Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Stability and Activity of Titanium Oxynitride Thin Films for the Electrocatalytic Reduction of Molecular Nitrogen to Ammonia at Different pH Values

Precious Chukwunenye, Ashwin Ganesan, Mojgan Gharaee, Kabirat Balogun, Qasim Adesope, Stella Chinelo Amagbor, Teresa D. Golden, Francis D'Souza, Thomas R. Cundari, and Jeffry A. Kelber

Department of Chemistry, University of North Texas, 1155 Union Circle, #305070, Denton, TX 76203-5017, USA.

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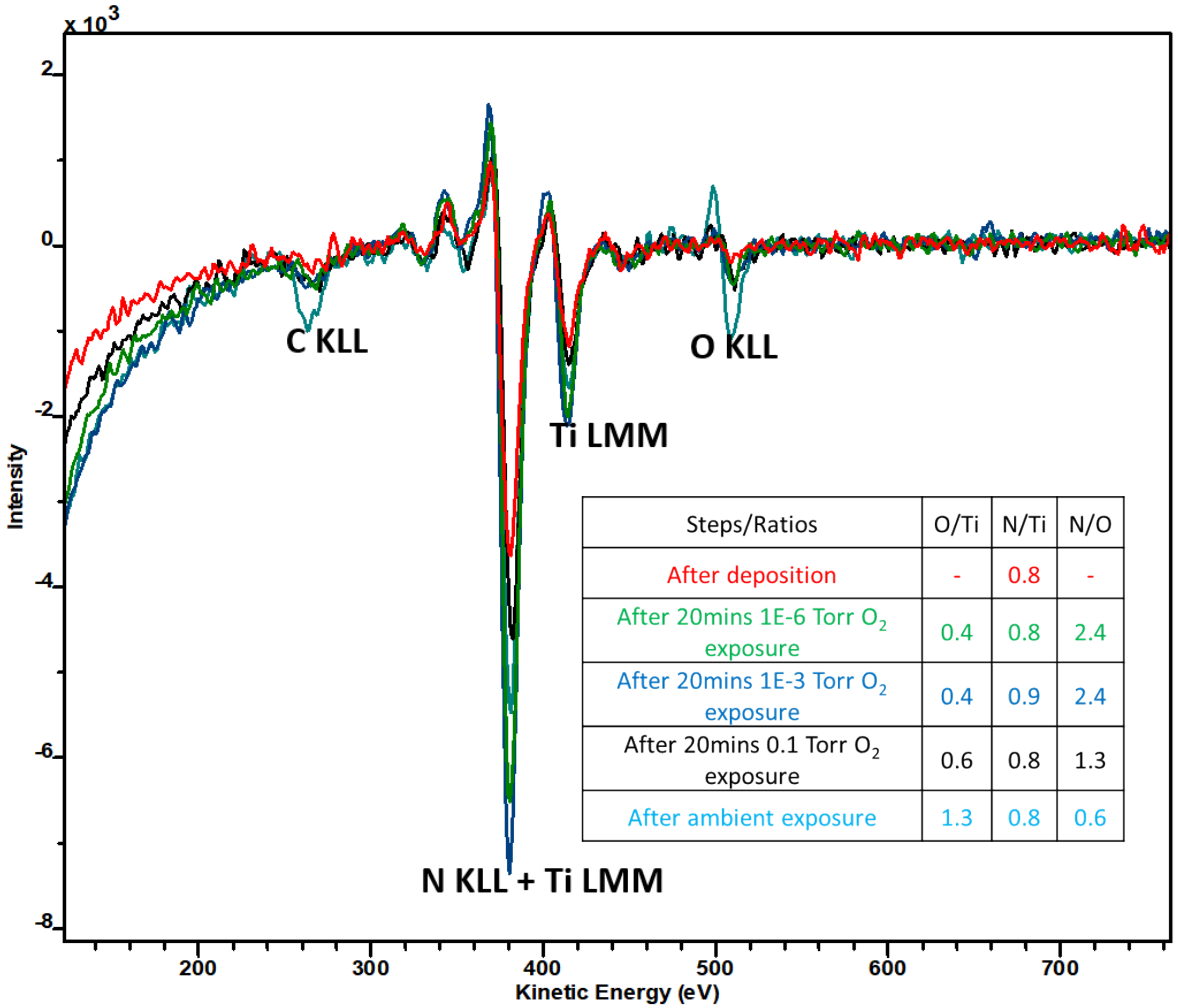

Steps/Ratios	O/Ti	N/Ti	N/O
After deposition	-	0.8	-
After 20mins 1E-6 Torr O_2 exposure	0.4	0.8	2.4
After 20mins 1E-3 Torr O_2 exposure	0.4	0.9	2.4
After 20mins 0.1 Torr O_2 exposure	0.6	0.8	1.3
After ambient exposure	1.3	0.8	0.6

Figure S1: In-situ AES spectra of TiN sample after deposition, subsequent oxygen exposure and ambient exposure.

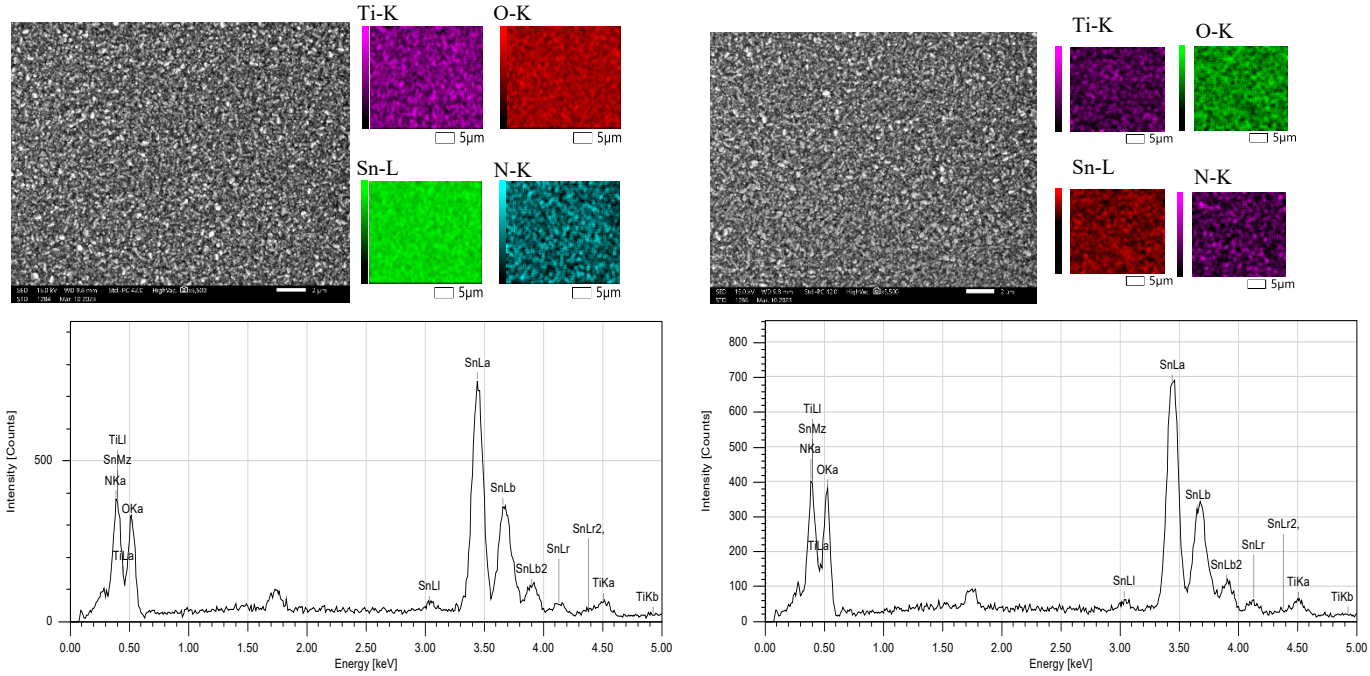

Figure S2: SEM-EDX of (a) TiN and (b) TiON sample.

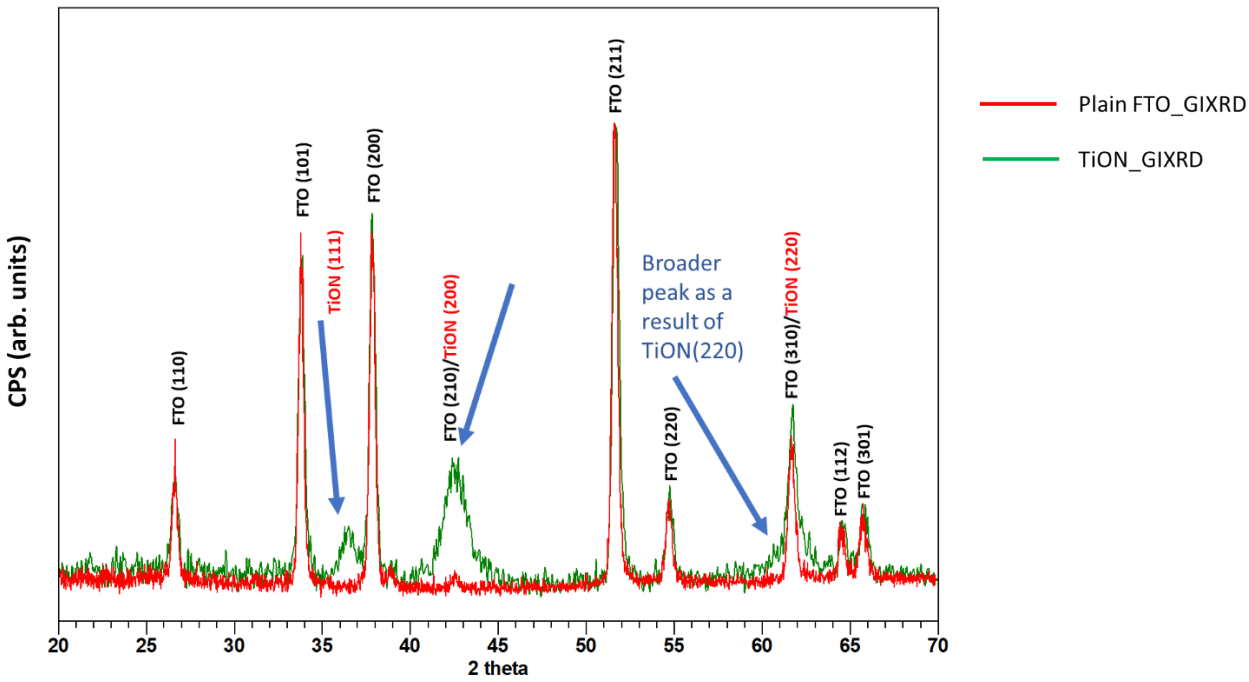

Figure S3: Overlaid grazing incidence XRD of plain FTO and titanium oxynitride.

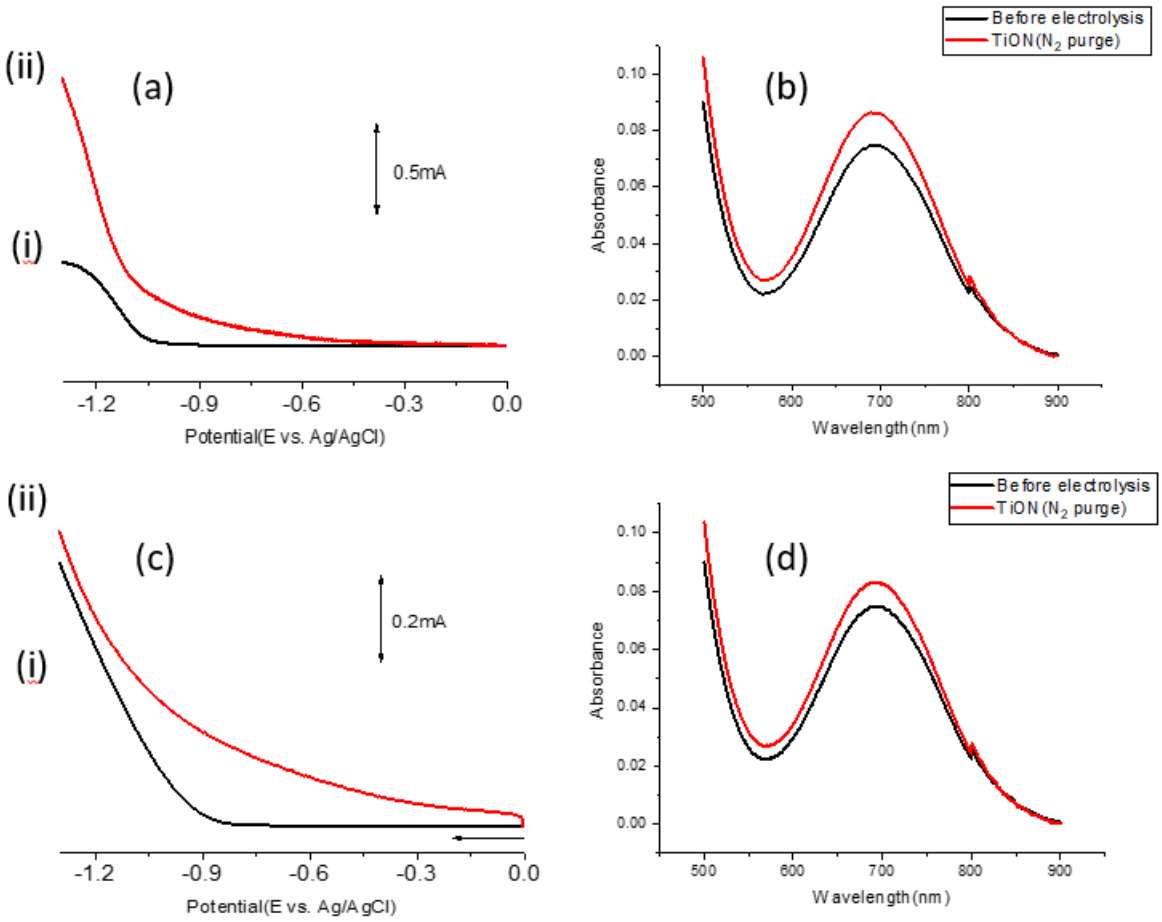

Figure S4: (a) LSV curves of (i) bare FTO and (ii) TiON sample (b) absorbance before and after electrolysis for the detection of ammonia in N_2 saturated solution of 0.1 M Na_2SO_4 solution at pH 7. In-situ AES N:O atomic ratio of film was 0.9 before ambient exposure (c) LSV curves of (i) bare FTO and (ii) TiON sample. (d) absorbance before and after electrolysis for the detection of ammonia in N_2 saturated solution in 0.1 M Na_2SO_4 solution at pH 10. In-situ AES N:O atomic ratio composition of film was 0.8 before ambient exposure.

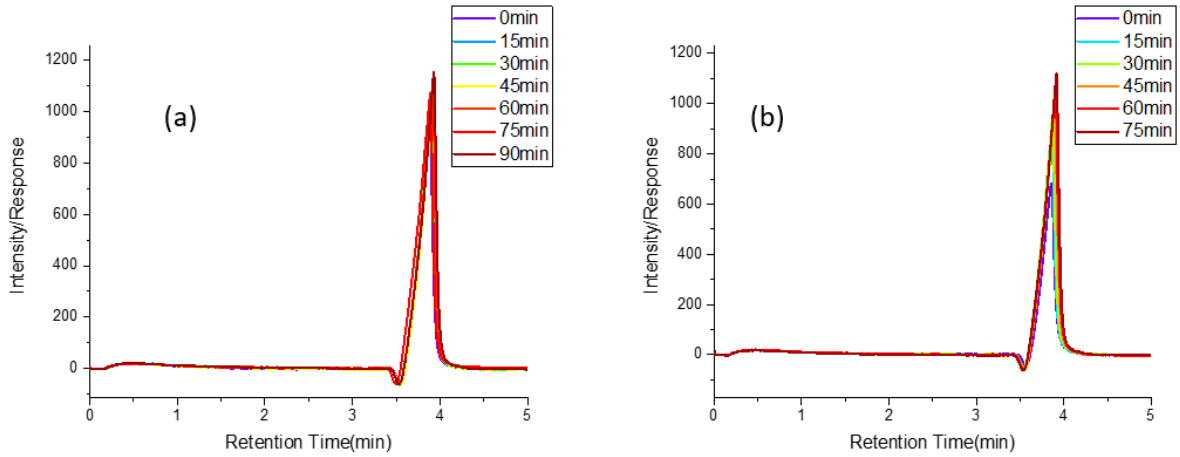

Figure S5: Gas chromatogram of TiON film in (a) pH 7 and (b) pH 10 during electrolysis for the detection of H_2 in N_2 environment in 0.1 M Na_2SO_4 solution.

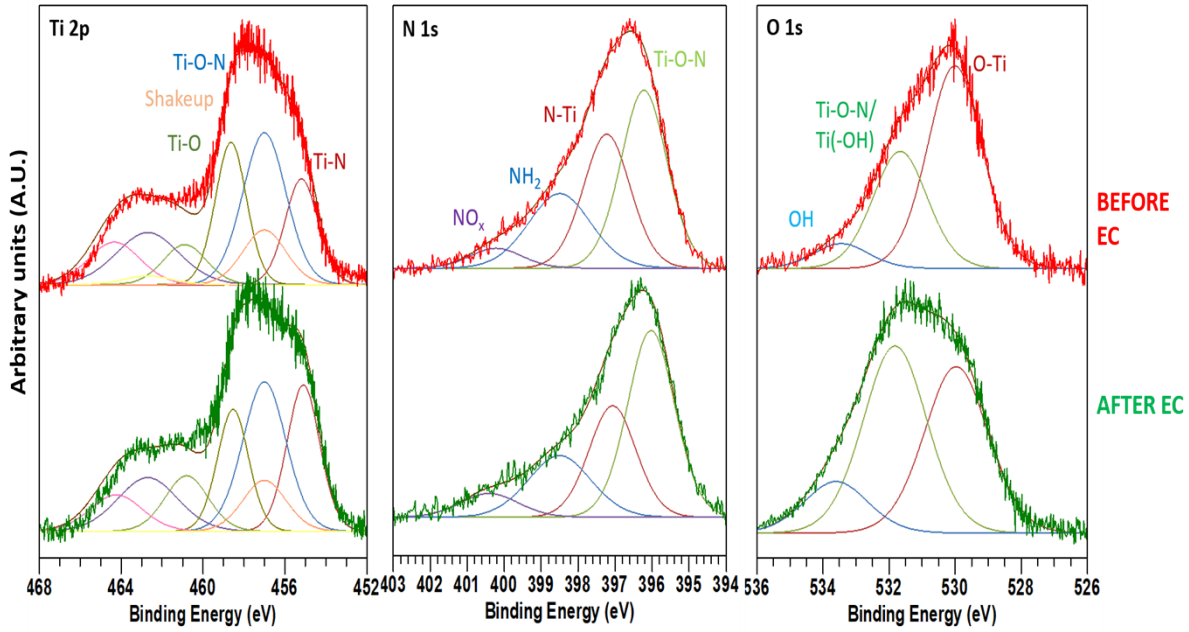

Figure S6: Ex-situ *XPS core level spectra of a TiON sample (a) before and (b) after 4.5 hr multicyclic voltammograms at -0.93 V in N_2 environment in 0.1 M Na_2SO_4 solution at pH 3.2. XPS-derived N:O ratios were 0.8 prior to and 0.4 after electrochemical cycling, respectively.*

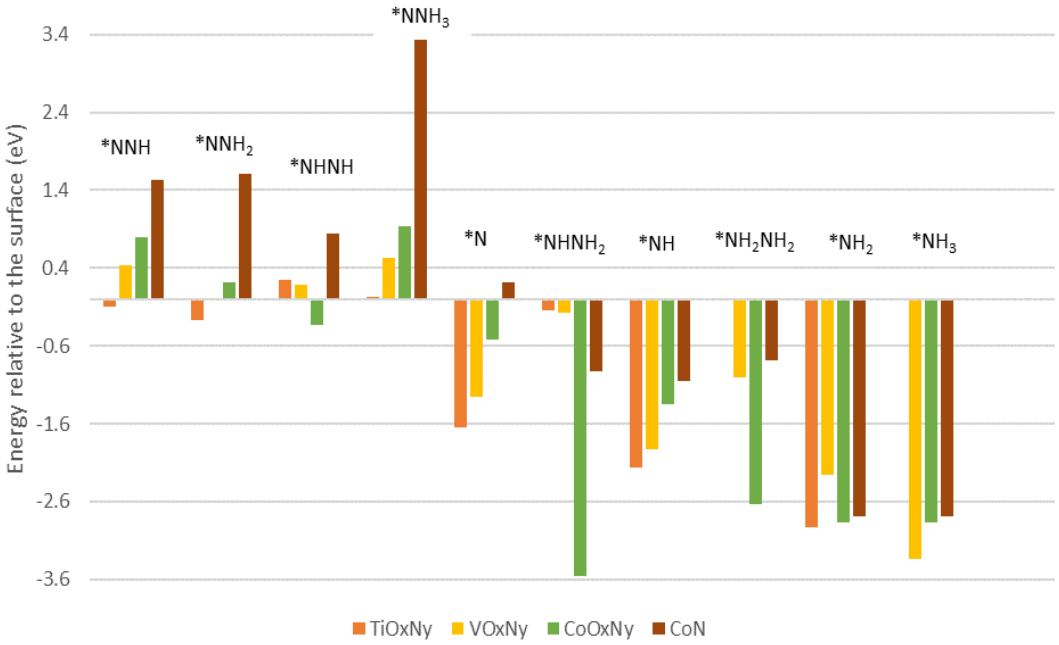

Figure S7: Energy calculation reaction (in eV) of $*N_aH_b$ surface intermediates for rs-TiO_xN_y (orange color), rs-VO_xN_y (yellow color), zb-CoO_xN_y (green color) and zb-CoN (red color) models