

## Supplementary Information: Table Captions

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| Sample                              | Lattice parameters (nm) |            |            | Cell volume (nm <sup>3</sup> ) | Average crystal size (nm) | $\chi^2$ | $R_{wp}$ | $R_p$ |
|-------------------------------------|-------------------------|------------|------------|--------------------------------|---------------------------|----------|----------|-------|
|                                     | <i>a</i>                | <i>b</i>   | <i>c</i>   |                                |                           |          |          |       |
| LaTiO <sub>2</sub> N <sup>(a)</sup> | 0.55699(1)              | 0.78648(1) | 0.56014(1) | 0.2454                         | 39                        | 2.27     | 9.30     | 6.64  |
| <i>Ca<sup>2+</sup>-backfilled</i>   |                         |            |            |                                |                           |          |          |       |
| 5% Ca <sup>2+</sup> <sup>(a)</sup>  | 0.55663(1)              | 0.78589(2) | 0.55987(1) | 0.2449                         | 46                        | 2.36     | 10.8     | 8.09  |
| 10% Ca <sup>2+</sup> <sup>(a)</sup> | 0.55641(1)              | 0.78609(1) | 0.55958(1) | 0.2448                         | 51                        | 1.79     | 9.87     | 7.25  |
| 20% Ca <sup>2+</sup> <sup>(b)</sup> | 0.55634(1)              | 0.78590(1) | 0.55884(1) | 0.2443                         | 72                        | 3.27     | 4.86     | 3.69  |
| 30% Ca <sup>2+</sup> <sup>(b)</sup> |                         |            |            |                                |                           |          |          |       |
| Phase 1 (59%)                       | 0.55873(2)              | 0.78418(2) | 0.55560(1) | 0.2434                         | 37                        | 1.62     | 4.28     | 3.33  |
| Phase 2 (41%)                       | 0.55449(1)              | 0.78125(1) | 0.55368(1) | 0.2399                         | 86                        |          |          |       |
| <i>Ca<sup>2+</sup>-substituted</i>  |                         |            |            |                                |                           |          |          |       |
| 5% Ca <sup>2+</sup> <sup>(a)</sup>  | 0.55632(1)              | 0.78590(1) | 0.55959(1) | 0.2447                         | 41                        | 1.99     | 9.37     | 6.61  |
| 10% Ca <sup>2+</sup> <sup>(a)</sup> | 0.55606(1)              | 0.78531(1) | 0.55900(1) | 0.2441                         | 42                        | 1.49     | 10.4     | 7.59  |
| 20% Ca <sup>2+</sup> <sup>(b)</sup> | 0.55558(1)              | 0.78404(1) | 0.55711(1) | 0.2427                         | 57                        | 2.59     | 5.77     | 4.36  |
| 30% Ca <sup>2+</sup> <sup>(b)</sup> | 0.55419(0)              | 0.78229(1) | 0.55589(1) | 0.2410                         | 75                        | 3.71     | 4.96     | 3.78  |
| <i>Ca<sup>2+</sup>-excessive</i>    |                         |            |            |                                |                           |          |          |       |
| 5% Ca <sup>2+</sup> <sup>(a)</sup>  | 0.55706(1)              | 0.78677(2) | 0.55976(1) | 0.2453                         | 47                        | 1.34     | 9.88     | 7.45  |

<sup>(a)</sup> X-rays from synchrotron source (0.501541 Å)

<sup>(b)</sup> X-rays from lab source (1.540598 Å)

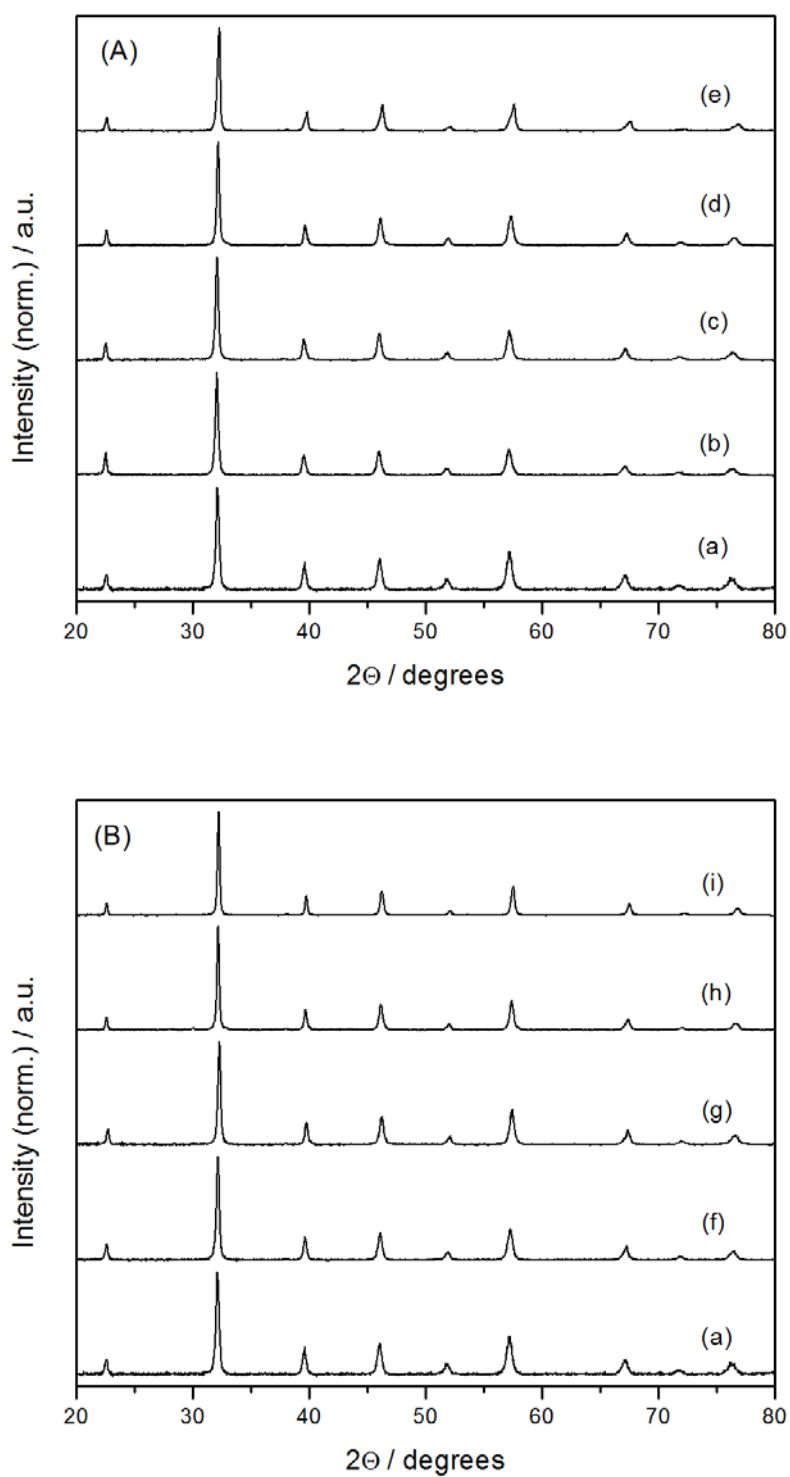
### Supplementary Information: Figure Captions

**Figure S1:** XRD pattern of the oxynitrides. (A)  $\text{Ca}^{2+}$ -backfilled  $\text{LaTiO}_2\text{N}$  with  $\text{Ca}^{2+}$  contents of (a) 0%, (b) 5%, (c) 10%, (d) 20%, and (e) 30%. (B)  $\text{Ca}^{2+}$ -substituted  $\text{LaTiO}_2\text{N}$  with  $\text{Ca}^{2+}$  contents of (a) 0%, (f) 5%, (g) 10%, (h) 20%, and (i) 30%.

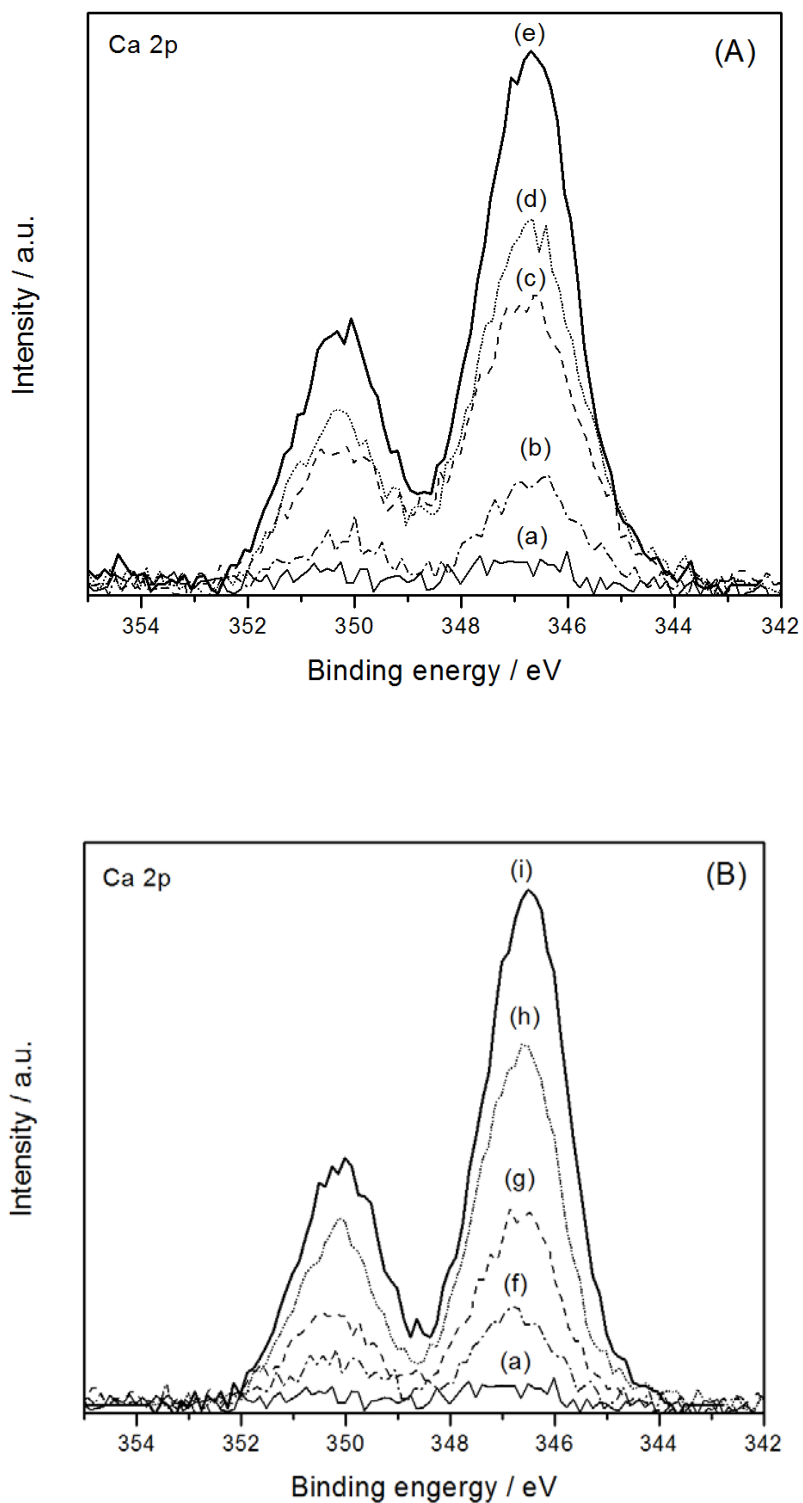
**Figure S2:** XPS detail spectra of the Ca 2p peak. (A)  $\text{Ca}^{2+}$ -backfilled  $\text{LaTiO}_2\text{N}$  with  $\text{Ca}^{2+}$  contents of (a) 0%, (b) 5%, (c) 10%, (d) 20%, and (e) 30%. (B)  $\text{Ca}^{2+}$ -substituted  $\text{LaTiO}_2\text{N}$  with  $\text{Ca}^{2+}$  contents of (a) 0%, (f) 5%, (g) 10%, (h) 20%, and (i) 30%.

**Figure S3:** XPS detail spectra of the Ti 2p peak with (a)  $\text{LaTiO}_{3.5}$ , (b) 30%  $\text{Ca}^{2+}$ -substituted, (c) 30%  $\text{Ca}^{2+}$ -backfilled, and (d) unsubstituted  $\text{LaTiO}_2\text{N}$ .

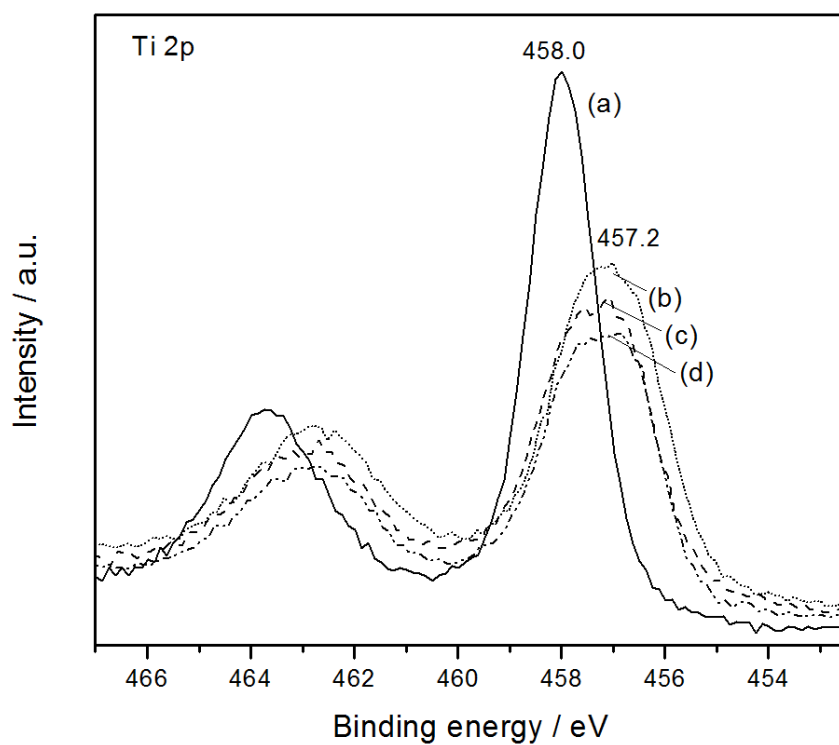
**Figure S4:** Diffuse reflectance spectra at  $\text{Ca}^{2+}$  contents of (A) 10%, (B) 20%, and (C) 30% with (a) unsubstituted, (b)  $\text{Ca}^{2+}$ -backfilled, and (c)  $\text{Ca}^{2+}$ -substituted  $\text{LaTiO}_2\text{N}$ .



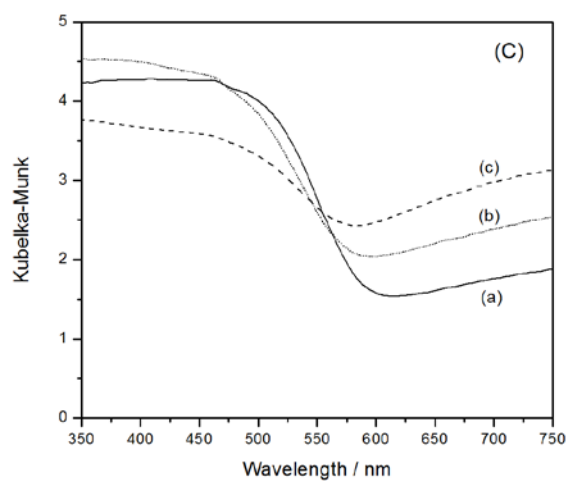
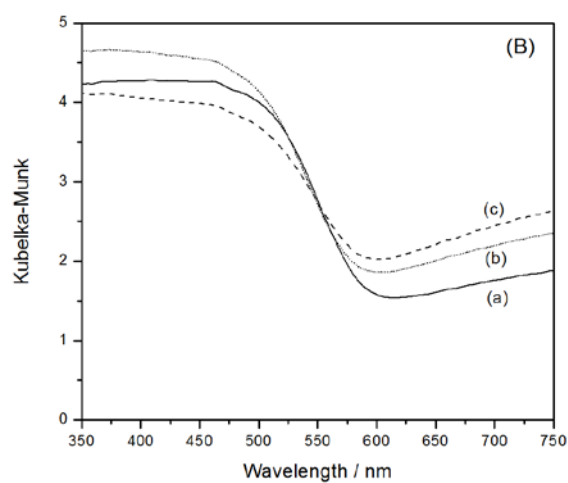
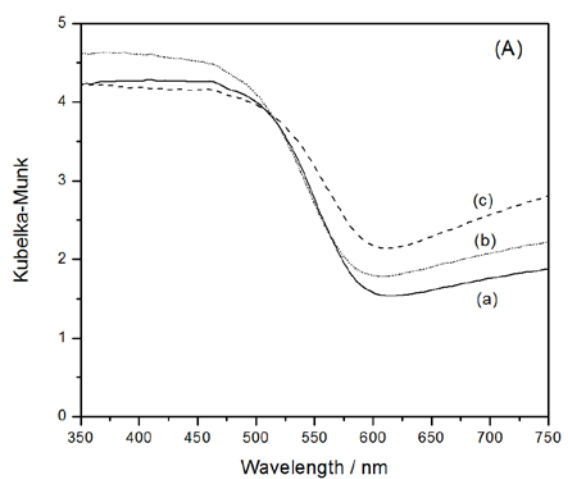
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