Structure, Electronic Properties, Morphology Evolution, and Photocatalytic Activity in $PbMoO_4$ and $Pb_{1-2x}Ca_xSr_xMoO_4$ (x= 0.1, 0.2, 0.3, 0.4 and 0.5) Solid Solutions

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Supporting Information

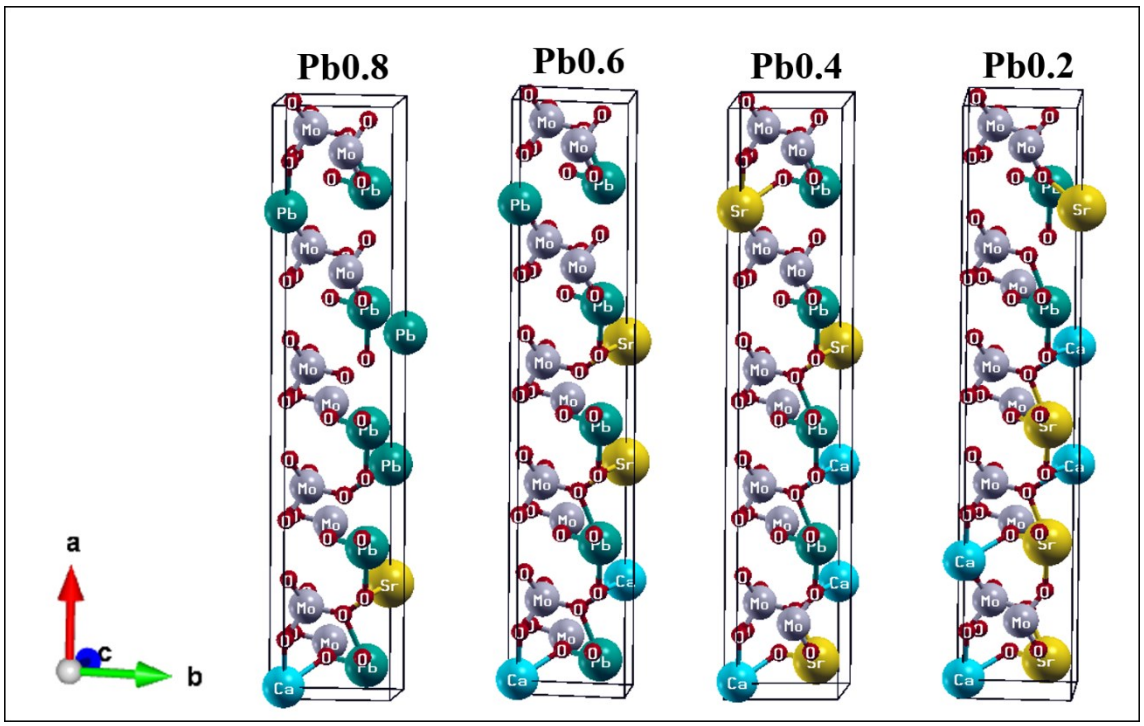

Figure S1. 5x1x1 supercell for $Pb_{1-2x}Ca_xSr_xMoO_4$ (Pb=0.8, Pb0.6, Pb0.4, Pb0.2) solid solutions.

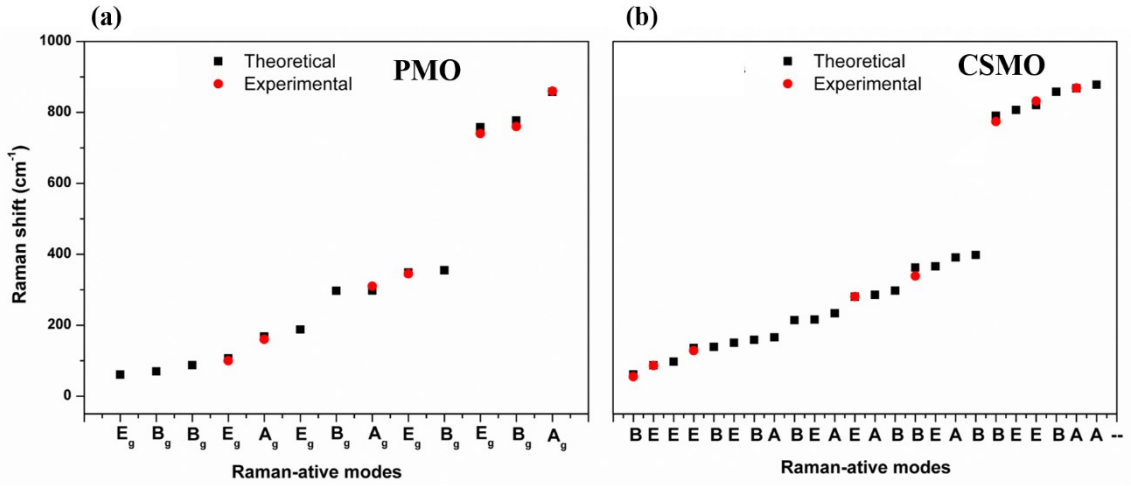

Figure S2. Theoretical and experimental values of the Raman modes for: (a) PMO, and (b) CSMO.

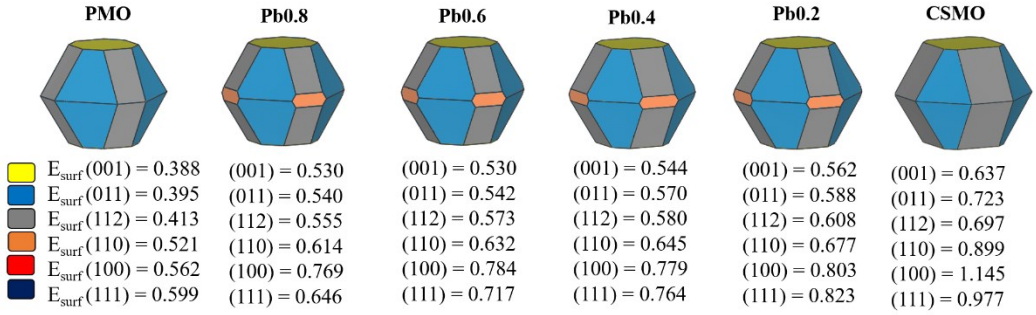

Figure S3. Values of E_{surf} in (J/m^2) and possible morphologies of PMO and $Pb_{1-2x}Ca_xSr_xMoO_4$ solid solutions. PMO (x=0), Pb0.8 (x=0.1), Pb0.6 (x=0.2), Pb0.4 (x=0.3), Pb0.2 (x=0.4), CSMO (x=0.5).

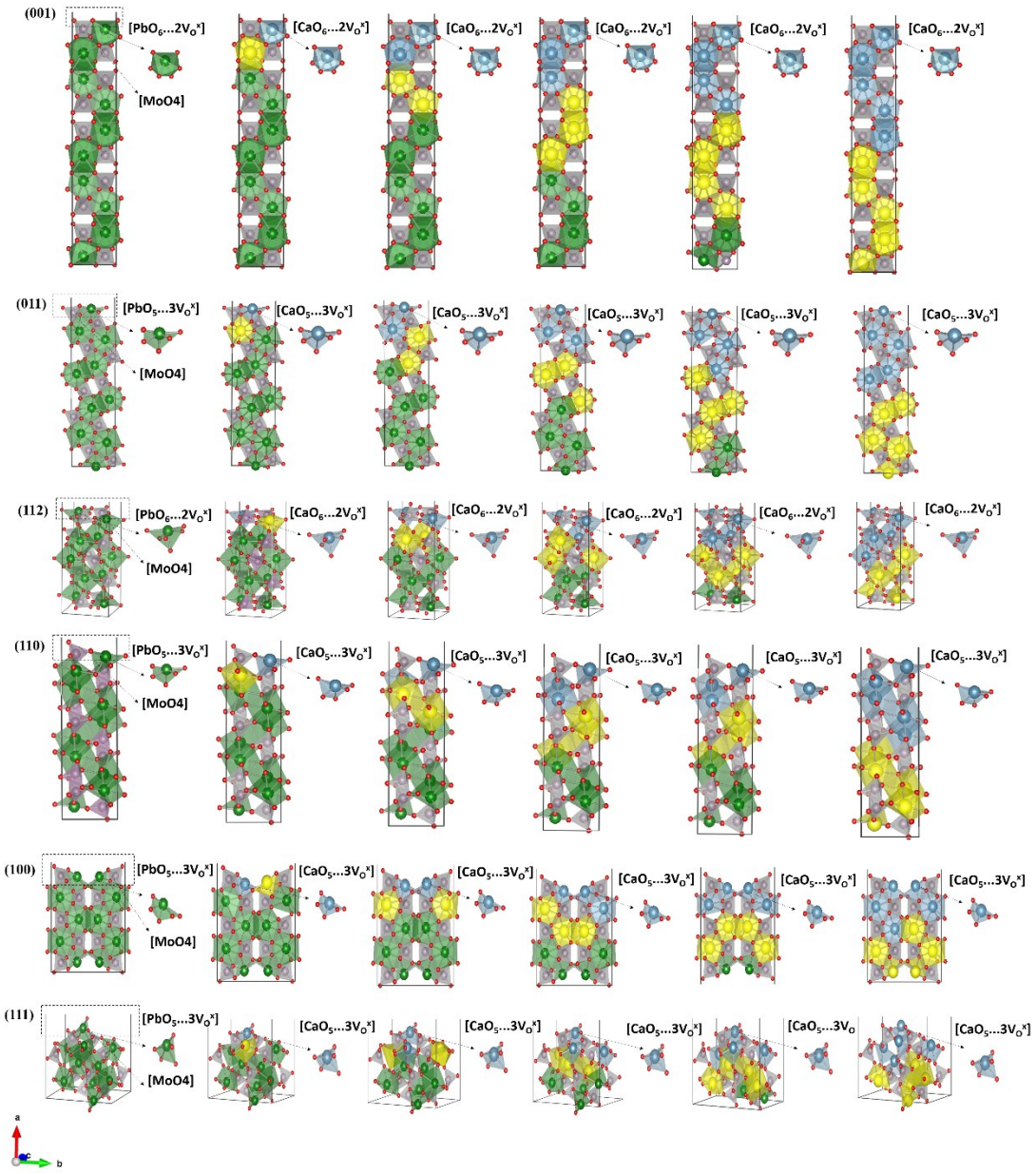

Figure S4. Schematic representations of surfaces: a) (001), b) (112), c) (100), d) (110), e) (111), and f) (011) for PMO and $Pb_{1-2x}Ca_xSr_xMoO_4$ (Pb=0.8, Pb0.6, Pb0.4, Pb0.2 and CSMO) solid solutions.

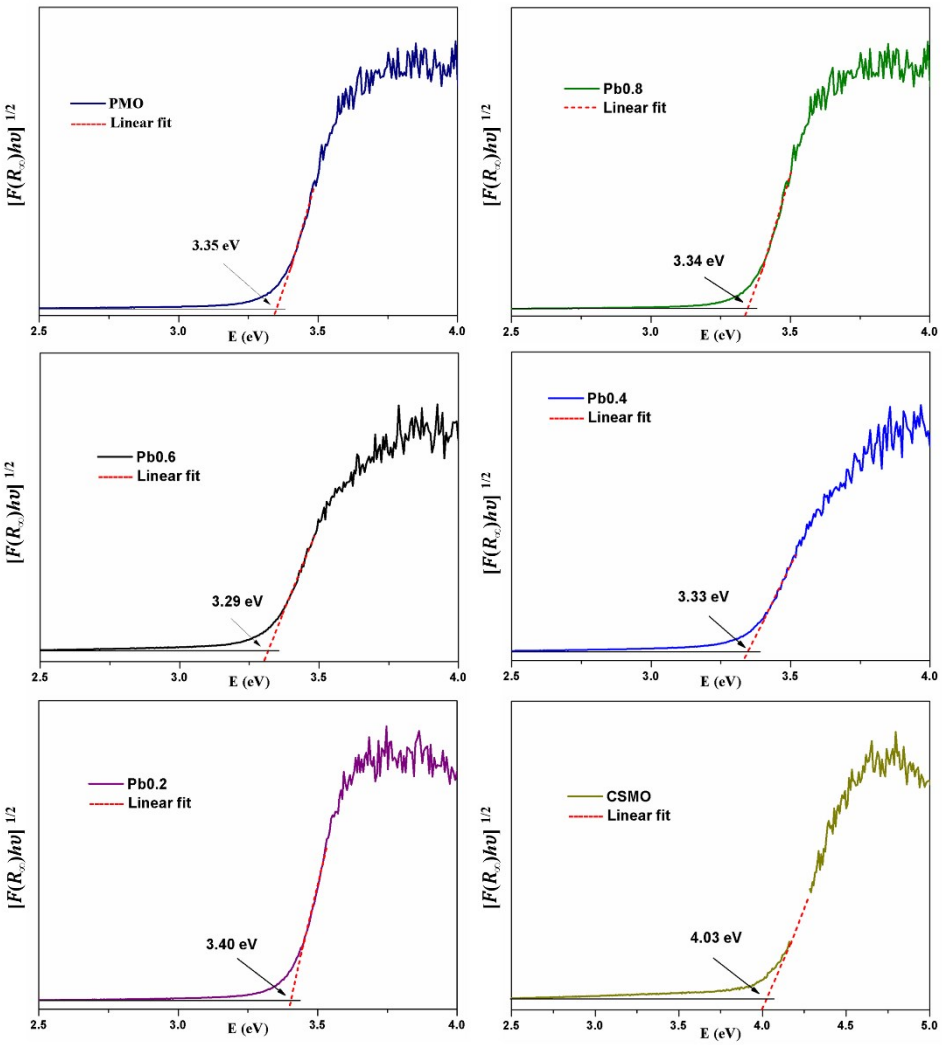

Figure S5. Calculated E_{gap} values by using the Wood and Tauc for PMO and $Pb_{1-2x}Ca_xSr_xMoO_4$ (Pb=0.2, Pb0.4, Pb0.6, Pb0.8 and CSMO) solid solutions.

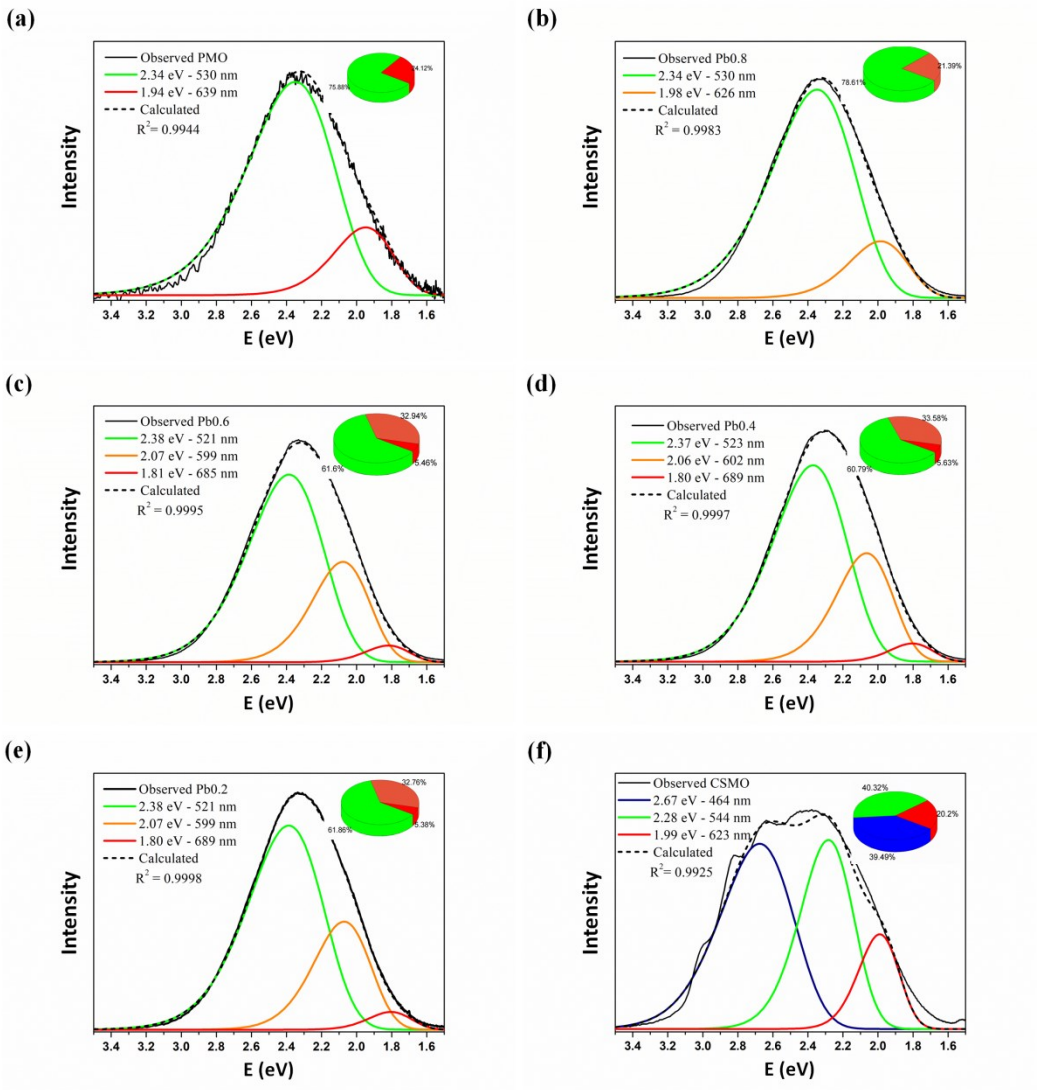

Figure S6. PL deconvolution curves: (a) PMO, (b) Pb0.8, (c) Pb0.6, (d) Pb0.4, (e) Pb0.2 and (f) CSMO.

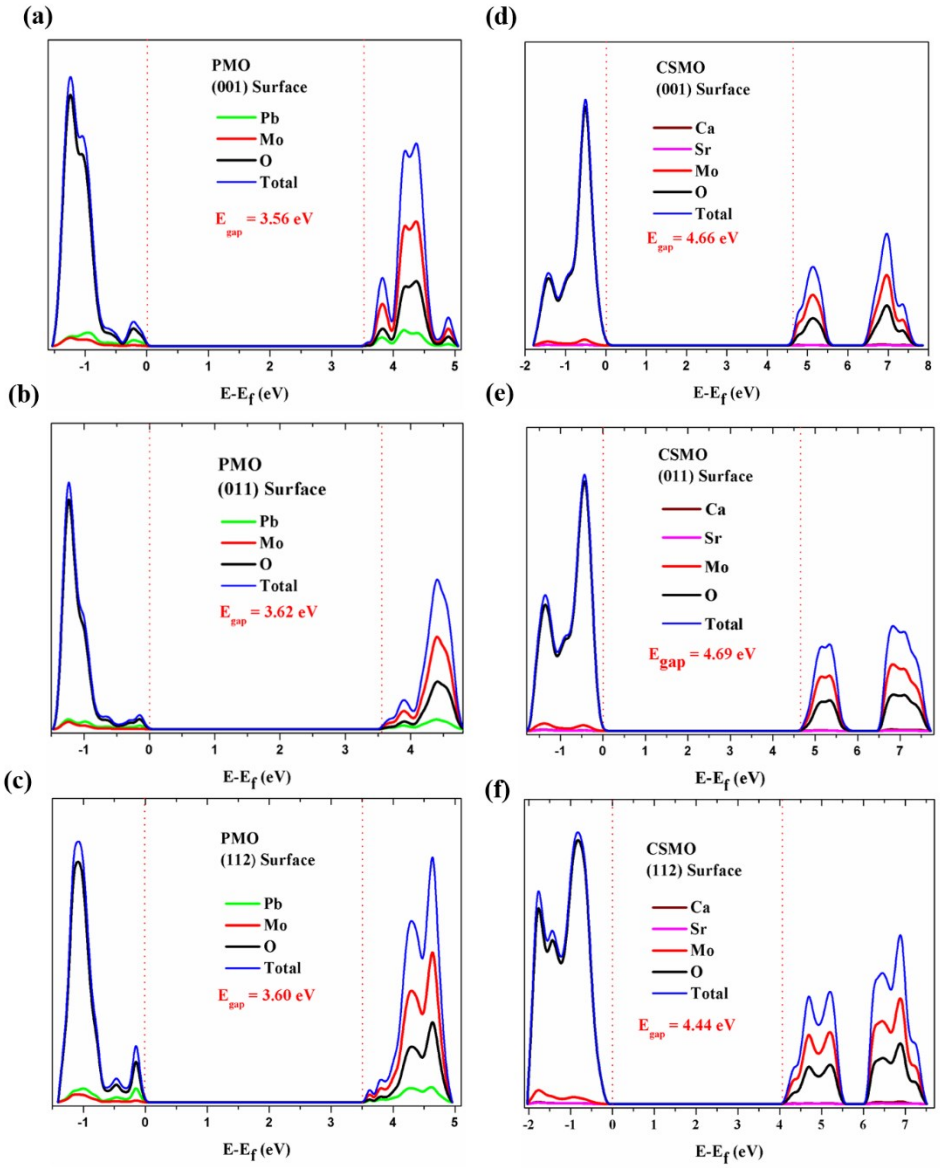

Figure S7. DOS of PMO surfaces (a) (001), (b) (011), (c) (112), and DOS of CSMO surfaces (d) (001), (e) (011), (f) (112).

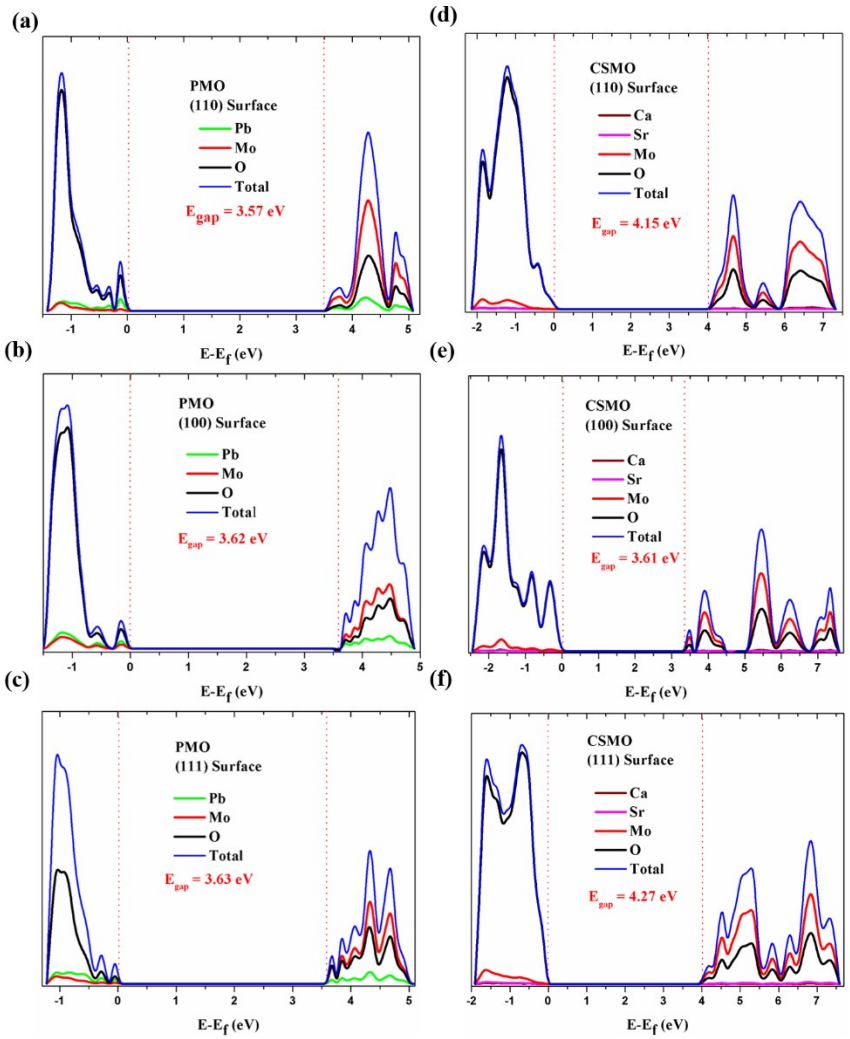

Figure S8. DOS of PMO surfaces (a) (110), (b) (100), (c) (111) and DOS of CSMO surfaces (d) (110), (e) (100), (f) (111).

Table S1. Theoretical values of the Pb-O, Ca-O, and Mo-O distances at the [PbO_6], [PbO_5], [CaO_6], [CaO_5] and [MoO_4] clusters at the exposed surfaces of the PMO and $Pb_{1-2x}Ca_xSr_xMoO_4$ (Pb= 0.2, Pb0.4, Pb0.6, Pb0.8 and CSMO) solid solutions in (Å) and the broken bond density (D_b) in (nm^{-2}).

Surface Bonds (Å)												
(001) Surface												
Samples	**PMO**	**Pb0.8**	**Pb0.6**	**Pb0.4**	**Pb0.2**	**CSMO**	**PMO**	**Pb0.8**	**Pb0.6**	**Pb0.4**	**Pb0.2**	**CSMO**
Bond (Å)	**[PbO_6]**	**[CaO_6]**	**[CaO_6]**	**[CaO_6]**	**[CaO_6]**	**[CaO_6]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**
2	2.494	2.383	2.376	2.399	2.372	2.398	1.777	1.786	1.782	1.787	1.784	1.789
2	2.533	2.449	2.445	2.454	2.446	2.413	1.860	1.850	1.861	1.848	1.861	1.836
2	2.692	2.652	2.445	2.654	2.671	2.560						
Surface area (nm^2)	0.305	0.305	0.305	0.305	0.305	0.290						
Broken bond number (N_b)	2	2	2	2	2	2						
D_b (nm^{-2})	6.557	6.557	6.557	6.557	6.557	6.896						
E_{relax}	0.134	0.046	0.103	0.193	0.271	0.095						
(011) Surface												
Samples	**PMO**	**Pb0.8**	**Pb0.6**	**Pb0.4**	**Pb0.2**	**CSMO**	**PMO**	**Pb0.8**	**Pb0.6**	**Pb0.4**	**Pb0.2**	**CSMO**
Bond (Å)	**[PbO_5]**	**[CaO_5]**	**[CaO_5]**	**[CaO_5]**	**[CaO_5]**	**[CaO_5]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**
1	2.338	2.277	2.268	2.267	2.269	2.302	1.779	1.798	1.844	1.795	1.791	1.795
2	2.403	2.347	2.345	2.348	2.348	2.320	1.789	1.803	1.822	1.800	1.798	1.796
3	2.498	2.389	2.382	2.396	2.379	2.336	1.823	1.813	1.798	1.816	1.821	1.821
4	2.568	2.419	2.432	2.419	2.428	2.400	1.853	1.836	1.791	1.841	1.845	1.831
5	2.588	2.471	2.529	2.492	2.527	2.433						
Surface area (nm^2)	0.371	0.371	0.371	0.371	0.371	0.380						
Broken bond number (N_b)	3	3	3	3	3	3						
D_b (nm^{-2})	8.086	8.086	8.086	8.086	8.086	7.894						
E_{relax}	0.294	0.052	0.558	0.600	0.661	0.397						
(112) Surface												
Samples	**PMO**	**Pb0.8**	**Pb0.6**	**Pb0.4**	**Pb0.2**	**CSMO**	**PMO**	**Pb0.8**	**Pb0.6**	**Pb0.4**	**Pb0.2**	**CSMO**
Bond (Å)	**[PbO_6]**	**[CaO_6]**	**[CaO_6]**	**[CaO_6]**	**[CaO_6]**	**[CaO_6]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**	**[MoO_4]**
1	2.450	2.344	2.342	2.343	2.327	2.329	1.775	1.780	1.794	1.793	1.794	1.779
2	2.456	2.380	2.422	2.420	2.444	2.358	1.791	1.791	1.795	1.795	1.795	1.791
3	2.519	2.431	2.483	2.460	2.472	2.411	1.837	1.833	1.830	1.827	1.836	1.830
4	2.552	2.502	2.513	2.533	2.481	2.486	1.842	1.850	1.847	1.849	1.845	1.838
5	2.703	2.525	2.547	2.590	2.499	2.500						
6	2.736	2.711	2.691	2.670	2.766	2.530						
Surface area (nm^2)	0.567	0.567	0.567	0.567	0.567	0.538						
Broken bond number (N_b)	4	4	4	4	4	4						
D_b (nm^{-2})	7.054	7.054	7.054	7.054	7.054	7.434						
E_{relax}	1.592	0.084	0.084	0.122	0.158	1.509						
(110) Surface												
Samples	**PMO**	**Pb0.8**	**Pb0.6**	**Pb0.4**	**Pb0.2**	**CSMO**	**PMO**	**Pb0.8**	**Pb0.6**	**Pb0.4**	**Pb0.2**	**CSMO**

Bond (Å)	[PbO_5]	[CaO_5]	[CaO_5]	[CaO_5]	[CaO_5]	[CaO_5]	[MoO_4]	[MoO_4]	[MoO_4]	[MoO_4]	[MoO_4]	[MoO_4]
1	2.343	2.309	2.323	2.316	2.320	2.470	1.735	1.739	1.817	1.739	1.738	1.747
2	2.389	2.404	2.428	2.476	2.412	2.517	1.801	1.813	1.888	1.815	1.816	1.805
3	2.455	2.409	2.436	2.828	2.436	2.544	1.842	1.857	1.738	1.845	1.847	1.847
4	2.554	2.443	2.433	2.829	2.436	2.554	1.889	1.872	1.845	1.890	1.889	1.872
5	2.856	2.451	2.484	2.841	2.480	2.608						
Surface area (nm^2)	0.478	0.478	0.478	0.478	0.478	0.498						
Broken bond number (N_b)	4	4	4	4	4	4						
D_b (nm^{-2})	8.368	8.368	8.368	8.368	8.368	8.032						
E_{relax}	1.861	0.103	0.121	0.157	0.199	0.330						

(100) Surface

Samples	PMO	Pb0.8	Pb0.6	Pb0.4	Pb0.2	CSMO	PMO	Pb0.8	Pb0.6	Pb0.4	Pb0.2	CSMO
Bond (Å)	[PbO_5]	[CaO_5]	[CaO_5]	[CaO_5]	[CaO_5]	[CaO_5]	[MoO_4]	[MoO_4]	[MoO_4]	[MoO_4]	[MoO_4]	[MoO_4]
1	2.303	2.258	2.263	2.255	2.282	2.213	1.730	1.731	1.731	1.737	1.730	1.739
2	2.329	2.285	2.290	2.287	2.308	2.268	1.806	1.796	1.812	1.807	1.809	1.812
3	2.256	2.309	2.320	2.300	2.308	2.298	1.846	1.850	1.837	1.842	1.847	1.835
4	2.800	2.396	2.471	2.434	2.471	2.395	1.878	1.877	1.875	1.858	1.875	1.848
5	2.839	2.423	2.475	2.458	2.508	2.453						
Surface area (nm^2)	0.676	0.676	0.676	0.676	0.676	0.640						
Broken bond number (N_b)	6	6	6	6	6	6						
D_b (nm^{-2})	8.875	8.875	8.875	8.875	8.875	9.375						
E_{relax}	0.573	0.028	0.166	0.183	0.246	0.746						

(111) Surface

Samples	PMO	Pb0.8	Pb0.6	Pb0.4	Pb0.2	CSMO	PMO	Pb0.8	Pb0.6	Pb0.4	Pb0.2	CSMO
Bond (Å)	[PbO_5]	[CaO_5]	[CaO_5]	[CaO_5]	[CaO_5]	[CaO_5]	[MoO_4]	[MoO_4]	[MoO_4]	[MoO_4]	[MoO_4]	[MoO_4]
1	2.351	2.283	2.365	2.283	2.322	2.492	1.763	1.790	1.732	1.799	1.795	1.785
2	2.364	2.292	2.368	2.307	2.377	2.496	1.808	1.806	1.856	1.801	1.806	1.793
3	2.422	2.445	2.435	2.431	2.457	2.521	1.820	1.816	1.861	1.808	1.815	1.817
4	2.528	2.457	2.450	2.446	2.465	2.538	1.836	1.822	1.831	1.832	1.817	1.825
5	2.854	2.497	2.481	2.471	2.531	2.667						
Surface area (nm^2)	1.004	1.004	1.004	1.004	1.004	0.994						
Broken bond number (N_b)	7	7	7	7	7	7						
D_b (nm^{-2})	6.972	6.972	6.972	6.972	6.972	7.042						
E_{relax}	1.220	0.073	0.115	0.166	0.220	0.301						

Table S2. Theoretical and experimental values of the E_{gap} for PMO and $Pb_{1-2x}Ca_xSr_xMoO_4$ (Pb=0.8, Pb0.6, Pb0.4, Pb0.2 and CSMO) solid solutions.

E_{gap} of the Bulk (eV)						
Samples	**PMO**	**Pb0.8**	**Pb0.6**	**Pb0.4**	**Pb0.2**	**CSMO**
Experimental	3.35	3.34	3.29	3.33	3.40	4.03
Theoretical	3.61	3.65	3.75	3.89	3.92	4.74

Table S3. Calculated values of the E_{gap} for PMO and $Pb_{1-2x}Ca_xSr_xMoO_4$ surfaces.

E_{gap} of the surfaces (eV)						
Surfaces	**PMO**	**Pb0.8**	**Pb0.6**	**Pb0.4**	**Pb0.2**	**CSMO**
(001)	3.56	3.56	3.57	3.56	3.64	4.66
(100)	3.62	3.59	3.61	3.81	3.99	3.61
(011)	3.62	3.65	3.7	3.8	4.06	4.69
(110)	3.57	3.61	3.67	3.66	4.0	4.15
(111)	3.63	3.69	3.68	3.79	3.96	4.27
(112)	3.60	3.64	3.69	3.77	3.97	4.44

Table S4. Calculated values (at atoms and clusters) of atomic Mulliken charge for PMO and CSMO bulk, and surfaces.

Bulk				**Surfaces**			
PMO		**CSMO**		**PMO (001)**		**CSMO (001)**	
Species	**Population**	**Species**	**Population**	**Species**	**Population**	**Species**	**Population**
Pb	1.26	Ca	1.62	$[PbO_6]$	-0.41	$[CaO_6]$	-0.29
Mo	1.67	Sr	1.85	$[MoO_4]$	0.42	$[MoO_4]$	0.28
O5	-0.24	1Mo	1.73	**(112)**		**(112)**	
O6	-0.24	2Mo	1.71	$[PbO_6]$	-0.36	$[CaO_6]$	-0.20
O7	-0.24	O5	-0.29	$[MoO_4]$	0.35	$[MoO_4]$	0.21
O8	-0.24	O6	-0.29	**(011)**		**(011)**	
O9	-0.24	O7	-0.29	$[PbO_5]$	-0.44	$[CaO_5]$	-0.29
O10	-0.24	O8	-0.29	$[MoO_4]$	0.35	$[MoO_4]$	0.17
O11	-0.24	O9	-0.29	**(110)**		**(110)**	
O12	-0.24	O10	-0.29	$[PbO_5]$	-0.18	$[CaO_5]$	-0.41
$[PbO_8]$	-0.69	O11	-0.29	$[MoO_4]$	0.16	$[MoO_4]$	0.12
$[MoO_4]$	0.69	O12	-0.29	**(100)**		**(100)**	
		$[CaO_8]$	-0.68	$[PbO_5]$	-0.20	$[CaO_5]$	-0.16
		$[SrO_8]$	-0.45	$[MoO_4]$	0.29	$[MoO_4]$	0.09
		1$[MoO_4]$	0.58	**(111)**		**(111)**	
		2$[MoO_4]$	0.56	$[PbO_5]$	-0.35	$[CaO_5]$	-0.49
				$[MoO_4]$	0.18	$[MoO_4]$	0.20

Table S5. The comparison of the photocatalytic activity of the prepared nanoparticle, Pb0.6, with other samples of the literature.

Sample	Dye / Concentration	kinetic constant (min^{-1})	Irradiation	References
P25	Methyl Orange 1.5×10^{-3} mol/L	6.0×10^{-3}	15 W, 365 nm, UV lamp	[1]
P25	RhB 1.0×10^{-5} mol/L	6.7×10^{-2}	25 W, 254 nm, UV lamp	[2]
PMO	RhB 1.0×10^{-5} mol/L	7.1×10^{-3}	18 W, UV lamp	[3]
Pb0.6	RhB 1.0×10^{-5} mol/L	2.0×10^{-2}	15 W, 254 nm, TUV Philip	This work

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2. W. Dong, C. W. Lee, X. Lu, Y. Sun, W. Hua, G. Zhuang, S. Zhang, J. Chen, H. Hou and D. Zhao, *Appl. Catal., B*, 2010, **95**, 197–207.
3. M. Shen, X. Zhang, K. Dai, H. Chen and T. Peng, *CrystEngComm*, 2013, **15**, 1146–1152.