Supporting Information
For

Title: Decoration of the layered manganese oxide birnessite by Mn(II/III) gives a new water oxidation catalyst with fifty-fold turnover number enhancement.

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Contents

Experimental……………………………………………………………………………..3
X-ray Powder Patterns…………………………………………………………………….. 6
SEM……………………………………………………………………………………….. 7
TEM……………………………………………………………………………………….. 8
XPS…………………………………………………………………………………………9
TOF from initial rates……………………………………………………………………… 15
Catalysis by recycled catalysts…………………………………………………………….. 19
Additional experimental data on birnessite samples………………………………………. 20

Experimental

General. Solutions were mixed by adding HCl solution to $KMnO_4$ via a New Era-1000 programmable syringe pump. X-ray powder patterns were acquired on an Bruker Kappa APEX II DUO diffractometer and Mo Kα radiation from a sealed molybdenum tube with a TRIUMPH monochromator. X-ray photoelectron spectra (XPS) of the dry samples were collected with a Scienta ESCA-300 at Lehigh University or a Thermo Scientific K-alpha+ at the University of Delaware. BET surface area was determined via a Micrometrics ASAP 202 Surface Area and Porosity Analyzer. For some depictions of the data, O_2 yield is compared with surface Mn density instead of surface area. Density of surface Mn atoms was calculated from the surface density of manganese atoms on the 001 face of birnessite (the most stable face) from the structure of crystalline birnessite. There are two Mn per rectangular C-face. The face has dimensions a and b = 5.149 Å and 2.843 Å respectively,[7] giving a surface density of two atoms per 14.63 $Å^2$ or 1 atom / 7.32 x 10^{-20} m^2. Converting to moles, this is 44,090 mol/m^2 which is used as a conversion factor to convert from BET area to mol surface Mn. TEM samples were prepared by depositing one drop of sonicated birnessite sample in water (100 mg/L) on a lacey carbon copper mesh TEM grid (400 mesh, Ted Pella) and allowed to air dry. Images were collected using a JEOL JEM-1400 microscope operating at 120 kV. SEM samples were prepared by depositing sample on carbon conductive tape mounted on aluminum stubs. Images were acquired on an Agilent 8500 FE-SEM operating at 1 kV. Elemental analysis was performed using a Thermo Scientific iCAP 7000 Series ICP-OES. Evolved oxygen was measured and recorded via a HACH LD101 Optical Dissolved Oxygen Probe.

Synthesis of high oxidation state birnessite. Hydrochloric acid (4M, 50.0mL) was added drop wise via a syringe pump at 1 mL/min to a heated and stirred (80^{o}C, 360 rpm) solution of potassium permanganate (0.200M, 250mL) in a 400mL beaker. Heating continued at 80^{o}C for an additional 0.5h after addition was completed. The resulting 300mL solution was then covered to prevent excessive evaporation overnight and aged for 15h at 50^{o}C before being washed via vacuum filtration with a fine frit five times to give B1, B5, and B6. These exact conditions were carried out for all samples in order to best control for consistent morphology, surface area and oxidation state. As seen in Table 1, synthesis of conditions yielded consistent surface areas for all three and similar oxidation states for B5 and B6. The difference between B1 and B5 and B6 is indicative of the chaotic nature the nucleation of the particles of this reaction as the same chloride concentrations does not necessarily correspond to the same oxidation state. Despite the extreme measures to ensure consistency, oxidation state can only be approximated. However, the use of the controlled, syringe pump addition improves both surface area and AOS consistency.

Synthesis of low oxidation state birnessite. Hydrochloric acid (2M, 50.0mL) was added drop wise via a syringe pump at 1 mL/min to a heated and stirred (80^{o}C, 360 rpm) solution of potassium permanganate (0.200M, 250mL) in a 400mL beaker. Heating continued at 80^{o}C for an additional 0.5h after addition was completed. The resulting 300mL solution was then covered to prevent excessive evaporation overnight and aged for 15h at 50^{o}C before being washed via vacuum filtration with a fine frit five times to give B2, B3, and B4. These exact conditions were carried out for all samples in order to best control for consistent surface area and oxidation state.

Comproportionation of birnessite for enriching surface with Mn(III). B5, Mn(3.77), birnessite (0.1818g) was stirred in a suspension of manganese(II) chloride (0.3264g, 1.650mmol) in 50mL of water for 20h. In addition to the birnessite, the centrifuged product contained a new phase of catalytically inactive Mn(III) nanoparticles based on TEM (Fig. S4a,c) and BET (surface area = 97.7 m^2/g). Vacuum filtration and washing of an aqueous suspension of this material removed the nanoparticles based upon TEM (Fig. d) and BET (33.4 m^2/g) to give product B5. Removal of the nanoparticle phase increased catalytic activity (TON) from 2506 to 5790 mmol O_2/mol surface Mn indicating the nanoparticle phase is not the active catalyst.

Oxygen evolution experiments. In general, 50 mg birnessite was stirred in a 15mL suspension of deionized water (purged with argon for at least 3h) in a 25mL filter flask under a nitrogen blanket. In trials with B2 and B4, 5 mg was used. 5mL of argon purged ammonium cerium(IV) nitrate (CAN, 0.4M, 2mmol) was added to the suspension via a10mL syringe. Induction period measurements were measured every second over a two minute period at which point the steady state was reached. Total lifetime and oxygen production measurements were taken in minute intervals over the course of 2.5h. All data points were normalized by sample surface area, manganese content, and zeroed to an initial minimum oxygen concentration value of zero. Comproportionated sample (B5) loading was decreased by a factor of five and normalized in order to keep the oxygen production within the range of the probe (max detection limit = 20.00 mg/mL; max observed = 9.02 mg/mL).. Each experiment was repeated in triplicate and averaged between trials. For some of the high AOS samples with low catalytic activities, a slight drop in O_2 concentration was observed upon injection of CAN. This is attributed to dilution of baseline oxygen in the birnessite suspension by the more recently-sparged CAN. This dip is not observed in the more active low AOS samples due to the immediate formation of O_2 upon mixing. TON is calculated as mmol O_2/amount of catalyst. TOF is calculated as the initial rate (Fig.S6)/amount of catalyst. (amount of catalyst quantity: mmol surface Mn, surface area (m^2) or mmol bulk Mn)

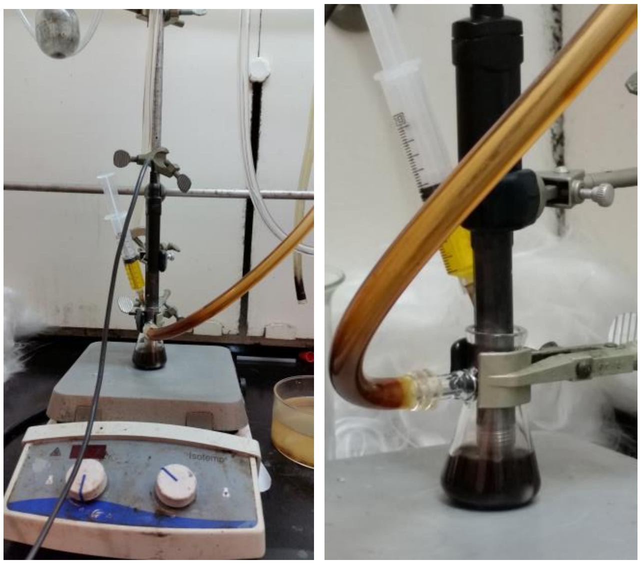


Figure S1. A dissolved oxygen probe monitors a stirred suspension of birnessite before and after injection of N_2-sparged ceric ammonium nitrate via syringe. The apparatus is protected from air-O_2 by flowing nitrogen into the side-arm of the flask, which exits through the top.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra (XPS) of the dry samples were collected using monochromatic Al Kα X-rays (148.7 eV) generated from a rotating anode were used with a high resolution, 300 mm mean radius hemispherical electrostatic analyzer. The base pressure of the analysis chamber was maintained at $1x10^{-9}$ Torr. Survey scans were collected using fixed pass energy of 300 eV and narrow scans were collected using a fixed pass energy of 150 eV. Data collected for the Mn $2p_{3/2}$ and O 1s spectral regions were peak fitted using Casa XPS software. To fit the Mn $2p_{3/2}$ region the procedure used by Nesbit and Banerjee was employed that takes into account the multiplet structure resulting from the presence of unpaired valence electrons in the 3d orbitals of manganese in the birnessite sample.[9] This fitting procedure relies on the theoretical calculations by Gupta of the expected XPS spectra from the free Mn(IV), Mn(III), and Mn(II) ions. The prior work showed that the calculated XPS spectra for the free ions (each containing 5 multiplet peaks) allowed the accurate fitting of experimental XPS Mn $2p_{3/2}$ data for birnessite.[9] The contributions of the Mn(IV) to the XPS data were fitted with peaks at 642.15, 643.19, 644.0, 645.05, and 646.06 eV using a relative peak area ratio of 1:0.63:0.32:0.10:0.06. Mn(III) contributions to the XPS data were fitted with peaks at 640.83, 641.53, 642.34, 643.36, and 644.73 eV with a relative peak area ratio of 1.0:0.71:0.42:0.30:0.30. Peak area ratios for each Mn-species were not changed during the fitting procedure. Peaks with a 50:50 Gaussian:Lorentzian contribution were used in the procedure and the full width half maximum for each peak was 1.15 eV. Using these parameters the spectral data was fitted by varying the relative contribution of individual set of multiplet peaks.

Determination of Mn content

To determine total Mn content, 0.50g of birnessite was dissolved in hydroxylamine hydrochloride (0.25M, 20mL) and diluted to 250mL. Mn content was then determined by analysis of an aliquot of the diluted solution by ICP-OES.

Average oxidation state of Mn

An oxalic acid-permangante back-titration[3] was used to determine the bulk AOS. First, Mn content was determined using the previous stated method. Second, a 0.50g sample of birnessite was completely dissolved in 5mL of 0.48M oxalic acid and 10.00mL H_2SO_4 to reduce all Mn species to Mn^{2+}. The excess oxalate was determined by back-titration at 70°C with a $KMnO_4$ (0.025M) solution. AOS was calculated according to both the titration result and the total amount of Mn determined from ICP-OES.

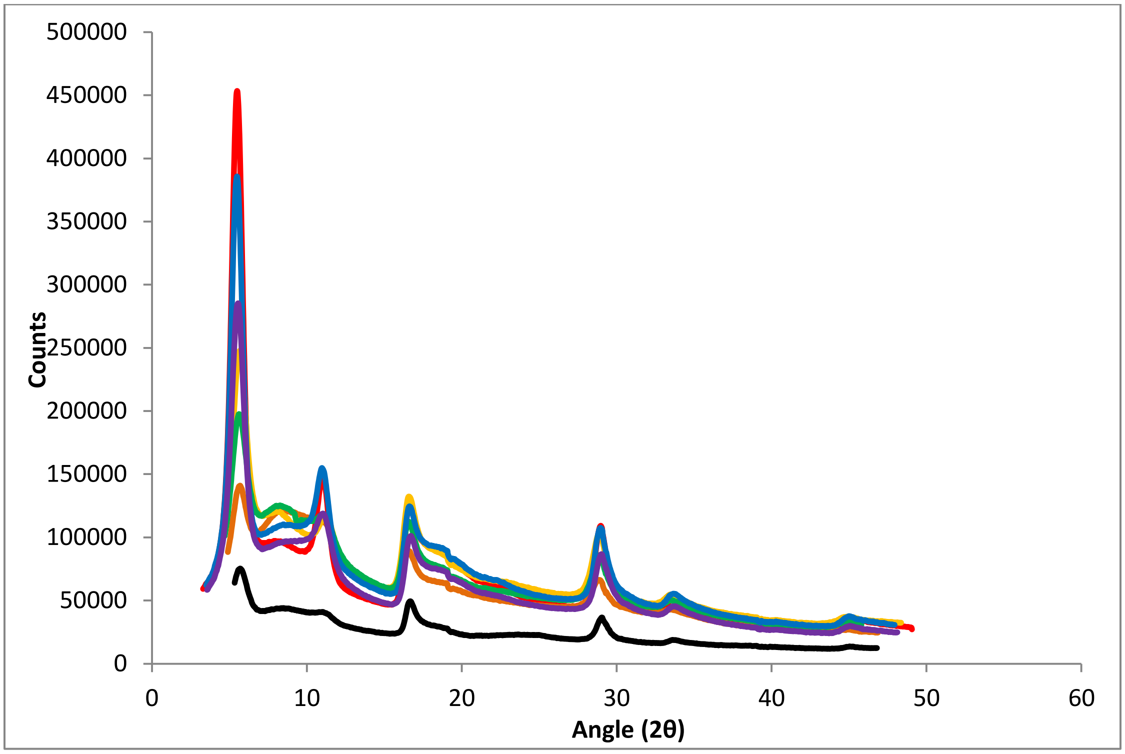


Figure S2. Powder X-ray diffraction pattern* of birnessite samples, λ = 0.71073- ●: 3.45(B1) ◆: 3.46 (B2) ■: 3.50(B3) ▲: 3.51(B4) ■: 3.77(B5) ◆: 3.78(B6) ◆: 3.49 (B5*). (*7*)

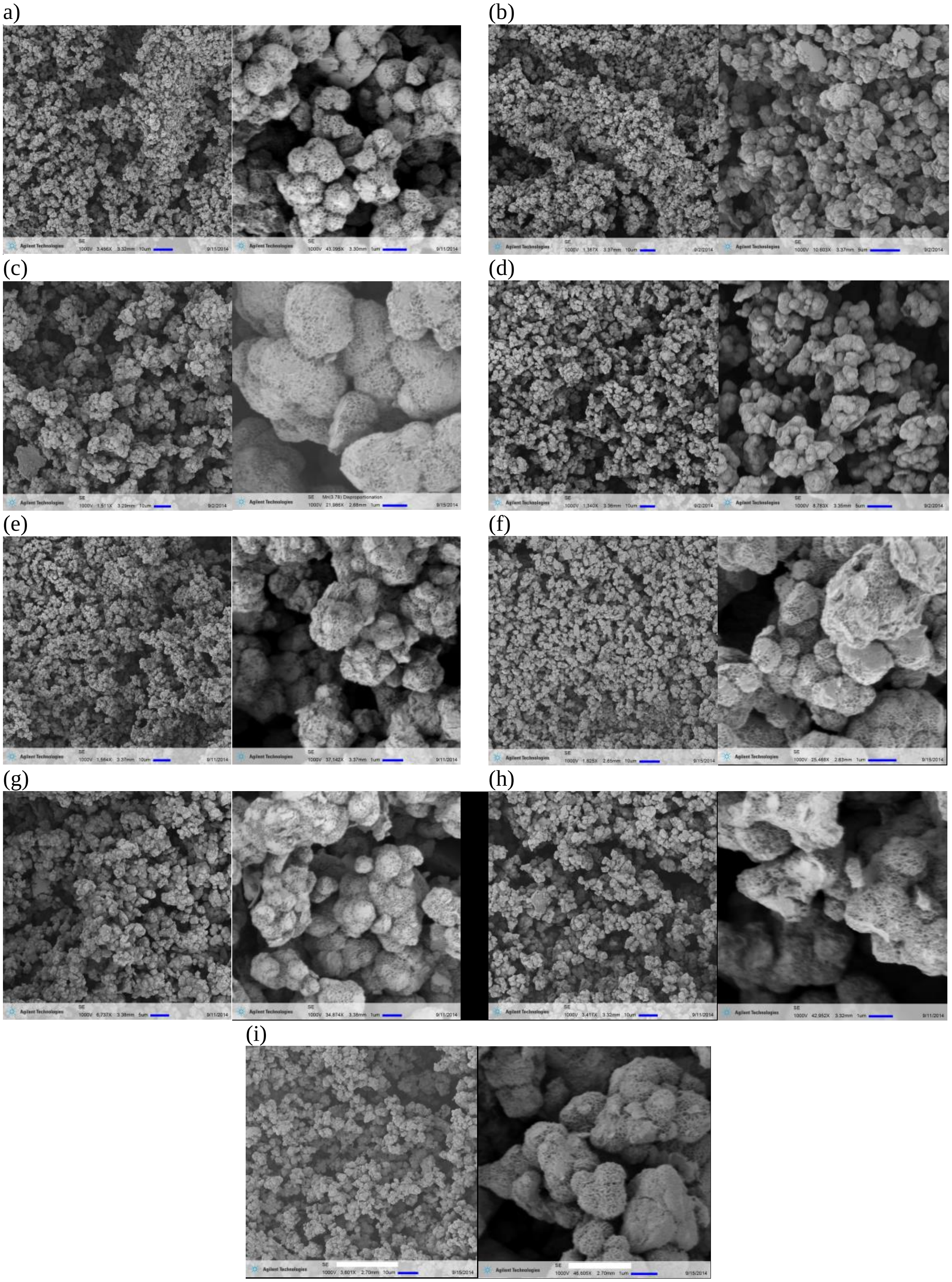


Fig. S3. SEM images of birnessite samples: (a.) B1- Mn(3.45); (b.) B2- Mn(3.46); (c.) B3- Mn(3.50); (d.) B4-Mn(3.51); (e.) B5- Mn(3.77); (f.) B6- Mn(3.78); (g.)B3 post-catalysis; (h.) B6 post-catalysis; (i.) B6* comproportionated.

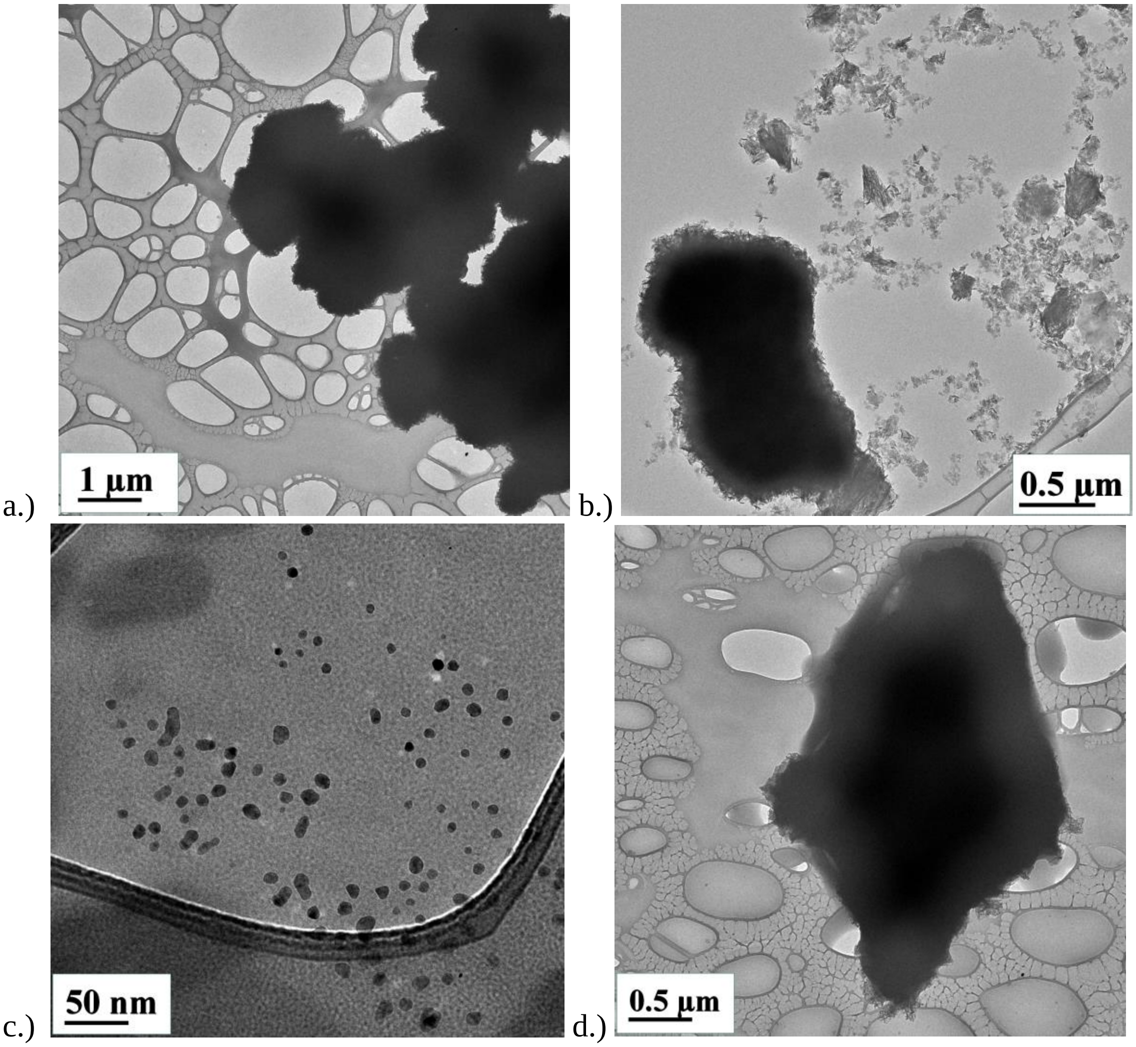


Figure S4. TEM images of (a.) birnessite ; (b) unwashed post-comproportionation sample; (c.) Mn(III) nanoparticle side products; (d.) pure comproportionated sample.

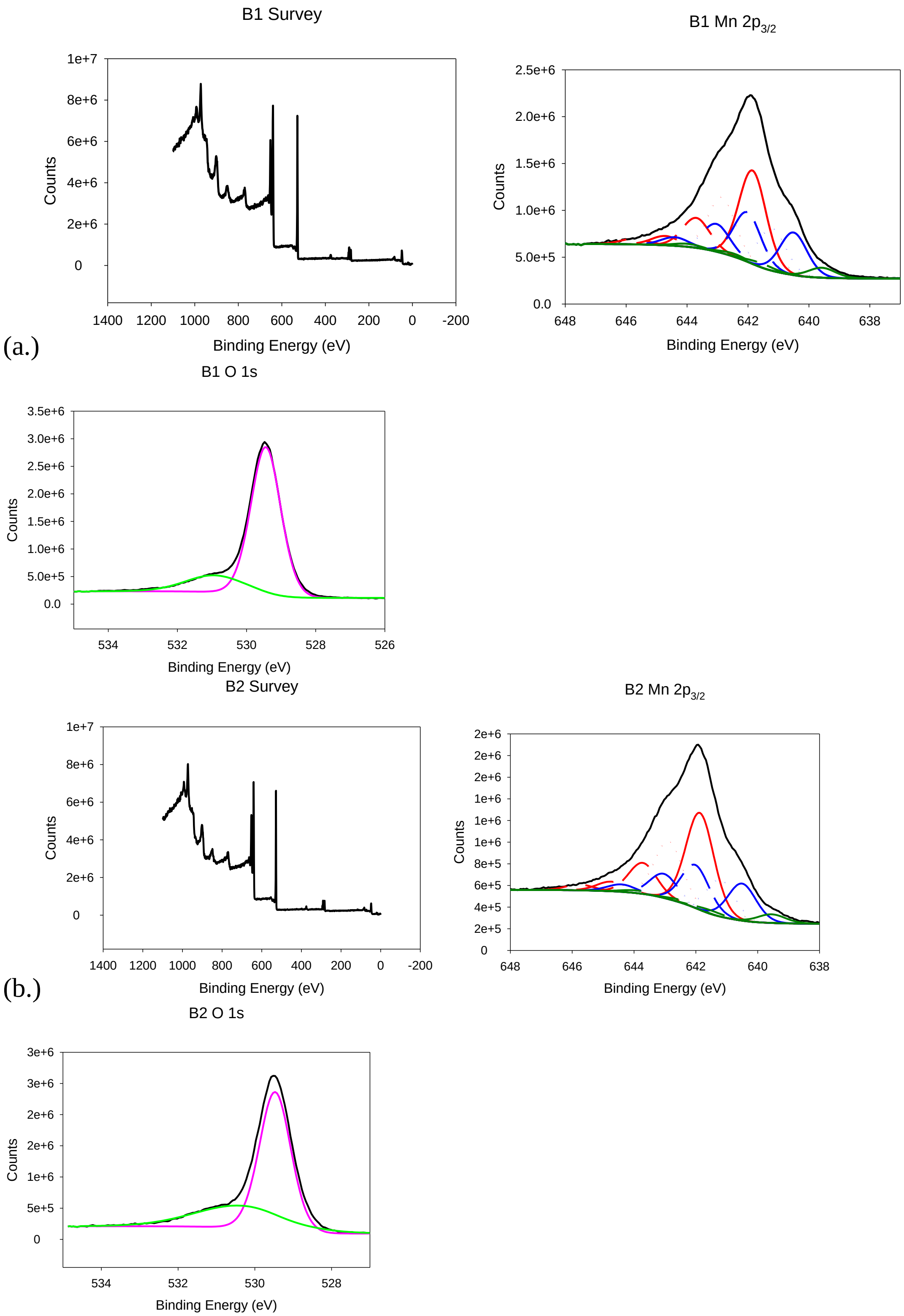
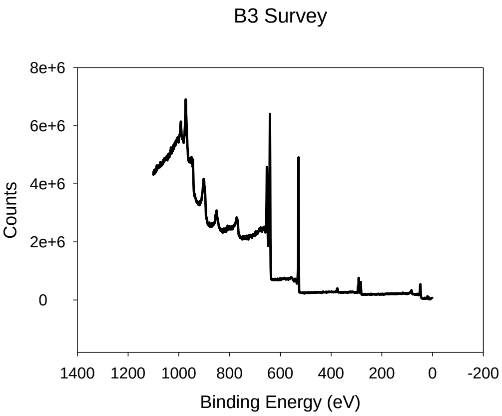
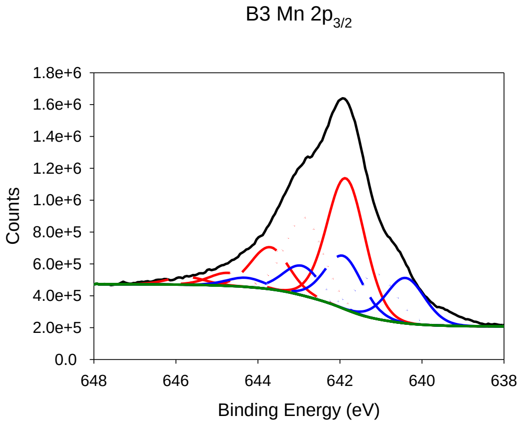
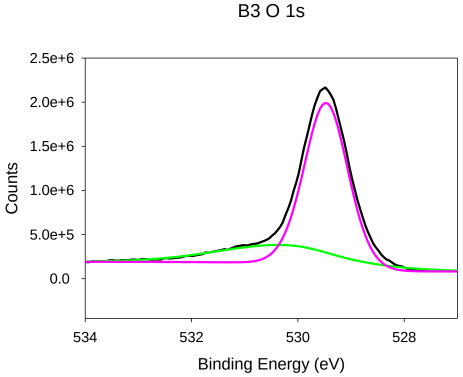


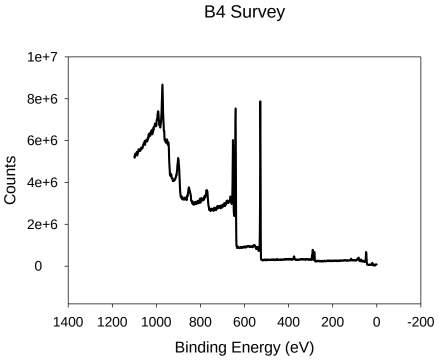
Figure S5. XPS spectra of- (a.) B1; (b.) B2; For Mn $2p_{3/2}$ spectra- Mn(IV) fittings are shown in red, Mn(III) fittings are shown in blue, and Mn(II) fittings are shown in dark green.[8]. For O 1s spectra, O^{2-} fits are shown in purple and OH^{-} fits are shown in green.[9]

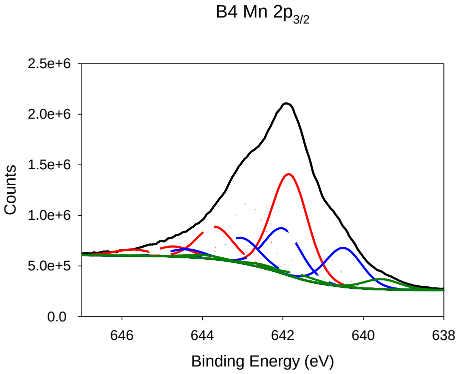




(c.)







(d.)

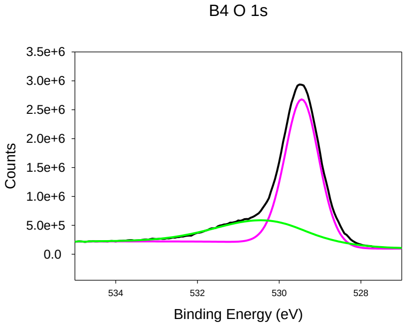
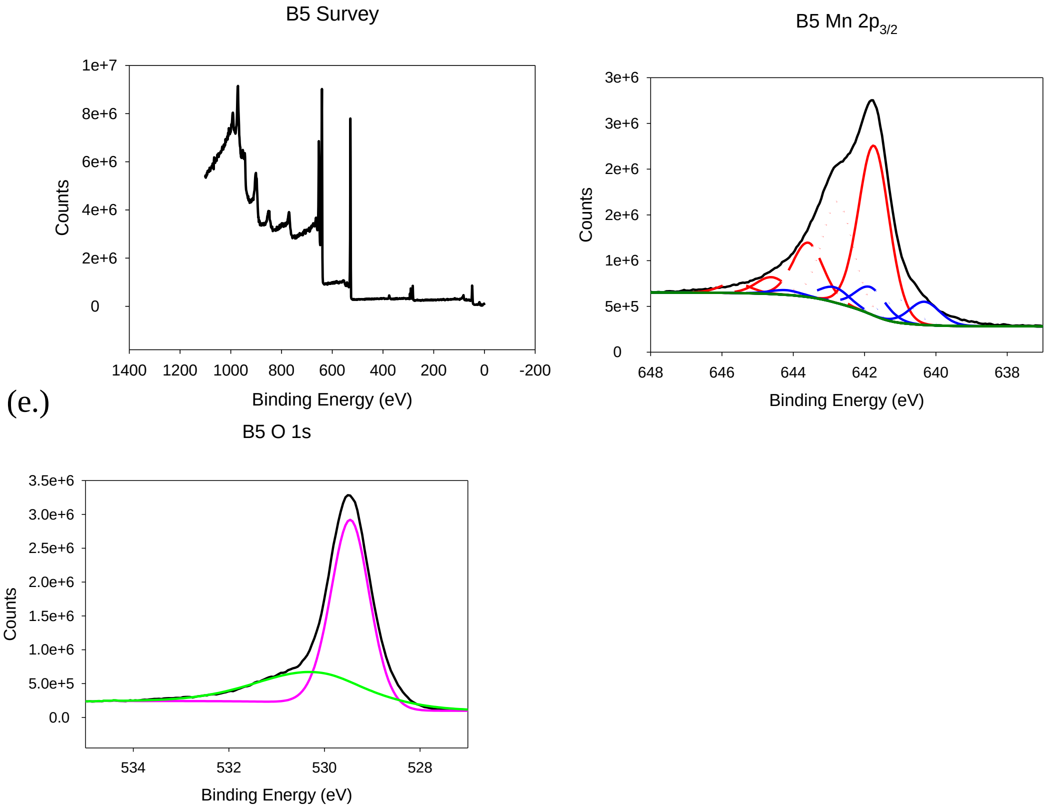


Figure S5 (cont). XPS spectra of- (c.) B3; (d.) B4; For Mn $2p_{3/2}$ spectra- Mn(IV) fittings are shown in red, Mn(III) fittings are shown in blue, and Mn(II) fittings are shown in dark green.[9] For O 1s spectra, O^{2-} fits are shown in purple and OH^{-} fits are shown in green.[9]



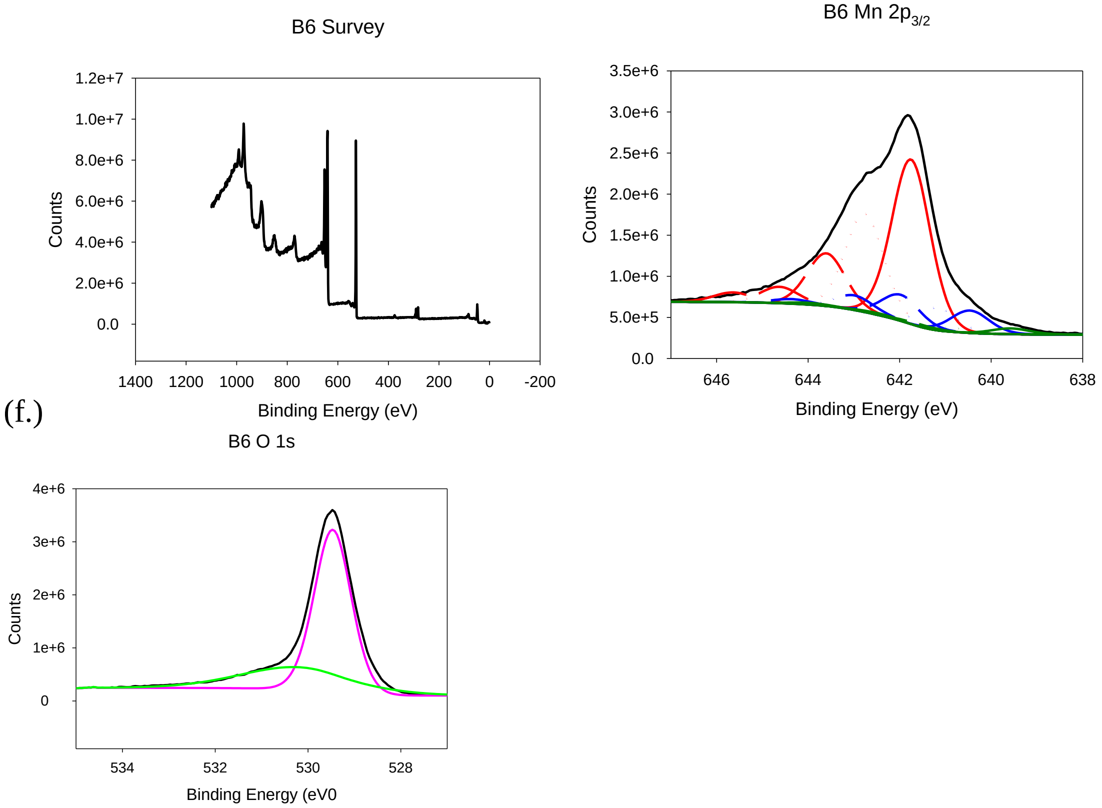


Figure S5 (cont). XPS spectra of (e.) B5; (f.) B6; For Mn $2p_{3/2}$ spectra- Mn(IV) fittings are shown in red, Mn(III) fittings are shown in blue, and Mn(II) fittings are shown in dark green.[9] For O 1s spectra, O^{2-} fits are shown in purple and OH^{-} fits are shown in green. [9]

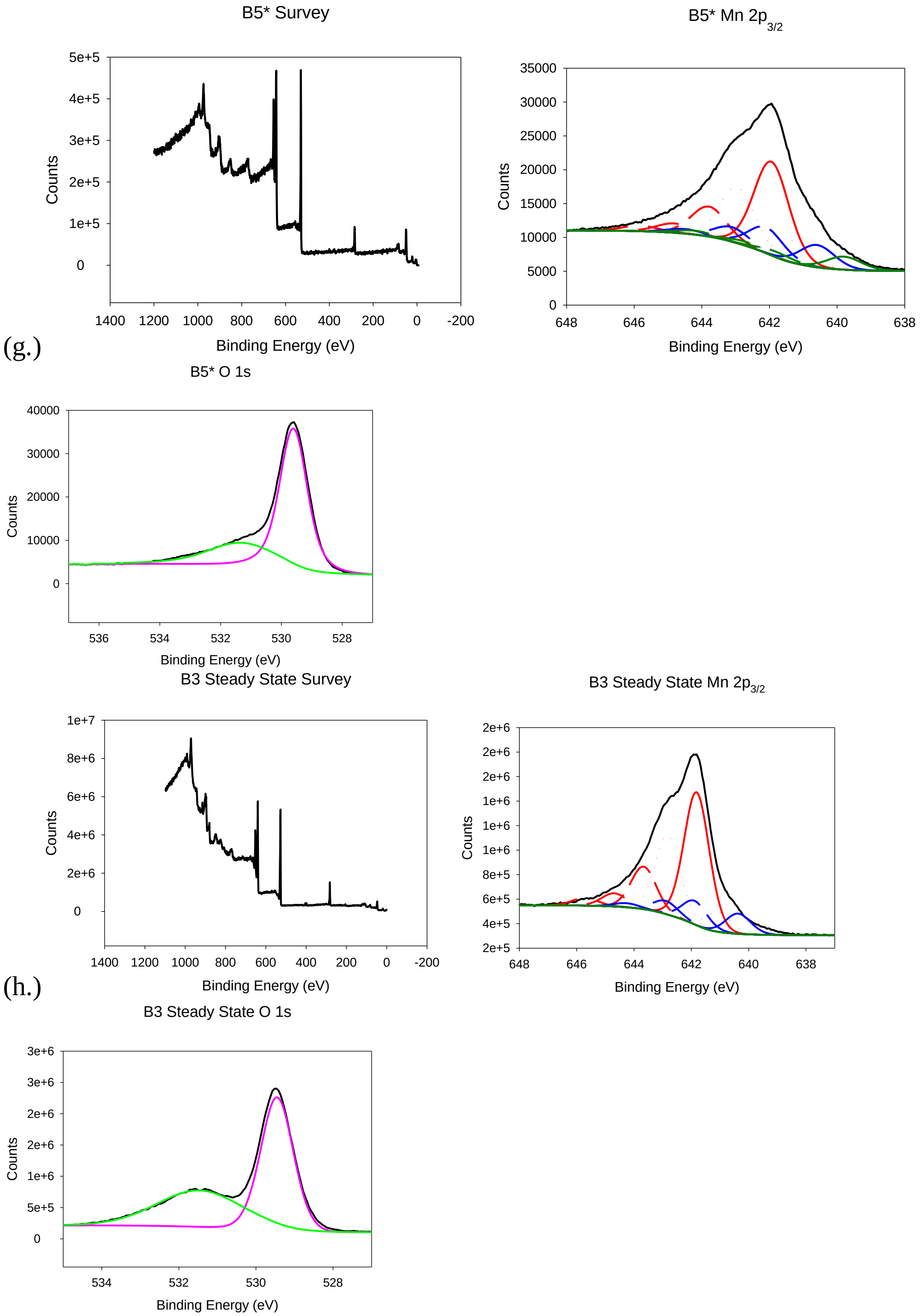
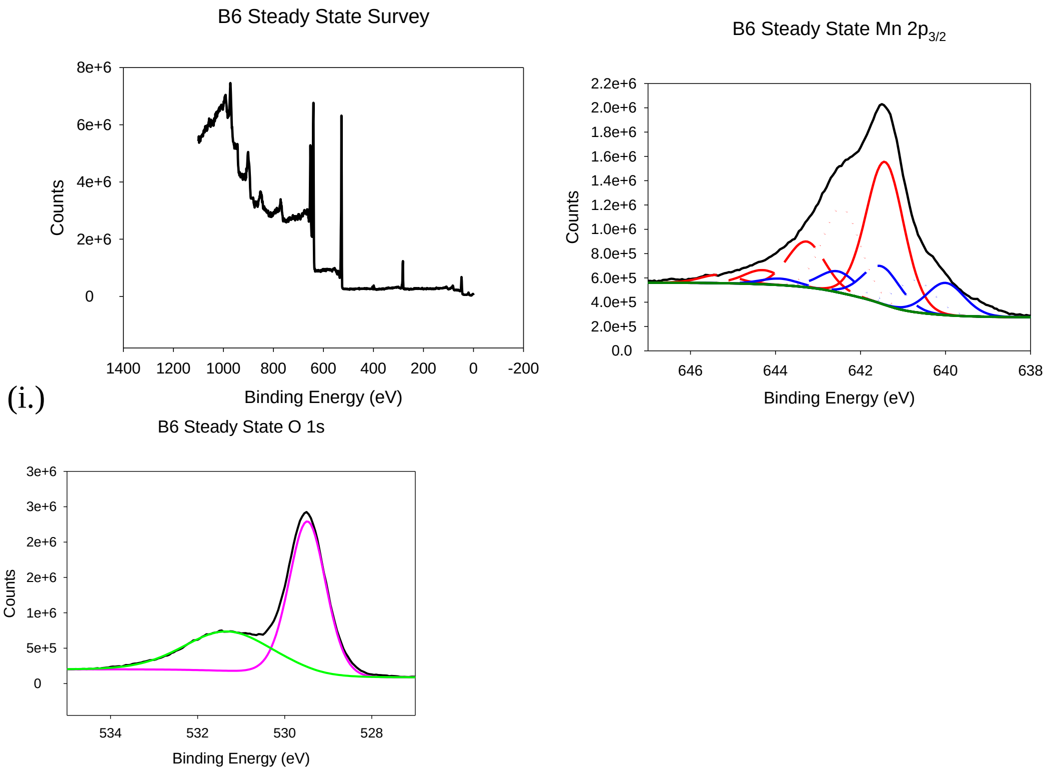


Figure S5 (cont). XPS spectra of (g.) B5*; (h.) B3 in its steady state; For Mn 2p$_{3/2}$ spectra- Mn(IV) fittings are shown in red, Mn(III) fittings are shown in blue, and Mn(II) fittings are shown in dark green.[9] For O 1s spectra, O^{2-} fits are shown in purple and OH^{-} fits are shown in green.[9]



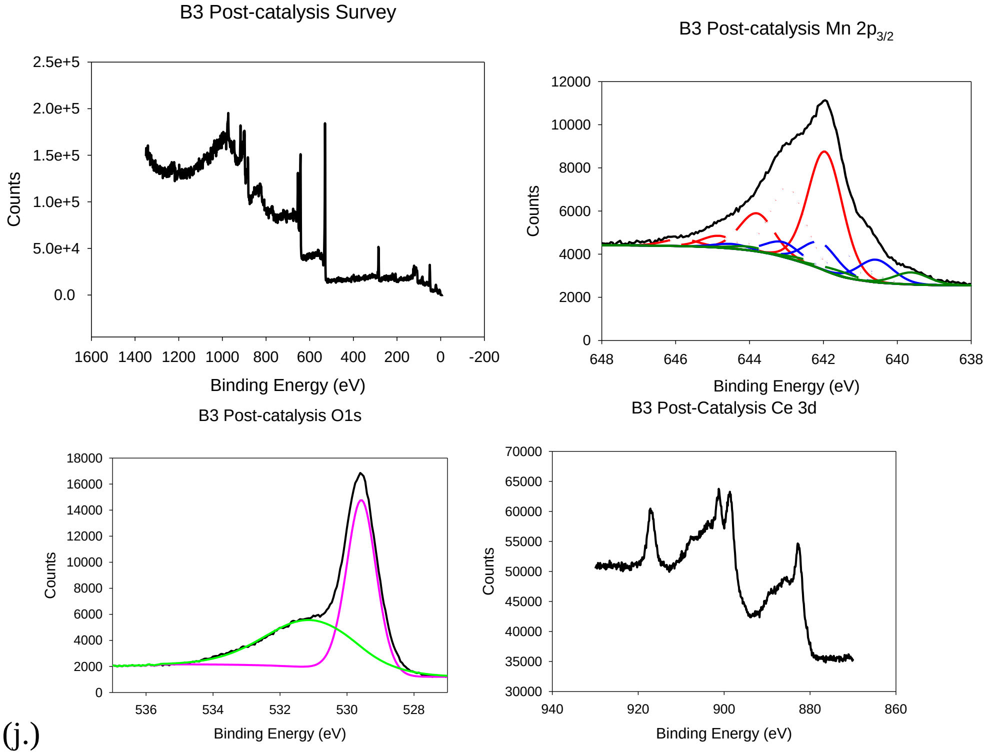
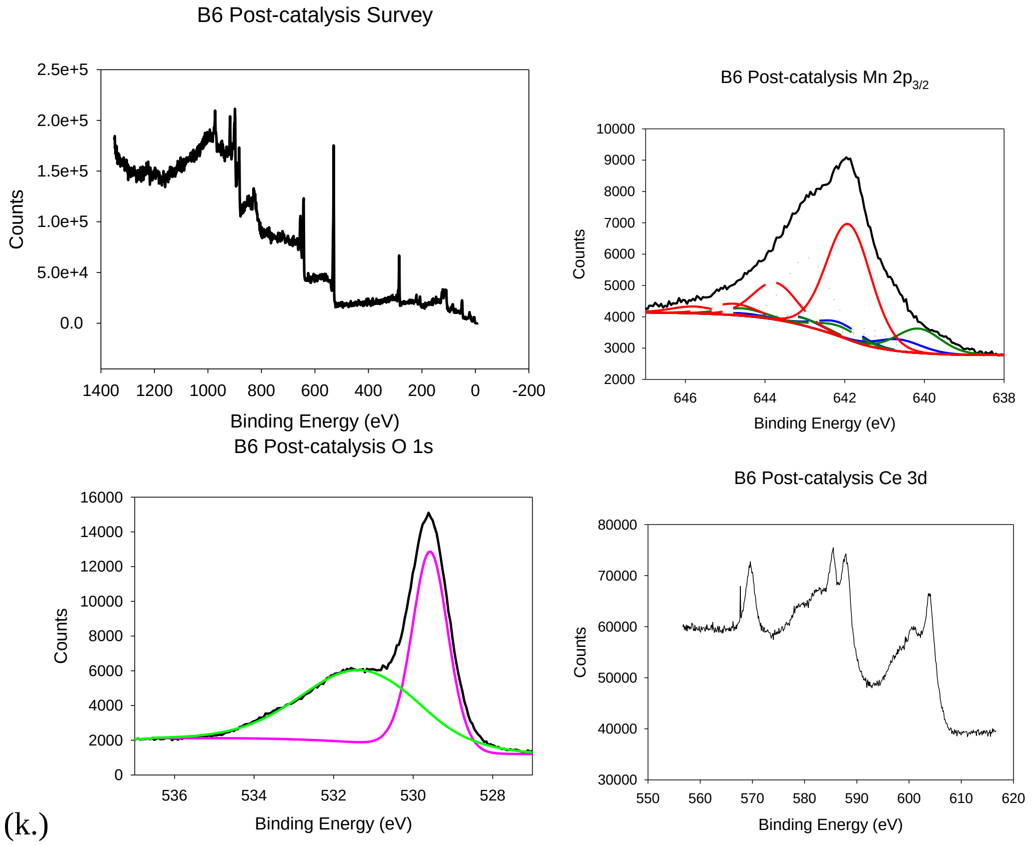
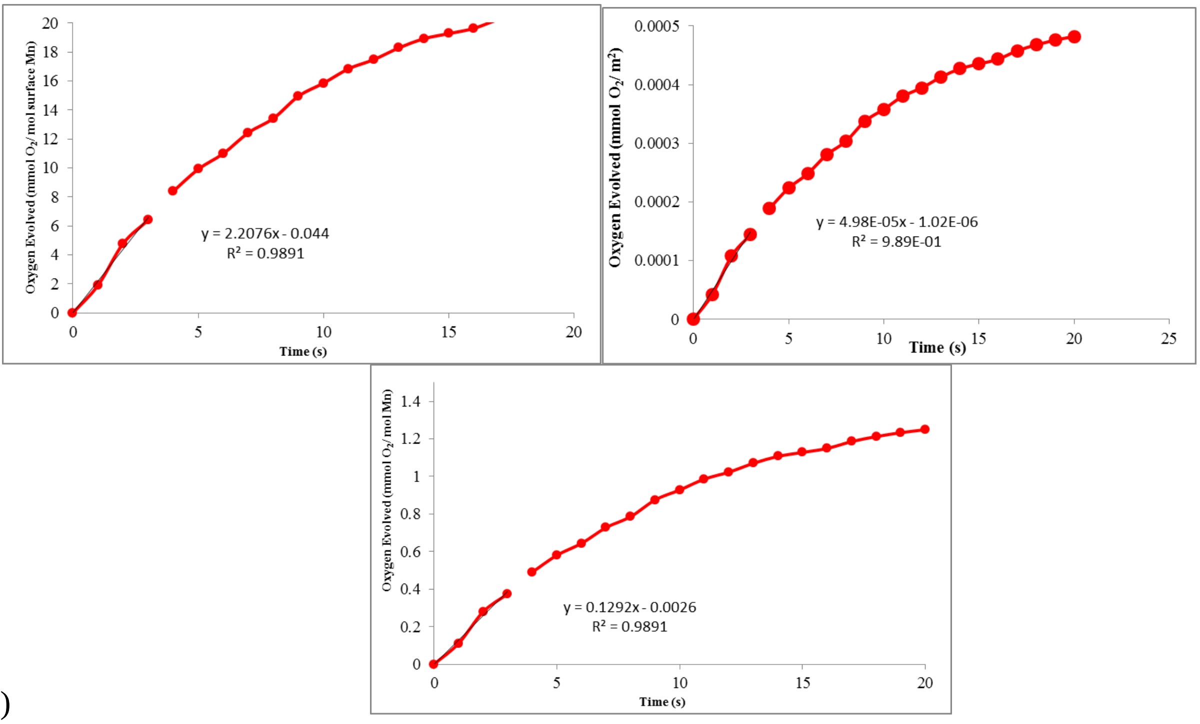


Figure S5 (Cont). XPS spectra of (i.) B6 in its steady state; (j.) B3 after catalysis; each with corresponding survey, Mn $2p_{3/2}$, and O 1s spectra. The Ce 3d spectra for (j.) shows evidence of adoption of cerium species on surface after catalysis. For Mn $2p_{3/2}$ spectra- Mn(IV) fittings are shown in red, Mn(III) fittings are shown in blue, and Mn(II) fittings are shown in dark green.[9] For O 1s spectra, O^{2-} fits are shown in purple and OH^- fits are shown in green.[9]

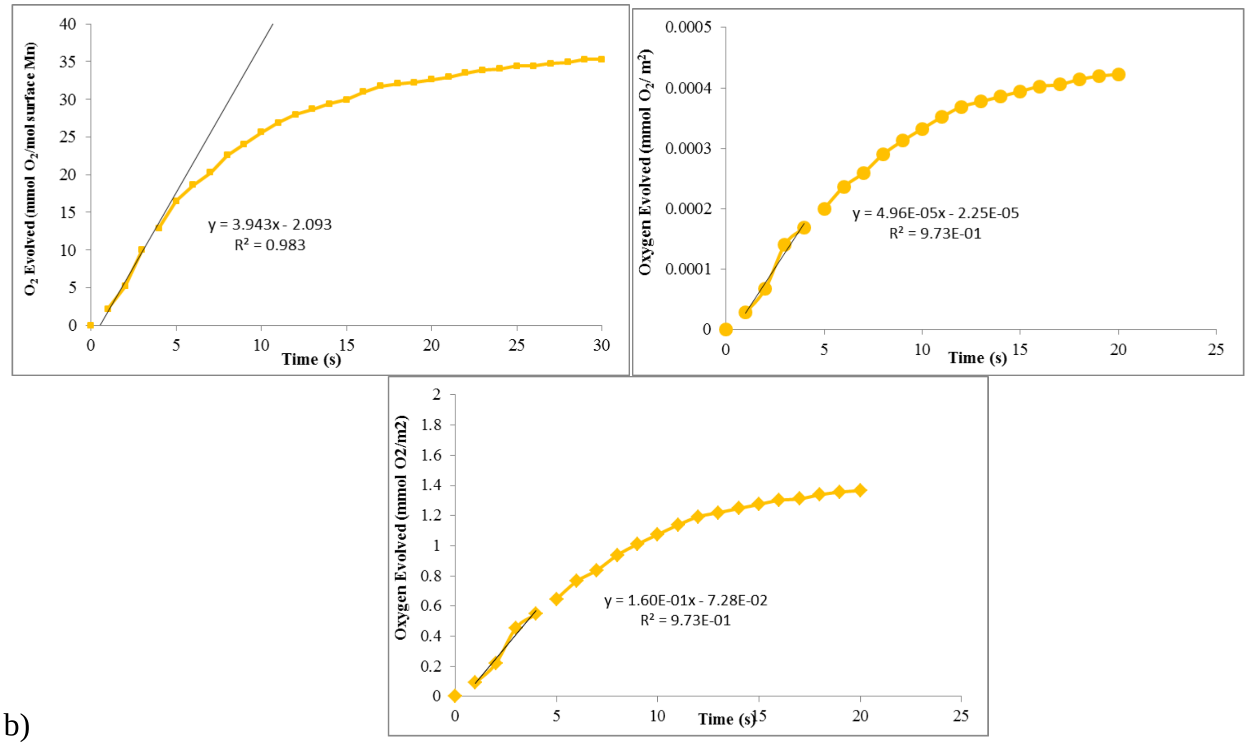


(k.)

Figure S5 (Cont). XPS spectra of (k.) B6 after catalysis with corresponding survey, Mn $2p_{3/2}$, and O 1s spectra. The Ce 3d spectra for (k.) shows evidence of adoption of cerium species on surface after catalysis. For Mn $2p_{3/2}$ spectra- Mn(IV) fittings are shown in red, Mn(III) fittings are shown in blue, and Mn(II) fittings are shown in dark green.[9] For O 1s spectra, O^{2-} fits are shown in purple and OH^- fits are shown in green.[9]

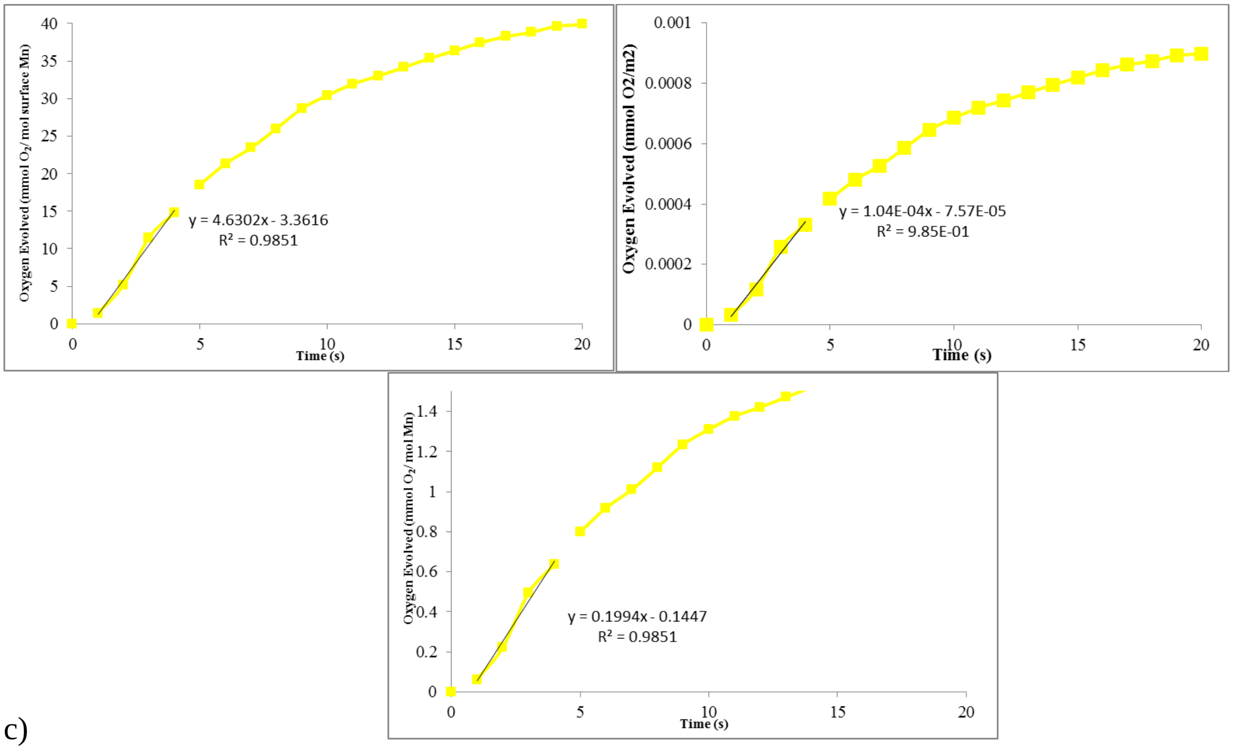


a)

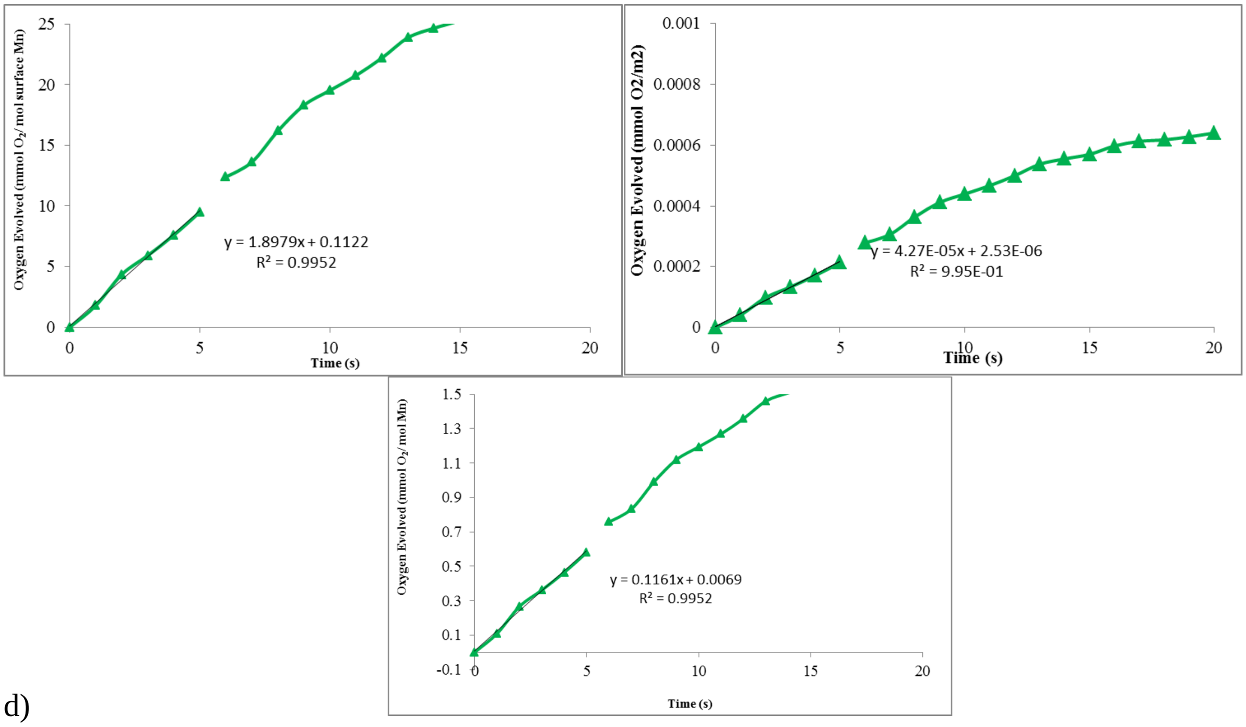


b)

Figure S6. Determination of turnover frequency for (a.)●: 3.45 [B1], (b.)◆: 3.46 [B2] normalized by surface Mn (left), surface area (right), and total mol Mn(bottom).

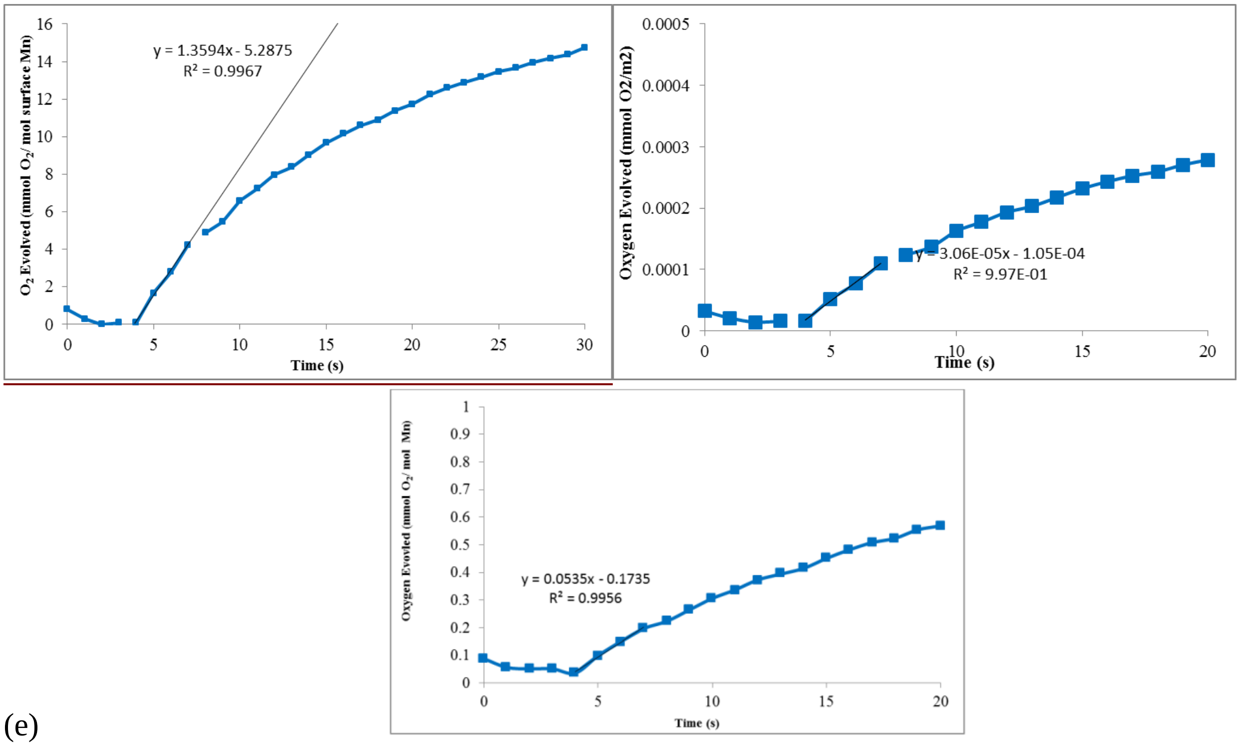


c)

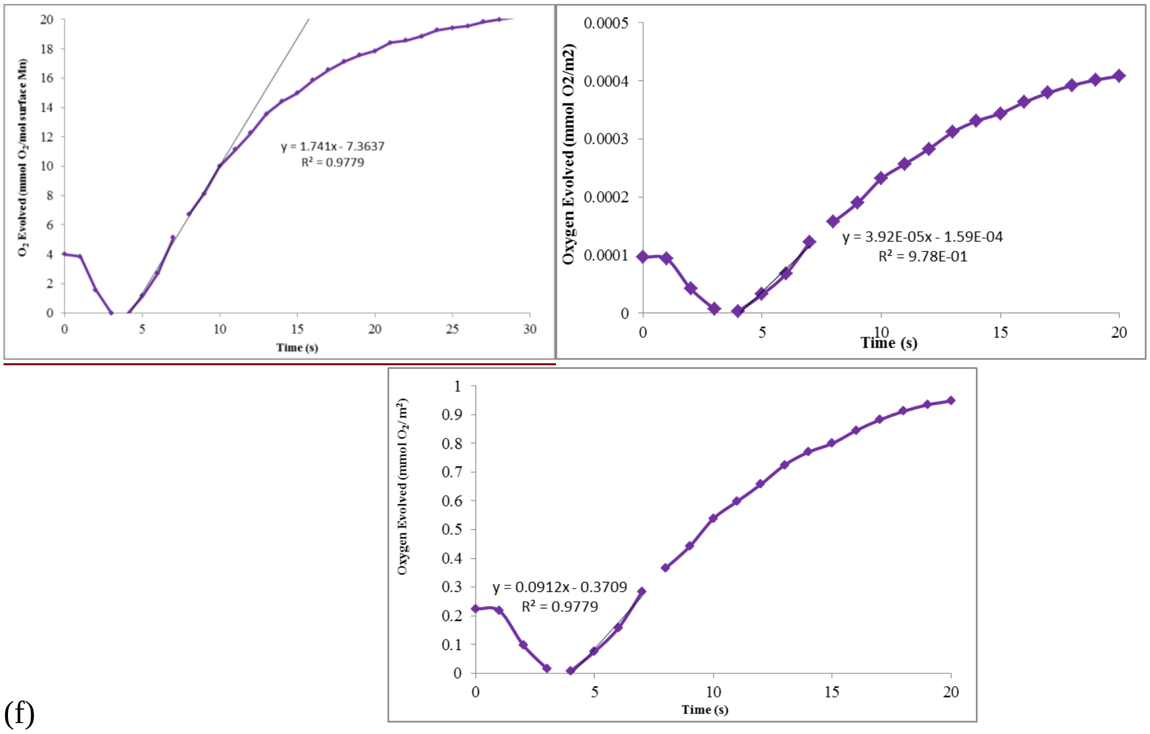


d)

Figure S6. Determination of turnover frequency for- (c.) 🟨: 3.50 [B3], (d) ▲: 3.51 [B4] normalized by surface Mn (left), surface area (right), and total mol Mn(bottom).

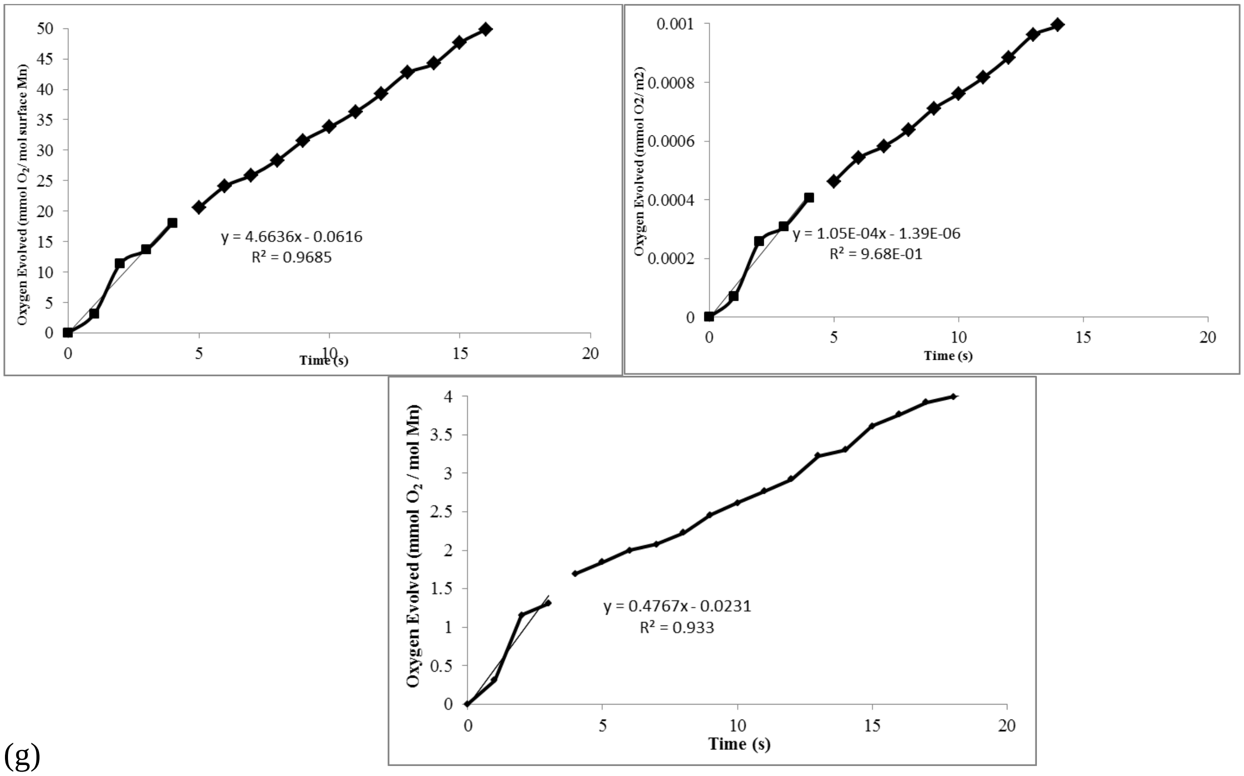


(e)



(f)

Figure S6 (cont). Determination of turnover frequency for (e.)■: 3.77 [B5],(f.)◆: 3.78 [B6] normalized by surface Mn (left), surface area (right), and total mol Mn(bottom).



(g)

Figure S6 (cont). Determination of turnover frequency for (g.)◆: 3.49 [B5*] normalized by surface Mn (left), surface area (right), and total mol Mn(bottom).

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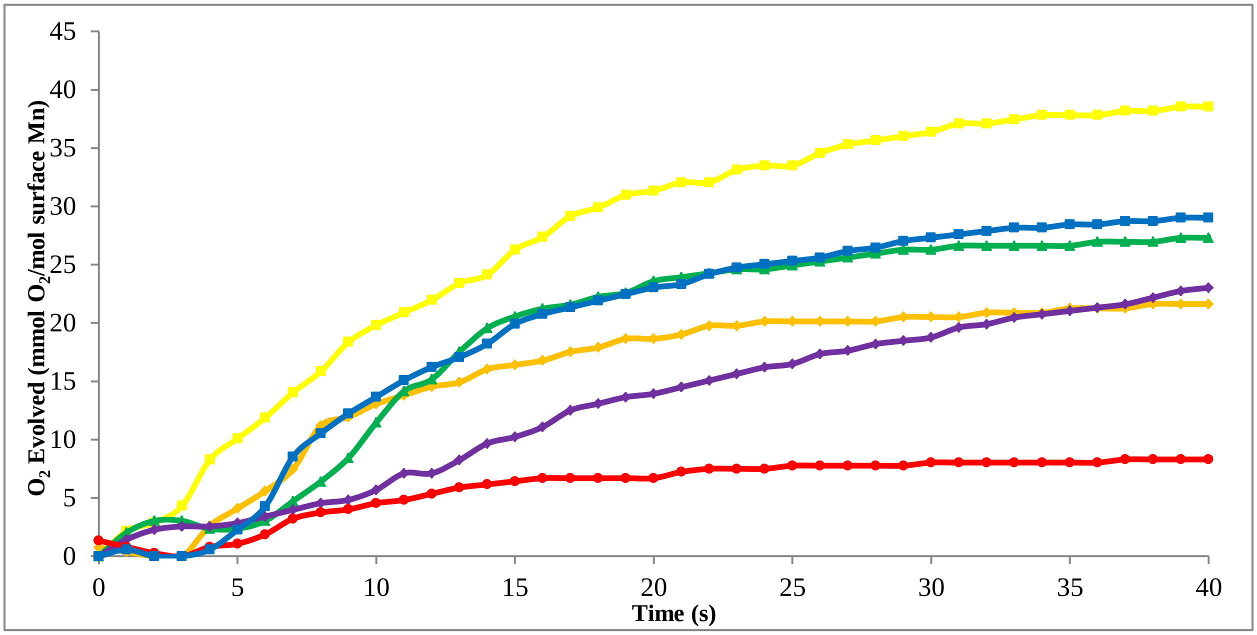

Figure S7. Catalytic O_2 evolution by recycled catalysts, which were collected, centrifuged, washed with water, and used again to catalyze water oxidation. All post-catalysis birnessite samples show an induction period. - ●: 3.45 [B1]-◆: 3.46 [B2]-■: 3.50 [B3]-▲: 3.51 [B4]-■: 3.77 [B5]-◆: 3.78 [B6].

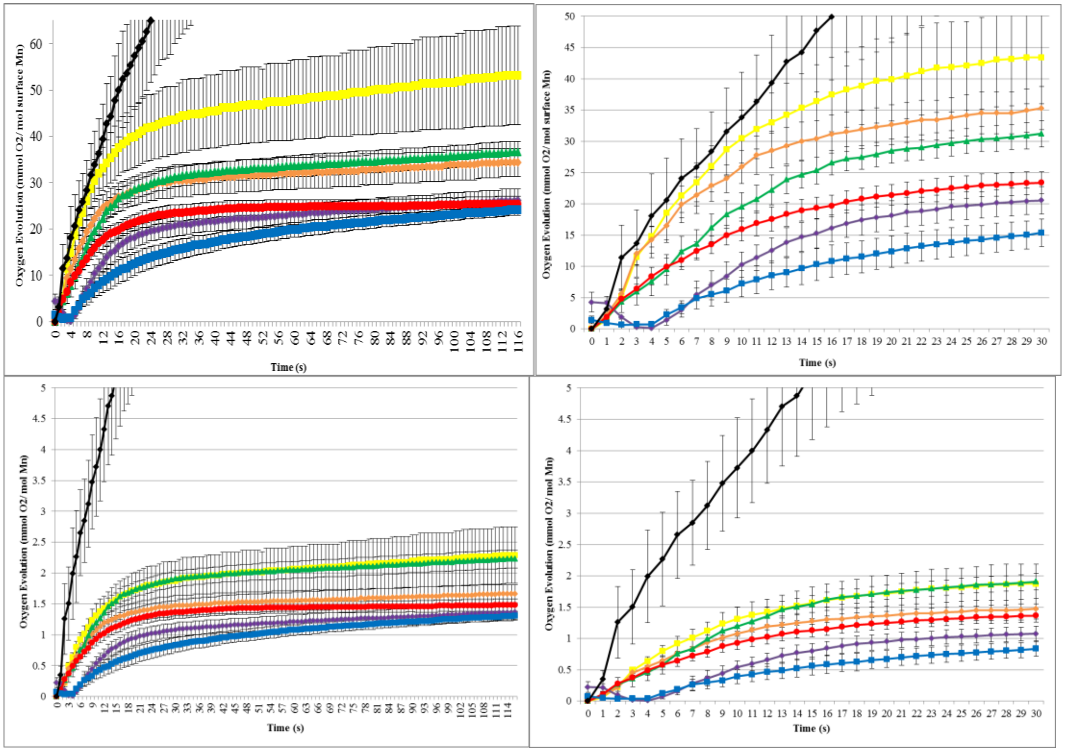

Figure S8. O_2 evolution measured by electrode dissolved oxygen probe with error bars for three trials. Concentrations of O_2 for each sample are normalized by the (a.) moles of surface Mn and (b.) the bulk moles of Mn Initial AOS(sample name): ●: 3.45(B1) ◆: 3.46 (B2) ■: 3.50(B3) ▲: 3.51(B4) ■: 3.77(B5) ◆: 3.78(B6) ◆: 3.49 (B5*).

Table S1. Experimental data for birnessite samples

Sample Name	AOS[a]	Mn(IV) (%)	Mn(III) (%)	Mn(II) (%)	O^{2-} (%)	OH^{-} (%)	Surface Area (m^2/g)[b]
B1	3.45	50.71	43.63	5.69	89.57	10.43	20.48
B2	3.46	53.62	39.67	6.94	85.20	14.80	14.56
B3	3.50	57.07	36.82	6.12	89.57	10.43	15.41
B4	3.51	55.21	40.88	3.92	82.68	16.32	16.47
B5	3.77	77.92	22.02	0.06	85.43	14.57	19.24
B6	3.78	78.57	21.92	0.00	71.61	29.39	19.37
B3-SS[c]	3.71	74.81	22.01	3.19	58.13	41.87	15.41
B6-SS	3.70	70.65	29.30	0.08	61.85	38.15	19.37
B3-PC[d]	3.57	66.67	24.50	8.83	53.85	46.06	15.41
B6-PC	3.48	67.73	13.47	18.80	53.94	46.06	19.37
B5*[e]	3.49	60.86	28.00	11.14	71.81	28.19	33.47
	3.04[f]	4.37[f]	94.62[f]	1.46[f]	51.56[f]	48.44[f]	97.30[f]
B5*-SS	3.44	59.93	26.37	13.70	83.41	16.59	33.74
B5*-PC	3.44	68.53	9.45	21.92	66.86	33.14	33.74

[a] AOS, manganese oxidation state percentages, and oxygen species were determined via XPS

[b] Surface area was determined by BET measurements.

[c] SS indicates measurements on samples recovered after reaching steady-state conditions (>30 s into catalysis).

[d] PC indicates post-catalysis samples, which were filtered, washed, and reused in a new catalysis test.

[e] A * is used to indicate that the sample has been enriched with Mn(III) by comproportionation of surface Mn(IV) with Mn(II) ions.

[f] Sample composition and BET surface area of comproportionated B5 sample before filtration: contains side product nanoparticles.

Table S2. Turnover numbers (TON) and turnover frequencies (TOF) of birnessite samples with esd.

	TON (mmol O_2/ mol surface Mn)	TOF (mmol O_2/ mol surface Mn*s)	TON (mmol O_2/ m^{-2})	TOF (mmol O_2/ m^{-2}*s)	TON (mmol O_2/ mol Mn)	TOF (mmol O_2/ mol Mn*s)
B1	145 ± 3.0	2.2 ± 0.45	(3.26 ± 0.06)x10^{-3}	(4.9 ± 1)x10^{-5}	8.6 ± 0.18	0.13 ± 0.026
B2	535 ± 6.3	3.1 ± 1.30	(1.20 ± 0.01)x10^{-2}	(4.9 ± 2)x10^{-5}	9.6 ± 0.30	0.15 ± 0.064
B3	225 ±- 20.5	4.6 ±1.50	(5.1 ± 0.46)x10^{-3}	(1.0 ± 0.3)x10^{-4}	9.0 ± 0.88	0.20 ± 0.068
B4	454 ± 4.7	1.9 ± 1.25	(1.01 ± 0.01)x10^{-2}	(4.2 ± 2.7) x10^{-5}	10.0 ± 0.28	0.12 ± 0.068
B5	178 ± 2.3	1.3 ± 0.91	(4.00 ± 0.06)x10^{-3}	(3.0 ± 2)x10^{-5}	9.8 ± 0.12	0.05 ± 0.049
B6	115 ± 5.0	1.7 ± 1.31	(2.57 ± 0.11)x10^{-3}	(3.9 ± 3)x10^{-5}	6.0 ± 0.26	0.09 ± 0.069
B5*	5800 ± 190.0	4.7 ± 3.50	0.130 ± 0.004	(1.0 ± 0.7) x 10^{-4}	640 ±20	0.50 ± 0.038

Table S3. Manganese content for bulk birnessite sample determined by ICP-OES.

	Birnessite Digested (mg)	ICP Read-out (mg/L)	Mn content (mg)	Mn content (mg Mn/ mg birnessite)
B1	50.5	0.872	21.8	0.431
B2	23.4	0.696	8.70	0.371
B3	50.9	0.901	22.5	0.442
B4	30.5	0.407	10.1	0.333
B5	50.0	0.872	21.8	0.436
B6	50.1	0.916	21.8	0.457
B5*, [a]	7.4[a]	11.6[a]	2.9[a]	0.375
B3PC	47.8	0.803	20.0	0.418
B6PC	30.4	0.552	13.8	0.453

[a] For B5* sample, second dilution (1.0mL to 100mL dilution) was not performed. Sample was digested in 20mL hydroxylamine hydrochloride and diluted to 250.0mL and run through the ICP-OES.

Table S4. Birnessite stoichiometries determined by ICP-OES, IC, and XPS.

	Simplified	Complete
B1	$K_{0.20}MnO_2$	$K_{0.20}Mn(IV_{0.50},III_{0.44},II_{0.06})O_{1.79}OH_{0.21}$
B2	$K_{0.31}MnO_2$	$K_{0.31}Mn(IV_{0.54},III_{0.40},II_{0.06})O_{1.70}OH_{0.30}$
B3	$K_{0.61}MnO_2$	$K_{0.61}Mn(IV_{0.57},III_{0.37},II_{0.06})O_{1.79}OH_{0.21}$
B4	$K_{0.90}MnO_2$	$K_{0.90}Mn(IV_{0.55},III_{0.41},II_{0.04})O_{1.65}OH_{0.35}$
B5	$K_{0.22}MnO_2$	$K_{0.22}Mn(IV_{0.78},III_{0.22},II_{0.00})O_{1.70}OH_{0.30}$
B6	$K_{0.18}MnO_2$	$K_{0.18}Mn(IV_{0.78},III_{0.22},II_{0.00})O_{1.43}OH_{0.57}$
B5*	$K_{0.20}MnO_2$	$K_{0.20}Mn(IV_{0.61},III_{0.28},II_{0.11})O_{1.43}OH_{0.57}$
B3-SS	$K_{0.010}MnO_2$	$K_{0.01}Mn(IV_{0.74},III_{0.22},II_{0.04})O_{1.16}OH_{0.84}$
B6-SS	$K_{0.021}MnO_2$	$K_{0.02}Mn(IV_{0.70},III_{0.29},II_{0.01})O_{1.22}OH_{0.76}$
B5*-SS	$K_{0.018}MnO_2$	$K_{0.018}Mn(IV_{0.59},III_{0.26},II_{0.13})O_{1.66}OH_{0.54}$
B3-PC	$K_{0.0020}MnO_2$	$K_{0.02}Mn(IV_{0.67},III_{0.24},II_{0.09})O_{1.06}OH_{0.94}$
B6-PC	$K_{0.0060}MnO_2$	$K_{0.20}Mn(IV_{0.68},III_{0.13},II_{0.19})O_{1.06}OH_{0.94}$
B5*-PC	$K_{0.012}MnO_2$	$K_{0.012}Mn(IV_{0.68},III_{0.10},II_{0.22})O_{1.34}OH_{0.66}$

Table S5. Catalytic loadings for turnover number (TON) and turnover frequency (TOF) trials. Trials were done in triplicate with masses weighed to ± 1 mg.

	TON birnessite loading (mg)	TOF birnessite loading (mg)
B1	50	50
B2	10	50
B3	50	50
B4	7	50
B5	50	50
B6	50	50
B5*	1	10