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Supplementary Materials

Photocatalytic Properties of $PbMoO_4$ Nanocrystals against Cationic and Anionic Dyes in Several Experimental Conditions

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Chapter Figure

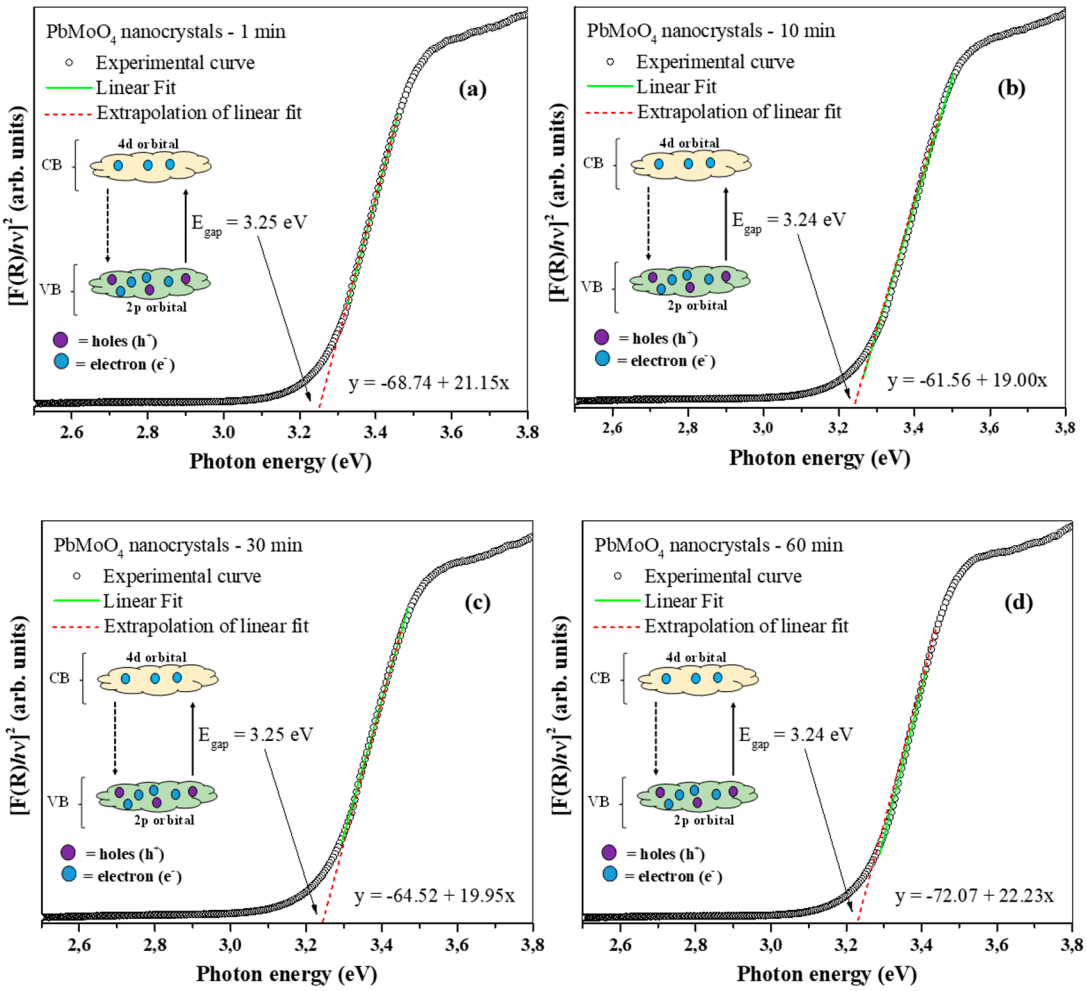

Figure S1. UV-vis spectra of $PbMoO_4$ nanocrystals synthesized at (**a**) 1 min, (**b**) 10 min, (**c**) 30 min and (**d**) 60 min by MH under 100 °C.

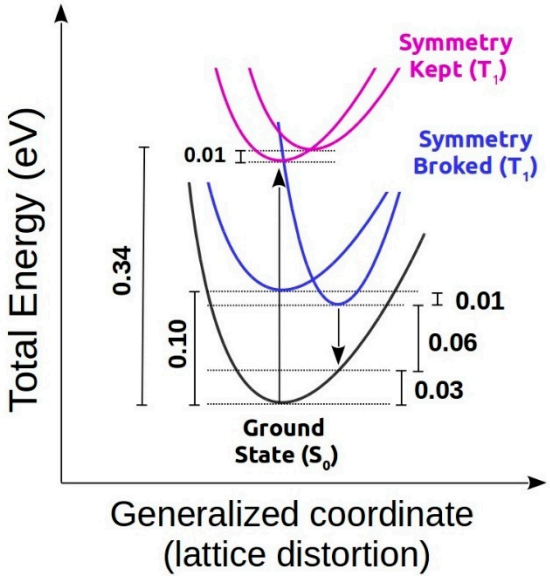

Figure S2. Calculated electronic (including dispersion) energy for stoichiometric $PbMoO_4$ in the singlet or triplet spin polarized solutions. The up vertical arrow indicates the spin polarization without atomic positions and lattice parameters relaxation. Despite the low energy difference, the energy may increase or decrease if the electronic correlation raise internal pressure while the lattice is frozen and the cations have partial reduction (delocalized solution). The energy decreases substantially with internal symmetry broken (vertical transition, blue curve), and a little more with lattice relaxation.

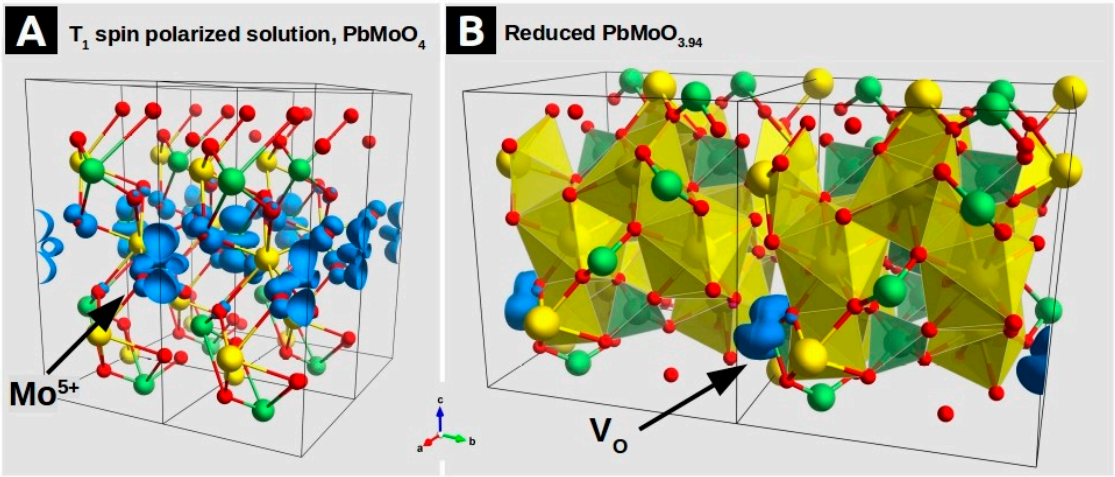

Figure S3. Electronic spin density isosurfaces of (**a**) stoichiometric $PbMoO_4$ in the spin polarized triplet solution, and (**b**) the supercell of reduced $PbMoO_{3.94}$, where only the local symmetry is broken with the oxygen vacancy (V_0) formation. In Figure (**a**) the conventional unit cell was replicated in [100] plan.

Chapter Table

Table S1 – Rietveld refinement results of $PbMoO_4$ nanocrystals.

Atoms	Wyckoff	Atomic coordinates		
		x	y	z
$PbMoO_4$ – 1min				
Pb	4b	0	0.25000	0.62500
Mo	4a	0	0.25000	0.12500
O	16f	0.23782	0.12102	0.04177
R_p = 8.45; R_{wp} = 11.0; R_e = 6.16 and χ^2= 3.165 and GOF = 1.77.				
$PbMoO_4$ – 10min				
Pb	4b	0	0.25000	0.62500
Mo	4a	0	0.25000	0.12500
O	16f	0.23634	0.11447	0.04513
R_p = 9.01; R_{wp} = 11.5; R_e = 6.97 and χ^2= 2.738 and GOF = 1.65.				
$PbMoO_4$ – 30min				
Pb	4b	0	0.25000	0.62500
Mo	4a	0	0.25000	0.12500
O	16f	0.23904	0.11805	0.04590
R_p = 10.0; R_{wp} = 12.5; R_e = 7.28 and χ^2= 2.960 and GOF = 1.72.				
$PbMoO_4$ – 60min				
Pb	4b	0	0.25000	0.62500
Mo	4a	0	0.25000	0.12500
O	16f	0.23963	0.11430	0.05048
R_p = 9.94; R_{wp} = 12.1; R_e = 7.36 and χ^2= 2.706 and GOF = 1.64.				

Table S2. Experimental and theoretical Raman active modes of $PbMoO_4$ nanocrystals synthesized and reported by literatures.

Assigment	This work		Moura et al. (2018) **(cm^{-1})**	Bomio et al. (2013) **(cm^{-1})**
	Experimental (cm^{-1})	Theoretical (cm^{-1})		
E_g	60	62.2	-	-
B_g		63.2	62	65
B_g	71	84.9	73	75
E_g	101	130.6	104	107
A_g	165	197.0	168	171
E_g	192	217.8	193	195
B_g	315	319.8	318	320
A_g		324.9	-	-
E_g	352	373.7	-	-
B_g		377.3	351	351
E_g	744	769.7	743	743
B_g	765	788.7	766	766
A_g	867	880.7	869	872

Table S3. Lattice parameters (**Å** and **Å³**), total energy differences per unit cell (eV), and electronic band gap (eV) of stoichiometric and reduced $PbMoO_4$.

Structure / State[a]	***a***	***b***	***c***	***V***	**ΔE/cell**
Stoichiometric system					
Ground S0 (fully relaxed) - reference	5.4168	5.4168	11.8200	346.82	0.00
Triplet T1 (frozen from ground S0) - delocalized					0.33
Triplet T1 (atomic positions relaxed from S0 structure)					0.34
Triplet T1 (symmetry broken, lattice frozen from S0)					0.10
Triplet T1 (symmetry broken, fully relaxed)[b]	5.2567	5.2591	11.5729	319.94	0.09
Ground S0 (electronic structure from full relaxed T1)					0.03
Reduced system					
VO (S0, frozen from stoichiometric bulk) - reference	5.4168	5.4168	11.8200	346.82	0.00
VO (T1, frozen from stoichiometric bulk)					0.02
VO (T1, atomic positions and lattice fully relaxed)[c]	5.4996	5.3398	11.8164	346.95	-0.02

Experimental parameters					
Experimental, single crystal	5.4312	5.4312	12.1065	357.12	-
Experimental, this work	5.4332	5.4332	12.1027	357.28	-

Legend: (a) S for singlet (diamagnetic), T for triplet (ferromagnetic); (b) alpha = beta = 90°; gamma = 89.87°; (c) alpha = 90.65°; beta = 90.24°; gamma = 90.89°.