Advances in Theoretical Calculation of Halide Perovskites for Photocatalysis

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Photocatalysis, which includes water splitting for hydrogen fuel generation, degradation of organic pollutants, and CO₂ reduction using renewable solar energy, is one of the most promising solutions for environmental protection and energy conversion. Halide perovskite has recently emerged as a new promising material for photocatalytic applications. The exploration of new efficient halide perovskite-based photocatalysts and understanding of photocatalytic reaction mechanisms can be revealed using theoretical calculations. The progress and applications of first-principles atomistic modeling and simulation of halide perovskite photocatalysts, including metal halide perovskites, halide perovskite heterojunctions, and other promising perovskite derivatives, are presented in this review. Critical insights into the challenges and future research directions of photocatalysis using halide perovskites are also discussed.

Keywords: first-principles calculations, photocatalysis, halide perovskites, density functional theory, heterojunctions

INTRODUCTION

As sustainable, inexhaustible, clean, and renewable energy, solar energy has been considered an attractive alternative for applications of heating systems and electricity production in the past decades. Driven by solar energy, photocatalysis is considered one of the most important routes for using solar energy since the pioneering work on TiO₂ for water splitting in 1972 (Fujishima and Honda, 1972). Photocatalytic processes are applied in four fields: water splitting, CO₂ reduction, degradation of organic compounds, and organic synthesis. Semiconductors have been the most used photocatalysts because of their intrinsic optical and electronic properties, from conventional binary semiconductor photocatalysts (i.e., g-C₃N₄, TiO₂, ZnO, CdS) (Yu et al., 2013; Jin et al., 2015; Ye et al., 2015; Adhikari et al., 2016; Cheng et al., 2018; Jaramillo-Páez et al., 2018; Yu et al., 2018) to ternary photocatalysts (i.e., BiVO₄, SrTiO₃, BaTi₄O₉) (Inoue et al., 1992; Kato and Kudo, 2002; Zeng et al., 2018; Andrei et al., 2020). However, conventional photocatalysts have drawbacks, such as large bandgap, high carrier recombination rate, and low light-absorption ability. It is critical to develop new photocatalysts with high photoconversion efficiency.

Metal halide perovskites with a chemical formula of ABX₃ (A = CH₃NH₃, CH(NH₂)₂, Cs; B = Pb, Sn; X = I, Br, or Cl) have recently attracted extensive research attention because of their extraordinary photophysical properties and performance, such as high visible-light absorption coefficients, long charge carrier diffusion lengths, high photoluminescence quantum yield, tunable bandgap, etc (Park et al., 2016; Zhang et al., 2018a; Shi and Jayatissa, 2018). Furthermore, combined with a diversity of A and B sites and ferroelectric and piezoelectric effects (Frost et al., 2014; Kanhere and Chen, 2014; Sun et al., 2016; Li et al., 2017; Zhu et al., 2019), ABX₃ halide perovskites are indubitably one of the most promising alternatives in photocatalytic applications (Zhu and Podzorov, 2015; Lee et al., 2018; Hong et al., 2019; Zhu et al., 2019; Chen et al., 2020).
First-principle atomistic modeling and simulation, such as density functional theory (DFT) and Green’s function-based many-body perturbation theory (GW), are fundamental means to investigate material properties by inputting the initial lattice structure and known atomic information. The DFT method is a calculation method based on Hohenberg-Kohn theorem and Kohn-Sham equation (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). When it comes to specific practical problems, it is necessary to consider several choices of exchange-correlation functional, such as Local Density Approximation (LDA), Generalized Gradient Approximation (GGA) and hybrid density functional method (Jones and Gunnarsson, 1989; Farr Robert, 1989).

LDA is mainly aimed at uniform electron gas, meaning that the charge density needs to change slowly in the order of local Fermi wavelength. In the calculation of Raman spectrum and phonon spectrum, LDA tends to a good performance. GGA optimizes the exchange-correlation and adds the gradient of charge density change to the exchange-correlation functional, giving more reasonable simulation results for heterogeneous electronic systems (Richard, 2004; Jiang et al., 2010). The commonly used GGA functionals are Perdew-Burke-Ernzerhof (PBE) (Kresse and Joubert, 1999) and Perdew-Wang (PW91) (Blöchl, 1994). However, GGA ignores the nonlocality of exchange, which usually underestimates the band gap. Therefore, hybrid density functional method is developed, which can improve the calculation accuracy based on the exact exchange energy obtained by Hartree-Fock approximation and the partial exact exchange energy obtained by mixed density functional theory. The commonly used methods are Heyd-Scuseria-Ernzerhof (HSE), PBE0, etc. (Perdew et al., 1996; Heyd et al., 2003). In addition, there are not only correction methods for electronic correlation (Grimme et al., 2010; Cao et al., 2012), such as dispersion interaction correction (DFT + D), self-interaction correction (DFT + U), but also correction methods for magnetic materials such as Spin orbit coupling (SOC) (Afsari et al., 2017; Sehgal, 2017).

GW method provides a more rigorous theoretical framework for the theoretical description of the electronic energy band structure of materials, which can give high-precision theoretical predictions for physically simple semiconductor materials, such as G0W0 method based on LDA/GGA self-consistent calculation (Aryasetiawan and Gunnarsson, 1998; Aulbur et al., 2000). However, there is still much room for improvement for physically more complex systems with stronger electronic correlation effects, because LDA/GGA often gives wrong description, which can lead to the wrong calculation of G0W0 (Aryasetiawan and Gunnarsson, 1995; Jiang, 2010; Jiang and Zhang, 2020). Many new methods have been developed to choose an appropriate starting point to calculate the reference Hamiltonian, such as G0W0 based on DFT + U or HSE (Miyake et al., 2006; Jiang et al., 2010), or quasi particle self-consistent GW, and fully self-consistent GW (van Schilfgaarde et al., 2006; Grumet et al., 2018). Among the above-mentioned methods, GGA-PBE in DFT calculation method is the most commonly used and inexpensive calculation method, because it does not cost so much computational power, while HSE and GW methods are more suitable for dealing with band gap calculation, and there are some problems such as complex program implementation and large amount of calculation.

First-principle methods can be used to explore the lattice constants, electronic structures, carrier mobility and diffusion lengths of photocatalyst, understand the reaction mechanism, and further predict new halide perovskite-based photocatalyst (Catlow et al., 2010; Luo and Daoud, 2015; Yu, 2019). The calculation of these properties is critical for optimizing the photocatalytic performance. Thus far, there has been limited research regarding the booming use of first-principles calculations to study halide perovskites as photocatalysts. Herein, we summarize the recent progress in the theoretical calculation study on halide perovskite-based photocatalysts (Figure 1), and focus on the link between calculated material properties and performance of photocatalysts, including 1) metal halide perovskites, 2) halide perovskite heterojunctions, and 3) other promising perovskite derivatives. Then, we discuss the challenges and future research directions of halide perovskite photocatalysis.

**THEORETICAL CALCULATION OF PROPERTIES OF HALIDE PEROVSKITE-BASED PHOTOCATALYSTS**

**Metal Halide Perovskites**

As is well known, for the ABX3 perovskites, the BX6 octahedra can be tilted and distorted at finite temperature or pressure (Glazer, 1972), and anharmonic effects are associated with the perovskite-phase transition (Buckeridge et al., 2013). Moreover, the bandgap of ABX3 perovskites can be tuned by chemical substitution (Sutton et al., 2016; Wang et al., 2019a). Several first-
principles investigations into ABX$_3$ structures have been conducted to explore their crystal structures, material stability properties, and defect physics. Most notably, the electronic and optical properties of ABX$_3$ perovskite as light absorbers in photocatalysis are critical, and several theoretical calculation studies have focused on the electronic energy-band structure, corresponding density of states (DOS), carrier mobility, and other electronic properties of halide perovskite-based photocatalyst.

One of the critical properties of a photocatalyst is its bandgap. Considering the utilization of visible light in the sunlight, the bandgap of $\sim$2 eV is desirable for photocatalytic reaction (Xiaobo et al., 2010). In addition, for CO$_2$ reduction, the position of conduction band minimum (CBM) should be lower than $-0.52$ eV (vs. NHE PH equals 0) (the energy barriers of reducing CO$_2$ to CO) (Kanhere and Chen, 2014; Schneider et al., 2012), that is more advantageous to the reduction reaction in thermodynamics. Angelis et al. first computationally investigated the MAPbX$_3$ hybrid halide perovskites in 2013 (Mosconi et al., 2013). They performed periodic DFT calculations within the GGA and found that the calculated bandgap values (MAPbI$_3$: $E_g = 1.57$ eV, MAPbBr$_3$: $E_g = 1.80$ eV, MAPbCl$_3$: $E_g = 2.34$ eV) agreed well with the experimental values. Figures 2A–C shows the optimized geometrical structures, calculated band structure, and DOS of MAPbI$_3$. Afterward, Umari developed an effective GW method incorporating SOC to accurately model the electronic properties of MAPbI$_3$ and MAPnI$_3$ (Umari et al., 2014). Furthermore, the photogenerated carrier transfer ability can be revealed by the calculated DOS. Sun et al. synthesized colloidal CsPbBr$_3$ quantum dots (QDs) as new photocatalytic material (Hou et al., 2017). To understand the advantages of the quantum size effect, they calculated the DOS of bulk CsPbBr$_3$ and atomic CsPbBr$_3$ QD slabs. Different from the bulk CsPbBr$_3$, the conduction band of CsPbBr$_3$ QDs was primarily contributed by the coupling of Cs $p$-states, Br $p$-states, and Pb $p$-states, whereas the valence band was constructed by the coupling of Cs $p$-states, Pb $s$-states, and Br $p$-states (as shown in Figure 2D).

Due to the increased DOS at CBM, more photogenerated carriers can reach CBM, resulting in more efficient photochemical conversion.

The last, but the most important issue is the photocatalytic mechanism. Metal halide perovskites have been successfully confirmed as efficient photocatalysts. However, it is difficult to develop improved perovskite materials without a thorough analysis of reaction mechanisms. Wang et al. derived the photocatalytic hydrogen evolution reaction (HER) mechanism using PBE functional of DFT, including the D3 van der Waals.
correction to account for London dispersion interactions (Zhang et al., 2018b). They constructed a supercell of the (010) surface of MAPbI3 in HI aqueous solution, and by comparing the activation barriers and reaction energies of different reaction pathways, they found that the Pb atoms and surface organic molecules play critical roles in the HER reaction. Furthermore, a two-step Pb-activated amine-assisted (PbAAA) reaction mechanism was proposed (Figure 2E), which is widely accepted and approved.

Tao et al. performed the DFT calculations with the PbAAA mechanism to explain the Br effect on the enhanced performance of the MAPb(I1-xBrx)3 photocatalytic HER process (Zhao et al., 2019a). Due to the smaller Br ionic radius, the Br-Pb bonds can be easily broken, and more Pb defect sites were formed for lowering the H-Pb absorption energy, and thus MAPb(I1-xBrx)3 shows a superb HER rate under visible light illumination.

Halide Perovskite Heterojunctions

To enhance the photocatalytic performance, the construction of halide perovskite heterojunctions with two-dimensional (2D) materials such as graphene, g-C3N4, and black phosphorus has caused extensive concern due to improved stability, more efficient carrier mobility, and regulated bandwidth (Xu et al., 2017; Ou et al., 2018; Wu et al., 2018; Zhao et al., 2019b; Guo et al., 2019; Paul et al., 2019; Wang, 2020). For the heterojunction calculations, the main problem is the understanding of the charge density difference and charge transfer process at the contacting interface.

Guo et al. used density-functional first-principles calculations with empirical dispersion corrections to investigate the interfacial interactions and electronic properties of graphdiyne/MAPbI3 heterostructures (Guo et al., 2019). By employing the projector-augmented wave (PAW) to describe the electron-core interaction, and GGA of PBE as the exchange-correlation functional, they found that the graphdiyne/MAPbI3 heterostructure was formed by van der Waals interaction, and the PbI2-terminated surface showed high stability when contacting graphdiyne. Combining HSE06 with SOC, the electronic properties including charge density difference, electron localization field, Bader charge, and electrostatic potential were analyzed, as shown in Figure 3A. The electron-hole separation is obviously enhanced due to the built-in electric field at the interface.

In addition to the van der Waals interaction of the heterostructure interface, Zhu et al. found that a significant covalent bond between CsPbBr3 and black phosphorus nanosheets was formed in the heterostructure by DFT calculation (Wang, 2020). Moreover, charge density difference analysis revealed that a directional electron transfer channel was generated reasonably between Pb and p elements, as shown in Figure 3B,C which was consistent with the experimental results. Furthermore, using ab initio atomistic thermodynamics
calculations, the possible mechanism of CO₂ reduction by CsPbBr₃ and black phosphorus nanosheet heterostructure was clarified. The black phosphorus nanosheets acted as the electron acceptor, which promoted the breaking of the C=O bonds and reduced the reaction barrier energy (Figure 3D).

**Other Promising Perovskite Derivatives**

The exploration of new photocatalysts is an important way to achieve high photocatalytic performance. And the new promising halide perovskites offer distinct advantages over the traditional perovskite materials (Volonakis et al., 2016; Liu et al., 2018; Maughan et al., 2018; Yan et al., 2018; Tang et al., 2019; Yue et al., 2020), such as substitution or mixing, double perovskites, and other perovskite derivatives. Theoretical calculation is a powerful tool to predict new functional perovskite materials suitable for photocatalysis and optimize the stoichiometric ratio of mixed halide perovskites. Especially when introducing the Goldschmidt tolerance factor \( t = \frac{(r_A + r_X)}{\sqrt{2} (r_B + r_X)} \) (where \( r_A, r_B \) and \( r_X \) refer to ionic radii for ions in \( A, B \) and \( X \) sites) (Goldschmidt, 1926), a useful parameter for basic formability prediction of any new materials with targeting perovskite structure, into the first-principle calculations, many studies have selected several promising perovskite materials from hundreds of compounds (Bartel et al., 2020; Fedorovskiy et al., 2020).

Xu et al. compared the catalytic efficiency of bulk CsPbBr₃ doped with different metals (Co., Fe, Ni, Cu, Ag, Mg, Mn, and Bi) and concluded that Co. and Fe doping could be ideal for CO₂ reduction (Tang et al., 2019). They specifically analyzed the adsorption-free energy using GGA of PBE functional with the PAW method. As shown in Figure 4A the ab initio molecular dynamics calculations indicated that Co− and Fe-doped systems showed stronger CO₂* adsorption energy (* refers to the adsorption site), which is the most important factor to determine the catalytic efficiency. Furthermore, using HSE06 with DFT + U correction to calculate the Hirshfeld charges and DOS of the strongly correlated effect of Co. atoms, they further illustrated the proposed reaction mechanism and confirmed that Co-doped CsPbBr₃ could be a great candidate for CO₂ reduction.

The toxicity of lead limits the wide commercialization of metal halide perovskite, and thus lead-free alternatives have recently attracted great attention, such as double perovskites \( (A_2BX_6 \text{ or } A_2B^{1+}B'^{3+}X_6) \) and other perovskite derivatives \( (A_3B_2X_6, A_3BX_5, A_4BX_3 \text{ etc.}) \), where Pb²⁺ cations are replaced using other metal cations, e.g., Na⁺, Ag⁺, Bi³⁺, and Sb³⁺. It is relatively difficult to experimentally synthesize thin films of these materials for...
photovoltaic and photocatalysis applications. However, the theoretical calculation is extremely useful because of its predicting power. For example, Cheetham et al. have used DFT calculations to compare the bandgaps and electronic structures of (MA)2B+1TiX6 (B+1 = e.g., K+, Ag+, Cu+1, Ti+1) and MAPbX₃, and found that the new double perovskite (MA)₂TL⁺¹BiBr₆, had strikingly isoelectronic properties with MAPbBr₃, as shown in Figure 4.2 (Deng et al., 2016). This study provided an intriguing alternative to the lead-containing MAPbX₃ for photoelectronic applications.

For the all-inorganic halide double perovskites, Giustino et al. (Volonakis et al., 2017) proposed a new promising halide double perovskites, Cs₂InAgX₆, with the direct band gaps between the visible and the ultraviolet as computed by the HSE06 and PBE0. Recently, Bartel et al. (Bartel et al., 2020) predicted 47 likely synthesizable compounds containing non toxic elements and with direct or nearly direct band gaps among the 311 cesium chloride double perovskites (Cs₂BB'Cl₆) compounds by computing with HSE06, and identified that the triple-alkali perovskites (where B refers to a group 1 alkali, and B' refers to a transition-metal cation) showed remarkable optical properties as computed by the GW-Bethe-Salpeter equation method. These studies are helpful to realize the future studies aim and synthesize more efficient photocatalyst with unique optoelectronic properties.

Besides the analyses of the structural, electronic and optical properties, first-principles calculations can also be used to predict phase transition temperatures, which have instructive significance on the exploration of new materials. Kye et al. calculated the bandgaps and optical properties of K₂SnX₆ (X = I, Br, Cl) in cubic, tetragonal, and monoclinic phases, and concluded that the cubic K₂SnBr₆ and monoclinic K₂SnI₆ can be promising candidates for light absorber materials (Jong et al., 2020). Moreover, they calculated the Helmholtz-free-energy differences among the above three phases, and gave the phase transition temperatures of K₂SnX₆, respectively.

As mentioned above, it is difficult to experimentally synthesize uniform thin films of double perovskites or other perovskite derivatives; however, nanocrystals or other nanostructures of these materials can be synthesized more easily. Furthermore, they are proved to be promising candidates because of their highly exposed surface. Geyer et al. developed Cs₂Sb₂Br₉ nanocrystals with significantly improved photocatalytic CO₂ production efficiency (Lu et al., 2020). Moreover, the analogous mechanism was observed using DFT calculations, as shown in Figures 4C-E. They calculated the surface energies and adsorption free energies of the (001) (1,000), and (201) surfaces of Cs₂Sb₂Br₉ as well as the (001) and (002) surfaces of CaPbBr₉, and found that the surfaces of Cs₂Sb₂Br₉ had a lower free-energy for the adsorption of COOH⁺ and CO⁺ intermediates because of the predominant defects, which suggested the enhanced catalysis activity.

As mentioned above, perovskite heterojunctions are usually endowed with optimized charge carrier dynamics for improved photocatalytic performance, and perovskite derivative heterojunctions are no exception (Feng et al., 2017; Guo et al., 2017; Wang et al., 2019b). By employing the DFT calculation, Kuang et al. (Wang et al., 2019b) investigated the electronic structures and interfacial properties in the Cs₂SnI₆/SnS₂ hybrid heterojunctions. Then, they revealed that a typical type II band alignment formed in the heterojunction, which was in accordance with the experimental values. Due to the facilitated charge separation between Cs₂SnI₆ and SnS₂ (i.e, holes from SnS₂ to Cs₂SnI₆ and electrons from Cs₂SnI₆ to SnS₂), the CO₂ photocatalytic reduction activity was unquestionably boosted.

We believed that the theoretical calculation of perovskite derivatives and heterojunction can help predict more direct or nearly direct band-gap materials and choose some more matching materials forming heterojunction with promoted the charge carrier mobility and reduced charge carrier recombination.

CONCLUSION AND OUTLOOK

Herein, we summarized current computational work on the halide perovskite-based photocatalyst. To reveal the underlying photocatalytic mechanisms, first-principles calculations were used to investigate the crystal structures, electronic properties, defect physics, and surface and interface interaction of perovskites. Furthermore, the promising potential of the first-principles material design for predicting new halide perovskites such as substitution or mixing, double perovskites, or other perovskite derivatives has also been demonstrated.

From our perspective, several critical issues and challenges still need to be overcome. First, several unique properties of halide perovskites, such as piezoelectric, and ferroelectric properties due to the anharmonicity in lattice dynamics should be illustrated and explored to promote the photocatalytic reaction efficiency. Second, the influence of structure on the photocatalytic performance of halide perovskite-based heterojunctions, such as the types of ligands, defects, dopants, and crystalline phases, needs to be further researched to improve the activity of the heterostructures. Third, theoretical analytical models of perovskite derivatives can be helpful to promote the charge carrier mobility and reduce charge carrier recombination.

AUTHOR CONTRIBUTIONS

XL proposed the research idea and manuscript; JF and CH performed check collection, collation and analysis; All authors reviewed the manuscript, have given approval to the final version of the manuscript, and confirmed the authorship to this work.

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REFERENCES

Adhikari, S. P., Hood, Z. D., More, K. L., Chen, V. W., and Lachgar, A. (2016). A Visible-Light-Active Heterojunction with Enhanced Photocatalytic Hydrogen Generation. ChemSusChem 9 (14), 1869–1879. doi:10.1002/cssc.201600424

Afari, M., Boochani, A., Hantezadeh, M., and Elahi, S. M. (2017). Topological Nature in Cubic Phase of Perovskite CsPbI3 by DFT. Solid State. Commun. 259, 10–15. doi:10.1016/j.ssc.2017.04.014

Andrei, V., Reuillard, B., and Reisner, E. (2020). Bias-free Solar Syngas Production by Integrating a Molecular Cobalt Catalyst with Perovskite-BiVO4 Tandems. Nat. Mater. 19 (2), 189–194. doi:10.1038/s41563-019-0501-6

Aryasetiawan, F., and Gunnarsson, O. (1995). Electronic Structure of NiO in the GWApproximation. Phys. Rev. Lett. 74 (16), 3221–3224. doi:10.1103/physrevlett.74.3221

Aryasetiawan, F., and Gunnarsson, O. (1998). The GW method. Rep. Prog. Phys. 61 (3), 237–312. doi:10.1088/0034-4885/61/3/002

Aubur, W. G., Jonsson, L., and Wilkins, J. W. (2000). “Quasiparticle Calculations in Solids,” in Solid State Physics. Editors H. Ehrenreich and F. Spaepen (Academic Press), 1–218. doi:10.1016/S0081-1947(08)60248-9

Bartel, C. J., Clary, J. M., Sutton, C., Vigil-Fowler, D., Goldsmith, B. R., Holder, A. M., et al. (2020). Inorganic Halide Double Perovskites with Optoelectronic Properties Modulated by Sublattice Mixing. J. Am. Chem. Soc. 142 (11), 5135–5145. doi:10.1021/jacs.9b12440

Böhlé, P. E. (1994). Projector Augmented-Wave Method. Phys. Rev. B 50 (24), 17953–17979. doi:10.1103/physrevb.50.17953

Borriello, I., Cantele, G., and Ninno, D. (2008). Ab Initio investigation of Hybrid Organic-Inorganic Perovskites Based on Tin Halides. Phys. Rev. B 77 (23), 235214. doi:10.1103/physrevb.77.235214

Brivio, F., Butler, K. T., Walsh, A., and Schlüter, M. V. (2014). Relativistic Quasiparticle Self-Consistent Electronic Structure of Hybrid Halide Perovskite Photovoltaic Absorbers. Phys. Rev. B 89 (15), 155204. doi:10.1103/physrevb.89.155204

Buckerman, J., and Navrotsky, M. (2018). 2D halide perovskite-based van der Waals heterostructures: contact evaluation and performance modulation. 2D Mater. 4 (3), 035009. doi:10.1088/2053-583X/aac3ac

Guo, Y., Xue, Y., Li, C., and Li, X. (2019). Electronic Properties of the Graphdiyne/CH3NH3PbI3 Interface: A First-Principles Study. physica status solidi (Rrl) 14 (1), doi:10.1002/pssr.201900544

Heyd, J., Scuseria, G. E., and Ernzerhof, M. (2003). Hybrid Functionals Based on a Screened Coulomb Potential. J. Chem. Phys. 118 (18), 8027–8121. doi:10.1063/1.1566060

Hohenberg, P., and Kohn, W. (1964). Inhomogeneous Electron Gas. Phys. Rev. 136 (B), B864–B871. doi:10.1103/physrev.136.B864

Hong, Z., Chong, W. K., Ng, A. Y. R., Li, M., Ganguly, R., Sun, T. C., et al. (2019). Hydrophilic Metal Halide Perovskites for Visible-Light Photoredox C–C Bond Cleavage and Dehydrogenation Catalysis. Angew. Chem. Int. Ed. 58 (11), 3456–3460. doi:10.1002/anie.201812225

Hou, J., Cao, S., Wu, Y., Gao, Z., Liang, F., Sun, Y., et al. (2017). Inorganic Colloidal Perovskite Quantum Dots for Robust Solar CO2 Reduction. Chem. Eur. J. 23 (40), 9481–9485. doi:10.1002/chem.201702237

Inoue, Y., Niijima, T., Asai, Y., and Sato, K. (1992). Stable Photocatalytic Activity of BaTiO3 Combined with Ruthenium Oxide for Decomposition of Water. J. Chem. Soc. Chem. Commun. (7), 579–580. doi:10.1039/c39920000579

Jaramillo-Paez, C. A., Navio, I. A., Hidalgo, M. C., and Macias, M. (2018). ZnO and ZnO:W Photocatalysts: Characterization and Photocatalytic Activity Assessing by Means of Three Substrates. Catal. Today 313, 12–19. doi:10.1016/j.cattod.2017.12.009

Ji, C., Sun, Z., Zeb, A., Liu, S., Zhang, J., Hong, M., et al. (2017). Bandgap Narrowing of Lead-Free Perovskite-type Hybrids for Visible-Light-Absorbing Ferroelectric Semiconductors. J. Phys. Chem. Lett. 8 (9), 2012–2012. doi:10.1021/acs.jpclett.7b00673

Jiang, H., Gomez-Abal, R., Rinke, P., and Scheffler, M. (2010). First-principles Modeling of Localized D States with the GW@LDA+U Approach. Phys. Rev. B 82 (4), 045108. doi:10.1103/physrevb.82.045108

Jiang, H. (2010). The GW Method: Basic Principles, Latest Developments and its Applications for D- and F–Electron Systems. Acta Phys. Chim. Sin. 26 (04), 1017–1033.

Jiang, H., and Zhang, M. (2020). Density-functional Theory Methods for Electronic Band Structure Properties of Materials. SCIENTIA SINICA Chim. 50 (1674–7224), 1344.

Jin, J., Yu, J., Guo, D., Cui, H., and Ho, W. (2015). A Hierarchical Z-Scheme CdS–WO3Photocatalyst with Enhanced CO2Reduction Activity. Small 11 (39), 5262–5271. doi:10.1002/smll.201500926

Jones, R. O., and Gunnarsson, O. (1989). The Density Functional Formalism, its Applications and Prospects. Rev. Mod. Phys. 61 (3), 689–746. doi:10.1103/revmodphys.61.689

Jong, U.-G., Yu, C.-J., and Kye, Y.-H. (2020). Computational Prediction of Structural, Electronic, and Optical Properties and Phase Stability of Double Perovskite K2SnX6 (X = I, Br, Cl). RSC Adv. 10 (1), 201–209. doi:10.1039/c9ta09332c
Kanhere, P., and Chen, Z. (2014). A Review on Visible Light Active Perovskite-Based Photocatalysts. *Molecules* 19 (12), 19995–20022. doi:10.3390/molecules19121995

Kato, H., and Kudo, A. (2002). Visible-Light-Response and Photocatalytic Activities of TiO2 and SrTiO3 Photocatalysts Codedoped with Antimony and Chromium. *J. Phys. Chem. B* 106 (19), 5029–5034. doi:10.1021/jp0255482

Kohn, W., and Sham, L. J. (1965). Quantum Density Oscillations in an Inhomogeneous Electron Gas. *Phys. Rev.* 137 (6A), A1697–A1705. doi:10.1103/physrev.137.a1697

Kresse, G., and Joubert, D. (1999). From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* 59 (3), 1758–1775. doi:10.1103/physrevb.59.1758

Lee, L. C., Huq, T. N., MacManus-Driscoll, J. L., and Hoye, R. L. Z. (2018). Research Update: Bismuth-Based Perovskite-Inspired Photovoltaic Materials. *APL Mater.* 6 (8), 084502. doi:10.1063/1.5029484

Luo, S., and Daoud, W. A. (2015). Recent Progress in Organic-Inorganic Halide Perovskites for Solar Cell Applications. *Chem. Soc. Rev.* 44 (1), 4467. doi:10.1039/c3cs41246f

Miyake, T., Zhang, P., Cohen, M. L., and Louie, S. G. (2006). Quasiparticle Energy Bands, Projector Augmented-Wave Method. *Phys. Rev. Lett.* 96 (3), 036402. doi:10.1103/physrevlett.96.036402

Perdew, J. P., Ernzerhof, M., and Burke, K. (1996). Rationale for Mixing Exact Exchange with Density Functional Approximations. *J. Chem. Phys.* 105 (22), 9982–9985. doi:10.1063/1.472933

Schrödinger, E. (1931). A New Method of Molecular Calculation. *Phys. Z.* 32, 856–862.

Schgel, M. L. (2017). Calculation of Spin Orbit Coupling of Tungsten (III) Complexes: A DFT Application. *Orient. J. Chem.* 33, 1045–1046. doi:10.13005/ojic/330263

Sun, S., Tominaka, S., Lee, J.-H., Xie, F., Bristowe, P. D., and Cheetham, Ak. (2016). Synthesis, crystal Structure, and Properties of a Perovskite-Related Bismuth Phase, (NH4)3Bi2Br9. *APL Mater.* 4 (3), 031101. doi:10.1063/1.4943680

Tang, C., Chen, C., Xu, W., and Xu, L. (2019). Design of Doped Cesium Lead Halide Perovskite as a Photo-Catalytic CO2 Reduction Catalyst. *J. Mater. Chem. A.* 7 (12), 6911–6919. doi:10.1039/c9ta05550a

Umari, P., Mosconi, E., and De Angelis, F. (2014). Relativistic GW Calculations on CH3NH3PbI3 and CH3NH3SnI3 Perovskites for Solar Cell Applications. *Scientific Rep.* 4 (1), 4467. doi:10.1038/srep04467

van Schilfgaarde, M., Kotani, T., and Faleev, S. (2006). Quasiparticle Self-Consistent GW Theory. *Phys. Rev. Lett.* 96 (22), 226402. doi:10.1103/physrevlett.96.226402

Volonakis, G., Filip, M. R., Haghighirad, A. A., Sakai, N., Weng, B., Snaith, H. J., et al. (2016). Lead-Halide Double Perovskites via Heterovalent Substitution of Noble Metals. *J. Phys. Chem. Lett.* 7 (7), 1254–1259. doi:10.1021/acs.jpclett.6b01376

Wang, K., Jin, Z., Liang, L., Bian, H., Wang, H., Feng, J., et al. (2019). Chlorine Doping for Black γ-CsPbI3 Solar Cells with Stabilized Efficiency beyond 16%. *Nano Energy* 58, 175–182.

Wang, X.-D., Huang, Y.-H., Liao, J.-F., Jiang, Y., Zhou, L., Zhang, X.-Y., et al. (2019). In Situ Construction of Cs2SnI6 Perovskite Nanocrystals/SnS2 Nanosheet Heterojunction with Boosted Interfacial Charge Transfer. *J. Am. Chem. Soc.* 141 (34), 13434–13441. doi:10.1021/jacs.9b04482

Xiaobo, C., Shen, S., Guo, L., and Mao, S. S. (2014). Semicontinuous Perovskite as a Photo-Catalytic CO2 Reduction Catalyst. *Appl. Catal. B: Envir.* 277, 119230. doi:10.1016/j.apcatb.2020.119230

Yan, J., Qiu, W., Wang, Z., Zhou, Q., Wang, L., Liu, Y., et al. (2018). Composite of CH3 NH3 PbI3 with Reduced Graphene Oxide as a Highly Efficient and Stable Visible-Light Photocatalyst for Hydrogen Evolution in Aqueous HI Solution. *Adv. Mater.* 30 (7), 1704342. doi:10.1002/adma.201704342

Yue, S., Wang, R., Wu, M.-Z., and Yuan, Y.-P. (2015). A Review on G-C3n4 for Photocatalytic Water Splitting and CO2 Reduction. *Appl. Catal. A: Gen.* 487, 77–88. doi:10.1016/j.apcata.2013.11.028

Zhi, S., and Jayatissa, A. (2018). Perovskites-Based Solar Cells: A Review of Recent Progress, Materials and Processing Methods. *Materials* 11 (5), 729. doi:10.3390/ma11050729

Zhu, X., Zong, X., and Li, Y. (2019). A CsPbBr3 Perovskite Quantum Dot/Graphene Oxide Composite for Efficient Visible Range Solar Cell Applications. *J. Mater. Chem. A.* 7 (27), 13902–13908. doi:10.1039/c9ta02751j

Zhu, X., Zong, X., and Li, Y. (2019). Silicon-Based Graphene Nanosheets for Photocatalytic CO2 Reduction. *Appl. Catal. B: Environ.* 277, 119230. doi:10.1016/j.apcatb.2020.119230
Zeng, S., Kar, P., Thakur, U. K., and Shankar, K. (2018). A Review on Photocatalytic CO2 Reduction Using Perovskite Oxide Nanomaterials. Nanotechnology 29 (5), 052001. doi:10.1088/1361-6528/aa9fb1
Zhang, J., Bai, D., Jin, Z., Bian, H., Wang, K., Sun, J., et al. (2018). 3D-2D-0D Interface Profiling for Record Efficiency All-Inorganic CsPbBr3 Perovskite Solar Cells with Superior Stability. Adv. Energ. Mater. 8 (15), 1703246. doi:10.1002/aenm.201703246
Zhang, Q., Ting, H., Wei, S., Huang, D., Wu, C., Sun, W., et al. (2018). Recent Progress in lead-free Perovskite (-like) Solar Cells. Mater. Today Energ. 8, 157–165. doi:10.1016/j.mtener.2018.03.001
Zhao, Y., Wang, Y., Liang, X., Shi, H., Wang, C., Fan, J., et al. (2019). Enhanced Photocatalytic Activity of Ag-CsPbBr3/CN Composite for Broad Spectrum Photocatalytic Degradation of Cephalosporin Antibiotics 7-ACA. Appl. Catal. B: Environ. 247, 37–69. doi:10.1016/j.apcatb.2019.01.090
Zhao, Z., Wu, J., Zheng, Y.-Z., Li, N., Li, X., Ye, Z., et al. (2019). Stable Hybrid Perovskite MAPb(I1−Br )3 for Photocatalytic Hydrogen Evolution. Appl. Catal. B: Environ. 253, 41–48. doi:10.1016/j.apcatb.2019.04.050
Zhu, X.-Y., and Podzorov, V. (2015). Charge Carriers in Hybrid Organic-Inorganic Lead Halide Perovskites Might Be Protected as Large Polaron. J. Phys. Chem. Lett. 6 (23), 4758–4761. doi:10.1021/acs.jpclett.5b02462
Zhu, X., Lin, Y., Martin, J. S., Sun, Y., Zhu, D., and Yan, Y. (2019). Lead Halide Perovskites for Photocatalytic Organic Synthesis. Nat. Commun. 10 (1), 2843. doi:10.1038/s41467-019-10634-x

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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