Supporting Information

Combinatorial Discovery of Lanthanum-Tantalum Oxynitride Solar Light Absorbers with Dilute Nitrogen for Solar Fuels Applications

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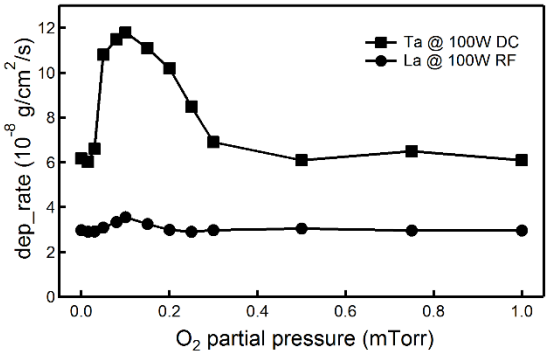

Figure S1. Deposition rate profiles of La (100W RF) and Ta (81W DC) as a function of O_2 partial pressure while maintaining 1.5 mTorr N_2 and a total working gas pressure of 6 mTorr.

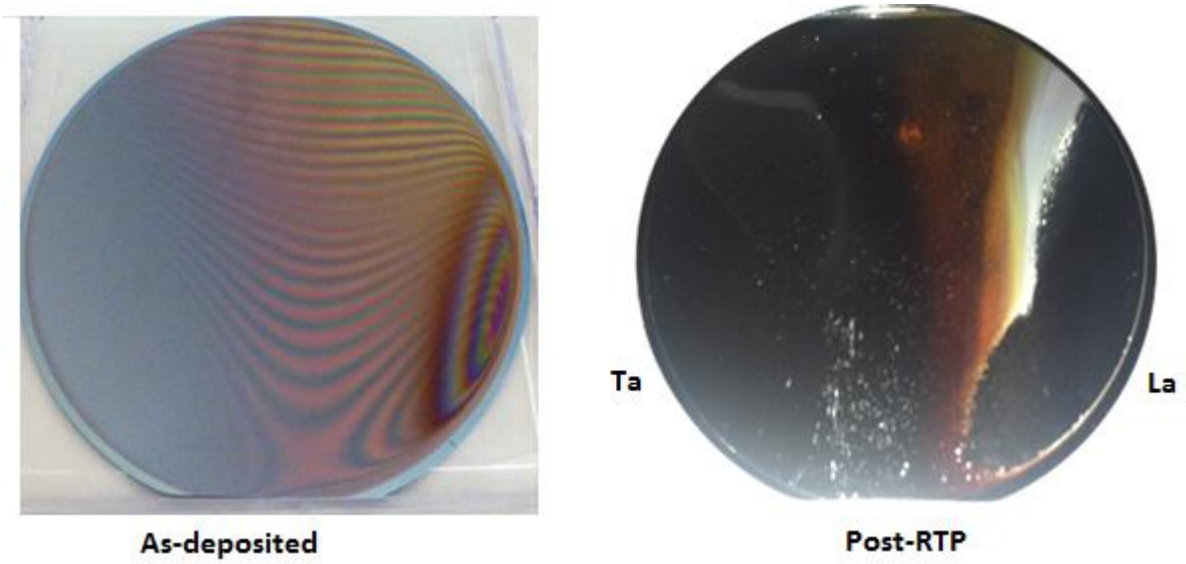

Figure S2. As-deposited and post-RTP images of the $La_xTa_{1-x}O_yN_z$ thin-film composition spread library.

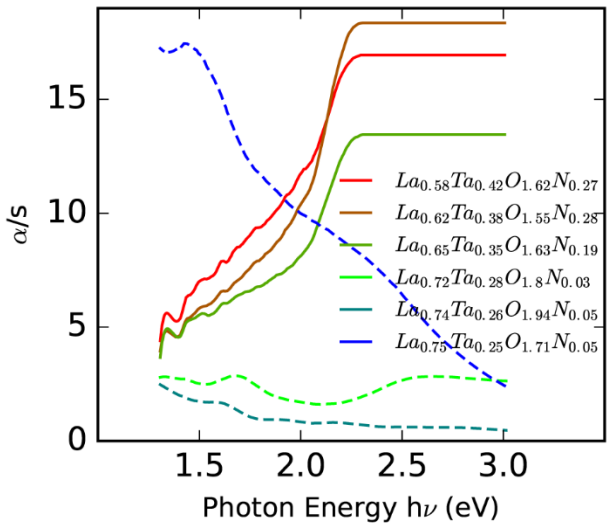

Figure S3. Plot of absorption coefficient (α) over scattering factor (s) as a function incident photon energy for several representative compositions in the $La_xTa_{1-x}O_yN_z$ library. For $0.72 \leq x \leq 0.75$ (dashed lines), the absorption coefficients are multiplied by 10 for ease of representation. For $0.58 \leq x \leq 0.65$, the diffuse reflectance signal was indistinguishable from dark noise at photon energies greater than 2.3 eV. For visualization purposes, we represent absorption in this region using a horizontal line.

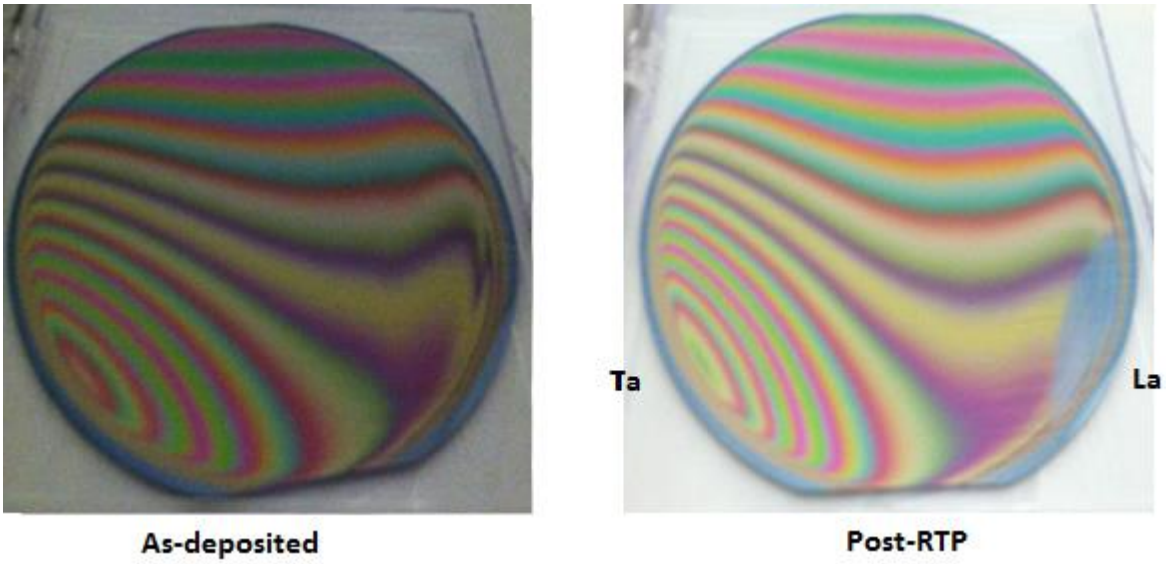

Figure S4. As-deposited and post-RTP images of a La-Ta-O thin-film composition spread library. Comparison with Figure S2 illustrates the importance of N in enabling visible light absorption.

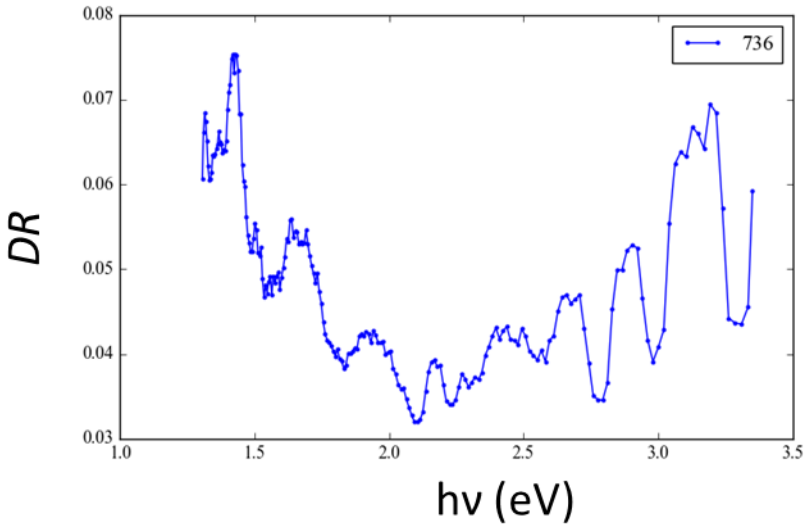

Figure S5. Diffuse-reflectance (*DR*) spectra for the La_3TaO_7 phase synthesized in the presence of oxygen only as a reactive gas during co-sputtering. This spectrum indicates no substantial light absorption with interference fringes providing the only detectable features. Comparison with Figure 4 highlights the visible light absorption induced by N_2 intercolation into La_3TaO_7.

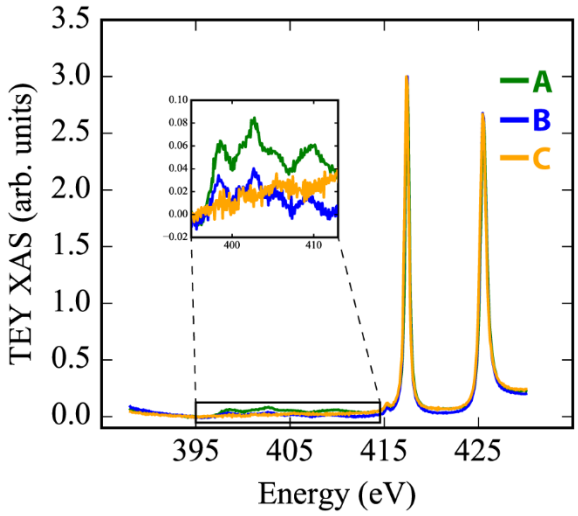

Figure S6. Figure showing TEY spectra for samples A, B, and C. Samples A and B that are phase pure $LaTaON_2$ exhibit nitrogen features similar to that observed for TFY (Figure 6). No nitrogen specific features are observed for Sample C consisting of phase pure La_3TaO_7.

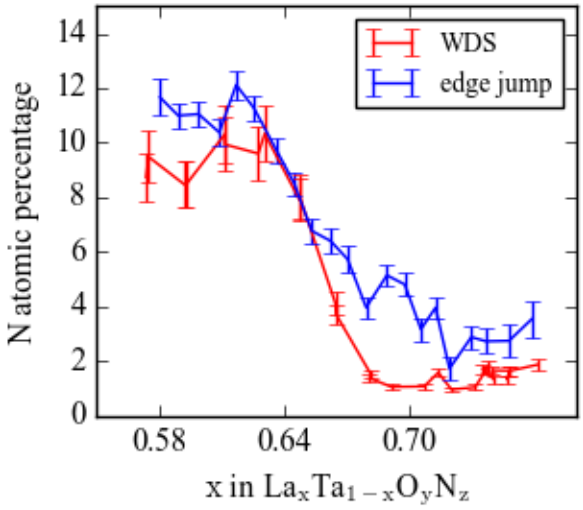

Figure S7. Nitrogen composition measurement using the relative edge jump from N K-edge TFY XANES overlaid with the WDS composition as a function of x in the $La_xTa_{1-x}O_yN_z$ library.

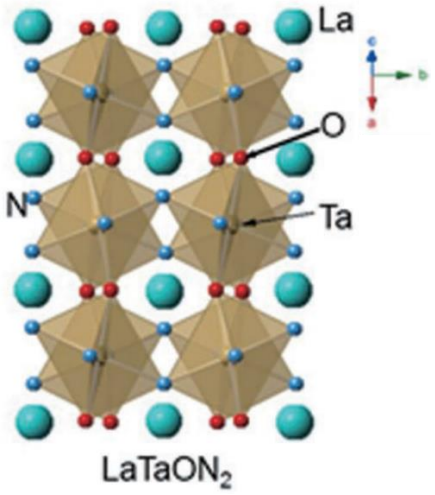

Figure S8. $LaTaON_2$ perovskite structure (reproduced from an open access source[1]) with the shortest Ta-N bond distance of 1.46 Å and the shortest La-N distance of 2.68 Å indicating that the contribution of La in the nitrogen chemical environment is small.

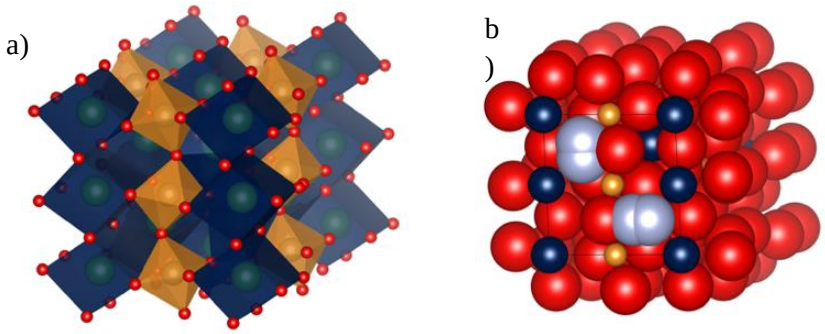

Figure S9. a) a. Polyhedral representation of La_3TaO_7 with LaO_8 in dark blue and TaO_6 in orange. Oxygen atoms are red in both images. b) Space filling representation of La_3TaO_7:N_2 with ionic radii and two possible configurations of intercalated N_2 in light blue. The black line indicates the unit cell.

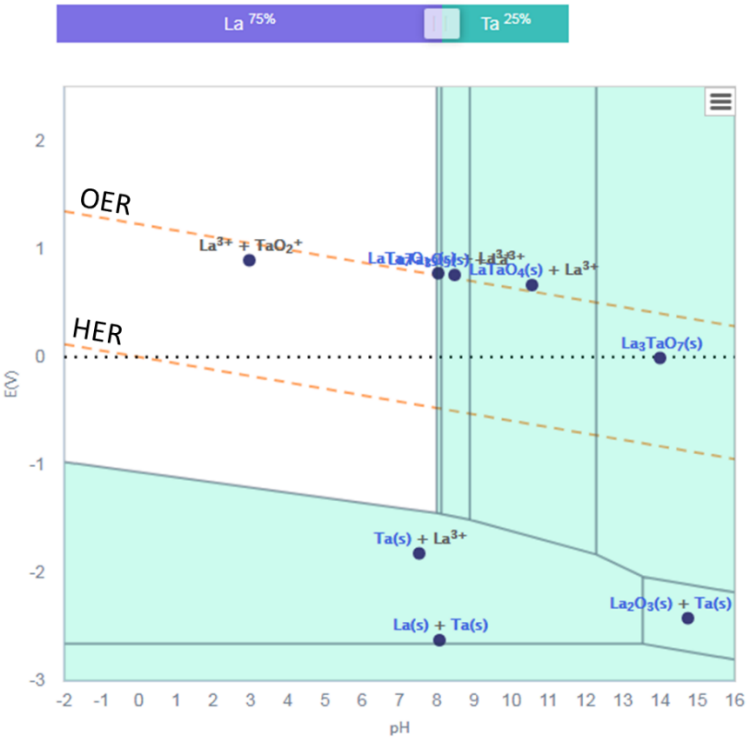

Figure S10. Pourbaix diagram calculated using the Materials Project Pourbaix App for La-Ta system at La:Ta=3:1, showing that La_3TaO7 is stable for a wide potential window that includes HER and OER potentials for pH > 11.5.

References

1. Pan, C.; Takata, T.; Nakabayashi, M.; Matsumoto, T.; Shibata, N.; Ikuhara, Y.; Domen, K., A complex perovskite-type oxynitride: the first photocatalyst for water splitting operable at up to 600 nm. *Angewandte Chemie* **2015,** *54* (10), 2955-9.