Single-crystalline Mn(III) Schiff base complex immobilized on silica-coated magnetic nanoparticles delivering enhanced electerochemical catalytic performance toward sulfide and alkene oxidation

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Characterization section

Table S1. Selected bond lengths [Å] and angles [°] for MnL(OAc).

Bond distances		Bond angles	
Mn1-O1	1.8630(14)	O1-Mn1-O2	91.36(7)
Mn1-O2	1.9251(15)	O1-Mn1-N2	178.81(7)
Mn1-N2	1.9925(16)	O2-Mn1-N2	87.67(7)
Mn1-O5	2.1188(16)	O1-Mn1-O5	92.39(6)
Mn1-N1	2.1289(17)	O2-Mn1-O5	159.56(6)
Mn1-O6	2.2870(16)	N2-Mn1-O5	88.76(6)
Mn1-C22	2.547(2)	O1-Mn1-N1	88.79(6)
O1-C1	1.318(2)	O2-Mn1-N1	108.61(7)
C1-C6	1.411(3)	N2-Mn1-N1	90.86(6)
C1-C2	1.422(3)	O5-Mn1-N1	91.56(6)
C2-O3	1.361(3)	O1-Mn1-O6	90.02(6)
C2-C3	1.369(3)	O2-Mn1-O6	100.55(6)
C3-C4	1.390(3)	N2-Mn1-O6	90.84(6)
C4-C5	1.371(3)	O5-Mn1-O6	59.37(6)
C5-C6	1.400(3)	N1-Mn1-O6	150.84(6)
C6-C7	1.449(3)	O1-Mn1-C22	90.74(7)
C7-N1	1.274(3)	O2-Mn1-C22	130.00(7)
N1-C8	1.470(2)	N2-Mn1-C22	90.42(7)
C8-C9	1.532(3)	O5-Mn1-C22	29.90(6)
C9-C19	1.527(3)	N1-Mn1-C22	121.38(7)
C9-C20	1.537(3)	O6-Mn1-C22	29.49(6)

C9-C10	1.538(3)	C1-O1-Mn1	123.49(12)
C10-N2	1.473(3)	O1-C1-C6	123.54(18)
N2-C11	1.293(3)	O1-C1-C2	117.95(18)
C11-C12	1.445(3)	C6-C1-C2	118.35(18)
C12-C13	1.411(3)	O3-C2-C3	125.1(2)
C12-C17	1.417(3)	O3-C2-C1	114.59(18)
C13-C14	1.375(4)	C3-C2-C1	120.3(2)
C14-C15	1.384(4)	C2-C3-C4	120.9(2)
C15-C16	1.375(3)	C5-C4-C3	119.9(2)
C16-O4	1.371(3)	C4-C5-C6	120.9(2)
C16-C17	1.420(3)	C5-C6-C1	119.54(19)
C17-O2	1.320(3)	C5-C6-C7	118.09(19)
O3-C18	1.419(3)	C1-C6-C7	122.16(18)
O4-C21	1.413(3)	N1-C7-C6	125.98(19)
O5-C22	1.273(3)	C7-N1-C8	118.12(17)
O6-C22	1.256(3)	C7-N1-Mn1	120.31(14)
C22-C23	1.490(3)	C8-N1-Mn1	121.47(13)
		N1-C8-C9	114.57(16)
		C19-C9-C8	110.84(17)
		C19-C9-C20	110.98(18)
		C8-C9-C20	107.04(17)
		C19-C9-C10	110.64(18)
		C8-C9-C10	111.26(17)
		C20-C9-C10	105.92(17)
		N2-C10-C9	113.35(16)
		C11-N2-C10	118.96(17)
		C11-N2-Mn1	122.67(14)
		C10-N2-Mn1	118.37(13)
		N2-C11-C12	125.77(19)
		C13-C12-C17	120.1(2)
		C13-C12-C11	119.0(2)
		C17-C12-C11	120.44(19)
		C14-C13-C12	120.7(2)
		C13-C14-C15	119.5(2)
		C16-C15-C14	121.6(2)

		C16-C15-H15A	119.2
		O4-C16-C15	118.1(2)
		O4-C16-C17	121.1(2)
		C15-C16-C17	120.7(2)
		O2-C17-C12	122.51(19)
		O2-C17-C16	120.02(19)
		C12-C17-C16	117.41(19)
		C17-O2-Mn1	123.62(13)
		C2-O3-C18	117.47(19)
		C16-O4-C21	116.97(18)
		C22-O5-Mn1	94.03(14)
		C22-O6-Mn1	86.82(13)
		O6-C22-O5	119.7(2)
		O6-C22-C23	121.6(2)
		O5-C22-C23	118.7(2)
		O6-C22-Mn1	63.69(12)
		O5-C22-Mn1	56.07(11)
		C23-C22-Mn1	174.29(18)

Symmetry transformations used to generate equivalent atoms:

angles [°] for MnL(OAc).

O(2)-Mn(1)-O(1)-C(1)	65.41(16)
O(5)-Mn(1)-O(1)-C(1)	-134.69(15)
N(1)-Mn(1)-O(1)-C(1)	-43.17(15)
O(6)-Mn(1)-O(1)-C(1)	165.97(15)
C(22)-Mn(1)-O(1)-C(1)	-164.55(16)
Mn(1)-O(1)-C(1)-C(6)	38.2(3)
Mn(1)-O(1)-C(1)-C(2)	-146.50(15)
O(1)-C(1)-C(2)-O(3)	3.3(3)
C(6)-C(1)-C(2)-O(3)	178.86(18)
O(1)-C(1)-C(2)-C(3)	-176.5(2)
C(6)-C(1)-C(2)-C(3)	-0.9(3)
O(3)-C(2)-C(3)-C(4)	-177.1(2)
C(1)-C(2)-C(3)-C(4)	2.6(4)
C(2)-C(3)-C(4)-C(5)	-1.4(4)
C(3)-C(4)-C(5)-C(6)	-1.5(4)
C(4)-C(5)-C(6)-C(1)	3.2(3)
C(4)-C(5)-C(6)-C(7)	178.0(2)
O(1)-C(1)-C(6)-C(5)	173.39(19)
C(2)-C(1)-C(6)-C(5)	-1.9(3)
O(1)-C(1)-C(6)-C(7)	-1.2(3)
C(2)-C(1)-C(6)-C(7)	-176.55(19)
C(5)-C(6)-C(7)-N(1)	170.1(2)
C(1)-C(6)-C(7)-N(1)	-15.2(3)
C(6)-C(7)-N(1)-C(8)	172.47(19)
C(6)-C(7)-N(1)-Mn(1)	-4.0(3)
C(7)-N(1)-C(8)-C(9)	136.83(19)
Mn(1)-N(1)-C(8)-C(9)	-46.7(2)
N(1)-C(8)-C(9)-C(19)	-61.6(2)
N(1)-C(8)-C(9)-C(20)	177.22(18)
N(1)-C(8)-C(9)-C(10)	61.9(2)
C(19)-C(9)-C(10)-N(2)	51.7(2)
C(8)-C(9)-C(10)-N(2)	-72.0(2)
C(20)-C(9)-C(10)-N(2)	172.00(18)
C(9)-C(10)-N(2)-C(11)	-115.9(2)

C(9)-C(10)-N(2)-Mn(1)	64.7(2)
C(10)-N(2)-C(11)-C(12)	169.89(19)
Mn(1)-N(2)-C(11)-C(12)	-10.8(3)
N(2)-C(11)-C(12)-C(13)	170.7(2)
N(2)-C(11)-C(12)-C(17)	-16.6(3)
C(17)-C(12)-C(13)-C(14)	1.0(3)
C(11)-C(12)-C(13)-C(14)	173.7(2)
C(12)-C(13)-C(14)-C(15)	-2.2(4)
C(13)-C(14)-C(15)-C(16)	0.9(4)
C(14)-C(15)-C(16)-O(4)	-173.8(2)
C(14)-C(15)-C(16)-C(17)	1.6(3)
C(13)-C(12)-C(17)-O(2)	178.6(2)
C(11)-C(12)-C(17)-O(2)	6.0(3)
C(13)-C(12)-C(17)-C(16)	1.4(3)
C(11)-C(12)-C(17)-C(16)	-171.17(19)
O(4)-C(16)-C(17)-O(2)	-4.8(3)
C(15)-C(16)-C(17)-O(2)	-180.0(2)
O(4)-C(16)-C(17)-C(12)	172.5(2)
C(15)-C(16)-C(17)-C(12)	-2.7(3)
C(12)-C(17)-O(2)-Mn(1)	31.7(3)
C(16)-C(17)-O(2)-Mn(1)	-151.18(15)
C(3)-C(2)-O(3)-C(18)	4.2(4)
C(1)-C(2)-O(3)-C(18)	-175.6(3)
C(15)-C(16)-O(4)-C(21)	-119.9(3)
C(17)-C(16)-O(4)-C(21)	64.7(3)
Mn(1)-O(6)-C(22)-O(5)	2.1(2)
Mn(1)-O(6)-C(22)-C(23)	-177.5(2)
Mn(1)-O(5)-C(22)-O(6)	-2.3(2)
Mn(1)-O(5)-C(22)-C(23)	177.3(2)

Symmetry transformations used to generate equivalent atoms:

Table S2. Hydrogen bonds for MnL(OAc) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(7)-H(7A)...O(5)#1	0.93	2.56	3.201(2)	126.4
C(10)-H(10A)...O(5)	0.97	2.58	3.138(3)	116.7
C(18)-H(18A)...O(6)#2	0.96	2.56	3.512(3)	171.8
C(21)-H(21B)...O(2)	0.96	2.37	2.983(3)	121.7

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1   #2 -x+1,y+1/2,-z+1/2

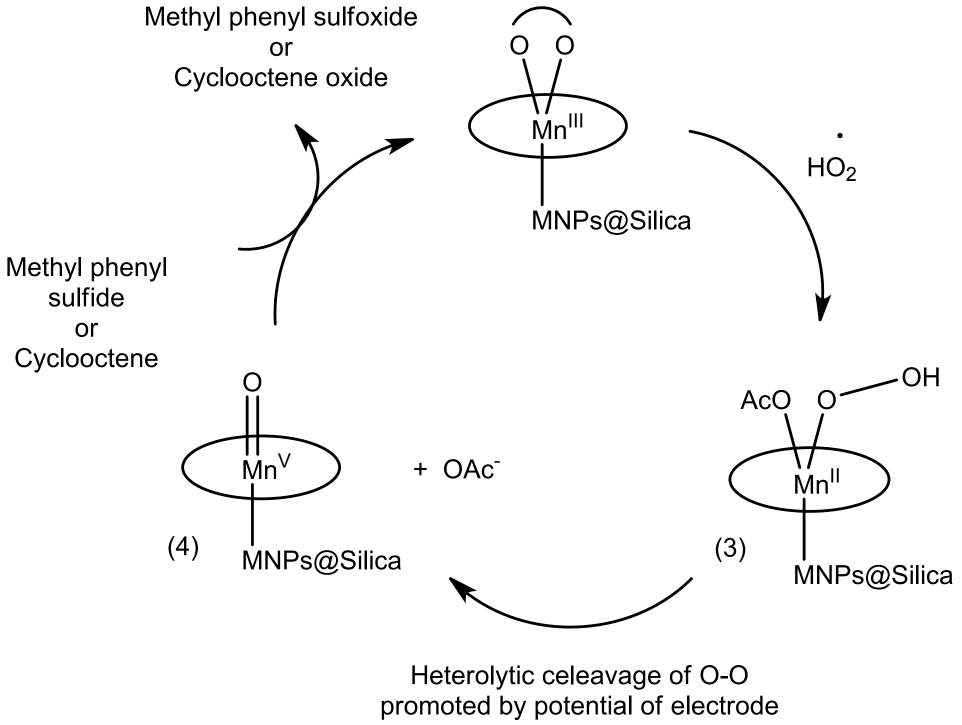
S2
Result and discussion section

The reaction proposed pathway is shown in Scheme 1. The reduction reaction of H_2O_2 in the presence of electrode depends on the solution conditions. In an acid solution, H_2O_2 is decomposed into H_2O and O_2 [1]. On the other hand, in neutral or alkaline solutions OH^- anions are produced [2,3]. Because the reaction mixture used in this experiment was maintained to be neutral, it is concluded that H_2O_2 was decomposed into OH^- ions by the reduction reaction (1) on the surface of glassy carbon electrode. The pH near the electrode surface may shift to be alkaline because of generation of OH^- ions and in this case, production of OH radicals in acidic or alkaline solutions has been reported [4].

Provided that OH radicals are generated, they can react with H_2O_2 to produce dioxidanyl radical (OOH radical) which can involve with the catalyst as follows [5]. The dioxidanyl radical could bind to the metal center of Fe_3O_4@SiO_2-[Mn^{III}L(OAc)] and cause one-electron electrochemical reduction of the Mn(III) complex, followed by the transfer of a second electron to form Fe_3O_4@SiO_2-[Mn^{II}(OOH)L(OAc)] adduct (3). Afterwards, as in previous reports, heterolytic cleavage of the O-O bond in the hydroperoxo intermediate, here seems to be activated by the potential of electrode, produces the oxo-species [Mn(V)Schiff base = O] (4) [5]. This high valent metal oxo species is highly activated, resulting the oxygen transfer to the desired substrates (sulfides of alkenes) [6,7].

$$(1)\quad H_2O_2 + e^- \longrightarrow \dot{O}H + OH^-$$

$$(2)\quad \dot{O}H + H_2O_2 \longrightarrow H\dot{O}_2 + H_2O$$



Scheme S1. Plausible mechanism for the electrochemical oxidation of sulfides and alkenes catalyzed by Fe_3O_4@SiO_2-[MnL(OAc)] in the presence of glassy carbon electrode.

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