Supporting Information

Tuning Electronic and Magnetic Properties of Catalytic Mn-mullite Oxide Sub-nanoclusters via MnO_n Polyhedron Units

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Detailed structural analysis of geometric structures of $(115)_n$:

For *n*=1, the most stable configuration is with one *T*-tetrahedron unit dispersed on the cluster surface with C_s symmetry. For *n*=2, the lowest-energy structure 2a with C_2 symmetry has two *T*-tetrahedron units. The structure 2b and 2c with low symmetry C_1 are less stable by 0.272eV and 1.934eV respectively, of which the higher-energy structure 2b with one two-fold Sm atom has two *T*-tetrahedron units, and the highest-energy structure 2c consists of two *S*-tetrahedron units. For *n*=3, the ground-state structure 3a prefers a C_2 symmetry with the Sm atoms gathered in nucleus, and with one *T*-tetrahedron unit and two *S*-tetrahedron units. The low symmetry (C_1) structure 3b and 3c are less stable by 2.191 eV and 2.983 eV respectively, of which the former

structure is formed with one *T*-tetrahedron unit and two *S*-tetrahedron units, and the latter structure with one *S*-tetrahedron unit and two *F*-pyramid units.

For *n*=4, the low-lying structures 4a, 4b and 4c all are all near planar. The lowest-energy structure 4a with C_1 symmetry consists of two *S*-tetrahedron units and two *F*-pyramid units. For comparison, the T-like structure 4b is higher by 0.911 eV with C_1 symmetry formed by two *T*-tetrahedron units, one *S*-tetrahedron unit and one *F*-pyramid unit. And the ring-like structure with C_4 symmetry is higher by 5.992 eV with four *F*-pyramid units. For *n*=8, the configurations all have low symmetry with C_1 point group, which are consisted of five *F*-pyramid units. The cluster 8a, with Sm atoms gathered in together, with MnO_5 units appearing in pairs, is the lowest energy structure. The low-lying isomers 8b and 8c are less stable by 2.471 eV and 3.022 eV, respectively.

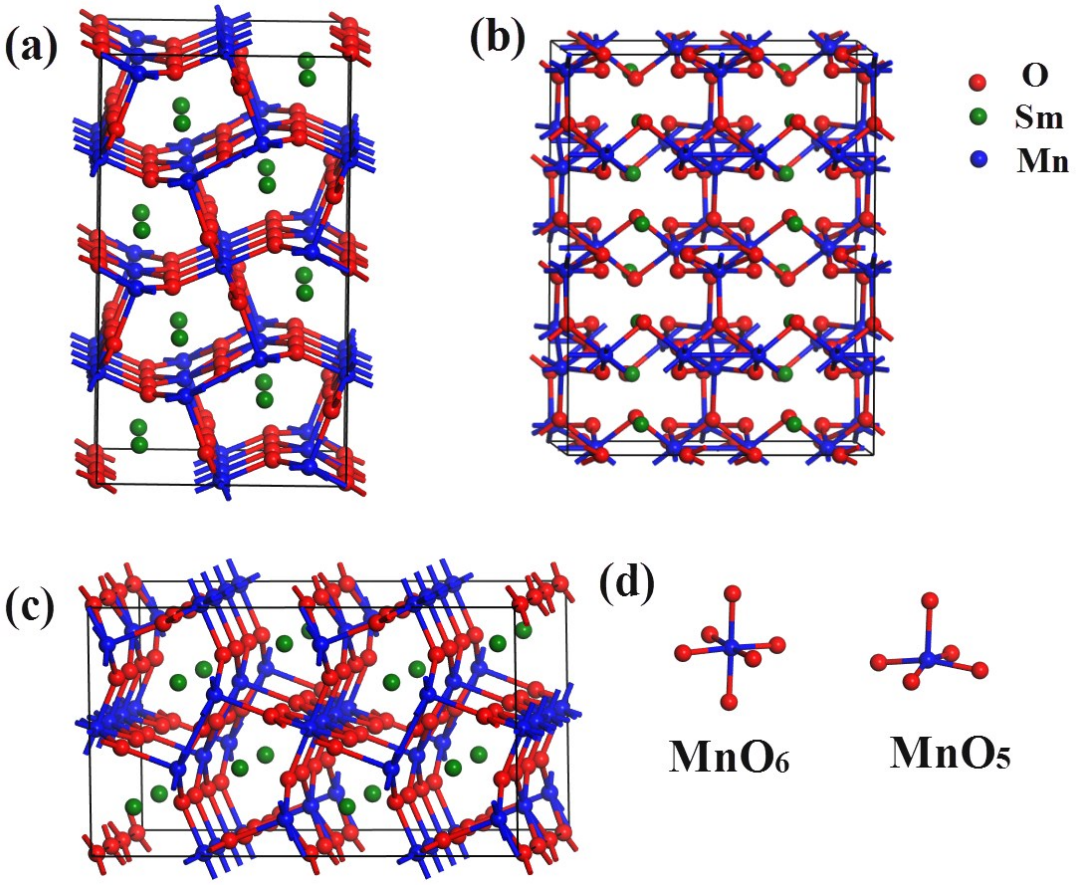

Fig.S1 The $SmMn_2O_5$ bulk structure from view of a (a), b (b), c (c) and the basic units octahedral (Mn_{oct}) and square pyramid (Mn_{pyr}) (d). Green, blue, and red spheres are Sm, Mn, and O atoms, respectively.

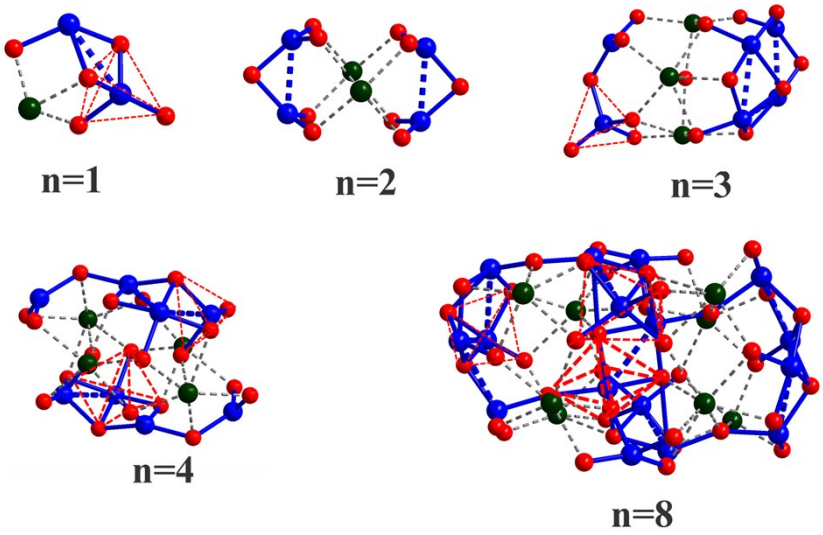

Fig.S2 The $Sm_1Mn_2O_5$ clusters with the MnO_n (n=4,5,6) units.Green, blue, and red spheres are Sm, Mn, and O atoms, respectively.

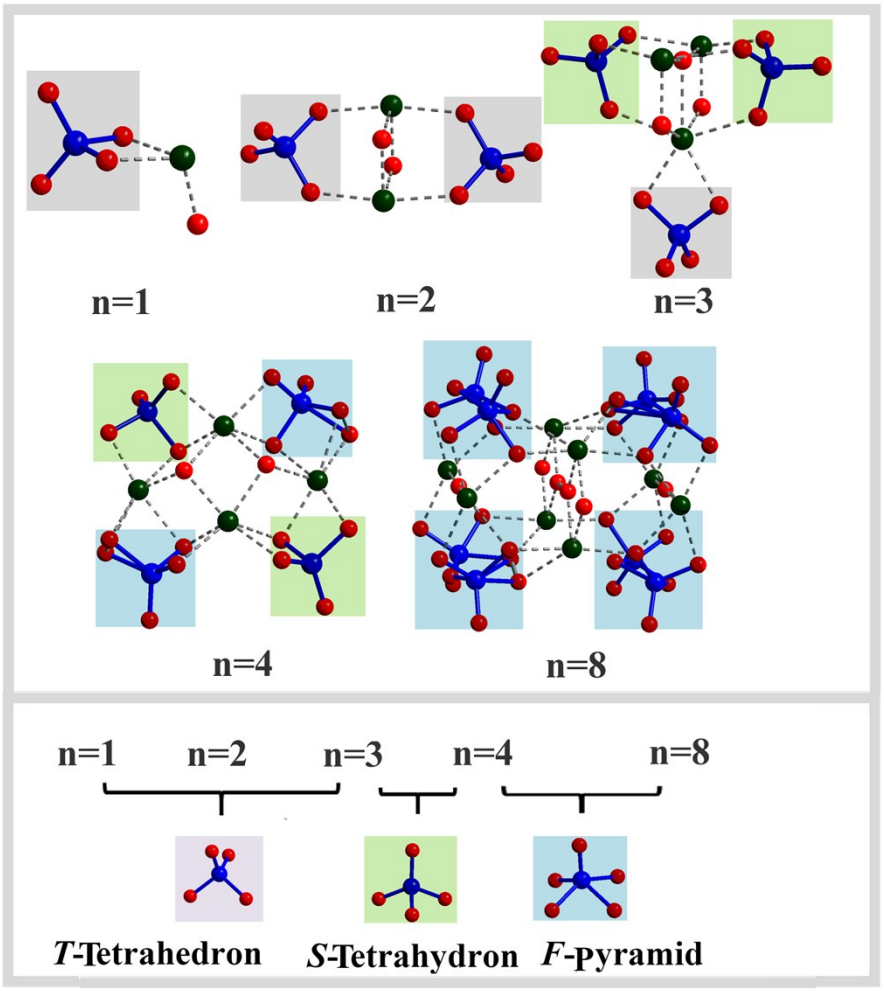

Fig.S3 The $Sm_1Mn_1O_5$ cluster with its MnO_n (n=4,5) units.

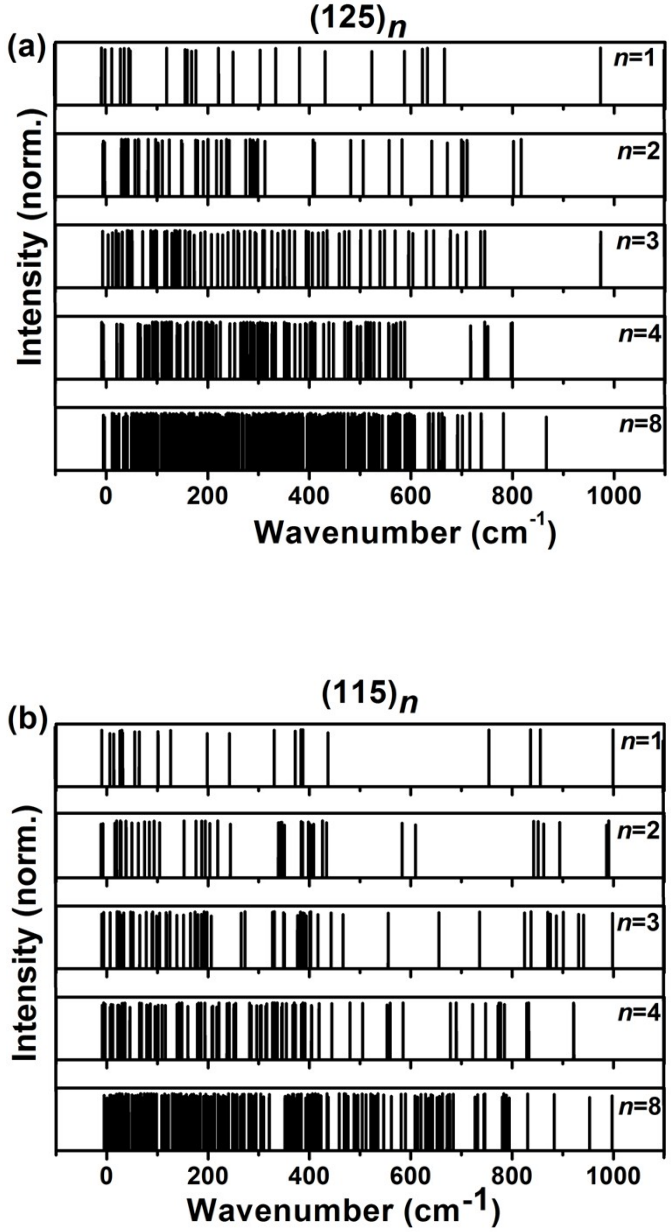

Fig.S4 vibrational frequencies for (a) (125)*n* and (b) (115)*n*.

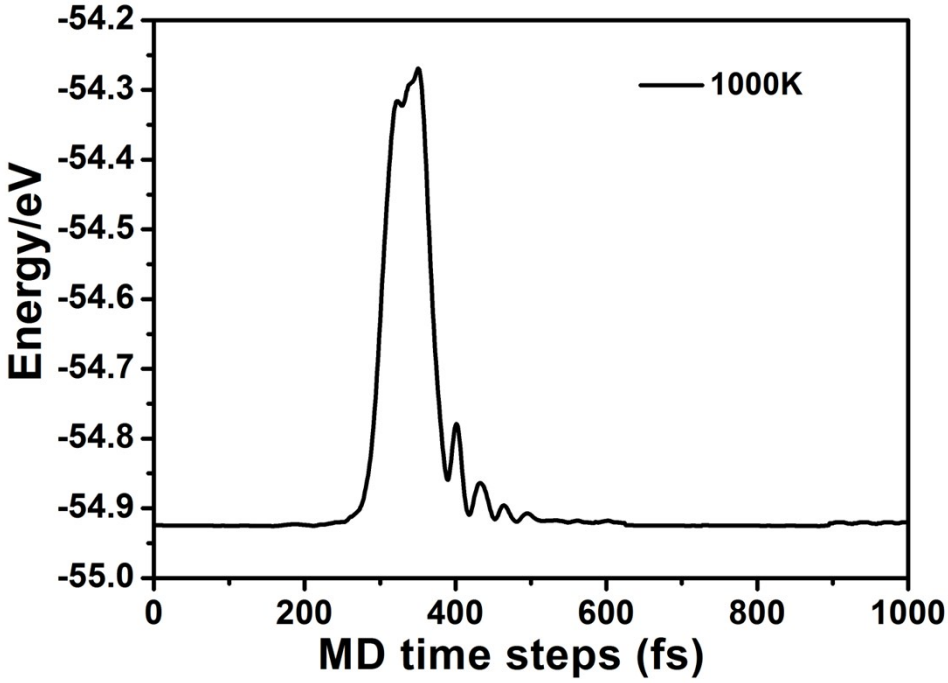

Fig.S5 The MD simulations at 1000 K with the time step 1 fs for $(125)_1$.

Table S1. The U value test.

U	Bandgap (eV)	Lattice Constant (Å)		
		a	b	c
1.0	0.69	7.28	8.53	5.66
2.0	1.04	7.31	8.55	5.68
2.2	1.09	7.31	8.55	5.68
2.4	1.13	7.31	8.55	5.69
2.6	1.19	7.31	8.56	5.69
2.7	1.21	7.32	8.56	5.69
2.8	1.26	7.32	8.56	5.70
3.0	1.28	7.33	8.56	5.70
4.0	1.42	7.33	8.56	5.70
Exp.	1.23[1]	-	-	-
	-	7.43[2]	8.59[2]	5.70[2]
	-	7.43[3]	8.58[3]	5.69[3]

Table S2. Bader Charge analyses for Mn atom in tetrahedron and/or pyramid units in $(115)_n$ clusters.

$(115)_n$	unit	Mn (e)
n=1	T-tetrahedron	4.60
n=2	T-tetrahedron	4.54
n=3	T-tetrahedron	4.54
	S-tetrahedron	4.53
n=4	S-tetrahedron	5.30
	F-pyramid	5.31
n=8	F-pyramid	5.35

Table S3. The main contributing orbital components of HOMO, HOMO-1 and LUMO for $(115)_n$ and $(125)_n$ clusters.

		HOMO	HOMO-1	LUMO
$(115)_n$	n=1	O-p_x	O-p_x	Mn-d_{xy}
				Mn-d_z^2
				O-p_y
	n=2	O-p_y	O-p_z	Mn-d_{xy}
				Mn-$d_{x^2-y^2}$
				O-$p_{z,y}$
	n=3	O-p_x	O-p_y	Mn-d_{xy}
				Mn-$d_{x^2-y^2}$
				O-p_x
	n=4	Mn-d_{xy}	Mn-d_{xy}	Mn-$d_{x^2-y^2}$
		O-$p_{z,x}$	O-p_z	O-p_z
			O-p_x	
	n=8	Mn-$d_{x^2-y^2}$	Mn-$d_{x^2-y^2}$	Mn-d_{z2}
		O-$p_{x,z}$	O-$p_{x,z}$	O-p_x
$(125)_n$	n=1	Mn-d_z^2	Mn-$d_{x^2-y^2}$	Mn-$d_{x^2-y^2}$
		O-p_y	O-$p_{y,z}$	O-p_z
	n=2	Mn-d_z^2	Mn-d_{xy}	Mn-$d_{x^2-y^2}$
				O-p_y
	n=3	Mn-$d_{x^2-y^2}$	Mn-$d_{x^2-y^2}$	Mn-$d_{x^2-y^2}$
		O-p_y	O-p_y	O-p_z
	n=4	Mn-$d_{x^2-y^2}$	Mn-$d_{x^2-y^2}$	Mn-$d_{x^2-y^2}$
		Mn-d_{xy}	O-$p_{y,z}$	Mn-d_{yz}
		O-p_z		O-p_y
	n=8	Mn-$d_{x^2-y^2}$	Mn-$d_{x^2-y^2}$	Mn-$d_{x^2-y^2}$
		Mn-d_{xy}	O-$p_{y,z}$	Mn-d_{z2}
		O-p_y		O-p_y

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