

# A generic method of visible light sensitization for perovskite-related layered oxides: Substitution effect of lead

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## Abstract

Nearly complete substitution of lead into layered perovskites is a generic method of visible light sensitization for these ultraviolet (UV)-active materials. Thus,  $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$  (Aurivillius phase),  $\text{K}_{0.5}\text{La}_{0.5}\text{Ca}_{1.5}\text{Nb}_3\text{O}_{10}$  (Dion–Jacobson phase), and  $\text{Sr}_3\text{Ti}_2\text{O}_7$  (Ruddlesden–Popper phase) are photocatalysts, all working under UV light, but their analogs containing lead ( $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ ,  $\text{K}_{0.5}\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.75}\text{Pb}_{0.75}\text{Nb}_3\text{O}_{10}$ , and  $\text{PbTiO}_3$ ) absorb visible light and exhibit photocatalytic activity of decomposition of water under visible light.

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## 1. Introduction

Photocatalysts convert solar energy into clean hydrogen energy by splitting water, and decompose harmful organic and inorganic pollutants. The remarkable progress of last decade in photocatalysis has been limited to ultraviolet (UV) light although visible light is far more abundant and thus a more useful region in the solar spectrum. The development of visible light photocatalysts, therefore, has become an important topic in the photocatalysis research today. Despite many efforts [1–4], the design of materials showing a high activity under visible light is still a main challenge in the field. One promising approach to develop new photocatalysts is the tuning of the optical properties of UV light active catalysts by substitutional doping, as demonstrated in  $\text{LaTiO}_2\text{N}$  [5],  $\text{TaON}$  [6],  $\text{Y}_2\text{Ta}_2\text{O}_5\text{N}_2$  [7],  $\text{Sr}_2\text{Nb}_2\text{O}_{7-x}\text{N}_x$  [8],  $\text{TiO}_{2-x}\text{C}_x$  [9–11], or  $\text{TiO}_{2-x}\text{N}_x$  [12] for anion doping, and in metal ion-implanted  $\text{TiO}_2$  [13],  $\text{TiO}_2$  or  $\text{SrTiO}_3\text{:Sb/Cr}$  [14], and  $\text{La}_2\text{Ti}_2\text{O}_7\text{:Cr/Fe}$  [15], for cation doping. However, this substitutional doping, in most of the cases, resulted in a small absorption in the visible light

region with the original band gap absorption intact, rather than a total red-shift of the band gap energy.

In search of photocatalysts with high photocatalytic activity under visible light irradiation, we have recently discovered that a novel oxide photocatalyst,  $\text{PbBi}_2\text{Nb}_2\text{O}_9$ , an Aurivillius-phase perovskite, is an efficient photocatalyst for water splitting into  $\text{O}_2$  or  $\text{H}_2$ , isopropyl alcohol degradation to  $\text{CO}_2$ , and production of photocurrent, all under visible light [16]. It is much more active than recently disclosed  $\text{TiO}_{2-x}\text{N}_x$  [12] in several photocatalytic reactions. The transition metal-based, perovskite-type oxides with  $d(0)$  electron configuration ( $\text{Nb}^{\text{V}}$ ,  $\text{Ta}^{\text{V}}$ , and  $\text{Ti}^{\text{IV}}$ ) are efficient photocatalysts for overall water splitting with high quantum yields under UV light [17–19]. Yet, visible-light responding perovskite-oxide photocatalysts are rare. In  $\text{PbBi}_2\text{Nb}_2\text{O}_9$ , the hybridization of  $\text{O}2p$  and  $\text{Pb}6s$  orbitals was proposed to be responsible for the visible light activity of the photocatalyst [16].

In the present work, we attempted to find out if this  $\text{PbBi}_2\text{Nb}_2\text{O}_9$  was an isolated example or one of general cases of visible light photocatalysis by perovskite-oxide materials containing lead. Thus, we have discovered that nearly complete substitution of lead into layered perovskites is a generic method of visible light sensitization for

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these UV-active materials. Our strategy was to shift the photocatalytic activity from UV into the visible light range, by high or complete substitution of cations in UV-active perovskite material with lead ion. This method of material preparation differs from the previously well-known substitutional doping methods where an element in the original material is substituted only to a minor degree (usually <10%). We investigated layered perovskite phases of the Aurivillius  $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ , Dion–Jacobson  $M[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$  and Ruddlesden–Popper  $(\text{A}_{n+1}\text{B}_n\text{O}_{3n+1})$  types [20–24]. This type of study is of crucial importance in visible light photocatalysis, because, if the substitution of Pb in any single member of a family can induce the desired change in electronic structure for visible-light photo-activity, then one can expect possibility of similar effect in other members of the family. This will reveal the photocatalytic candidacy of several unexplored materials. Thus, we have found that, in all the three structure type examples, representative of each structure type, a non-visible light absorbing, non-photocatalytically active lead-free phase can be converted by lead substitution into a visible light absorbing, visible light photocatalytically active phase. We report here on the importance of this substitution in obtaining visible-light active layered photocatalysts. We believe that the results would provide a directional guide for exploratory study of other member materials of interest.

## 2. Experimental section

The perovskite-related layered oxides for each structure type (see Table 1) were prepared by the conventional solid state reactions. For each perovskite system, the stoichiometric mixtures of appropriate salts, viz.  $\text{K}_2\text{CO}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$  were mixed and ground in ethanol. The pelletized powders were calcined at 1273–1473 K for 48 h in static air. Thus obtained layered oxides were further converted into active

photocatalysts by loading them with 0.1 wt% of Pt, via an incipient wetness impregnation.

The finally obtained photocatalysts were characterized for their physico-chemical properties. The structural phases were determined by X-ray diffraction (Mac Science Co., M18XHF). The diffuse reflectance spectra of the photoactive compounds were recorded on UV-vis spectrophotometer (Shimadzu UV 2401), to monitor the effect of Pb substitution on the band gap of parent layered oxide.

Apart from structural and optical studies, photocatalytic properties were also evaluated on the basis of the test reactions; the photoreduction/photooxidation of  $\text{H}_2\text{O}$  to  $\text{H}_2/\text{O}_2$ . Accordingly, the tests were carried out separately using methanol as a sacrificial electron donor and  $\text{Ag}^+$  as a sacrificial electron acceptor, respectively. The photocatalytic reactions were carried out at room temperature under normal pressure in a closed circulation system using a Xe-arc lamp (450 W) equipped with UV cut-off filter ( $\lambda \geq 400$  or 420 nm) placed in an inner irradiation-type pyrex reaction cell. The  $\text{H}_2$  evolution was determined in aqueous solution (200 ml) containing 0.3 g catalyst and 30 ml methanol. The photooxidation was performed in aqueous  $\text{AgNO}_3$  solution (0.05 M, 200 ml) containing 0.3 g catalyst. The evolved amounts of  $\text{H}_2$  and  $\text{O}_2$  were analyzed by gas chromatography (TCD, molecular sieve 5 Å column and Ar carrier). The quantum yields (QY) were calculated using the following equation:  $\text{QY} = 2 \times \text{number of } \text{H}_2 \text{ or } 4 \times \text{number of } \text{O}_2 \text{ generated per number of photon absorbed by photocatalyst.}$  The number of absorbed photons was determined by light flux meter (1815-C, Newport) with the light sensor attached to the photocatalytic reactor. First, the light absorbed by the whole photocatalytic reactor system was obtained by the difference in light flux with and without the photocatalytic reaction between the light source and the light sensor. The loss of light intensity due to scattering and absorption by materials in the light path other than the photocatalyst was determined for the same reactor containing suspended

Table 1  
Band gap energies and photocatalytic activities for  $\text{H}_2$  and  $\text{O}_2$  evolution for different structure types

Structure type	Phase	$E_g$ (eV)	Photoreduction		Photooxidation	
			$\text{H}_2$ evolution ( $\mu\text{mol h}^{-1}$ )	$\Phi_{\text{H}_2}$ (%)	$\text{O}_2$ evolution ( $\mu\text{mol h}^{-1}$ )	$\Phi_{\text{O}_2}$ (%)
Aurivillius	$\text{CaBi}_4\text{Ti}_4\text{O}_{15}$	3.36	0	—	0	—
	$\text{PbBi}_4\text{Ti}_4\text{O}_{15}$	3.02	11.2	0.27	433	21
	$\text{CaBi}_2\text{Nb}_2\text{O}_9$ <sup>a</sup>	3.18	—	—	—	—
	$\text{PbBi}_2\text{Nb}_2\text{O}_9$ <sup>b</sup>	2.88	3.2	0.4	520	29
Dion–Jacobson	$\text{K}_{0.5}\text{La}_{0.5}\text{Ca}_{1.5}\text{Nb}_3\text{O}_{10}$	3.44	0	—	0	—
	$\text{K}_{0.5}\text{La}_{0.5}\text{Ca}_{0.75}\text{Pb}_{0.75}\text{Nb}_3\text{O}_{10}$	3.09	Traces	—	124	6
	$\text{K}_{0.5}\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.75}\text{Pb}_{0.75}\text{Nb}_3\text{O}_{10}$	3.06	Traces	—	168	8
Ruddlesden–Popper	$\text{Sr}_3\text{Ti}_2\text{O}_7$	3.31	0	—	0	—
	$\text{PbTiO}_3$	2.98	13.6	0.33	523	28

<sup>a</sup>Photocatalytic activity not measured.

<sup>b</sup>Photocatalytic activity measured with light source equipped with an UV cut-off filter ( $\lambda > 420$  nm).

$\text{La}_2\text{O}_3$  powders (instead of the photocatalyst), which did not absorb visible light. The net absorption by the photocatalyst was obtained by the difference of these two values.

### 3. Results and discussions

Fig. 1 shows the UV-visible diffuse reflectance spectra along with respective XRD patterns for lead-free and lead-

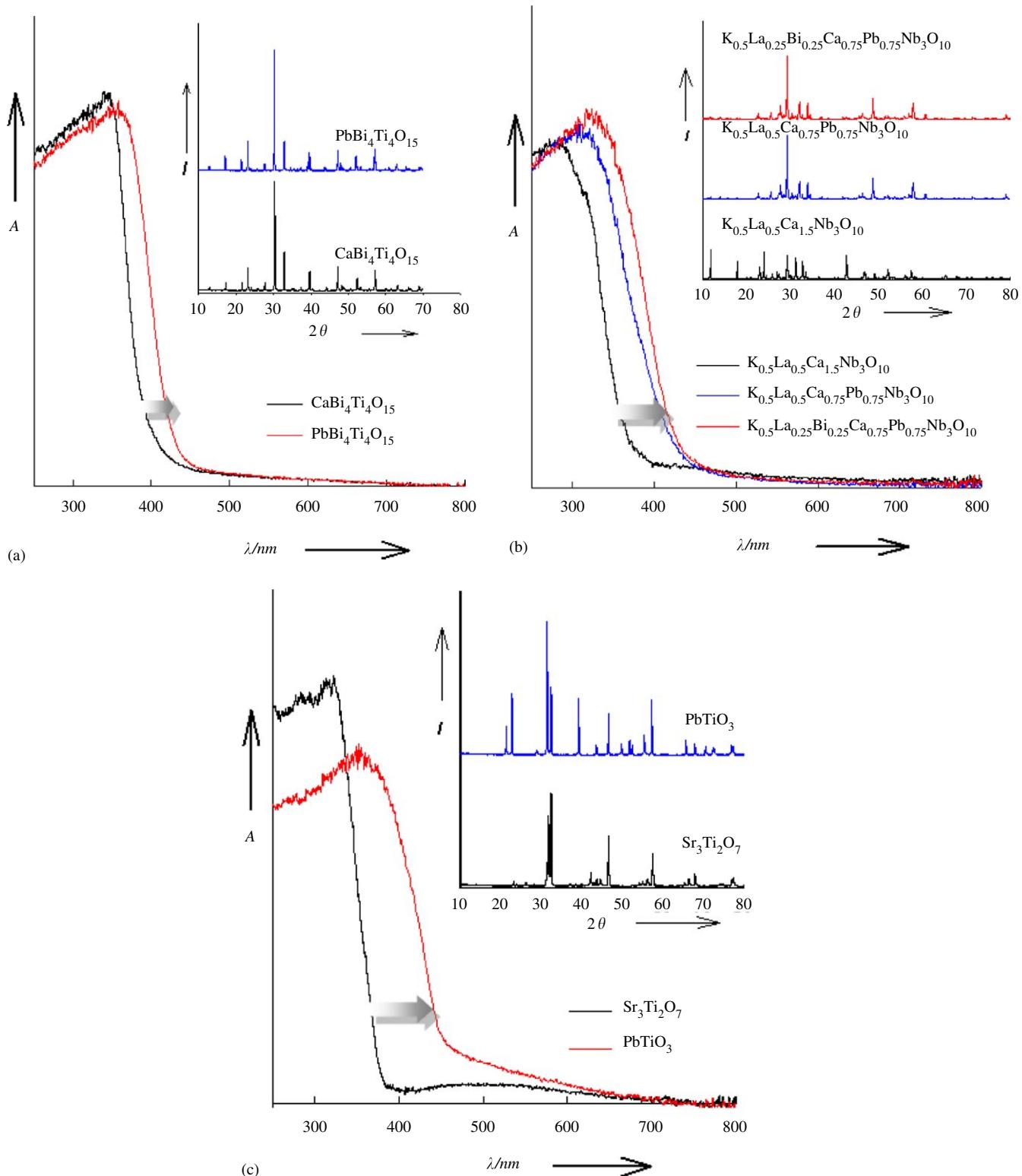


Fig. 1. UV-VIS diffuse reflectance spectra and XRD patterns of the Aurivillius phases: (a)  $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ ,  $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ ; Dion–Jacobson phases; (b)  $\text{K}_{0.5}\text{La}_{0.5}\text{Ca}_{1.5}\text{Nb}_3\text{O}_{10}$ ,  $\text{K}_{0.5}\text{La}_{0.5}\text{Ca}_{0.75}\text{Pb}_{0.75}\text{Nb}_3\text{O}_{10}$ , and  $\text{K}_{0.5}\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.75}\text{Pb}_{0.75}\text{Nb}_3\text{O}_{10}$ ; the Ruddlesden–Popper phase; and (c)  $\text{Sr}_3\text{Ti}_2\text{O}_7$ , illustrating the effect of Pb (and Bi)-substitution.

substituted compounds of Aurivillius, Dion–Jacobson and Ruddlesden–Popper phases. The analysis of absorption spectra reveals that upon lead substitution a significant red-shift (see Table 1) in absorption edge is induced. XRD patterns in the inset of the figure confirm that metal replacement with lead ions in the crystal lattice does not change the high crystallinity, although some changes in crystal structure were observed. Thus it is evident from Fig. 1 that when Ca ions (*A*-site) are completely/partially substituted with Pb ions in: (i) Aurivillius crystal-like  $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$  with  $a = 5.4324 \text{ \AA}$ ,  $b = 5.4152 \text{ \AA}$ ,  $c = 40.78 \text{ \AA}$  [22] and, (ii) Dion–Jacobson crystal-like  $\text{K}_{0.5}\text{La}_{0.5}\text{Ca}_{1.5}\text{Nb}_3\text{O}_{10}$ , i.e. with space group *Cmcm*, with  $a = b = 3.9 \text{ \AA}$ ,  $c = 29.65 \text{ \AA}$  [23], or (iii) when Sr ions (*A*-site) are substituted with Pb ions in Ruddlesden–Popper crystal-like  $\text{Sr}_3\text{Ti}_2\text{O}_7$ , i.e. with space group *I4/mmm*,  $a = b = 3.90 \text{ \AA}$ ,  $c = 29.65 \text{ \AA}$  [24]; then the resulting materials indeed absorb visible light. Specifically in  $\text{K}_{0.5}\text{La}_{0.5}\text{Ca}_{1.5}\text{Nb}_3\text{O}_{10}$  the effect is further augmented when half of La (*M*-site) is further substituted by Bi. The Aurivillius phase maintains its layered perovskite structure even after lead substitution as shown in Fig. 1a and in Ref. [16]. Yet, the lead-containing Dion–Jacobson and Ruddlesden–Popper phases show structural changes as clearly observed in the inset of Fig. 1b and c. Although the structural analysis of the substituted phase has not been done, the lead-substituted Dion–Jacobson  $\text{K}_{0.5}\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.75}\text{Pb}_{0.75}\text{Nb}_3\text{O}_{10}$  may not even be a single phase. Yet, independent of the initial structure types chosen and irrespective of structural changes upon the substitution, the lead-substitution induces a red shift ( $\geq 0.3 \text{ eV}$ ) in absorption edge making the material absorb the visible radiation. Furthermore, these materials show single sharp edges extending to visible light region. However, doped materials usually exhibit two absorption edges; the main edge due to the initial oxide in UV-region and a shoulder due to doping elements in the visible light region [5–12,14,15]. This total red-shift of the band gap energy is a desirable attribute for active photocatalytic materials.

Interestingly, this kind of tuning of the optical absorption, induced by lead substitution, was also found to shift the photocatalytic activity of these phases into the visible region. Table 1 displays the results of photocatalytic water decomposition carried out under visible light ( $\lambda \geq 420 \text{ nm}$  for  $\text{PbBi}_2\text{Nb}_2\text{O}_9$  and  $\lambda \geq 400 \text{ nm}$  for all other phases) in the presence of sacrificial agents. The photocatalysis studies on a given set of compounds demonstrate that lead substitution does shift the photocatalytic activity into visible region of electromagnetic radiation. These activities were also stable during ca. 100 h of continuous runs. Hence, in contrast to the lead-free, visible-light inactive counterparts, the lead-containing compounds show a considerable activity for the photoreduction of  $\text{H}_2\text{O}$  into  $\text{H}_2$  and for the photooxidation of  $\text{H}_2\text{O}$  into  $\text{O}_2$  under visible light. All compounds, however, showed overall water splitting activities into  $\text{H}_2$  and  $\text{O}_2$  (in a stoichiometric mole ratio of 2:1) under UV light even in the absence of sacrificial

agents. It can be noted that of all the lead-containing phases described in Table 1,  $\text{PbTiO}_3$  phase, with  $\text{H}_2$  and  $\text{O}_2$  evolution rates of 13.6 and  $523 \mu\text{mol h}^{-1}$ , respectively, is the most active catalyst. Further in case of oxides with Aurivillius-type phases, lead-containing compounds  $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$  and  $\text{PbBi}_2\text{Nb}_2\text{O}_9$  show a significant activity with rates of  $11.2 \mu\text{mol H}_2\text{h}^{-1}/433 \mu\text{mol O}_2\text{h}^{-1}$  and  $3.2 \mu\text{mol H}_2\text{h}^{-1}/520 \mu\text{mol O}_2\text{h}^{-1}$ , while their lead-free counterparts show no visible light activity at all. The lead-containing compound of Dion–Jacobson phase,  $\text{K}_{0.5}\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.75}\text{Pb}_{0.75}\text{Nb}_3\text{O}_{10}$  is considerably less active. For this compound, an  $\text{O}_2$  evolution rate of  $168 \mu\text{mol h}^{-1}$  and only traces of hydrogen could be observed. The calculated quantum yields for the  $\text{O}_2$  evolution for lead containing phases are  $\text{PbBi}_2\text{Nb}_2\text{O}_9$  (29%),  $\text{PbTiO}_3$  (28%),  $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$  (21%) and  $\text{K}_{0.5}\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.75}\text{Pb}_{0.75}\text{Nb}_3\text{O}_{10}$  (8%). Similarly only lead-containing compounds ( $\text{PbBi}_2\text{Nb}_2\text{O}_9$ ,  $\text{PbTiO}_3$  and  $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ ) exhibit a non-zero quantum yield for  $\text{H}_2$  evolution unlike their lead-free counterparts. Thus it is clear from above comparative study that lead ion plays a vital role in displaying the photocatalytic activity in the visible light range.

In order to examine and understand the novel role of lead-containing layered structures, we performed the electronic band structure calculations [25]. The calculations were based on the full potential linearized augmented plane wave (FLAPW) method. This uses the generalized gradient approximation (GGA) within the density functional theory and is known for yielding high accuracy results for many electrons system. The Wien97 package was used for this

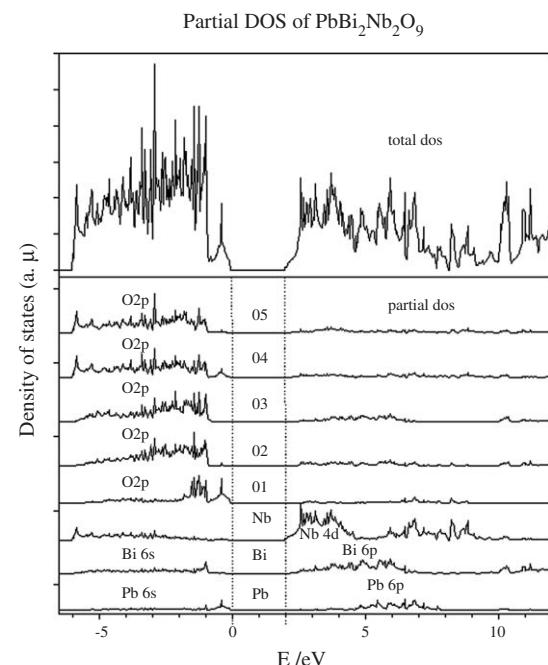


Fig. 2. Calculated total and partial density of states (DOS) of  $\text{PbBi}_2\text{Nb}_2\text{O}_9$ . The conduction and valence bands of the compound consist of empty Nb4d and occupied O2p orbital, with the latter hybridized with Pb6s and Bi6s, giving the smaller band gap compared to compounds that do not contain Pb and Bi in their structure.

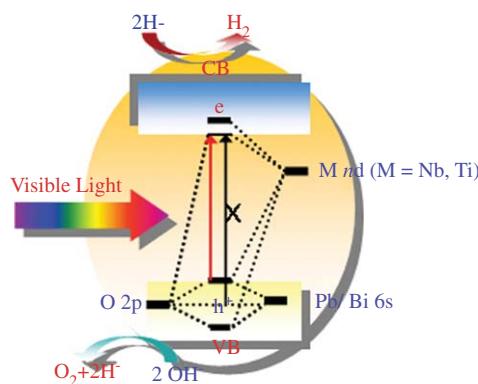


Fig. 3. Schematic band energy diagram of lead or bismuth substituted perovskite-related oxides.

study for the calculations. The result illustrated in Fig. 2 ascertains that in the lead-free compounds, the empty  $\text{Nb}4d$  or  $\text{Ti}3d$  orbital and the occupied  $\text{O}2p$  orbital are contributing to the formation of conduction and valence bands, respectively. However for the lead-containing compounds, an additional hybridization of the occupied  $\text{Pb}6s$  and  $\text{O}2p$  orbital seem to result in a narrower band gap. This hybridization would push up the position of the valence band giving the smaller band gap compared to their respective lead-free counterparts. The  $\text{Bi}6s$  orbital is also located nearby and seems to form hybridization with  $\text{O}2p$  orbitals ( $\text{O}2$ ,  $\text{O}3$  and  $\text{O}5$  in Fig. 2), although this hybridized band of  $\text{Bi}6s$  and  $\text{O}2p$  is located below the top of the valence band. The schematic diagram of Fig. 3 illustrates the above statements.

Finally, above experimental and theoretical considerations predict the novelty of role of lead (or bismuth) in converting the UV active photocatalyst into visible-light active photocatalyst. There is only a handful of undoped, single phase visible-light active materials reported recently in the literature such as  $\text{BiVO}_4$  [26],  $\text{RbPb}_2\text{Nb}_3\text{O}_{10}$  [27,28], and  $\text{CaBi}_2\text{O}_4$  [29]. It is not a coincidence that these materials contain either lead or bismuth. Based on the presented data it can be concluded that lead (or bismuth) substitution can be a successful and generic strategy to develop new photocatalysts active under visible light.

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