Supplementary Information (SI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2025

Electronic Supplementary Information for

Titanium Nitride Prepared by the Urea-Glass Synthesis Gives an Active Electrocatalyst for the Oxygen Reduction Reaction

Wanrui Xie, † Ryan D. Van Daele, † Allison Kattz, Leo Ellenson, Fengrui Qu, and Bart M. Bartlett*

Department of Chemistry, University of Michigan, 930 N. University Avenue, Ann Arbor, MI 48109 United States

Corresponding author email address: bartmb@umich.edu

Table of Contents

Experimental section for single crystal growth, data collection, and structure determination

Single colorless plate-shaped crystals of Ti(IV)chloride-urea complex were used as supplied. A suitable crystal with dimensions 0.14 × 0.09 × 0.04 mm^3 was selected and mounted on a dtrek-CrysAlisPro-abstract goniometer imported rigaku-d*trek images diffractometer. The crystal was kept at a steady T = 85 K during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Olex2 1.5-alpha (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2019/3 (Sheldrick, 2015) using full matrix least squares minimization on $\boldsymbol{F^2}$.

Crystal Data. $C_{31}H_{110}Cl_4N_{24}O_{31}Ti_4$, M_r = 1648.82, monoclinic, $P2/n$ (No. 13), a = 9.6426(2) Å, b = 17.1560(4) Å, c = 22.1236(6) Å, β = 90.520(2)°, $\alpha = \gamma$ = 90°, V = 3659.72(15) $Å^3$, T = 85 K, Z = 2, Z' = 0.5, μ(Cu K_α) = 5.738, 52589 reflections measured, 6785 unique (R_{int} = 0.1171) which were used in all calculations. The final wR_2 was 0.2828 (all data) and R_1 was 0.0948 (I≥2 σ(I)).

Table S1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å²×10^3) for Ti(IV)chloride-urea complex. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij}.

Atom	x	y	z	U_{eq}
Ti1	5757.5(10)	6861.1(6)	7798.5(4)	30.5(3)
Ti2	6838.7(10)	8223.5(6)	6790.1(4)	31.1(3)
Cl1	1916.3(17)	9004.6(11)	9651.8(8)	57.8(5)
Cl2	2509(3)	3992.3(19)	5683.2(12)	108.9(11)
O00G	2500	4207(3)	7500	53.5(17)
O1	4713(4)	5976(2)	7322.8(18)	36.5(9)
O2	3856(4)	7155(2)	8067.1(17)	34.8(8)
O3	5777(4)	6074(2)	8523.7(18)	37.9(9)
O4	6672(4)	7531(2)	8282.8(17)	32.3(8)
O5	7500	6364(3)	7500	31.9(11)
O6	5712(4)	7496(2)	7146.3(16)	30.5(8)
O7	7500	8652(3)	7500	33.3(11)
O8	5247(4)	8993(2)	6712.3(19)	40.9(9)
O9	6049(4)	7881(2)	5955.5(17)	35.7(9)
O10	7987(4)	9038(2)	6290.4(19)	41.0(9)
N1	4420(6)	4936(3)	6718(3)	48.6(13)
N2	5686(6)	5977(3)	6392(2)	48.4(13)
N3	1962(5)	7648(3)	8518(2)	45.7(13)
N4	4096(5)	8097(4)	8796(3)	50.3(14)
N5	5379(8)	5155(4)	9217(3)	68.9(19)
N6	3733(8)	5439(5)	8506(3)	83(3)
N7	5097(8)	9725(4)	7558(3)	72(2)
N8	3599(6)	9897(4)	6741(3)	59.6(16)
N9	7581(6)	7067(3)	5500(3)	46.0(12)
N10	5609(7)	7481(4)	4999(3)	62.1(17)
N11	6520(6)	9506(4)	5565(3)	51.4(14)
N12	8769(6)	9931(4)	5634(3)	59.5(16)
C1	4922(6)	5646(3)	6829(3)	33.7(12)
C2	3320(5)	7625(3)	8449(3)	35.0(12)
C3	5009(7)	5556(4)	8737(3)	42.1(14)
C4	4678(6)	9527(4)	7002(3)	44.6(14)
C5	6401(6)	7481(4)	5503(3)	40.1(13)
C6	7742(6)	9477(4)	5840(3)	41.7(14)
C7	2500	3545(6)	7500	99(4)
C8	2680(20)	3110(5)	6957(5)	142(5)

Table S2: Anisotropic Displacement Parameters (×10^4) for Ti(IV)chloride-urea complex. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti1	32.7(5)	33.6(5)	25.2(6)	-0.1(4)	0.4(4)	-1.3(4)
Ti2	32.5(5)	35.5(5)	25.3(6)	2.8(4)	-1.9(4)	-0.1(4)
Cl1	52.5(9)	69.8(11)	50.9(10)	-29.0(8)	-8.9(7)	13.2(7)
Cl2	128(2)	126(2)	72.5(16)	-56.7(16)	-18.5(15)	60.4(18)
O00G	82(5)	30(3)	48(4)	0	20(3)	0
O1	38(2)	41(2)	31(2)	-0.3(17)	-1.0(16)	-5.8(16)
O2	34.5(19)	43(2)	27(2)	-1.7(16)	-2.8(15)	-3.2(16)
O3	42(2)	40(2)	31(2)	3.5(17)	2.6(16)	-0.8(17)
O4	34.2(18)	36.5(19)	26(2)	0.9(15)	-1.1(14)	2.9(15)
O5	32(3)	33(3)	30(3)	0	-4(2)	0
O6	37.9(19)	31.7(18)	21.9(19)	-5.2(14)	-3.9(14)	-0.7(14)
O7	33(3)	35(3)	32(3)	0	3(2)	0
O8	42(2)	45(2)	36(2)	3.3(18)	-6.3(17)	2.7(17)
O9	43(2)	40(2)	24(2)	1.5(16)	-1.2(15)	-0.4(16)
O10	38(2)	46(2)	39(2)	11.0(18)	-2.8(17)	-2.5(17)
N1	62(3)	43(3)	41(3)	-9(2)	11(2)	-9(2)
N2	62(3)	57(3)	26(3)	-3(2)	8(2)	-14(3)
N3	32(2)	63(3)	43(3)	-17(3)	-1(2)	2(2)
N4	37(3)	70(4)	45(3)	-25(3)	13(2)	-5(2)
N5	87(5)	73(4)	47(4)	32(3)	-3(3)	-18(4)
N6	89(5)	92(5)	66(5)	33(4)	-26(4)	-54(4)
N7	80(5)	62(4)	73(5)	-25(4)	-24(4)	20(3)
N8	56(3)	58(4)	64(4)	-3(3)	-13(3)	19(3)
N9	49(3)	52(3)	37(3)	-8(2)	-2(2)	6(2)
N10	61(4)	84(5)	41(3)	-6(3)	-17(3)	1(3)
N11	48(3)	61(3)	44(3)	25(3)	-6(2)	-11(3)
N12	49(3)	70(4)	59(4)	32(3)	-3(3)	-16(3)
C1	42(3)	26(2)	33(3)	-7(2)	6(2)	-7(2)
C2	30(3)	45(3)	30(3)	-6(2)	-2(2)	1(2)
C3	56(4)	44(3)	26(3)	2(2)	6(3)	-10(3)
C4	42(3)	41(3)	51(4)	-4(3)	-8(3)	8(3)
C5	50(3)	45(3)	26(3)	1(2)	-2(2)	-6(3)
C6	46(3)	47(3)	32(3)	13(3)	-3(2)	-9(3)
C7	193(12)	39(5)	66(7)	0	63(8)	0
C8	302(16)	39(4)	85(7)	-15(4)	100(9)	-16(7)

Table S3: Bond Lengths in Å for Ti(IV)chloride-urea complex.

Atom	Atom	Length/Å
Ti1	O1	2.099(4)
Ti1	O2	1.997(4)
Ti1	O3	2.097(4)
Ti1	O4	1.797(4)
Ti1	O5	2.002(2)
Ti1	O6	1.808(4)
Ti2	Ti2[1]	3.3795(19)
Ti2	O4[1]	1.872(4)
Ti2	O6	1.837(4)
Ti2	O7	1.843(2)
Ti2	O8	2.030(4)
Ti2	O9	2.076(4)
Ti2	O10	2.103(4)
O00G	C7	1.136(12)
O1	C1	1.248(7)
O2	C2	1.280(7)
O3	C3	1.252(7)
O8	C4	1.248(8)
O9	C5	1.263(7)
O10	C6	1.269(7)
N1	C1	1.332(7)
N2	C1	1.348(7)
N3	C2	1.321(7)
N4	C2	1.341(8)
N5	C3	1.312(9)
N6	C3	1.343(9)
N7	C4	1.335(9)
N8	C4	1.345(8)
N9	C5	1.341(8)
N10	C5	1.346(8)
N11	C6	1.322(8)
N12	C6	1.344(8)
C7	C8[2]	1.427(8)
C7	C8	1.427(8)

––––

[1]3/2-x,+y,3/2-z; [2]1/2-x,+y,3/2-z

Table S4: Bond Angles in ° for Ti(IV)chloride-urea complex.

Atom	Atom	Atom	Angle/°
O2	Ti1	O1	83.93(16)
O2	Ti1	O3	86.37(16)
O2	Ti1	O5	168.89(18)
O3	Ti1	O1	85.35(16)
O4	Ti1	O1	172.74(17)
O4	Ti1	O2	96.21(16)
O4	Ti1	O3	87.41(17)
O4	Ti1	O5	93.48(15)
O4	Ti1	O6	95.65(17)
O5	Ti1	O1	85.78(15)
O5	Ti1	O3	88.64(15)
O6	Ti1	O1	91.58(16)
O6	Ti1	O2	94.00(17)
O6	Ti1	O3	176.85(16)
O6	Ti1	O5	90.45(15)
O4[1]	Ti2	Ti2[1]	78.27(12)
O4[1]	Ti2	O8	170.13(18)
O4[1]	Ti2	O9	91.11(16)
O4[1]	Ti2	O10	88.17(17)
O6	Ti2	Ti2[1]	79.69(11)
O6	Ti2	O4[1]	93.62(17)
O6	Ti2	O7	96.12(16)
O6	Ti2	O8	91.65(17)
O6	Ti2	O9	88.62(16)
O6	Ti2	O10	173.30(16)
O7	Ti2	Ti2[1]	23.50(15)
O7	Ti2	O4[1]	93.81(16)
O7	Ti2	O8	93.92(17)
O7	Ti2	O9	172.93(19)
O7	Ti2	O10	90.19(16)
O8	Ti2	Ti2[1]	110.93(13)
O8	Ti2	O9	80.66(16)
O8	Ti2	O10	85.68(17)
O9	Ti2	Ti2[1]	163.57(11)
O9	Ti2	O10	84.89(16)
O10	Ti2	Ti2[1]	107.01(12)
C1	O1	Ti1	133.4(4)
C2	O2	Ti1	137.1(3)
C3	O3	Ti1	138.1(4)
Ti1	O4	Ti2[1]	136.7(2)
Ti1	O5	Ti1[1]	129.5(3)
Ti1	O6	Ti2	137.9(2)
Ti2	O7	Ti2[1]	133.0(3)
C4	O8	Ti2	140.3(4)
C5	O9	Ti2	139.5(4)
C6	O10	Ti2	135.3(4)
O1	C1	N1	121.1(5)
O1	C1	N2	122.0(5)
N1	C1	N2	116.9(5)
O2	C2	N3	120.2(5)
O2	C2	N4	122.2(5)
N3	C2	N4	117.6(5)
O3	C3	N5	121.3(6)
O3	C3	N6	120.4(6)
N5	C3	N6	118.1(6)
O8	C4	N7	121.9(6)
O8	C4	N8	117.9(6)
N7	C4	N8	120.1(6)
O9	C5	N9	121.6(5)
O9	C5	N10	120.2(6)
N9	C5	N10	118.2(6)
O10	C6	N11	122.9(5)
O10	C6	N12	118.5(6)
N11	C6	N12	118.6(6)
O00G	C7	C8[2]	121.5(6)
O00G	C7	C8	121.5(6)
C8	C7	C8[2]	117.0(11)

[1]3/2-x,+y,3/2-z; [2]1/2-x,+y,3/2-z

Table S5: Torsion Angles in ° for Ti(IV)chloride-urea complex.

Atom	Atom	Atom	Atom	Angle/°
Ti1	O1	C1	N1	156.5(4)
Ti1	O1	C1	N2	-21.9(9)
Ti1	O2	C2	N3	-178.0(4)
Ti1	O2	C2	N4	0.8(10)
Ti1	O3	C3	N5	179.3(5)
Ti1	O3	C3	N6	-6.0(11)
Ti2[1]	Ti2	O6	Ti1	-21.3(3)
Ti2	O8	C4	N7	-2.1(12)
Ti2	O8	C4	N8	179.1(5)
Ti2	O9	C5	N9	6.1(10)
Ti2	O9	C5	N10	-171.7(5)
Ti2	O10	C6	N11	0.3(11)
Ti2	O10	C6	N12	-179.4(5)
O1	Ti1	O6	Ti2	-143.4(3)
O2	Ti1	O4	Ti2[1]	-136.4(3)
O2	Ti1	O6	Ti2	132.6(3)
O3	Ti1	O4	Ti2[1]	137.5(3)
O4	Ti1	O6	Ti2	35.9(3)
O4[1]	Ti2	O6	Ti1	56.1(3)
O4[1]	Ti2	O7	Ti2[1]	-48.36(12)
O5	Ti1	O4	Ti2[1]	49.1(3)
O5	Ti1	O6	Ti2	-57.6(3)
O6	Ti1	O4	Ti2[1]	-41.7(3)
O6	Ti2	O7	Ti2[1]	45.70(12)
O7	Ti2	O6	Ti1	-38.1(3)
O8	Ti2	O6	Ti1	-132.2(3)
O8	Ti2	O7	Ti2[1]	137.78(13)
O9	Ti2	O6	Ti1	147.1(3)
O10	Ti2	O7	Ti2[1]	-136.54(12)

––––

[1]3/2-x,+y,3/2-z

Table S6: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Ti(IV)chloride-urea complex. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij}.

Atom	x	y	z	U_{eq}
H1A	3933	4692.92	6994.17	58
H1B	4575.9	4711.04	6367.47	58
H2A	5145.31	6173.63	6118	58
H2B	6181.99	6344.77	6550.62	58
H3A	1442.34	7329.67	8315.43	55
H3B	1584.88	7980.08	8759.56	55
H4A	4649.68	8367.06	8571.54	60
H4B	3570.8	8414.58	8995.76	60
H5A	6180.32	5248.29	9396.06	83
H5B	4824.64	4793.06	9360.2	83
H6A	3432.42	5727.92	8203.08	99
H6B	3197.6	5074.22	8657.35	99
H7A	5929.32	9558.42	7616.9	86
H7B	5081.97	10224.06	7592.86	86
H8A	3382.48	9687.35	6398.08	71
H8B	2891.3	9870.08	6977.69	71
H9A	8132.67	7070.73	5819.65	55
H9B	7804.58	6792.66	5179.83	55
H10A	5664.42	7033.09	4823.5	75
H10B	4757.34	7565.8	5095.66	75
H11A	5834.45	9211.4	5691.76	62
H11B	6393.2	9818.58	5253.91	62
H12A	9288.51	9673.42	5388.3	71
H12B	8409.53	10322.55	5444	71
H8C	1788.4	2885.1	6830.54	212
H8D	3351.83	2691.39	7027.46	212
H8E	3020.08	3456.27	6638.16	212

Table S7: Solvent masking (PLATON/SQUEEZE) information for Ti(IV)chloride-urea complex.

No	x	y	z	V	e	Content
1	-0.091	0.500	0.321	1556.0	477.4	$16CH_3CH_2OH$, $8H_2O$

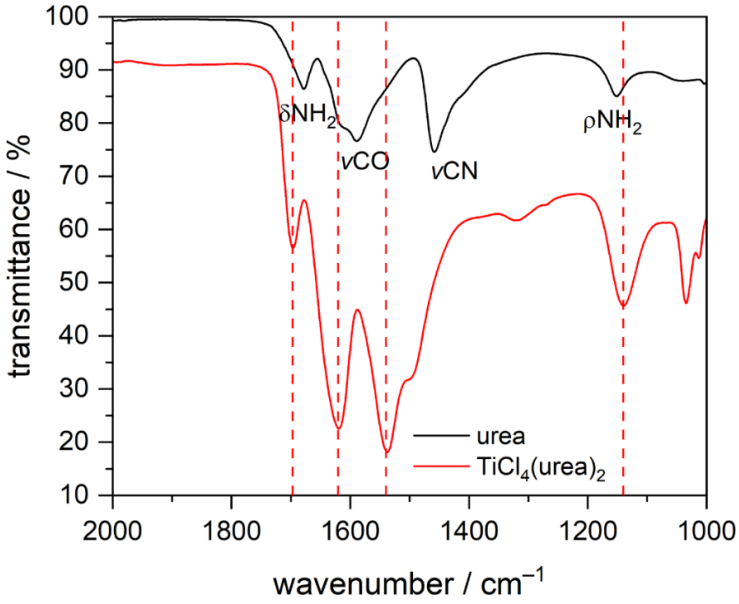

Figure S1. ATR-IR characterization of $TiCl_4(OC(NH_2)_2)_2$ precursor.

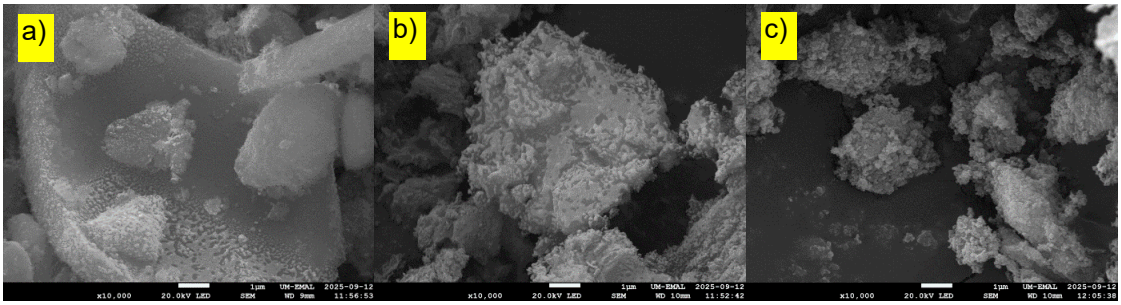

Figure S2. SEM characterization; 20.0 keV, 10 mm working distance, JOEL-SEM EMAL, 10,000× magnification of TiN synthesized from: a) the urea-glass method TiN, b) a direct solventless reaction, and c) a $TiCl_4(OC(NH_2)_2)_2$ complex.

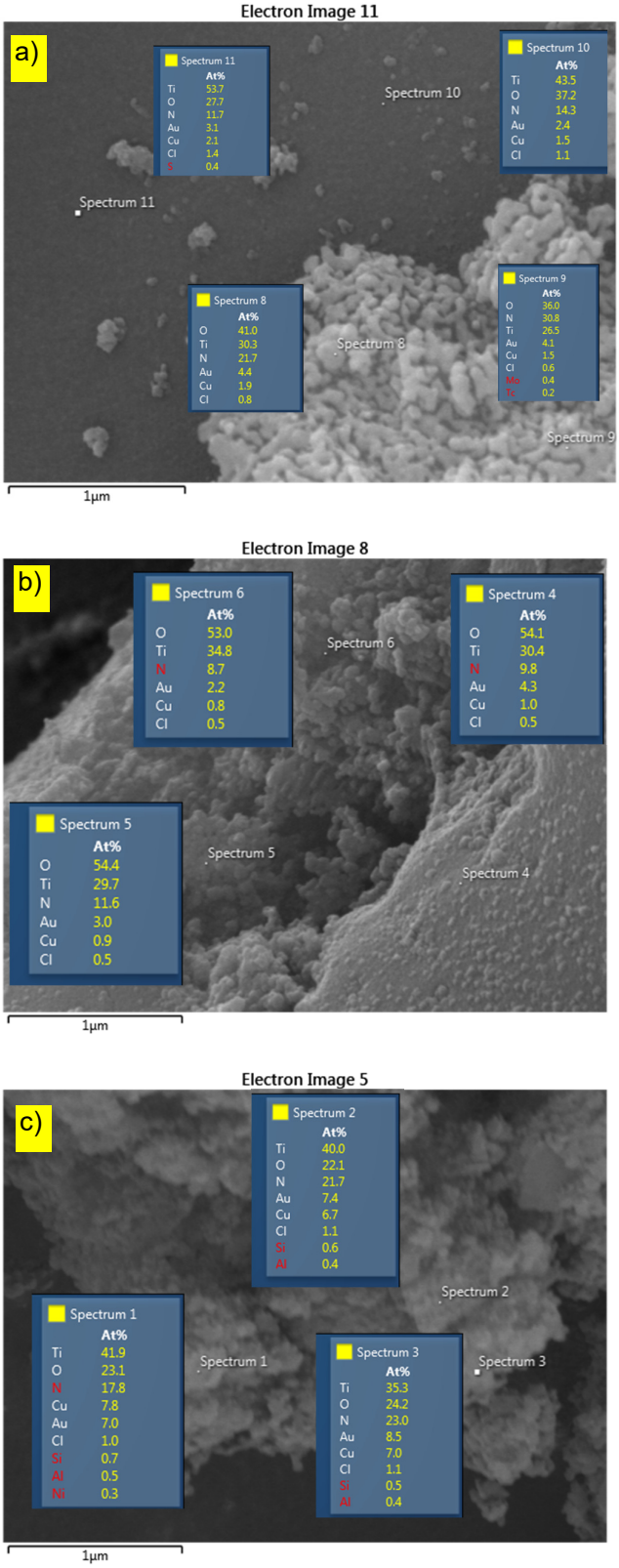

Figure S3. Energy Dispersive X-ray Spectroscopy Characterization of TiN synthesized from: a) the urea-glass method TiN, b) a direct solventless reaction, and c) a $TiCl_4(OC(NH_2)_2)_2$ complex.

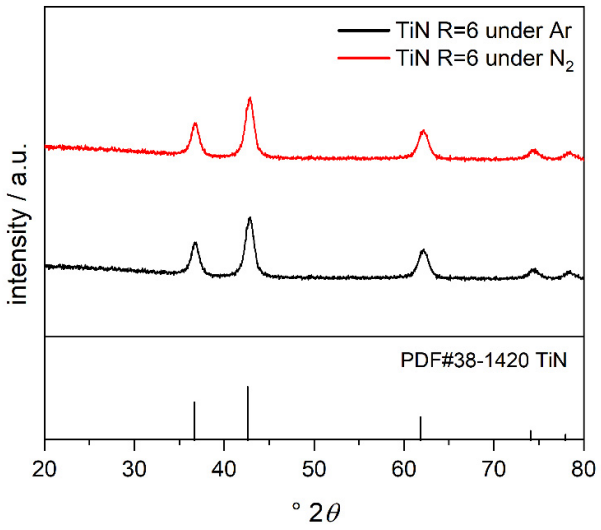

Figure S4. XRD patterns of TiN synthesized from the urea-glass method with a urea-to-titanium (IV) chloride ratio of 6 under N_2 and Ar atmospheres.

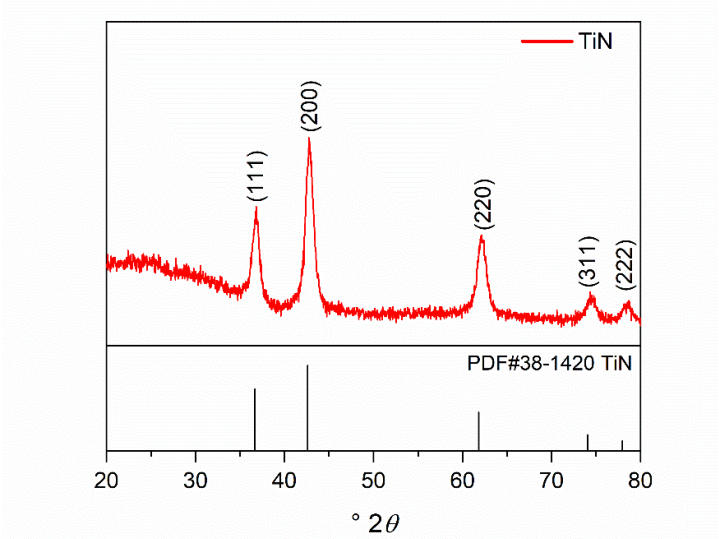

Figure S5. XRD of the solid material obtained from annealing the isolated urea-glass $[Ti_4(\mu\text{-}O)_6(OC(NH_2)_2)_{12}]^{4+}$ precursor complex at 750 ºC under N_2 atmosphere.

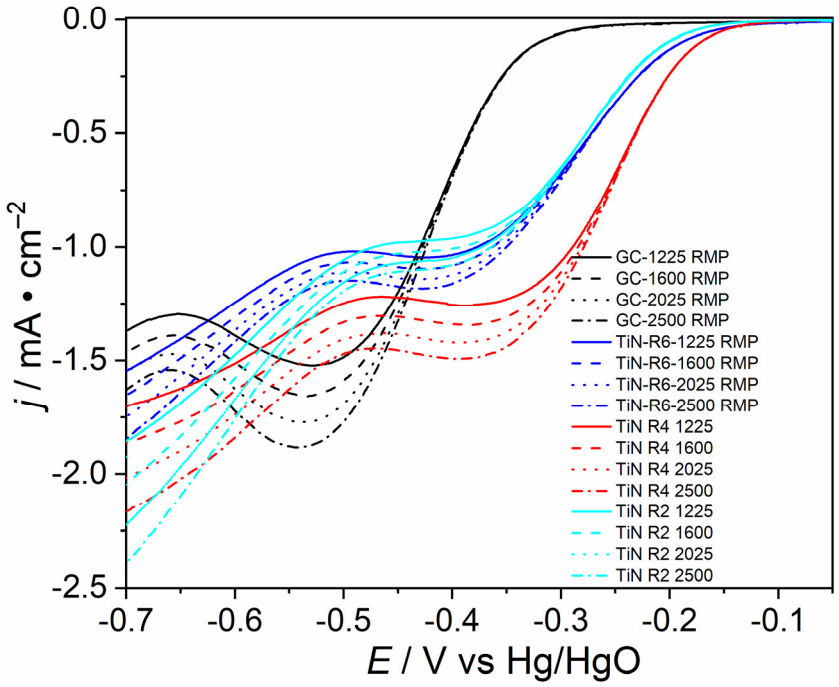

Figure S6. LSV traces on an RDE of urea-glass synthesized TiN (R=2, R=4, and R=6).

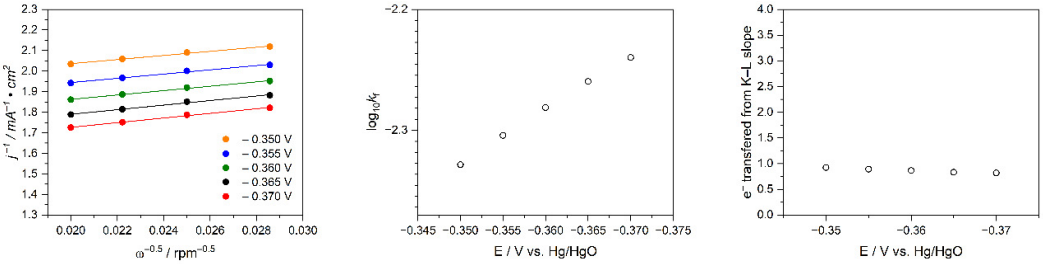

Figure S7. Electrochemical kinetics of TiN prepared by a direct solventless reaction: a) Kouteký-Levich plot, b) electron transfer numbers, and c) the forward constant rate.

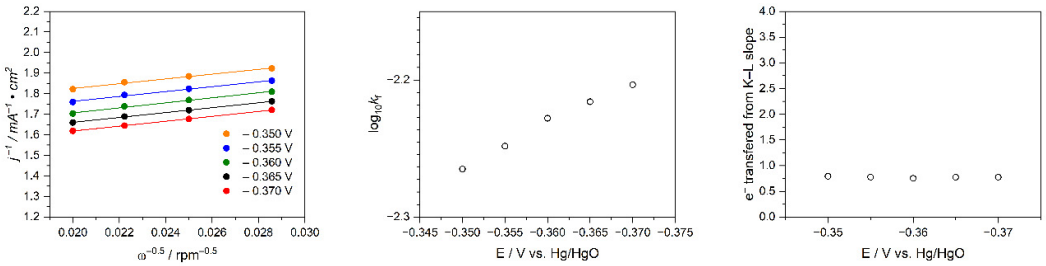

Figure S8. Electrochemical kinetics of TiN prepared from a $TiCl_4(OC(NH_2)_2)_2$ complex: a) Kouteký-Levich plot, b) electron transfer numbers, and c) the forward constant rate.

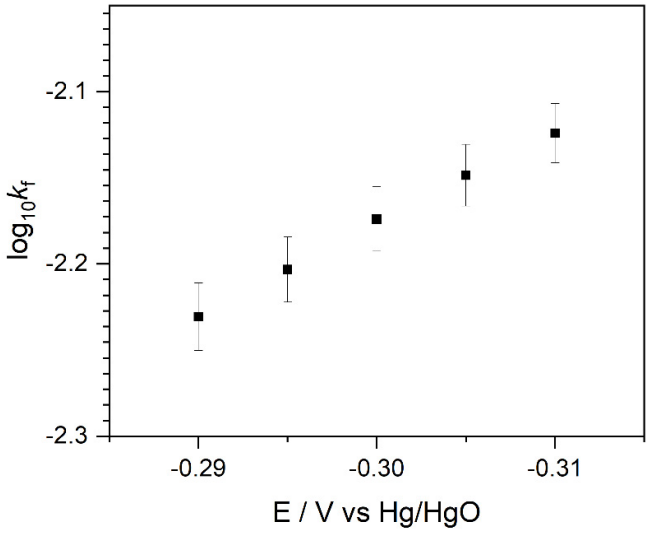

Figure S9. Mean and standard deviation of triplicate RDE tests for urea–glass–synthesized TiN.

Table S7. Mean and standard deviation for forward rate constant (k_f)

E/V vs. Hg/HgO	Trial 1 k_f(cm/s)	Trial 2 k_f (cm/s)	Trial 3 k_f (cm/s)	Mean(cm/s)	Standard Deviation
-0.29	0.00584	0.00617	0.00565	0.00588	2.63×10^{-4}
-0.295	0.00626	0.00654	0.006	0.00627	2.70×10^{-4}
-0.3	0.00675	0.00697	0.0064	0.0067	2.87×10^{-4}
-0.305	0.00714	0.00738	0.0068	0.00711	2.91×10^{-4}
-0.31	0.00758	0.00778	0.0072	0.00752	2.95×10^{-4}

Figure S10. Permanganate test for H_2O_2 product produced from TiN synthesized from: a) the urea-glass method TiN, b) a direct solventless reaction, and c) a $TiCl_4(OC(NH_2)_2)_2$ complex.

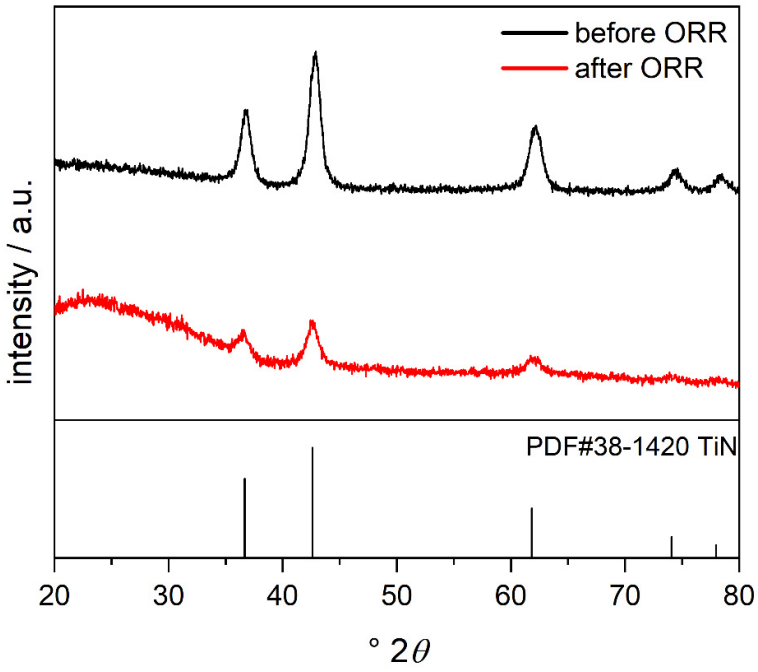

Figure S11. XRD pattern of TiN synthesized from the urea-glass method before and after conducting the ORR.

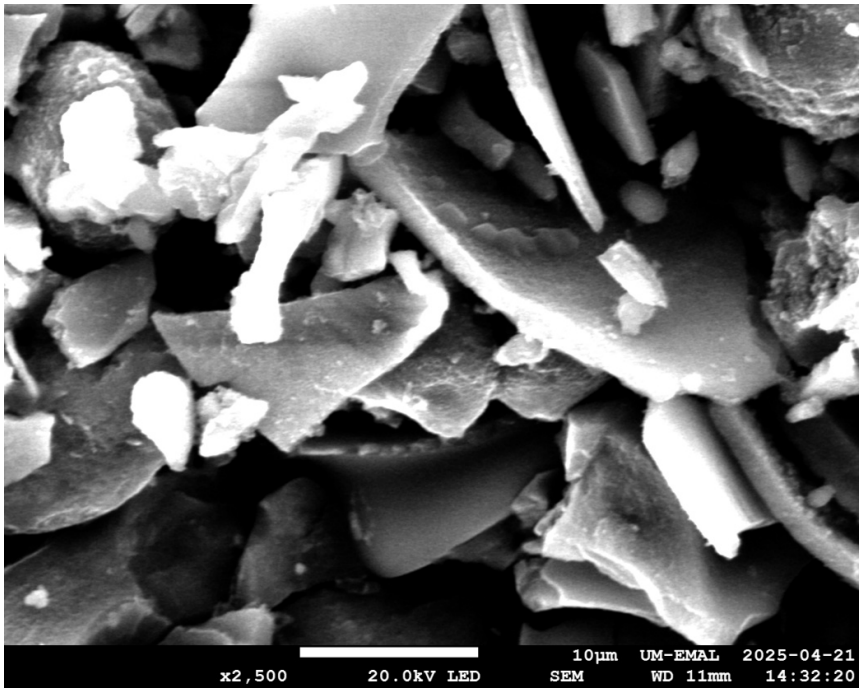

Figure S12. SEM image of TiN synthesized from the urea-glass method after the ORR.

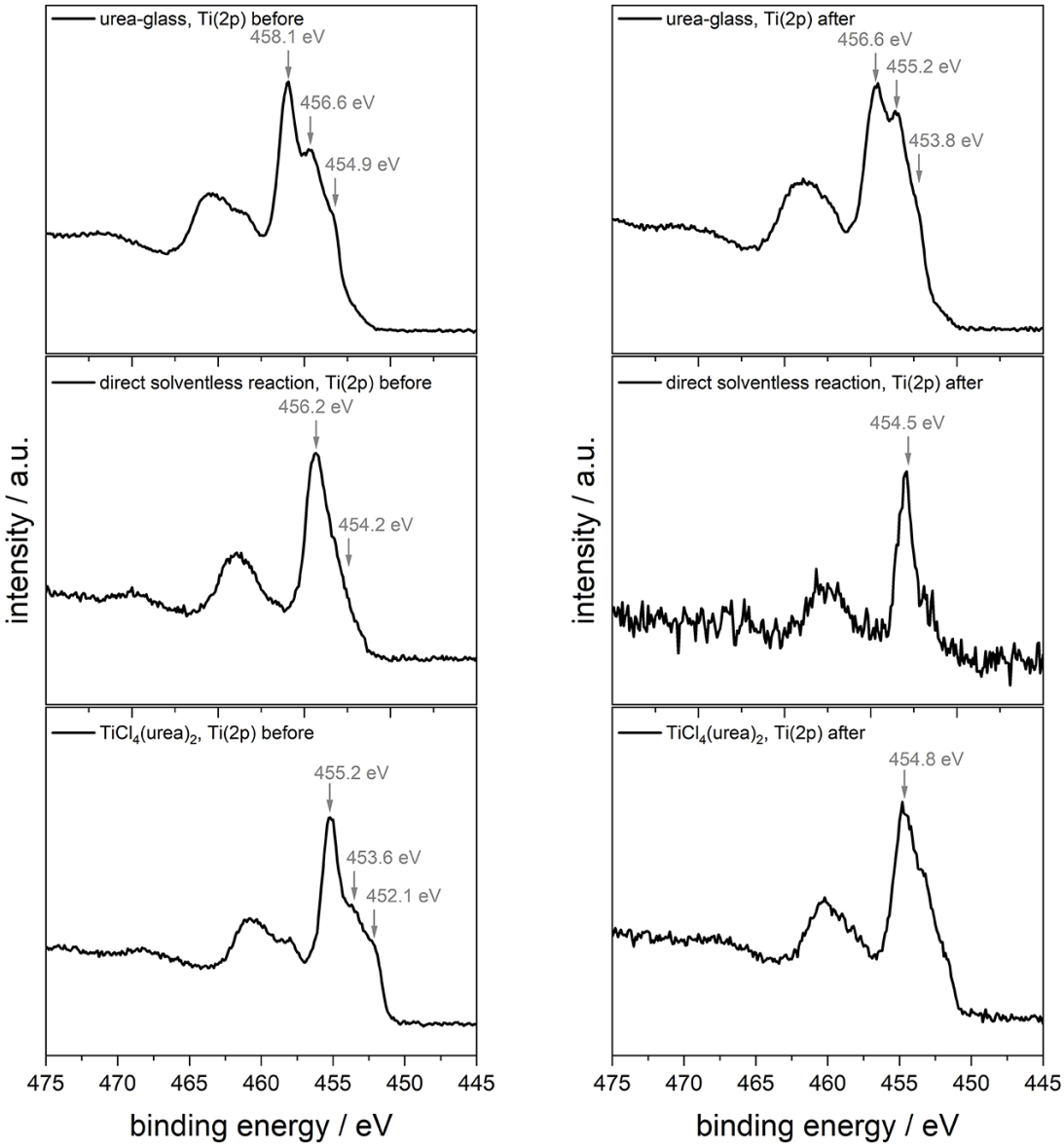

Figure S13. Ti(2p) XPS spectra of TiN synthesized from the urea–glass method, a direct solventless reaction, and a $TiCl_4(OC(NH_2)_2)_2$ complex before (left) and after (right) ORR. Peak assignments were made from inflection points in first derivative plots.

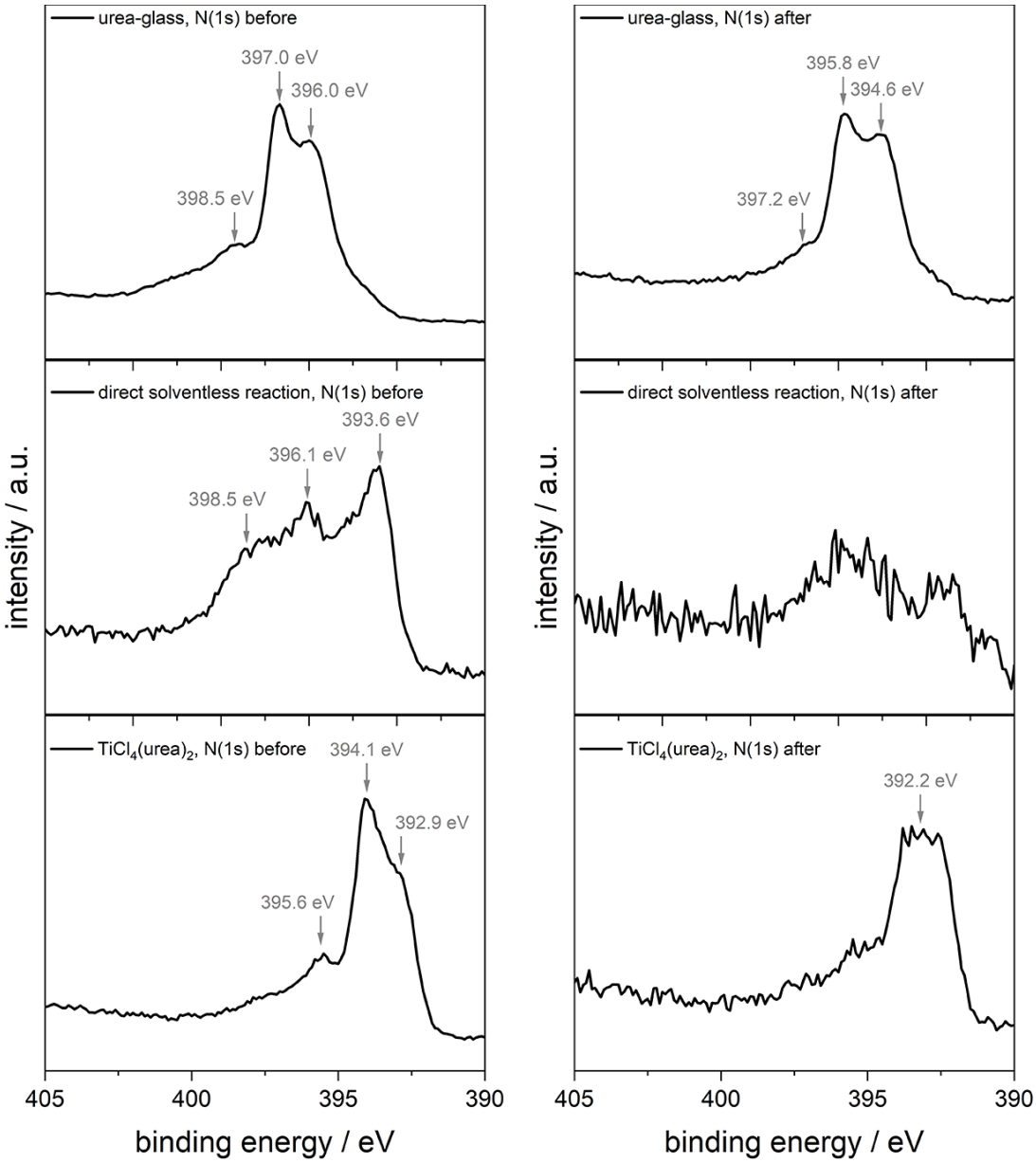

Figure S14. N(1s) XPS spectra of TiN synthesized from the urea–glass method, a direct solventless reaction, and a $TiCl_4(OC(NH_2)_2)_2$ complex. The left spectra were taken before ORR and the right spectra were collected after ORR. Peak assignments were made from inflection points in first derivative plots.

Citations

1. CrysAlisPro Software System, Rigaku Oxford Diffraction, (2024).

2. DTREK_VERSION=d*TREK version 9.9.9.4 W9RSSI – Aug 22 (2012).

3.O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

4.Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3-8.

5.Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.