Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synthetic manganese-calcium cluster similar to the catalyst of Photosystem II: Challenges for biomimetic water oxidation

Younes Mousazade,[a] Mohammad Reza Mohammadi,[b] Robabeh Bagheri,[c] Rahman Bikas,[*d] Petko Chernev,[e,f] Zhenlun Song,[c] Tadeusz Lis,[g] Milosz Siczek,[g] Nader Noshiranzadeh,[h] Stefan Mebs,[e] Holger Dau,[e] Ivelina Zaharieva,[e] and Mohammad Mahdi Najafpour[*a,i,j]

[a]*Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran*
[b]*University of Sistan and Baluchestan, Department of Physics, 98167-45845, Zahedan, Iran*
[c]*Surface Protection Research Group, Surface Department, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, 519 Zhuangshi Road, Ningbo 315201, China*
[d]*Department of Chemistry, Faculty of Science, Imam Khomeini International University, 34148-96818, Qazvin, Iran*
[e]*Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany*
[f]*Uppsala University, Department of Chemistry - Ångströmlaboratoriet, Lägerhyddsvägen 1, 75120 Uppsala, Sweden*
[g]*Faculty of Chemistry, University of Wrocław, 14. Joliot-Curie, 50-383, Wrocław, Poland*
[h]*Department of Chemistry, Faculty of Science, University of Zanjan, 45371-38791 Zanjan, Iran*
[i]*Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran*
[j]*Research Center for Basic Sciences & Modern Technologies (RBST), Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran*
Corresponding authors: Tel: (+98) 28 3390 1368; E-mail: bikas@sci.ikiu.ac.ir (RB); Tel: (+98) 24 3315 3201; E-mail: mmnajafpour@iasbs.ac.ir (MMN)

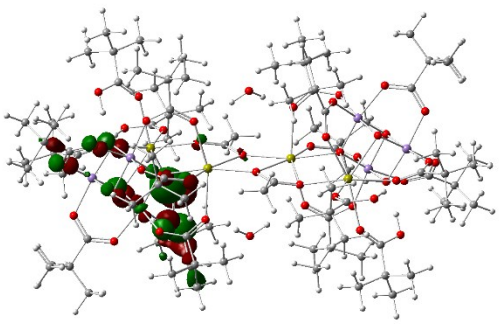
Table S1 Selected bond lengths and bond angles around the metal ions in the crystal structure of **1**.

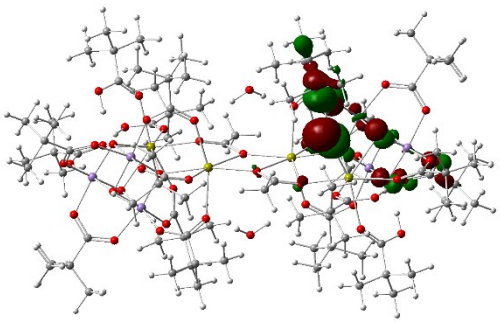
Bond	**Length (Å)**	**Bond**	**Angle (°)**
Mn1—Mn2	2.7448(8)	O3—Mn1—O2	87.88(11)
Mn1—Mn3	2.7281(9)	O3—Mn1—O1	85.74(11)
Mn2—Mn3	2.8548(9)	O2—Mn1—O1	85.22(10)
Mn1—Ca1	3.3990(10)	O3—Mn1—O2A	95.08(11)
Mn2—Ca1	3.3888(12)	O2—Mn1—O2A	96.51(11)
Mn2—Ca2	3.6079(16)	O1—Mn1—O2A	178.11(11)
Mn3—Ca1	3.3763(11)	O3—Mn1—O1J	89.09(11)
Mn3—Ca2	3.8038(19)	O2—Mn1—O1J	172.40(11)
Mn1—O3	1.813(2)	O1—Mn1—O1J	87.61(11)
Mn1—O2	1.844(2)	O2A—Mn1—O1J	90.70(11)
Mn1—O1	1.890(2)	O3—Mn1—O1I	172.95(11)
Mn1—O2A	1.897(3)	O2—Mn1—O1I	87.92(10)
Mn1—O1J	1.963(3)	O1—Mn1—O1I	88.27(11)
Mn1—O1I	1.981(2)	O2A—Mn1—O1I	91.01(11)
Mn2—O1	1.879(2)	O1J—Mn1—O1I	94.38(11)
Mn2—O2	1.859(2)	O4—Mn2—O2	90.18(11)
Mn2—O4	1.856(2)	O4—Mn2—O1	80.92(10)
Mn2—O2G	1.898(3)	O2—Mn2—O1	85.10(10)
Mn2—O2F	1.908(3)	O4—Mn2—O2G	100.53(11)
Mn2—O2I	1.978(3)	O2—Mn2—O2G	169.10(11)
Mn3—O1	1.895(2)	O1—Mn2—O2G	94.49(11)
Mn3—O3	1.838(3)	O4—Mn2—O2F	99.38(11)
Mn3—O4	1.863(2)	O2—Mn2—O2F	87.17(11)
Mn3—O2B	1.917(3)	O1—Mn2—O2F	172.27(11)
Mn3—O2H	1.919(3)	O2G—Mn2—O2F	93.05(12)
Mn3—O2J	1.982(3)	O4—Mn2—O2I	169.10(10)
Ca1—O2	2.444(2)	O2—Mn2—O2I	85.04(10)
Ca1—O3	2.483(3)	O1—Mn2—O2I	88.90(10)
Ca1—O4	2.574(3)	O2G—Mn2—O2I	84.06(11)
Ca1—O1A	2.531(3)	O2F—Mn2—O2I	90.18(11)
Ca1—O1B	2.304(3)	O3—Mn3—O4	91.64(11)
Ca1—O1C	2.354(3)	O3—Mn3—O1	84.88(11)
Ca1—O1D	2.400(3)	O4—Mn3—O1	80.30(10)
Ca1—O1E	2.420(3)	O3—Mn3—O2B	90.91(12)
Ca2—O4	2.379(2)	O4—Mn3—O2B	101.91(11)
Ca2—O1C	2.668(3)	O4—Mn3—O2H	95.19(11)
Ca2—O2C	2.427(3)	O1—Mn3—O2H	96.17(12)
Ca2—O1F	2.288(4)	O2B—Mn3—O2H	87.76(13)
Ca2—O1G	2.329(3)	O3—Mn3—O2J	86.13(12)
Ca2—O1H	2.331(4)	O4—Mn3—O2J	167.59(11)
Ca2—O1W	2.789(19)	O1—Mn3—O2J	87.34(11)
Ca1—Ca2	4.1094(16)	O2B—Mn3—O2J	90.35(12)
Ca2—Ca2^{i}	3.818(2)	O2H—Mn3—O2J	87.18(12)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

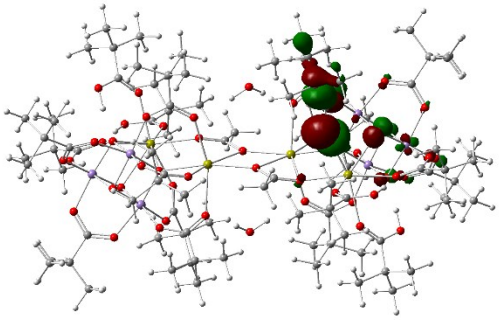
Table S2. Parameters obtained by the simulation of the k^3-weighted EXAFS spectra. The simulated spectra correspond to the Fourier-transformed EXAFS spectra shown in Fig. S7. To avoid over- parameterization, the Debye-Waller parameter (ó) was set to 0.067 Å. The amplitude reduction factor, S_0^2, was fixed to 0.7. R-factor filtered was 15 and 14 for **1** and the operated sample, respectively.

sample		Mn-O	Mn-Mn	Mn-C	Mn-O	Mn-Ca
1	Distance [Å]	1.89± 0.01	2.77± 0.01	2.91± 0.04	3.16± 0.05	3.29± 0.04
	Coordination number	6.4 ± 0.3	2.1 ± 0.4	4.5 ± 1.9	2.0 ± 1.9	0.9 ± 0.7
After operation	Distance [Å]	1.89± 0.01	2.81± 0.01	----------	----------	3.01± 0.01
	Coordination number	6.0 ± 0.3	3.0 ± 0.3	----------	----------	2.3±0.4

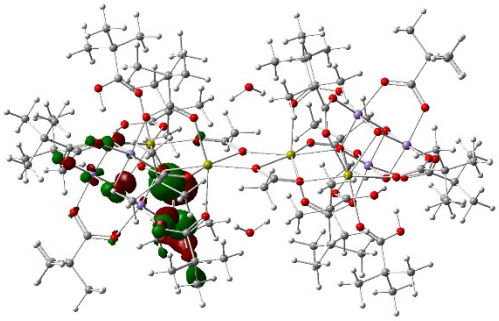




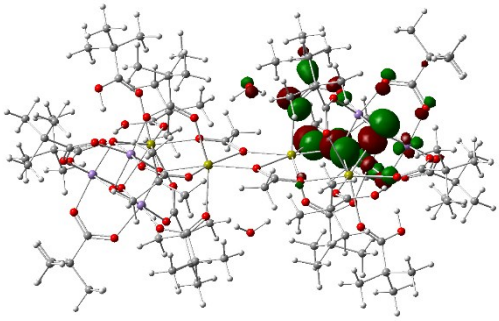
α-HOMO-3



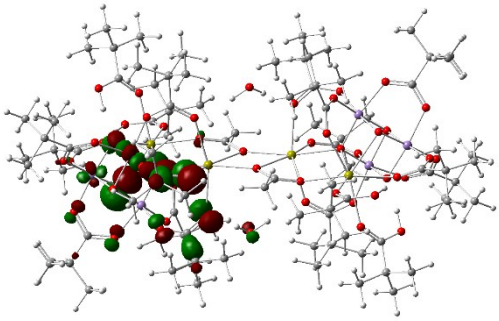
β-HOMO-3



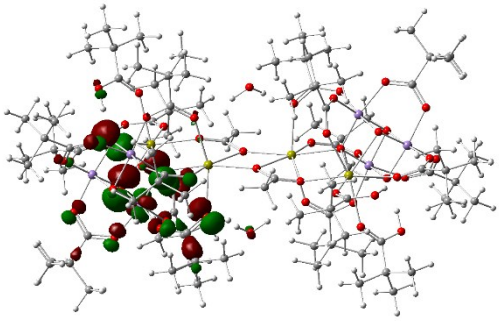
α-HOMO-2



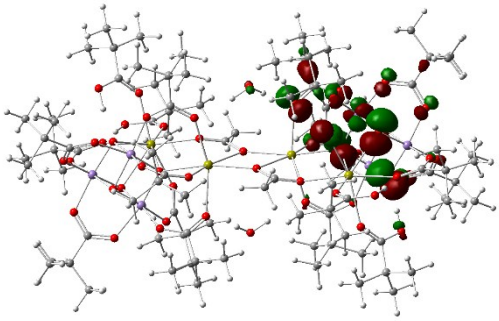
β-HOMO-2



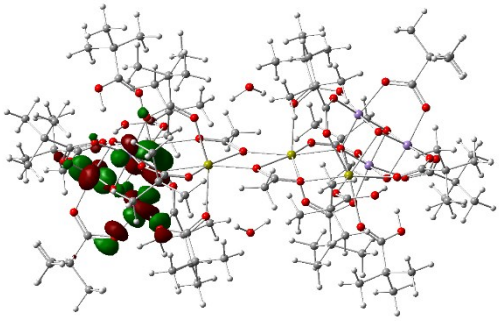
α-HOMO-1



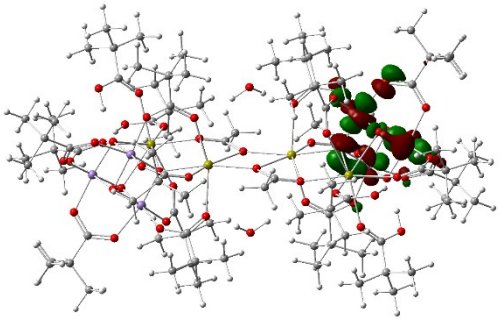
β-HOMO-1



α-HOMO

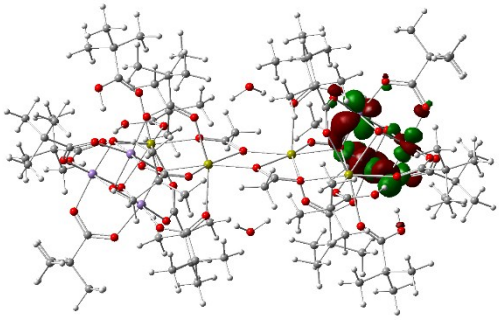


β-HOMO

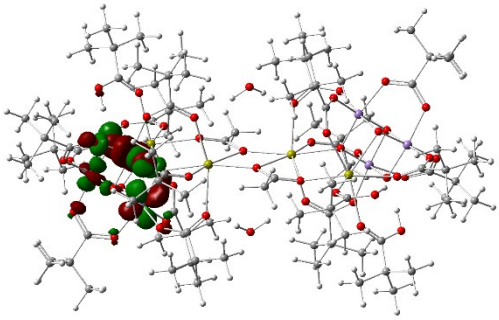


α-LUMO

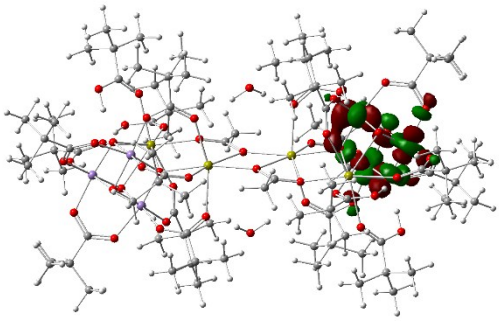
β-LUMO



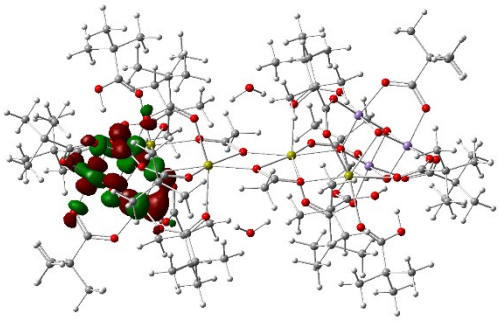
α-LUMO+1



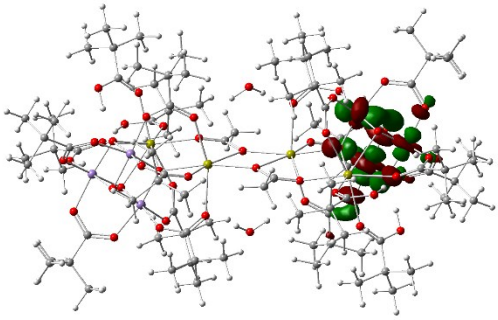
β-LUMO+1



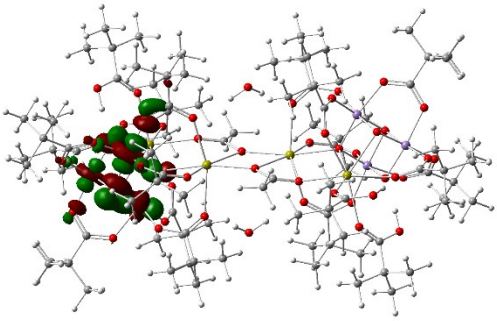
α-LUMO+2



β-LUMO+2

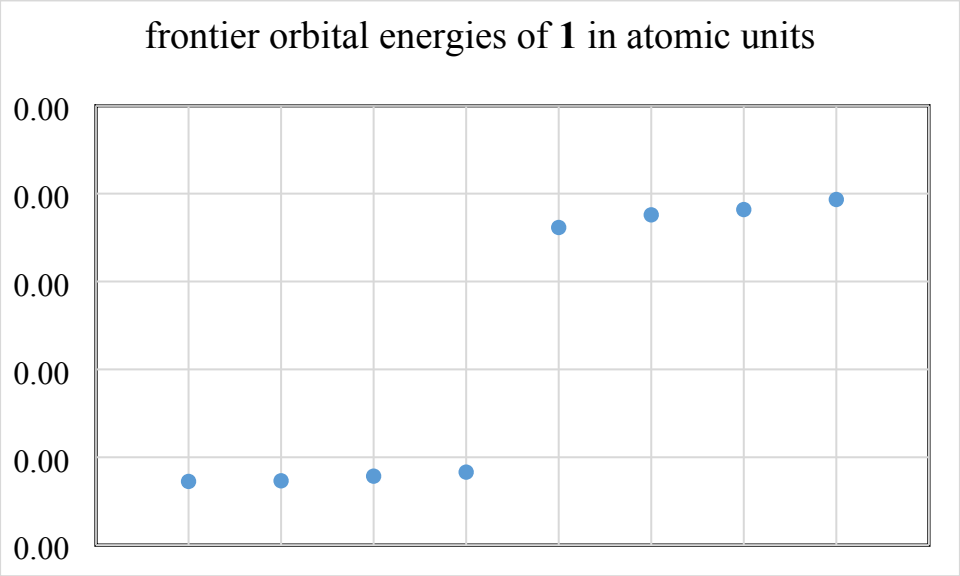


α-LUMO+3



β-LUMO+3

Fig. S1. Electronic distribution of frontier orbitals of **1**.



The HOMO-LUMO gap is 0.139 a.u. (3.79 eV)

Fig. S2 Frontier orbital energies of **1**.

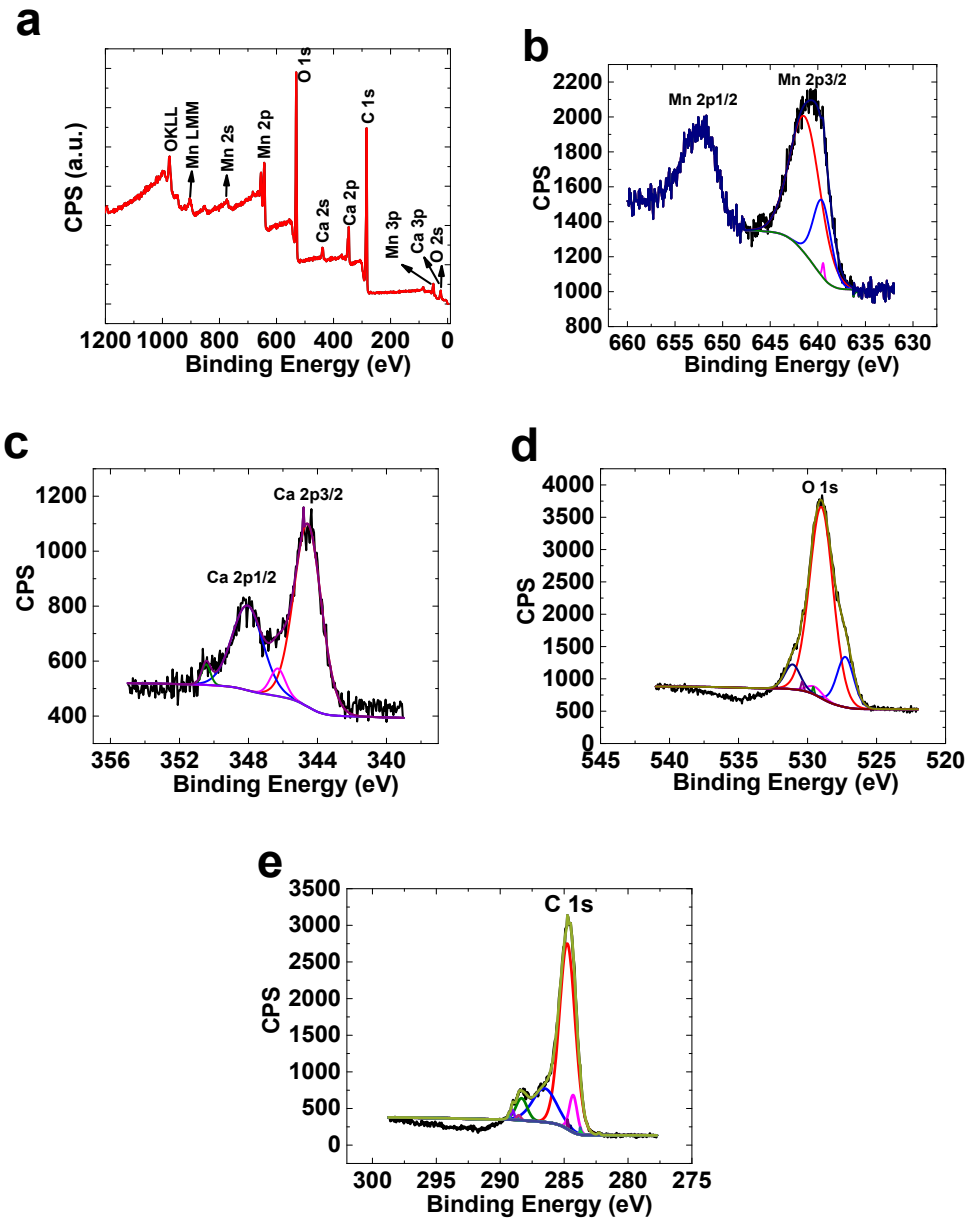


Fig. S3 XPS for **1** before water oxidation.

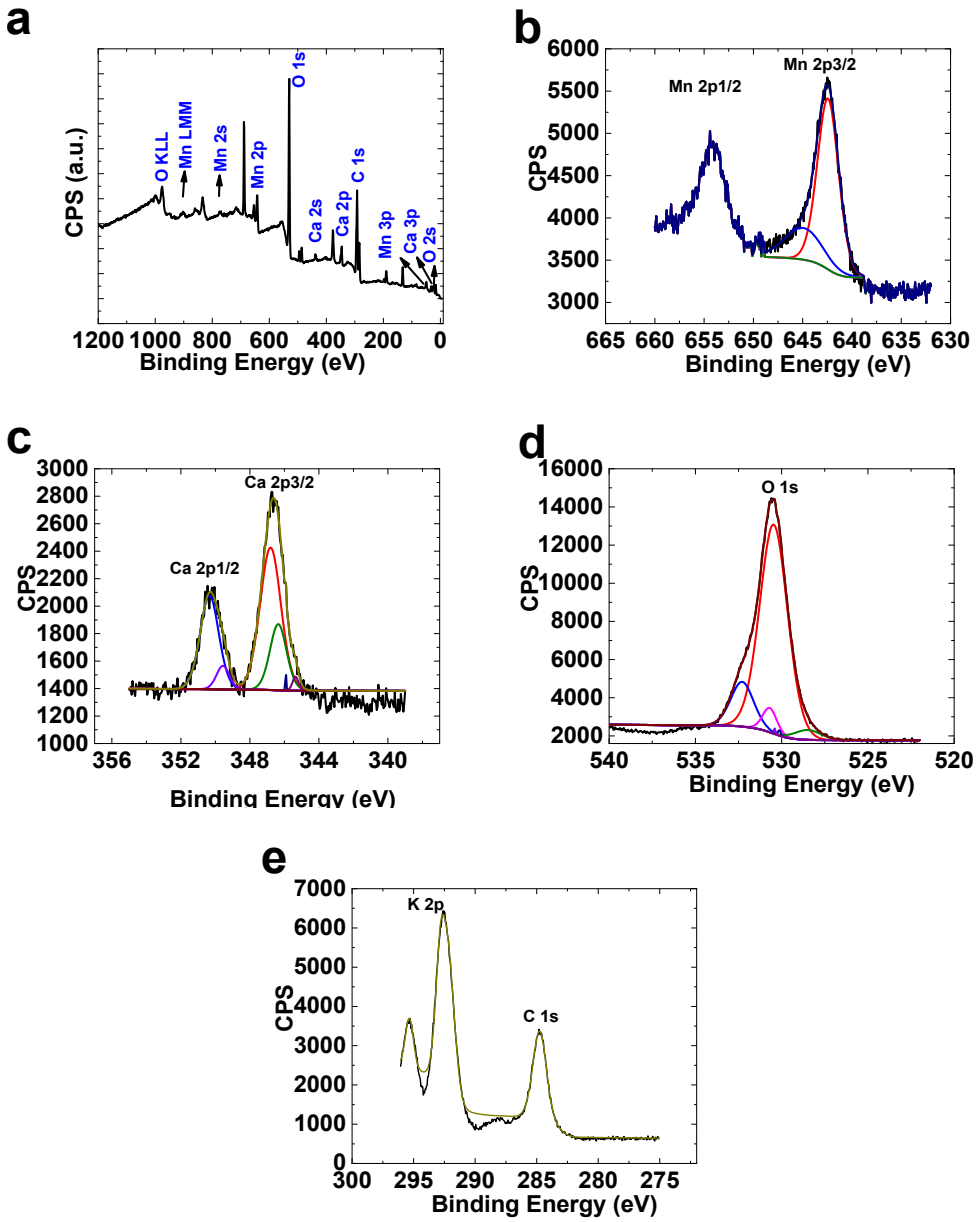


Fig. S4 XPS for **1** after the water-oxidation reaction. The amperometry was performed in the presence of **1** at 1.8 V in 25.0 mL of the phosphate buffer (1.0 M, pH=11.0).

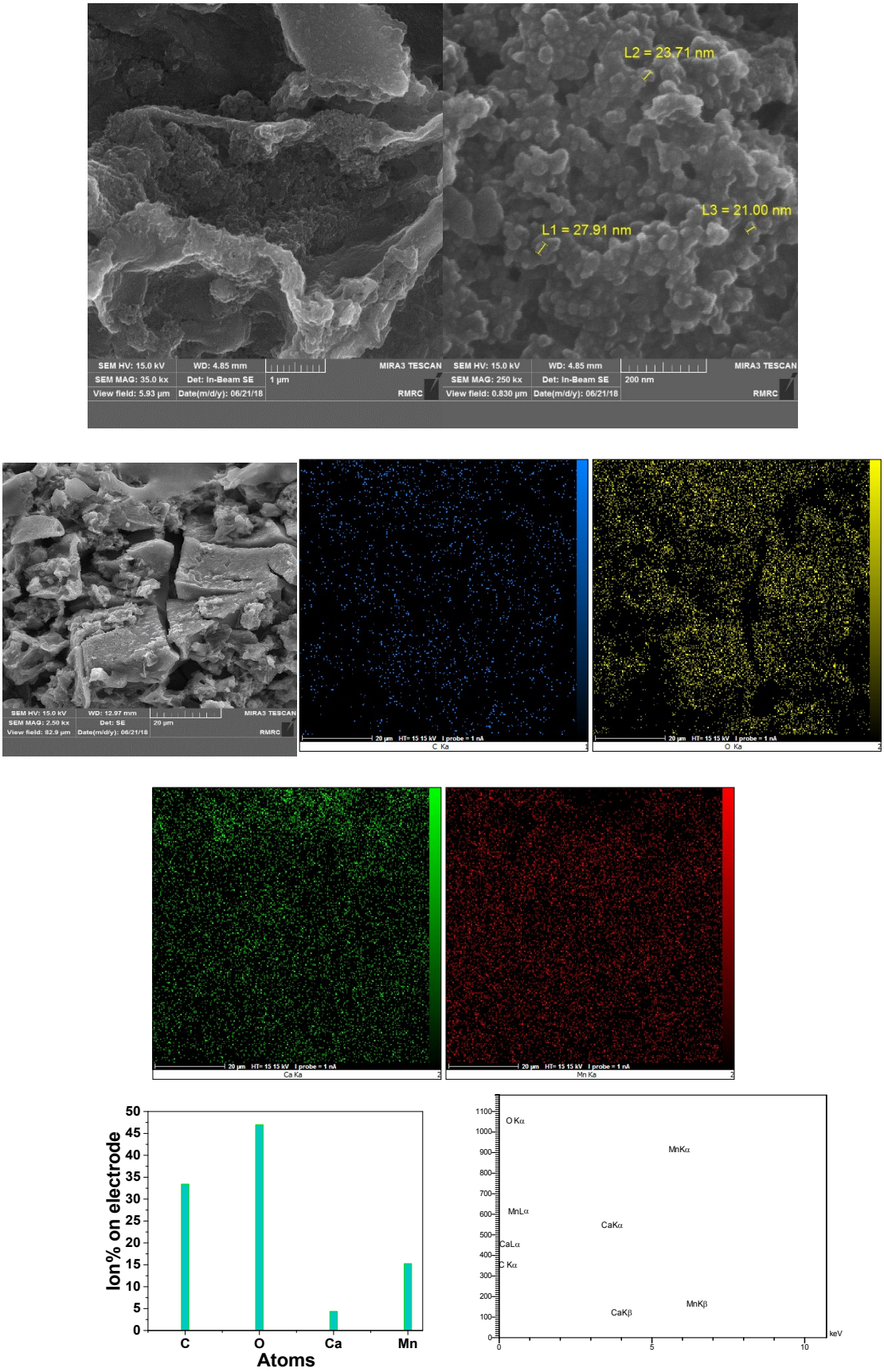


Fig. S5 SEM images of **1** after water-oxidation reaction (a,b). EDX-mapping and spectrum for **1** after water oxidation. The amperometry was performed at 1.8 V for 1.5 hours.

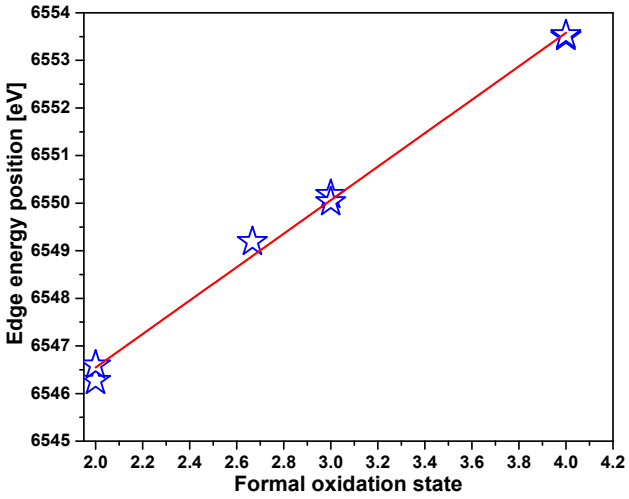


Fig. S6 Mn *K*-edge XANES of $Mn^{II}O$, $Mn^{II}CO_3$, Mn_3O_4, $Mn^{III}{}_2O_3$, α-$Mn^{III}{}_2O_3$, $Mn^{IV}O_2$ and β-$Mn^{IV}O_2$ were measured as a reference to determine the oxidation state of **1** (initial compound) and after operation.

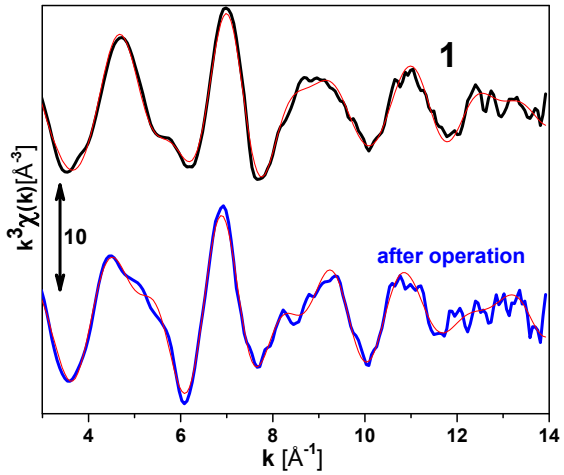


Fig. S7 k^3-weighted χ(k) of EXAFS spectra of **1** (black) and the obtained compound at 1.8 V the phosphate buffer (1.0 M, pH=11.0; blue). The thick lines and the thin red lines show the experimental data and simulations, respectively. The fit parameters for the simulations are given in Table S3. Phase shift not corrected.