Electronic Supplementary Material (ESI) for Nanoscale Advances.


# Defect Engineering of Two-dimensional Nb-based Oxynitrides for Visible-light-driven Water Splitting to Produce $H_2$ and $O_2$

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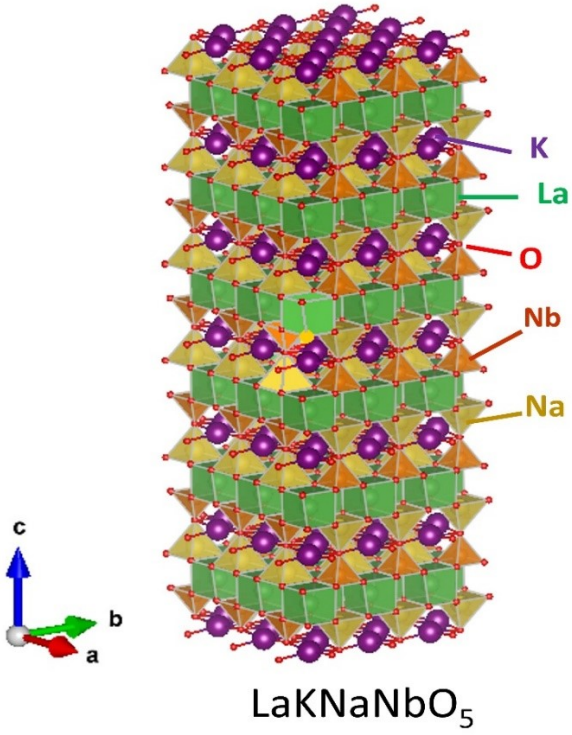
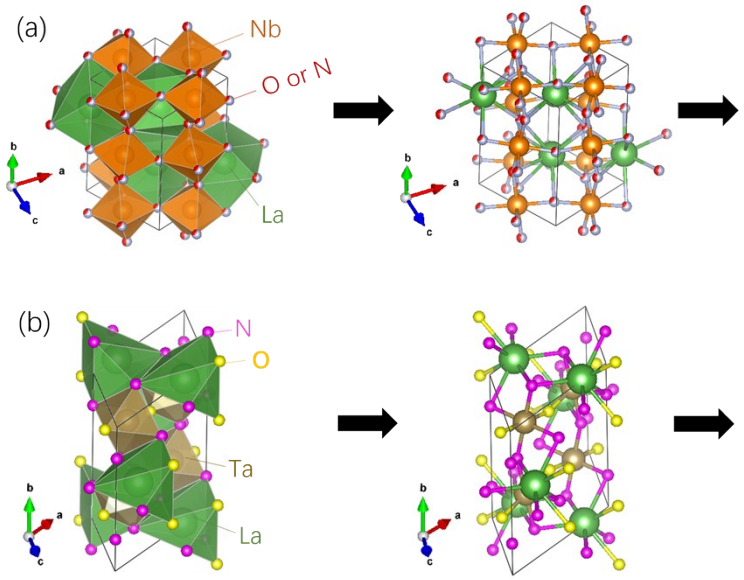



**Figure S1.** Crystal structure of $LaKNaNbO_5$.




| a(Å) | b(Å) | c(Å) |
|---|---|---|
| 5.7221 | 8.0684 | 5.7428 |
| α | β | γ |
| 90° | 90° | 90° |

Orthorhombic structure

| a(Å) | b(Å) | c(Å) |
|---|---|---|
| 8.0922 | 8.0603 | 5.7118 |
| α | β | γ |
| 90° | 134.8150° | 90° |

Monoclinic structure

**Figure S2.** Crystal structure of $LaNbON_2$ and $LaTaON_2$ with polyhedral and ball and stick model and the corresponding unit cell parameters.

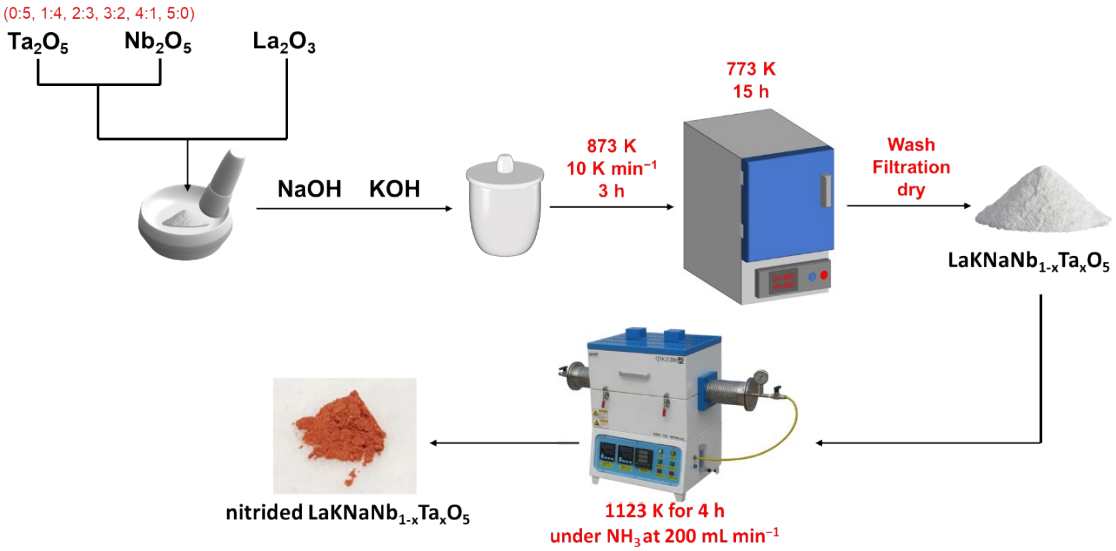



**Figure S3**. The synthesis procedure scheme of $LaKNaNb_{1-x}Ta_xO_5$ oxide precursors and nitrided $LaKNaNb_{1-x}Ta_xO_5$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0).

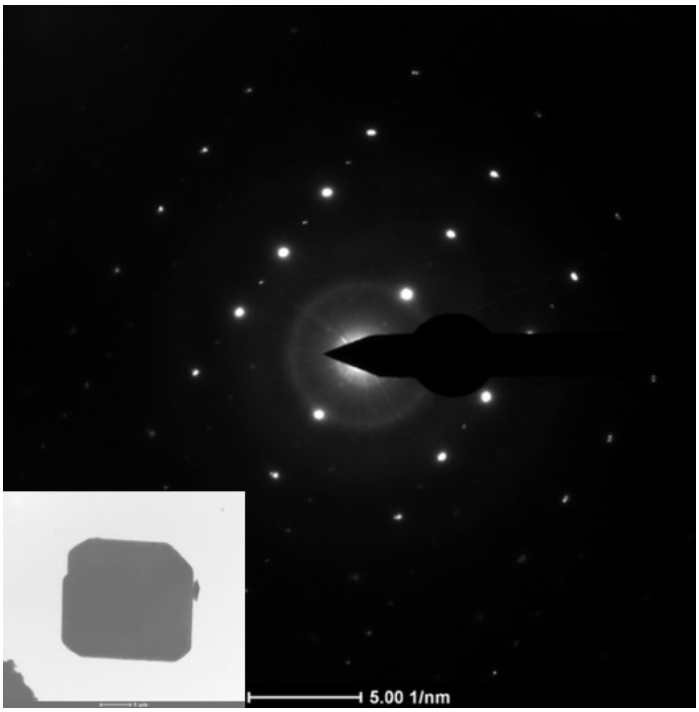



**Figure S4.** TEM image (inset) of the layered $LaKNaNb_{1-x}Ta_xO_5$ heated at 873 K for 3 h and maintained at 773 K for 15 and corresponding electron diffraction pattern.

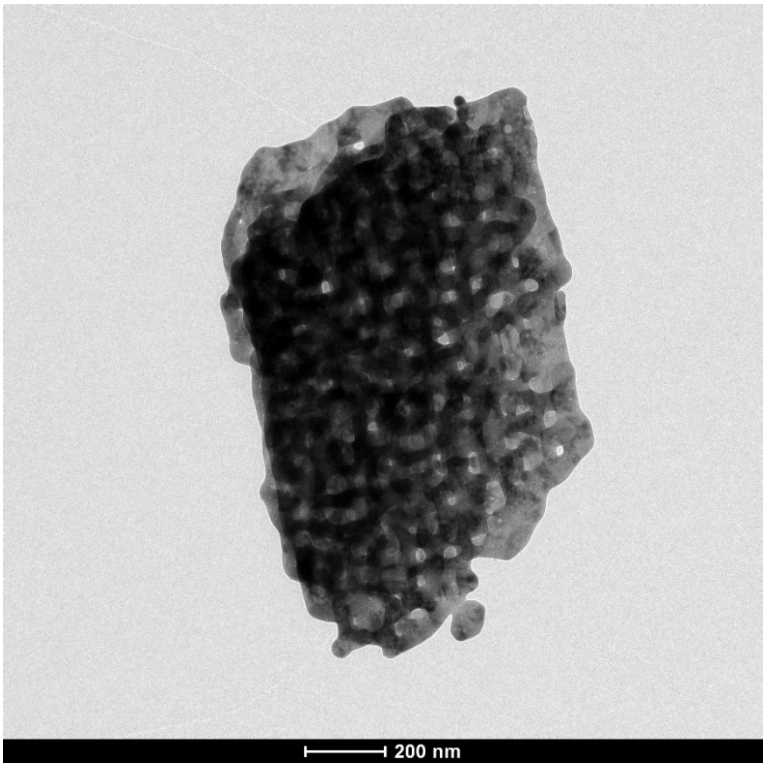



**Figure S5.** TEM image of the layered $LaKNaNb_{0.8}Ta_{0.2}O_5$ after nitridation at 1123 K for 4 h.

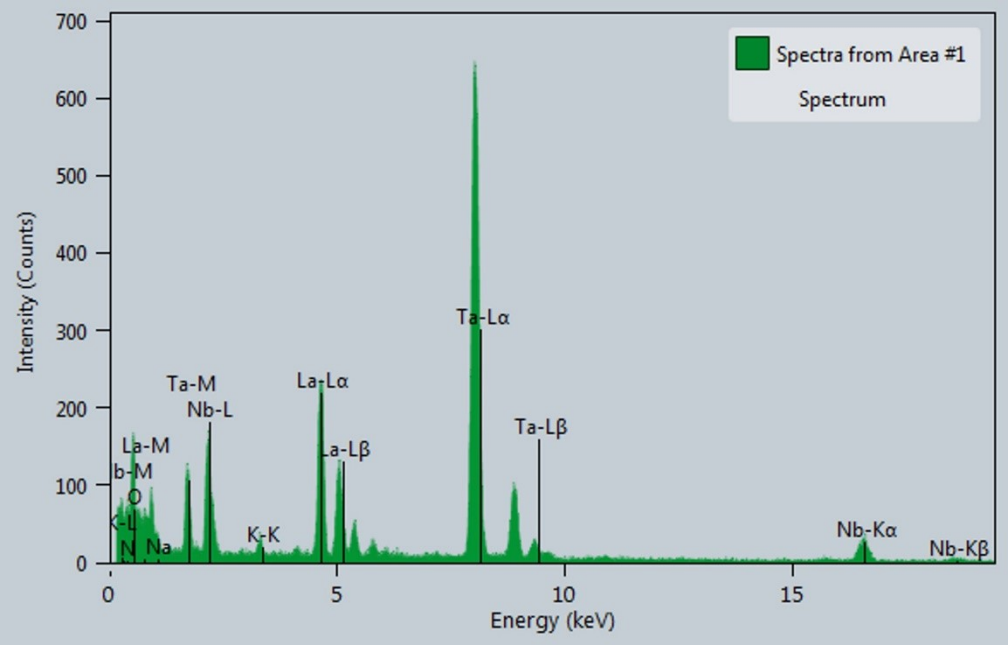



**Figure S6.** The EDS spectra of $LaKNaNb_{0.8}Ta_{0.2}O_5$ after nitridation at 1123 K for 4 h.

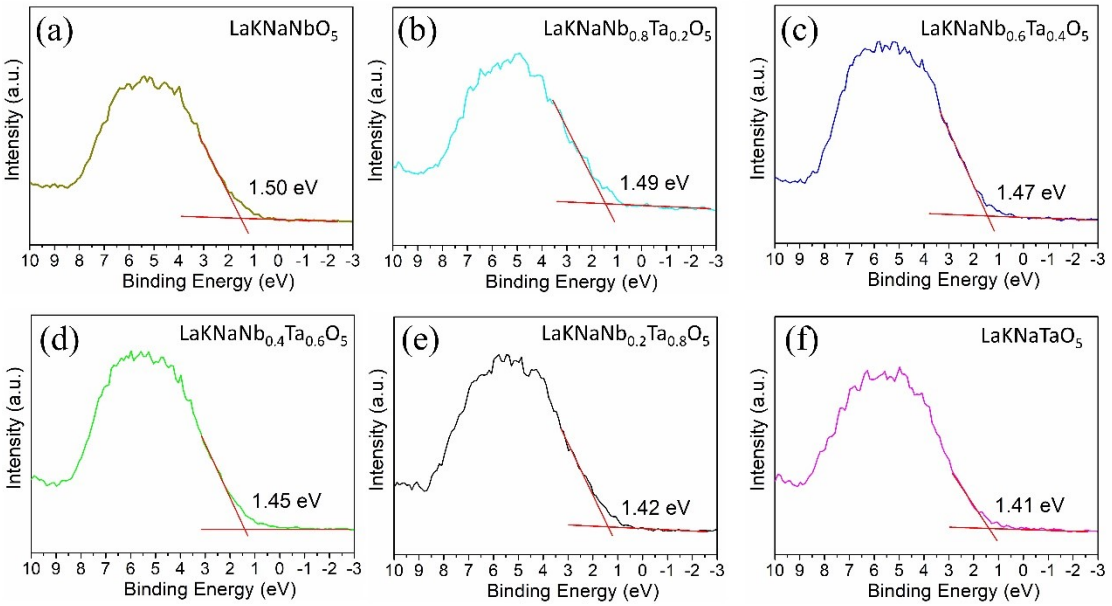



**Figure S7.** Valence band XPS spectra of (a) $LaKNaNbO_5$, (b) nitrided $LaKNaNb_{0.8}Ta_{0.2}O_5$, (c) nitrided $LaKNaNb_{0.6}Ta_{0.4}O_5$, (d) nitrided $LaKNaNb_{0.4}Ta_{0.6}O_5$, (e) nitrided $LaKNaNb_{0.2}Ta_{0.8}O_5$ and (f) nitrided $LaKNaTaO_5$.

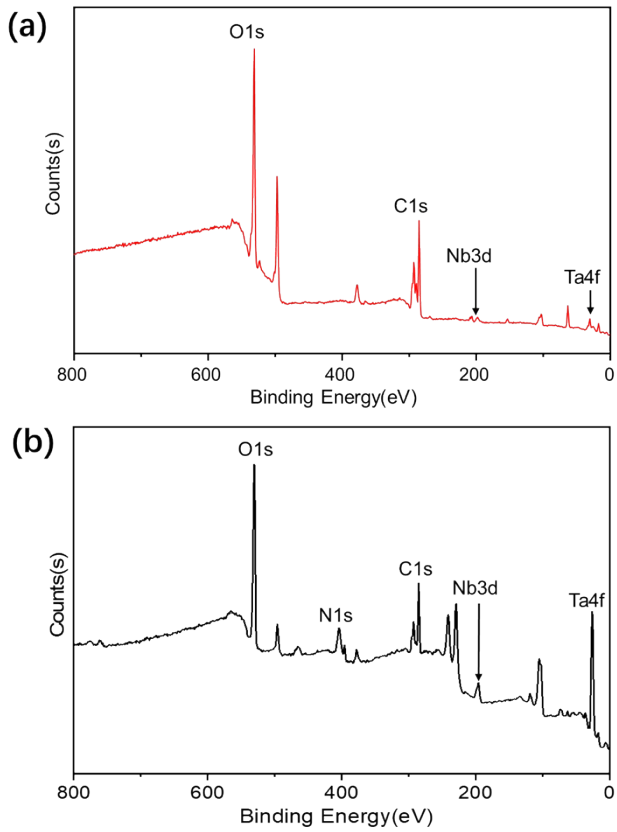



**Figure S8.** XPS survey spectra of (a) $LaKNaNb_{0.8}Ta_{0.2}O_5$ and $LaKNaNb_{0.8}Ta_{0.2}O_5$ nitrided at 1123 K for 4 h.

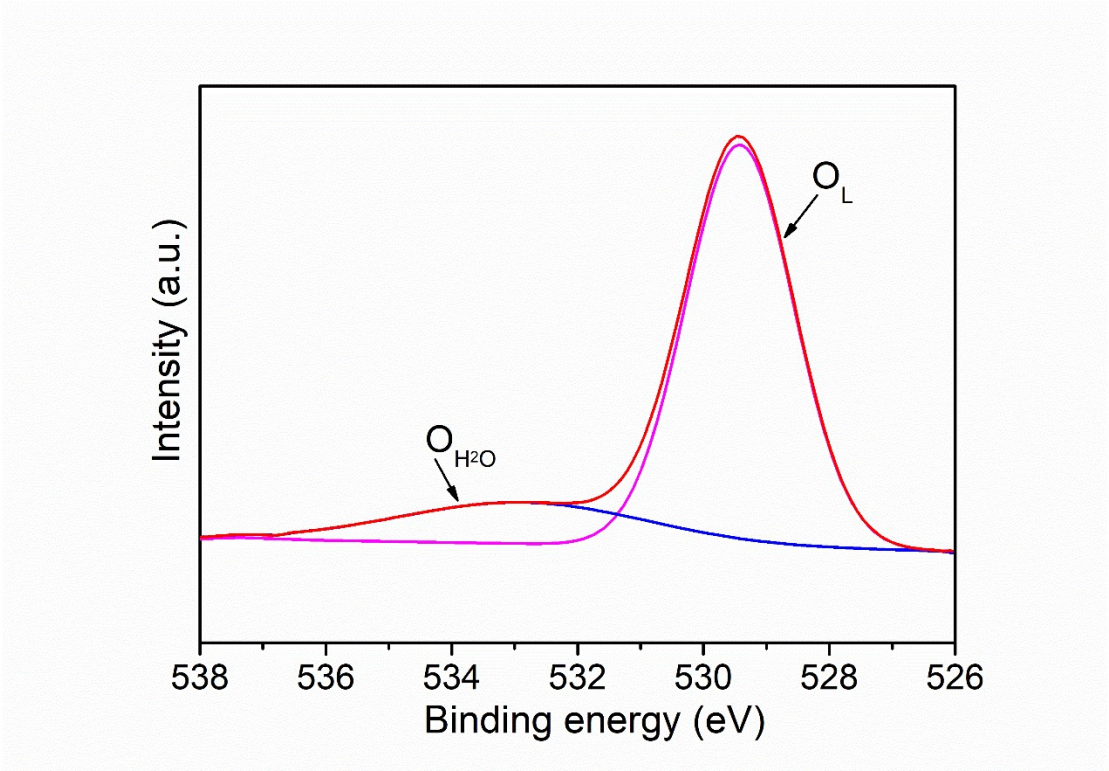



**Figure S9.** High-resolution XPS spectra of O 1s for $LaKNaNbO_5$

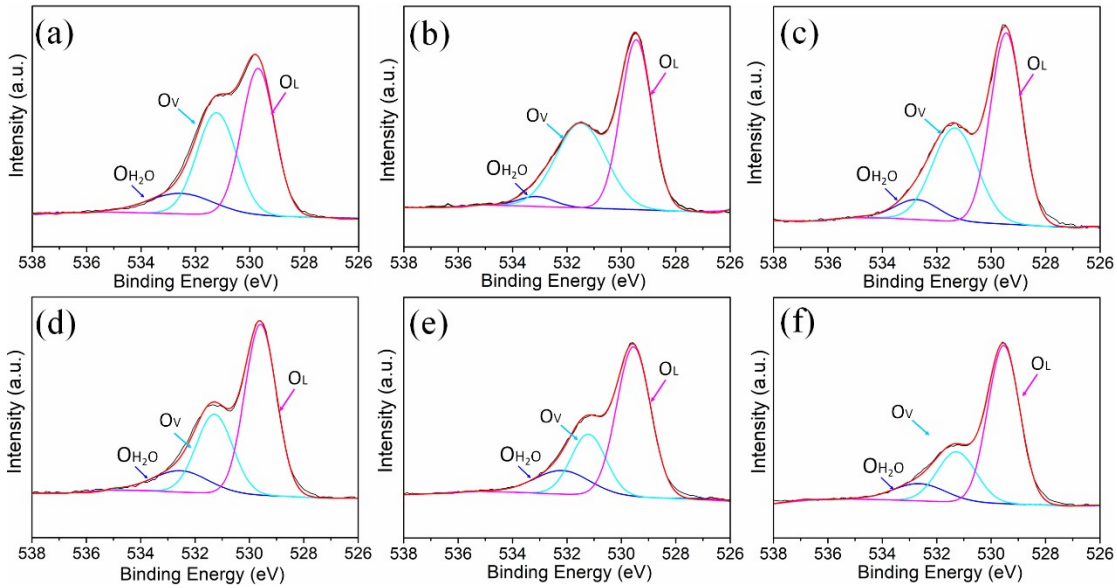



**Figure S10.** High-resolution XPS spectra of O 1s for the nitrided $LaKNaNbO_5$ (a), the nitrided $LaKNaNb_{0.8}Ta_{0.2}O_5$ (b), the nitrided $LaKNaNb_{0.6}Ta_{0.4}O_5$ (c), the nitrided $LaKNaNb_{0.4}Ta_{0.6}O_5$ (d), the nitrided $LaKNaNb_{0.2}Ta_{0.8}O_5$ (e) and the nitrided $LaKNaTaO_5$ (f) nitrided at 1123 K for 4 h.

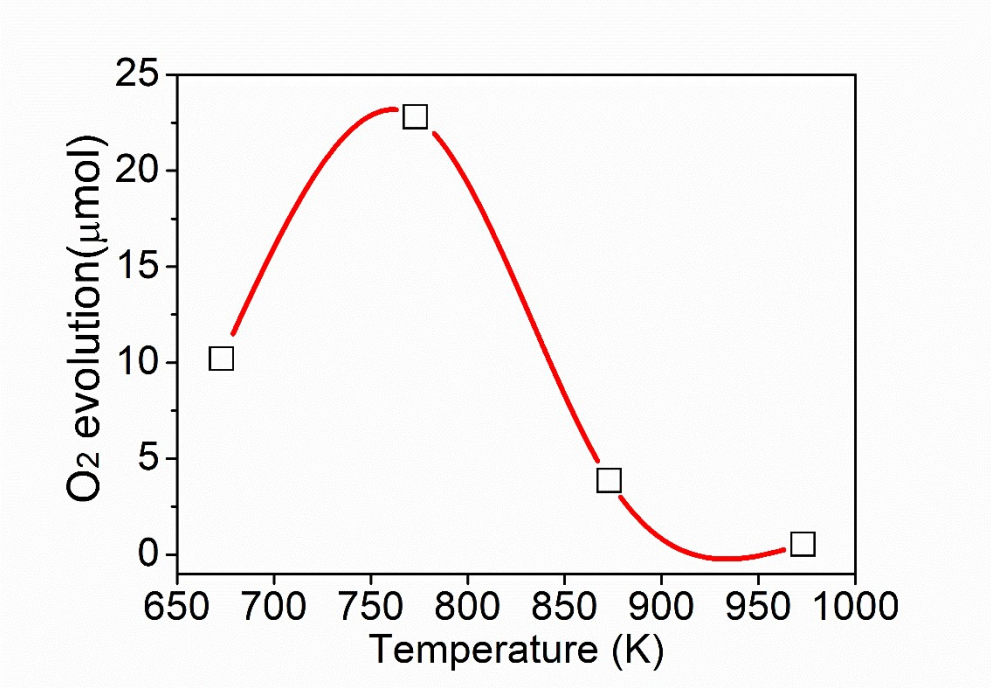



**Figure S11.** $O_2$ evolution rates for $CoO_x$ modified the nitrided $LaKNaNbO_5$ treated at different temperature for 2 h.

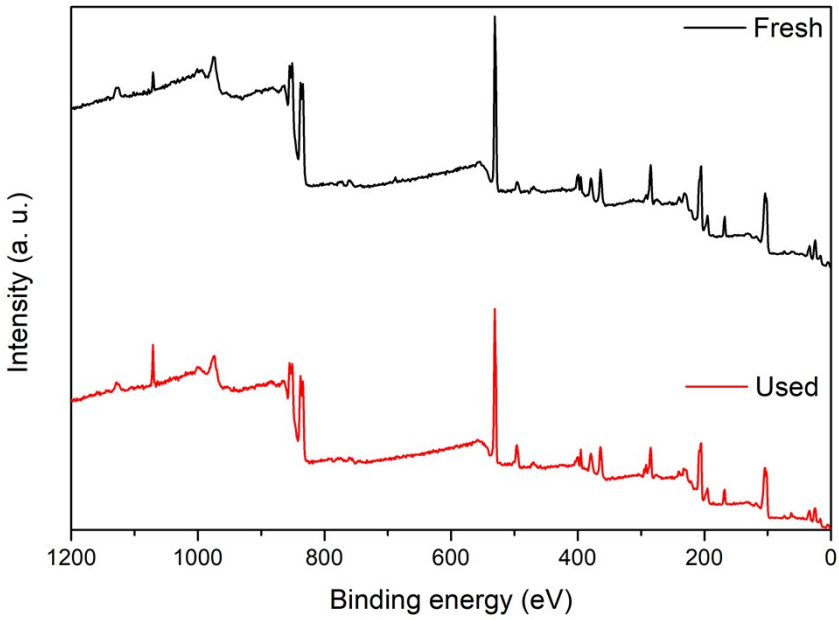



**Figure S12**. XPS survey of fresh and used nitrided $LaKNaNb_{0.8}Ta_{0.2}O_5$ after photoreaction.

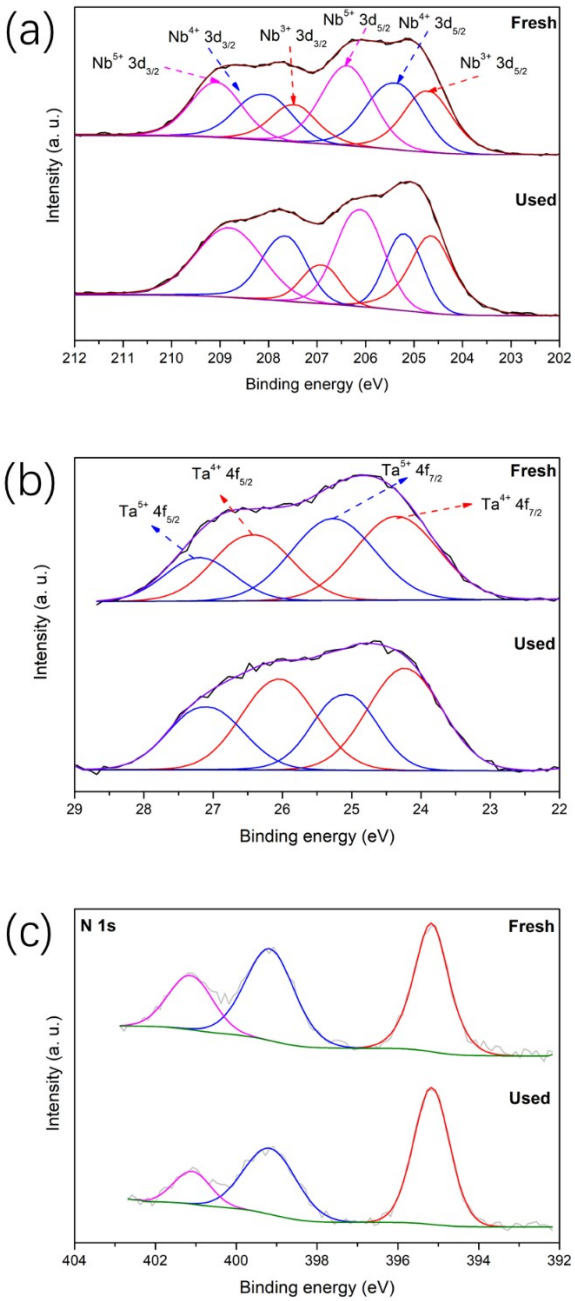



**Figure S13**. XPS Nb 3d (a), Ta 4f (b) and N 1s (c) of fresh and used nitrided $LaKNaNb_{0.8}Ta_{0.2}O_5$ after photoreaction.

**Table S1.** The values of bandgap, VBE and CBE calculated from UV-vis DRS and VB-XPS spectra.

| Samples | Bandgap (eV) | VBE (eV) | CBE (eV) |
|---|---|---|---|
| $LaKNaNbO_5$ | 1.77 | 1.50 | -0.27 |
| $LaKNaNb_{0.8}Ta_{0.2}O_5$ | 1.84 | 1.49 | -0.35 |
| $LaKNaNb_{0.6}Ta_{0.4}O_5$ | 1.86 | 1.47 | -0.39 |
| $LaKNaNb_{0.4}Ta_{0.6}O_5$ | 1.89 | 1.45 | -0.44 |
| $LaKNaNb_{0.2}Ta_{0.8}O_5$ | 1.96 | 1.42 | -0.54 |
| $LaKNaTaO_5$ | 2.12 | 1.45 | -0.67 |

**Table S2.** Fractions of Nb species obtained from the XPS Nb 3d deconvolution regions for the nitrided $LaKNaNb_{1-x}Ta_xO_5$.

| Samples | Nb 3d $_{3/2}$ | | | Nb 3d $_{5/2}$ | | |
|---|---|---|---|---|---|---|
| | $Nb^{5+}3d_{3/2}$ | $Nb^{4+}3d_{3/2}$ | $Nb^{3+}3d_{3/2}$ | $Nb^{5+}3d_{5/2}$ | $Nb^{4+}3d_{5/2}$ | $Nb^{3+}3d_{5/2}$ |
| $LaKNaNbO_5$ | 8.51% | 9.80% | 15.59% | 9.43% | 25.69% | 30.98% |
| $LaKNaNb_{0.8}Ta_{0.2}O_5$ | 4.37% | 17.64% | 12.62% | 11.18% | 24.67% | 29.52% |
| $LaKNaNb_{0.6}Ta_{0.4}O_5$ | 13.78% | 11.23% | 21.35% | 11.13% | 23.25% | 19.25% |
| $LaKNaNb_{0.4}Ta_{0.6}O_5$ | 15.41% | 15.21% | 11.37% | 17.88% | 20.92% | 19.21% |
| $LaKNaNb_{0.2}Ta_{0.8}O_5$ | 26.98% | 12.48% | 9.14% | 24.41% | 15.75% | 11.24% |
| $LaKNaTaO_5$ | 0 | 0 | 0 | 0 | 0 | 0 |

**Table S3.** Fractions of Ta species obtained from the XPS Ta 4f deconvolution regions for the nitrided $LaKNaNb_{1-x}Ta_xO_5$.

| Samples | Ta 4f $_{5/2}$ | | Ta 4f $_{7/2}$ | |
|---|---|---|---|---|
| | $Ta^{5+}$ 4f $_{5/2}$ | $Ta^{4+}$ 4f $_{5/2}$ | $Ta^{5+}$ 4f $_{7/2}$ | $Ta^{4+}$ 4f $_{7/2}$ |
| $LaKNaNbO_5$ | 0 | 0 | 0 | 0 |
| $LaKNaNb_{0.8}Ta_{0.2}O_5$ | 11.32% | 32.58% | 17.96% | 38.14% |
| $LaKNaNb_{0.6}Ta_{0.4}O_5$ | 12.39% | 30.95% | 24.33% | 32.33% |
| $LaKNaNb_{0.4}Ta_{0.6}O_5$ | 19.08% | 27.76% | 24.50% | 28.66% |
| $LaKNaNb_{0.2}Ta_{0.8}O_5$ | 23.56% | 22.22% | 28.71% | 25.51% |
| $LaKNaTaO_5$ | 33.39% | 11.92% | 40.76% | 13.92% |

**Table S4.** Fractions of O species obtained from the XPS O1s deconvolution regions for the nitrided $LaKNaNb_{1-x}Ta_xO_5$.

| **Samples** | **Area（$O_L$）** | **Area（$O_V$）** | **Area（$O_{H2O}$）** |
|---|---|---|---|
| $LaKNaNbO_5$ | 47.67% | 43.27% | 9.06% |
| $LaKNaNb_{0.8}Ta_{0.2}O_5$ | 53.45% | 39.00% | 7.55% |
| $LaKNaNb_{0.6}Ta_{0.4}O_5$ | 54.81% | 37.48% | 7.71% |
| $LaKNaNb_{0.4}Ta_{0.6}O_5$ | 57.07% | 30.51% | 12.42% |
| $LaKNaNb_{0.2}Ta_{0.8}O_5$ | 59.72% | 25.03% | 15.25% |
| $LaKNaTaO_5$ | 65.88% | 20.75% | 13.37% |

**Table S5.** Photocatalytic $H_2$ and $O_2$ evolution rates over the nitrided $LaKNaNb_{1-x}Ta_xO_5$ at 1123 K for 4 h.

| Samples | $H_2$ evolution rate | $O_2$ evolution rate |
|---|---|---|
| $LaKNaNbO_5$ | 0.2635 umol/h | 18.6485 umol/h |
| $LaKNaNb_{0.8}Ta_{0.2}O_5$ | 1.4836 umol/h | 22.8087 umol/h |
| $LaKNaNb_{0.6}Ta_{0.4}O_5$ | 3.3684 umol/h | 14.9002 umol/h |
| $LaKNaNb_{0.4}Ta_{0.6}O_5$ | 4.7403 umol/h | 5.9927 umol/h |
| $LaKNaNb_{0.2}Ta_{0.8}O_5$ | 6.9226 umol/h | 2.6307 umol/h |
| $LaKNaTaO_5$ | 19.3713 umol/h | 0.4457 umol/h |

**Table S6.** The XPS peak contents of nitride $LaKNaTa_{0.8}Nb_{0.2}O_5$ before and after 15 hours reaction.

| | Name | Peak BE | Height CPS | FWHM eV | Area (P) CPS.eV | Atomic % | Peak Type |
|---|---|---|---|---|---|---|---|
| **Fresh** | C 1s | 284.8 | 25911.8 | 2.66 | 100441 | 61.41 | Standard |
| | N 1s | 394.91 | 16502.7 | 1.01 | 60060 | 23.58 | Standard |
| | Nb 3d | 205.59 | 39381.6 | 3.03 | 177463 | 10.97 | Standard |
| | Ta 4f | 24.83 | 12381.2 | 3.49 | 69693.1 | 4.03 | Standard |
| | **Name** | **Peak BE** | **Height CPS** | **FWHM eV** | **Area (P) CPS.eV** | **Atomic %** | **Peak Type** |
| **Used** | C 1s | 284.8 | 19785.4 | 2.56 | 89630 | 63.49 | Standard |
| | N 1s | 395.2 | 15287.4 | 1.07 | 46031.9 | 20.94 | Standard |
| | Nb 3d | 205.72 | 36628.6 | 2.71 | 163111 | 11.69 | Standard |
| | Ta 4f | 25.12 | 8925.04 | 3.61 | 58018.3 | 3.88 | Standard |