Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

The CeO_2 supported multi-nuclear Nb_xS_y clusters for hydrogen evolution reaction

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Table S1. The calculated cohesive energy.

	E_c (eV/atom)
2H-NbS_2	-5.50
Nb_3S_4	-4.94
Nb_4S_3	-4.73
Nb_4S_4	-5.06

Table S2. The Bader charge and magnetic moment of inner-layer Ce^{4+} and reduced Ce^{3+} on Nb_xS_y/CeO_2.

		Ce^{4+}		**Ce^{3+}**	
Nb_3S_4/CeO_2	Bader charge (e)	9.60	9.89	9.90	9.89
	Magnetic moment (μ_B)	0.00	0.96	0.97	0.96
Nb_4S_3/CeO_2	Bader charge (e)	9.60	9.94	9.93	9.94
	Magnetic moment (μ_B)	0.00	0.95	0.96	0.96
Nb_4S_4/CeO_2	Bader charge (e)	9.60	9.87	9.88	
	Magnetic moment (μ_B)	0.00	0.97	0.97	

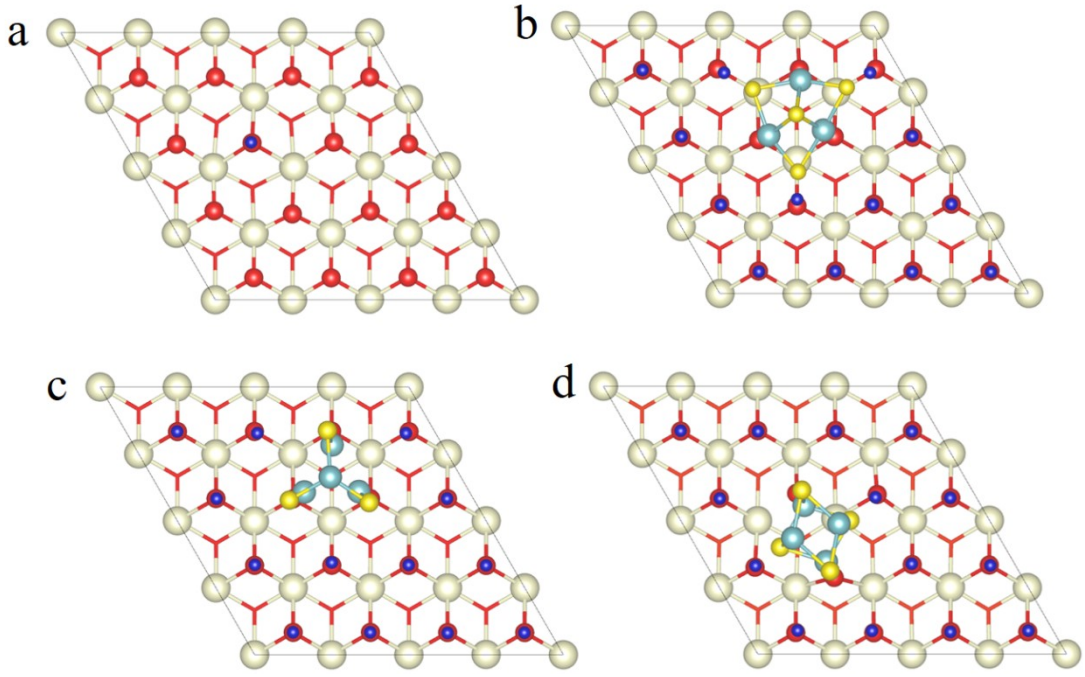

Figure S1. The optimized structures with different coverage of H atoms. (a) the CeO_2 with 6.25% coverage, (b) the CeO_2+Nb_3S_4 with 100% coverage, (c) the CeO_2+Nb_4S_3 with 100% coverage, (d) the CeO_2+Nb_4S_4 with 100% coverage.

Table S3. The Ce^{3+} of CeO_2+Nb_xS_y with different H coverage.

coverage	0%	6.25%	0%	100%	0%	100%	0%	100%
μ_B	CeO_2		CeO_2+Nb_3S_4		CeO_2+Nb_4S_3		CeO_2+Nb_4S_4	
Ce_1^{3+}	-	0.97	0.96	0.96	0.95	0.97	0.97	0.97
Ce_2^{3+}	-	-	0.97	0.96	0.96	0.97	0.97	0.97
Ce_3^{3+}	-	-	0.96	0.96	0.96	0.97	-	0.97
Ce_4^{3+}	-	-	-	0.97	-	0.97	-	0.97
Ce_5^{3+}	-	-	-	0.97	-	0.97	-	0.97
Ce_6^{3+}	-	-	-	0.96	-	0.97	-	0.97
Ce_7^{3+}	-	-	-	0.96	-	0.97	-	0.97
Ce_8^{3+}	-	-	-	0.97	-	0.97	-	0.97
Ce_9^{3+}	-	-	-	0.97	-	0.97	-	0.97
Ce_{10}^{3+}	-	-	-	0.97	-	0.97	-	0.97
Ce_{11}^{3+}	-	-	-	0.97	-	0.96	-	0.97
Ce_{12}^{3+}	-	-	-	0.97	-	0.97	-	0.97
Ce_{13}^{3+}	-	-	-	0.97	-	0.97	-	0.97
Ce_{14}^{3+}	-	-	-	0.96	-	0.97	-	0.97
Ce_{15}^{3+}	-	-	-	0.96	-	0.93	-	0.97
Ce_{16}^{3+}	-	-	-	0.97	-	0.96	-	0.97

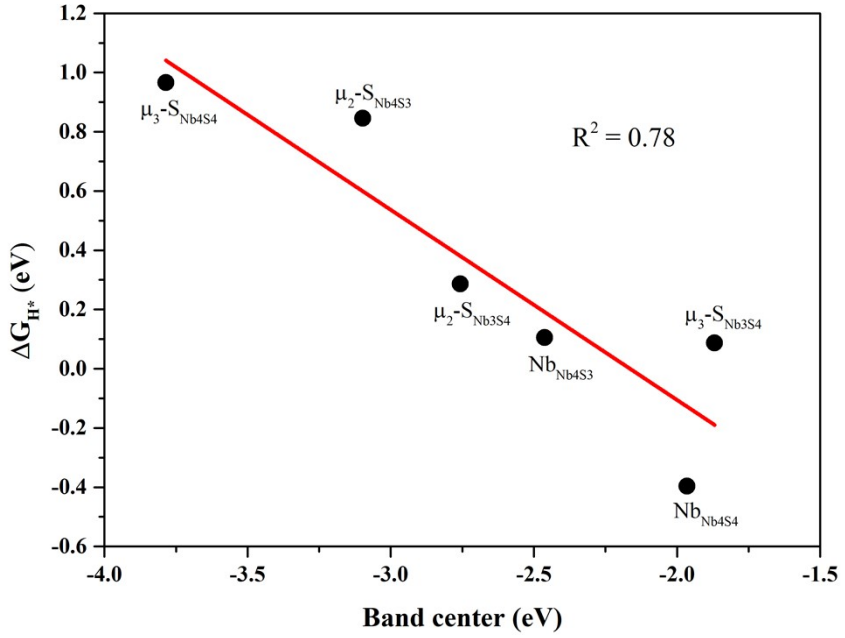

Fig. S2 The relation between ΔG_{H*} and the *p*/*d* band center of edge atoms on Nb_xS_y/CeO_2.

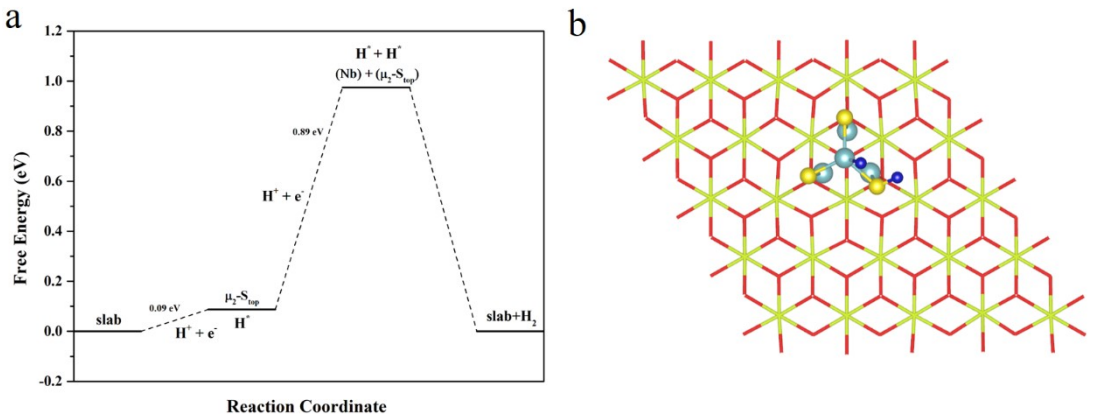

Fig. S3 (a) The calculated reaction pathways with Volmer-Tafel reaction mechanisms of Nb_4S_3/CeO_2 and (b) the optimized structure of Nb_4S_3/CeO_2 with two H^* absorption.