



Sustaining energy systems using metal oxide composites as photocatalysts

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Article
Open Access
Published

ABSTRACT

Among the various types of metal organic frameworks (MOFs), the metal-oxide-based ones fulfill all the essential criteria such as strong bonding, organic linking units, and highly crystalline nature, properties required to be effective photocatalysts to serve environmental remediation. Moreover, the even spread of active sites and semiconductor properties make the MOFs ideal for absorbing irradiation from UV as well as visible light sources. Metal oxide composites with carbon based materials, especially, show high photocatalytic activity toward the degradation of organic dyes. Considering the relatively low cost of metal oxide semiconductors compared to pure metallic nanoparticles, metal oxide composites can provide a great alternative as photocatalysts especially considering the adjustable bandgaps and synergistic effects. Therefore, the metal oxide application as the photocatalysts in industry and technology in terms of techno-economic advantage is attracted. In this study, energy sustainability and solving carbon-related issues through metal oxide-based materials are discussed. This study aims to review metal oxide composites including metal oxide-MOFs and metal oxide-carbon material compositions as photocatalysts, application, merits in environmental and energy systems performances, and its contribution as an influential factor for sustainable development.

Keywords

- Metal-oxide
- Metal oxide-MOFs composition
- Metal oxide-carbon material composition
- Photocatalysts
- Storage systems materials
- Sensors
- Carbon dioxide reduction
- Environmental sustainability

Received: July 20, 2021; Revised: August 07, 2021; Accepted: August 12, 2021; Published: August 20, 2021

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1. Introduction

In a novel approach, MIL-125-NH₂ was doped with Ag₃VO₄ and Ag₂WO₄ NPs, which reduced the bandgap of the MIL from 2.65 eV to 2.56 eV and 2.27 eV, respectively. The organic dyes MB and RhB were degraded under visible light irradiation was more than the MIL by about 2.1 to 4.9 times [1]. Incorporation of Fe₃O₄ NPs into the MIL-100 by a solvothermal process afforded core/shell encapsulation. The as-prepared Fe₃O₄@MIL-100, due to its magnetic property, permitted easy recovery of the photocatalysts from the reaction medium in the breakdown of MB dye [2]. Another semiconductor metal oxide ZnO, has been under research for potential photocatalytic applications as part of MOF composites. ZnO@MOF-46 and ZnO@ZIF-8 have been investigated as potential candidates for wastewater treatment to remove MB and Cr(VI), respectively. In the case of ZnO@MOF-46 photocatalyst, the role of °OH was prominent in accelerating the decolorization of MB. The dye was degraded up to 81% in 3h under UV irradiation which was a significant improvement over the 41.5% and 51% in the presence of individual ZnO and MOF-46, respectively [3]. The formation of ZnO@ZIF-8 core-shell heterostructures depended on the concentration of 2-methylimidazole during its synthesis using ZnO colloidal spheres as templates. Selective reduction of Cr(VI) was observed due to the selective adsorption and permeation induced by ZIF-8 shell. On the other hand, MB molecules

could neither be adsorbed onto its surface nor be permeated into the MOF, which led to the selectivity of Cr(VI) over MB [4]. Fast degradation of RhB was reported by Mahmoodi et al. who utilized a two-step process to obtain the photocatalyst Ag/AgCl@CFNMT. The synthesis involved initial magnetization of the MOF NH₂-MIL-125(Ti) (NMT) by CoFe₂O₄ followed by an in situ deposition/photo-reduction technique to assemble Ag/AgCl onto the surface of CoFe₂O₄/NMT (CFNMT). The synergistic effect observed between the Ag/AgCl and CFNMT regions propelled a superfast degradation under LED visible light. Photodegradation ability of 89% was achievable with this nanocomposite even after seven cycles, and its easy separation from the reaction medium was due to the magnetic properties [5].

Considering the relatively low cost of metal oxide semiconductors compared to pure metallic nanoparticles, the composites 'MO@MOF' can provide a great alternative as photocatalysts especially considering the adjustable bandgaps and synergistic effects [6]. The addition of dye sensitizers to this combination can further enhance the photocatalytic activity of the metal oxide semiconductor. In this context, Xie et al. [7] reported the introduction of MOF as a sensitizer for anatase TiO₂. ADA-Cd crystals, when mixed physically with TiO₂ at specific proportion, yielded ADA-Cd/TiO₂, which was efficient for the task of



degrading organic dyes under irradiation of visible light via photocatalysis. The bandgap of ADA-Cd/TiO₂ being 3.14 eV, provided an excellent example as to how the fabrication of metal oxide-MOFs can tune the absorption of light. This modified bandgap provided the perfect platform for the photocatalytic activity of ADA-Cd/TiO₂ toward organic dyes under visible light, which could not be matched by either TiO₂ (3.20 eV) or ADA-Cd (3.04 eV) alone. This observation confirmed the synergistic mechanism between the TiO₂ and the coordinated ADA-Cd MOFs. Electrons present in the conduction band of TiO₂ were found to take up O₂ from the atmosphere and oxidize it into the form of key oxidative species. The holes present in the valence band of the MOF, in tandem with °OH resulting from another mechanism, assisted the photodegradation [7]. Selective removal of cationic dyes was achieved by Fe₃O₄@HPU-9 composites having core-shell structures. The removal of R6G could be performed continuously for several cycles without the need for centrifugal separation of the catalyst [8]. A simple technique of fabricating Fe₃O₄/Cu₃(BTC)₂ by controlling the rate of ligand addition was demonstrated by Zhao et al. The synthesized metal oxide-MOF composite was tested for its catalytic activity in removal of MB from water in the pH range of 2–11. Due to the development of negative charge on the adsorbent at higher pH values, the electrostatic interaction between these and the cationic dye was found to be higher but not the major cause of adsorption. Rather, the π-π stacking and hydrophobic interactions between the Fe₃O₄/Cu₃(BTC)₂ surface and MB resulted in the adsorption that followed the pseudo-first order kinetic model. This system also provided a low cost alternative to other adsorbents [9]. Engineering metal-Organic frameworks (MOFs) for controlled delivery of physiological gaseous transmitters discussed in [10], tried to propose an emerging field to develop signaling molecule-releasing MOFs with practical applications.

Poly aromatic hydrocarbons (PAHs) are one of the major environmental pollutants arising out of rapid industrialization and their extraction mechanisms remain under intense research. MOFs have also been researched under this field and very recently, Li et al. have synthesized Fe₃O₄@MIL-101 nanocomposites made up of Fe₃O₄ core and MIL-101 (Cr) MOF shell as a viable material for negligible-depletion magnetic solid-phase extraction (nd-MSPE) of PAHs dissolved freely in aquatic bodies. π-π interactions, π-complexation and hydrophobic interactions between the nanocomposites and PAHs resulted in remarkable lowering the time for extraction equilibrium to less than 60 min. Competitive substances like DOM and DOM-associated PAHs are not adsorbed while the PAHs can be detected up to 0.08–0.82 ng L⁻¹ and adsorbed due to the porous structure of the nanocomposites [11].

Soil contaminant pesticides such as organophosphorus glyphosate (C₃H₈NO₅P) are extremely harmful to aquatic plants and microbes and hence their detection is of

immense value for environmental remediation. In this context, the work of Yang et al. provides a Zr-MOF based composite that can detect glyphosate at concentrations up to 0.093 mg/L. The Zr-OH groups were found to act as the functional groups in the composite Fe₃O₄@SiO₂@UiO-67 owing to their high affinity toward the phosphate groups. The electron transfer between the Fe₃O₄ and UiO-67 components was hindered to a large extent by the intervening SiO₂. As a consequence, the detection was possible at such a low limit of glyphosate concentration. The binding of the adsorbent with the phosphate groups was indicated by a distinct change in the fluorescence intensity at 315 nm [12]. Metal-oxide based materials and photocatalysts were also applied for carbon dioxide reduction through systematic steps as [13]:

- Adsorption of reductant and CO₂ onto the metal oxide catalyst surface;
- Adsorption of sunlight on the perovskite leading to electron-hole separation;
- Transfer of photogenerated charges to the surface and reaction with adsorbed CO₂ and water;
- Desorption of products.

Danish et al. introduced semiconductor metal oxides such as TiO₂, ZnO, WO₃, BiVO₄ and Fe₂O₃ for photoelectrochemical water splitting and photoelectrochemical (PEC) water splitting as solar-driven water splitting methods to produce hydrogen gas in the context of environmentally friendly and sustainable energy production [14]. Antibiotics being highly toxic toward microbial life can cause substantial damage to environment. As a consequence, the removal of antibiotics is an area of focused research. Highly crystalline 1D MIL-100(Fe)/TiO₂ nanoarrays were synthesized by Xiang He et al. for tetracycline removal at an efficiency of 90.79%. The degradation carried out in quartz cuvette under ambient conditions displayed good recyclability of the catalyst, which was recorded to be twice as high as pure titanium oxide, even after five cycles [15]. Ciprofloxacin is a common antibiotic that is among the most persistent pharmaceuticals present in wastewaters and needs efficient removal. In view of this, Moradi et al. developed magnetic metal-organic framework sorbents Fe₃O₄@MIL-100(Fe) and Fe₃O₄@MOF-235(Fe) for CIP removal which that occurred in a spontaneous and endothermic manner. While Fe₃O₄@MIL-100(Fe) displayed both chemisorption and physisorption, the latter only showed physisorption. Phase separation was also easily achieved on using the Fe₃O₄@MIL-100(Fe) composite [16].

Heavy metal removal using 'MO@MOF' composites was demonstrated by employing the magnetic Fe₃O₄@UiO-66 produced by the epitaxial method. A lot of micropores and a large surface area attributed to the composites' core-shell structure allowed for multi-layer heterogeneous adsorption of As (V) up to 73.2 mg per gram of the adsorbent. The inclusion of the ferrosferric oxide provided good

thermal stability in pseudo-second-order kinetics and easy separation from the medium due to its magnetic nature [17]. Used as a disinfectant widely, and especially during the large-scale breakout of infectious diseases, Hypochlorous acid (HClO) finds its way into the environment, leading to severe ramifications. Therefore, the detection of HClO levels is an important step toward limiting its usage. Ma et al. developed ZIF-8/RhB-CDs/Fe₃O₄ as a ratiometric and magnetic probe for fluorimetric detection of HClO. While Rhodamine B carbon dots and ferrosferric oxide are the guest particles in this system, the MOF ZIF-8 acts as the platform to house these. The role of the MOF also extends to the adsorption of the analyte HClO. Extreme fluorescence quenching at 580 nm, almost thrice as much as the RhB-CDs probe, confirmed the detection even at a LOD of 6.7 μM. The role of Fe₃O₄ was to provide easy magnetic separation of the nanoprobles [18].

2. Metal oxide-carbon material composites as photocatalysts

Balancing The rise of polymers, carbon fibers, graphene oxides, fullerenes, nanotubes, quantum dots and other carbon-based materials has opened up many research opportunities and their practical applications. Research on environmental remediation has also seen the use of such materials in conjugation with other materials through interface engineering, doping, surface functionalization, and coordination, for achieving effective results.

Metal oxide composites with carbon-based materials, especially, show high photocatalytic activity toward the degradation of organic dyes. In one such example, dispersion of Pt particles in the composite of ZnO/CFs. The Pt@ZnO NRs/CFs composites were prepared via a three-step route involving atomic layer deposition of Pt, hydrothermal growth, and magnetron sputtering. Synergistic effect between the Pt NPs and the ZnO nanorods facilitated easy electron transfer at their interface and impeded the electron-hole recombination to a great extent. Therefore, the photocatalytic activity in the degradation of organic dyes increased tremendously, as shown in the case of methyl

orange degradation. The hierarchical structure provided the necessary stability [19]. Bark derived from Konar tree was used to make activated carbon further used in preparing modified ZnO nanoplates. Under visible light irradiation, this ZnO-AC composite showed great catalytic activity in removing ClF from aqueous solution [20]. In another instance, direct hydrothermal method was used to synthesize ZnO NPs decorated nitrogen-doped graphite carbon sheets from peach fruit juice. These ZnO@N-Cs were used to determine the effectiveness in MB removal and the results revealed these composites to be more than 95% efficient for the purpose. Use of natural bio-waste as the raw material for the synthesis, neutral aqueous solution for the degradation study and a degradation time of less than 60 minutes suggested these composites to be ideal for practical purposes [21].

Different ratios of ZnO nanorods and graphene oxide were used to prepare ZnO-rGO NCs. Among these, the ZnO-5% rGO displayed very good photocatalytic activity for the degradation of RhB. It was six times more than pure ZnO NPs and two times more than ZnO-5% rGO(H). In the degradation of phenol, activity enhancement was thrice that of ZnO-5% rGO(H). The significant aspect of these NCs was that they could work in the photodegradation of both the positively charged MB and the negatively charged phenol species in aqueous medium. Higher surface area and a higher separation between the electron hole pairs result in the heightened activity in photodegradation. Different key radicals were formed during the degradation of phenol and MB, which suggested the versatility of the prepared NCs [22]. Hydrothermal and sol-gel methods were used by Jo et. al. to prepare a series of binary and ternary titania based nanocomposites. Homogeneous dispersion of Co₃O₄ over the surface of TiO₂ NPs resulted in remarkable increase in visible light driven photocatalysis. The degradation of oxytetracycline (OTC) and Congo red (CR) in aqueous medium was further improved by modifying this TiO₂-Co₃O₄ nanocomposite with GO-nanosheets in trace amount. The electron-hole recombination was effectively prevented by the addition of GO, while the combination of TiO₂ and Co₃O₄ modulated the bandgap (Figure 1) [23].

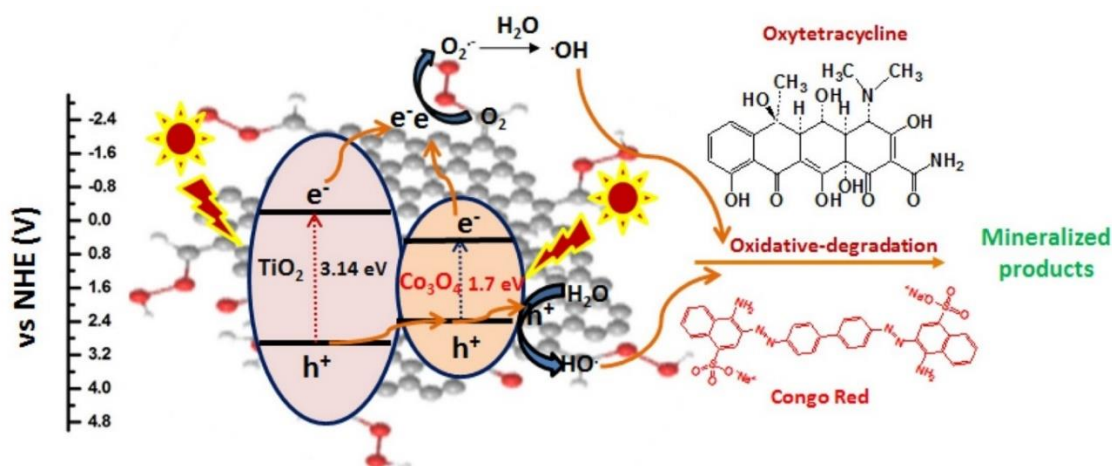


Figure 1. Photocatalysis mechanism of OTC and CR by ternary titania based nanocomposites [23].

A well-regulated hydrothermal synthesis was used to obtain the composites of 2D- WO_3 sheets and reduced GO. Under sunlight, these rGO/ WO_3 NCs displayed photodegradation of MB and RhB, which was found to be better than that of pure WO_3 [24]. Uniform dispersion of WO_3 sticks inside the graphene sheets was achieved by hydrothermal process that resulted in the WO_3 NR/G composites. The variant with 7% G ($\text{WO}_3/\text{G}-7$) exhibited the most efficient photodegradation of MB under visible light irradiation. The reason for the same was considered to be the decrease in the bandgap energy in WO_3 [25]. Taha et al. synthesized WO_3 -CNF NCs employing an electrospinning method along with carbonization. The incorporation of CNF into the metal oxide semiconductor provided a way to develop high-efficiency NCs that displayed photocatalytic properties in the degradation of MB, MO, and MG in aqueous medium [26]. The synthesis of composites containing carbon nanodots and WO_3 via a hydrothermal process was reported by Song et al. Efficient light-harvesting and superior electron-hole separation, as a result of the synergistic effect between the metal oxide and the carbon dots, were the hallmark of this system which made the C-dots/ WO_3 as efficient photocatalysts for the degradation of RhB under visible light irradiation [27]. Effective degradation of Indigo carmine (IC) and MB were realized under sunlight by the ultrasonically prepared WO_3 -GO NCs. The activity was better than the pure and, therefore, a significant achievement in the easy synthesis active photocatalyst composites of metal oxides and graphene [28]. Polyvinylidene fluoride and polyvinylpyrrolidone were used as the base material to support TiO_2 NPs. Electrospinning technique was used to fabricate the PVDF-PVP base wherein the PVP could be dissolved to increase the total surface area and make way for the reactive species to access the TiO_2 NPs. This arrangement provided both stability and enhancement of performance as demonstrated by the photo degradation of MB which worked with high efficiency even after 10 cycles [29].

Degradation of 2,4 dichlorophenol is extremely important since this contaminant causes liver and kidney related problems in addition to nervous system damage in humans. In this direction, the synthesis of $\text{Fe}_3\text{O}_4@\text{GO}@\text{MIL}-100$ (Fe) composite by Gong et al. is an interesting report. Degradation efficiency of 100% in 60 minutes in the presence of hydrogen peroxide was achieved owing to the fast transfer of photogenerated electrons between all the three components, i.e. Fe_3O_4 , MIL, and GO. Due to their magnetic properties, the composites could also be recovered with an external magnetic field [30]. Pesticides dissolved in water bodies pose a serious threat to the aquatic as well as other life forms. Therefore, their removal is an important topic of research. In his direction, Liu et. al. synthesized a composite Fe_3O_4 - GO- β -CD/HKUST. This combination of metal oxide, copper-based MOF, and graphene oxide proved to be an excellent photocatalyst for the degradation of removal of ne

onicotinoid insecticides, namely thiamethoxam imidacloprid acetamiprid, nitenpyram, dinotefuran, clothianidin, and thiacloprid. The removal was achieved from tap water which showed the practiced use of this composite [31]. Graphene-like carbon nitride ($\text{g-C}_3\text{N}_4$) was used to prepare Z-scheme photocatalyst composite $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$ for studying its effectiveness in degrading phenol. The results showed it to be better than both Bi_2O_3 and $\text{g-C}_3\text{N}_4$ when used individually [32]. Wu and coworkers synthesized stable perovskite-type $\text{LaFeO}_3/\text{g-C}_3\text{N}_4$ quasi-polymeric heterostructure via the calcination method. The delayed electron-hole recombination was identified as the reason behind the increase in the bed lifetime of the charge carriers. Therefore, a Z-scheme charge carrier pathway ensued owing to the interaction at the p-n heterojunction interface. This resulted in 16.9 times the greater photocatalytic activity of $\text{LaFeO}_3/\text{g-C}_3\text{N}_4$ compared to pristine $\text{g-C}_3\text{N}_4$ in the degradation of the dye Brilliant Blue. Hydroxyl radicals, holes, and superoxide radicals were the primary reactive species in the process [33].

Jain and coworkers demonstrated heavy metal removal by metal oxide-carbon materials composites. The employed the co-precipitation method to synthesize the ZnO/AC composites for the elimination of Cd (II), Cu(II), and Cr (VI) species from tap water. Electrostatic attraction between the functional groups -COOH and OH, present on the surface of adsorbent composites. The heavy metals were ascertained on the reason behind the removal of these metals [34]. Removal of Uranium is essential due to its radioactive nature and the occasional leakages that have happened over the years. To detect and remove Uranium from the aqueous sources, Guo et al. synthesized a magnetic ZIF-CD adsorbent. These $\text{Fe}_3\text{O}_4\text{-CMC}@Z1\text{F}-8@\text{CD}$ composites displayed better adsorption (173.60 mg/g) compared to the $\text{Fe}_3\text{O}_4\text{-CMC}@Z1\text{F}$ (96.02 mg/g). The greater adsorption was attributed to the large surface area and abundant N/O containing functional groups present on the surface of the carbon dots [35].

Foul odor in the environment is a problem that needs immediate solutions. To achieve this goal, research has to been going on of developing e-noses to which can identify the malodorous substances. With an emphasis on long-term applications, metal oxide-based gas sensors (Figaro type) have been reported to be the most suitable [36]. Romain et al. worked for 3 years to establish the usefulness of tin oxide sensor arrays for identifying malodorous gases. Wastewater, paint shops, compost, and printing setups were found to be the sources that contributed mostly to the release of malodorous gases [37]. Humidity Changes were found to be crucial in the identification of different reducing gases by using SnO_2 gas sensors. Therefore, the humidity calibration for e-noses equipped with SnO_2 was prescribed to be time-dependent by Lonescu et al. to achieve desired improvements in the performance of these e-noses [38].

3. Energy sustainability and solving carbon-related issues through metal oxide-based materials

Energy conversion and storage are significant challenges faced by the modern world due to excessive industrialization. Therefore, low cost and high-efficiency catalysts are the need of the hour. In this context, metal oxides have been actively researched as viable options. Other applications of metal oxides in the energy sector include photoanodes for PEC Water splitting, intercalation cathodes for lithium-ion batteries, electrode materials for fuel cells, solar cells, supercapacitors, and electrochemical cells [39].

Simple metal oxides such as TiO_2 , ZnO , WO_3 , BiVO_4 , Fe_2O_3 have been found application as photoanodes for photoelectrochemical splitting of water, while NiO , Co_3O_4 , and IrO_2 were reported to be efficient catalysts for water oxidation through electrocatalysis. The recent surge in nanotechnology has paved the way for various kinds of nanoparticles to develop sustainable and recyclable systems for energy conversion and storage. Dye-sensitized solar cells have been reported wherein ZnO and TiO_2 nanoparticles have found use owing to their large surface area and electron transport abilities [40]. Doping has been one of the most favorite techniques of researchers worldwide. Both metal and non-metal dopants can be used to modulate the band gaps in the semiconductor metal oxides like

ZnO , TiO_2 , Ta_2O_5 , which makes it easier to access the visible light for carrying out photocatalysis [41,42].

Another Important strategy has been the introduction of intrinsic oxygen vacancies into the metal oxides. Methods have been explored to synthesize oxygen-deficient metal oxides to achieve PEC water splitting, usage in supercapacitors, solar cells, fuel cells, and LIBs. Such defects can modulate electronic and optical properties due to the rearrangement of inherent donor densities. The most common metal oxides that can be tuned in this manner are Fe_2O_3 , WO_3 , BiVO_4 , and TiO_2 [43]. Treatment of TiO_2 nanowire arrays by hydrogen leads to oxygen vacancies during annealing at high temperatures. The reduction of Ti^{4+} to Ti^{3+} by hydrogen results in the formation of these vacancies since the overall charge is balanced. PEC performance of these oxygen vacancies containing TiO_2 -NWs coated electrodes was found to be significantly better than untreated TiO_2 -NWs [44]. Photoelectrode performance can be increased several folds by introducing oxygen defects that can synchronize with other complementary systems. One such report was published by Wang and coworkers in which they combined a microbial fuel cell with a PEC cell. Therefore, a self-sustained system for hydrogen gas liberation was obtained, which functioned continuously due to the TiO_2 electrode that worked in the presence of solar light (Figure 2 [45]).

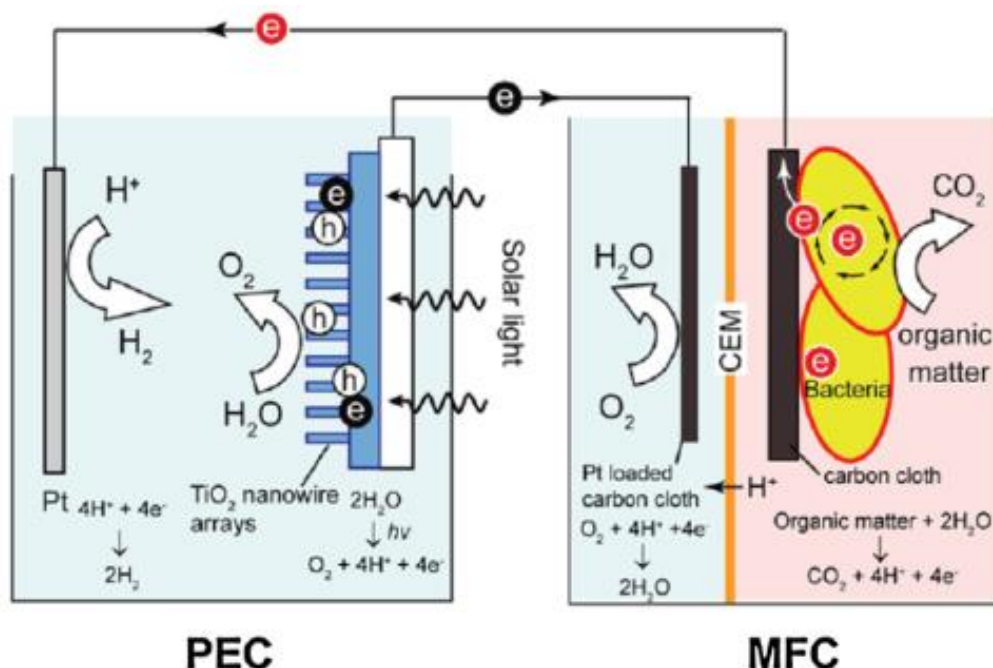


Figure 2. Schematic illustration of a PEC-MFC device [45].

TiO_2 electrodes have been under investigation for increasing the efficiency of dye sensitized solar cells. TiO_2 rutile NWs were found to improve the efficiency of DSSC from 0.28% to 0.45% for solar energy conversion. Hydrogen treatment of Degussa P25 resulted in oxygen vacancies that improved the solar energy conversion of DSSC to 13%. Under natural sunlight, the enhancement was

9.30%. The reason behind this improvement was ascertained to be the increase in electron density as a result of hydrogenation [46]. As a low-cost alternative to platinum, WO_3 has been explored by Cheng et al. to operate as the counter electrode in DSSC. Since I_3^- gets reduced to I^- during a complete cycle of electron transfer in DSSC, it is very important to have sites that can absorb I_3^- and reduce it to

I. The introduction of oxygen vacancies proved to be beneficial for this purpose. Thus, the use of WO_3 and the introduction of oxygen vacancies therein resulted in a tremendous increase in conversion efficiency from 0.63% to 5.43% [47].

Supercapacitor efficiency can be significantly improved by oxygen defective metal oxides as demonstrated by Lu and coworkers, who used hydrogen treated TiO_2 as a scaffold to support MnO_2 nanoparticles, which act as pseudocapacitive materials. These nanoparticles were fabricated into MnO_2 cores on top of which the H- TiO_2 were assembled. The as-prepared H- TiO_2 @ MnO_2 core-shell NWs were used as a positive electrode in flexible solid-state asymmetric devices. With a slighter modification, MnO_2 was replaced by carbon and the resulting H- TiO_2 @C core-shell NWs were used as the negative electrode. A high specific capacitance (1.396F/g) and a voltage window of 1.8V was the characteristic feature of these supercapacitor devices [48]. Studies on the percentage of oxygen vacancies in MoO_3 and the resulting influence on its capacitive performance revealed that the faster Kinetics of the oxygen-deficient MoO_3 was directly related to the concentration of vacancies. Structural stability was also observed as a result of these defects. Therefore, repeated intercalation and de-intercalation of lithium was could be performed with very good cycling efficiency [49].

Liang and coworkers demonstrated application of oxygen-deficient Metal Oxide in lithium-ion batteries. They reduced TiO_2 with hydrogen and the resultant TiO_2 inverse opal showed improvement in conductivity since the hydrogen-reduced TiO_2 acted as an efficient current collector for S cathode. The oxygen vacancies enhanced S-Ti-O bridges that acted as a medium for the sulfur-titanium oxide interaction while the 3D framework of TiO_2 made the transport of Li ions and electrons easier. Therefore, the system achieved a high specific capacity of 1250 mAh/g. The oxygen deficiency was found to be the reason behind the excellent rate capability and reversible capacity due to the heightened electrical conductivity [50]. The zero/low emissions at ordinary temperatures and possessing high power densities make fuel cells promising sources of clean energy. Yet, costly catalysts, durability issues, and poor reliability hamper the commercialization of fuel cells. In this context, metal oxide-based materials have been found to solve the issue of catalysis to a large extent. For instance, upon annealing MnO_2 in oxygen or argon atmosphere afforded nanocrystals of oxygen defective MnO_2 , which displayed ORR catalytic activity characterized by positive onset potential, low peroxide production, and greater current density. All of these parameters were found to be better than pure MnO_2 because of the reduction in the kinetic barrier [51].

In a first of its kind, zero-dimensional CdS QDs were combined with 2D ZnO nanosheets which resulted in the formation of heterostructures. In the presence of ultrasonic waves and NaOH, a hydrothermal process was used

to assemble a microflower-like structure for the 2D ZnO NSs upon which the CdS QDs were deposited by the process of successive ionic-layer absorption and reaction. The resultant CdS/ZnO heterostructures were very effective in generating hydrogen by water splitting. A Z-scheme photocatalytic system that promoted electron-hole separation was at the core of the excellent catalytic ability of this heterostructure that was further enhanced by the fine-sized 0D CdS and 2D ZnO and their intimate contact that diminished the migration resistance [52].

Energy storage is as important as energy generation. The batteries used traditionally lack the efficiency needed for the 21st century energy needs and cause severe pollution by leaking heavy metals and other toxic compounds into the environment. Therefore, other smart methods for storing energy, are being researched for quite some time. In the pursuit of preparing wearable energy storage devices, Lee et al. designed conductive textile with excellent toughness and high porosity via a two-step process wherein a metal oxide was coated onto the surface of cotton, followed by pyrolysis. The synthesized PCT-MO_x/ZnCl₂ composite textile (MO_x = V₂O₅, Al₂O₃, ZnO) were found to display unusual material toughness among with, the one prepared with V₂O₅ was the best. Introduction of V₂O₅ and ZnCl₂ modified the graphene-like sheets in PCT to V-mediated cross-linked turbostatic carbon sheets and this was the reason behind the increase in material toughness. The PCT-V₂O₅/ZnCl₂ was developed into a flexible solid-state supercapacitor using PVA-H₂SO₄ as the gel electrolyte. The as-prepared supercapacitor was found to possess an energy density (2.24 mWh/cm³) 3 times that of commercial supercapacitors, along with a power density (585 mW/cm³) that is nearly twice as much as that of commercial Lithium ion batteries. This finding is expected to open up further research in a bid to develop wearable energy storage devices that can be commercialized at reasonable cost by using widely available metal oxides precursors [53].

Rapid climate change over the last century has led researchers as well as industries to think of new ways to remove the excess carbon accumulation in the atmosphere. In this attempt, several fields of research have emerged out among which, carbon dioxide photoreduction occupies a prominent place. The major criterion for any photocatalyst to work effectively in reducing CO₂ lies in the extent of the gas it can adsorb. MOFs have been found suitable in this context since they possess Lewis acid sites to adsorb the CO₂ molecules over the most abundant N₂ gas molecules, from the atmosphere. MOFs can also house other sites with various functional groups and metals, to acts as centers for the catalytic activity [54]. The high adsorption capability of MOFs was combined with the favorable photocatalytic activity of TiO_2 to produce MOF/ TiO_2 systems for carbon dioxide reduction. By coating the nanocrystalline TiO_2 onto the $\text{Cu}_3(\text{BTC})_2$ core, Xiong et al. developed as core-shell photocatalyst $\text{Cu}_3(\text{BTC})_2$ @ TiO_2

for selectively producing CH₄ from CO₂ with a 5-fold enhancement over pure TiO₂ [55]. Other examples of incorporating metal oxides into MOFs to achieve CO₂ reduction have also been reported. These include Zn₂GeO₄/Mg-MOF-74, O-ZnO/Uio-66-NH₂, O-ZnO/rGO/Uio-66-NH₂, PCN-224(Cu)/TiO₂, and QS-Co₃O₄HoMSs(ZIF-67). Among these, the titanium and cobalt oxide based catalysts were reported to work under Xenon lamp, in water as the reaction medium, the ZnO based ones required the addition of acetonitrile or NaHCO₃ to the reaction medium for their activity [56].

Conversion of CO₂ into useful fuels and other valuable precursors for industries is a great way to reduce the carbon footprint and cut the cost of production in a single shot. Therefore, carbon dioxide to methanol conversion could be economically viable if low-cost catalytic systems can be developed. In this context, Senanayake and coworkers reported the synthesis of CeO_x/Cu(111) and ZnO/Cu(111) catalysts for the easy conversion of CO₂ to methanol via stabilization of the intermediate CO₂^{δ-} species. The role of metal oxide was especially investigated, and they found that the deposition of CeO_x and ZnO NPs on the Cu(111) surface decreases the activation energy for the methanol synthesis from 25 kcal/mol on pristine Cu(111) to 13 and 16 kcal/mol on CeO_x/Cu(111) and ZnO/Cu(111), respectively. Moreover, strong metal-oxide

interactions were observed as a result of the inverse oxide/metal configuration. Ce³⁺ was established as the site for stabilizing the intermediate CO₂^{δ-} species. Overall, the metal-metal oxide interfaces, CeO_x-Cu and ZnO-Cu, were considered critical in the hydrogenation of CO₂ [57].

Use of oxygen-deficient metal oxides for reducing CO₂ into useful chemicals has been demonstrated by Gao et al. in their report about the partially oxidized atomic cobalt layer that displayed excellent selectivity (90%) for formate production. With an overpotential of 0.24 V, this metal oxide system is an outstanding one in terms of CO₂ reduction catalysis. The difficulty in ascertaining the possible mechanism was due to the difficulty in identifying active sites, which in turn, was because of the mixture of cobalt oxide and metallic cobalt particles in the system [58]. However, such systems can provide further insights and pave the way for designing better photocatalysts if the role of oxygen deficiency present therein, can be investigated.

Interfacial charge transfer was observed in the case of LaFeO₃-TiO₂ nanocomposites prepared by Humayun et al. Increased specific surface area, and improved harvesting of visible light, in addition to N-doping were also considered to be causes behind the efficiency shown by this system (Figure 3) [59].

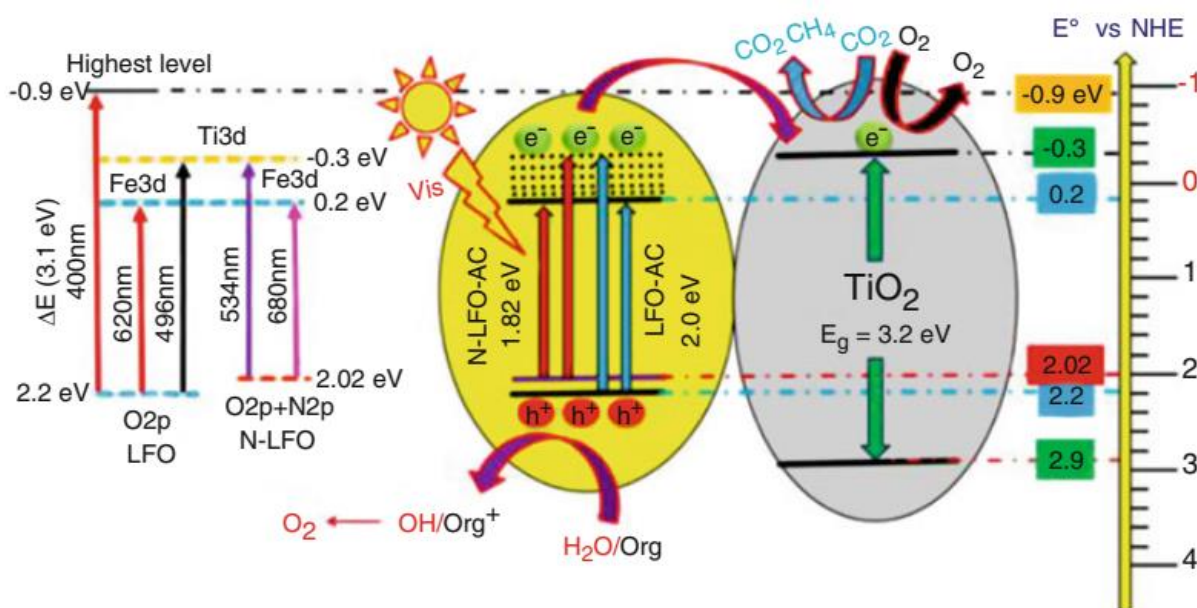


Figure 3. Interfacial charge transfer in LaFeO₃-TiO₂ nanocomposites catalyzed photoreduction of CO₂ [59].

A heterojunction photocatalyst g-C₃N₄/NaNbO₃ also displayed good photocatalytic carbon dioxide reduction wherein the carbon nitride provided the light harvesting ability while the metal oxide provided the necessary bandgap for the process. An artificial photosynthetic system reported by Zhou et al. was found to have mimicked the real leaves as a result of its 3D structural features. Sunlight as the energy source, carbon dioxide as the carbon

source and water as the electron donor was achieved through this 3D APS architecture. SrTiO₃ was identified as the active site for breakdown of CO₂, and cocatalysts like Pt, Ag, Au, and Cu were found to be suitable for loading. Interestingly, this system was found to have morphological similarities with natural leaf. Therefore, construction of such systems is quite promising in neutralizing the excess carbon content in the environment.

4. Conclusion

Metal-oxide-based materials that demonstrate various properties such as electrical, magnetic, mechanical, optical, catalytic, etc., gained significant importance in various parts of industrial applications. Metal-organic frameworks (MOFs) consist of metallic ions and organic ligands, which have gained substantial interest due to their techno-economic advantages with relatively low cost of metal oxide semiconductors than pure metallic nanoparticles that can provide great alternative photocatalysts especially considering the adjustable bandgaps and synergistic effects. Also, the oxide-MOFs-based compositions have high porosity high surface area with adjustable pore size from the features perspective. Recently MOFs and carbon-based metal oxides are considered for a wide range of applications. Specifically, their application for energy suitability can be counted for hydrogen energy and battery applications for storage catalysts systems, fuel and solar cells, sensors, pyroelectric, etc., applications at industry scale, and more importantly, supercapacitors applications. Therefore, this study reviews the subject to develop essential information that the subject will pursue in the next phase in details of frameworking, planning, modeling, design, and application of metal-oxide-based materials in energy environmental sustainability.

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