Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
This journal is © The Owner Societies 2012

A theoretic insight on catalytic activity promotion of CeO_2 surface by Mn doping

Wanglai Cen, Yue Liu*, Zhongbiao Wu*, Haiqiang Wang, Xiaole Weng

Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, China

E-mail: yueliu@zju.edu.cn (Y. Liu); zbwu@zju.edu.cn (Z. B. Wu)

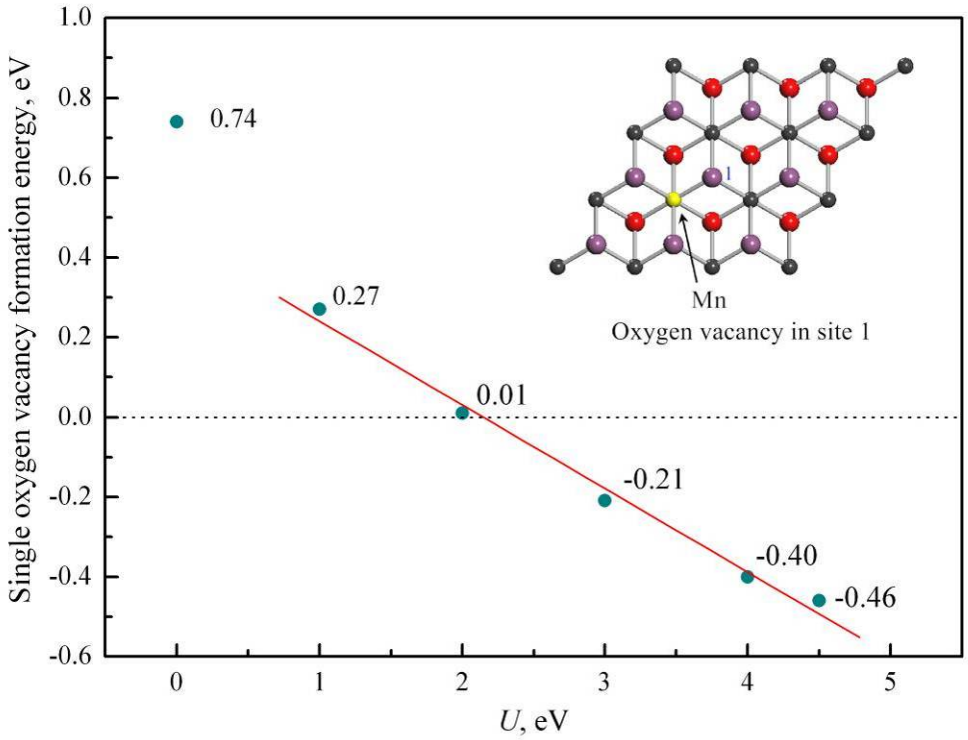

Fig. S1 Single oxygen vacancy formation energy for U = 0 ~ 4.5 eV. The formation energies were labeled with aside the data points. Inset: oxygen vacancy site in MnCe labeled 1.

This journal is © The Owner Societies 2012

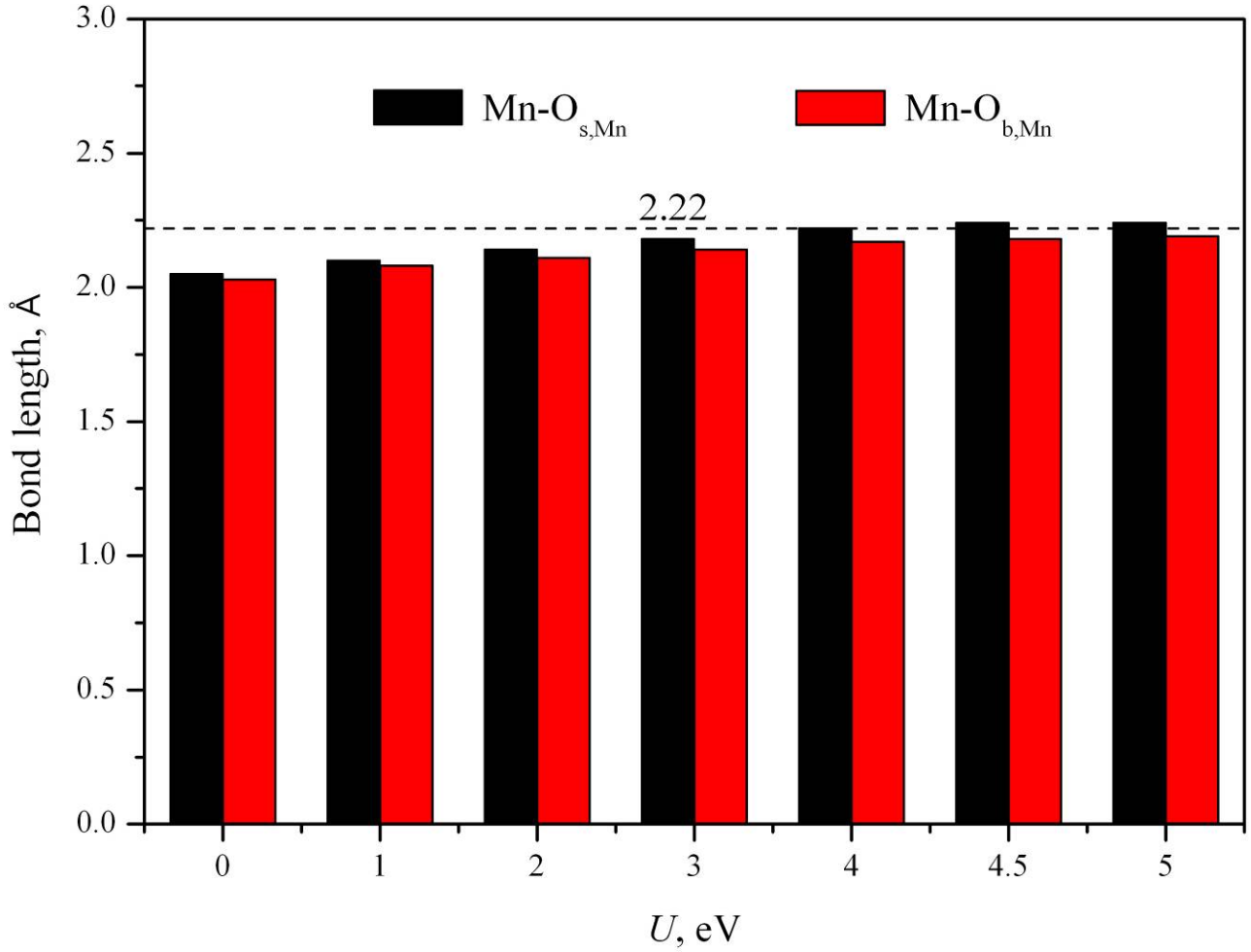

Fig. S2 Selected Mn-O bond lengths in vMnCe with oxygen vacancy in site 1.

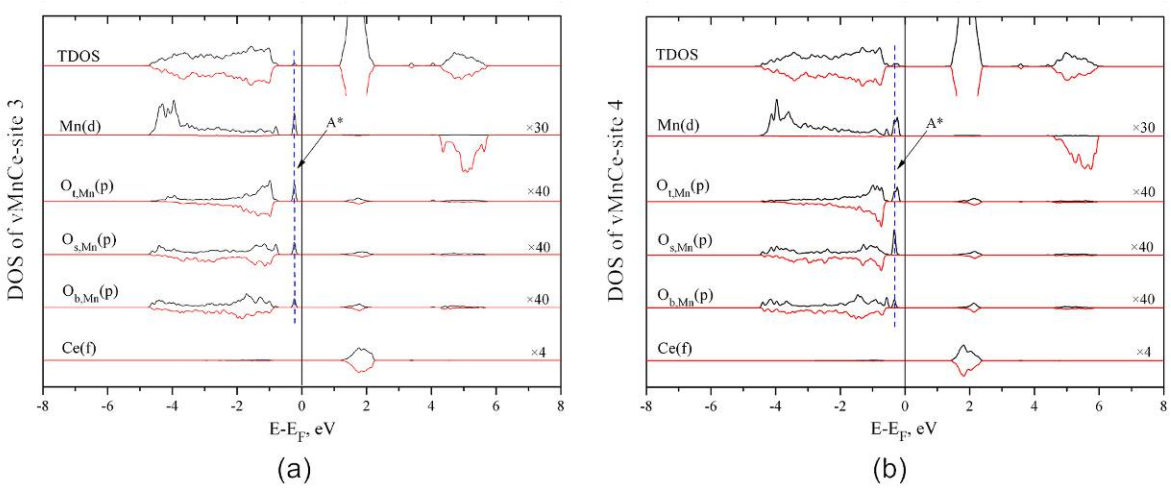

Fig. S3 Total and partial DOS of vMnCe with oxygen vacancy in site 3 and 4. The blue dashed lines labeled as A* are Mn 3*d*-O 2*p* gap states acting as electrons buffer instead of Ce 4*f*. Fermi level is set to be zero point.

This journal is © The Owner Societies 2012

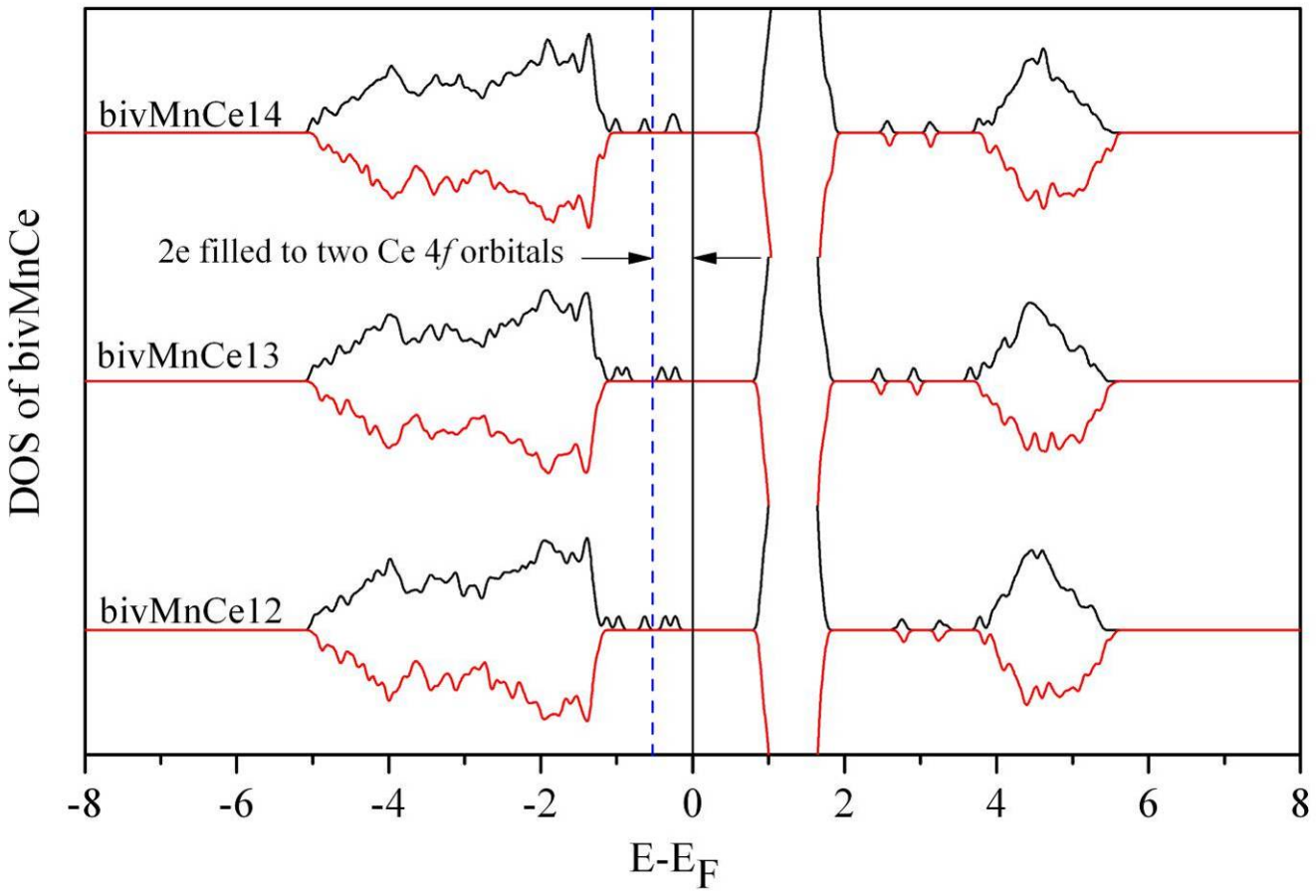

Fig. S4 DOS of bivMnCe with two oxygen vacancies at sites 1-2, 1-3 and 1-4. All the populations of the occupied Ce 4f states are 2 e by DOS integration.

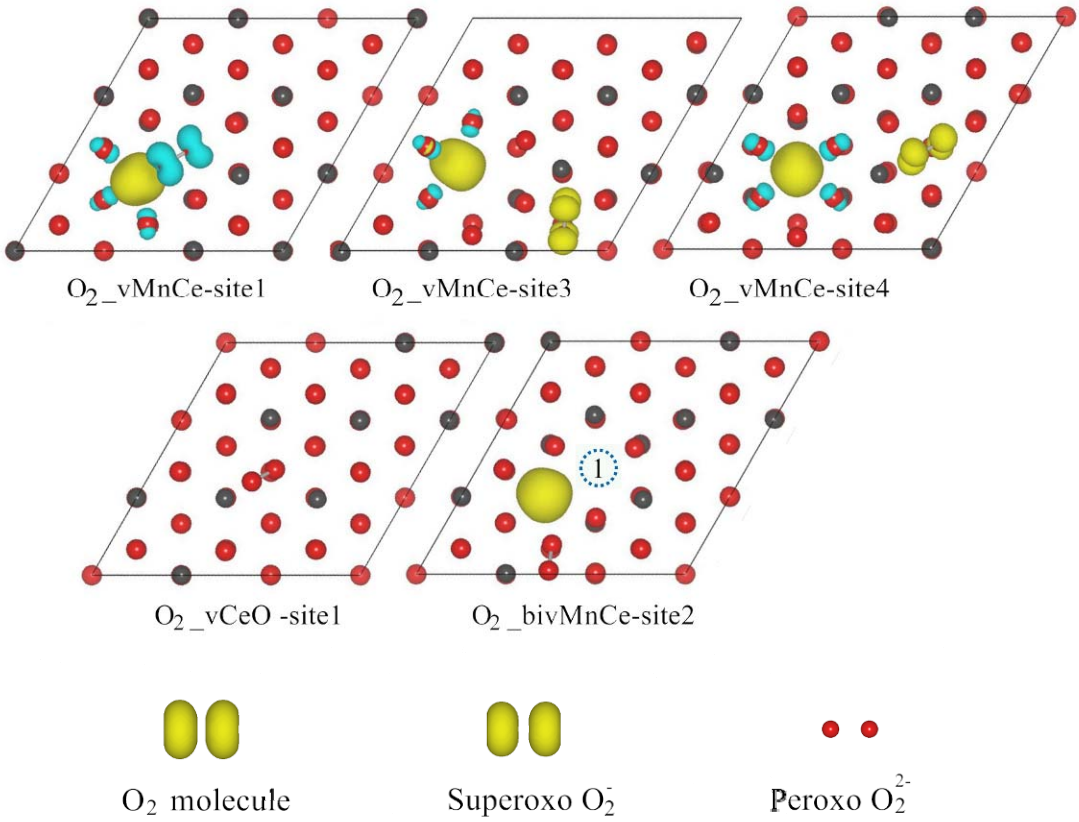

Fig. S5 Spin charge density of: O_2_vMnCe with O_2 molecule adsorbed at oxygen vacancy site 1, 3 and 4, O_2_$vCeO_2$ at site 1, O_2_bivMnCe at site 2, free O_2 molecule, superoxo O_2^-, and peroxo O_2^{2-}. The isovalue is 0.05 e/Å^3. The *p*-like spin-polarized charge density distribution of the adsorbed O_2 on vMnCe indicates O_2^- specie. The spin-unpolarized charge density distribution of the adsorbed O_2 on bivMnCe and vCeO2 indicates O_2^{2-} specie.

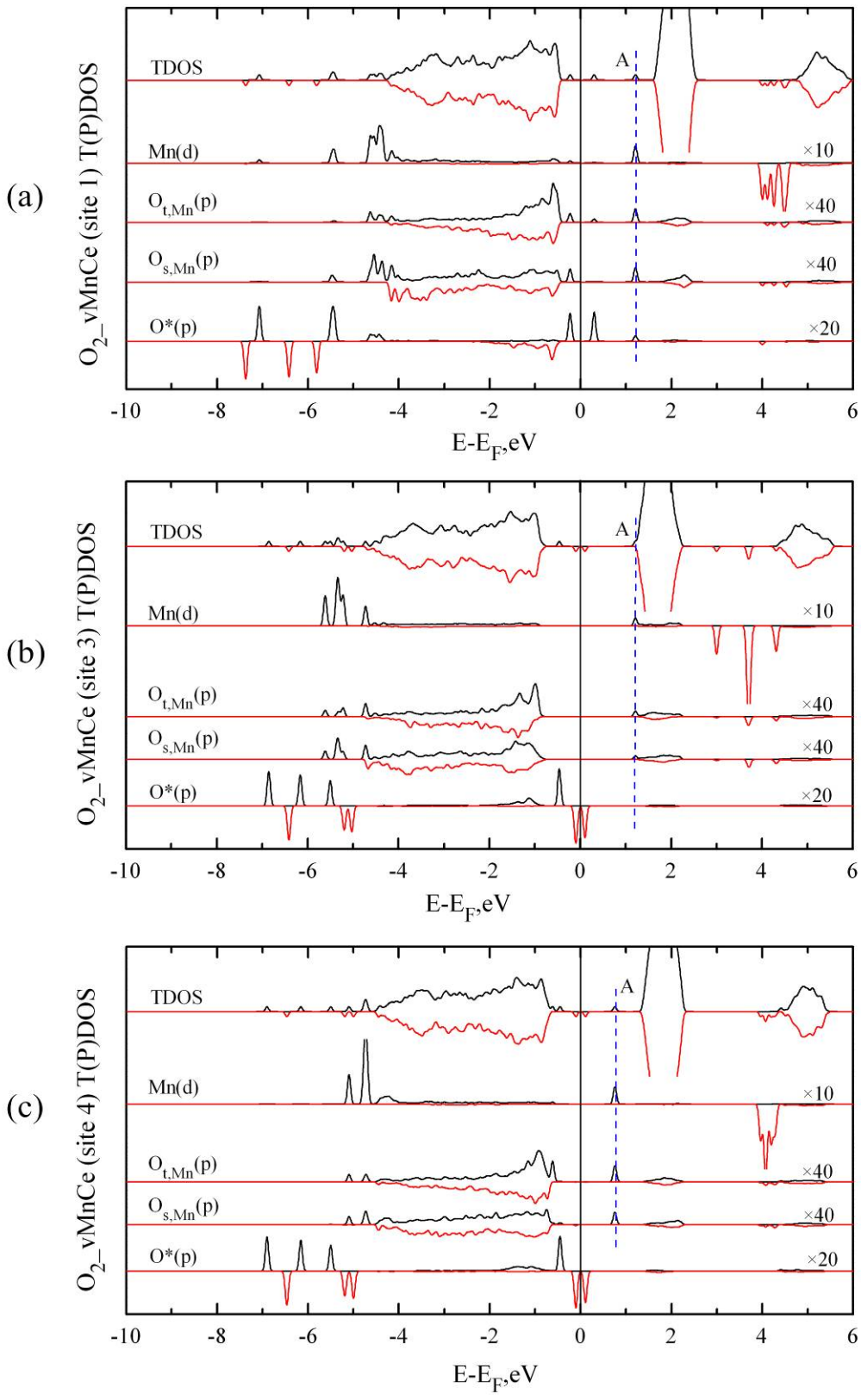

Fig. S6 DOS of O_2_vMnCe with oxygen molecule adsorbed on different vacancy sites. Mn 3*d*-O 2*p* gap state is marked by the dashed line A.

This journal is © The Owner Societies 2012

Table S1 Population with different Wigner Seitz radiuses for MnCe and vMnCe at U = 4.5 eV for Mn 3*d*.

Items	vMnCe		MnCe	
Wigner Seitz radius, Å	default[c]	1[d]	default	1
Mn 3*d* in VB，e	4.73	4.29	4.45	4.07
Mn 3*d*-O 2*p* gap state in PDOS, e				
$O_{t,Mn}$ 2*p*	0.167	0.185	0.194	0.214
$O_{s,Mn}$ 2*p*	0.171	0.187	0.133	0.145
$O_{b,Mn}$ 2*p*	0.108	0.118	-	-
$(O_{t,Mn} + O_{s,Mn}) \times 3$[a]	-	-	0.981	1.077
$O_{b,Mn}$ 2*p* + $O_{t,Mn}$ 2*p* × 2 + $O_{s,Mn}$ 2*p* × 3[b]	0.955	1.049	-	-
Mn 3*d*	0.383	0.373	0.317	0.311
Sum	1.338	1.422	1.298	1.388
Mn 3*d*-O 2*p* gap state in TDOS, e	1.999	1.999	1.999	2.000

a: the MnCe slab is in C_{3v} symmetry, so there are three equivalent atoms each of the $O_{t,Mn}$ and $O_{s,Mn}$ atoms;

b: there are one $O_{b,Mn}$ atom, two $O_{t,Mn}$ atoms and three $O_{s,Mn}$ atoms as shown in Fig. 1a and b.

c: all the radiuses are employed as default in the pseudopotential files: Mn 1.323 Å, Ce 1.323 Å, O 0.820 Å.

d: all the radiuses for Ce, Mn and O atoms are set to be 1 Å.

Table S2 Calculated properties of adsorbed O_2 and Mn in O_2_vMnCe

Adsorption site	Bond length, Å	Stretching frequency, cm^{-1}	Magnetic moment, μ_B		
			O_2^*	Mn	Mn in vMnCe
1	1.32	1134	-1.04	4.09	4.70
3	1.35	1119	0.92	3.90	4.71
4	1.34	1119	0.93	4.12	4.72