Supplementary Materials for

Novel Antimonate Photocatalysts MSb_2O_6 (M = Ca, Sr and Ba): A Correlation between Packing Factor and Photocatalytic Activity

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1. Literature on Photocatalytic Compounds

A literature survey of the photocatalytic activity and structure factor is summarized in Table S1 and Table S3. Packing factor (PF) was computed using the crystallographic data of unit cell volumes and coordination numbers reported in the literature (i.e., the papers that reported photocatalysis or other papers/handbook/database on structures). The value of band gap (E_g) was taken from the same report(s) on photocatalytic activity. Where applicable, additive used (RuO_2, Pt or NiO) is specified.

2. Additional materials

Additional materials besides MSb_2O_6 (M = Ca, Sr, Ba) for photocatalytic evaluation in our experiments were synthesized by solid state reaction or precipitation using high purity (Sinoreg., 99.5%) starting materials unless noted otherwise. (See descriptions on individual materials below.) The calcination temperature and time were chosen to yield comparable BET surface areas for powders of different compounds in the same series. Phase identification was performed by X-ray powder diffraction (XRD) and only single phase powders were used. The optical band gaps were estimated from the UV-Vis diffuse reflection spectra.

(1) TiO_2: Commercial anatase TiO_2 was heat-treated at 500 ^oC and 950 ^oC, respectively, to acquire anatase and rutile phases with similar surface area.

(2) $BiNbO_4$: Two polymorphs (orthorhombic and triclinic) were prepared by solid state reactions between Bi_2O_3 and Nb_2O_5 at 900 ^oC to 1100^oC (orthorhombic) and 1250^oC (triclinic).

(3) $M$$TiO_3$ (M = Mg, Ca, Sr and Ba): These compounds were synthesized by precipitation of metal (M) salt on TiO_2 particles. A stoichiometric amount of TiO_2 (Degussa P25) was suspended in 200 mL of $M(NO_3)_2$ aqueous solution with $[M^{2+}]$ = 0.5 mol/L and 1 mL PEG (molecular weight: 200) was added. Next, 55 mL of aqueous solution of Na_2CO_3 with $[CO_3^{2-}]$ = 2 mol/L was added dropwise into the suspension under vigorous stirring. The precipitates were repeatedly filtered and washed in water, then calcined at 850 ^oC to 1050 ^oC for 6 h.

(4) $(BaO)(TiO_2)_n$ (n = 1, 2 and 4): These compounds were prepared by solid state reactions between $BaCO_3$ and TiO_2 at 1250^oC for 12 h to 18 h.

(5) $(CaO)(TiO_2)_n$ (n = 1, 2 and 4): These compounds were prepared by solid state reactions between $CaCO_3$ and TiO_2 at 1400^oC for 12 h.

(6) MNb_2O_6 (M = Mg, Ca, Sr and Ba): These compounds were synthesized by solid state reactions between MCO_3 and Nb_2O_5 at 1450^oC for 12 h.

(7) MSb$_2$O$_6$ (M = Ca, Sr and Ba): These compounds were synthesized by solid state reactions between M(NO$_3$)$_2$ and Sb$_2$O$_3$ at 1150^{o}C for 24 h.

(8) MWO$_4$ (M = Ca, Sr and Ba): These compounds were synthesized by solid state reactions between MCO$_3$ and WO$_3$ at 850^{o}C to 950^{o}C.

(9) MBiO$_2$Cl (M = Ca, Sr and Ba): These compounds were prepared by solid state reactions between BiOCl and MCO$_3$ at 780^{o}C for 12 h to 20 h.

(10) (SrO)$_m$(Bi$_2$O$_3$)$_n$: Compounds of Sr$_2$Bi$_6$O$_{11}$, SrBi$_4$O$_7$, SrBi$_2$O$_4$, and Sr$_2$Bi$_2$O$_5$ were prepared by solid state reactions between SrCO$_3$ and Bi$_2$O$_3$ at 650^{o}C to 780^{o}C for 12 h to 28 h.

Table S1 Photocatalytic compounds from the literature, grouped to illustrate the perfect correlation between photocatalytic activity and packing factor (PF).

Catalyst	E_g (eV)	Crystal system	Space group	PF (%)	Measurement	Activity	Ref.
NaTaO$_3$ KTaO$_3$	3.96 3.42	Orthorhombic Cubic	- Pm3m	80.46 85.03	UV, water splitting	Na > K	S1
LiTaO$_3$ NaTaO$_3$ KTaO$_3$	4.7 4.0 3.6	Rhombohedral Orthorhombic Cubic	R3c - Pm-3m	68.99 80.46 85.03	UV, water splitting	Li > Na > K	S2-S4
CaTa$_2$O$_6$ SrTa$_2$O$_6$ BaTa$_2$O$_6$	4.0 4.4 4.1	Orthorhombic Orthorhombic Orthorhombic	Pnma Pbam Pnma	63.11 62.13 62.42	UV, water splitting	Sr > Ba > Ca	S2,S5
MgTa$_2$O$_6$ BaTa$_2$O$_6$	- -	Tetragonal Orthorhombic	P4$_2$/mnm Pnma	65.35 62.42	UV, water splitting	Ba > Mg	S4
KTaO$_3$	3.9	Cubic	Pm3m	85.03	UV, water	K$_2$ > K	S6

$K_2Ta_2O_6$	4.5	Cubic	Fd3m	67.87	splitting		
$Pt/CaTaO_2N$ $Pt/SrTaO_2N$ $Pt/BaTaO_2N$	2.5 2.1 2.0	Orthorhombic Cubic Cubic	Pnma - -	76.71 75.61 78.27	Vis, water splitting	Sr > Ca ≈ Ba	S7
$NaNbO_3$ $KNbO_3$	3.08 3.14	Orthorhombic Orthorhombic	Pbma Cm2m	78.60 83.38	UV, water splitting	Na > K	S1
$Pt/NiNb_2O_6$ $Pt/NiTa_2O_6$	2.20 2.30	Orthorhombic Tetragonal	Pbcn $P4_2/mnm$	66.49 65.45	UV, water splitting	Ta > Nb	S8
$Pt/AgNbO_3$ $Pt/AgTaO_3$	2.80 3.40	Orthorhombic Monoclinic	- -	67.42 67.88	UV, O_2 evolution	Nb > Ta	S9
$NiO/Sr_2Nb_2O_7$ $NiO/Sr_2Ta_2O_7$	3.90 4.60	Orthorhombic Orthorhombic	Cmcm Cmcm	56.13 55.07	UV, water splitting	Ta > Nb	S10
$Pt/BiNbO_4$ $Pt/BiTaO_4$	2.64 2.74	Orthorhombic Triclinic	Pnna P1	57.60 58.93	UV, water splitting	Nb > Ta	S11
$Pt/InVO_4$ $Pt/InNbO_4$ $Pt/InTaO_4$	1.90 2.50 2.60	Orthorhombic Monoclinic Monoclinic	Cmcm P2/c P2/c	53.57 63.36 63.72	UV-Vis, water splitting	V > Nb > Ta	S12
$Pt/BaZn_{1/3}Nb_{2/3}O_3$ $Pt/BaZn_{1/3}Ta_{2/3}O_3$ $Pt/BaNi_{1/3}Nb_{2/3}O_3$ $Pt/BaNi_{1/3}Ta_{2/3}O_3$	3.82 4.50 3.35 3.89	Cubic Hexagonal Cubic Hexagonal	Pm-3m P-3m Pm-3m P-3m	74.09 74.20 74.32 74.46	UV, water splitting	ZnNb > ZnTa > NiNb > NiTa	S13
$Zn_3V_2O_8$ $Mg_3V_2O_8$ $Ni_3V_2O_8$	2.92 3.02 2.25	Tetragonal Tetragonal Tetragonal	Abam Abam Abam	68.98 69.56 71.69	Vis, O_2 evolution	Zn > Mg > Ni	S14
$Mg_{2.5}VMoO_8$ $Zn_{2.5}VMoO_8$	- -	Orthorhombic Orthorhombic	Pnma $P2_12_12_1$	61.33 60.41	Vis, O_2 evolution	Zn > Mg	S15
Ga_2BiNbO_7 In_2BiNbO_7	2.57 2.52	Cubic Cubic	Fd-3m Fd-3m	55.31 56.69	UV, water splitting;	Ga > In;	S16

					Vis, MB degradation	Ga > In	
Bi_2YTaO_7 Bi_2LaTaO_7	2.23 2.17	Cubic Cubic	Fd-3m Fd-3m	54.37 52.76	UV, water splitting; Vis, MB degradation	La > Y; La > Y	S17
$Sr(In_{1/2}Nb_{1/2})O_3$ $Ba(In_{1/2}Nb_{1/2})O_3$	3.62 3.30	Cubic Cubic	Pm3m Pm3m	72.83 75.24	UV-Vis, MB degradation	Sr > Ba	S18
$Sr(In_{1/3}Nb_{1/3}Sn_{1/3})O_3$ $Ba(In_{1/3}Nb_{1/3}Sn_{1/3})O_3$	3.48 3.00	Cubic Cubic	Pm3m Pm3m	72.84 75.49	UV-Vis, MB degradation	Sr > Ba	S18
$Ba(In_{1/3}Pb_{1/3}Nb_{1/3})O_3$ $Ba(In_{1/3}Pb_{1/3}Ta_{1/3})O_3$	1.48 1.50	Cubic Cubic	Pm3m Pm3m	75.51 76.71	UV-Vis, MB degradation	In > Ta	S19
$CaIn_2O_4$ $SrIn_2O_4$ $BaIn_2O_4$	- - -	Orthorhombic Orthorhombic Monoclinic	Pnam Pnam $P2_1/a$	59.98 61.36 62.90	Vis, MB degradation	Ca > Sr > Ba	S20
$RuO_2/CaIn_2O_4$ $RuO_2/SrIn_2O_4$ $RuO_2/BaIn_2O_4$	- - -	Orthorhombic Orthorhombic Monoclinic	Pnam Pnam $P2_1/a$	59.98 61.36 62.90	UV-Vis, water splitting	Ca > Sr > Ba	S21
$RuO_2/LiInO_2$ $RuO_2/NaInO_2$	- -	Tetragonal Trigonal	$I4_1/amd$ R-3m	64.39 59.81	UV-Vis, water splitting	Na > Li	S22
Pt/Anatase-TiO_2 Pt/Rutile-TiO_2	3.20 3.00	Tetragonal Tetragonal	- -	64.55 70.45	UV, water splitting	Anatase > Rutile	S23
Li_2TiO_3 $Na_2Ti_3O_7$ $K_2Ti_8O_{17}$	- - -	Monoclinic Monoclinic Monoclinic	C2/c $P2_1/m$ C2/m	70.76 63.05 63.85	UV, MB degradation	Na > K > Li	S24
$RuO_x/Na_2Ti_6O_{13}$ $RuO_x/K_2Ti_6O_{13}$ $RuO_x/Rb_2Ti_6O_{13}$	3.36 3.26 3.13	Monoclinic Monoclinic Monoclinic	C2/m C2/m C2/m	61.65 63.84 65.36	UV, water splitting	Na > K > Rb	S25
$RuO_x/Na_2Ti_3O_7$	3.51	Monoclinic	$P2_1/m$	63.05	UV, water	$Ti_6 > Ti_3$	S25

$RuO_x/Na_2Ti_6O_{13}$	3.36	Monoclinic	C2/m	61.65	splitting		
$RuO_x/K_2Ti_2O_5$ $RuO_x/K_2Ti_4O_9$ $RuO_x/K_2Ti_6O_{13}$	- 3.46 3.26	Monoclinic Monoclinic Monoclinic	- C2/m C2/m	70.51 68.21 63.84	UV, water splitting	$Ti_6 > Ti_4 > Ti_2$	S25
$RuO_2/BaTi_4O_9$ $RuO_2/Ba_4Ti_{13}O_{30}$ $RuO_2/Ba_2Ti_9O_{20}$ $RuO_2/Ba_6Ti_{17}O_{40}$	- - - -	Orthorhombic Orthorhombic Monoclinic Monoclinic	Pnmm Abma $P2_1/m$ A2/a	65.27 66.43 68.10 68.93	UV, water splitting	$Ti_4 > Ti_{13} > Ti_9 > Ti_{17}$	S26
$RuO_2/BaTi_4O_9$ $RuO_2/K_2Ti_4O_9$	- -	Orthorhombic Monoclinic	Pnmm C2/m	65.27 68.21	UV, water splitting	Ba > K	S27
$NiO_x/La_2Ti_2O_7$ $NiO_x/Pr_2Ti_2O_7$ $NiO_x/Nd_2Ti_2O_7$	3.82 2.99 3.65	Monoclinic Monoclinic Monoclinic	$P2_1$ $P2_1$ $P2_1$	63.66 64.48 64.56	UV, water splitting	La > Pr > Nd	S28
$RuO_2/Ca_2Sb_2O_7$ $RuO_2/Sr_2Sb_2O_7$	- -	Orthorhombic Orthorhombic	Imma Imma	65.41 64.45	UV, water splitting	Sr > Ca	S29
$Ca_2Sb_2O_7$ $Sr_2Sb_2O_7$	4.02 3.86	Orthorhombic Orthorhombic	Imma Imma	65.41 64.45	UV, MO degradation	Sr > Ca	S30
RuO_2/Ca_2SnO_4 RuO_2/Sr_2SnO_4 RuO_2/Ba_2SnO_4	- - -	Orthorhombic Tetragonal Tetragonal	Pbam I4/mmm I4/mmm	63.01 63.79 64.62	UV, water splitting	Ca > Sr > Ba	S29
$Pt/SrCrO_4$ $Pt/BaCrO_4$	2.44 2.63	Monoclinic Orthorhombic	$P2_1/n$ Pnma	61.18 59.19	Vis or UV, water splitting	Ba > Sr	S31
$Pt/CuMn_2O_4$ $Pt/ZnMn_2O_4$	1.40 1.23	Tetragonal Tetragonal	$I4_1/amd$ $I4_1/amd$	65.07 62.15	Halogen lamp, water splitting	Zn > Cu	S32
Bi_2MoO_6 Bi_2WO_6	2.70 2.80	Orthorhombic Orthorhombic	- -	58.19 58.69	Vis, O_2 evolution	Mo > W	S33
ZnS CdS	3.70 2.50	- -	- -	67.88 56.99	UV, MO and Rhodamine 6G	Cd > Zn	S34

					degradation		
ZnS CdS	- -	- -	- -	67.88 56.99	UV, water splitting	Cd > Zn	S35
Pt/CdS Pt/$NaInS_2$	2.40 2.30	- Trigonal	- R-3m	56.99 70.74	Vis, water splitting	Cd > NaIn	S36

Table S2 Photocatalytic compounds from the literature, grouped to illustrate exceptions to the correlation between photocatalytic activity and packing factor (PF). The exceptions are marked by * under "Activity" and explained in note a to f.

Catalyst	E_g (eV)	Crystal system	Space group	PF (%)	Measurement	Activity	Ref.
Pt/Bi_2InTaO_7 Pt/Bi_2FeTaO_7 Pt/Bi_2GaTaO_7	2.92 2.42 3.01	Cubic Cubic Cubic	- - -	53.13 57.04 56.12	UV, water splitting	In > Fe >*[a] Ga	S37
Pt/$CaCo_{1/3}Nb_{2/3}O_3$ Pt/$SrCo_{1/3}Nb_{2/3}O_3$ Pt/$BaCo_{1/3}Nb_{2/3}O_3$	2.80 2.46 2.46	Monoclinic Cubic Cubic	- Pm3m Pm3m	76.70 79.21 77.54	Vis (λ ≥ 420 nm), water splitting	Ba >*[b] Ca > Sr	S38
$CaIn_{0.5}Nb_{0.5}O_3$ $SrIn_{0.5}Nb_{0.5}O_3$ $BaIn_{0.5}Nb_{0.5}O_3$	4.17 3.96 3.51	Orthorhombic Cubic Cubic	Pama Pm3m Pm3m	68.71 72.83 75.24	Pt loading, UV, water splitting; NiO_x loading, Vis (λ ≥ 420 nm), water splitting	Ca > Sr > Ba; Ba >*[c] Ca > Sr	S39
$RuO_2/BaTi_4O_9$ $RuO_2/BaTi_5O_{11}$ $RuO_2/BaTi_2O_5$ $RuO_2/BaTiO_3$	3.70 3.80 3.70 3.70	Orthorhombic Monoclinic Monoclinic Cubic	Pnmm $P2_1/n$ C2/m Pm-3m	65.27 68.96 70.97 82.24	UV, water splitting	$BaTi_4O_9$ > $BaTi_2O_5$ >*[d] $BaTi_5O_{11}$ > $BaTiO_3$	S40
$Sr(In_{1/3}Nb_{1/3}Pb_{1/3})O_3$ $Ba(In_{1/3}Nb_{1/3}Pb_{1/3})O_3$	3.10 1.48	Cubic Cubic	Pm3m Pm3m	75.21 75.51	UV-Vis or Vis, MB and 4-Chlorophenol degradation	Ba >*[e] Sr	S18

$NaTaO_3$	3.96	Orthorhombic	-	80.46	UV, water splitting	Ta >*[f] Nb	S1
$NaNbO_3$	3.08	Orthorhombic	Pbma	78.60			
$KTaO_3$	3.42	Cubic	Pm3m	85.03	UV, water splitting	Ta >*[f] Nb	S1
$KNbO_3$	3.14	Orthorhombic	Cm2m	83.38			

a. Fe absorbs more light due to d^5 configuration of Fe^{3+}.

b. Ca compound, having a higher E_g, absorbs less light when using a visible light source.

c. All compounds have relatively high E_g, hence inefficient light absorption when using a visible light source.

d. Crystallinity of $BaTi_5O_{11}$ was reported to be poor.

e. Large difference in E_g makes comparison difficult; Ba compound has a much lower E_g and more absorption.

f. The considerably larger E_g of the Ta compounds implies a higher conduction band minimum, hence a higher reduction potential for H^+/H_2.

3. The UV-Vis spectra for the antimonates

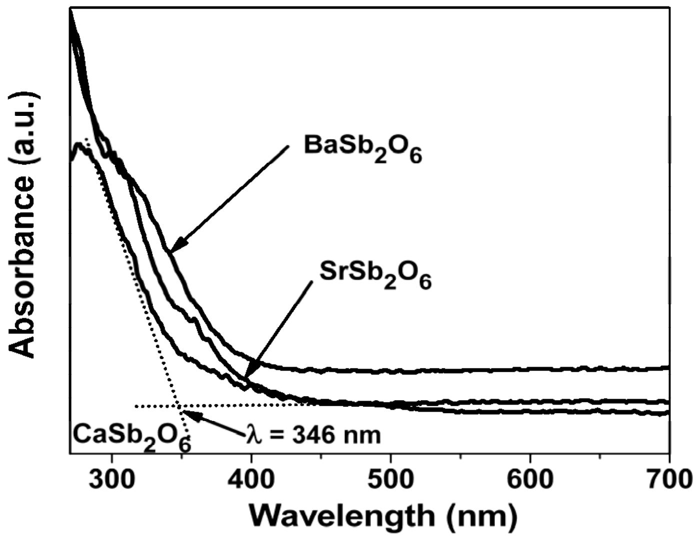

Fig. S1 UV-Vis for the antimonates photocatalysts*

* As shown in Fig. S1, the light absorbance starts at about 350 nm for all the antimonate samples, while a uniform red shift of absorbance edge is observed in the order of $CaSb_2O_6$ (λ = 346 nm), $SrSb_2O_6$ (λ = 349 nm), and $BaSb_2O_6$ (λ = 358 nm). So

the intrinsic band gaps of $CaSb_2O_6$, $SrSb_2O_6$ and $BaSb_2O_6$ are estimated at 3.59 eV, 3.55 eV and 3.46 eV, respectively, using the widely-applied equation:

$$Eg\ (eV) = 1241\ /\ \lambda\ (nm).$$

4. The MB mineralization measurements

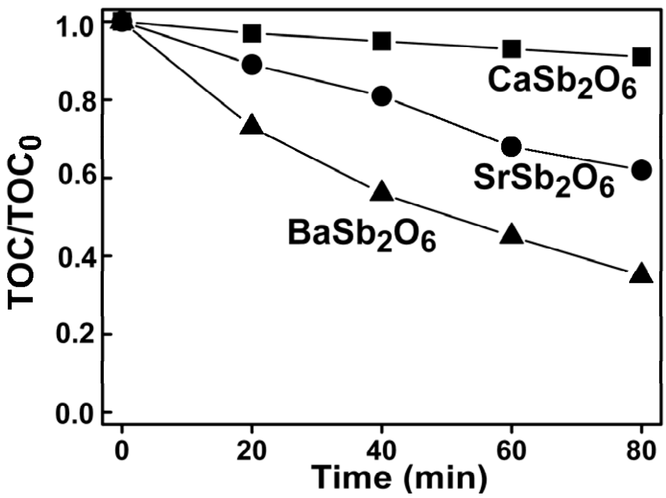

Fig. S2 MB mineralization over antomonate photocatalysts under UV-irradiation (Cat: 0.6 g, MB: 4.5 mg, H_2O: 300 mL)*

* The MB mineralization results show that $BaSb_2O_6$ is most active while $CaSb_2O_6$ is least. The dye mineralization degrees after the reaction time of 80 min, are about 65% for $BaSb_2O_6$, 38% for $SrSb_2O_6$, and 9% for $CaSb_2O_6$, respectively.

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