Harnessing Metal-organic frameworks in sensitized light harvesting devices: a review

Sandeep Kumar Sharma,

Assistant Professor, SGGS, Chandigarh-India.

Abstract: Metal organic frameworks are emerging as an efficient group of materials whose diverse and tunable structures make them paragon for use in photovoltaic applications. Owing to their tunable properties *viz*. efficient light harvesting, flexible fabrication and highly porous nature, their utilization in photovoltaic devices is proved to be an epitome to combat energy crisis, which the world is facing due to continuously diminishing energy sources. Several studies focused to enhance the electrical conductivity of MOFs by its successful hybridization with various conducting materials like metal ions, carbon nano-tubes and graphene etc. This review thus covered the brief findings exploring the fabrication of MOFs and its composites as different components of various solar cell technologies especially the dye-sensitized solar cells that improved the overall performance of these photovoltaic cells.

Keywords: MOFs, photovoltaics, DSSC, power conversion efficiency

1. Introduction: The development of solar energy harvesting systems is a need of the hour to meet the future goals of global energy requirements. Various types of solar cells are being developed to improve the technological and commercial viabilities of solar energy as the most promising energy sector in coming decades. The vast majority of the solar panels (about 90%) are based on silicon which is now a mature technology. In the recent decades, some alternative solar cell technologies, including dye-sensitized solar cells (DSSCs), organic photovoltaics, perovskite photovoltaics, and inorganic quantum dot solar cells, have garnered stimulating and intense research and development efforts in academia and industry. Metal-organic frameworks (MOFs) are more or less crystalline, highly porous and hierarchical chemical structures that are formed by the reaction of coordination of suitable metal ions and multidentate organic linkers [1-4]. A wide flexibility with the selection of constituents (metal ions as well as organic counterparts) and the chemistry of their coordination have allowed the realization of infinite varieties of MOFs with tunable structures, geometries, pore sizes, and functionalities. For a long period of time, MOFs were investigated mostly in applications exploiting host-guest chemistry. These applications included the storage of various fuel and toxic gases, adsorption of harmful analytes, drug delivery cargos, etc. [5-7]. The activity of metal centres or the existence of specific functionalities in MOFs has been exploited in other applications like catalysis [8, 9], photocatalysis [10-12], sensors [13], and electrochemical devices [14-16]. MOFs have been investigated by various researchers in the field of photovoltaics. Their stability exhibited in response to light exposure has established some classes of MOFs as promising semiconductor materials for photovoltaics applications. Though most of the synthesized MOFs are insulating in nature, some special examples have been reported with improved electron transfer rates, which is a key factor for fabricating

photovoltaic devices. With latest research in this field, the utility of MOFs is now a well-established fact in refining the properties of the next-generation photovoltaic devices such as dye-sensitized solar cells (DSSC). Some MOF based core-shell structures also show much promise in this field. Various blends of metal ions and ligands can be explored to improve the light absorption properties of MOFs which will result in the enhancement of their performance photovoltaic devices. Some nanoporous MOFs have been proven useful for the absorption of visible spectrum of light which is vital for the fabrication of efficient solar cells. The porous nature of MOF based solar cells has also been suggested to tackle the problems of charge recombination, thereby offering opportunities of attaining higher values of open circuit potentials. Furthermore, the MOFs can be combined with other nanomaterials such as quantum dots, carbon nanotubes and porphyrin dyes, which allow significant improvements in their photovoltaic performance. In recent years, MOFs have also attracted great attention in the arena of Perovskite solar cells. The use of MOF nanocrystals opens up new ways of enhancing the crystallinity and morphological domains of the Perovskite thin films. The incorporation of porous MOF structures with 3-D Perovskite material is likely to affect the important features of such cells including their stability, absorption coefficient, and carrier mobility.

The extension of the applications of MOFs in photovoltaics is a research activity that has attracted extensive attention during the past decade. Nonetheless, the photovoltaic applications of MOFs are still in early stages [17-21]. Most of reports available discuss about the generation of photocurrent from MOF based half cells. Some researchers have proposed the designing of fully devised MOFs solar cells but such directions have yet to find solutions to the limitation of poor performance. This review brings in limelight the different properties of MOFs which can be exploited for its successful application in photovoltaics over the years. Furthermore, it describes the areas which are to be targeted to improve the MOF component in its successful utilization of generating power efficient photovoltaic devices as discussed under following heads:

2. Photovoltaic applications of metal-organic frameworks (MOFs)

As discussed earlier also, MOFs prominently act as insulators at low temperatures. However, in some studies, certain conditions and combinations (of metal center and linkers) have been identified that articulated the possible semiconducting nature of MOFs. In one of the first research works on this direction, Xamena et al. studied MOF-5 and proposed the possible reasons of its semiconducting properties [22]. These authors experimentally studied properties like charge density and electrostatic potential of MOF-5. Based on the current-voltage (I-V) behavior and photocurrent spectrum, they reported that MOF-5 could yield quantum dot like properties, which were ascribed to presence of ZnO metal clusters. The optical properties of MOF-5 were tuned based on the presence of inorganic semiconductor ZnO quantum entities (for example, dots or wires) in proximity with organic molecules. As such, the above report was the starting point that encouraged subsequent explorations to investigate the potential of various other MOFs in photovoltaics.

Alvaro et al. [23] also conducted studies to investigate the semiconducting properties of MOF-5. In their work, MOF-5/DMF paste was deposited on a transparent ITO (indium tin oxide) electrode which was then used in a photovoltaic solar cell, also containing a platinum counter electrode. As analyzed with a solar simulator (525 W, AM 1.5 filter), the open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), and fill factor (FF) of the MOF-5/DMF containing cell were assessed as 0.33 V, 0.7 μA, and 44%, respectively. The research group of Kobayashi has studied a dithiolene based MOF known as Cu[Ni(pdt)$_2$] MOF (where pdt^{2-} = pyrazine-2,3-dithiolate) for its p-type semiconductivity, optical band gap, and redox behaviour [24]. The strong metal-ligand orbital interactions in the above MOF were accounted for the observed electronic conductivity. Based on the diffuse reflectance spectral studies, Cu[Ni(pdt)$_2$] was proposed to possess an optical band gap value of around 2 eV. Furthermore, it was also established that Cu[Ni(pdt)$_2$] could deliver a conductivity of the range of 10^{-8}S/cm (measured at room temperature conditions). Interestingly, the doping of I$_2$ was reported to cause an enhancement in the above conductivity to 4 orders of magnitude, while there was no effect on the porosity of the MOF. Al$_2$(BDC)$_3$ MOF was also studied for its possible semiconductivity [25]. Al$_2$(BDC)$_3$ has a large porosity which allowed this MOF to be incorporate photoactive guests (e.g., (1,4-dimethoxybenzene)) within its intra crystalline space. Authors constructed a dye sensitized solar cell with the above MOF consisting of gold as a counter electrode. The values of important DSSC performance parameters, for example short circuit current density (J_{SC}) and open circuit potential (V_{OC}) were estimated as 36.2 μA/cm^2 and 361.339 mV, respectively. The band gap of MOFs such as that of Zn-MOFs, can be tuned by certain strategies [26]. These strategies may include a change in the cluster size of SBU, i.e., secondary building unit (SBU) or by selecting organic linkers of varying conjugated bonds. Usman et al. [27] have recently proposed the self-assembly of [Sr(Hbtc)(H$_2$O)] MOF which is a 3D framework having a the band gap of 2.3 eV. Interestingly, this value of band gap is comparable to other common semiconductors including CdSe, CdTe, ZnTe, and GaP.

Though certain MOFs have been reported for their optical band gaps, it is not a clear indication of their conductivity or semiconductivity. It may not be possible to realize the charge delocalization in MOFs with desired efficiency. Thus, MOFs may not be termed as actual semiconductors. Their main role in photovoltaics or in DSSCs should be the absorption of photons just like the plant chromoplasts.

3. Optical and charge transfer characteristics of MOFs

Optical response of any material through band gap modification is a critical experimental need to develop the material for photovoltaic applications. Such modifications in the optical responses can be achieved via rational functionalization of linking units; for example in case of titanium-based MOFs (MIL-125 as an example) [28]. Studies with density function theory (DFT) based computations have revealed that the optical characteristics of MIL-125 can be tailored so as to allow the light absorption with this material in the visible light region once a rational selection is ensured for the substituent group of the aromatic linker. Kent et al. [29] have reported the building of photoactive Ru(II)-bpy (bpy = 2,2'-bipyridine) and then prepared some microscale

MOFs which were found to possess "antenna" like characteristics and thus offered high efficiencies of electron transfer (>98%). Such an efficient rate of electron transfer at the MOF/solution interface could be demonstrated on the basis of both oxidative and reductive types of quenching in the photoluminescence intensities of MOFs. The reason for the process was associated with the fast rate of energy migration occurring over several of hundreds nanometers. The above research work was a proof that the MOFs can serve as an attractive material for the harvesting the light.

Zn-based MOF is another example of a as host framework wherein the incorporation of methyl viologen as a guest molecule was reported to improve the overall electron transfer characteristics [30]. Followed by this, various other strategies have been reported to address of challenges of charge recombination. These methods can be listed as the manipulation of structural arrays, adjustments in the donor–acceptor connections, and making variation within the distances between the radical ion pairs. Methyl viologen loaded Zn-MOF was claimed as one of the first MOF driven material with host–guest type of interaction capability, leading to the phenomenon of photo and thermally induced electron transfer.

Cd/Zn-based MOFs were investigated for their optical properties with the help of simulation software. The conditions of their synthesis, chemical bonding, electronic structure, environmental stability, and potential usability in photovoltaic were investigated [31]. Computational approaches with pseudo-potential generalized gradient approximation-Perdew, Ernzerhof (GGA-PBE), and Burke functions were taken up with the aid of the Vienna ab initio simulation package (VASP) code. The results demonstrated that the optical features and properties of Cd/Zn-based MOF-5 (as analyzed on the CASTEP module, Material Studio 5.0) should follow a semiconductor-type behavior with an estimated band gap of the magnitude of about 3.6 eV.

4. Light harvesting potential of MOFs

The linker characteristics define the light harvesting capabilities of MOFs to a great extent. A large number of the linkers used for the synthesis of different MOFs are primarily capable to absorb light from ultraviolet to blue regions. In recent years, researchers have proposed the synthesis of MOFs with special linkers, such as 2,5-dihydroxyterephthalic acid (H$_4$DOBDC) and 2-amino terephthalic acid (NH$_2$-bdc) which displayed exciting potential towards the harvesting of light even from visible spectrum [32]. The generation of electron-hole pairs in MOFs is associated with the presence of the conjugated π-electrons and their related transition which take place from chromophores to metal centres. For instance, H$_4$DOBDC has been used in the synthesis of a p-type semiconducting MOF, known as NTU-9 (a Ti(IV) based MOF). This MOF has been found characterized with capability of visible-light driven photo-response [33]. NTU-9 MOF favours strong light absorption over visible spectrum region (e.g., absorption approaching to 750 nm) and possesses a bandgap of 1.72 eV. The photo-electrochemical studies with NTU-9 have revealed its photoactivity under the illumination of visible light (wavelength > 400 nm).

Another MOF, named as UiO-66-NH$_2$, has been synthesized via the coordination ofZr$_6$O$_{32}$ units with NH$_2$-bdc (or also known as 2-aminoterephthalate). This MOF was also found to have potential towards the light absorption from the visible region [34]. The researchers carried out UV-vis diffuse reflectance studies and characterized the above MOF to possess an optical bandgap of around 2.75 eV (measured at an absorption band-edge of 450 nm).

As already explained, the choice of organic linker plays a crucial role on the light absorption behaviour of many MOFs. Apart from this, the inorganic units can also play their role. For instance, inorganic Fe$_3$-μ_3-oxo clusters were reported to assist in improving the absorption of visible light absorption from Fe(III)-MOF [35]. Importantly, the researchers in the above study observed the Fe(III)-MOFs to possess the capability of absorbing photons with a comparable efficiency to that of the commonly used semiconductor based photocatalysts, including TiO$_2$. The degradation of Rhodamine 6G in the aqueous solutions was taken as an evidence towards an efficient photocatalytic performance of the Fe(III)-MOFs.

The broadening of light absorption capability of MOFs has also been attempted by adopting the strategy of forming their composites with other suitable and compatible materials, which may be listed as graphene, quantum dots, carbon nanotubes, and semiconductor metal oxide nanoparticles. As an example, a ZnO@ZIF-8 heterostructure was found to possess a noticeable photo-electrochemical response [36]. The heterostructure was synthesized by utilizing ZnO nanorods, which acted both as a source of Zn^{2+} ions and a template in order to facilitate the formation of ZIF-8. The above template based method was found as an advantageous experimental approach to realize the synthesis of core−shell heterostructures. As an added advantage, the method could facilitate a straightforward control on the size and morphology of the final product. The excitation of the core-shell material with light of <380 nm resulted in the generation of photo generated carriers within the ZnO nanostructure. These charge carriers were suggested to get recombined or they could migrate to the surface-trapping sites as well so as to interact with redox species which were present over the surface or within the solution. As such, ZnO@ZIF-8 nanorod system was found useful to enhance the photocurrent response, attributable to the presence of ZIF-8 which minimized the losses pertaining to recombination of charge carriers.

Jin et al [37] have investigated the light harvesting features of some porphyrin-MOFs. The coupling of these MOFs with CdSe/ZnS (core/shell) QDs (quantum dots) was useful to further enhance the light harvesting capability. The above group of researchers articulated the transfer of photon-generated excitons (within the QDs) toward the MOFs and that too in in resonance energy form. The successful energy transfer from QDs to MOF was verified with the aid of photoluminescence (PL) studies. The above type of QD-MOF arrangements can allow the absorption of light even in spectral regions over which the MOFs alone would sustain little absorptivity [38]. The process governing the absorption of light by the QD-MOF hybrids was explained with the help of time-resolved emission studies. The first step of the process involved the photo excitation of QDs, which is followed, as a second step, by the transfer of energy to the MOFs. The energy transfer efficiency was assessed to be greater than 80%.

5.   MOFs functioning as quasi-solid electrolyte in DSSCs

The enhancement in a DSSC performance can be achieved by using MOF based electrolytes in quasi-solid DSSCs. MOF skeleton-based gel electrolytes have been investigated to seek the development of highly efficient quasi-solid-state DSSCs [39]. The reaction of Al^{3+} with 1,3,5-benzenetricarboxylate (H_3BTC) could yield the synthesis of a sponge-like porous material, termed as metal–organic gel (MOG). The above synthesized material exhibited an excellent ability to allow the accommodation of a variety of common electrolyte ingredients. Hence, the MOG based electrolytes could penetrate within the photoanode film so as to facilitate a good interfacial contact. When experimental conditions were optimized, the gel-state cells displayed improved short circuit current density. Hence, a high conversion efficiency of greater than 8.60% was achievable.

6.   MOFs for the development of Counter and Working electrodes of DSSCs

In recent past, researchers have explored the applications of MOFs to develop efficient electrode systems for DSSCs. Apart from photoanodes, the use of MOFs in counter electrodes has also been taken up with equal interest. To cite an example, the idea of a Pt-free DSSC was floated by demonstrating the use of ZIF-67 [40]. In this work, the MOF was first synthesized via surfactant-assisted method followed by its conversion to cobalt sulfide (CoS) nanoparticles. ZIF-67 was composed of cobalt cations (metal source) and 2-methylimidazole (organic linker). It was first converted to yield CoO_x having a pore size of 0.34 nm; the desired product CoS was then prepared via sulfide conversion. The use of the CoS as a novel material to form counter electrode proved useful to yield a solar-to-electricity conversion efficiency of about 8.1%. Zinc-imidazolate framework-8 (ZIF-8) has been used for interfacial modification of DSSCs [41]. This post-treatment approach was found to allow useful enhancement in the open circuit potential (V_{oc}) of the cell. In the above work, TiO_2 interface was first modified with sensitizer dyes, over which the layers of ZIF-8 were grown. The MOF modified surface was again subjected to dye-sensitization. Thus prepared TiO_2/dye/ZIF-8/dye surface was then tested for photovoltaic performance. These researchers summarized that a growth time of ZIF-8 for seven minutes and the two-time post-treatment of photoanode could yield optimum photovoltaic performance. The enhancement in V_{oc} and electron lifetimes was accounted for by the energy barrier effect of ZIF-8. It was possible that absorption of dyes over ZIF-8 layer could have led to a negative influence over the electron injection. Nonetheless, the very first step of pre-anchoring a layer of dye over the TiO_2 surface contributed in maintaining the efficiency of the photocurrent output. As an important benefit, more number of dyes molecules adsorbed within the porous ZIF-8 network ultimately could contribute to improve the values of short-circuit photocurrent (J_{SC}).

MOF-5 and MOF-177 films have also been investigated as the working electrodes for applications in the dye sensitized solar cells. Feldblyum and coworkers have investigated the photo-electrochemical response of MOF-5 and MOF-177 [42]. They grew the MOF films on tin oxide substrates (fluorine-doped) which were also having readily available terminal carboxylic acid functional groups. This electrochemical cell was constructed by using platinum wire as the counter and Ag/Ag^+ as the quasi-reference electrodes. The illumination of the above

MOF film with white light was seen to produce significant photocurrents. Note that acetonitrile was used as an electrolyte in the above study. In general, the TiO_2-based DSSCs deliver V_{OC} values of the order of 0.7-0.8 V. There is a need to further improve these values to a theoretical maximum value of 0.95 V. In this context also, the MOF-based working electrodes have been proven useful. Their use is advocated to improve the open circuit voltage of dye-sensitized solar cells. For instance, the layers of zinc imidazolate framework (ZIF-8) were coated over a TiO_2 electrode [43]. The electrode was characterized with current-voltage (I–V) studies, and the researchers found an increase in the value of Voc, which was accounted for by the reduction in the events of interfacial charge recombination. The authors further observed a linear dependency of V_{OC} values over the thickness of the ZIF-8 coating layers. Hence, the magnitude of the V_{OC} values was rationally controlled by regulating the growth time of the MOF layer. As the results of the above research indicated, an initial V_{OC} value of 741 with the use of plain TiO_2 photoanode could be improved to 796 mV after the putting on ZIF-8 layers, grown for 40 minutes. As a limitation of the design, the above modification of TiO_2 electrode with ZIF-8 caused a decrease in the short circuit current because the modified TiO_2/ZIF-8 electrode restricted the injection or transfer of electrons from the dye molecules into the CB (conduction band) edge of the TiO_2. The layer-by-layer (LBL) film assembly technique was proposed to grow the layers of a copper-based MOF, whose potential as a light-absorbing layer in the TiO_2-based solar cells was then investigated [44]. The conductivity of the layer and the efficiency of charge-transfer reaction across the interface of TiO_2/MOF/electrolyte were further enhanced through iodine doping. The electron transportation property of the above design was found dependent upon the appropriateness of the assembly of MOF over the TiO_2 film. The researchers performed several layer deposition of the Cu-MOF film to cover the TiO_2 surface. Experimental evidences were presented to prove that Cu-MOF did not lose its main structural properties even after the process of film coating. The authors further assessed the photovoltaic performance of the resulting electrodes, having different film thicknesses. The existence of energy gap between HOMO and LUMO within the iodine-doped copper MOFs was exploited to fabricate a liquid junction photovoltaic cell. Some researchers have also used copper-based MOFs in order to sensitize the TiO_2-MWCNTs/FTO composite photoanode films [45]. Here again, the conductivity of Cu-MOF was improved via iodine doping. An enhanced conductivity of the modified Cu-MOF resulted in the attainment of efficient power conversion efficiency; showing almost 60% increase compared to the reference cells. The above study also elaborated the current-voltage profiles of the cells in following configurations: (i) FTO-glass/TiO_2/electrolyte/Pt, (ii) FTO-glass/TiO_2/Cu-MOF/electrolyte/Pt, and (iii) FTO-glass/TiO_2-MWCNTs/Cu-MOF/electrolyte/Pt. Based on the favorable results obtained, the researchers of the above study articulated that an optimized selection of the type of MOF and the thickness of its layering can improve the overall photovoltaic characteristics.

A number of researchers have floated the idea of utilizing MOFs as precursors to obtain other useful semiconducting nanomaterials and nanostructures, which would show better photovoltaic potential than the conventionally processed ones. In this context, Li *et al.* proposed the synthesis of hierarchical ZnO microparticles (300–500 nm) as MOF-5 precursor was allowed to decompose under high temperature [46]. These

ZnO particles were used to form a scattering layer over photoanode of a DSSC. The application of such bilayer structures proved useful as an optical scattering layer, which in turn, was responsible for enhancing the capture and retainment of incident photons. Further, it should be noted that the sub micrometer size particles should be better alternatives to function as optical scattering layer. When compared to a reference cell (FTO/ZnO), the use of ZnO parallelepipeds (obtained by calcination of MOF-5 at 525 °C) allowed the realization of a cell (FTO/ZnO/MOF-5) that delivered around 16.5% improvement in the power conversion efficiency.

7. MOFs as materials in Perovskite solar cells

Perovskite solar cells are amongst the fast-advancing solar cell technologies in recent years. Their design essentially involves a perovskite structure possessing a light harvesting active layer. The hybrid organic or inorganic Pb (lead) or Sn (tin) halides-based materials are commonly used to design perovskite cells. The application of mesoporous structures is important to develop solid-state perovskite that can achieve an efficiency exceeding 10%. Some of the MOFs bear matching topologies as those of inorganic perovskites. Further, some MOFs can also possess other interesting properties, e.g., the cohabitation of ferroelectric and the magnetic ordering. The above favorable features of MOFs have been integrated in newer types of Perovskite solar cells. For instance, a small crystal sized MOF-525 was incorporated within a perovskite structure. The resulting structural composite inflicted a significant feature enhancement, i.e., in terms of crystallinity and morphology of the perovskite thin film [47]. When 5 v/v% suspension of MOF-525 (20 mg/mL) was added, the use of the resulting MOF/perovskite composite in a solar was found to improve the following device characteristics: 12% enhancement of average power conversion efficiency, achievement of a high value of open-circuit voltage (0.93 V), a high short-circuit current density (23.04 mA/cm^2), and a fill factor (FF) of 0.60. The improvement in the above key cell parameters meant that the MOF modified perovskite cell yielded the power conversion efficiency in excess of 10%. Vinogradov et al. have also worked on the development of MOF inspired perovskite solar cells [48]. They reported the application of a hydrothermally prepared TiO_2–MIL-125 composite. In this research work, a depleted type of perovskite/TiO_2–MOF (a heterojunction) solar cell was assembled, which delivered a power conversion efficiency of 6.4%. The mixing of 3% of MIL-125 in TiO_2 was enough to deliver the enhanced values of V_{OC} (0.85 mV), J_{SC} (10.9 mA/cm^2), FF (0.69), and photocurrent response (39 µA/cm^2). The density functional theory (DFT) simulations have also been performed by some researchers to put forth the evidences toward the increasing significance of MOFs in the development of new age perovskite solar cells [49].

8. Overview of literature on MOF-Based DSSCs

The development of DSSCs has experienced various stages of research and continues improvements. Of the different configurations of DSSCs, the use of Porphyrins as photosensitizers has allowed the achievement of sufficiently high cell efficiencies. Nonetheless, the current DSSC technology faces a serious limitation of undesired charge recombination. Such unwanted charge recombination take place between the injected electrons and the acceptor molecules/species present in the redox species containing electrolyte. In case of latest or modern

porphyrin molecular structure based DSSCs, researchers are attempting to select/synthesize suitable molecularly engineered structures that can control the recombination events. The harvesting of solar spectrum, just beyond the UV region, has also been considered critical to improve the solar cell efficiencies. In this context, photosensitizers like green grass, organogelator materials with relatively low molecular mass, functionalized organic dyes, special metal oxide nanostructures (e.g., ZnO rectangular prisms), nanorods, and metal-organic frameworks have also been developed as highly efficient options to help broadening the absorption of light from UV to visible to NIR ranges. The application of semiconductor nanocrystals, such as metal di and mono chalcogenides (e.g., MoS_2, WS_2, CdS, PbS, CdSe, PbSe, etc.), graphene and carbon dots, and carbon nanotubes, has also been demonstrated to the design better electrode systems in the direction of development of modern solar cells. The attraction or the rate of transfer of charge carriers toward the opposite electrodes is one of the main factors to govern and decide the overall photocurrent accumulation efficiency of the dye sensitized solar cells. This desirable property of a DSSC is achieved with the use of special electrode materials like porous and nanocrystalline materials. Such electrode materials help in development of photoanodes with reduced charge recombination losses when compared to the use of other electrode materials. The use of porous and nanocrystalline materials can enhance the charge separation at semiconductor-electrolyte interface.

MOFs are known as one of the most porous structures known in the modern material science era, Because of their highly porous network, MOFs have attracted wide research attention in diverse technological applications, which range from gas storage and separation, catalysis, chemo- and bio-sensing, drug loading and drug delivery, etc. MOFs can also absorb light and they can play a vital role in encompassing other guest molecules. As a result, MOFs and their composite structures have attracted noteworthy research consideration in the field of photovoltaics as well. In the field of DSSCs also, MOFs have been explored in different ways, as elaborated in Table 1. A majority of those examples points out toward the usefulness of MOFs in the designing of better photoanodes and counter electrodes. In fact, MOFs have been converted to other metal oxide materials through pyrolysis, which have been proven better counter electrode materials than the normally processed similar types of materials. The deployment of MOFs in the development of photoanodes has also been reported useful to improve the design of DSSCs in terms of parameters like open circuit voltage (V_{OC}) and short circuit current. An improvement of these two important cell parameters has a direct beneficiary effect on the power conversion efficiency of a DSSC.

Table 1: Summary of applications of MOFs in DSSCs

Material composition	Performance Parameters				Type of component
	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF	η (%)	
MOF- converted in to cobalt sulfide nanoparticles	14.7	784	0.71	8.1	Counter electrode
FTO/TiO$_2$/Cu-MOFs	1.22	430	0.51	0.27	Photoanode
FTO/TiO$_2$/MWCNT/Cu-MOFs	1.95	480	0.51	0.46	Photoanode
DMB@ Al$_2$(BDC)$_3$	36.20	361	0.40	-	Photoanode
ZIF-8/TiO$_2$	9.67	756	0.71	5.21	Photoanode
ZnO parallelepipeds prepared from MOF	8.13	663	0.68	3.67	Scattering layer of photoanode
Zr-based porphyrin MOF (MOF-525)	23.04	930	0.60	12	Perovskite thin film hetero-junction
Perovskite/TiO$_2$/MIL-125 heterojunction	10.9	850	0.69	6.4	Hetero-junction

The application of MOFs in the development of counter electrodes helps in enhancing the overall external surface areas, while also improving roughness factors. These two factors make the MOF based counter electrodes a better alternative than the conventionally used Platinum electrodes. The replacement of Platinum has also been advocated with an aim of developing new ecofriendly Pt-free dye sensitized solar cells. MOFs are also known for their high chemical and thermal stabilities, which should encourage the development of environmentally sustainable and long-shelf life DSSCs when compared to other types of dye sensitized solar cell systems.

9. Applications of MOF composite in DSSCs and allied applications

In light of interesting features of MOFs with respect to their photovoltaic applications, researchers have further extended their efforts to augment the light-harvesting properties of MOFs by combining them with other functional advanced materials. As an example of this, MOFs have been combined with quantum dots (QDs). MOF-QD composites offer certain important advantages. MOFs provide higher stability to the QDs, while QDs could harvest more number of photons due to quantum confinement in them. MOF-QD hybrids have been proposed for energy storage, energy production, and photovoltaics. QD/MOF composites based energy storage devices show higher surface area and deliver superior performance. Wakaoka et *al.* [50] have reported the

encapsulation of CdSe QDs in the pores of MIL-101(Al)-NH$_2$ MOF. Different fluorescent emissions of the above nanocomposite were possible. This was possible by varying the particle sizes. Buso and co-workers [51] also worked on the preparation of a QD/MOF-5 hybrid system for the size selective detection of thiol. They used a variety of QDs, such as CdSe, CdS, Cd$_{0.5}$Zn$_{0.5}$S, and ZnS QDs. As the ethane-thiol molecules entered into the MOF pores, they diffused through the network and ultimately reached to the surface of the embedded QDs to react and yield a quenching behavior. Lu *et al.* [52] have reported the incorporation of PVP-capped nanoparticles of CdSe and CdTe QDs into the ZIF-8 matrix. A two-step growth coupled with spin-coating method was used for the deposition of catalytic, magnetic and semiconductor QD/MOF hybrid thin films. The above composite was suggested to be a futuristic optical sensor which would be suitable for further commercialization. CdSe/Eu-MOF composite has been used for detection of different categories of explosives [53]. A carbon QD (CQD)/ZIF-8 composite, synthesized by incorporating poly (ethylenimine)-capped CQDs into the MOF matrix, has been used for the sensing of copper on the basis of quenching phenomenon.

Apart from many allied applications, MOF-QD composites have also been explored for their photoactivity. A CdS/MIL-101 composite has been photo-deposited in presence of 0.5 wt% of Pt particles to synthesize a ternary type of Pt@CdS/MIL-101 composite material that was investigated for the photocatalytic evolution of hydrogen under the influence of visible light irradiation [54]. CdS/UiO-66-NH$_2$ has been used for achieving the visible-light assisted oxidation of benzyl alcohol in to benzaldehyde, wherein molecular oxygen was suggested to act as the oxidant [55]. The composite had better photocatalytic performance than bare framework, commercially available CdS, as well as their physical mixture. The results proved that the interface between the two components was very important factor to boost the photocatalytic activity of CdS. The encapsulation of CdS QDs within ZAVA (i.e., Zn based low molecular weight hydrogel) has been reported to produce CdS@ZAVA-Cl MOFs with fluorescent properties [56]. This composite's photocatalytic ability to generate hydrogen gas was evaluated under irradiation with visible light. Platinum was used as a co-catalyst and ethanol acted as a sacrificial reagent. To summarize, the above composite showed a stable photocatalytic activity for 12 cycles. Li *et al.* [57] have proposed the synthesis of a core-shell Cu$_3$(BTC)$_2$@TiO$_2$ composite, which displayed high photocatalytic reduction efficiency for CO$_2$ and CH$_4$. Compared to bare TiO$_2$, the composite could drive 5 times higher conversion rates for photocatalytic production of CH$_4$ from CO$_2$. The above composite was also found selective for hydrogen as compared to other individual components. MOF-QD composites deliver light harvesting properties and catalyze the conversion of solar energy into electrical/chemical energy. Jin *et al.* [58] have reported the use of QD@MOF composites for efficient light-harvesting. They reported the mechanism of the energy transfer from semiconductor QDs to the MOF counterpart. Fluorescence lifetimes of QD were found shortened after their coating on the MOF surface. As such, the above research demonstrated that a proper selection of MOF composition or QD size can allow control on the light harvesting efficiency of the resulting composite. A close proximity of the QD with MOF permitted highly efficient energy transfer. The charge

transfer characteristics and light-harvesting capabilities of MOF-QD composites are also opening up new opportunities in quantum dot DSSCs.

Recently, a MOF-QD nanocomposite has been reported using CdTe QDs and a titanium-based MOF known as NTU-9 [59]. The CdTe/NTU-9 composite displayed a broad light absorption and could yield rapid (1/2 hours) and visible light-based photocatalytic removal of a dye (rhodamine 6G). The application of the composite as a photoanode material in a QD (quantum dot) sensitized solar cell (QDSSC) was also investigated. A 1.5% improvement relative to the QD alone was reported in the power conversion efficiency. The above effect was associated with some material features, such as broadened light absorption, chemical and thermal stability, and good photocatalytic and photovoltaic characteristics. A europium-MOF (Eu-MOF) has also been used in conjunction with CdTe QDs to develop a new type of photoanode system [60]. A DSSC made with Eu-MOF/CdTe composite provided an enhancement in the short circuit current density, e.g., from 19.8 (CdTe QD alone) to 28.45 mA/cm² (Eu-MOF/CdTe). The power conversion efficiency of the Eu-MOF/CdTe based DSSC was reported to be 3.02%.

10. Emergence of MOF-Carbon (Graphene/Carbon Nanotubes) in energy and solar cell applications

The addition or incorporation of graphene and carbon nanotubes (CNTs) into titanium dioxide (TiO₂) film in a DSSC has been suggested to enable more efficient electron transfer as a result of excellent electrical conduction properties of graphene and CNTs [61]. The formation of composites of MOFs with graphene and CNTs is also useful in enhancing the electric field of the devices. As a result of synergistic and added properties of MOFs and graphene/CNTs, one can expect accelerated electron transfer rate, and subsequently an enhanced power conversion efficiency of the device.

10.1. Composites of MOFs with Graphene

MOFs have been acknowledged as intriguing photosensitizer materials on account of their immensely-ordered structures and fascinating light-harvesting properties. MOFs can substitute dye molecules to sensitize TiO₂ in dye sensitized solar cells (DSSCs) by serving two-fold functions, i.e., (i) absorption of light and (ii) injection of electrons into the TiO₂ film. Many MOFs, reported in literature, have been documented to possess an insulating nature. In some recent years, some researchers have proposed ideas to introduce electrical conduction in MOFs. For instance, the co-presence of graphene in MOF matrices can significantly augment the electrical conductivity of the resulting composite materials.

Graphene and graphene-based materials have attracted immense attention due to the extraordinary structural, morphological, mechanical, catalytic, and electronic properties of their 1-atom-thick sheets. Graphite is a common source of graphene. It can be visualized as a 3D crystal comprising of graphene layers. Various attempts to convert graphite into graphene layers have been made. Most of such research reports advocates the

use of graphite oxide (GO) as the starting material. Graphene is typically characterized with a layered structure made up with a non-stoichiometric chemical composition. Lately, graphene has been very popularly used to prepare and design numerous other types of nanocomposites which display improved optical and electronic properties. The layers in graphene are stacked (i.e., joined) together with an approximate interlayer distance from 6-12 Å, depending upon the extent of hydration. In one of the recent works, Kaur et al. have reported the application of a MOF-graphene composite as a promising photo-sensitizer material in DSSCs [62].

10.2. Composites of MOFs with carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) are widely acknowledged for their hallmarks like high electrical and thermal conductivities, paired with low densities and high mechanical robustness. So far, a limited number of examples of MOF-CNT composites have been developed and that too with prime focus on hydrogen storage, supercapacitors, and humidity sensors.

MOF-CNT composites can be produced in distinct forms. On one hand, intensely intergrown composites of MOF particles that have crystallized around CNTs can be used as electrode materials in batteries or in thermoelectric applications. On the other hand, thin films of the composites can be embedded on individual substrates. Electrochemical ORR (oxygen reduction reaction) particularly in the basic media is a principal reaction, often encountered when studying the electrochemical energy conversion and storage devices. Such device may include fuel cells, metal-air batteries, and chlor-alkali electrolysis cells with air-depolarized cathode. Hence, there is a substantial interest in the synthesis of electrocatalysts that can exhibit high performance and should remarkably stimulate the kinetics of ORR. The network formed around MOFs and CNTs appreciably promotes the electrical conductivity (i.e., charge transfer) as well as the stability of ORR systems. The process of gas diffusion through the orderly-porous MOF structure has been accounted for by the above observed advantageous properties.

It has been suggested that the inclusion of carbon nanotubes (single walled or multi walled CNTs) into the TiO_2 film electrode of a DSSC can lead to even more prominent electron transfer because of the contribution from CNTs which have then own outstanding electrical properties [63]. It has also been verified that insertion of CNTs into solar cell electrodes causes an enhancement in the electric field of the devices. As a result of the accelerated electron transfer rate after the introduction of CNTs, the overall power-conversion efficiency of the devices is augmented. As an example, Lee et al. introduced CNTs into a Cu-MOF sensitized solar cell with an objective to increase the functioning of the cell [64]. The addition of CNTs contributed to boost the power-conversion efficiency of the cell by approximately 60%. The mixing of CNTs improved the electric field of the cell. In fact, the presence of CNTs ensured a higher intensity of electric field, accounted for by the improved rate of charge-separation at the TiO_2/MOF/electrolyte interface of the solar cell. The improved electric field

accelerated the charge-transfer process and thus reduced the recombination process. The electron-transfer rate was augmented due to the adaptable functionalities of the MWCNTs.

The literature review on the subject has revealed different aspects where MOFs and its composites could be successfully exploited in Photovoltaics. However, there are only few important facts about the status of MOF-Carbon nanostructure based DSSCs. The research in this particular domain is still in early stages, though some researchers have successfully demonstrated an excellent utility of MOF-Carbon in improving several performance parameters of DSSCs, which is the area of further research that is to be exploited in future to generate more efficient and economical photovoltaic structures.

References:

1. Du, M., Z.-H. Zhang, L.-F. Tang, X.-G. Wang, X.-J. Zhao and S. R. Batten (2007). Molecular Tectonics of Metal–Organic Frameworks (MOFs): A Rational Design Strategy for Unusual Mixed-Connected Network Topologies. *Chemistry – A European Journal,* **13**(9): 2578-2586.

2. He, J., J.-X. Zhang, G.-P. Tan, Y.-G. Yin, D. Zhang and M.-H. Hu (2007). Second Ligand-Directed Assembly of Photoluminescent Zn(II) Coordination Frameworks. *Crystal Growth & Design*, **7**(8): 1508-1513.

3. Zhang, H.-M., H. Wu, Y.-Y. Liu, J. Yang, D.-W. Kang and J.-F. Ma (2015). Syntheses, structures, gas adsorption and reversible iodine adsorption of two porous Cu(ii) MOFs. *CrystEngComm*, **17**(7): 1583-1590.

4. Wang, H., D. Zhang, D. Sun, Y. Chen, L.-F. Zhang, L. Tian, J. Jiang and Z.-H. Ni (2009). Co(II) Metal−Organic Frameworks (MOFs) Assembled from Asymmetric Semirigid Multicarboxylate Ligands: Synthesis, Crystal Structures, and Magnetic Properties. *Crystal Growth & Design,* **9**(12): 5273-5282.

5. Liu, S., L. Sun, F. Xu, J. Zhang, C. Jiao, F. Li, Z. Li, S. Wang, Z. Wang, X. Jiang, H. Zhou, L. Yang and C. Schick (2013). Nanosized Cu-MOFs induced by graphene oxide and enhanced gas storage capacity. *Energy & Environmental Science,* **6**(3): 818-823.

6. Meek, S. T., J. A. Greathouse and M. D. Allendorf (2011). Metal-Organic Frameworks: A Rapidly Growing Class of Versatile Nanoporous Materials. *Advanced Materials,* **23**(2): 249-267.

7. Howarth, A. J., M. J. Katz, T. C. Wang, A. E. Platero-Prats, K. W. Chapman, J. T. Hupp and O. K. Farha (2015). High Efficiency Adsorption and Removal of Selenate and Selenite from Water Using Metal–Organic Frameworks. *Journal of the American Chemical Society*, **137**(23): 7488-7494.

8. Luz, I., F. X. Llabrés i Xamena and A. Corma (2010). Bridging homogeneous and heterogeneous catalysis with MOFs: "Click" reactions with Cu-MOF catalysts. *Journal of Catalysis,* **276**(1): 134-140.

9. Ma, L., C. Abney and W. Lin (2009). Enantioselective catalysis with homochiral metal–organic

frameworks. *Chemical Society Reviews*, **38**(5): 1248-1256.

10. Wang, D., R. Huang, W. Liu, D. Sun and Z. Li (2014). Fe-Based MOFs for Photocatalytic CO_2 Reduction: Role of Coordination Unsaturated Sites and Dual Excitation Pathways. *ACS Catalysis,* **4**(12): 4254-4260.

11. Gascon, J., M. D. Hernández-Alonso, A. R. Almeida, G. P. M. van Klink, F. Kapteijn and G. Mul (2008). Isoreticular MOFs as Efficient Photocatalysts with Tunable Band Gap: An Operando FTIR Study of the Photoinduced Oxidation of Propylene. *ChemSusChem*, **1**(12): 981-983.

12. Li, Y., H. Xu, S. Ouyang and J. Ye (2016). Metal–organic frameworks for photocatalysis. *Physical Chemistry Chemical Physics*, **18**(11): 7563-7572.

13. Meyer, L. V., F. Schönfeld and K. Müller-Buschbaum (2014). Lanthanide based tuning of luminescence in MOFs and dense frameworks – from mono- and multimetal systems to sensors and films. *Chemical Communications*, **50**(60): 8093-8108.

14. Liu, W. and X.-B. Yin (2016). Metal–organic frameworks for electrochemical applications. *TrAC Trends in Analytical Chemistry,* **75**: 86-96.

15. Li, W.-J., M. Tu, R. Cao and R. A. Fischer (2016). Metal–organic framework thin films: electrochemical fabrication techniques and corresponding applications & perspectives. *Journal of Materials Chemistry A*, **4**(32): 12356-12369.

16. Patwardhan, S. and G. C. Schatz (2015). Theoretical Investigation of Charge Transfer in Metal Organic Frameworks for Electrochemical Device Applications. *The Journal of Physical Chemistry C,* **119**(43): 24238-24247.

17. Kaur, R., K.-H. Kim, A. K. Paul and A. Deep (2016). Recent advances in the photovoltaic applications of coordination polymers and metal organic frameworks. *Journal of Materials Chemistry A*, **4**(11): 3991-4002.

18. Ullman, A. M., J. W. Brown, M. E. Foster, F. Léonard, K. Leong, V. Stavila and M. D. Allendorf (2016). Transforming MOFs for Energy Applications Using the Guest@MOF Concept. *Inorganic Chemistry*, **55**(15): 7233-7249.

19. Lee, D. Y., D. V. Shinde, S. J. Yoon, K. N. Cho, W. Lee, N. K. Shrestha and S.-H. Han (2014). Cu-Based Metal–Organic Frameworks for Photovoltaic Application. *The Journal of Physical Chemistry C,* **118**(30): 16328-16334.

20. Kumar, P., V. Bansal, A. Deep and K.-H. Kim (2015). Synthesis and energy applications of metal organic frameworks. *Journal of Porous Materials,* **22**(2): 413-424.

21. Bildirir, H., V. G. Gregoriou, A. Avgeropoulos, U. Scherf and C. L. Chochos (2017). Porous organic polymers as emerging new materials for organic photovoltaic applications: current status and future

challenges. *Materials Horizons,* **4**(4): 546-556.

22. Llabrés i Xamena, F. X., A. Corma and H. Garcia (2007). Applications for Metal−Organic Frameworks (MOFs) as Quantum Dot Semiconductors. *The Journal of Physical Chemistry C,* **111**(1): 80-85.

23. Alvaro, M., E. Carbonell, B. Ferrer, F. X. Llabrés i Xamena and H. Garcia (2007). Semiconductor Behavior of a Metal-Organic Framework (MOF). *Chemistry – A European Journal*, **13**(18): 5106-5112.

24. Kobayashi, Y., B. Jacobs, M. D. Allendorf and J. R. Long (2010). Conductivity, Doping, and Redox Chemistry of a Microporous Dithiolene-Based Metal−Organic Framework. *Chemistry of Materials*, **22**(14): 4120-4122.

25. Lopez, H. A., A. Dhakshinamoorthy, B. Ferrer, P. Atienzar, M. Alvaro and H. Garcia (2011). Photochemical Response of Commercial MOFs: $Al_2(BDC)_3$ and Its Use As Active Material in Photovoltaic Devices. *The Journal of Physical Chemistry C,* **115**(45): 22200-22206.

26. Lu, W., Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle Iii, M. Bosch and H.-C. Zhou (2014). Tuning the structure and function of metal–organic frameworks via linker design. *Chemical Society Reviews,* **43**(16): 5561-5593.

27. Usman, M., S. Mendiratta, S. Batjargal, G. Haider, M. Hayashi, N. Rao Gade, J.-W. Chen, Y.-F. Chen and K.-L. Lu (2015). Semiconductor Behavior of a Three-Dimensional Strontium-Based Metal–Organic Framework. *ACS Applied Materials & Interfaces,* **7**(41): 22767-22774.

28. Hendon, C. H., D. Tiana, M. Fontecave, C. Sanchez, L. D'arras, C. Sassoye, L. Rozes, C. Mellot-Draznieks and A. Walsh (2013). Engineering the Optical Response of the Titanium-MIL-125 Metal–Organic Framework through Ligand Functionalization. *Journal of the American Chemical Society*, **135**(30): 10942-10945.

29. Kent, C. A., D. Liu, A. Ito, T. Zhang, M. K. Brennaman, T. J. Meyer and W. Lin (2013). Rapid energy transfer in non-porous metal–organic frameworks with caged Ru(bpy)32+ chromophores: oxygen trapping and luminescence quenching. *Journal of Materials Chemistry A,* **1**(47): 14982-14989.

30. Hu, S., L. Lv, S. Chen, M. You and Z. Fu (2016). Zn-MOF-Based Photoswitchable Dyad That Exhibits Photocontrolled Luminescence. *Crystal Growth & Design*, **16**(12): 6705-6708.

31. Yang, L.-M., P. Ravindran, P. Vajeeston and M. Tilset (2012). Properties of IRMOF-14 and its analogues M-IRMOF-14 (M = Cd, alkaline earth metals): electronic structure, structural stability, chemical bonding, and optical properties. *Physical Chemistry Chemical Physics*, **14**(14): 4713-4723.

32. Liang, R., L. Shen, F. Jing, W. Wu, N. Qin, R. Lin and L. Wu (2015). NH2-mediated indium metal–organic framework as a novel visible-light-driven photocatalyst for reduction of the aqueous Cr(VI). *Applied Catalysis B: Environmental*, **162**: 245-251.

33. Gao, J., J. Miao, P.-Z. Li, W. Y. Teng, L. Yang, Y. Zhao, B. Liu and Q. Zhang (2014). A p-type Ti(iv)-based metal–organic framework with visible-light photo-response. *Chemical Communications*, **50**(29): 3786-3788.

34. Shen, L., W. Wu, R. Liang, R. Lin and L. Wu (2013). Highly dispersed palladium nanoparticles anchored on UiO-66(NH2) metal-organic framework as a reusable and dual functional visible-light-driven photocatalyst. *Nanoscale,* **5**(19): 9374-9382.

35. Shi, L., T. Wang, H. Zhang, K. Chang, X. Meng, H. Liu and J. Ye (2015). An Amine-Functionalized Iron(III) Metal–Organic Framework as Efficient Visible-Light Photocatalyst for Cr(VI) Reduction. *Advanced Science*, **2**(3): 1500006.

36. Zhan, W.W., Q. Kuang, J.Z. Zhou, X.J. Kong, Z.X. Xie and L.S. Zheng (2013). Semiconductor@Metal–Organic Framework Core–Shell Heterostructures: A Case of ZnO@ZIF-8 Nanorods with Selective Photoelectrochemical Response. *Journal of the American Chemical Society,* **135**(5): 1926-1933.

37. Jin, S., H.-J. Son, O. K. Farha, G. P. Wiederrecht and J. T. Hupp (2013). Energy Transfer from Quantum Dots to Metal–Organic Frameworks for Enhanced Light Harvesting. *Journal of the American Chemical Society*, **135**(3): 955-958.

38. Aguilera-Sigalat, J. and D. Bradshaw (2016). Synthesis and applications of metal-organic framework–quantum dot (QD@MOF) composites. *Coordination Chemistry Reviews*, **307**: 267-291.

39. Fan, J., L. Li, H.-S. Rao, Q.-L. Yang, J. Zhang, H.-Y. Chen, L. Chen, D.-B. Kuang and C.-Y. Su (2014). A novel metal–organic gel based electrolyte for efficient quasi-solid-state dye-sensitized solar cells. *Journal of Materials Chemistry A*, **2**(37): 15406-15413.

40. Hsu, S.-H., C.-T. Li, H.-T. Chien, R. R. Salunkhe, N. Suzuki, Y. Yamauchi, K.-C. Ho and K. C. W. Wu (2014). Platinum-Free Counter Electrode Comprised of Metal-Organic-Framework (MOF)-Derived Cobalt Sulfide Nanoparticles for Efficient Dye-Sensitized Solar Cells (DSSCs). *Scientific Reports*, **4**: 6983.

41. Li, Y., C. Chen, X. Sun, J. Dou and M. Wei (2014). Metal–Organic Frameworks at Interfaces in Dye-Sensitized Solar Cells. *ChemSusChem*, **7**(9): 2469-2472.

42. Feldblyum, J. I., E. A. Keenan, A. J. Matzger and S. Maldonado (2012). Photoresponse Characteristics of Archetypal Metal–Organic Frameworks. *The Journal of Physical Chemistry C*, **116**(4): 3112-3121.

43. Li, Y., A. Pang, C. Wang and M. Wei (2011). Metal–organic frameworks: promising materials for improving the open circuit voltage of dye-sensitized solar cells. *Journal of Materials Chemistry*, **21**(43): 17259-17264.

44. Lee, D. Y., D. V. Shinde, S. J. Yoon, K. N. Cho, W. Lee, N. K. Shrestha and S.-H. Han (2014). Cu-Based Metal–Organic Frameworks for Photovoltaic Application. *The Journal of Physical Chemistry C,* **118**(30):

16328-16334.

45.　Lee, D. Y., C. Y. Shin, S. J. Yoon, H. Y. Lee, W. Lee, N. K. Shrestha, J. K. Lee and S.-H. Han (2014). Enhanced photovoltaic performance of Cu-based metal-organic frameworks sensitized solar cell by addition of carbon nanotubes. *Scientific Reports,* **4**: 3930.

46.　Li, Y., Z. Che, X. Sun, J. Dou and M. Wei (2014). Metal–organic framework derived hierarchical ZnO parallelepipeds as an efficient scattering layer in dye-sensitized solar cells. *Chemical Communications*, **50**(68): 9769-9772.

47.　Chang, T.-H., C.-W. Kung, H.-W. Chen, T.-Y. Huang, S.-Y. Kao, H.-C. Lu, M.-H. Lee, K. M. Boopathi, C.-W. Chu and K.-C. Ho (2015). Planar Heterojunction Perovskite Solar Cells Incorporating Metal–Organic Framework Nanocrystals. *Advanced Materials*, **27**(44): 7229-7235.

48.　Vinogradov, A. V., H. Zaake-Hertling, E. Hey-Hawkins, A. V. Agafonov, G. A. Seisenbaeva, V. G. Kessler and V. V. Vinogradov (2014). The first depleted heterojunction TiO2–MOF-based solar cell. *Chemical Communications,* **50**(71): 10210-10213.

49.　Ghosh, S., D. Di Sante and A. Stroppa (2015). Strain Tuning of Ferroelectric Polarization in Hybrid Organic Inorganic Perovskite Compounds. *The Journal of Physical Chemistry Letters, 6*(22): 4553-4559.

50.　Wakaoka, T., K. Hirai, K. Murayama, Y. Takano, H. Takagi, S. Furukawa and S. Kitagawa (2014). Confined synthesis of CdSe quantum dots in the pores of metal–organic frameworks. *Journal of Materials Chemistry C*, **2**(35): 7173-7175.

51.　Buso, D., J. Jasieniak, M. D. H. Lay, P. Schiavuta, P. Scopece, J. Laird, H. Amenitsch, A. J. Hill and P. Falcaro (2012). Highly Luminescent Metal–Organic Frameworks Through Quantum Dot Doping. *Small*, **8**(1): 80-88.

52.　Lu, G., S. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Qi, Y. Wang, X. Wang, S. Han, X. Liu, J. S. DuChene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S. C. J. Loo, W. D. Wei, Y. Yang, J. T. Hupp and F. Huo (2012). Imparting functionality to a metal–organic framework material by controlled nanoparticle encapsulation. *Nature Chemistry*, **4**(4): 310-316.

53.　Kaur, R., A. K. Paul and A. Deep (2014). Nanocomposite of europium organic framework and quantum dots for highly sensitive chemosensing of trinitrotoluene. *Forensic Science International*, **242**: 88-93.

54.　He, J., Z. Yan, J. Wang, J. Xie, L. Jiang, Y. Shi, F. Yuan, F. Yu and Y. Sun (2013). Significantly enhanced photocatalytic hydrogen evolution under visible light over CdS embedded on metal–organic frameworks. *Chemical Communications,* **49**(60): 6761-6763.

55.　Shen, L., S. Liang, W. Wu, R. Liang and L. Wu (2013). CdS-decorated UiO–66(NH2) nanocomposites fabricated by a facile photodeposition process: an efficient and stable visible-light-driven photocatalyst for

selective oxidation of alcohols. *Journal of Materials Chemistry A*, **1**(37): 11473-11482.

56. Saha, S., G. Das, J. Thote and R. Banerjee (2014). Photocatalytic Metal–Organic Framework from CdS Quantum Dot Incubated Luminescent Metallohydrogel. *Journal of the American Chemical Society*, **136**(42): 14845-14851.

57. Li, R., J. Hu, M. Deng, H. Wang, X. Wang, Y. Hu, H.-L. Jiang, J. Jiang, Q. Zhang, Y. Xie and Y. Xiong (2014). Integration of an Inorganic Semiconductor with a Metal–Organic Framework: A Platform for Enhanced Gaseous Photocatalytic Reactions. *Advanced Materials,* **26**(28): 4783-4788.

58. Jin, S., H.-J. Son, O. K. Farha, G. P. Wiederrecht and J. T. Hupp (2013). Energy Transfer from Quantum Dots to Metal–Organic Frameworks for Enhanced Light Harvesting. *Journal of the American Chemical Society*, **135**(3): 955-958.

59. Kaur, R., A. Rana, R. K. Singh, V. A. Chhabra, K.-H. Kim and A. Deep (2017). Efficient photocatalytic and photovoltaic applications with nanocomposites between CdTe QDs and an NTU-9 MOF. *RSC Advances*, **7**(46): 29015-29024.

60. Kaur, R., A. L. Sharma, K.-H. Kim and A. Deep (2017). A novel CdTe/Eu-MOF photoanode for application in quantum dot-sensitized solar cell to improve power conversion efficiency. *Journal of Industrial and Engineering Chemistry*, **53**: 77-81.

61. Kilic, B., S. Turkdogan, A. Astam, O. C. Ozer, M. Asgin, H. Cebeci, D. Urk and S. P. Mucur (2016). Preparation of Carbon Nanotube/TiO2 Mesoporous Hybrid Photoanode with Iron Pyrite (FeS2) Thin Films Counter Electrodes for Dye-Sensitized Solar Cell. *Scientific Reports*, **6**: 27052.

62. Kaur, R., K.-H. Kim and A. Deep (2017). A convenient electrolytic assembly of graphene-MOF composite thin film and its photoanodic application. *Applied Surface Science*, **396**: 1303-1309.

63. Yen, C.-Y., Y.-F. Lin, S.-H. Liao, C.-C. Weng, C.-C. Huang, Y.-H. Hsiao, C.-C. M. Ma, M.-C. Chang, H. Shao, M.-C. Tsai, C.-K. Hsieh, C.-H. Tsai and F.-B. Weng (2008). Preparation and properties of a carbon nanotube-based nanocomposite photoanode for dye-sensitized solar cells. *Nanotechnology*, **19**(37): 375305.

64. Lee, D. Y., C. Y. Shin, S. J. Yoon, H. Y. Lee, W. Lee, N. K. Shrestha, J. K. Lee and S.-H. Han (2014). Enhanced photovoltaic performance of Cu-based metal-organic frameworks sensitized solar cell by addition of carbon nanotubes. *Scientific Reports,* **4**: 3930.