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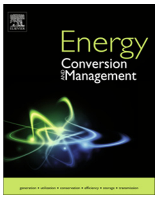

Computational study on oxynitride perovskites for CO_2 photoreduction

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ABSTRACT

The photocatalytic conversion of CO_2 into chemical fuels is an attractive route for recycling this greenhouse gas. However, the large scale application of such approach is limited by the low selectivity and activity of the currently used photocatalysts. Using first principles calculations, we report on the selection of optimum oxynitride perovskites as photocatalysts for photoelectrochemical CO_2 reduction. The results revealed six perovskites that perfectly straddle the carbon dioxide redox potential; namely, $BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$, $LaTiO_2N$, $BaNbO_2N$, and $SrNbO_2N$. The electronic structure and the effective mass of the selected candidates are discussed in details, the partial and total density of states illustrated the orbital hybridization and the contribution of each element in the valence and conduction band minima. The effect of cation size in the ABO_2N perovskites on the band gap is investigated and discussed. The optical properties of the selected perovskites are calculated to account for their photoactivity. Moreover, the effect of W doping on improving the selectivity of perovskites toward specific hydrocarbon product (methane) is discussed in details. This study reveals the promising optical and structural properties of oxynitride perovskite candidates for CO_2 photoreduction.

1. Introduction

More energy from sunlight strikes the earth in one hour than all of the energy consumed on the planet in one year. Thus, the challenge modern society faces is not one of identifying a sustainable energy source, but rather one of capitalizing on the vast solar resource base. Of the various storage solutions considered in recent years, solar fuels, in which sunlight is converted into chemical energy, are particularly attractive because of the long shelf-life of such fuels and their ready integration with the existing fuel storage and delivery infrastructure [1–6].

Recently, there has been a significant interest in recycling the undesirable by-products of fossil fuel combustion; especially CO_2. Conversion of CO_2 into a high-energy content, storable and portable fuel, suitable for use in the current hydrocarbon-based energy infrastructure, is an attractive pathway [7–12]. However, this process is energy intense and will only be useful if a renewable energy source is used for that purpose [9]. A possible sustainable avenue is to use photocatalysts for the conversion of CO_2 into useful hydrocarbons with the help of solar energy [13]. A useful carbon cycle involving only H_2O and CO_2 is very promising in this regard. This is simply to mimic Nature that has provided us with an amazing strategy, photosynthesis, to utilize CO_2 while replenishing oxygen and providing fuels. One great advantage of having water in the proposed artificial photosynthesis process is that water is as an electron donor [14], which can provide electrons and protons to facilitate reactions (1)–(5) below:

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \tag{1}$$

$$HCOOH + 2H^+ + 2e^- \rightarrow HCHO + H_2O \tag{2}$$

$$HCHO + 2H^+ + 2e^- \rightarrow CH_3OH \tag{3}$$

$$CH_3OH + 2H^+ + 2e^- \rightarrow CH_4 + H_2O \tag{4}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{5}$$

However, the artificial photosynthetic conversion of CO_2 is hindered by some factors [15–17], such as the thermochemically unfavorable one-electron reduction potential of CO_2 ($E^\circ = -1.9\ V_{NHE}$), the low solubility of CO_2 in water (33 mM at 298 K and 1 atm), the strong oxidation power of photogenerated holes (or OH radicals), during the photocatalytic process, that can react with intermediates conversion products, and the competition with H_2 generation (H^+/H_2O potential is $-0.41\ V_{NHE}$ whereas CO/CO_2 potential is $-0.52\ V_{NHE}$ at pH 7). Various approaches [14,18–23] have been attempted to surpass the above mentioned limitations. However, the electrode material is still playing the major role in determining the nature of the resulting conversion products and their selectivity. The surface properties (e.g., roughness, porosity,

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dislocations, vacancies and defects), crystal orientation (hence preferential adsorption of reactants and intermediates on specific facets), surface impurities, and electronic configuration are the most determinant factors affecting the catalytic activity of a particular photocatalyst. In this regard, the band edge positions and the bandgap of the semiconductor electrode with respect to the redox potentials of CO_2 as well as the different hydrocarbon species are very essential factors to be taken into account when selecting the photocatalyst. Based on that consideration, many researchers have investigated the use of different photocatalysts to achieve higher visible light activities. Canfield and Frese [24] were able to achieve CO_2 reduction to methanol using p-GaAs and p-InP photoelectrodes in a CO_2-saturated solution of Na_2SO_4. Similarly, formation of methanol together with formic acid and formaldehyde was reported by Blajeni et al. [25] using single-crystal p-GaP and p-GaAs photoanodes. Among many tested powder semiconductors (TiO_2, ZnO, CdS, SiC, and WO_3) suspended in CO_2-saturated water illuminated by a Xe lamp, the formaldehyde and methanol yield was highest in the presence of SiC [26]. This behavior can be attributed to the relative position of the SiC conduction band (CB) with respect to the $HCHO/H_2CO_3$ redox potential. No methanol was detected upon the use of WO_3 as a catalyst, which can be attributed to the position of the CB that is lower than the $HCHO/H_2CO_3$ redox potential. Similarly, strontium titanate [27], with a higher conduction band-edge position compared to the redox potential of CH_3OH/H_2CO_3, could effectively reduce CO_2 dissolved in an aqueous electrolyte indicating the influence of band-edge positions on CO_2 reduction.

Regarding the photocatalyst band gap, in theory, for the splitting of both CO_2 and H_2O, the bandgap should be at least 1.33 eV. Considering the major sources of energy loss (entropy change, by-product formation, etc.), a band gap between 2 and 2.4 eV should be optimal [28]. Consequently, the maximum attainable efficiency will be limited to about 17% [28]. However, the reported efficiencies to date are still much lower. In this regard, there are ongoing efforts to extend the absorption capability of the stable semiconductor photocatalyst to the visible region of the solar spectrum so that to achieve a band gap closer to the target, 2–2.4 eV. In this regard, because of the high potential energy of the metal–nitrogen bond compared to the metal–oxygen bond [7], transition metal oxynitrides [13,15–17,19,29]have been identified as an alternative class of materials that can efficiently be used for CO_2 reduction. This difference in bond energy resulted in narrower band gap energies in oxynitrides compared to their metal oxide counterparts.

Based on the above analysis, the aim of the current work was to investigate the possibility of using oxynitride perovskite materials as photocatalysts, enabling the construction of high performance, affordable, and air-stable inorganic photoelectrochemical devices for CO_2 conversion into useful hydrocarbons. Herein, we use density functional theory (DFT) screening to identify such oxynitride perovskites. The screening strategy for selecting the oxynitrides perovskites throughout this paper is classified into three sections: (1) the band edge positions for different perovskites *versus* the potential electrode were calculated; (2) the band structure and density of states together with the effective mass of electrons and holes were investigated, and (3) the dielectric function for the selected oxynitrides was calculated, from which the other optical properties were identified.

2. Computational methods

For all calculations presented in this paper, we used the DFT calculations in the frame work of CASTEP [30], and GPAW codes [31,32]. All the investigated perovskites are used in their standard ABO_2N cubic structure form [33], where A and B are the metal cations forming the perovskite, and O, N refer to oxygen and nitrogen anions, respectively, as shown in Fig. 1. Before the bandgap calculations, a full relaxation is performed for the atomic and lattice parameters for all the perovskites using the generalized gradient approximation (GGA) [34]. The functional used is RPBE with a cutoff energy of 380 eV. The k-points sampling was 5 × 5 × 5. All the relaxed structures were set to be optimized until the forces converged to 0.05 eV/Å for each crystal. For the band gap calculations, we used the so called PBE0 XC functional as implemented in CASTEP. The density of states (DOS) was also investigated using the same optimized electronic structures. The effective mass of electrons and holes was extracted from the previously calculated band structures from the inverse of the second derivative at the conduction and valence band minima, respectively, for each crystal structure. The difference between the k points was selected to get a parabolic valence and conduction bands at these minima. Reliable calculations for the bandgap is required for the screening study, which are performed using the so-called GLLB-Sc functional [35,36]. This was demonstrated to predict the magnitude of the bandgap for a large selection of oxynitride perovskites, with a maximum deviation of 0.4 eV from the experimentally reported values. This accuracy is sufficient and crucial for the success of our screening study. For the reduction of carbon dioxide to specific hydrocarbons, we investigated the doping of perovskite with various amounts of tungsten. A supercell of the optimized structure for $BaTaO_2N$, with 16 N, 32 O, 16 Ba, and 16 Ta atoms, is used. The W atoms are doped by replacing the Ta cations with ratios of (1 W/15Ta) and (2 W/14Ta). This gives doping concentrations of (6.8% W) and (14.2% W), respectively. As we are mainly focusing on the conduction band edge for the reduction of CO_2 to other hydrocarbons, we used the PBE0 hybrid functional in this section. This functional contains a combination of exact exchange energy and GGA approximation terms as presented by Eq. (6).

$$E_{XC}^{PBE0} = \frac{1}{4}E_X^{HF} + \frac{3}{4}E_X^{PBE} + E_C^{PBE} \tag{6}$$

where E_X^{HF} is the Hartree-Fock (HF) exchange energy, E_X^{PBE} and E_C^{PBE} are the PBE exchange and correlation energies, respectively. Thus, it correctly assigns the position of the unoccupied band energies, which provide a reliable estimation of the conduction band edge for CO_2 conversion [37].

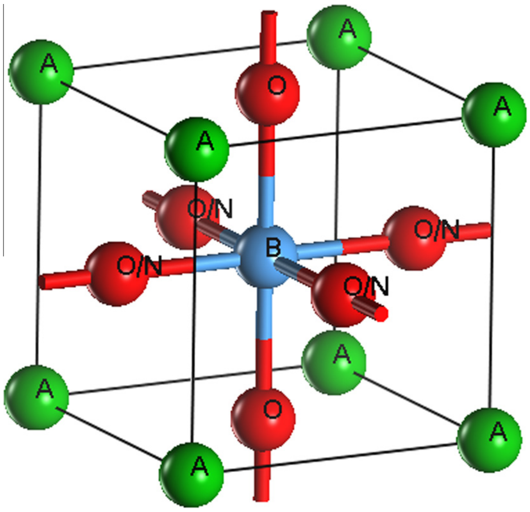

Fig. 1. Oxynitride perovskite crystal structure for ABO_2N; O/N represents the atomic positions for oxygen and nitrogen atoms, with 0.5 occupancy for each.