Supporting Information – 8 pages

Aliovalent Gallium Dopants Remove Ti^{3+} Defects and Improve Photocatalytic and Photoelectrochemical Water Oxidation Properties of $LaTiO_2N$

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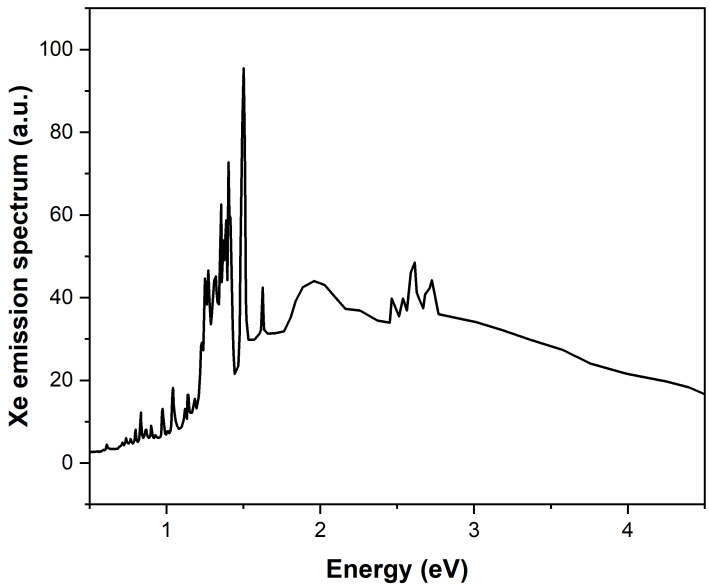


Figure S1. Emission spectrum of 300 W Xe arc lamp. The irradiance was calibrated to 100 mW cm^{-2} using the photocurrent from a commercial polycrystalline silicon photovoltaic cell.

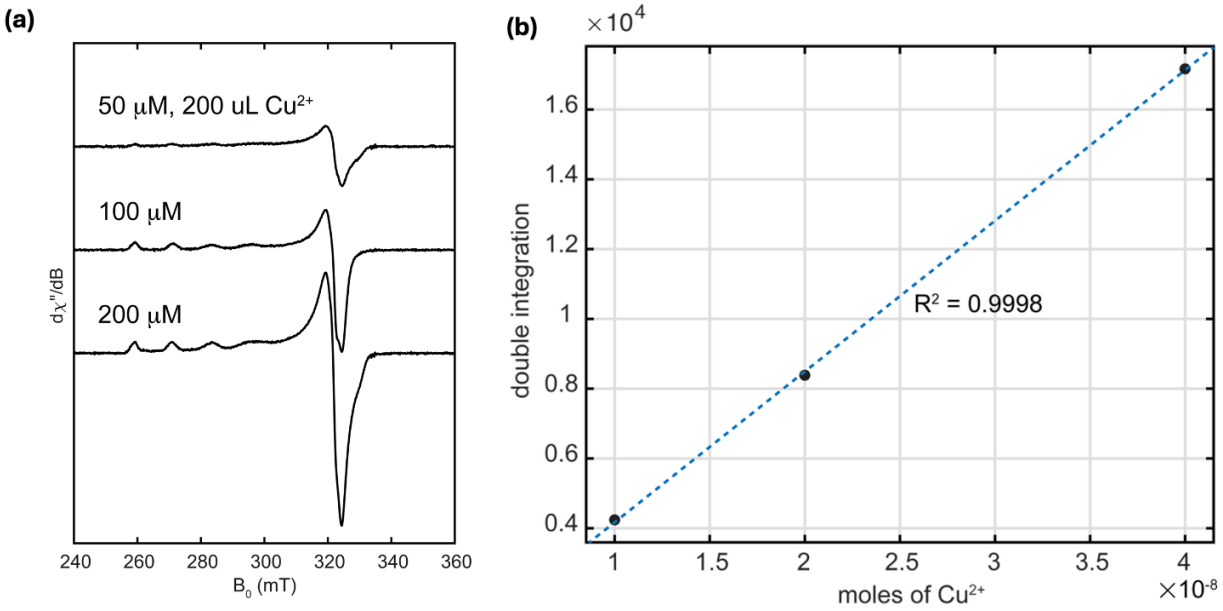


Figure S2. EPR spectra of $CuSO_4$ solutions in 20/80vol% ethylene glycol/H_2O and plot of EPR peak area versus $CuSO_4$ concentration.

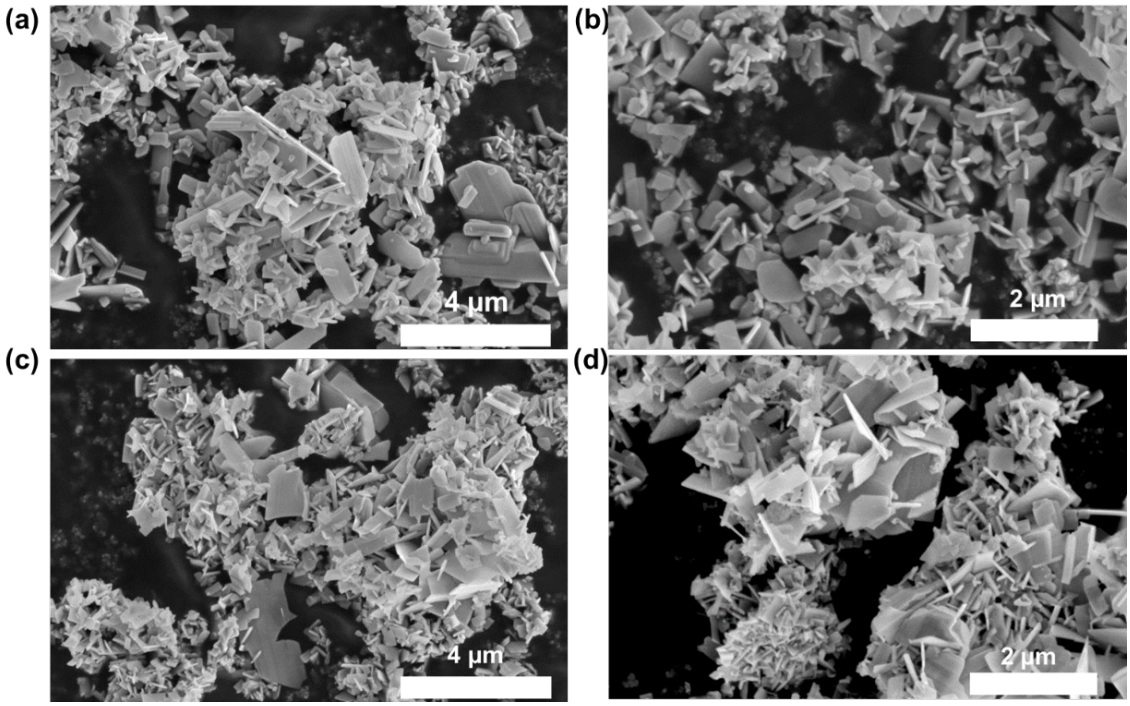


Figure S3. SEM images of $La_2Ti_2O_7$ and Ga-doped $La_2Ti_2O_7$ with different Ga concentrations. (a) $La_2Ti_2O_7$; (b) 2% Ga-$La_2Ti_2O_7$; (3) 5% Ga-$La_2Ti_2O_7$ and (d) 10% Ga-$La_2Ti_2O_7$.

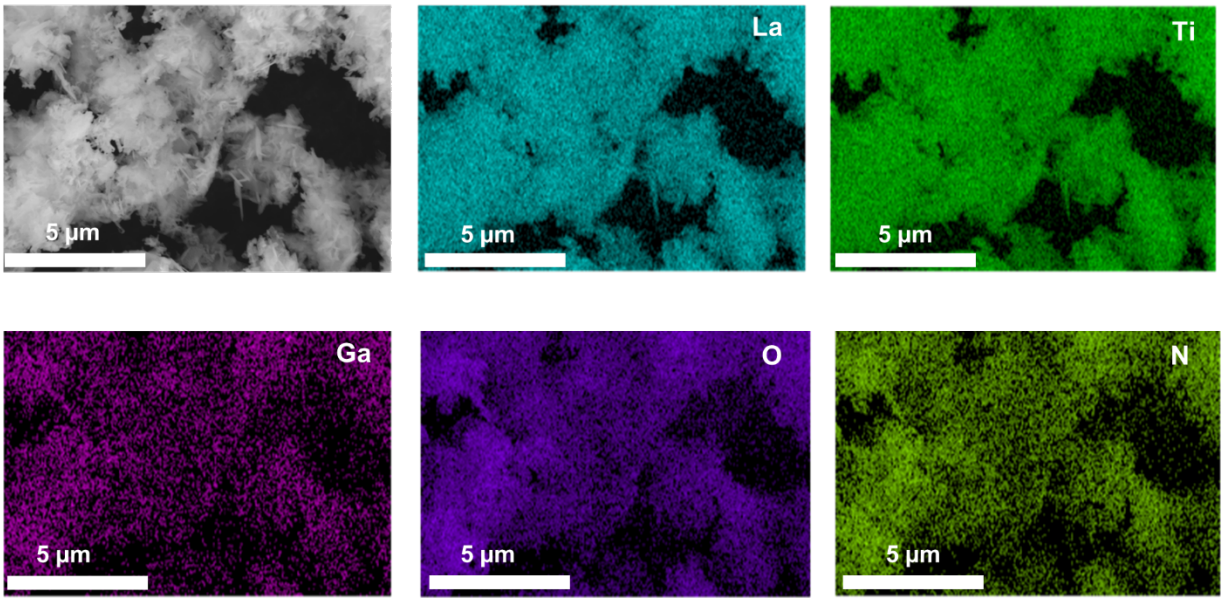


Figure S4. SEM-EDS elemental maps of 5% Ga-doped $LaTiO_2N$.

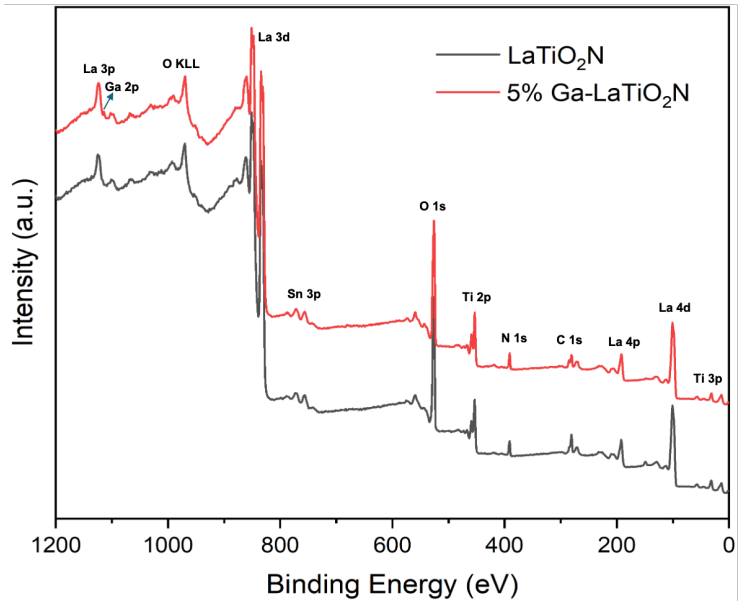
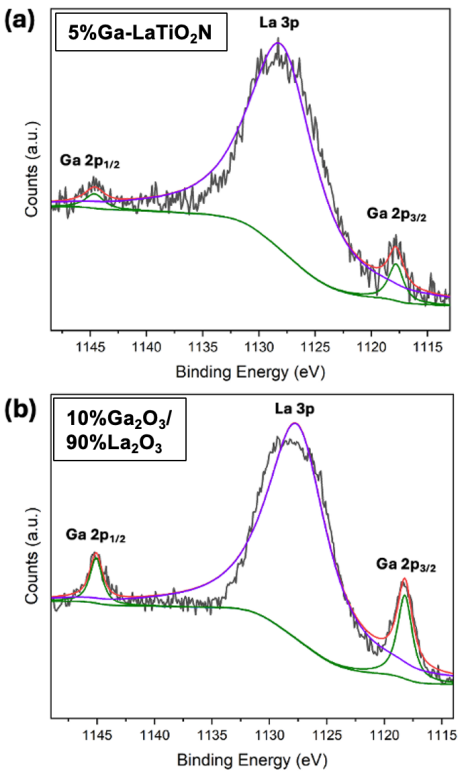


Figure S5. Survey XPS data for $LaTiO_2N$ and 5%Ga-$LaTiO_2N$. The Sn signal originates from the FTO substrate.



Peak	Position	Area
Ga $2p_{1/2}$	1144.6	1712.434
Ga $2p_{3/2}$	1117.8	3504.301
La 3p	1128.0	85019.520

Area ratio of Ga/La = (1712.434 + 3504.301)/85019.520 = 0.0614

Peak	Position	Area
Ga $2p_{1/2}$	1145.0	5621.022
Ga $2p_{3/2}$	1118.0	12270.130
La 3p	1127.6	126111.700

Area ratio of Ga/La = (5621.022 + 12270.130)/126111.700 = 0.14

Figure S6. High resolution XPS spectra and peak fits in the Ga 2p region for (a) 5%Ga-$LaTiO_2N$ and for (b) a homogeneous mixture of pure La_2O_3 and pure Ga_2O_3 (1:10 Ga/La mole ratio) with corresponding data in tables. The 10%(mol) Ga containing reference sample has an observed Ga : La XPS peak area ratio of 0.14. Based on the 0.0614 Ga : La XPS peak area ratio, the Ga concentration of the 5%Ga-doped $LaTiO_2N$ is 4.38%.

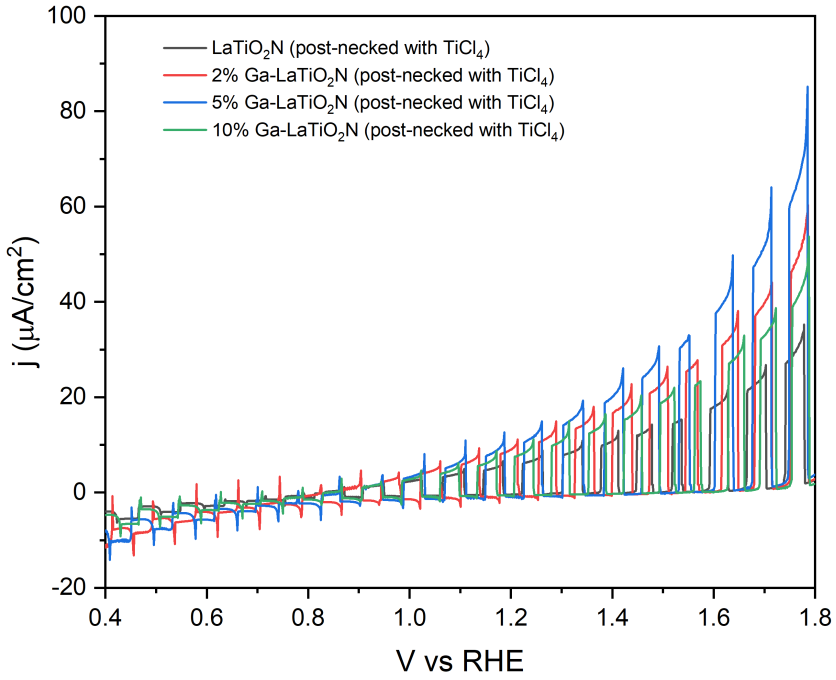


Figure S7. Linear sweep voltammetry (LSV) scans for $LaTiO_2N$ and Ga-doped $LaTiO_2N$ photoelectrodes under chopped at 100 mW cm^{-2} visible light (λ ≥ 420 nm) in 0.5 M Na_2SO_4 electrolyte.

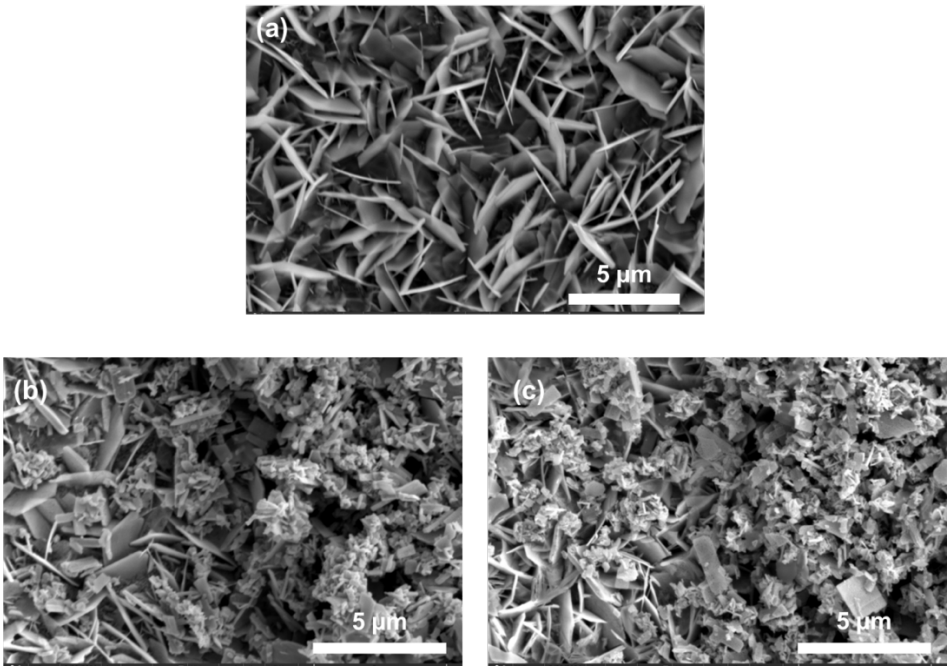


Figure S8. SEM images of (a) ZnO on FTO, (b) at the edges of FTO/ZnO/$LaTiO_2N$, and (c) for FTO/ZnO/5% Ga-doped $LaTiO_2N$.

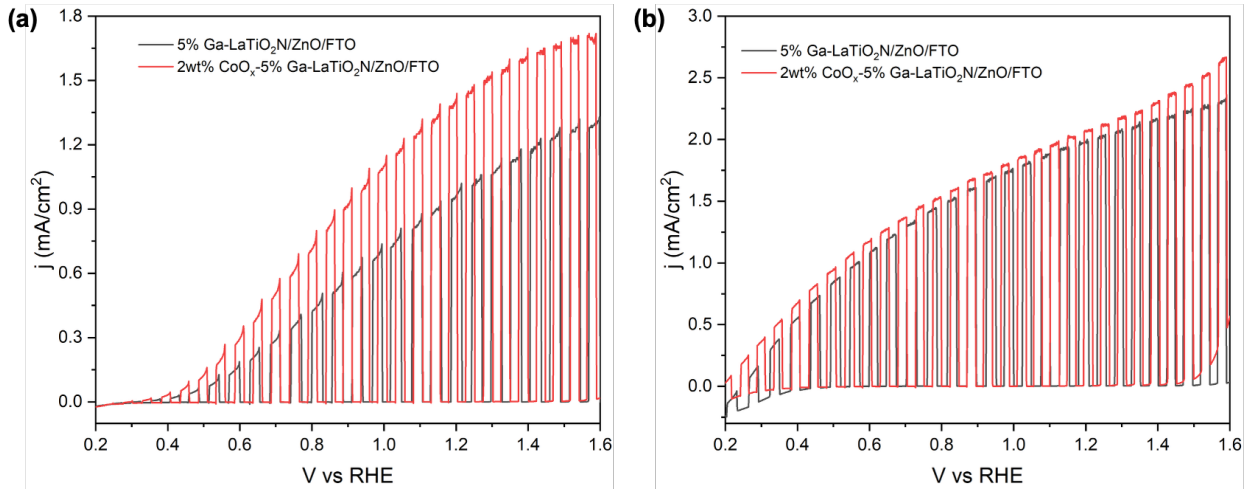


Figure S9. Linear sweep voltammetry (LSV) scans for photoelectrodes containing 5% Ga-doped FTO and 2 wt% CoO_x loaded 5% Ga-$LaTiO_2N$ under 100 mW cm^{-2} illumination from a 300 W Xe arc lamp in (a) 0.5 M Na_2SO_4 electrolyte and (b) 1 M NaOH electrolyte.

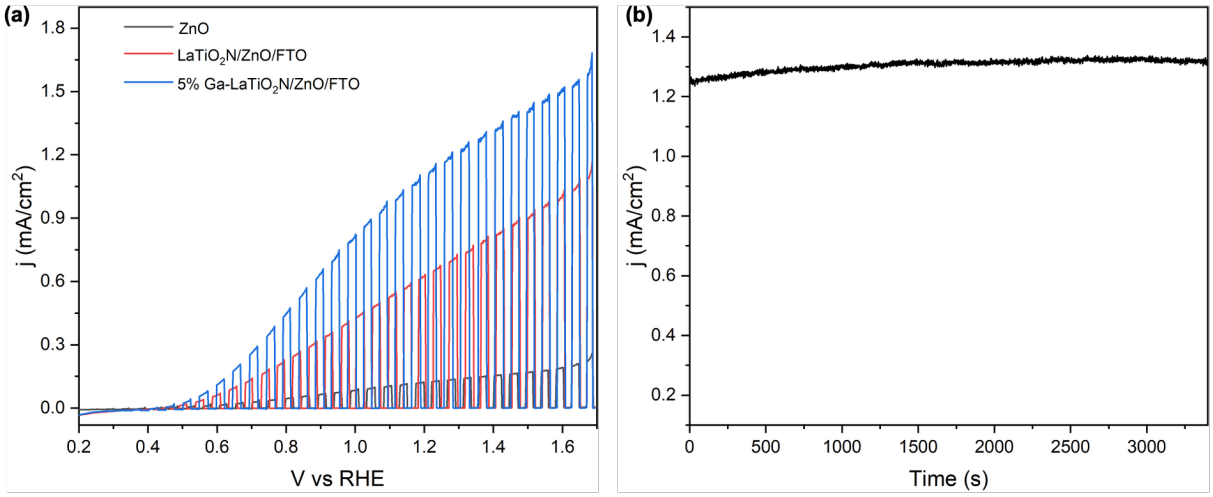


Figure S10. (a) PEC performance of as-prepared FTO/ZnO/$LaTiO_2N$ and 5% Ga-$LaTiO_2N$/ZnO/FTO photoelectrodes under under 100 mW cm^{-2} illumination (back illumination) in 0.5 M KBi electrolyte (pH=13). (b) Stability assessment for FTO/ZnO/5% Ga-$LaTiO_2N$ photoelectrode through chronoamperometric measurements at 1.30 V vs RHE in 0.5 M KBi solution (pH=13) under 100 mW cm^{-2} illumination. Based on a current of 1.2 mA cm^{-2} over a 3250 s period, 10 μmol of O_2 were evolved, corresponding to a turnover number of 3.7 for a ~1.0 μm thick $LaTiO_2N$ film on the 1.0 cm^2 electrode.

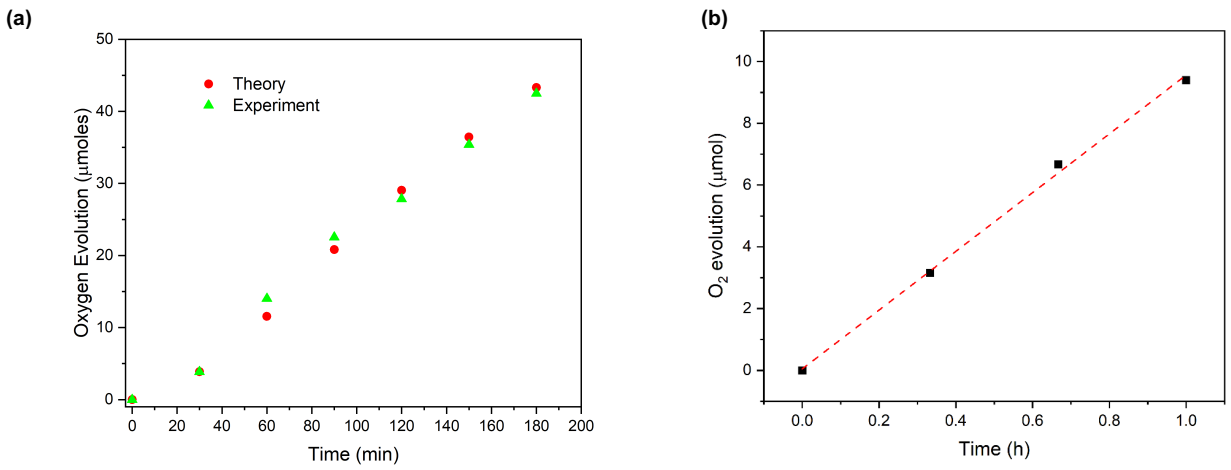


Figure S11. (a) Faradaic efficiency of FTO/ZnO/5%Ga-$LaTiO_2N$ photoelectrode in KBi solution. Oxygen values are summarized in **Table S1**. (b) O_2 evolution from 100 mg of 2 wt % CoO_x-loaded 5% Ga-doped $LaTiO_2N$ in 100 mL of 0.5 M $AgNO_3$ aqueous solution under 400 nm LED illumination (spectrum in **Figure S12**, light intensity: 15 mW cm^{-2}. Illumination area: 1.32 cm^2). Oxygen values are summarized in **Table S2**.

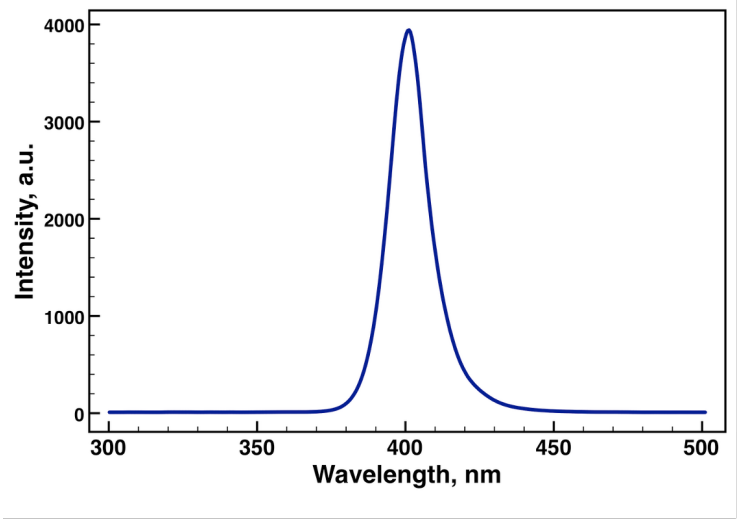


Figure S12. 400 nm LED emission spectrum (FWHM: ~ 15.4 nm).

Table S1. Oxygen Evolution data for FTO/ZnO/5%Ga-$LaTiO_2N$ photoelectrode

Time/min	O_2/μmol (experiment)	O_2/μmol (Theory)
0	-	-
30	3.86	3.86
60	14.02	11.55
90	22.55	20.83
120	27.86	29.04
150	35.37	36.45
180	42.49	43.30

Table S2. GC analysis for the AQE measurement. The photoreactor has a direct connection to the gas chromatograph (GC).

Time (min)	Integration area of O_2 gas peak	O_2/μmol
0	0	0
20	5.89	3.32
40	11.51	6.79
60	15.41	9.59