Electronic Supplementary Information

Exploring the Effect of *B*-Site Al^{3+}-Mg^{2+} Dual Substitution on Optoelectronic, Surface, and Photocatalytic Properties of $BaTaO_2N$†

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Table S1. Al:Mg-(co)substituted $BaTaO_2N$ configurations at the total substituent content of 50 at.%, corresponding chemical compositions, structural parameters, and band gap values calculated by DFT-HSE12s.

Designation	Chemical compositions	Lattice constants *a b c*, Å	Cell volume *V,* Å^3	Band gap, eV
BTON*	$BaTaO_2N$	4.111	69.487	1.49 (Γ-Γ)
BTON:Al (50 at.%)	$BaTa_{0.5}Al_{0.5}O_2N$	4.050; 4.050; 4.033	66.151	1.61(M-Γ); 1.66 (Γ-Γ)
BTON:Mg (50 at.%)	$BaTa_{0.5}Mg_{0.5}O_2N$	4.071; 4.071; 4.232	70.137	2.01(M-Γ); 2.02(Γ-Γ)
BTON:Al:Mg (25:25 at.%)	$BaTa_{0.5}Al_{0.25}Mg_{0.25}O_2N$	4.073; 4.099; 4.108	68.584	1.44 (X-Y); 1.84 (Γ-Γ)
BTON:Al:Mg (37.5:12.5 at.%)	$BaTa_{0.5}Al_{0.375}Mg_{0.125}O_2N$	4.063; 4.063; 4.088	67.485	1.36 (Γ-Γ)
BTON:Al:Mg (12.5:37.5 at.%)	$BaTa_{0.5}Al_{0.125}Mg_{0.375}O_2N$	4.065; 4.065; 4.184	69.137	1.54 (Γ-Γ)

*M. Hojamberdiev, R. Vargas, Z.C. Kadirova, K. Kato, H. Sena, A.G. Krasnov, A. Yamakata, K. Teshima, M. Lerch, Unfolding the Role of *B* Site-Selective Doping of Aliovalent Cations on Enhancing Sacrificial Visible Light-Induced Photocatalytic H_2 and O_2 Evolution over $BaTaO_2N$, *ACS Catal.* **2022**, *12*, 1403−1414.

Table S2. Calculated effective masses of electrons and holes in pristine and (co)substituted $BaTaO_2N$ models along specific directions in the reciprocal space.

Model		m_e^*/m_0			m_h^*/m_0		
BTON (HSE12s)	direction	Γ→X	Γ→M	Γ→R	Γ→X	Γ→M	Γ→R
	calculation	0.363	0.449	0.374	0.535	0.238	0.233
	average		0.395			0.335	
BTON:Al (50 at.%)	direction	Γ→X		Γ→M	M→X	M→Γ	
	calculation	0.306		0.324	1.017	1.599	
	average		0.315			1.308	
BTON:Mg (50 at.%)	direction	Γ→X		Γ→M	M→X	M→Γ	
	calculation	0.320		0.328	1.254	1.492	
	average		0.324			1.373	
BTON:Al:Mg (25:25 at.%)	direction		Y→S		X→Γ	X→S	
	calculation		0.308		0.628	7.618	
	average		0.308			4.123	
BTON:Al:Mg (37.5:12.5 at.%)	direction	Γ→X		Γ→M	Γ→X	Γ→M	Γ→Z
	calculation	0.335		0.338	1.090	1.223	0.908
	average		0.336			1.074	
BTON:Al:Mg (12.5:37.5 at.%)	direction	Γ→X		Γ→M	Γ→X	Γ→M	Γ→Z
	calculation	0.342		0.347	1.840	1.895	3.195
	average		0.345			2.310	

Table S3. Details of the calculation of the band edge potentials by DFT.

Parameter/ Element	Ba	Ta		O		N		Al	Mg
Electron affinities, eV*	-0.50	0.32		1.46		0.07		0.46	-0.15
First ionization energies, eV*	5.20	7.89		13.62		14.53		5.99	7.65
Compound	$BaTaO_2N$	$BaTa_{0.5}Al_{0.5}O_2N$		$BaTa_{0.5}Mg_{0.5}O_2N$		$BaTa_{0.5}Al_{0.25}Mg_{0.25}O_2N$		$BaTa_{0.5}Al_{0.375}Mg_{0.125}O_2N$	$BaTa_{0.5}Al_{0.125}Mg_{0.375}O_2N$
Electronegativity of semiconductor, χ	5.254	5.129		5.207		5.168		5.148	5.187
Electronic transition type	direct	indirect	direct	indirect	direct	direct	direct	direct	direct
E_g, eV	1.49	1.61	1.66	2.01	1.36	1.54	1.84	1.54	1.36
E_{CB}, eV	0.01	-0.18	-0.20	-0.30	-0.03	-0.08	-0.25	-0.08	-0.03
E_{VB}, eV	1.50	1.43	1.46	1.71	1.33	1.46	1.59	1.46	1.33

*R.G. Pearson, Absolute Electronegativity and Hardness: Application to Inorganic Chemistry, *Inorg. Chem.* 27 (1988) 734–740.

Table S4. Adsorption energies of water and methanol molecules on the $BaTaO_2N$ (110) surfaces with Al-, Mg-, andAl-Mg (co)substitution.

Structures (adsorbate)	Mg, %	Al, %	E_{ads}, kcal·mol^{-1}	Water: dE_{ads}/dN_i, kcal·mol^{-1}	Methanol: dE_{ads}/dN_i, kcal·mol^{-1}
$BaTaO_2N$ (water adsorption)	5	0	-67.18	-2.26	
	2.5	2.5	-68.79	-2.34	
	2.5	2.5	-68.95	-2.37	
	0	5	-71.10	-2.67	
	0	0	-65.92	-2.53	
	1.5	3.5	-69.57	-2.34	
	3.5	1.5	-67.49	-2.52	
$BaTaO_2N$ (water-methanol adsorption)	5	0	-73.16	-2.56	-5.23
	2.5	2.5	-76.86	-2.49	-6.14
	0	5	-78.81	-2.69	-5.25
	0	0	-72.73	-2.29	-5.04
	2.5	2.5	-75.37	-2.33	-4.95
	1.5	3.5	-76.79	-2.58	-5.62
	3.5	1.5	-74.94	-2.41	-5.62

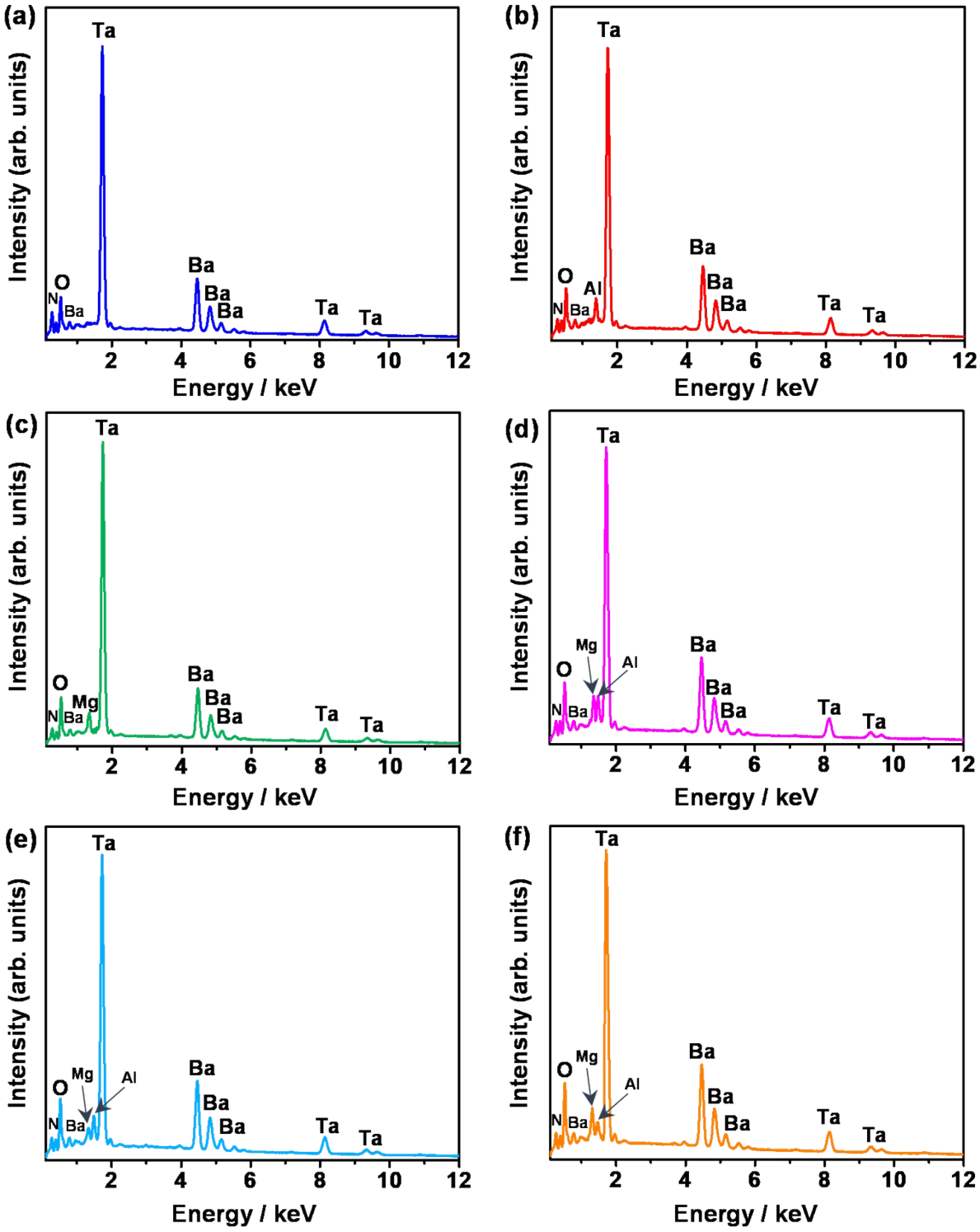

Figure S1. EDX spectra of BTON1 (a), BTON2 (b), BTON3 (c), BTON4 (d), BTON5 (e), and BTON6 (f).

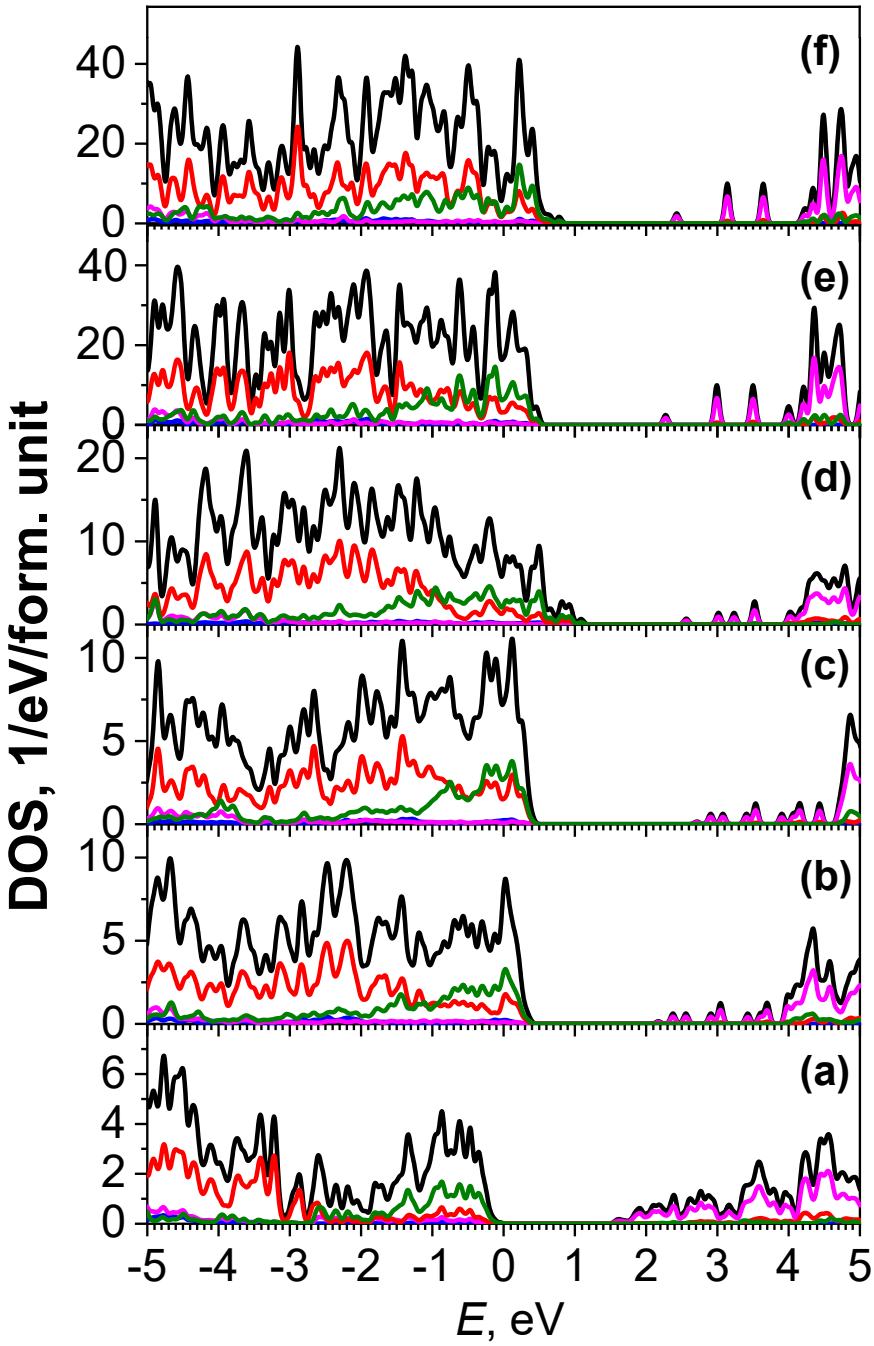

Figure S2. Total and partial density of states (a) BTON [32], (b) BTON:Al (50 at.%), (c) BTON:Mg (50 at.%), (d) BTON:Al:Mg (25:25 at.%), (e) BTON:Al:Mg (37.5:12.5 at.%), and (f) BTON:Al:Mg (12.5:37.5 at.%). The Fermi level is set at 0 eV.

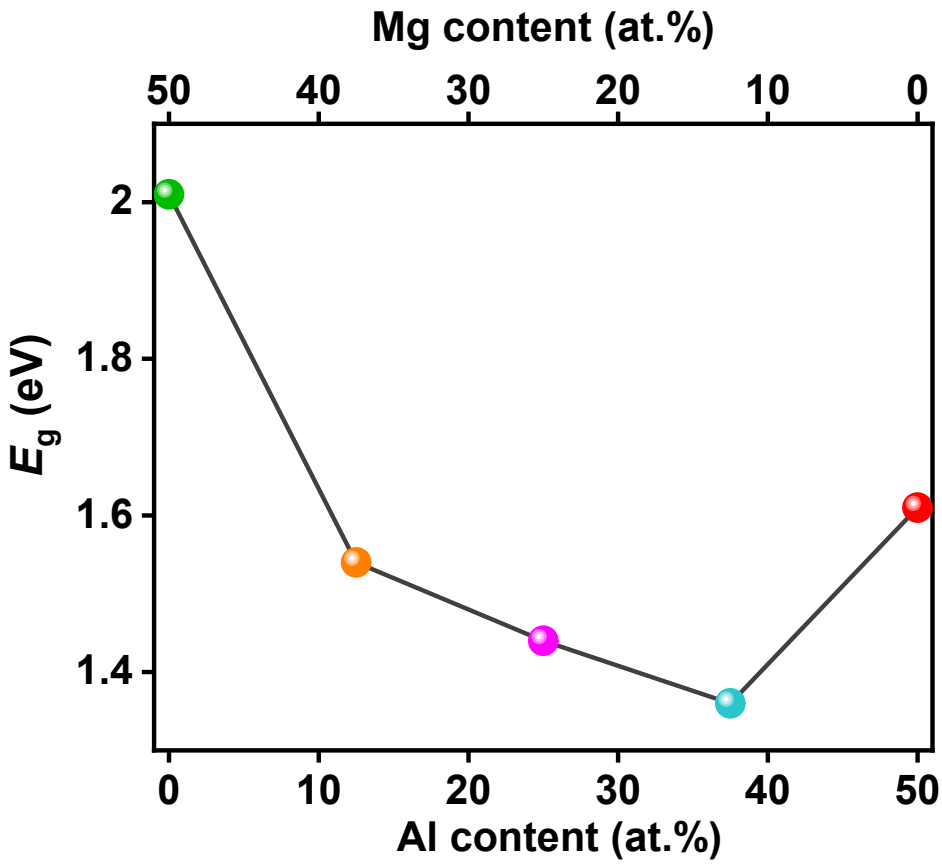

Figure S3. DFT-HSE12s-predicted band gap values of pristine and (co)substituted $BaTaO_2N$ models as functions of Al and Mg contents.

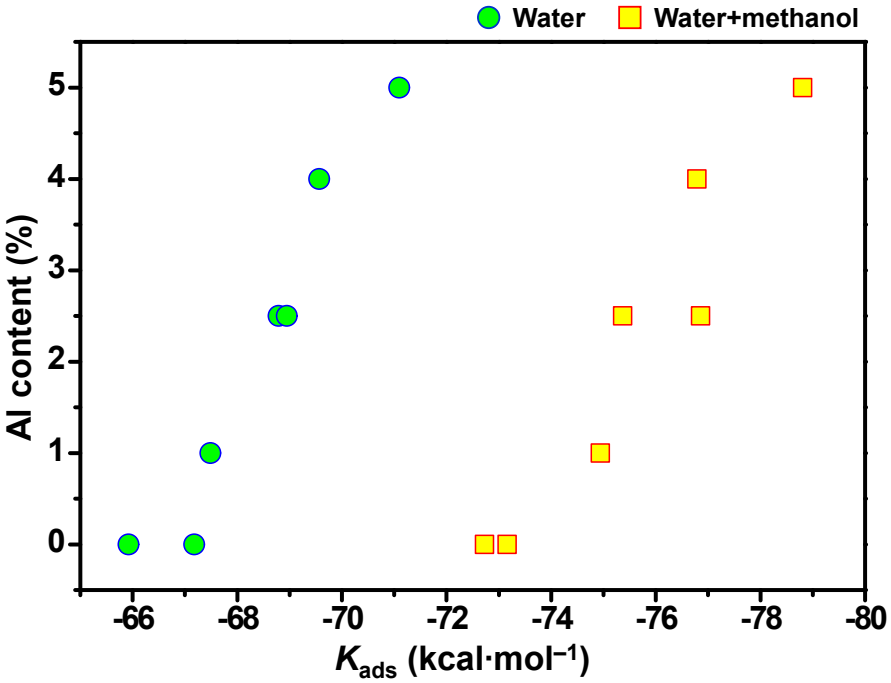

Figure S4. Effect of aluminum substitution on adsorption energy of water and water+methanol molecules on the $BaTaO_2N$ (110) surfaces.