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Density Functional Theory Study of Metal-Organic Frameworks for Enhancement of Photo-Anode Properties

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The optoelectronic properties of dye zinc and titanium-based metal-organic framework (MOF) compounds with regard to their application as photo-anode material characterized in solar cells were investigated. Analyses of the optoelectronic properties were performed on the MOF single crystal unit cell with adsorbed dye to determine the electronic and optical properties of the relevant materials. The electronic and optical properties were predicted by density functional theory (DFT) calculations. The results show that the absorption of light occurs for the examined MoF compounds from the near UV to the (visible) blue spectral range, at optical band gap sizes from 2.8 eV up to 3.88 eV. Dye sensitization of MOF with eosin Y or crown ether gave additive UV-Vis spectra. An improvement in band gap or an improved electron injection could be archived as well. Moreover, the light absorption does not solely depend on the linkers used, but also from the metal atoms in the secondary building unit. The fluorescence of MOFs depends on the linker and especially on the linker coordination and their rotation relative to each other. The utilizations of MOFs and their derivatives as electrodes, photoactive materials, charge carriers and additives in different solar cells are highlighted.

Keywords: *MOF, ZnO/crown, TiO_2/eosin Y, dye-sensitized, solar cell.*

1. Introduction

The shortage of energy reserves, especially oil, has caught the attention of many nations. The global oil production maximum, also called peak Oil, can be reached in a short time. After reaching this peak, the global demand for oil can no longer be met[1,2]. Consequently, an enormous increase in oil price can happen. It is therefore of paramount of importance to develop new technologies, to ensure continued energy supply. In this regard, renewable energies are often to be used[3]. These include biomass, hydropower, wind power, geothermal energy and the solar energy. Solar energy can be used in the form of heat (solar thermal) or by converting it into electrical energy (photovoltaic). It has been shown that the share of renewable energy has increased in the ten past years from 1.9% (1990) to 20.2% (2021) in final energy consumption. Photovoltaic (PV) represents 4.1% from the final energy supply from renewable energies[4,5].

The direct use of solar radiation energy with PV attracts worldwide attention and has always attracted the attention of researchers on themselves[6]. On the one hand, this may be due to the variety of physical processes related to PV technologies. On the other hand, the meaning of PV goes far beyond a mere scientific interest. For the development of a worldwide sustainable society is access to economically usable, regenerative energy sources a crucial factor[7], with global energy demand since steadily increasing over the years. Solar energy has the greatest potential here, the future to serve global needs for renewable energy sources[8-10], as they are a decentralized and virtually unlimited source. Moreover, the reserves conventional energy sources such as coal, gas and oil limited their use inseparable from global warming caused by the greenhouse effect – mainly through released carbon dioxide (CO_2) – is connected. PV on the other hand is free of carbon dioxide emissions during operation. The Energy content that reaches the earth's surface within one hour is about that total annual energy demand of mankind. Apart from these PVs offer ecological and economic importance. Natural scientists a wide field of interesting physics for practical basic research. The different generations of solar cells with their different technological approaches include very advanced concepts and thus cover a wide range of topics in the field of physical chemistry, surface and interface physics and materials science[11]. The dynamic of charge carriers, such as their generation, recombination, energetic relaxation and their transport are the fundamental processes within each solar cell, which with suitable time-resolved measurement methods can be followed to get a deeper to gain an understanding of the light-induced processes and their interaction. The dynamic processes - depending on the device - extend across a time range from a few femtoseconds (10) to the low range of seconds.

The currently commercially available panels made of silicon. However, various disadvantages are presented[12]. Therefore, critics attribute the expensive and poisonous manufacturing process that is necessary to produce high-purity silicon, must be handled. Therefore, new, promising

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materials that can serve as a photo-anode in injection solar cells are needed.

Two decades ago, the dye, based on a natural process, developed by Grätzel was used to synthesis solar cell with breakthrough application. The cells became stable further developed and optimized for a wide range of application prospects[13].

Solar cells can be made not only from silicon crystals, but also from conductive plastics and dye molecules. These can even be flexible and cheaper, but don't deliver as much power due to the low efficiency (less than five percent). However, with the indoline dyes, the titanium dioxide layers can be built up thinner than before. This increases the mobility of electrons and ions, which should be as good as possible for a high yield. In terms of efficiency, dye cells cannot yet compete with monocrystalline silicon cells, but in principle they can be produced much more cheaply[13].

In 1999, Yaghi discovered a new class of materials, the so-called metal-organic frameworks (MOFs)[14,15]. Because of their outstanding properties such as the high surface area, due to its very small pores, and the possibility of producing MOFs with different building blocks and functionalities, MOFs represent a promising material for photo-anodes in solar cells. By construction the zinc (or titanium)-based metal-organic frameworks, MOFs can be proximity to the optoelectronic and electrochemical behavior of zinc oxide. To consider the electronic properties of a crystalline solid, the valence band and conduction band are of the greatest importance in the structure. In this case, the valence band is used completely or partially with electrons occupied energetically highest energy band. That energetic higher-lying energy band that is partially or not occupied by electrons is called the conduction band. The occupation of the energies levels with electrons is described by a Fermi-Dirac statistic. In conductors, the valence and conduction bands overlap. Thus, the electrical conductivity based on the developed energy band model as a possibility of excitation of electrons from the valence band describe in the free conduction band. Even with a partial occupation, the Electrical conductivity is detected in the valence band. This results from the occupation of the otherwise free, highest energy states of the valence band[16].

The increasing investigation of conductive MOF development, the further exploration of structures-performance relationships as well as the increasing understanding of the working mechanism of MOFs and MOF derivatives in solar cells, together with the effective support from theoretic studies, will exclusively inspire further design and development of novel MOFs and MOF derivatives for applications in different solar cells with enhanced performance in the near future[17]. MOFs can be photosensitive due to light absorption by the organic component or the metal oxide node. Photoexcitation of the light absorbing units generates a ligand-to-metal charge-separation state that can lead to photocatalytic activity[18].

The targeted manipulation of MOFs is an interesting concept for the development of tailored material properties, opening new possibilities not only in the fields of sorption and catalysis, but also in the control of more sophisticated physical properties such as band gap, magnetic, and electrical properties. So far, there has been little effort to characterize intrinsic or intentionally created defects of various types. MOFs have been successfully used to increase the stability of solar cells[19].

MOFs have been utilized in solar cell as an additive in electron and hole transport layers, interface modifiers, or hybrid perovskite/MOF absorbers. MOFs have been mostly incorporated into the solar cell to enhance their environmental stability, such as oxygen and moister resistance, together with sequestration of lead leakage different MOF incorporation strategies into the solar cell were introduced by different groups[20].

Moreover, MOFs have novel method has been implemented in order to minimize the Pb leakage perovskite solar cells by forming water-insoluble solids[21].

Exceeding the theoretical yield limit requires PV components with several energy levels to cover the widest part of the spectrum solar. There are several approaches and concepts to achieve possibly these components, some of which are involve nanomaterials or nanostructuring semiconductors[22,23].

Other high yield strategies intervene the nanostructuring of semiconductors composed of elements of groups II-VI, III-V or IV-IV. In effect, reducing the size of semiconductor crystals to nanometric sizes gives them special features such as quantum confinement. For example, the band gap width can be modulated depending on the size of the nanocrystal, which allows absorb and convert more photons and/or generate more carriers. Materials can be structured as nanotubes or nanowires, wells or quantum dots. The PV devices can be cells with tandem, intermediate band, photon conversion or with hot carriers. Theoretically, they are likely to allow conversion yields greater than 40%. Thanks to the development of nanotechnology, the realization of these structures is now possible, but their implementation in real PV cells is still a challenge, both in terms of design and of the principle of operation[24].

The central task of the present work is designing novel materials based on both: dyes and transition metal based-MOFs to demonstrate the possibility to synthesis of ZnO/crown, TiO_2/eosin Y hybrid layers and to study the electronic and optical properties of the newly designed materials.

2. Calculation Method

The results of this work were obtained with the Vienna Ab-Initio Simulation Package[25,26], VASP for short version 5.1.39. VASP solves the (generalized) Kohn-Sham equations in k-space, where the interaction between electrons and Ions are treated using the PAW method[27,28], which offers precision comparable to all-electron representations (e.g. FLAPW[28,29]). The VASP underlying implementation of the GWA as part of the PAW method is described in detail in other work[27].

The optical spectra, including many-body effects within the framework of the BetheSalpeter equation, were calculated using routines based on VASP[30,31]. The optical transition matrix elements were partly in the longitudinal, partly calculated in the transversal approximation, where for the considered materials no appreciable influence on the oscillator strengths existed. The numerical details and convergence parameters are summarized in other work[32].

3. Results and Discussion

Figure 1 shows the optimized crystal structure of MOF-crown and MIL-125-eosin. Calculations with DFT method have shown that the linker functionalization can contribute to the stability of the relevant MOF system. In the MOF materials, the electronic properties are determined by the coordination of the zinc (titanium) cation to the central one oxygen of the secondary building unit (SBU). Because of this, MOFs can be viewed as zinc oxide quantum dots and should have properties a semiconductor with a relatively large band gap compared to zinc oxide.

The reason for this is that the electronic states of the conduction band edge are mainly states of 2p orbitals, as evident in Figure 2. This is how the lower conduction band formed from orbitals of the linker, only the carbon atom

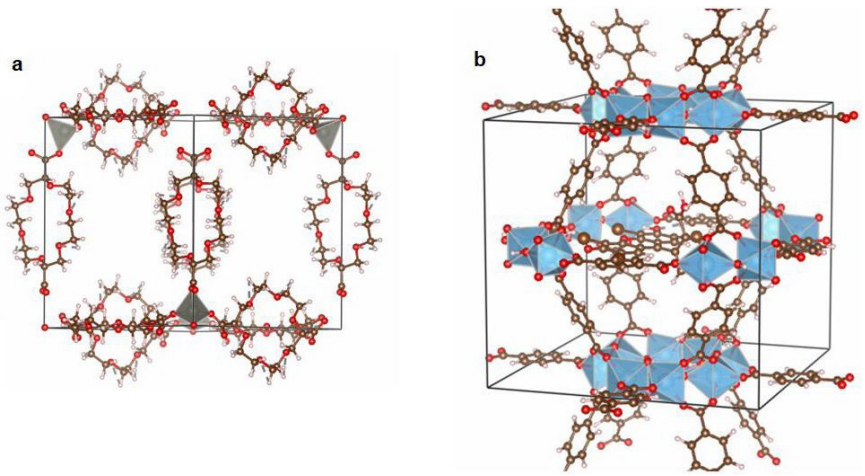
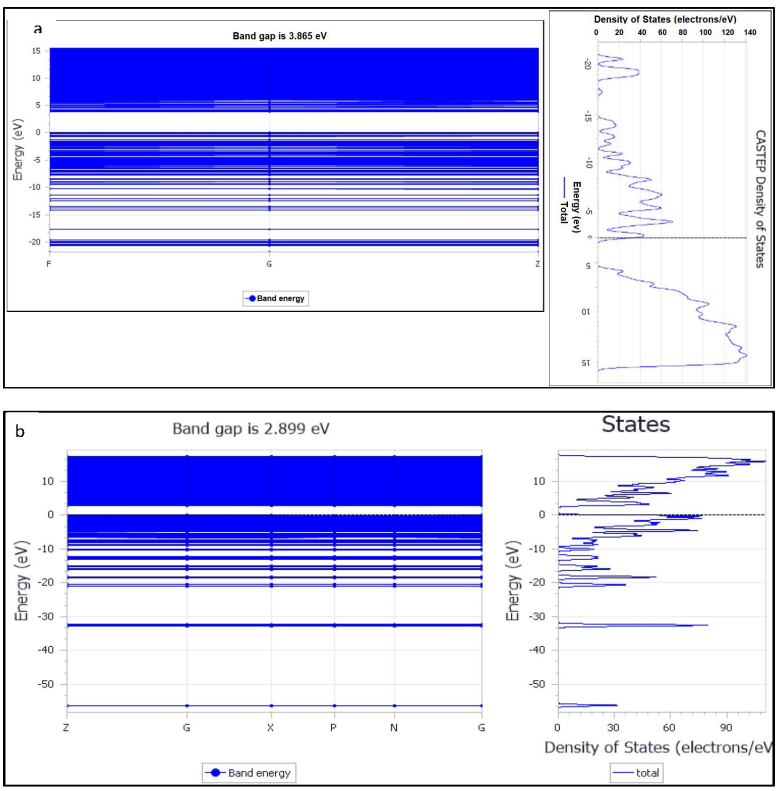


Figure 1. Crystal structure of MOF-crown (a) and MIL-125 eosin (b).



Figures 2. The bands structures of MOF-crown (a) and MIL-125-erosin (b) respectively.

via which the zinc cation coordinated to the linker is shared between the linker and SBU. The upper valence band is also bounded by the linker orbitals, the coordinating oxygen between linker and metal cation and the central oxygen atom in the middle of the SBU. Simulation results show that the band gap of MOF-crown is about 3.8 eV, while it decreases by almost 1eV for MIL-125-erosin. From these results it can be seen that the electronic states that shape the band gap and thus determine the band edges are dominated by the C2p orbital. This means the linker are mainly responsible for the size of the band gap. i.e. MOF band gap is determined by size of the HOMO-LUMO transition of the linkers used. The band gap of the MOF becomes smaller when linker is conjugated with eosin in the MOF system. This can also be achieved by using a longer linker. The aromatic rings of the linkers in the MOF are also freely rotatable and can be placed in the in-plane conformation also accept twists of up to 90[33,34]. Table 1 summarizes the parameters of the unit cell of each material.

The as-made porous carbon skeleton layer was deposited with TiO_2 nanoparticles and then used as the ETL to improve the photogenerated electron transport rate of PSCs[35]. As a result, the PCE of the carbon-skeleton-based n-i-p PSC device was enhanced from 14.25% to 17.32%[17].

The zinc-oxo clusters often behave as in as zinc oxide quantum dots. Therefore, an interaction and a decreasing reflectivity are in not alarming in UV-Vis area and also do not point to contamination with zinc oxide. It is clearly visible in Figure 3a that the MOF-crown band edge is around 125 nm. The experimentally determined IRMOFs band edges are always in the range of 311-314 nm. This t deviation is due to the presence of crow ether linker. Nonetheless, the band gap edge of MIL-125, Figure 3b, is about 620 nm clearly much higher than that of MOF-crown. Moreover, the reflectivity of MIL-125-erosin is almost 4 times higher than that of MOF-crown across the entire solar spectrum[36,37]. A good material for solar cell application must have a high reflectivity and low resistivity (i.e. high conductivity) generally calculated over all solar spectra.

Figure 4 shows the electric conductivity of both MOF-crown (a) and MIL-125-erosin (b) across entire spectrum. It is clear that the conductivity of both materials as similar to that of other MOF materials. However, the conductivity of MIL-125 is almost double that of MOF-crown. This could be explained as a result of presence of both Ti oxide cluster and erosin in the structure of MIL-125[38,39].

The propagation speed of an electromagnetic wave (speed of light) is typically lower in matter than in a vacuum. The dimensionless quantity n, the so-called refractive index, describes the propagation speed in matter relative to the propagation speed in vacuum[1] and is a material constant[2]. A beam of light changes at oblique incidence between two media with different refractive index, the physical phenomenon of refraction occurs, i.e. at the boundary between the directions of the light beam changes between the two media[3]. There is the refraction greater, the more the two refractive indices differ from each other. This phenomenon is exploited with magnifying glasses or by the Use of glass or plastics with a high refractive index[4].

Figure 5 represents the refractive index of both materials in consideration. It is clear that the refractive index of

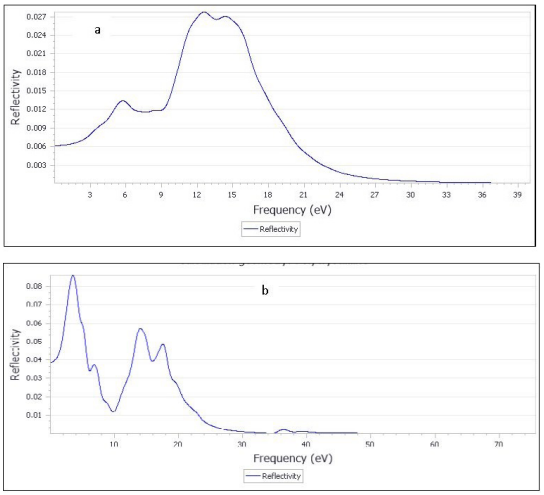


Figure 3. UV-Vis spectra of pure MOF-crown (a) and MIL-125-erosin (b). The band edges are 125 nm for MOF-crown, and 620 for MIL-125-eosin.

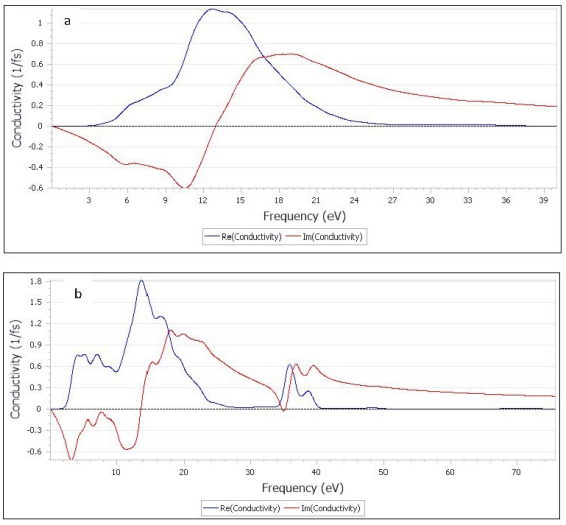


Figure 4. The conductivity as a function of frequency of MOF-crown (a) and MIL-125-erosin (b).

Table 1. Parameters of the unit cell of each material.

Materials	a (Å)	b (Å)	c (Å)	α	β	γ
MOF-crown	17.577	17.577	17.577	90.0°	90.0 °	90. °
MIL-125 eosin	19.082	19.082	18.127	90.0 °	90.0 °	90. °

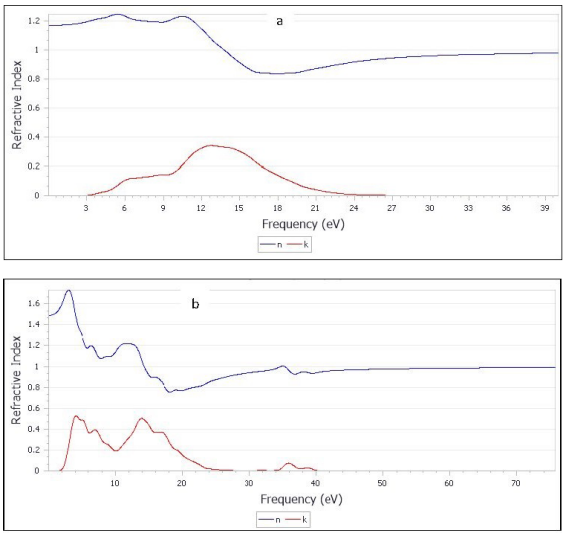


Figure 5. The refractive index as a function of frequency of MOF-crown (a) and MIL-125-erosin (b).

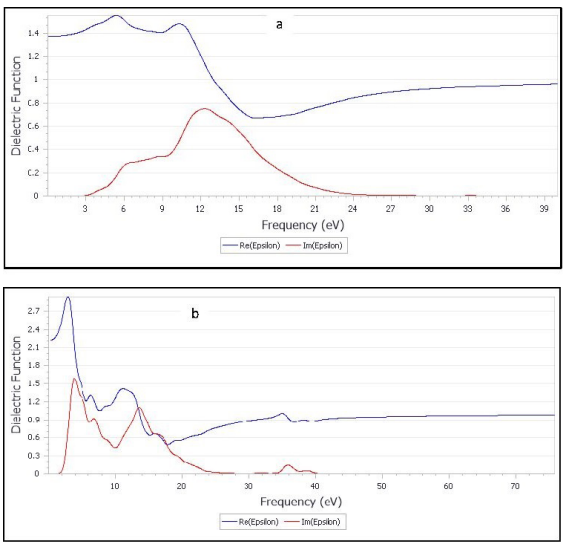


Figure 6. The dielectric function of MOF-crown (a) and MIL-125-erosin (b).

MIL-125-eosin is higher than that of MOF-crown across intern spectrum. Therefore, MIL-125 is more preferable for solar cell applications[40-42].

The dielectric function of a semiconductor is determined by the following factors influenced: the course of the energy bands (near IR, visible range, UV), optical phonons (mid and far IR), free charge carriers (entire IR range) and impurities (far IR). This experiment deals exclusively with the first point. The absorption at the fundamental band edge can first be described by a simple model by taking a direct one semiconductor with a parabolic valence band and conduction band (VB and CB) and is obtained in this model. Using this simple model the dielectric function of both materials was calculated and presented in Figure 6. It is clear that that materials MIL-125-eosin is more preferable for solar cell applications[43]. The efficiency of the photochemical reaction of a soluble compound can be expressed by the quantum yield as a ratio of the number of photoproduct molecules formed and the number of photons absorbed as an absolute one size can be determined. For solids, however, absolute quantum yield measurements are not possible due to light scattering and reflection. However, a useful parameter is the conversion of incident light in photoproduct" (incident light to photoproduct conversion), which is equivalent to specifying the efficiency of Solar cells[44]. These apparent quantum yields may depend on parameters that affect light scattering, such as particle size or structure of the photo reactor but at least they provide a quantitative value for the efficiency of the photo-catalytic process.

4. Conclusion

The field of PVs is increasingly opening up to concepts involving the use of nanostructures. These nanostructures can intervene in relation to their optical properties, in particular confinement effects quantum, which will make it possible to modulate the widths of forbidden bands and to create new materials without affecting their chemical composition. This is how a very wide range of new possibilities available to researchers, who could make it possible to develop high-performance multi junctions solely based on the use of quantum size effects. They can also intervene on the geometric dimension by allowing a much finer mesh of space than it was with traditional structures. This meshing makes it possible to exploit PV components, which could not operate at conventional scales in the micron range to a few hundreds of microns. This is particularly the case for dye cells and organic cells. They can then be used for management optics of the PV devices, in order to allow the confinement of the electromagnetic radiation in increasingly finer areas, at the closer to conversion centers.

In the present work, the optoelectronic and electrochemical properties of newly designed Zinc/Titanium-based metal-organic frameworks were characterized with regard to their application as photo-anode material in injection solar cells. Analyses of the optical and optoelectronic properties of the MOFs were performed using DFT calculations. DFT calculations were employed to determine the band gap, refractive index, reflectivity and dielectric function of the relevant materials.

Frameworks from the near UV to the blue (visible) spectral range, with optical band gap sizes from 2.8 eV up to 3.75 eV. Dye sensitization of the MOF-125 with eosin Y or resulted in additive UV-Vis spectra. An increase of band gap or an improved electron injection could not be determined. The MOF-crown showed that the light absorption does not depend exclusively on the linkers used, but also from the metal atoms in the SBUs. DFT calculations have shown that the fluorescence of MOFs is linker-based. It could also be shown that the fluorescence is still dependent on many factors and could be concluded that the fluorescence especially of the linker coordination and their rotation relative to each other.

Moreover, our results show that the material of eosin Y-encapsulated titanium-based MOF can offer the best materials in term of opt-electric properties.

Finally, nanomaterials and nanostructures will surely have a decisive role to play in the development of new PV

devices with very high efficiency (> 50%) based on new concepts involving the conversion of photons, the generation of excitons multiple, the direct collection of electron-hole pairs before thermal processing in future so-called "hot carrier" devices, as well as the concept of intermediate bands.

5. References

1. Florini A. The International Energy Agency in global energy governance. Glob Policy. 2011;2:40-50.
2. Stritzke S, Trotter PA, Twesigye P. Towards responsive energy governance: lessons from a holistic analysis of energy access in Uganda and Zambia. Energy Policy. 2021;148:111934.
3. Stritzke S, Jain P. The sustainability of decentralised renewable energy projects in developing countries: learning lessons from Zambia. Energies. 2021;14(13):3757.
4. Zeng S, Liu Y, Liu C, Nan X. A review of renewable energy investment in the BRICS countries: history, models, problems and solutions. Renew Sustain Energy Rev. 2017;74:860-72.
5. Arantegui RL, Jäger-Waldau A. Photovoltaics and wind status in the European Union after the Paris Agreement. Renew Sustain Energy Rev. 2018;81:2460-71.
6. Hu X, Li X, Li G, Ji T, Ai F, Wu J et al. Recent progress of methods to enhance photovoltaic effect for self-powered heterojunction photodetectors and their applications in inorganic low-dimensional structures. Adv Funct Mater. 2021;31(24):2011284.
7. Owusu PA, Asumadu-Sarkodie S. A review of renewable energy sources, sustainability issues and climate change mitigation. Cogent Eng. 2016;3(1):1167990.
8. Dincer F. The analysis on photovoltaic electricity generation status, potential and policies of the leading countries in solar energy. Renew Sustain Energy Rev. 2011;15(1):713-20.
9. Kabir E, Kumar P, Kumar S, Adelodun AA, Kim K-H. Solar energy: potential and future prospects. Renew Sustain Energy Rev. 2018;82:894-900.
10. Chandel R, Chandel SS, Malik P. Perspective of new distributed grid connected roof top solar photovoltaic power generation policy interventions in India. Energy Policy. 2022;168:113122.
11. Saga T. Advances in crystalline silicon solar cell technology for industrial mass production. NPG Asia Mater. 2010;2(3):96-102.
12. Pizzini S. Towards solar grade silicon: challenges and benefits for low cost photovoltaics. Sol Energy Mater Sol Cells. 2010;94(9):1528-33.
13. Ghosh S, Yadav R. Future of photovoltaic technologies: a comprehensive review. Sustain Energy Technol Assess. 2021;47:101410.
14. Safaei M, Foroughi MM, Ebrahimpoor N, Jahani S, Omidi A, Khatami M. A review on metal-organic frameworks: synthesis and applications. Trends Analyt Chem. 2019;118:401-25.
15. Dutta A, Pan Y, Liu J-Q, Kumar A. Multicomponent isoreticular metal-organic frameworks: principles, current status and challenges. Coord Chem Rev. 2021;445:214074.
16. Islamoglu T, Ray D, Li P, Majewski MB, Akpinar I, Zhang X et al. From transition metals to lanthanides to actinides: metal-mediated tuning of electronic properties of isostructural metal–organic frameworks. Inorg Chem. 2018;57(21):13246-51.
17. Chen B, Yang Z, Jia Q, Ball RJ, Zhu Y, Xia Y. Emerging applications of metal-organic frameworks and derivatives in solar cells: recent advances and challenges. Mater Sci Eng Rep. 2023;152:100714.
18. Dhakshinamoorthy A, Asiri AM, García H. Metal–Organic Framework (MOF) compounds: photocatalysts for redox reactions and solar fuel production. Angew Chem Int Ed. 2016;55(18):5414-45.
19. Nevruzoglu V, Demir S, Karaca G, Tomakin M, Bilgin N, Yilmaz F. Improving the stability of solar cells using metal–organic frameworks. J Mater Chem A Mater Energy Sustain. 2016;4(20):7930-5.
20. Pourshaban E, Golobostanfard MR. Recent development in MOFs for perovskite-based solar cells. In: Gupta RK, Nguyen TA, Yasin G, editors. Metal-organic framework-based nanomaterials for energy conversion and storage. Amsterdam: Elsevier; 2022. p. 507-34.
21. Wu S, Li Z, Li M-Q, Diao Y, Lin F, Liu T et al. 2D metal–organic framework for stable perovskite solar cells with minimized lead leakage. Nat Nanotechnol. 2020;15(11):934-40.
22. Ariga K. Nanoarchitectonics: what's coming next after nanotechnology? Nanoscale Horiz. 2021;6(5):364-78.
23. Terna AD, Elemike EE, Mbonu JI, Osafile OE, Ezeani RO. The future of semiconductors nanoparticles: synthesis, properties and applications. Mater Sci Eng B. 2021;272:115363.
24. Kshirsagar B, Jaykhedkar N, Jain K, Kishor S, Shah V, Ramaniah LM et al. Green CsSnX3 (X= Cl, Br, I)-derived quantum dots for photovoltaic applications: first-principles investigations. J Phys Chem C. 2021;125(4):2592-606.
25. Kresse G, Hafner J. *Ab initio* molecular dynamics for liquid metals. Phys Rev B. 1993;47(1):558-61.
26. Kresse G, Furthmüller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys Rev B. 1996;54(16):11169-86.
27. Hafner J. *Ab-initio* simulations of materials using VASP: density-functional theory and beyond. J Comput Chem. 2008;29(13):2044-78.
28. Hafner J. Materials simulations using VASP: a quantum perspective to materials science. Comput Phys Commun. 2007;177(1-2):6-13.
29. Sun G, Kürti J, Rajczy P, Kertesz M, Hafner J, Kresse G. Performance of the Vienna ab initio simulation package (VASP) in chemical applications. J Mol Struct THEOCHEM. 2003;624(1-3):37-45.
30. Wang V, Xu N, Liu J-C, Tang G, Geng W-T. VASPKIT: a user-friendly interface facilitating high-throughput computing and analysis using VASP code. Comput Phys Commun. 2021;267:108033.
31. Rani P, Dubey GS, Jindal VK. DFT study of optical properties of pure and doped graphene. Physica E. 2014;62:28-35.
32. Suo Z, Dai J, Gao S, Gao H. Effect of transition metals (Sc, Ti, V, Cr and Mn) doping on electronic structure and optical properties of CdS. Results Phys. 2020;17:103058.
33. Pham HQ, Mai T, Pham-Tran N-N, Kawazoe Y, Mizuseki H, Nguyen-Manh D. Engineering of band gap in metal–organic frameworks by functionalizing organic linker: a systematic density functional theory investigation. J Phys Chem C. 2014;118(9):4567-77.
34. Musho T, Li J, Wu N. Band gap modulation of functionalized metal–organic frameworks. Phys Chem Chem Phys. 2014;16(43):23646-53.
35. Zhang Z, Luo X, Wang B, Zhang J. Electron transport improvement of perovskite solar cells via a ZIF-8-derived porous carbon skeleton. ACS Appl Energy Mater. 2019;2(4):2760-8.
36. Yin W, Tao C-A, Wang F, Huang J, Qu T, Wang J. Tuning optical properties of MOF-based thin films by changing the ligands of MOFs. Sci China Mater. 2017;61(3):391-400.
37. Zhao Q, Liuxue Z, Wang X, Jia X, Xu P, Zhao M et al. Simultaneous efficient adsorption and photocatalytic degradation of methylene blue over iron(III)-based metal–organic frameworks: a comparative study. Transit Met Chem. 2019;44:789-97.
38. Xie LS, Skorupskii G, Dincă M. Electrically conductive metal–organic frameworks. Chem Rev. 2020;120(16):8536-80.
39. Li C, Zhang L, Chen J, Li X, Sun J, Zhu J et al. Recent development and applications of electrical conductive MOFs. Nanoscale. 2021;13(2):485-509.
40. Keppler NC, Hindricks KDJ, Behrens P. Large refractive index changes in ZIF-8 thin films of optical quality. RSC Advances. 2022;12(10):5807-15.

41. Chong X, Kim K-J, Ohodnicki PR, Li E, Chang C-H, Wang A. Ultra-short near-infrared fiber-optic sensors for carbon dioxide detection. IEEE Sens J. 2015;15(9):5327-32.
42. Huang Y, Tao C-A, Chen R, Sheng L, Wang J. Comparison of fabrication methods of metal-organic framework optical thin films. Nanomaterials. 2018;8:676.
43. Warmbier R, Quandt A, Seifert G. Dielectric properties of selected metal–organic frameworks. J Phys Chem C. 2014;118(22):11799-805.
44. Navalón S, Dhakshinamoorthy A, Álvaro M, Ferrer B, García H. Metal–organic frameworks as photocatalysts for solar-driven overall water splitting. Chem Rev. 2023;123(1):445-90.