Electronic Supplementary Materials (ESI)

New Reaction between Common Compounds: When Lead Oxide meets Formaldehyde

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(1) Experiment details:

Reaction between Lead oxide and formaldehyde: 1mmol PbO (Sinopharm Chemical Reagent Co., Ltd., China) was dispersed into 10ml X% HCHO aqueous solution (X%: volume percent, X=4, 10, 20, 40) to get a yellow suspension at 25°C. After 6h stirring, a white powder product was obtained by centrifuging and drying under vacuum at 40 °C overnight.

Reaction between Lead oxide and diols: 1mmol PbO was dispersed into 10ml 10% diols (diols= ethylene glycol, glycerin, 1,2-propanediol, 1,3-propanediol and 1,4-butanediol, 10%: volume percent) aqueous solution to get a yellow suspension at 25°C. After 6h stirring, the product was obtained by centrifuging, washed with deionized water. Finally, the precipitate was dried under vacuum at 40 °C overnight.

(2) Material characterization:

UV/Vis adsorption spectra were measured with a Shimadzu UV-2450 spectrophotometer in the diffuse/reflectance mode. The Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Thermo Nicolet 380 spectrometer. The morphology of the samples was observed by field emission scanning electron microscopy (FE-SEM) on a JSM-6700F electron microscope (JEOL, Japan). Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-1230 operated at 80 Kv. HRTEM images and SAED patterns were recorded on the TECNAI G2 F20 operated at 200 KV. Elemental analyses were performed with Vario MICRO CHN elemental analyser (EA). The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 409 PG/PC analyzer (N_2, ramp rate: 10 °C/min).

(3) DFT calculations

Major part of the density functional theory (DFT) calculation was carried out using Gaussian 09W program[1] (as molecular calculations). The Becke-three-parameter-Lee-Yang-Parr hybrid functional was employed.[2-5] The Los Alamos effective core potentials (ECP) was used for Pb,[6] and the 1s to 5s, 5p, 5d electrons were replaced by the ECP. The Dunning-Huzinaga full double zeta (D95) basis set was used for C, H, and O atoms and the valence electrons of Pb.[7] In the search of reaction paths, the transition state (TS) was characterized first, and then the Intrinsic Reaction Coordinate (IRC) analysis was carried out for the both directions, i.e., reactant and product. Since the step width of

IRC is very small, the IRC analysis was restricted at the neighbor of the TS. At the end point of IRC, it was followed by usual optimization. The plane-wave based DFT calculation was also conducted using the Castep program, [8] and the unit cell of Fig.2B. The Perdew, Burke and Ernzerhof (PBE) functional[9] was used together with the ultra-soft core potentials.[10] The basis set cut-off energy was set to 300 eV. The electron configurations of atoms are H: $1s^1$, C: $2s^2 2p^2$, O: $2s^2 2p^4$, and Pb: $5d^{10} 6s^2 6p^2$. As shown in Fig.S2A, all the atomic coordinates were optimized, and the lattice constants were fixed. The optimized dimer structure of $(PbO_2CH_2)_2$ was reused for the harmonic frequency calculation by Gaussian 09W as a molecule. Fig.S2B shows the band dispersion and density of states. The band gap was estimated to be 2.17 eV as the difference between the VBM and CBM.

(4) XRD refinements

The X-ray powder diffraction spectra were collected on a Rigaku D/Max-2550pc powder diffractometer, using CuKα (λ for Kα=1.54059 Å) radiation at 40 kVand 250 mA. The scans were run from 5.0 to 90.0° (2θ), with an increasing step size of 0.02° and counting time duration of 2 s for each step. Data were processed using the MDI-Jade version 9.0 software.

The XRD pattern of the sample was shown in Figure S1. After testing many times, we concluded that it could not be identified as a known crystal structure reported in the PDF4-2012 database. Instead, the XRD pattern was indexed by Jade 9.0 as monoclinic crystal system and $P2_1$ (4#) space group. Full pattern profile fitting in Figure S1 gave unit cell parameters of a=6.972(1)Å, b=20.318(3)Å, c=5.176(1)Å, β=94.165(14)º,V=731.42$Å^3$. Attempts to solve the structure using the direct method and simulated annealing method, but all failed. However, all suggested solutions from direct methods, suggested two oxygen atoms coordinated Pb. However, Rietveld refinements and subsequent difference Fourier maps did not reveal consistent enough oxygen or other atom positions to finalized the refinements. Some minor difference (intensity of some powder diffraction peaks) between the XRD patterns of the product and the calculated one was due to preferred orientation of sample.

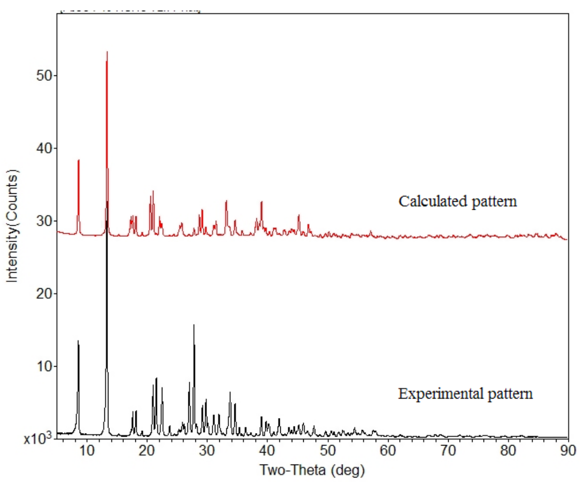


Fig. S1 Full pattern profile fitting of XRD pattern

Table.S1 Elemental analysis of $PbCH_2O_2$

	C%(weight)	H%(weight)	nH:nC
Experiment result	5.01	0.984	2.36
Calculation result	4.74	0.791	2

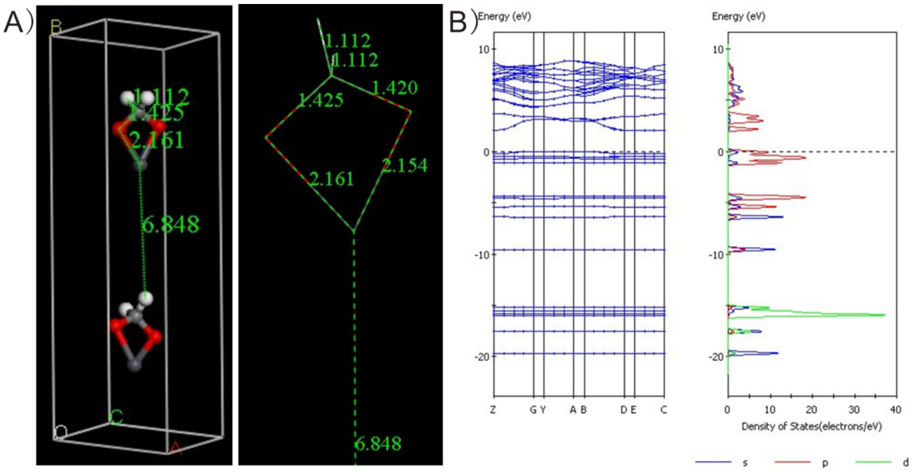


Fig. S2 A) The optimized structure of $(PbO_2CH_2)_2$ unit cell with typical bond lengths; B) band dispersion and DOS of PbO_2CH_2

Table.S2 Experimental and DFT calculation results of FT-IR frequency for $PbCH_2O_2$

Function Groups	FT-IR frequency (cm^{-1})	
	Experimental results	DFT calculation results
$\nu(CH_2)$	2770	2847
	2690	2829
$\nu(COO)$	1584	1551
$\delta(CH_2)$	1402	1383
	1338	
ν(Pb-O-C)	1050	1001
	983	943
	770	719

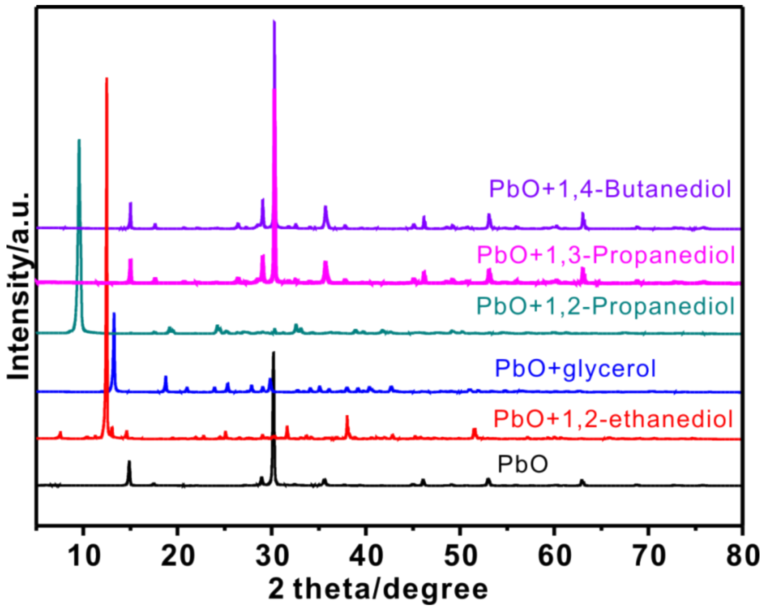


Fig. S3 XRD patterns of PbO+diols

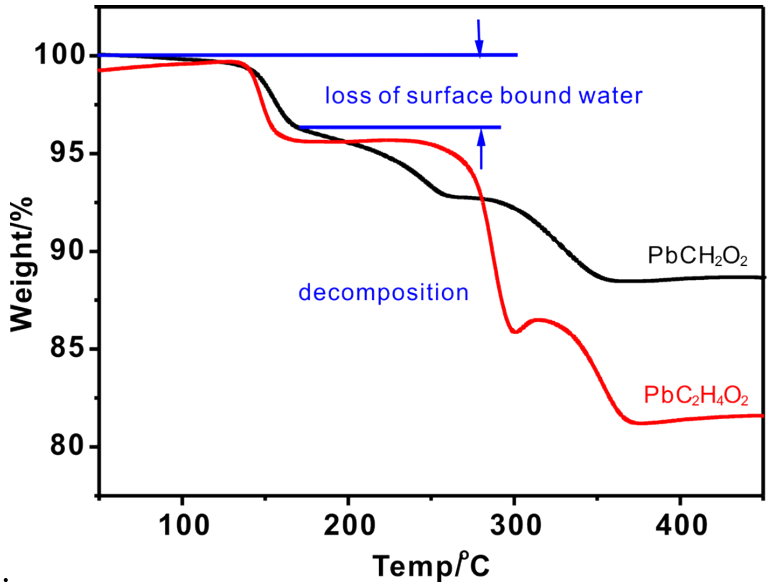
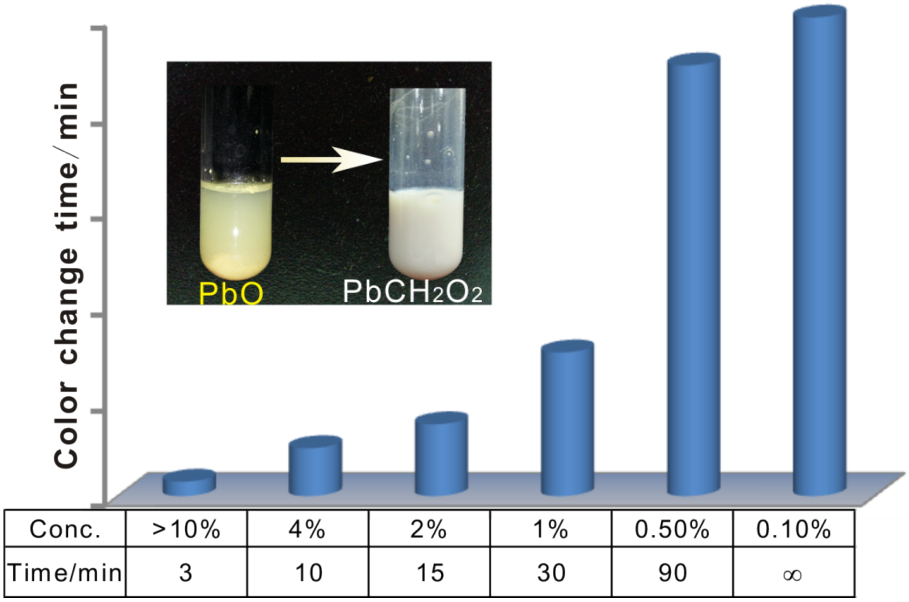


Fig. S4 TG of $PbCH_2O_2$ and $PbC_2H_4O_2$



Conc.	>10%	4%	2%	1%	0.50%	0.10%
Time/min	3	10	15	30	90	∞

Fig. S5 Color change time of 1mmol PbO+ 10ml X% HCHO(X=0.10, 0.50, 1, 2, 4, 10, 20, 40)

References

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