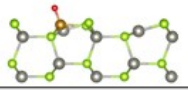
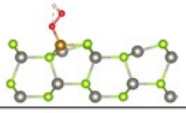
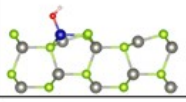
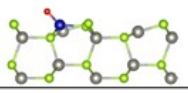
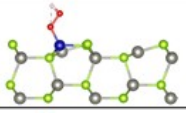
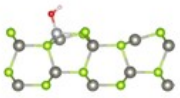
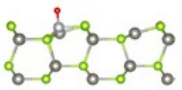
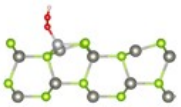
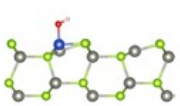
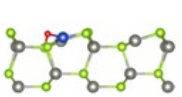
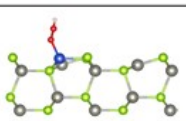
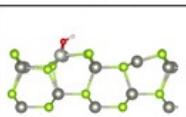
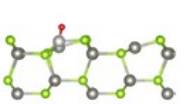
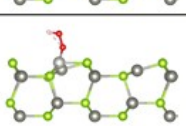
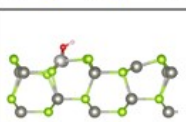
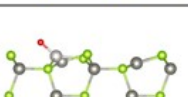
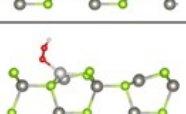
Systems	*OH	*O	*OOH
Fe-doped ZnSe			
Co-doped ZnSe			
Ni-doped ZnSe			
Cu-doped ZnSe			
Pd-doped ZnSe			
Pt-doped ZnSe			

Figure S4. Side views of the optimized *OH, *O and *OOH adsorption configurations of Fe, Co, Ni, Cu, Pd and Pt doped ZnSe nanostructures for OER/ORR.

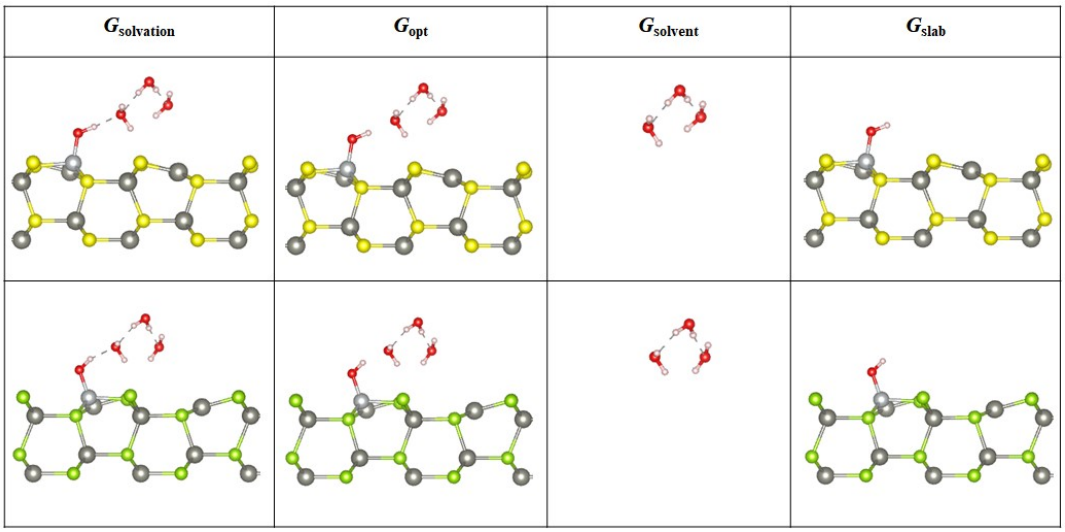


Figure S5. The illustration of the stabilization of adsorbed *OH intermediate on the surface of Ni doped ZnS and ZnS nanostructures due to the favorable solvent interaction. The G_{opt} refers to the optimized geometry with explicit solvent, $G_{solvent}$ refers to the solvent water molecules, G_{slab} refers to the slab without solvent, and $G_{solvation}$ refers to the estimated stabilization of the system gains from the favorable interaction of the solvent with the surface. And $\Delta G_{solvation}$ can be obtained by the equation : $\Delta G_{solvation} = G_{opt} - (G_{solvent} + G_{slab})$.

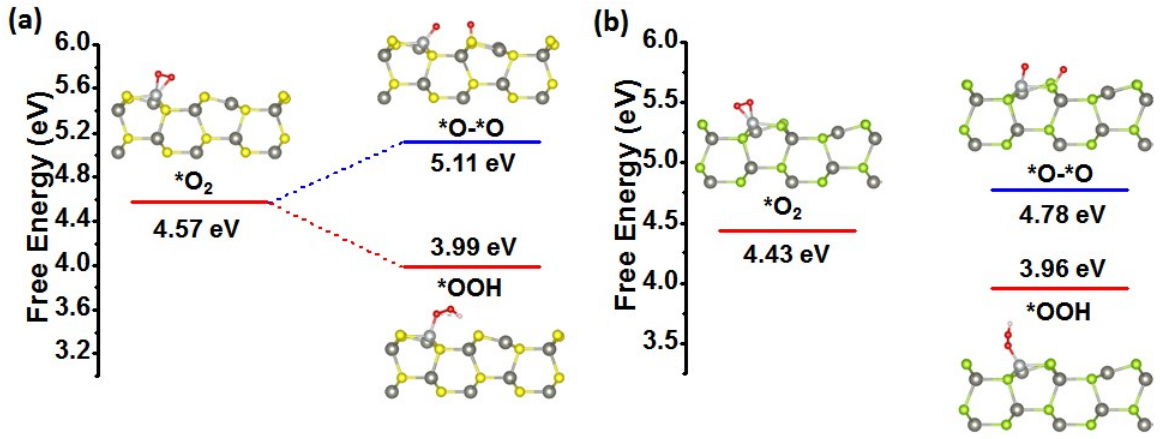


Figure S6. The calculated free energy changes of O_2 dissociative pathway ($*O_2$ to two *O) and associative pathway ($*O_2$ to *OOH) for Ni doped (a) ZnS and (b) ZnSe nanostructures. The $*O_2$ to two *O step is an endothermic reaction signified by the increase of free energy, while $*O_2$ to *OOH is an exothermic reaction showing a decrease of free energy.

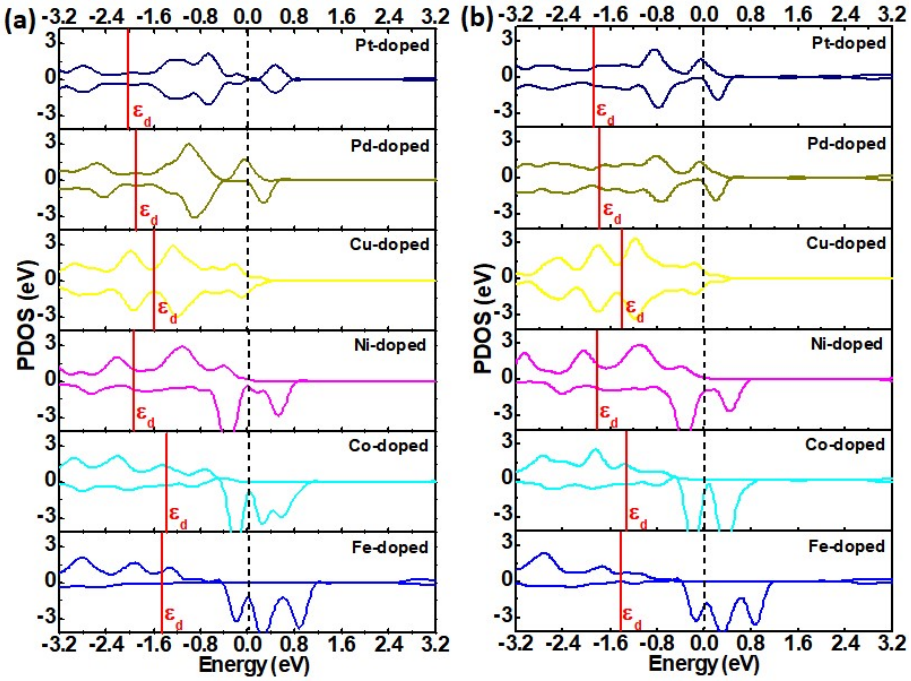


Figure S7. Partial density of states (PDOS) of d orbitals for TM doped (a) ZnS and (b) ZnSe nanostructures, the d-band centers (ε_d) are also labeled for TM atom, from Fe to Pt.