

## Supporting Information

### Effect of Mg<sup>2+</sup> Substitution on Photocatalytic Water Splitting Activity of LaMg<sub>x</sub>Nb<sub>1-x</sub>O<sub>1+3x</sub>N<sub>2-3x</sub>

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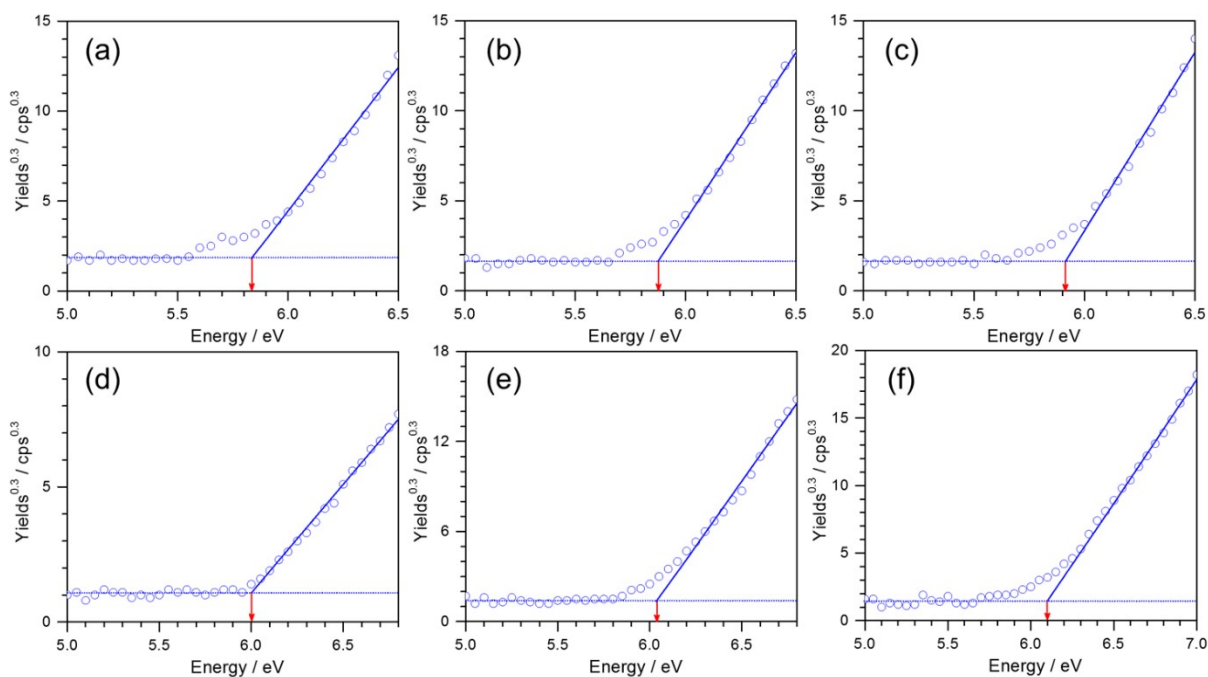
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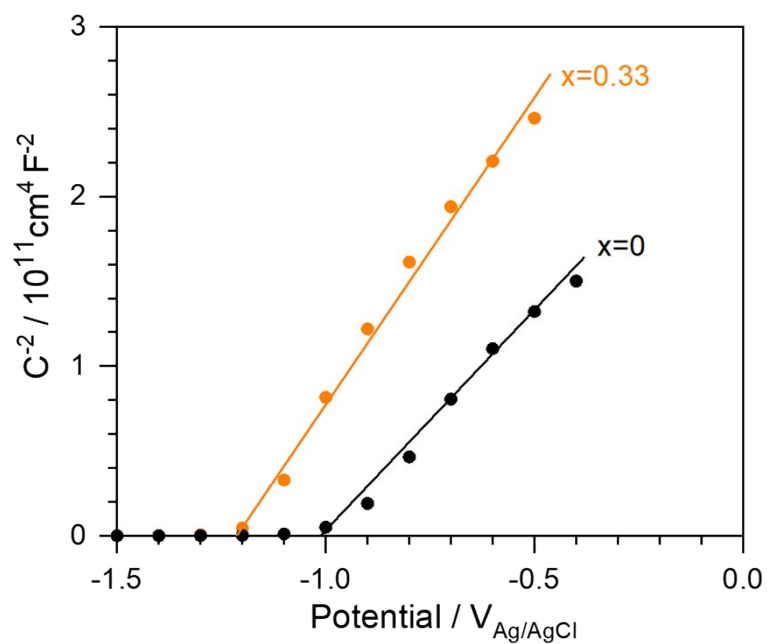
**Table S1.** Bulk elemental compositions for the synthesized  $\text{LaNbON}_2$  and  $\text{LaMg}_{1/3}\text{Nb}_{2/3}\text{O}_2\text{N}$  photocatalysts, prepared by thermal nitridation of the corresponding oxides at 1123 K for 8 h.

	Atomic ratio <sup>a)</sup>		
	La	Mg	Nb
$\text{LaNbON}_2$	1.00	-	1.09
$\text{LaMg}_{1/3}\text{Nb}_{2/3}\text{O}_2\text{N}$	1.00	0.34	0.68

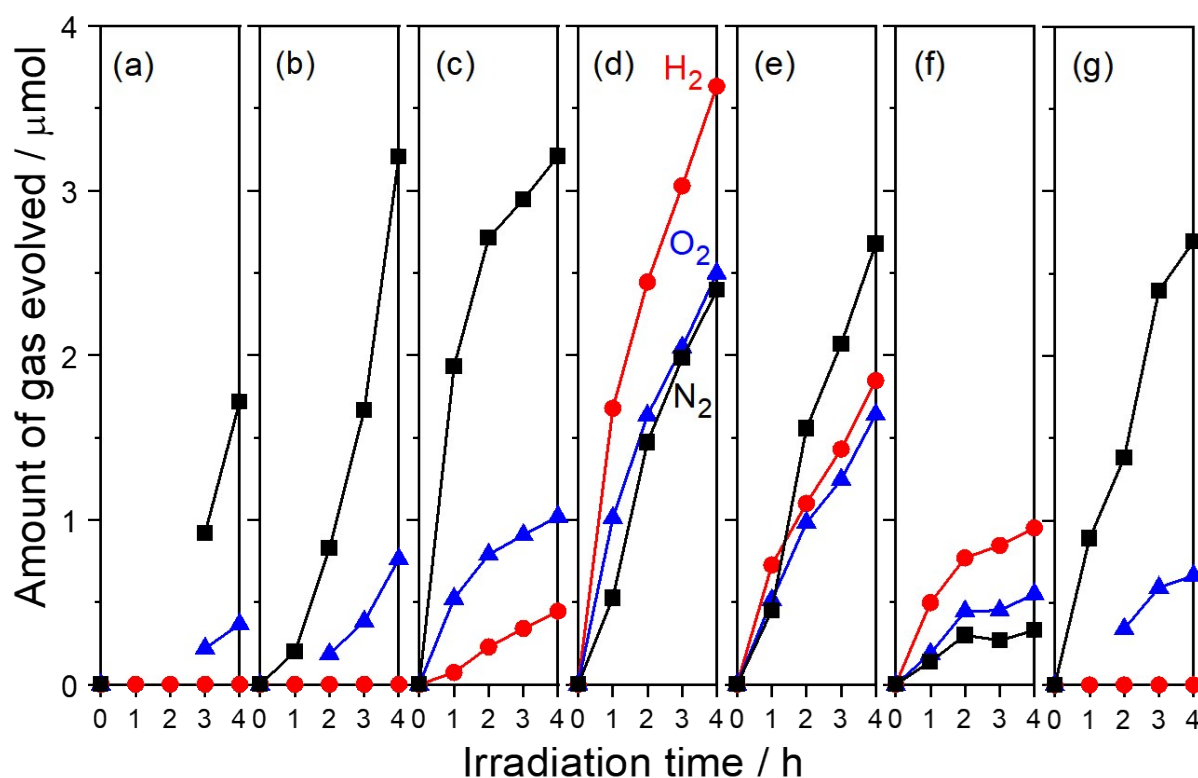
<sup>a)</sup> Determined by ICP-OES analysis.



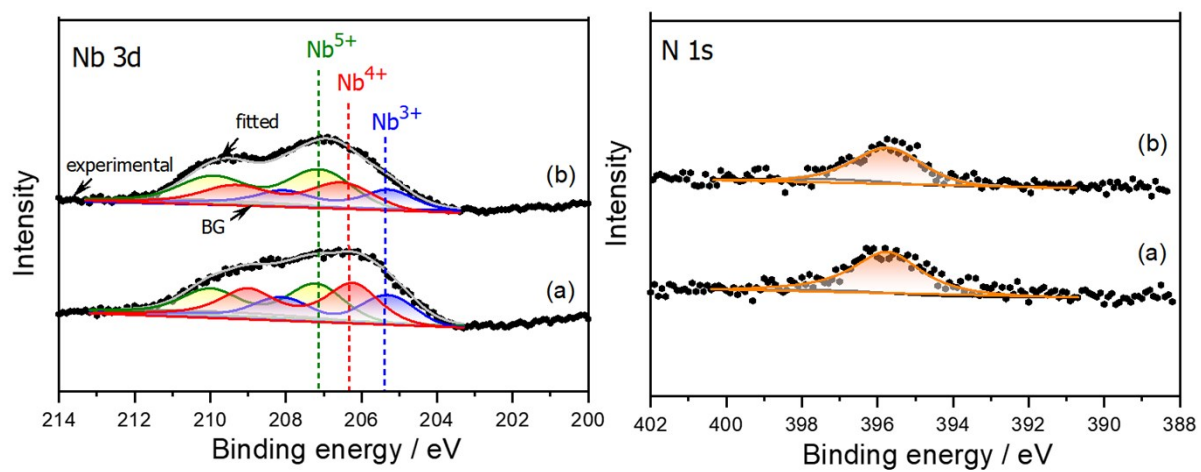
**Figure S1.** Photoelectron spectra in air acquired from  $\text{LaMg}_x\text{Nb}_{1-x}\text{O}_{1+3x}\text{N}_{2-3x}$  series with  $x =$  (a) 0, (b) 0.10, (c) 0.20, (d) 0.33, (e) 0.40 and (f) 0.50, prepared by thermal nitridation of the corresponding oxides at 1123 K for 8 h. The intersection of the background and yield lines indicates the valence band maximum (VBM) potential for each compound.



**Figure S2.** Mott-Schottky (MS) plots for bare  $\text{LaMg}_x\text{Nb}_{1-x}\text{O}_{1+3x}\text{N}_{2-3x}$  electrodes with  $x = 0$  and  $0.33$  at pH 13 at a frequency of 1 kHz. Pt wire and Ag/AgCl electrodes were used as a counter and reference electrodes, respectively. The measurements were carried out in an Ar-saturated 0.5 M potassium borate (KBi) aqueous electrolyte under dark condition. The MS plots were recorded by cathodically sweeping the potential with an AC amplitude of 15 mV.



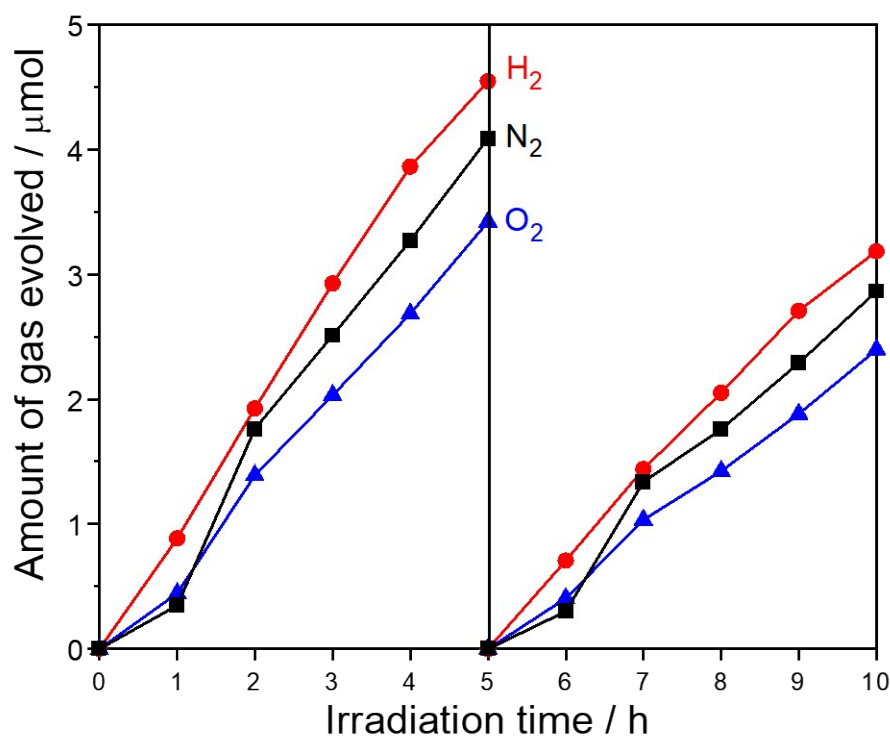
**Figure S3.** Gas evolution during water splitting on 0.2 g portions of  $\text{RhCrO}_y\text{-CoO}_z/\text{LaMg}_x\text{Nb}_{1-x}\text{O}_{1+3x}\text{N}_{2-3x}$  photocatalysts with  $x =$  (a) 0, (b) 0.1, (c) 0.2, (d) 0.33, (e) 0.4 and (f) 0.5, and (g) a blank trial without a catalyst. Data were acquired in a top-irradiation-type reaction vessel including 150 mL of pure water under 300 W Xe lamp irradiation ( $\lambda > 380$  nm). The oxynitride surfaces were modified with 0.2 wt%  $\text{RhCrO}_y$  and 0.1 wt%  $\text{CoO}_z$  as cocatalysts for  $\text{H}_2$  and  $\text{O}_2$  evolution, respectively.



**Figure S4.** Narrow-scan Nb 3d and N 1s XPS spectra obtained from  $\text{LaMg}_{1/3}\text{Nb}_{2/3}\text{O}_2\text{N}$  particles (a) before and (b) after water splitting reaction.

**Table S2.** Surface compositions of  $\text{LaMg}_x\text{Nb}_{1-x}\text{O}_{1+3x}\text{N}_{2-3x}$  photocatalysts with  $x = 0, 0.20, 0.33, 0.40$  and  $0.50$  as determined from the Nb 3d and N 1s XPS spectra in Figure 5 and Figure S4.

Mg <sup>2+</sup> contents	Surface N/Nb ratio	Fractions of surface Nb species			
		Nb <sup>5+</sup> /Nb <sub>total</sub>	Nb <sup>4+</sup> /Nb <sub>total</sub>	Nb <sup>3+</sup> /Nb <sub>total</sub>	(Nb <sup>4+</sup> +Nb <sup>3+</sup> )/Nb <sub>total</sub>
0	-	0.23	0.25	0.52	0.77
0.2	-	0.32	0.29	0.40	0.68
0.33	1.39	0.39	0.30	0.31	0.61
0.33, after reaction	1.41	0.39	0.31	0.30	0.61
0.4	-	0.47	0.31	0.21	0.52
0.5	-	0.73	0.26	0.00	0.26



**Figure S5.** Gas evolution during water splitting on 0.24 g portions of RhCrO<sub>y</sub>-CoO<sub>z</sub>/LaMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>2</sub>N catalysts in a top-irradiation-type reaction vessel including 150 mL of pure water and 0.2 g La<sub>2</sub>O<sub>3</sub> under visible light irradiation (300 W Xe lamp;  $\lambda > 420$  nm). The oxynitride surfaces were modified with 0.6 wt% RhCrO<sub>y</sub> and 0.3 wt% CoO<sub>z</sub> as cocatalysts for H<sub>2</sub> and O<sub>2</sub> evolution, respectively. After a 5 h reaction the vessel was evacuated and another 5 h reaction was carried out in the same manner.