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Boosting oxygen reduction reaction activity of dual-atom catalysts on N-doped graphene by regulating the N coordination environment

Lei Li,*[a,b] Xiaoxia Wu,[a,b] Qiuying Du,[a,b] Narsu Bai[a,b], and Yuhua Wen*[c]

[a] *Modern Physics research center, College of Physics and Electronic Information, Inner Mongolia Normal University, Hohhot 010022, China. E-mail: lilei@imnu.edu.cn.*

[b] *Inner Mongolia Key Laboratory for Physics and Chemistry of Functional Materials, Hohhot 010022, China.*

[c] *Department of Physics, Xiamen University, Xiamen 361005, China. E-mail: yhwen@xmu.edu.cn.*

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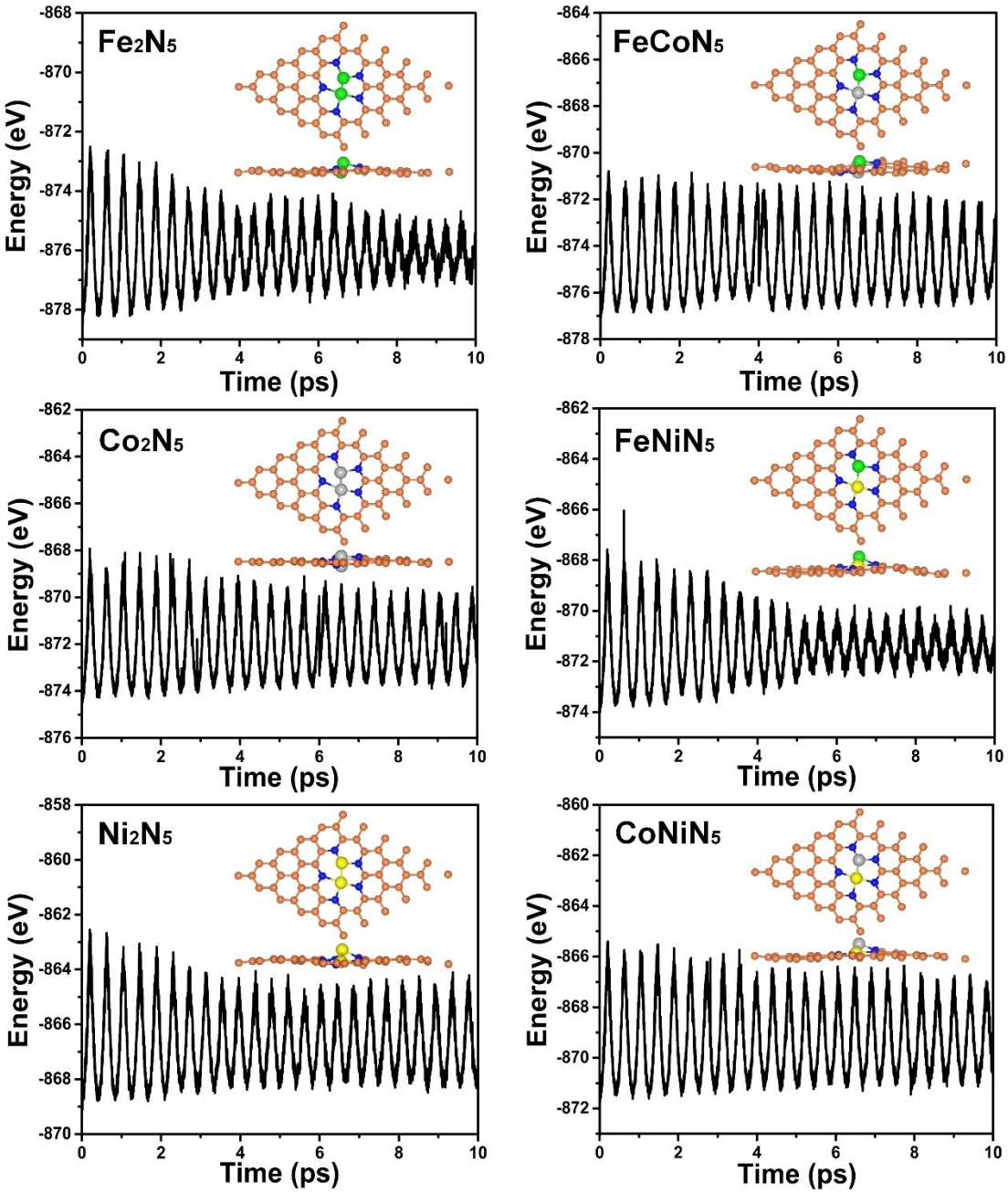

Fig. S1 Evolution of energy with the elapsed time for AIMD simulations of $M_1M_2N_5$ at 300 K. Inserts are top and side views of the snapshot of atomic configuration at 10 ps. The orange, blue, green, gray, and yellow balls denote C, N, Fe, Co, and Ni atoms, respectively.

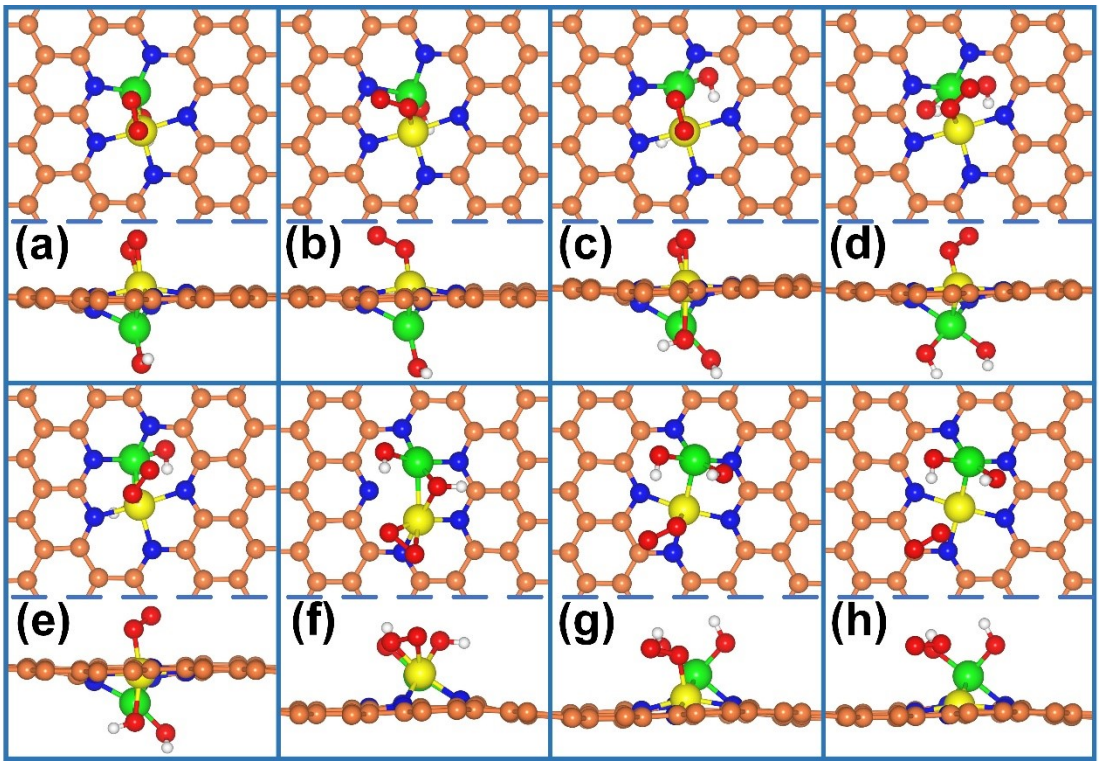

Fig. S2 Schematic illustration of the adsorption structures of O_2 molecular. (a)-(b) DS of $Co_2N_5(OH)$ and other $M_1M_2N_5(OH)$ structures. (c)-(e) DS of $Fe_2N_5(OH_2)$, $Co_2N_5(OH_2)$, and other $M_1M_2N_5(OH_2)$ structures. (f)-(h) RS of $Fe_2N_5(OH_2)$, $Co_2N_5(OH_2)$/$FeCoN_5(OH_2)$, and other $M_1M_2N_5(OH_2)$ structures. The orange, blue, green, yellow, red, and white balls denote C, N, M_1, M_2, O, and H atoms, respectively.

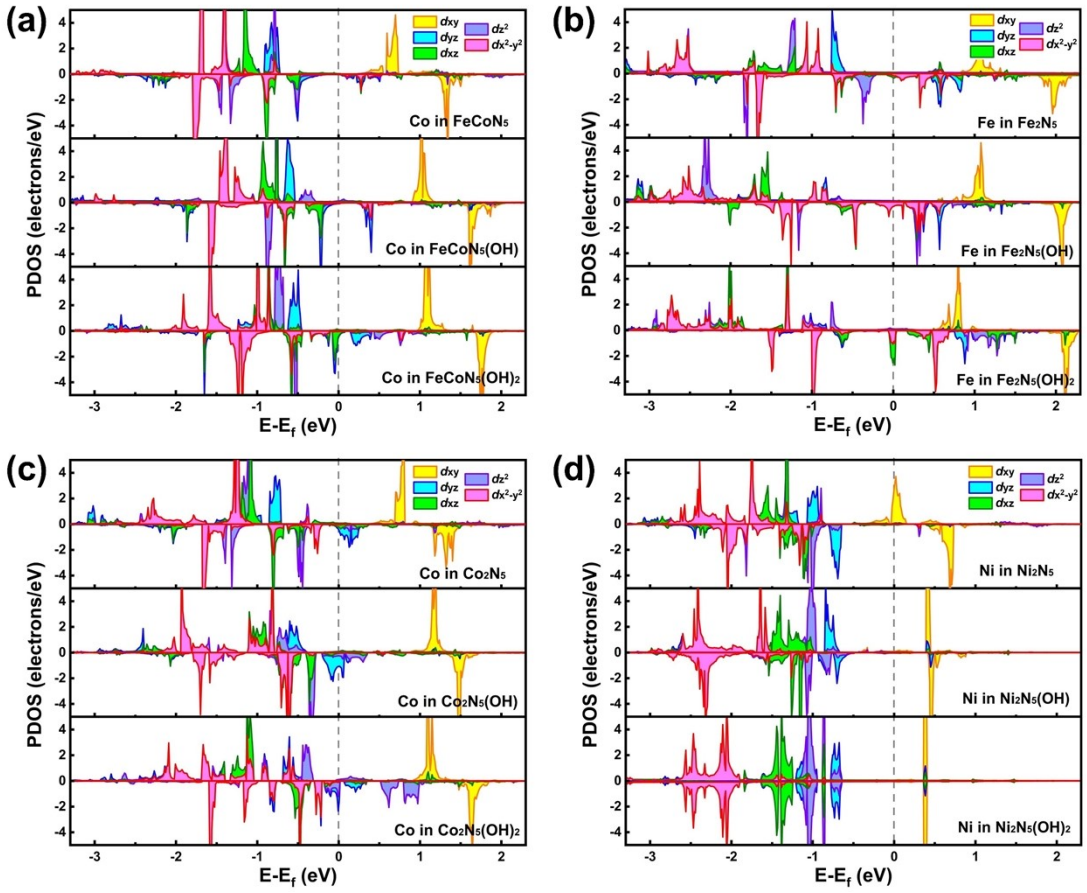

Fig. S3 The PDOS of *d* orbitals of M_2 atom in different structures. The dashed line indicates the Fermi level.

Table S1. Formation energy (E_f) for $M_1M_2N_5$, binding energy (E_b) between metal atoms and N_5-coordinated graphene, and cohesive energy (E_{coh}) for the metal bulk.

Model	E_f**(eV)**	E_b**(eV)**	E_{coh}**(eV)**	**Model**	E_f**(eV)**	E_b**(eV)**	E_{coh}**(eV)**
Fe_2N_5	-5.46	5.11	4.14	$FeCoN_5$	-6.32	5.54	4.64
Co_2N_5	-6.78	5.77	5.13	$FeNiN_5$	-5.60	5.18	4.51
Ni_2N_5	-5.84	5.30	4.88	$CoNiN_5$	-6.30	5.53	5.01

Table S2. Adsorption energy (E_{ads}) of the reaction intermediates (*OOH, *O, and *OH) on different catalysts.

Model	E_{ads}(eV)			Model	E_{ads}(eV)		
	*OOH	*O	*OH		*OOH	*O	*OH
Fe_2N_5	-3.25	-6.07	-4.27	$FeCoN_5$	-3.07	-5.64	-4.15
$Fe_2N_5(OH)$	-1.64	-5.38	-3.49	$FeCoN_5(OH)$	-2.06	-5.09	-3.33
$Fe_2N_5(OH_2)$	-2.04	-4.45	-3.07	$FeCoN_5(OH_2)$	-1.71	-4.02	-2.86
Co_2N_5	-3.10	-5.70	-3.99	$FeNiN_5$	-2.99	-6.15	-4.39
$Co_2N_5(OH)$	-2.39	-5.33	-3.72	$FeNiN_5(OH)$	-2.04	-4.91	-3.39
$Co_2N_5(OH_2)$	-1.73	-3.72	-2.85	$FeNiN_5(OH_2)$	-1.08	-3.01	-2.22
Ni_2N_5	-2.69	-4.92	-3.94	$CoNiN_5$	-3.23	-5.73	-4.17
$Ni_2N_5(OH)$	-1.92	-3.90	-3.02	$CoNiN_5(OH)$	-1.94	-4.32	-3.11
$Ni_2N_5(OH_2)$	-0.95	-2.80	-2.05	$CoNiN_5(OH_2)$	-0.92	-2.82	-2.04

Table S3. Distance of the M–O bond (d_{M-O}) for the most stable adsorption structures of reaction intermediates ($*O_2$, *OOH, *O, and *OH) on different catalysts.

Model	d_{M-O}(Å)				Model	d_{M-O}(Å)			
	$*O_2$	*OOH	*O	*OH		$*O_2$	*OOH	*O	*OH
Fe_2N_5	1.824 1.817	1.820 2.057	1.797 1.816	1.775	$FeCoN_5$	1.821 1.811	1.822 2.049	1.729 1.843	1.807
$Fe_2N_5(OH)$	1.849 1.857	1.880	1.783 1.793	1.947 2.056	$FeCoN_5(OH)$	1.858 1.864	1.814	1.731 1.829	1.819
$Fe_2N_5(OH_2)$	1.816 1.982	1.786	1.651	1.829	$FeCoN_5(OH_2)$	1.828	1.816	1.652	1.830
Co_2N_5	1.817 1.810	1.822 1.990	1.699 1.827	1.760	$FeNiN_5$	1.810 1.808	1.817	1.604	1.799
$Co_2N_5(OH)$	1.854 1.830	1.800	1.747 1.778	1.907 2.052	$FeNiN_5(OH)$	1.840	1.774	1.652	1.815
$Co_2N_5(OH_2)$	1.855	1.858	1.653	1.824	$FeNiN_5(OH_2)$	1.895	1.845	1.692	1.829
Ni_2N_5	1.794 1.849	1.793	1.711 1.889	1.778	$CoNiN_5$	1.829 1.804	1.816 2.009	1.606	1.759
$Ni_2N_5(OH)$	1.875	1.836	1.712	1.826	$CoNiN_5(OH)$	1.858	1.791	1.701 1.857	1.806
$Ni_2N_5(OH_2)$	1.959	1.877	1.695	1.853	$CoNiN_5(OH_2)$	1.933	1.859	1.696	1.836

Table S4. Bader charge transfer (Δq) for different structures. Note that the minus sign denotes electron loss.

Model	Δq(e)			Model	Δq(e)		
	M_1	**M_2**	***OH**		**M_1**	**M_2**	***OH**
Fe_2N_5	-0.69	-0.73		$FeCoN_5$	-0.77	-0.62	
$Fe_2N_5(OH)$	-0.89	-0.88	0.50	$FeCoN_5(OH)$	-1.04	-0.65	0.55
$Fe_2N_5(OH_2)$	-1.06	-1.07	1.02	$FeCoN_5(OH_2)$	-1.14	-0.73	0.98
Co_2N_5	-0.60	-0.67		$FeNiN_5$	-0.66	-0.60	
$Co_2N_5(OH)$	-0.82	-0.71	0.48	$FeNiN_5(OH)$	-1.06	-0.65	0.55
$Co_2N_5(OH_2)$	-0.93	-0.91	0.95	$FeNiN_5(OH_2)$	-1.16	-0.68	0.98
Ni_2N_5	-0.56	-0.63		$CoNiN_5$	-0.61	-0.63	
$Ni_2N_5(OH)$	-0.78	-0.70	0.51	$CoNiN_5(OH)$	-0.84	-0.67	0.49
$Ni_2N_5(OH_2)$	-0.94	-0.75	0.97	$CoNiN_5(OH_2)$	-1.00	-0.71	0.96