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Towards visible-light water splitting Photocatalysts: Band engineering of two-dimensional $A_5B_4O_{15}$ perovskites

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ABSTRACT

Photocatalytic water splitting is a promising route to achieve renewable hydrogen production. In this work, a series of $A_5B_4O_{15}$ (A=Ca, Sr, Ba; B=V, Nb, Ta) layered perovskite materials, were investigated through density functional theory computations. We revealed that changing B ions can modify the band gap, and A-ion substitution can tune the band-edge position. Therefore, through A/B ion combination, we can realize the band engineering of $A_5B_4O_{15}$ materials. Electron/hole effective mass and water adsorption of $A_5B_4O_{15}$ materials were also explored. Further investigations suggest that $Ca_5V_4O_{15}$ nanosheet, with an appropriate band gap and an optimal band-edge position, would be a promising photocatalyst for visible-light water splitting.

1. Introduction

Photocatalytic water splitting has attracted tremendous attention as a potential route to address energy and environment related issues [1,2]. Since the first realization of water splitting without any applied electric power by Fujishima and Honda [3], significant breakthrough has emerged to boost the performance [4–7]. However, currently most industrial hydrogen is still produced from fossil fuels, and present photocatalytic systems are not economical for industrial hydrogen production [8]. The absence of stable photocatalysts that can operate under visible light with high efficiency is a critical obstacle for commercial photocatalytic water splitting [9,10].

Perovskite materials stand out as promising photocatalysts for water splitting [8,11–13]. The high stability of perovskite-like structures enables myriad A- and B-site ion combinations, and offers enormous flexibility for performance optimization [12]. For example, water splitting activity was found in $ATaO_3$ (A=Li, Na, and K) [14], $Sr_2M_2O_7$ (M=Nb and Ta) [15], $A_mB_mO_{3m+2}$ (m=4, 5; A=Ca, Sr, La; B=Nb, Ti) [16], and $A_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ (A=K, Rb, Cs; x=0, 0.5, 1) [17]; visible-light-driven photocatalytic performances were also observed in $NaBiO_3$ [18], Cu(II)-$(Sr_{1-y}Na_y)(Ti_{1-x}Mo_x)O_3$ [19], and $(Ag_{0.75}Sr_{0.25})(Nb_{0.75}Ti_{0.25})O_3$ [20].

As layered perovskite materials with B-site vacancies [21,22], $A_5B_4O_{15}$ is of particular interest as water splitting photocatalysts. In 2005, water splitting activity was found for both $Sr_5Ta_4O_{15}$ [23] and $Ba_5Ta_4O_{15}$ [24]. Later, a quantum yield as high as 17% was achieved for $NiO_x/Ba_5Nb_4O_{15}$ by Miseki et al., who systematically investigated $A_5Nb_4O_{15}$ (A=Sr, Ba), and $ALa_4Ti_4O_{15}$ (A=Ca, Sr, Ba) [25,26]. By comparison, the quantum yield of nanocrystalline TiO_2 is 16% [27]. Further, the H_2 production rate was improved in $Ba_5Ta_4O_{15}$ with 0.2 wt% nitrogen doping, due to the enhanced visible light absorbance [28]. Chen et al. revealed that H_2 evolution on $Pt/Sr_5Ta_4O_{15-x}N_x$ and O_2 evolution on $CoO_x/Sr_5Ta_4O_{15-x}N_x$ under visible light irradiation [29]. Enhanced photocatalytic activity for $BaLa_4Ti_4O_{15}$ was reported by Negishi et al. [30,31] by loading ultra-small gold clusters. Li et al., proposed that P–Mo co-doped $Ba_5Nb_4O_{15}$ could own visible light activity [32]. Experimentally, Marschall et al. [33] prepared $Ba_5Ta_4O_{15}$, $Ba_5Ta_2Nb_2O_{15}$ and $Ba_5Nb_4O_{15}$ nanofibers and demonstrated their ability to generate hydrogen without cocatalysts.

The realization of two-dimensional (2D) nanosheet morphology, which shows several advantages as water splitting photocatalysts [9,34–37], is feasible for $A_5B_4O_{15}$ materials due to the layered structure. Zhu et al. [38] reported that $Ba_5Ta_4O_{15}$ monolayers prepared through a hydrothermal route under low temperatures without templates exhibited better photocatalytic performance than the bulk. Park et al. investigated the H_2 evolution on bulk $Ba_5Nb_4O_{15}$, $Ba_5Nb_4O_{15}$ nanosheets with ~30 nm thickness and $Ba_5Nb_4O_{15}$ nanosheets with ~6 nm thickness, and revealed that the water splitting activity increased with decreasing the

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nanosheet thickness [39]. The reduced physical dimension facilitates the diffusion of electron/hole to the surface to participate the photocatalytic reaction; therefore, 2D materials generally shows lower electron-hole recombination rate than their bulk counterparts [40]. Also, 2D nanosheets have much larger surface areas that could promote the adsorption of H_2O, H^+ and OH^- [34].

$A_5B_4O_{15}$ materials have versatile structures of perovskites and can also be fabricated into monolayer nanosheets, which makes them rather promising as water splitting photocatalysts. However, few studies have been performed on the electronic structure of $A_5B_4O_{15}$ and several questions remain open. For example, how would A/B ions influence the electronic structure and how would quantum confinement effect modify the band gap of $A_5B_4O_{15}$? Does the material possess visible light absorption capability? Especially, the band edge positions of $A_5B_4O_{15}$, which are critical for photocatalysts, are unexplored. In this work, we systematically investigated the electronic properties of $A_5B_4O_{15}$ (A=Ca, Sr, Ba; B=V, Nb, Ta) bulks and nanosheets through density functional theory (DFT) computations. The lattice parameters and band structures between bulk and nanosheets were compared to illustrate their relation. The influence of changing A/B ions on band gap and band edge position was investigated, as well as effective mass and water adsorption. In light of these analyses, we predicted that $Ca_5V_4O_{15}$ nanosheets are promising visible light photocatalysts for water splitting.

2. Computational details

All DFT computations were performed by using projector augmented wave (PAW) [41] method as implemented in Vienna *ab initio* simulation package (VASP) [42]. Lattice parameters and atomic coordinates were optimized with generalized gradient approximation (GGA) as implemented by Perdew, Burke and Ernzerhof (PBE) [43]. Spin polarization and plane-wave energy cutoff of 550 eV were employed for all computations. Spin-orbital coupling shows trivial influence on band gaps; therefore, it is not adopted in our computations. HSE06 hybrid functional [44,45] was applied for the computation of band edge positions and accurate band gaps. K-point separation of 0.025 $Å^{-1}$ for PBE calculations and 0.04 $Å^{-1}$ for expensive HSE06 computations was employed. The band edge position relative to the vacuum level was evaluated by electrostatic potential alignments. For the calculations of convex hull, a correction scheme of formation enthalpy proposed by Jain et al. [46] was adopted. Effective mass for both electrons and holes was evaluated through the equation:

$$m^* = \hbar^2\left(\frac{d^2E}{dk^2}\right)^{-1}$$

The calculated effective mass was represented in the unit of m_0 (electron rest mass). For the calculation of water adsorption, $2 \times 2 \times 1$ supercells and Monkhorst-Pack grids of $3 \times 3 \times 1$ k-points were adopted for nanosheets.

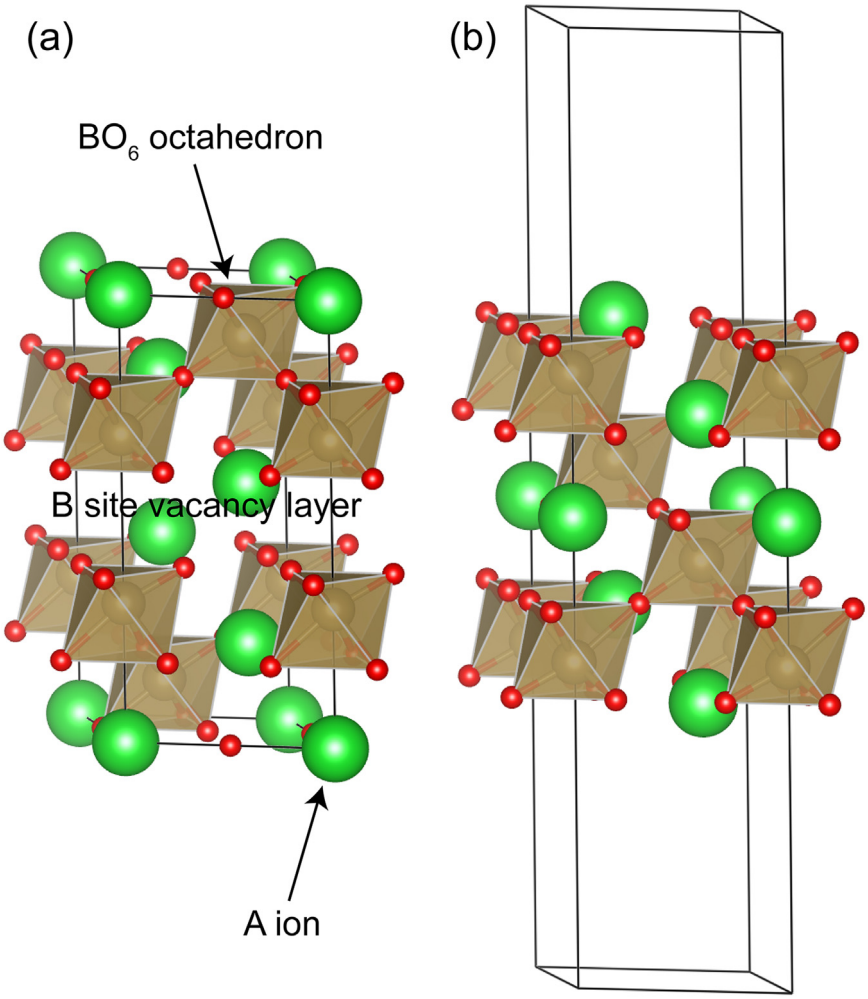

Fig. 1. Crystal structures of $A_5B_4O_{15}$ (a) bulk and (b) nanosheet.