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Advances in metal-based vanadate compound photocatalysts: synthesis, properties and applications

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ABSTRACT

Among the ongoing research on photocatalysis under visible-light, it has been shown that doped or hybrid catalysts are more active than a single catalyst alone. However, problems including visible light absorption, a low quantity of energetic sites on surfaces, and rapid recombination of the photo-electron hole pair produced by light have prohibited photocatalysts from being used in a practical and widespread manner. To overcome these problems, synthesis of nanostructure hybrid catalyst using several methods has attracted much attention. Several procedures have been suggested for the preparation of photocatalysts with the desired structure and morphology. Preparation methods similar to partial modification may lead to diverse structures and qualities. In this regard, the development of efficient, low-cost photocatalysts and rapid synthesis is the most important issues that should be considered. This review discusses various methods and mechanisms that work with the modification of vanadium compounds as photocatalysts to progress their photocatalytic efficiency. In addition, the effects of synthesis temperature, solution pH and concentration on the photocatalytic performance are also described in detail.

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1. Introduction

Many problems, such as environmental pollution and insufficient energy resources, have forced scientists to find appropriate solutions. The technology of using photocatalysts is one of the new solutions that have been welcomed in developed countries. Photocatalysis process involves reactions that occurs using light and semiconductors which has recently attracted much attention. Solar energy is a readily available and free resource that may be used to deliver energy to

industries as a viable alternative to fossil fuels. Other technologies, such as photocatalysis, photovoltaics, smart materials and environmental purification, have been used with solar energy [1-4]. The production of hydrocarbon fuel such as methanol and dimethyl ether by photocatalysis technology has been studied in last decade [5]. Carbon dioxide (CO₂) activation by photoreduction to methane (CH₄) under visible light illumination [6] is the newest photocatalysis techniques without releasing toxic byproducts [7]. The elimination of

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Fig. 1. Photocatalyst applications.

halogenated organic compounds and other volatile organic compounds (VOCs) from water using photocatalysis can be used effectively [8]. Personal care products and pharmaceuticals as emerging contaminants are present in surface water and wastewater, groundwater and even drinking water have been treated effectively using various photocatalysts [9]. Photocatalysts are the best platform for chemical reactions that are normally either difficult or impossible to occur [10]. The increasing development of photocatalysts has grown exponentially in recent years, and its applications can be seen in a wide range of research in Fig. 1.

The main difference between these types of catalysts and conventional heat catalysts is that heat catalysts are activated by heat and accelerate the reaction, while photocatalysts are activated by photons and light energy. These materials absorb sun light to provide higher energy to perform such reactions [11]. In photocatalysts, the main factor of photocatalytic activity (PCA) is the ability of the catalyst to form electron-hole pairs that produce free radicals and are capable of secondary reactions. Photocatalysts are able to decompose harmful substances in the sun containing UV rays [12]. Understanding and optimizing the properties of existing photocatalysts will increase the exploitation of these materials. Despite more than four decades of continuous effort, research in the field of photocatalytic materials is still in its infancy and photocatalytic expansion is still a challenge because of the weak oxidation capacity and the inadequate amount of active sites. Currently, TiO₂ is often used as a photocatalyst because of its high oxidation and reduction ability compared to semiconductors such as WO₃, ZnO, ZnS, SrO₂, CdS and F-TiO₂, as well as TiO₂ polymorphism, the anatase phase has the most photocatalytic performance [13]. Superoxide (O₂^{•-}) radicals, hydroxyl radicals (•OH) and H⁺ holes are responsible for catalyzing the oxidation reactions produced by TiO₂ and other photocatalysts (Fig. 2). In semiconductors, the band gap contains energy levels to which valence electrons cannot be promoted [14]. This band is much smaller in semiconductors than in non-conductors. This allows the capacitance layer electrons in

semiconductors to be easily transmitted to the conduction band by the application of heat or light. This property makes multiple applications for semiconductors predictable. The reason for the popularity of TiO₂ is its low price, high stability, natural abundance, excellent optical properties and environmental friendliness [15]. A desirable photocatalyst should have high surface area, resistant to photo-corrosion, thermal and optical stable, narrow band gap energy, high mechanical strength, non-toxic and so on. In addition to TiO₂, ZnO has been investigated due to its morphology and catalytic structure [16]. In the design of new photocatalysts, goals such as preventing the recombination of electron hole pairs and improving the absorption of light in the visible confine should be considered. In addition, another approach can be mentioned that expanding the edge of photocatalytic light sorption prevents the recombining of electron/hole pairs and increases the photocatalytic efficiency [17]. TiO₂ is synthesized in various forms such as nanotubes, nanorods, nanowires, etc. and can be mixed with CeO₂ [18], Fe₂O₃ [19], SiO₂ [20], AgVO₃ and Ag₃VO₄ [21], BiVO₄ [22], ZnBi₂O₄ [23]. Zeolites are also used as supporting materials due to consequently their large surface area and porous structure and, high heat adsorption, maintaining structural stability, acidic form and adjustable acidity that can decrease the electron/hole pair recombination [24].

Photocatalytic processes are generally divided into homogeneous and heterogeneous categories [25] and all photocatalysts are essentially semiconductors. In this regard, semiconductors operate in three main stages of the catalytic process, which takes place in heterogeneous operations: 1) Excitation of the bond to form an electron-hole pair, 2) transfer of charge carriers to the photocatalyst surface; and 3) creating energetic sites for the next oxidation and reduction action [26]. Therefore, the electronic structure, bulk structure and surface structure of photocatalysts strongly affect the photocatalytic performance. This means that photocatalysts must have a narrow bandgap and intense oxidation and reduction capabilities. The first case shows that a small band can increase the photo-responsiveness of catalysts for a wider

Fig. 2. Schematic of photocatalytic process and different types of materials on the basis of band gap.

range of sunlight usage. Since the photodegradation is proportional to the load on the catalyst in heterogeneous photocatalytic reactions, the optimum photocatalyst concentration must be determined to prevent the use of extra photocatalyst [27]. The efficiency of photocatalysts are affected by co-catalysts morphology, degree of crystallinity, specific surface area (SSA) and surface acidity, so it should be expanded in this field. The specific surface area of a photocatalyst depend on the porosity, pore size distribution, shape and roughness. Vanadate-base compounds are widely used in photocatalysis process due to their fascinating features but there are some challenges such as high band gap energy, reusability, fast electron/hole pair recombination rate and poor activity in visible light [28]. In this regard, a group of vanadate composites ($M^{3+}VO_4$), where M^{3+} is +3 charge metal cation such as Fe^{3+} , In^{3+} , and Ag^{3+} have been summarized. This study provides new insights into the use of vanadium compounds in the synthesis of well-defined photocatalysts with excellent performance to increase photocatalytic efficiency to remove contaminants, splitting water and hydrocarbon production and so on. The crystal constructions and the optical features of photocatalysis are briefly investigated.

2. Synthesis strategies

Photocatalytic performance depends greatly on the adsorption properties of the photocatalyst. There are several methods for preparing metal oxide nanoparticles. Methods such as co-precipitation, solid state synthesis, microwave synthesis, hydrothermal method, electrochemical, sol-gel technique, thermal decomposition procedure, arc discharge method, etc. are used for this purpose.

2.1. Precipitation method

Among the available techniques, the precipitation method is the simplest and cost-effective concept, because it does not need high pressure and high temperature. The particle structure and crystalline size can be easily changed by moderating the pH of medium and high samples can be prepared at the same time [29]. During precipitation method, the raw materials must be mixed in a solution to form the desired sediment, and parameters such as temperature and aging time must be optimized in the desired amount to achieve the required

precipitate. In this process, a solution containing a precipitating substance, usually hydroxide, is mixed with a solution containing the desired oxide cation. Then the sediments are fired (vanadate, hydroxide, or carbonate). Chemical precipitation methods contain homogeneous precipitation, direct precipitation and co-sedimentation. Preparation of photocatalyst with this method is often used for nanoscale synthesis [30]. The difference between these methods is in the number of cations. If there is only one cation in the solution, it is called the direct precipitation process, while for the co-precipitation procedure; there are several cations in the mixture. Also, co-precipitation and hydrolysis method can be used for uniform distribution of nanomolite powders (~100 nm). Compared to direct precipitation and co-sedimentation techniques, homogeneous precipitation has advantages of good homogeneity of core and precipitation. Usually a substance is used as a precipitating agent in the homogeneous precipitation process [31].

The efficiency of a chemical precipitation process depends on several parameters such as the type and concentration of ionic metals present in the solution, the precipitate used, the reaction conditions (mostly the acidity of the solution) and the presence of other components that may prevent the precipitation reaction. The precipitation method has advantages such as simplicity, reproducibility, low cost, and ability to modify the surface chemistry which in this regard can be used in the production of large-scale photocatalysts [32]. However, the aging of the sediment often takes more than 24 hours and the weakness of this method is time consuming. By modifying the synthesis conditions, the properties of the products can be controlled. The ratio of raw materials can have a small impact the crystallinity, particle size, band gap and ability to absorb light [33].

The co-precipitation technique is most widely used to prepare a uniform mixture of two or more uniform blends via the precipitation operation, which is one of the great routs for the preparation of nano-sized compounds including two or more types of cation in the form of hydroxide, carbonates, oxalates, or citrates [34]. Then, by calcining these precipitates at suitable temperatures, the required nano-powder is obtained. Because the required calcination temperature is low, sedimentation leads to smaller particle sizes. However, in each synthesis specific conditions and different precursor reactions are used.

Through the co-precipitation technique, homogeneous nanocomposites with uniform distribution can be achieved by various chemical reactions in solution [35].

2.2. Microwave/ultrasonic-assisted synthesis

High-intensity ultrasound can be used to produce new material, providing an unusual path for known material without high temperature, high pressure, or long reaction time [36]. In this method, the interaction between molecules occurs with electromagnetic radiation and the electromagnetic energy is converted into thermal energy. This technique can be used as an efficient and harmless technique for synthesizing materials. Acoustic cavities can be created by ultrasonic waves, and this phenomenon in the production and modification of nanomaterials has been able to produce photocatalysts with efficient structures. This idea evaluates the benefits, challenges, and future prospects of metal-based photocatalysts with the aim of degrading pollutants.

2.3. Hydrothermal and solvothermal method

Hydrothermal synthesis can be considered as a technique for preparing water-soluble crystals in hot and pressurized water in a crystallization vessel called autoclave made of stainless steel. The hydrothermal method can be used to produce crystals that are not stable at the melting point. It is also useful for producing materials with high vapor pressures at their melting points because the reactions take place in an aqueous medium. The hydrothermal technique has been expanded for the synthesis of highly crystalline nanomaterials. Influential parameters in this method include the type and concentration of raw materials, solvents, stabilizing agents and reaction temperature and time, which have an important effect on product quality. With this method, large crystals with good quality can be produced in one-step process and at the same time their composition ratio can be controlled. This is one of the advantages of the hydrothermal method compared to the co-precipitation method, which is performed at low temperatures and usually produces weak crystalline nanoparticles, but hydrothermal methods have relatively low product yields [37]. Also, the need for costly sealed autoclaves lined with Teflon and the impossibility of observing the crystal as it grows if steel pipes are used are among the disadvantages of the hydrothermal method. Some materials prepared by hydrothermal method have higher photocatalytic degradation efficiency, for example, BiPO_4 prepared by hydrothermal synthesis has been reported to possess high efficiency of the optical holes in the capacitance band. Photocatalytic synthesis of these materials by hydrothermal method shows better performance in photodegradation of contaminants compared to non-hydrothermal process [38].

The production of semiconductor nanomaterials through solvothermal routes is an ideal synthesis method. Reaction temperature, pH and additives, aging time, morphology, crystalline phase and particle size of products are controlled by adjusting solvents. This method is one of the important solutions for the synthesis of bismuth-based photocatalysts [39] with exposed active agents, 3D hierarchical microstructures and surface defects. Generally, photocatalysts prepared using the solvothermal method execute better and are more acceptable for specialized applications than other methods. But low production due to long synthesis time and batch characteristics because of the use of special autoclaves is the main weakness of this method.

2.4. Sol-gel method

In chemistry, the sol-gel operation is a way of synthetic approaches to producing high quality solids such as MONPs (metal oxide nanoparticles) as well as mixed oxide composites from micro and nano molecules. This method, which is performed in five stages including hydrolysis, multiple compaction (condensation), aging & drying (supercritical, thermal or freeze drying) and thermal separation, has extraordinary control over the contexture and surface quality of the final product [40]. The sol-gel method has the advantages of short soaking times, high purity of products, low reaction temperature, and high stability, and is considered as one of the promising methods for artificial photocatalysts. Additionally, the photocatalytic ingredients prepared by the sol-gel method usually have thermal stability and uniform distribution. Consequently, sol-gel technique has attracted much attention in the synthesis of vanadate-based photocatalysts [41].

3. Metal-based vanadate photocatalysts

Vanadate is a compound consisting of vanadium oxyanion, which is usually in the maximum oxidation state of +5. So far, many applications have been found for ternary vanadate one-dimensional, including the production of lithium batteries, electrochemical sensors and photocatalytic process as well as its good electrochemical and photocatalytic properties [42, 43]. Vanadates have attracted a lot of attention in photocatalysis applications due to their attractive structural features. Vanadates are especially described with a close band gap and simple preparation methods [44]. A layered vanadium type such as BiVO_4 has attracted considerable attention as a photocatalyst with the help of visible light. There are many semiconductors that have a high ability to absorb visible light [45], but among them, bismuth vanadate (BiVO_4), which has band gap of 2.4–2.5 eV, due to its controllable crystalline aspect and specific electronic structure, has excellent potential for organic degradation and water oxidation. However, the photocatalytic efficiency of BiVO_4 is still relatively weak because of slow oxidation of water, the low electron transfer rate, poor mobility of the charge carrier and poor surface adsorption content [46]. Therefore, various solutions to progress its photocatalytic efficiency have been investigated, such as morphological engineering [47], primary doping, defect formation and semiconductor bonding and so on.

BiVO_4 is much more efficient than TiO_2 because it absorbs more light content due to the TiO_2 surface area, which is about 0.1 that of BiVO_4 nanocrystals. Loading platinum nanoparticles on the surface of BiVO_4 can help as an excellent charge collector and transporter, preventing the recombining of electron-generated hole pairs and eliminating more active sites in the procedure [48]. Moreover, additional acceleration on the electron is made possible by the Schottky energy barrier with loading Pt on the surface of the particles, hence increasing the hydroxylation reaction at the photocatalyst surface. It is widely accepted that the photocatalytic process in semiconductors is accompanied by the absorption of photons directly through the band gap to excite electrons from the valence band to the conduction band in the particles, and then the holes and separated electrons are transferred to the particle outside. This process begins with the light absorption with energy equitable to or higher than the energy of the semiconductor band gap. It means that the activator of the photocatalyst is a narrow band gap. The branched BiVO_4 nanocrystalline photocatalytic particles have band gap energy of approximately 2.5 eV while a titania band gap

energy of 3.7 eV. The narrower BiVO₄ band gap compared to titanium makes the excitation of BiVO₄ electrons from the capacitance band to the conduction band better by absorbing visible light as well as ultraviolet light and making solar energy more efficient [49]. Electrons are excited by visible light irradiation from the valence band (VB) to the conduction band (CB), creating electropositive holes in the valence band. Then, by transferring the generated holes and electrons to the outside of the BiVO₄ nanostructures, the reaction with O₂ and water takes place and 'O²⁻ and 'OH radicals are produced, respectively. In this process, electrons and holes first migrate in two different ways: (1) electrons produced by light are trapped in mastoids or surface pores and transferred to platinum nanocrystals through the Schottky barrier through additional haste. As a result of this extra force, the electrons can quickly combine with oxygen to create 'O²⁻ radicals. (2) The photogenerated holes migrate on the nanocrystals surface mastoids, respectively, and then combine with water to form 'OH radicals. The produced 'OH and 'O²⁻ radicals react mostly in H₂O to break down ciprofloxacin particles into H₂O and CO₂ or further intermediates [50]. However, the complicated mechanism of this reaction for the photodegradation procedure of ciprofloxacin is not fully understood. Singh et al. showed how to use the thin structure of bismuth vanadate and titanium dioxide as an efficient photocatalyst to photogenerate electron hole pairs and to achieve corrosion resistance, both of which factors are important prerequisites for a photoelectrode to attain high photoelectrochemical performance [22]. By using the thin structure of BiVO₄ and TiO₂ as photocatalysts and hydrogen purification, a significant improvement in the optical density of tape engineering can be achieved. The increase in photoelectrochemical performance is due to the facilitation of the hole transfer to the electrode surface and the increase in light absorption in the TiO₂ substrate [51]. This is an example of how hydrogenation can be used to create the structural properties of BiVO₄/H:TiO₂, leading to improvements in similar compounds [52].

Due to defects in the one-component photocatalytic structure, comprehensive attempts have been made over the years to configure photocatalysts, for example, to form heterogeneous type-II nanocomposites using two or three semiconductors to enhance charge separation and increase photocatalytic efficiency [53]. The construction of a suitable heterojunction photocatalytic compound can separate electrons and holes in two different places, which in turn increases the lifespan of photogenerated carriers. Ag₃PO₄ is a hopeful photocatalyst because its band gap energy is placed in the visible light span (E_g~2.4 eV), so it is a good alternative for replacing titania which is active only under ultraviolet light [54]. Since the crystal aspect is related to the semiconductor photocatalytic efficiency, a new BiVO₄/Ag₃PO₄/polyaniline polymer photocatalyst with heterojunction system aspect has been investigated by Chen et al. [55]. The preparation method of this photocatalyst is the precipitation of Ag₃PO₄ in the most active form of BiVO₄ and then the combination of polyaniline polymer (PANI). Since morphological engineering can reach active face selective exposure, and heterojunction fabrication can significantly increase the efficiency of singular semiconductor charge separation, heterojunction engineering and simultaneous morphology modification are thought to be a practical strategy for potentially improving photocatalytic efficiency. Ag₃PO₄ with high quantum efficiency in sunlight is a suitable semiconductor for photocatalytic decomposition of organic contaminants, because of its intense oxidizing capability of VB holes [56, 57]. But photo corrosion under

visible light and dissolution in aqueous solution seriously impede its widespread use. Theoretically, the selective deposition of cocatalysts on BiVO₄ could improve photocatalytic performance because of the highly active shape providing more BiV₄ polyatomic orbits that could be used as multiple electron transition channels and energetic sites.

By analyzing the energy level, it was found that the gap between CB of BiVO₄ and CB of g-C₃N₄ (energy band gap of ~2.74 eV) is much great, positively impacting the recombination of e⁻/h⁺ (electron/hole) [58]. This would cause photoinduced electrons in CB of BiVO₄ to be rapidly transferred to valence band of g-C₃N₄, leaving rich electrons in CB of g-C₃N₄ and holes in VB of BiVO₄ to take part in the redox action. Therefore, it may lead to an unmediated direct Z-scheme photocatalytic series [59]. The direct Z-scheme of BiVO₄/g-C₃N₄ results in high-efficiency separation of electrons and photogenerated holes, therefore greatly improving photocatalytic efficiency. This general strategy can be used to design other high-performance Z-scheme direct photocatalysts. The results showed that the direct Z-scheme of BiVO₄/g-C₃N₄ affects the charge separation, and results in significant photocatalytic activity for BiVO₄/g-C₃N₄ composites under visible light illumination. Therefore, it provides very powerful oxidation and reduction ability. Another study found that 3D g-C₃N₄ showed increased exciton resolution, better mobility and separation of charge carriers than g-C₃N₄ nanosheets, which implies the way for more electron transport in 3D morphology [60]. In particular, g-C₃N₄ nanosheets had a notably reduction in activity (less than 44%) because of the accumulation of nanosheets, while 3D g-C₃N₄ did not show significant inactivation, which confirms its high stability for the overall water splitting reaction [61]. In another study by Nguyen et al., the effect of g-C₃N₄ nanosheet/Ag₃BiO₃ on the decomposition of organic matter was investigated, and the activity and satiability of this binary photocatalyst were attributed to effective transfer and separation photogenerated charges from g-C₃N₄ to Ag₃BiO₃ and the presence of semiconductor with a small bang gap [62].

The direct solid-state Z-scheme heterojunction photocatalytic construction system was used in the water splitting and removal of organic pollutants. As previously mentioned, pores (h⁺), superoxide radicals ('O²⁻) and hydroxyl radicals ('OH) are the main reaction factors in photocatalytic performance. The rate of electron-hole pair regeneration can be inhibited by forming a new system of Z-scheme heterojunction system. Synthetic Z-scheme V₂O₅/g-C₃N₄ can greatly increase photocatalytic activity compared to pure g-C₃N₄ and V₂O₅. Hong et al. have shown that V₂O₅ amount has a major effect on the photocatalytic activity of V₂O₅/g-C₃N₄ precursor photocatalysts. If the amount of V₂O₅ is more than 1.0% by weight, the photocatalytic activity decreases [63]. The result shows that direct fabrication of heterojunctions V₂O₅/g-C₃N₄ with a direct Z-scheme can improve the separation of the photogenized electron-hole pair. This photocatalyst can be used to decompose contaminants such as RhB (rhodamine B), TC (tetracycline), methylene blue (MB) and methyl orange (MO) under visible light. The photocatalytic decomposition of phenol and methyl orange (MO) in the aqueous solution was investigated with g-C₃N₄/Ag₂VO₂PO₄ and found to be approximately 3 to 4 times more active than g-C₃N₄ and Ag₂VO₂PO₄ [64]. Also g-C₃N₄/Ag₂VO₂PO₄ is able to break down 30% of the phenol under 240 minutes disposal to visible light irradiation. Injection of electrons from the Ag₂VO₂PO₄ conduction band into the g-C₃N₄ valence band suppresses the quick recombination procedure and extends the charge carrier life, thus improving the photocatalyst effect. Using the photocurrent graph, it is

found that the $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{VO}_2\text{PO}_4$ photocurrent density is much higher than that of pure $\text{g-C}_3\text{N}_4$ and $\text{Ag}_2\text{VO}_2\text{PO}_4$. The ratio of this difference in $\text{g-C}_3\text{N}_4$ is 8 times and in $\text{Ag}_2\text{VO}_2\text{PO}_4$ is 20 times. The photostability of $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{VO}_2\text{PO}_4$ does not decrease after 6 cycles, this confirmed the excellent combination in terms of photodegradation performance. This can be attributed to the direct Z-scheme heterogeneity between $\text{g-C}_3\text{N}_4$ and $\text{Ag}_2\text{VO}_2\text{PO}_4$, which efficiently results in charge separation. Recent advances have been made in the field of photocatalytic organic synthesis based on two-dimensional semiconductor with surface defect engineering. [65]. Zhang et al. used $\text{Ag}@\text{AgVO}_3$ nanowires/graphene/protonated $\text{g-C}_3\text{N}_4$ nanosheets ($\text{Ag}@\text{AgVO}_3/\text{rGO}/\text{PCN}$) for the photocatalytic degradation of phenol, MB, and MO. This three-compound photocatalyst is efficient for the degradation of organic pollutants under sunlight irradiation because of the intense visible light absorption of $\text{1D Ag}@\text{AgVO}_3$ nanowires, electronic conductivity of two-dimensional graphene with outstanding physical and chemical properties [66], wide surfaces and fast transmission, and the separation of fast load interfaces [67]. The large surface area of $\text{Ag}@\text{AgVO}_3/\text{rGO}/\text{PCN}$ heteroconjugates is due to the one-dimensional $\text{Ag}@\text{AgVO}_3$ bridge nanowires as the distance between 2D PCN and GO nanosheets of graphene oxide nanosheets to prevent the accumulation of both nanoplates and the creation of three-dimensional porous structures. The 2D nanosheet form of photocatalysts have many substantial superiorities over common three-dimensional nanoparticle photocatalysts, containing amended light absorption specifications, shortening of hole and electron transfer routes to the surface of photocatalysts (therefore, undesirable recombination of the electron-hole pair is minimized), and numerous defects of surface, the possibility of modulating the band and facilitating the transfer of charge from the semiconductor to the absorbers [68].

It is reported that the Z-scheme $\text{BiVO}_4\text{-Ru}/\text{SrTiO}_3\text{:Rh}$ composite photocatalyst is useful for solar water splitting and the photocatalytic activity forcefully depend on the synthesis method [69]. Photocatalytic activity also depends on pH, so that in acidic conditions it is higher than neutral pH due to weak interaction between BiVO_4 and $\text{SrTiO}_3\text{:Rh}$ particles. Therefore, the result of heat treatment in the air should be investigated for the physical mixture, as heat treatment can establish a great contact between $\text{Ru}/\text{SrTiO}_3\text{:Rh}$ and BiVO_4 when both materials are blended together. However, heat treatment has an adverse effect on photocatalytic activity because cocatalytic degradation occurs and the mixture activity of BiVO_4 and $\text{Ru}/\text{SrTiO}_3\text{:Rh}$ is completely reduced under heat treatment. Also, the result of heat treatment in the air on the Composite-LSR mixture ($\text{BiVO}_4\text{:Ru}$ 0.7 wt%/ $\text{SrTiO}_3\text{-Rh}$ 1%), which shows the highest activity, has been investigated and the result has shown that its activity also decreases with heat treatment. In the process of water splitting using $\text{BiVO}_4\text{-Ru}/\text{SrTiO}_3\text{:Rh}$ under sunlight illumination, photocatalytic activity depends on the aqueous solution pH. Neutral pH conditions can provide the highest and most stable activity. However, the optimum pH value depends on the ratio of BiVO_4 and $\text{Ru}/\text{SrTiO}_3\text{:Rh}$ mixture. To maintain an equipose among the negative and positive effects of pH, an appropriate pH value of 7 is considered.

Studies by Min et al. have shown that $\text{FeVO}_4/\text{TiO}_2$, $\text{BiVO}_4/\text{TiO}_2$, $\text{InVO}_4/\text{TiO}_2$, and $\text{Ag}_3\text{VO}_4/\text{TiO}_2$ heterostructure photocatalysts have a marked change in the absorption band compared to the P25 (TiO_2) and differed notably, which is attributed to the transfer charge between TiO_2 and vanadate. These photocatalysts have a stronger structure in

the range of 400–600 nm. Because TiO_2 has higher energy levels than BiVO_4 , Ag_3VO_4 , and FeVO_4 , direct intinction of electrons into the titania conductor band facilitated the transfer to the conduction band BiVO_4 , Ag_3VO_4 , and FeVO_4 , and expanded the applications of these photocatalytic species. The photocatalytic activity of vanadium/ TiO_2 nanostructures using Rh.B decomposition under visible light illumination is remarkably higher than that of TiO_2 . Moreover, $\text{InVO}_4/\text{TiO}_2$ heterostructure composite exhibits great performance among other heterostructure composites. In a study by Yan et al., the outcome of InVO_4 photocatalytic particle size on its performance was investigated and it was found that InVO_4 nanocrystals performs better than that of InVO_4 microspheres [70]. Shen et al. also considered a hydrothermal pathway for the synthesis of RGO-InVO_4 nanostructures and proved that proper integration of RGO and InVO_4 provides better photocatalytic performance than InVO_4 and RGO alone. [71]. In this regard, a closed system at relatively high temperatures and internal pressures has been used to minimize defects, which recovers the π -conjunction graphene bond. The reason for the increase in efficiency of $\text{InVO}_4\text{-RGO}$ has been attributed to the increase in surface area and the scattered nature of the RGO as support and catalyst. The entry of InVO_4 nanoparticles into the RGO prevents the graphite structure from forming on top of each other. Metal nanoparticles, acting as a spacer, increase the distance between the sheets, thus making both sides of the RGO accessible, which in turn ensures that the specific surface area is high. The photocatalytic effect of InVO_4 can also be enhanced by combining BiVO_4 and CNQDs ($\text{g-C}_3\text{N}_4$ quantum dots) as these help to effectively separate electron pairs and increase photocatalytic efficiency for water treatment under visible light illumination. Additionally, coating $\text{g-C}_3\text{N}_4$ quantum dots can enhance the performance of visible light attraction, which is moreover useful for nanostructures to be capable to photolysis rhodamine B, so increasing the photocatalytic efficiency of the $\text{BiVO}_4/\text{InVO}_4/\text{CNQDs}$ nanocomposite [72]. Another important parameter for examining photocatalysts is their stability in multiple cycles. Stability is one of the most important factors in selecting photocatalysts to promote their practical application. The results of the stability test show that the degradation rate of $\text{BiVO}_4/\text{InVO}_4/\text{CNQDs}$ photocatalysts decreased slightly after 280 minutes of repeated five-step irradiation. The photocatalytic mechanism of the $\text{BiVO}_4/\text{InVO}_4/\text{CNQDs}$ composite revealed that under visible light illumination, after the incorporation of hydroxyl radical 2-propanol, and hole ammonium oxalate the degradation rate of Rh B had low reduction, indicating that holes and 'OH' groups were involved but not main radical groups. However, the decomposition of Rh B was notably suppressed in the attendance of the 4-benzoquinone 'O²⁻' group inhibitor. Thus, the 'O²⁻' radical activated species were the main reactive oxygen species for the $\text{BiVO}_4/\text{InVO}_4/\text{CNQDs}$ photocatalyst in Rh B mixture under sunlight. One of the available metal oxides, NiO nanostructure [73], has been used as a semiconductor with a stable band gap [74] in photocatalytic processes. The photocatalytic activities of NiO/InVO_4 and single InVO_4 were investigated by Lin et al. for the water splitting in Pyrex glass container under visible light illumination [75]. After loading NiO, numerous holes are made on the surface of InVO_4 photocatalyst, which facilitated the production of hydrogen gas. For the preparation of NiO nanoparticles, semi-solid complexes of nickel anthranilic acid with solid state decomposition can be used [76].

Wei et al. have constructed microsphere $\text{n-BiVO}_4/\text{p-Ag}_2\text{S}$ photocatalyst by depositing p-type Ag_2S on n-type BiVO_4 (Fig. 3) and have proved

Fig. 3. The photocatalysis enhancement mechanism of p-n heterojunction photocatalyst.

that this three-dimensional photocatalyst performed better than Ag_2S and BiVO_4 for the decomposition of tetracycline (TC) under visible light illumination [77]. With low levels of Ag_2S , carrier trapping sites increase, which increases carrier life span, thus improving photocatalytic activity. Conversely, if the Ag_2S deposition amount is too high, an overload of Ag_2S may block the transfer of electrons produced by the light and thus reduce the exposure of the active site due to the high overlap of the Ag_2S particles. TC degradation is a first-order reaction and has been shown using 0.3-p- n- $\text{BiVO}_4/\text{p-Ag}_2\text{S}$ to be 15 and 5 times faster than Ag_2S and BiVO_4 , respectively. Increasing the separation yield of photogenerated charges and increasing the life of the charge carrier leads to increased photocatalytic performance.

Copper oxide is a p-type semiconductor with much higher conduction band energy than conventional semiconductors [78]. In current $\text{Cu}_2\text{O}/\text{BiVO}_4$ composites, Cu_2O is a semiconductor with bandwidth of 2.0 eV and has a remarkable ability to absorb sunlight. The heterogeneous nanostructures of the p-n $\text{Cu}_2\text{O}/\text{BiVO}_4$ bond, which are synthesized by the growth of Cu_2O nanoparticles on pre-produced BiVO_4 nanostructures by junction a polyol technique with a hydrothermal procedure, are also associated with significantly efficient electron hole separation and excellent photocatalytic activity compared to the individual BiVO_4 nanocrystals for the decomposition of MB and phenol under visible light illumination [79]. The p-n junction shape between n-type BiVO_4 and p-type Cu_2O semiconductors can increase the photocatalytic activity of heterogeneous $\text{Cu}_2\text{O}/\text{BiVO}_4$ nanostructures. In this combination, increasing the separation of charge by nanoparticles by contacting Cu_2O with the holes and electrons produced by light, gives enough time to participate in photocatalytic reactions and leads to increase efficiency.

One of the most greatly used materials in the field of photocatalysis is black phosphorus (BP), which has been extensively studied due to its

adjustable band gap, high hole mobility and wide optical absorption range [80]. However, because of the low separation efficiency of the charge carriers caused by the photo, pristine black phosphorus can be combined with other materials to show good photocatalytic activity. Inspired by nature, a new photocatalytic system has been developed based on the artificial Z-scheme with a two-dimensional (2D) structure of black phosphorus (BP)/ BiVO_4 . There is an effective charge separation that oxidizes and reduces water in BiVO_4 and BP, respectively. For this purpose, BP nanoflakes were synthesized via an ultrasonication exfoliation procedure, while BiVO_4 nanosheets were prepared via the hydrothermal method. Zhu et al. were able to achieve the desired rate of O_2 and H_2 production in BP/ BiVO_4 of about 102 and $160 \times 10^{-6} \text{ mol g}^{-1} \text{ h}^{-1}$ under $>420 \text{ nm}$ light illumination, without the use of sacrifice or external bias factors [81]. Compared to other systems such as BP/ Co_3O_4 and $\text{BiVO}_4/\text{Co}_3\text{O}_4$, BP/ BiVO_4 has been shown to exhibit better photocatalytic activity even without any sacrificial agents. Moreover, as light intensity decreases, both H_2 and O_2 production are reduced. But the products of H_2 and O_2 are not linear with photon intensities. The concentrations of electrons and holes for BiVO_4 and BP/ BiVO_4 are reduced to multi-exponential due to the recombination of the charge in a short time. Charge concentrations for pure BP are also reduced because of the rapid recombination of holes and electrons produced in pure BP in a short time. BiVO_4 and BP are both fully capable of generating electrons and holes under irradiation visible light more than 400 nm. Electrons trapped in shallow and deep sites have the short lifespan and long lifespan of components, respectively, before recombination between CB electrons and VB holes. Due to the load transfer path from conduction band of BiVO_4 to the adjacent valence band of black phosphorus, the shorter lifetime is for BP/ BiVO_4 . Table 1 summarizes the photocatalytic results of vanadate-base compounds under different conditions.

Table 1. Comparison of photoatalytic effects of vanadate.

Photocatalyst	Synthesis Method	Irradiation time	pH	Efficiency	Band gap	Target	Light source	Notes	Ref.
Pt–BiVO ₄	Facile microwave-assisted	60 min	3	Ciprofloxacin degradation ratio of 91.97%	2.35 eV	Degradation of CIP	150 W tungsten halogen lamp 360–760 nm	The degradation of CIP was carried out at 35 °C in a photochemical container.	[48]
BiVO ₄ /Ag ₃ PO ₄ /PANI–6% (polymer polyaniline)	In-situ	60 min		Degradation efficiency of 85.92%	2.4–2.5 (BiVO ₄)	Wastewater treatment	300 W xenon lamp, 420 nm cut-off filter	Prior to reaction, the mixture should be stirred vigorously in the dark for 30 min to achieve the adsorption-desorption equilibrium.	[55]
Z-scheme C ₃ N ₄ /BiVO ₄	g– Mixed calcination procedure	300 min	7	Degradation efficiency of 85%		Degradation of RhB	500 W xenon lamp, λ>420 nm	Na ₂ SO ₄ was used as the supporting electrolyte.	[59]
Z-scheme C ₃ N ₄ /V ₂ O ₅ heterojunctions	g– In-situ	60 min		95.5% degradation of RhB	2.3 eV (V ₂ O ₅)	Degradation of RhB and TC	250 W xenon lamp, a 420 nm cutoff filter	Metalless g-C ₃ N ₄ bulk powders were prepared by heat treatment of melamine.	[63]
g–C ₃ N ₄ /Ag ₂ VO ₂ PO ₄ Z-scheme	Hydrothermal method for Ag ₂ VO ₂ PO ₄ , g–C ₃ N ₄ by heating melamine	120 min		40% photodegraded	~2.74 eV for g–C ₃ N ₄	Degradation of phenol and MO solution	1000 W halogen lamp, a JB 420 cutoff filter λ>420 nm	To prepare g–C ₃ N ₄ /Ag ₂ VO ₂ PO ₄ heterojunction photocatalyst, powders were added into deionized water, followed by 30 min of ultrasonication. The mixture was heated in an oven and dried at 200 °C for 3 h.	[64]
Ag:AgVO ₃ /rGO/PCN (protonated g–C ₃ N ₄ nanosheets)	Electrostatic self-assembly	120 min		~98.9% MB degradation		Degradation of methylene blue (MB)		MO ~86% in 20 min, phenol ~81% in 60 min was decomposed.	[67]
BiVO ₄ –Ru/SrTiO ₃ :Rh Z-scheme composite	Impregnation procedure, liquid–solid state reaction		7	Quantum yield of 1.6% under 420 nm		Water splitting	300 W Xe lamp, a cut-off filter and cold mirror	Photocatalytic process was mainly performed in a closed gas circulation system and an irradiation cell with a Pyrex window.	[69]
Reduced graphene oxide (RGO)–InVO ₄	Hydrothermal method for InVO ₄ , sonication for RGO	120 min	8		2.0 eV for InVO ₄	Removal of methyl orange and Cr (VI)	Xe lamp	The whole process can be carried out under mild conditions.	[71]
InVO ₄ /BiVO ₄ /CNQDs (g–C ₃ N ₄ quantum dots)		40 min	3	100% of the Rh B was degraded.	2.70 eV for CNQDs	Degradation of rhodamine B (RhB)	300 W Xe lamp, λ>420 nm		[72]
NiO/InVO ₄	Solid-state reaction method	120 min		The apparent quantum yield was 56%	3.6–4.0 eV for NiO	Water splitting	500 W halogen lamp	Pyrex glass reactor equipped with cooling water	[75]
n-BiVO ₄ /p–Ag ₂ S, n–p heterojunction	Precipitation			The degradation efficiency of 0.3-p-Ag ₂ S/n-BiVO ₄ can be achieved 90%.	2.3 eV for 0.3-p-Ag ₂ S/n-BiVO ₄	Degradation of tetracycline	500 W Xe lamp, a cut-off filter (420 nm)	The photocatalyst should be dispersed in 50 ml of tetracycline (20 mg/L), stirred for 1 hour in the dark to achieve equilibrium of absorption and desorption.	[77]

Table 1. Continued.

Photocatalyst	Synthesis Method	Irradiation time	pH	Efficiency	Band gap	Target	Light source	Notes	Ref.
p–n junction Cu ₂ O/BiVO ₄	Hydrothermal method	240 min	7	97.3% of MB was degraded	2.0 eV for Cu ₂ O	Degradation of methylene blue (MB) and phenol	300-W Xe lamp coupled with a UV cut off filter (>420 nm)	Cu ₂ O nanoparticles were grown on the BiVO ₄ nanocrystals by a polyol method.	[79]
Heterostructure of black phosphorus (BP)/BiVO ₄ (2D)	Ultrasonication exfoliation method for BP, hydrothermal method for BiVO ₄ nanosheets	180 min		The apparent quantum efficiency (AQE) of H ₂ production is around 0.89%.		Oxidation of water	>420 nm light irradiation		[81]
V ₂ O ₅ nanorods/graphene oxide (GO)	Sonochemical process	90 min		98% degradation of Victoria Blue dye		Degradation of VB (Victoria Blue dye)			[82]
InVO ₄ /TiO ₂ heterostructure	Ion impregnate	30 min	7		2.1 eV for InVO ₄	Rh.B and benzoic acid (BA) degradation	LED lamp, 8 W		[83]
FeVO ₄ /TiO ₂ heterostructure		30 min	1				LED lamp, 8 W	There is a significant absorption of 540 to 800 nm for the FeVO ₄ sample.	[83]
Ag ₃ VO ₄ /TiO ₂ heterostructure		30 min	7				LED lamp, 8 W	The absorption edge of the Ag ₃ VO ₄ is about 600 nm.	[83]
BiVO ₄ /TiO ₂ heterojunction	Hydrothermal method	60 min				RhB degradation	LED lamp (4 W)		[84]
BP/BiVO ₄ /Co ₃ O ₄ (agent: AgNO ₃)	Hydrothermal method	180 min		AQE of H ₂ production is around 4.45%.		Water splitting	Visible light (>420 nm)		[85]
BP/BiVO ₄ /Co ₃ O ₄ (agent: ethylenediaminetetraacetic acid: EDTA)	Hydrothermal method	180 min		AQE of H ₂ production is around 6.5%.		Water splitting	Visible light (>420 nm)		[85]
Nanoporous BiVO ₄ /Bi ₂ S ₃ nanosheets	Hydrothermal method	40 min	1.7		<2.03 eV	Water splitting	300 W Xe lamp and AM 1.5	Loading FeOOH could enhance the photoelectrochemical water splitting ability.	[86]
BiVO ₄ /ZnFe ₂ O ₄	Multiple strategy	40 min	13		~ 2.0 eV	Water splitting		When Co ²⁺ was added, the resulting much more stable photocurrent	[87]
Mo:BiVO ₄ /Au	Multiple strategy		7	Incident photon-to-electron conversion efficiency (IPCE) 41%	1.23 eV	Hydrogen production	AM 1.5G light (100 mW cm ⁻²)	By adding a semiconductor underlayer, the designed structure overcomes the reflection losses of light.	[88]
WO ₃ /BiVO ₄ , CoPi core-shell nanostructured	Glancing angle deposition (GLAD) electrochemical deposition	180 min	7	Hydrogen generation efficiency of 8.1%		Water splitting	Sunlight	Cell temperature of 50 °C	[89]

Table 1. Continued.

Photocatalyst	Synthesis Method	Irradiation time	pH	Efficiency	Band gap	Target	Light source	Notes	Ref.
W/Fe-co-doped nanoparticles BiVO ₄ loaded with MOF MIL-100	BiVO ₄ by drop-casting MIL-100(Fe) by hydrothermal method		7	IPCE of 52.6%		Water splitting	300 W xenon lamp	Ambient conditions apply	[90]
Pt/MnO _x /BiVO ₄	Impregnation method	60 min				Degradation of MO and RhB	300 W Xe lamp ($\lambda > 420$ nm)	IO ₃ ⁻ as an electron acceptor	[91]
Pt/Co ₃ O ₄ /BiVO ₄	Photo-deposition method	60 min		160.3 $\mu\text{mol h}^{-1}$ of O ₂ evolution		Water oxidation	300 W Xe lamp ($\lambda > 420$ nm)		[91]
CdS/Bi ₄ V ₂ O ₁₁	Facile in-situ growth method	120 min	7.5	77% activity	2.21 eV	Pollutant degradation	250 W, with a 420 nm cutoff filter	Bi ₄ V ₂ O ₁₁ prepared by solvothermal method.	[92]
Mn ₂ V ₂ O ₇	Hydrothermal process	240 min	7	90.6% degradation	2.79 eV	Degradation of methylene blue	100 mW/ml of solar power	Polymer polyvinyl pyrrolidone (PVP) as the surfactant and adjusting the pH value	[93]
AgBr-Ag-BiVO ₄	Hydrothermal procedure	180 min				Bacterium inactivation and organic pollution treatment	300 W Xe lamp, a 420 nm cutoff filter	The mass percentage of Ag in the total Ag and BiVO ₄ is 3 wt %.	[94]
BVO/BFO (bismuth vanadate/bismuth ferrite)	Multiple strategy	90 min	9.5	99% of TC degradation	1.92 eV for BFO	TC degradation	250 W Xe lamp ((Oriol), a 420 nm cutoff filter)	Process efficiency enhanced with increasing solution pH.	[95]
Ag ₂ Sr(VO ₃) ₄	Solid state method	180 min		O ₂ -evolution rates of 8 $\mu\text{mol.h}^{-1}$	2.4 eV	Water oxidation	$\lambda > 400$ nm, 300 W, Xe arc lamp, L42 cut-off filter)		[96]
Sr(VO ₃) ₂	Solid state method	180 min		O ₂ -evolution rates of 12 $\mu\text{mol.h}^{-1}$	2.7 eV	Water oxidation	$\lambda > 400$ nm, 300 W, Xe arc lamp, L42 cut-off filter)		[96]

4. Applications

4.1. Water splitting

Water splitting to produce hydrogen and oxygen on a photocatalyst under visible light illumination is a hopeful method to produce clean, large-scale hydrogen. Photocatalysis has proven to be the latest technology that can aid in providing solution to energy storage. A potential solution to compensate for the lack of energy is to use solar energy as an endless primary source of energy combined with semiconductor photocatalytic systems. Visible light makes up the bulk

of the solar spectrum, so its use can revolutionize the development of photocatalyst applications [97, 98]. One of the most important fuels is hydrogen, which is a promising and renewable chemical fuel due to its high energy density and environmentally friendly [99]. Clean generation of H₂ by water splitting using a semiconductor photocatalyst and solar energy, without relying on fossil reserves, is a new technology [60] which is a target pursued by chemists over the past decade. Half of the solar energy at the earth surface is in the visible region ($400 < \lambda < 800$ nm), so the efficient use of visible light is essential to achieve large-scale practical H₂ production by photocatalytic water splitting [100]. The advantage of photocatalytic water splitting is that no sacrificial reagent is required to produce hydrogen and oxygen

[101]. This process is a competitive low-cost technology for large-scale use compared to traditional industrial hydrogen production, including natural gas or methane steam reforming. Achieving a stable, low-cost, non-toxic photocatalyst with the desired solar-hydrogen conversion efficiency is critical to achieving widespread use of this sustainable technology. The overall H_2O splitting into H_2 and O_2 is an endothermic reaction that requires 1.23 V energy [102]. One of the important parameters of this process is the H_2 production rate, which is affected by various factors. For efficient conversion of solar energy by a semiconductor-based photocatalyst, the photocatalyst must have a suitable band gap that will not only efficiently absorb light but also a suitable conduction band (CB) and valence band (VB) levels for water-splitting redox reactions [103]. Furthermore, a desirable photocatalyst must be highly effective at isolating and transmitting light-generated charges [104]. Unfortunately, it suffers from recombination photogenerated holes and electrons, which reduces the efficiency of the solar to hydrogen (STH) [105]. The photocatalytic hydrogen production of a ternary composite is significantly improved compared to a single composite. The increase in activity depends mainly on the Schottky effect and the heterogeneous Z-scheme photosynthesis system, in which the effective charge separation is WO_3 as a hole collector and Au as an electron collector. Also, the effect of Surface Plasmon Resonance (SPR) in Au further increases charge separation and visible light absorption. The high decomposition efficiency of H_2O in the synthetic structure depends on the direct electronic structure of the Z-scheme of ternary photocatalyst and the spatial oxidation units separated from the Z-scheme, which greatly increases the lifespan of the electrons produced by the light and the holes, and prevents the reversibility of the reaction [106]. The constructed direct Z-scheme photocatalysts, which imitate nature's photosynthetic process, have many advantages, such as enhanced light absorption, spatially isolated reductive and oxidative active sites, and well-preserved intense redox capability, which contribute to photocatalytic efficiency [107]. Some parameters such as catalyst dose, pH values, water source and symbiotic ions affect the photocatalytic performance. Achieving 30% in terms of quantum performance at 600 nm for water splits into H_2 and O_2 has not yet been achieved because a limited number of photocatalysts have been used for water splitting. The Rh-BiVO₄ photocatalyst has responded to split water to about 500 nm. However, to achieve higher quantum performance, we need to work on producing new and superior photocatalyst materials for clean energy production. There are also beneficial opinions for the construction of other new types of metal hydroxide photocatalysts that act by combining anion replacement and cation doping in the visible region [108].

4.2. CO_2 reduction

The photocatalytic conversion technology of CO_2 to carbonaceous chemicals [109] can be used to prepare feedstock for many processes, which is a promising solution to reduce greenhouse gases and storing energy [110]. Understanding the reaction mechanism of CO_2 and especially the active site of the photocatalyst can help develop the application of photocatalysts [111]. Because CO_2 is an inert gas, it has the tendency to reduce multi-electrons reaction in photocatalysis and determines the high complexity of the reaction for study. Research has shown that increasing photocatalyst activity helps increase CO_2 uptake capacity, better absorption of visible-light, and charge transfer from covalent triazine-based framework (CTF) to CO_2 molecules [112].

To make effective use of visible light and overcome large-scale defects in metal oxides, several visible light-reactive catalysts have emerged, such as CsPbBr₃ QD/GO [113], doped NaTaO₃ [114], Fe-doped ZnO [115] and BiOBr-GO [116]. Studies have shown that monomeric photocatalysts always lose their photocatalytic activity under the influence of inherent defects such as structural defects, photo corrosion, and rapid recombination of charge carriers produced by light. There are some ways to improve the photocatalytic activity of monomers that can be useful for the industrialization of photocatalysts [117]. For this purpose, conventional methods such as heterogeneous fabrication with other metals, combination with semiconductors, molecular and elemental doping and preparation of nanocomposite have been used so far [118].

4.3. Air and water purification

To remove contamination, industrial plants must eliminate synthetic organic dyes from wastewater before its discharging into natural water sources. The photodecomposition of pollutants in air and water is an exciting research interest in photocatalysis [119]. In the field of gas phase photocatalysis, four main uses can be proposed: indoor air, outdoor air, processing gases and soluble pollutants [120]. Each of these applications has special characteristics that can affect the type of optical reactor and the composition of the photocatalyst used compared to other treatments [121]. Photocatalytic conversion of organic compounds such as benzene in polluted ambient air in the presence of TiO₂ has been considered [122]. In photocatalytic reactions, several factors such as organic class, water, catalyst type, radiation and oxygen are involved, which complicate the process. Thus, the operational parameters related to each of these factors clearly affect the efficiency of the photocatalytic process. Fig. 4 depicts the mechanism for wastewater treatment.

Several studies have been reported in the use of heterogeneous photocatalysis in the decomposition/elimination of contaminants in the aqueous solution, which includes contaminants such as dyes [123–125], herbicides/pesticides, aromatic compounds, phenols [126] and pharmaceutical effluents [126]. Ciprofloxacin (CIP) and levofloxacin are widespread antibiotics used in the treatment of various infections and has been detected in the aquatic environment recently [127]. Its presence in the environment can simulate bacterial resistance and is a risk to the environment, so it should be eliminated from the water. One of the possible ways for antibiotic treatment is to degrade it in a photocatalytic process [128]. The advantages of removing the residual dye in wastewater by photocatalytic decomposition include as mild photocatalytic conditions, less need for chemical reagents and decomposition of artificial organic dyes into small non-toxic molecules [129]. TiO₂-coated nanoparticles absorb natural sunlight at 980 nm and convert it to ultraviolet and blue light, which is suitable for photocatalytic activation [130]. In this regard, organic dyes such as methylene blue (MB), methyl orange (MO) and rhodamine can be degraded. Photocatalyst must possess high absorption properties and photocatalytic activity before it can be suitable in the removal of recalcitrant organic pollutants in water. Adsorption properties play an important role in the decomposition of methylene blue due to the interaction between methylene blue and photocatalyst molecules [131]. Semiconductors such as Fe₂O₃, WO₃, ZnO and, TiO₂ have band gap in the range of 2.2–3.2 eV show unsatisfactory photocatalytic properties due to high band gap energy and restrict their practical application.

Fig. 4. The mechanism of wastewater treatment.

Incorporating metal ions into their lattice will assist in without negative electron transfer makes them more sensitive to a wide range of solar spectra. By changing the structure of the band gap, the removal of contaminants can be increased. The dye contents can be degraded into a degradable product by binary metal oxide photocatalysts prepared by different procedure. The ternary composite is highly efficient against the photocatalytic oxidation of rhodamine B and methylene blue. For photocatalytic oxidation of rhodamine B and methylene blue, the ternary composite has a high efficiency [132]. Wide band gaps are present in most photocatalysts and cause them to be active only in the UV region. The solar spectrum contains only about 4% of ultraviolet illumination. Semiconductors with white color and wide band gaps need to be modified because they do not absorb in the visible range of the spectrum. Photocatalysts can be modified by using methods such as surface modification, composite or pair materials, metallic and non-metallic doping, and metal complexes to perform better performance [133].

The photocatalytic reaction occurs at the photocatalyst surface and the acid-base properties of the reaction medium have a significant effect on the process efficiency [134]. The pH variation of the environment causes the surface charge of the photocatalyst to be distributed, given that it will have a positive or negative charge level in relation to the reference value for each substance. Therefore, the efficiency of catalytic activity arises from the amphoteric behavior of materials and its effect on the absorption of organic matter on the substrate. The reaction rate of the photocatalytic process is a function of the photocatalyst mass unit if reach to a certain level, after that, the mass of photocatalyst doesn't affect the reaction rate. In these reactions, it has been proven that the reaction rate increases with increasing organic bed concentration according to the law of velocity.

The active sites of the catalyst are easily occupied in conditions of high concentrations of organic matter [135]. Therefore, a slight increase in the initial concentration of the substrate reduces the adsorption capacity of the photocatalyst and reduces the reaction rate.

The main purpose of altering the morphologies of photocatalyst is to reduce its band gap and increase the light response to the visible zone, as well as the recombination reduction of the electron/hole pair and increase the photocatalytic activity of semiconductors. In an effort to develop effective methods for the removal of lethal contaminants from wastewater and water treatment, the focus is on the development of a binary metal oxide catalyst supported for the photocatalytic oxidation process used in wastewater [136, 137]. In this regard, doping with

correct choice of the metal ions and its optimum concentration, can be used to change the chemical, physical, optical and photocatalytic properties of raw materials in a complex way [138]. It also maintains charge separation from the electron/hole pair and keeps the photocatalyst excited for longer. However, at high concentrations, the metal can proceed as a recombination agent and disrupt the photocatalytic process [139]. Photocatalytic activity can be enhanced by increasing surface area and porosity [140], composite constitution, methodology and crystallite size reduction. The dose of photocatalyst used plays a significant role in the photocatalytic activity for pollutant degradation.

4.4. Nitrogen fixation

Nitrogen fixation is the operation by which molecular N_2 gas is turn into reactive and biological species of nitrogen, which is a fundamental process on a global scale for survival [141]. Nitrogen fixation is a reaction performed by the Haber-Bosch process in industry to produce biomolecules. This process requires intense reaction conditions (temperature above 300°C and pressure 15MPa) that consume a lot of energy [142]. Therefore, researchers were looking for an environmentally friendly method with moderate conditions to reduce energy consumption and a reasonable cost for nitrogen fixation [143]. Photocatalysis has shown great capability in N_2 fixation as an eco-friendly technology with solar energy as the power source in the reaction process [144]. Today, the design of nanostructured photocatalysts has expanded because it provides improved photocatalytic activity due to the separation and transfer of their photogenerated effect [145]. The photocatalytic activity of nanocomposites strongly depends on the shape of the loading particles, the optical band gap and the concentration of the defect [146]. Nanostructured photocatalysts often have higher specific surface area and more active sites compared with their bulk counterparts, thus being able to excite N_2 molecules. It is important to select materials that can replace nitrogen voids with the photocatalytic stabilizing ability of N_2 . [147]. New research on Z-scheme photocatalytic systems has made semiconductor material design more logical and practical [148], which not only solves the problem of insufficient light absorption and faster recombination, but also offers chemists a wide range of perspectives. But, the selection of suitable semiconductor materials, insufficient absorption of visible light and low quantum efficiency still limit practical applications. In addition, to achieve fine-tuning at the junction of support and other photocatalysts, it is important to inspect the

nanoparticle anchor on the support surface. Various pathways should be considered to adjust the functional capacity of the surface to enhance anchorage capability, as effective migration and separation of photocarriers is only possible through the surface bonding of intact nanocomposites.

5. Conclusions

In this review, we presented recent advances in the characterization, synthesis, and photocatalytic applications of vanadate photocatalysts, particularly in the field of energy supply and pollutant degradation. Over the past five years, some interesting studies on vanadate photocatalysts have been reported and highlighted. Many solutions, such as energy band engineering, doping, heterojunction structure, surface moderating, and conjunct catalyst bonding, have been used to increase light absorption, modify charge carriers, progress photocatalytic resistance, and hasten surface reaction kinetics. Several vanadate compounds as a photocatalysts have been designed and prepared, including Pt-BiVO₄, Z-scheme BiVO₄, heterojunction BiVO₄, InVO₄, FeVO₄ heterostructure, Ag₃VO₄, VO₄-based ternary composites. These photocatalysts are good candidates for purposes such as water distribution, pollutant degradation, water treatment, CO₂ reduction, N₂ stabilization and organic synthesis.

The electronic structure of the catalyst and the exposed surfaces can greatly affect the photocatalytic efficiency because photocatalytic reactions occur on the catalyst surface. Reducing electron-hole pair recombination and promoting electron transmit proficiency, both of which can generally be realized in defect-rich 2D systems, are other steps towards enhanced photocatalytic efficiency. As it turned out, the heterojunction Z-scheme design system has a better result for photocatalytic hydrogen production. In particular, the network construction of independent 3D nanotubes can enhance the separation performance of photocatalysts. Also, doping on some vanadium compounds such as BiVO₄ by semiconductors such as WO₃, NiO and CdS and using perovskite-based composites will be an important step towards achieving the goals.

However, most of the photocatalysts only respond to ultraviolet light for water splitting. Commercializing photocatalysts requires the participation of various specialized groups such as materials scientists, band gap engineers, chemists and chemical engineers. It is important to develop visible-light-responsive photocatalysts in order to harvest sunlight efficiently. Further research is needed to form binary and ternary composites to absorb light in the visible region and increase degradation by preventing electron recombination with less catalyst and time. Then, new opportunities are created to address the challenges effectively with the use of modified composites. Decreased catalytic activity over time is a usual problem for all photocatalysts, becoming a barrier to their industrial applications. The main problem to work out involves the synthesis of a large-scale, high-performance vanadate photocatalyst with high photocatalytic efficiency. For example, highly crystalline products with suitable defects exposed and active aspects were difficult to obtain in the precipitation method. The production of atomic-thick vanadium-based materials, or the conversion of nanosheets to monolayers through peeling, is a new strategy that could be used in the future. Of course, this approach is challenging because the interlayer of vanadate-based photocatalysts are absorbed by electrostatic interaction instead of van der Waals forces.

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