MODIFICATION METHODS TO ENHANCE THE PERFORMANCE OF TiO$_2$ IN PHOTOCATALYSIS

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With industrial development and changes in human lifestyle, organic pollution has become an increasingly serious problem, posing a serious threat to the ecological environment and human health. As an emerging advanced oxidation process, titanium dioxide–based photocatalysis has shown unparalleled potential in solving environmental pollution problems due to its stable catalyst properties, mild reaction conditions, environmental friendliness and low cost. However, titanium dioxide is limited in its photocatalytic efficiency by the fact that it can only be excited by ultraviolet light, its carriers are easily compounded and its adsorption capacity is weak. In order to improve the photocatalytic degradation efficiency of organic pollutants, the properties of titanium dioxide can be enhanced by means of modification. This article mainly reviews several major modification methods and research progresses of semiconductor titanium dioxide materials for the degradation performance of organic pollutants in the environment, and focuses on the advantages of the new Metal Organic Frameworks/ titanium dioxide composite system in enhancing the degradation performance of organic pollutants. Finally, the application prospects and key issues of Metal Organic Frameworks/ titanium dioxide materials in photocatalytic treatment of organic pollution problems are presented.

1. Organic pollutants in the environment

With the development of society and technology, people's standard of living has continued to rise, benefiting from advances in industrial technology. However, with the unbridled expansion of industries such as transportation, construction, chemicals and mining and the accelerated urbanisation process, the excessive consumption of natural resources and the generation of large amounts of hazardous waste threaten human health and the safety of the environment (Bhatt et al., 2021; Gang et al., 2021). Organic pollutants, in particular, have become a typical category of pollutants of greatest concern to researchers due to their high toxicity, strong accumulation and difficulty in degradation (Lan et al., 2021; Samanta et al., 2019).

According to previous ecological investigations, organic pollutants have been present in the environment for a long time and they are not only difficult to biodegrade but also have a high rate of transport (Ajiboye et al., 2021). These toxic organic pollutants are

present in the environment in different forms, such as in water, soil and air. These organic pollutants mainly include Volatile Organic Compounds (VOCs) such as phenolics, aldehydes, petroleum–based substances (Liu et al., 2020; Okoh, 2020), insecticides (Zhang et al., 2018), pesticides, etc. It also includes some non–volatile organic compounds such as dyes (Wang et al., 2016), antibiotics, humic substances, surfactants, etc.

Compared to non–volatile organic pollutants, VOCs tend to be more biotoxic and migratory. According to the World Health Organization (WHO), VOCs are usually organic compounds with a boiling point of 50–260 °C at atmospheric pressure (WHO, 2010). The sources of VOCs are widely distributed and can be divided into outdoor sources and indoor sources. Outdoor sources include: agricultural production, automobile manufacturing, textile manufacturing, electronic component manufacturing, petrochemicals, vehicle exhaust emissions, preservatives, pesticides, etc. Indoor sources include: furniture supplies, office supplies, printers, plumbing materials, insulation materials, etc (Skjevrak et al., 2003).

VOCs are harmful to the ecological environment and human health, and some VOCs (e.g., chlorofluorocarbons) can destroy the ozone layer and thus contribute to the greenhouse effect.VOCs are also precursors to the production of atmospheric fine particulate matter (PM2.5) and urban photochemical smog, and under light, they react photochemically with atmospheric nitrogen oxides to produce photochemical smog, which causes damage to the environment and is detrimental to human health. Wastewater containing VOCs (e.g., preservatives containing high concentrations of formaldehyde) can cause the death of fish and aquatic plants leading to the destruction of the entire aquatic environment (Guimarães et al., 2012). High concentrations of VOCs can cause many serious diseases such as acute leukemia, central nervous system poisoning, and asthma in children, and even low concentrations of VOCs can cause various chronic diseases such as respiratory and cardiovascular diseases in humans after a certain period of exposure, and even produce serious hazards such as carcinogenesis (Bishop, 2008). Therefore, the control and management of VOCs are of great importance for the protection of human health and ecological environment.

Many technologies have been used to reduce the emission of VOCs into the environment: adsorption, condensation, membrane filtration, ozone oxidation, high–temperature combustion, thermal catalysis, biological purification, and low–temperature plasma technology (Jeong et al., 2005; Mamaghani et al., 2017). However, most of these treatment technologies are for high concentrations of VOCs and require special equipment and space, high treatment costs, long treatment cycles, and can cause a lot of secondary pollution. However, the current severe groundwater pollution and indoor air pollution problems are usually low concentration and large scale pollution, so the above mentioned cleaning technologies are not promising to be used in this realistic context.

Photocatalysis has received widespread attention and development since 1972, when the Japanese scientist Akira Fujishima discovered that TiO_2 electrodes could crack H_2O under light to produce hydrogen (Fujishima & Honda, 1972). Photocatalytic technology has the advantages of low energy consumption, high degradation efficiency for

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On-line ISSN 2521-151X

low concentrations of pollutants, can be performed at ambient temperature and pressure, and is universal for polluting pollutants. Therefore, this method is very promising for treating low concentration organic pollutants in the environment.

2. Basic principles of photocatalysis and promising photocatalysts for degrading organic pollutants in the environment

2.1 The basic principle of multi–phase photocatalysis

Photocatalytic reaction is a complex process. Photocatalysts can excite photogenerated electrons (e^-) and photogenerated holes (h^+) after absorbing light energy, and then the photogenerated electrons and holes interact with water molecules and oxygen on the surface of the photocatalyst, which in turn form superoxide radicals ($\cdot O_2^-$), hydrogen peroxide (H_2O_2), singlet oxygen ($^1O_2$), and hydroxyl radicals ($\cdot OH$) and other strongly oxidizing reactive species (Figure 1) (Nosaka & Nosaka, 2017). It is generally believed that the photocatalytic degradation of organic pollutants is dominated by these photoactive species.
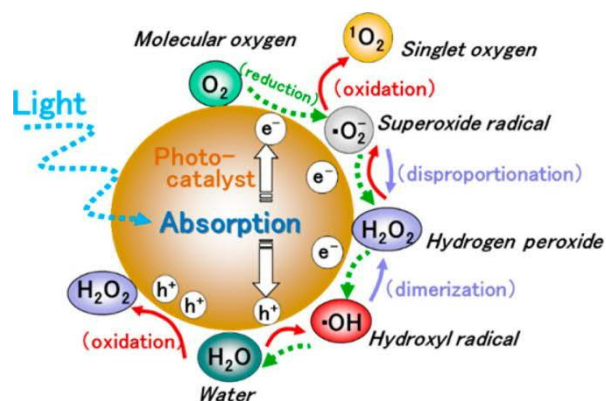

Fig. 1. Mechanism of semiconductor photocatalytic reaction (Nosaka & Nosaka, 2017).

Due to the strong Coulomb forces between photogenerated electrons and photogenerated holes, a portion of the photogenerated electrons and holes will be compounded during their migration to the photocatalyst surface, and the energy released after compounding is lost in the form of fluorescence, phosphorescence and heat. Therefore, the activity of photocatalysts is inextricably linked to the separation and migration efficiency of photogenerated electrons and photogenerated holes. Therefore, enhancing the separation and migration of photogenerated electrons and holes and thus reducing their complexation is an effective means to enhance the photocatalytic activity.

2.2 Photocatalysts

In recent years, there has been a great progress in the research on the fabrication of efficient semiconductor–based photocatalysts (Wang et al., 2020; Yeh et al., 2016). Different photocatalysts have different oxidation and reduction capabilities due to their different positions of the highest molecule occupied orbital (HOMO) as well as the lowest molecule occupied orbital (LUMO), i.e., different potentials in the valence band (VB) and conduction band (CB), and the energy band positions of several mainstream catalysts are shown in Figure 2 (Li et al., 2016).

This is because the thermodynamic driving force in the photocatalytic process strongly depends on the relative relationship between the potential of the CB/ VB of the semiconductor photocatalyst used and the redox potential of the target species. Therefore, the more negative CB position of the semiconductor favors the reduction reaction, while the more positive VB position of the semiconductor favors the oxidation

reaction. Therefore, it is generally believed that semiconductors with sufficient positive VB potential are more suitable as photocatalysts for degrading organic pollutants such as VOCs, such as metal oxide
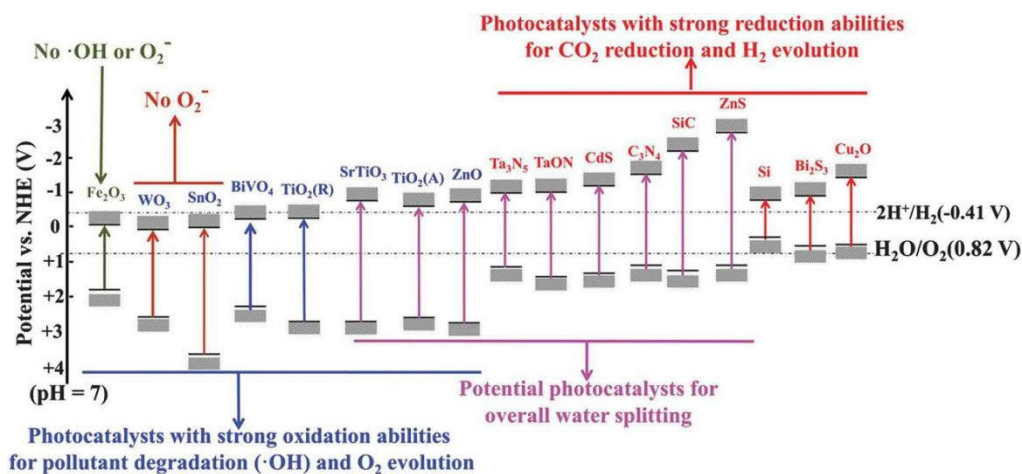

Fig. 2. *Energy band location map of mainstream semiconductor photocatalysts (Li et al., 2016).*

photocatalysts (TiO_2, ZnO, Fe_2O_3), chalcogenide photocatalysts ($SrTiO_3$), spinel photocatalysts ($ZnAl_2O_4$, $BaAl_2O_4$), bismuth–based photocatalysts ($BiVO_4$, Bi_2WO_6, BiOCl and BiOBr), etc.

Interestingly, TiO_2 semiconductor photocatalysts, as the first discovered photocatalytic materials, have been hotly researched in the field of photocatalysis. TiO_2 exists in three different crystalline forms, anatase phase, rutile phase and slate phase.

All three crystalline forms of TiO_2 can be easily synthesized under conventional laboratory conditions. Among them, the rutile phase is the most thermodynamically stable one, and the anatase and slate phases transform to rutile phase when the calcination temperature exceeds 600 °C. All three crystalline forms are coordinated with one Ti^{4+} and six O^{2-} to form TiO_6 ortho–octahedra.

As shown in Figures 3 for the three different crystal structures of TiO_2, the band gap of anatase phase TiO_2 is 3.2 eV, the band gap of rutile phase TiO_2 is 3.0 eV, and the band gap of plagioclase phase TiO_2 is about 3.2 eV (Koelsch et al., 2004).

Generally, TiO_2 in anatase and rutile phases possess higher catalytic activity, which is attributed to their excellent energy band positions.

As shown in Figure 3, the positions of the valence and conduction bands of TiO_2 ensure the simultaneous formation of hydroxyl radicals (·OH), superoxide radicals (·O_2^-), and hydrogen peroxide (H_2O_2) at pH=7. All these active species have been shown to play an important role in the photocatalytic degradation of organic compounds (Chen et al., 2010; Wen et al., 2015).

Compared to other semiconductor materials, they have the advantages of high activity, low cost, non–toxicity, and high stability (Chen et al., 2012).

Therefore, TiO_2 is considered as one of the most promising photocatalysts in the field of environmental purification.
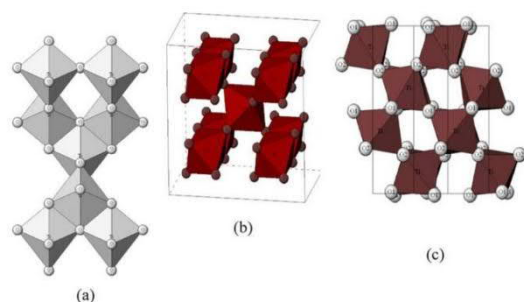
Fig. 3. *Crystal structure of TiO$_2$ (a) Anatase phase (b) Rutile phase (c) Plate titanite phase. Reprinted with permission from Advanced Industrial Science and Technology (AIST)*

3. Methods for improving photocatalytic activity

TiO$_2$ as a promising semiconductor photocatalyst, although it has numerous advantages over other photocatalysts, its development is currently constrained by some defects. Firstly, TiO$_2$ is a broadband semiconductor material, which can only be excited by UV light (λ<387 nm), however, the energy of UV light only accounts for 4–5 % of the total energy of sunlight, so TiO$_2$ has the problems of low quantum efficiency and low utilization of light energy. In addition, the crystal structure of TiO$_2$ leads to its small specific surface area and poor adsorption ability to pollutants. Based on this, researchers have used various methods to study the modification of TiO$_2$, mainly including constructive morphology, ion doping, surface modification and construction of composite materials.

3.1 Morphology and structural modification

Porous materials, including TiO$_2$ with mesoporous, multilayered, and hollow structures, can be prepared by regulating the growth conditions of TiO$_2$. preparing porous materials not only increases the specific surface area of TiO$_2$ and the number of active sites, but also increases the reflection of light in the multilayered structure and improves the utilization of light energy (Réti et al., 2017). In addition, due to the quantum size effect, the band gap of TiO$_2$ can be adjusted when reducing the size of nanoparticles to the nanoscale, extending its optical response range (Alivisatos, 1996).

Kondo et al. (2008) prepared submicron spherical hollow anatase TiO$_2$ particles of uniform size using polystyrene templates, and the resulting sample had a specific surface area greater than 70 m^2/g and was 1.8 times more active than commercial P25 in the degradation of gaseous isopropanol under UV light.

Alosfur et al. (2018) prepared mesoporous nano–TiO$_2$ hollow spherical structures with high surface area by microwave method, and the sample had a specific surface area of about 172.3 m^2/g and degraded methylene blue up to 99% under UV light for two hours, which was much higher than commercial anatase.

Li et al. (2007) used TiOSO$_4$ as a precursor to synthesize sea urchin structured TiO$_2$ hollow spheres using a template–free solvothermal method, which enables the regulation of the hollow cavity size, and this hollow structure facilitates multiple reflections of UV light, thus greatly improving the photocatalytic activity of TiO$_2$ in the degradation of phenol.

3.2 Elemental doping

Doping or element doping is a widely used modification method, which mainly includes metal ion doping and non–metal element doping.

Metal ion doping mainly involves replacing Ti^{4+} in TiO$_2$ with transition metal ions and rare earth metal ions. Doping with rare earth ions can greatly extend the

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On-line ISSN 2521-151X

photoresponse range of TiO_2 and thus improve its solar energy utilization.

Reszczyńska et al. (2015) synthesized a series of TiO_2 rare earth ions by sol–gel method. It was shown that the rare earth ions Er^{3+} and Yb^{3+} can effectively promote the absorption and utilization of visible light by photocatalysts. Er/Yb–TiO_2 successfully decomposed phenol under visible light illumination at $\lambda > 450$ nm.

Obregón et al. (2013) prepared Er^{3+} doped TiO_2 materials by hydrothermal method, which showed good photocatalytic activity in both the liquid–phase decomposition of phenol and the gas–phase decomposition of toluene. It was found that the presence of Er^{3+} leads to the expansion of the TiO_2 lattice and Er^{3+} can act as an electron slot under UV light to promote the electron–hole separation. In addition, the upconversion property of Er^{3+} can utilize visible light or even near–infrared light, which greatly improves the light energy utilization of TiO_2 and thus the photocatalytic efficiency of the material.

Non–metal doping refers to the replacement of oxygen atoms in TiO_2 with elements such as C, N and S. By doping with nonmetallic elements, new charges are introduced in the lattice, leading to the formation of defects or changes in the type of defects affecting the band gap of TiO_2, thus expanding the absorption range of the material for sunlight.

Xu et al. (2006) prepared C–doped TiO_2 by hydrothermal method using $TiCl_4$ and glucose. It was shown that the catalytic efficiency of carbon–doped TiO_2 was 8–13 times higher than that of pure titanium dioxide.

Li et al. (2005) experimentally demonstrated that C doping leads to the generation of Ti^{3+} and oxygen vacancies are formed around Ti^{3+}. The energy band of the oxygen vacancy is located between the conduction band and valence band of TiO_2, thus achieving the modulation of the band gap of TiO_2.

Asahi et al. (2001) demonstrated by first–principles quantum calculations and found by X–ray photoelectron spectroscopy that doping nitrogen instead of oxygen into the TiO_2 lattice can effectively reduce the band gap and thus improve the photocatalytic activity.

Diwald et al. (2004) treated TiO_2 single crystals with NH_3 gas at 870 K to obtain N–doped TiO_2. It has been determined that photon absorption in the range of 2.4 eV~3.0 eV is significantly enhanced in N–doped TiO_2.

3.3 Surface modification

Unlike elemental modifications (doping), surface modifications usually involve the deposition of nanoparticles on the photocatalyst surface. The most commonly used are precious metal nanoparticles such as Ag, Au, Pt, Pd, etc. This is attributed to the unique surface plasmon resonance effect (SPR effect) of precious metal nanoparticles. When the energy and momentum of the incident light meet specific conditions, the electrons freely vibrating on the metal surface interact with photons to oscillate collectively, and the energy of the incident light is absorbed by the electrons, and the absorbed energy can be injected into the semiconductor, and the SPR effect can improve the efficiency of the system for visible light utilization (Han et al., 2017). On the other hand, due to the high Fermi energy level of noble metals, they can act as electron potential wells, and the photogenerated electrons from semiconductor excitations are

easily transferred to noble metals, thus promoting the separation of photogenerated electron holes and improving the quantum efficiency (Christopher et al., 2011). In addition, some noble metal atoms dispersed on the catalyst surface can act as the active center of the catalytic reaction, thus enhancing the catalytic reaction efficiency.

Weon et al. (2018) prepared Pt/ TiO_2 nanoparticles for the degradation of toluene and found that the photocatalytic activity of Pt/ TiO_2 catalysts was significantly enhanced compared to pure TiO_2, but Pt/ TiO_2 tended to deactivate in cycling experiments.

Tian & Tatsuma (2005) deposited Au nanoparticles (Au–TiO_2) on the surface of porous TiO_2 and found that Au nanoparticles were photoexcited and excited electrons were transferred from Au to TiO_2 conduction band due to plasmon resonance effect, and Au–TiO_2 showed high catalytic oxidation efficiency for ethanol and methanol under visible light.

Zeng et al. (2018) prepared Ag nanowires and TiO_2 composite photocatalysts (Ag@TiO_2) by a solvothermal method and found that Ag@TiO_2 degraded acetaldehyde with 72% efficiency, which was double the degradation efficiency of pure TiO_2. The authors of this paper concluded that the Ag@TiO_2 catalyst could not only broaden the photoresponse range of the catalyst through the SPR effect of Ag, but also effectively promote the separation of photogenerated electron–hole pairs.

3.4 Creating composite materials

The preparation of composite materials is an effective way to utilize the advantages of different materials to construct high–performance catalysts. By choosing a suitable composite material and TiO_2, it can effectively improve the electron–hole separation efficiency, extend the light absorption range of the catalyst or enhance the adsorption capacity of the catalyst. Due to the variety of semiconductors and their different properties, the preparation of composite materials has been widely studied. At present, the common composite systems are semiconductor/ TiO_2 system, carbon material/ TiO_2 composite system and porous material/ TiO_2 composite system.

3.4.1 Semiconductor/ TiO_2

Most of the semiconductor/ TiO_2 composites are constructed with narrow bandgap semiconductors to expand the light absorption range of the material, while the formed heterojunctions promote the separation of electron–hole pairs.

Helaïli et al. (2009) prepared xCu_yO_z/ TiO_2 composite catalysts and investigated their degradation of the dye methyl orange. It was found that the Cu/ Cu_2O/ CuO catalyst had the highest catalytic activity under visible light, while 0.5 Cu_yO_z/ TiO_2 showed the strongest catalytic degradation under simulated sunlight (UV–vis). This study analyzed the global mechanism of electron injection between nanomaterials and concluded that CuO can act as an intermediary for electron transfer from Cu_2O to TiO_2, thus reducing the loss of charge during conduction.

Niu et al. (2012) prepared g–C_3N_4/ TiO_2 composite photocatalysts with high catalytic activity for both methylene blue and Cr^{4+} ion removal by thermal conversion method. It was found that g–C_3N_4 extended the response range of the catalyst to visible light and the heterojunction facilitated the electron transfer between g–C_3N_4 and TiO_2.

Zhou et al. (2013) prepared TiO_2 nanoribbon heterostructures (TiO_2@MoS_2) coated with MoS_2 nanosheets with 3D

Water and Water Purification Technologies. Scientific and Technical News

On-line ISSN 2521-151X

hierarchical configuration by hydrothermal method, and the catalysts showed high photocatalytic hydrogen production activity and strong adsorption ability to organic dyes, and exhibited high activity in photocatalytic degradation of dye molecules.

3.4.2 Carbon material/ TiO₂

Carbon materials have good electrical conductivity, large specific surface area, and are often used to enhance catalyst performance by compounding with photocatalysts. Carbon materials include a variety of structures such as activated carbon, graphene, carbon quantum dots, carbon nanotubes, and fullerenes.

Hu et al. (2018b) used a composite of carbon quantum dots and titanium oxide (CQD/ TiO₂) and found that carbon quantum dots could improve both the adsorption ability of the material to organic matter and the separation of electrons and holes in TiO₂.

Lin et al. (2018) prepared a reduced graphene oxide and titanium dioxide composite photocatalyst (rGO–TiO₂) by hydrothermal method to investigate the degradation performance of gas–phase acetaldehyde and o–xylene, and found that the degradation efficiency of rGO–TiO₂ for o–xylene was higher than that for acetaldehyde under the same experimental conditions than that of pure TiO₂. The reason for this is that the π–bonds of graphene are more favorable for the adsorption of benzene rings.

Sun et al. (2013) prepared TiO₂ nanosheet/ graphene sheet heterostructures by a solvothermal method, which produced a tight interfacial contact between TiO₂ nanosheet and graphene sheet layers, and the materials showed high photocatalytic activity for the degradation of both rhodamine B and 2,4–dichlorophenol, and the experimental results demonstrated the key role of nanomaterial dimension in the interfacial charge transfer process.

3.4.3 Porous material/ TiO₂

The use of SiO₂, zeolite, diatomite and other large specific surface area materials and TiO₂ composite can improve the adsorption performance of the catalyst by using the large specific surface area of the porous materials, and also improve the dispersion of TiO₂. Therefore, the construction of porous materials/ TiO₂ can effectively improve the performance of photocatalysts.

Ullah et al. (2015) prepared SiO₂@TiO₂ core–shell structure by low–temperature hydrothermal method to obtain highly dispersed TiO₂ loaded catalysts. This method can effectively control the particle morphology and crystallinity, and the synthesized SiO₂@TiO₂ core–shell structures enhance the light absorption utilization by extending the optical paths inside the particles, and have higher photocatalytic activity and good cyclability compared to unloaded TiO₂.

Jansson et al. (2015) prepared a series of zeolite/ TiO₂ composites for the degradation of pollutants in the gas phase and investigated the effects of TiO₂ content, zeolite structure (zeolite Y and ZSM–5) and Si/ Al ratio on the structural properties, adsorption capacity and photodegradation activity of zeolite/ TiO₂ composites. The results of this study showed that the nature of the pollutants and the physicochemical properties of zeolites have a great influence on the adsorption capacity and photocatalytic performance of the composites, and that reasonable regulation of the zeolite and TiO₂ ratios can reduce the formation of by–products.

However, inorganic porous materials with large specific surface area such as SiO₂, zeolite, and molecular sieve usually lack light

Water and Water Purification Technologies. Scientific and Technical News

On-line ISSN 2521-151X

absorption and photochemical excitation properties. Therefore, they cannot change the energy band structure of catalytic materials, and they cannot expand the spectral sensitivity of the materials.

3.5 MOFs/ TiO₂

Metal Organic Frameworks (MOFs) are a class of porous materials with periodic network structures constructed by self–assembly of organic ligands with metal nodes bridged by coordination bonds (Batten et al., 2008; Jiao et al., 2019). Similar to zeolites and inorganic porous molecular sieves, MOFs are porous materials with large specific surface area. However, MOFs are composed of a wide variety of metal nodes and organic ligands with diverse structures and coordination modes.

Compared with conventional porous materials, MOFs have the advantages of rich structure, chemically functionalizable, ultra–high specific surface area, and dimensionally tunable morphology (Jiao et al., 2019). On the other hand, the pore channels of MOFs materials are composed of metal nodes and organic ligands arranged periodically, and MOFs have higher activity and selectivity for organic reactions compared to materials such as inorganic porous zeolites or molecular sieves. Therefore, MOFs have become a hot research topic in the fields of gas adsorption, gas storage, gas separation, and drug slow release (Falcaro et al., 2016).

Due to the unique structural properties of MOFs, they exhibit photochemical properties similar to those of typical semiconductors such as TiO₂ and ZnO. Under light irradiation, the electrons of MOFs are excited from HOMO (highest occupied molecular orbital) orbitals to LUMO (lowest unoccupied molecular orbital) orbitals (A. Nasalevich et al., 2014; Karthik et al., 2018),

which can be attributed to the organic ligands and metal ions/ clusters in MOFs materials of photoresponsiveness. Therefore, MOFs materials are considered very promising for research applications in the field of photocatalysis (Horiuchi et al., 2012).

3.5.1 Structure of MOFs

The composition of MOFs generally includes metal nodes (metal ions or metal clusters) and organic ligands, and the structures are shown in Figure 4. Since the metal nodes and organic ligands constituting MOFs are diverse and abundant in origin, they are easy to be functionalized. Therefore, by changing the synthesis conditions, the geometric configuration of the secondary structural units, the shape of the organic ligands or the size of the organic ligands, different morphological structures and specific functionalities of MOFs materials can be obtained. Thus, the physicochemical properties of MOFs may be very diverse, which determines their applications in various fields.
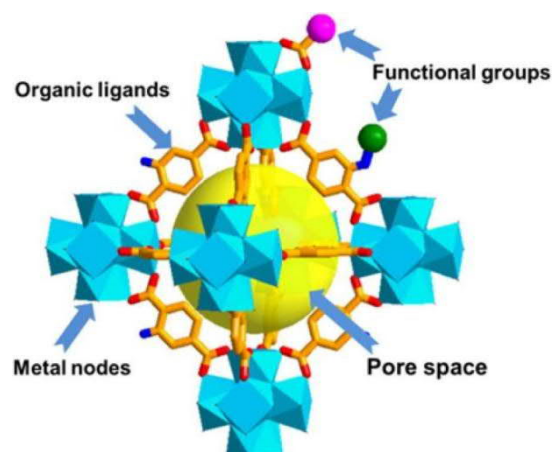

Fig. 4. *Schematic structure of MOFs (Jiao et al., 2019).*

The metal nodes of MOFs materials are usually transition metals (Slater & Cooper, 2015), which are mainly due to the fact that transition metals contain a large number of empty d and f electron orbitals with

coordination numbers ranging from 2 to 7, which can construct different secondary building units (SBUs), such as tetrahedra, octahedra, and dodecahedra. With the continuous research, metal nodes have been extended from the traditional transition metals to alkali metals and alkaline earth metals, further expanding the variety of MOFs. The common secondary structural units are shown in Figure 5.
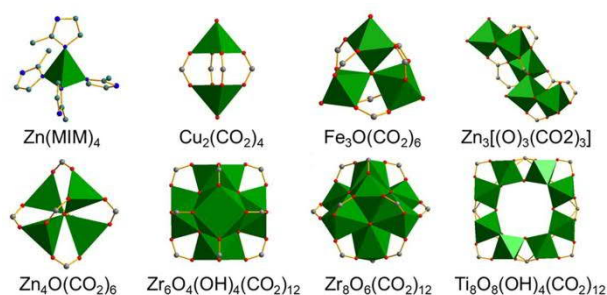

Fig. 5. Common secondary building units (Jiao et al., 2019).

The organic ligands used to connect metal nodes are usually organic nitrogen–containing heterocyclic small molecules and organic carboxylic acid–containing smal molecules. In addition, the structures of the molecules acting as ligands are highly variable and capable of incorporating many functionalized groups (Furukawa et al., 2013). Thus, the synthesized MOFs materials are rich in ligand structures, and the common ligands are shown in Figure 6.
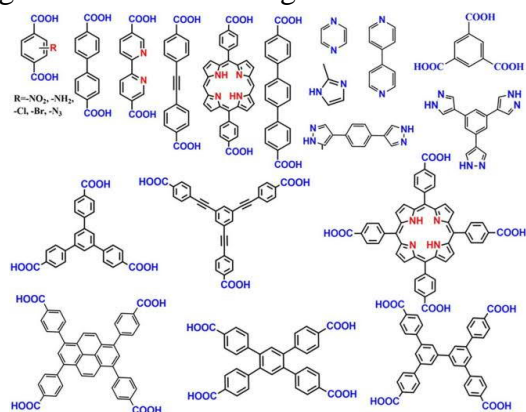

Fig. 6. Common organic ligands (Jiao et al., 2019).

Most of the current methods for the synthesis of metal–organic skeletons are solvothermal methods. In addition, microwave, ultrasonic and electrochemical methods have been reported in a few cases (Forster et al., 2002; George et al., 2017).

However, most MOFs are very sensitive to water, especially those that remain structurally stable in acidic or alkaline environments are very rare (Devic & Serre, 2014). Only very limited literature has reported MOFs materials that are stable in a wide range of PH and also in acidic or alkaline solutions (Dong et al., 2015).The main reason for the structural disruption of MOFs in humid environments is that the metal nodes building MOFs are relatively reactive and the metal centers, which are electrophilic reagents, ligated with oxygen (nucleophilic reagents) of water molecules in the environment, thus destroying the crystal structure of MOFs. Thus, the strength of the coordination bonds between their metal nodes and organic ligands is an important indicator of the water stability of MOFs materials (Low et al., 2009). Nevertheless, in recent years, MOFs materials with high thermal and chemical stability have been reported (Wang et al., 2015).

3.5.2 Adsorption properties of MOFs for VOCs

MOFs have excellent adsorption performance for various types of VOCs (such as formaldehyde, benzene, alcohols, ketones, etc.), and their adsorption performance is much higher than that of traditional adsorbents such as activated carbon, molecular sieve and zeolite. Thanks to the excellent structural tunability of MOFs materials, the adsorption performance of MOFs materials still has great potential for

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On-line ISSN 2521-151X

improvement. Therefore, many researchers have been working on the mechanistic studies

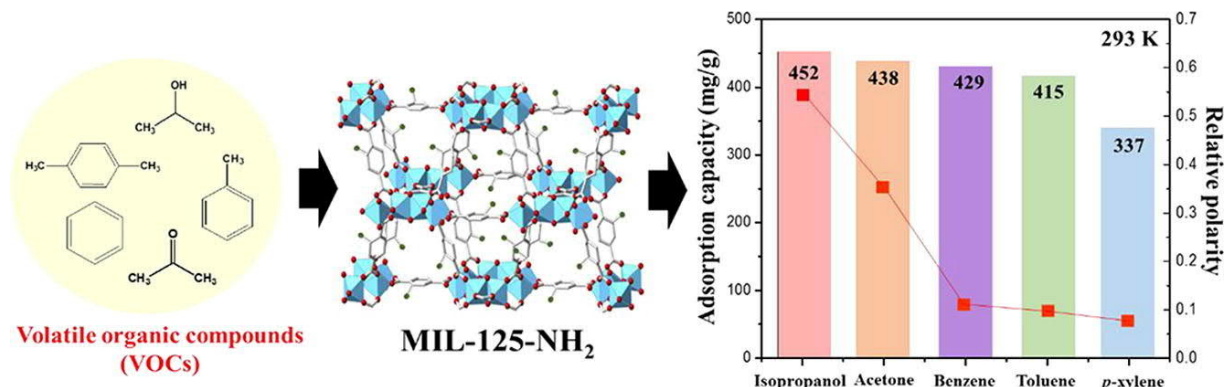and modifications for MOFs materials to improve their adsorption capacity.

Fig. 7. Adsorption performance of MIL–125–NH$_2$ for different polar VOCs (Kim et al., 2018).

Kim et al. (2018) used MIL–125–NH$_2$ for the adsorption of formaldehyde, and the adsorption of formaldehyde by MIL–125–NH$_2$ was 19.14 times that of MIL–125, 21.16 times that of UiO–66 and 23.65 times that of MIL–101 due to the action of amino groups and the microporous structure. Also, this group used MIL–125–NH$_2$ for the adsorption of xylene, toluene, benzene, acetone and isopropanol. The results showed that the adsorption of MIL–125–NH$_2$ on them increased with their polarity (Figure 7).
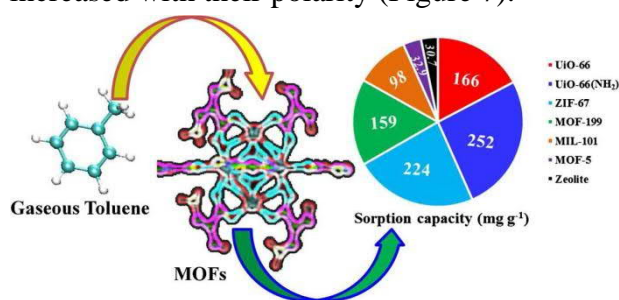

Fig. 8. The adsorption capacity of different MOFs materials for toluene (Vellingiri et al., 2017).

Vellingiri et al. (2017) investigated the adsorption of toluene by a series of MOFs materials (UiO–66, UiO–66(NH$_2$), ZIF–67, MOF–199, MOF–5, and MIL–101(Fe)) (Figure 8). The results showed that the two

MOFs, UiO–66–NH$_2$ and ZIF–67, have relatively high toluene adsorption capacity due to their –NH bonds and easy formation of hydrogen bonds with toluene compared with other MOFs materials.

Hu et al. (2018a) prepared MOF materials with hydrophobic properties by combining dopamine and UiO–66 using a mechanochemical method. The results showed that the N–liganded UiO–66 (labeled as M–UiO–66 (Zr–N3.0)) showed significantly higher adsorption of acetaldehyde and chlorobenzene compared to UiO–66 and UiO–66–NH$_2$, while its adsorption of water was 20% and 47% lower compared to UiO–66 and UiO–66–NH$_2$, respectively. In addition, the rate diffusion constants of chlorobenzene on M–UiO–66 (Zr–N3.0) were 7.8 and 40 times higher than those of UiO–66 and UiO–66–NH$_2$, respectively.

Zhang et al. (2019a) prepared a series of microporous–mesoporous UiO–66 materials using P123 as a template and used them for toluene adsorption. The results showed that the porous structure facilitated mass transfer and thus improved its toluene adsorption capacity, which was 2.6 times higher than that

Water and Water Purification Technologies. Scientific and Technical News

On-line ISSN 2521-151X

of UiO–66. The group (Zhang et al., 2019b) also used CTAB as a template agent to prepare UiO–66 materials with defects, and CTAB–UiO–66–0.5 had higher toluene adsorption capacity compared with UiO–66, and the toluene adsorption capacities of CTAB–UiO–66–0.5 and UiO–66 were 275 mg/g and 151 mg/g, respectively, which were mainly attributed to the ligand deficiency to promote the mass transfer of toluene and the existence of π–π forces between the adsorbed toluene and UiO–66.
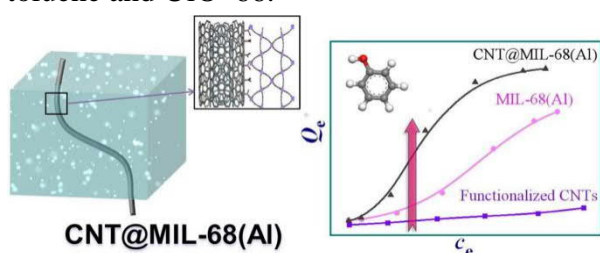

Fig. 9. *Schematic structure of CNT@MIL–68(Al) and its adsorption activity on phenol (Han et al., 2015).*

Han et al. (2015) reported the use of MIL–68(Al) for the adsorption of phenol from water and the modification of MIL–68(Al) using carbon nanotubes (CNT). The results showed that the CNT@MIL–68(Al) composites were effective in enhancing the adsorption capacity of phenol from water. And the authors proposed π–π interaction and hydrogen bonding as the main adsorption mechanism (Figure 9).

3.5.3 Synthesis and properties of TiO_2/ MOFs composites

In summary, MOF materials have excellent adsorption properties for VOCs and can be used to enhance the selective adsorption of specific VOCs by modulating the functional groups of organic ligands. In addition, MOFs have unique light–absorbing properties and semiconductor–like properties, so TiO_2/ MOF composites prepared by combining MOFs and titanium dioxide have great application prospects in the field of photocatalytic treatment of VOCs. TiO_2/ MOFs composites have the following advantages: MOFs can greatly increase the specific surface area of TiO_2, thus promoting the adsorption of TiO_2 on VOCs; MOFs can play the role of photosensitizers to achieve effective light utilization and extend the light absorption ability of TiO_2 to the UV region; the HOMO and LUMO orbitals of MOFs can couple with the TiO_2 valence and conduction bands, thus promoting the separation of photogenerated electrons and holes. Recently, many research teams have prepared composites with better photocatalytic activity than pure TiO_2 by compounding MOFs with TiO_2.

Li et al. (2014) synthesized $Cu_3(BTC)_2@TiO_2$ composites for CO_2 reduction, and the experimental results showed that photogenerated electrons could be effectively transferred from the semiconductor to the MOFs, which not only facilitated charge separation on the semiconductor but also provided excited state electrons to the gas molecules adsorbed on the MOFs (Figure 10). In addition, CO_2 is easily trapped by the micropores of MOFs, which also improves the activity and selectivity of the composites for the photocatalytic reduction of CO_2.
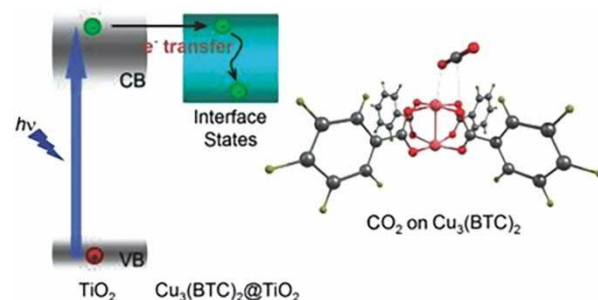

Fig. 10. *Photocatalytic mechanism of $Cu_3(BTC)_2@TiO_2$ composite (Li et al., 2014).*

Zeng et al. (2016) prepared TiO_2/ ZIF–8 composites by a simple sonochemical method to composite ZIF–8 on the surface of TiO_2 nanofibers (Figure 11). The results showed that the photocatalytic degradation of RhB was substantially improved due to the formation of N–Ti–O bonds between ZIF–8 and TiO_2 nanofibers, which enhanced the thermal stability, controllable crystallinity, and promoted the effective electron–hole separation of the composite. Moreover, the UV–Vis absorption spectroscopy results of TiO_2/ ZIF–8 composites indicated that the incorporation of ZIF–8 photosensitizer extended the TiO_2 spectral response to visible light.

Fig. 10. Preparation process and photocatalytic activity of TiO_2/ ZIF–8 composites (Zeng et al., 2016).

3.5.4 Application prospects and critical issues of MOFs/ TiO_2 composites

In summary, we can prove the following points. The catalytic activity of photocatalysts can be effectively improved by preparing MOF/ TiO_2 composites. Existing studies show that MOF/ TiO_2 composites have quite promising applications in the fields of photocatalytic water decomposition, photocatalytic carbon dioxide reduction, degradation of organic dyes, degradation of inorganic toxic gases, selective conversion of organic matter, photocatalytic degradation of VOCs, etc. However, the research of MOF/ TiO_2 nanostructures in the field of

photocatalysis is still in the initial stage, and there is still some distance from the stage of real practical application. At present, there are still some urgent problems to be solved. Firstly, the mechanism of MOF/ TiO_2 photocatalysis is still unclear, especially the charge transfer mechanism between MOF materials and TiO_2 needs to be further explored. Secondly, the light utilization rate of MOF/ TiO_2 composites is still low. Although many MOF/ TiO_2 composites have extended the light absorption capability to the visible region, a large fraction of light still cannot be utilized, indicating that there are still many opportunities to improve the optical properties of photocatalysts. Third, the photocatalytic reactions involved in MOF/ TiO_2 photocatalysts are sensitive to environmental conditions such as pH, temperature or relative humidity, which can affect the success of practical applications of MOF/ TiO_2 photocatalysts.

4. Conclusions

Compared with traditional organic pollution treatment methods, titanium dioxide photocatalysis has the advantages of low cost, high efficiency, and environmental friendliness. This work reviews typical modification methods to enhance the degradation performance of TiO_2 against organic pollutants, including: morphological construction, elemental doping, surface modification, and creation of composite materials. These modification methods can enhance the performance of TiO_2 in terms of adsorption, photo–quantum efficiency, and photo–absorption, thus effectively enhancing the ability of TiO_2 photocatalysts to degrade organic pollutants. In addition, this work also explores the research progress of MOF/ TiO_2 composite photocatalysts in the field of

organic pollution treatment. The results show that MOF/ TiO_2 composite photocatalysts can inherit the excellent optical properties and superb adsorption performance of MOFs, while also possessing the advantages such as strong redox activity of TiO_2. Therefore, MOF/ TiO_2 composite photocatalysts are expected to take TiO_2 photocatalysis to a new level. However, at present, MOF/ TiO_2 photocatalysis still faces problems such as low light utilization and poor stability. Therefore, other modification methods should be combined to further improve the MOF/ TiO_2 photocatalytic material system.

Acknowledgments

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МЕТОДИ МОДИФІКАЦІЇ ДЛЯ ПІДВИЩЕННЯ ЕФЕКТИВНОСТІ TiO₂ У ФОТОКАТАЛІЗІ

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З розвитком промисловості та зміною способу життя людей забруднення органічними речовинами стає все більш серйозною проблемою, що становить серйозну загрозу для екологічного середовища та здоров'я людей. Як новий передовий процес окиснення, фотокаталіз на основі титан (IV) оксиду показав неперевершений потенціал у вирішенні проблем забруднення навколишнього середовища завдяки стабільним властивостям каталізатора, м'яким умовам реакції, екологічності та низькій вартості. Однак фотокаталітична ефективність титан (IV) оксиду обмежена тим, що він може бути збуджений лише ультрафіолетовим світлом, але його носії легко рекомбінують і його адсорбційна здатність є слабкою. Властивості титан (IV) оксиду можна покращити шляхом модифікації для підвищення ефективності фотокаталітичної деградації органічних забруднювачів. У цій статті в основному розглянуто кілька основних методів модифікації та результати досліджень напівпровідникових матеріалів на основі титан (IV) оксиду для деградації органічних забруднювачів у навколишньому середовищі, а також зосереджено увагу на перевагах нової композитної системи металоорганічних каркасів/ титан (IV) оксиду у підвищенні ефективності деградації органічних забруднювачів. У статті представлені перспективи використання та ключові питання застосування матеріалів металоорганічні каркаси/ титан (IV) оксид у фотокаталітичному очищенні від органічних забруднень.

Ключові слова: *деградація органічних забруднювачів, композити, модифікація, органічні забруднювачі, титан (IV) оксид, фотокаталіз*