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A critical review on surface modified nano-catalysts application for photocatalytic degradation of volatile organic compounds

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Abstract

Surface modification of nano-catalyst got significant attention due its outstanding photocatalytic performance with minimum secondary pollution. Photocatalytic oxidation (PCO) is a promising technology for removing volatile organic compounds (VOCs) due to its higher activity with minimum secondary pollution. In this review, we have selected literature from the Web of Science database for nearly 10 years, with most of our sources spanning the past 5 years. Current review study summarizes the recent reports of nano-catalyst surface modification technology, including overcoming the internal and external limitations of nano-catalyst, and improving the method of photocatalytic degradation of VOCs. Additionally, we found that surface modification greatly enhances the catalytic performance of the nano-catalyst, which is beneficial for the degradation of VOCs. There are some limitations including low catalytic activity and catalyst stability. So, in future research, new methods of preparing catalysts and improving their overall catalyst performance should be managed and paid more attention.

Keywords: Photocatalytic oxidation; Nano-catalyst; Surface modification; Volatile organic compounds; Surface chemistry;

1.Introduction

Air quality has received a widespread attention due to its injurious effects on living organism. Industries, such as petroleum refining [1], chemical production [2], synthetic resin [3], clothing dyeing [4-6], leather processing [7], pharmaceutical industry [2, 8], insecticide production [9], coating and adhesive manufacturing [10], spraying [11], printing [4, 12], electronic component manufacturing [2, 5, 13] releasing significant amount of volatile organic compound (VOC) which ultimately effects the air quality **(Fig. 1)**. Due to easy diffusivity, toxicity and volatility, VOCs can cause irreversible damage to human health [14-16]. The adverse effects of VOCs on human health include not only acute irritation to the eyes and lung but also chronic diseases such as asthma, gastrointestinal diseases, cardiovascular diseases and cancer [17-20].

To overcome devastating effects of VOCs, several efficient purification techniques of VOCs has been developed. Such as incineration, condensation, adsorption, photocatalytic oxidation (PCO), ozone-catalytic oxidation and membrane separation [21]. Comparing with these techniques, PCO has many advantages such as room-temperature operation, high activity, and no secondary pollution which made PCO an auspicious technique[22]. Besides, PCO is a powerful air purification technology that destroys VOCs, by photocatalysis under the irradiation of ultraviolet (UV) and sunlight, converting them to water, carbon dioxide and detritus.

Commonly used photocatalysts material for purification of VOCs includes TiO_2, ZnO, WO_3, V_2O_5, ZnS and CdS [23-25]. To date, nanotechnology has made exponential progress [26-28]. Nanomaterials (NMs) are widely used in the field of environmental remediation [29]. Nowadays, TiO_2 has a large number of applications photocatalysis [30-33], due to its high photocatalytic efficiency, stability under extreme conditions, and suitable edge potential to act as active centers for catalytic reactions [34-36]. However, the performance of these nano-catalyst is not efficient. For example, compared with other semiconductor materials, TiO_2 has a wider band gap and higher carrier recombination rate which limit the photocatalytic process to the UV region of the spectrum [31, 37].

Recently, the techniques of modifying nano-catalyst include (i) the use of compound semiconductors i.e., semiconductors made from two or more elements, (ii) catalyst immobilization on solids such as silica or polymeric supports, (iii) use of co-catalysts, (iv) dye sensitization, and (v) surface doping is being applied to fill the shortcomings of nano-catalyst. These techniques not only enable catalyst to increase visible light utilization efficiency but also increase the lifetime of photoexcited carrier pairs [38-42].

Previously published articles give a detailed introduction to the processes for modification of various nano-catalysts [43-46]. However, there is no comprehensive review on the impact of modification of nano-catalysts by the different methods on their efficiency and capability to eliminate VOCs. The purpose of this review is thus to classify the techniques according to the surface modification method and review the new features of the modified photocatalyst. Furthermore, new features of the modified photocatalyst are briefly discussed. Photocatalysis fundamentals, factors that affect the catalytic performance of the photocatalyst, and the modification

technology has been illustrated. Through these studies, we can explore the limitations of the current catalysts and use this to further improve the performance of the catalysts, with the overarching goal of contributing to the improved elimination of environmental VOC pollution by nano-catalysis in the future.

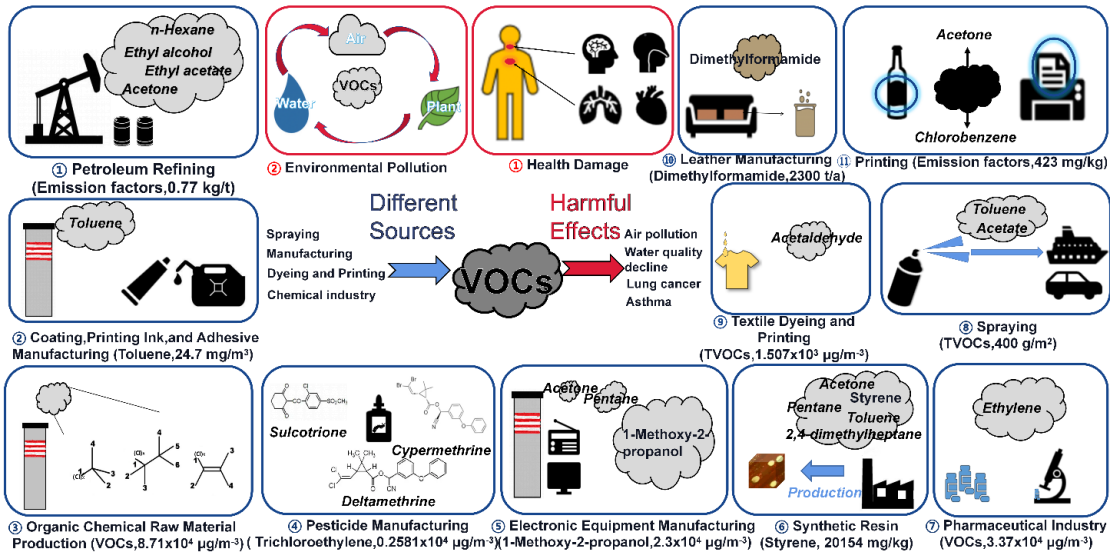

Fig 1. Illustration of industries releasing VOCs in air, concentration obtained from [47-57].

2. Mechanism behind photocatalytic oxidation of VOCs

The photocatalytic reaction is a complex process, which begins with the absorption of a large amount of visible light on the surface of the material. When the energy of the absorbed photon is not less than the energy of the semiconductor band gap photon (Eg), the electrons existing in valence bands (VB) will be excited into the empty conduction bands (CB), such that holes are left behind in the VB [58]. The following uses TiO_2 as an example to analyze the electrons and holes generation process:

$$TiO_2 + hv \rightarrow e^-(TiO_2) + h^+(TiO_2) \quad (1)$$

There are three possible processes for electrons and holes :(1) Separate and move to the surface of the material to have an opportunity to participate in redox reaction (2) Trapped by defect sites. (3) Recombine and release energy. However, the second and the third process do not promote the photocatalytic reaction, and only the first process can drive reduction and oxidation [59]. Before driving the redox reaction, the charge needs to undergo separation, thermalization, trapping, recombination, and transport [60] **(Fig. 2)**. Interfacial charge transfer may directly eliminate VOCs through oxidation or generate hydroxyl radicals and superoxides [61]. The process can be depicted as follows equations (2)-(8) [62]:

$$h^+(TiO_2) + H_2O \rightarrow TiO_2 + H^+OH^\bullet \quad (2)$$

$$h^+(TiO_2) + OH^- \rightarrow TiO_2 + OH^\bullet \quad (3)$$

$$e^-(TiO_2) + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \quad (4)$$

$$O_2^{\bullet-} + H^+ \rightarrow H_2^\bullet \quad (5)$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (6)$$

$$e^-(TiO_2) + H_2O_2 \rightarrow OH^- + OH^\bullet \quad (7)$$

$$VOC + O_2 + OH^\bullet \rightarrow H_2O + CO_2 + other\ products \quad (8)$$

Current model is difficult to explain due to the complex charge transfer process. Understanding the underlying mechanisms, will help us to find new photocatalysts for application in VOCs degradation.

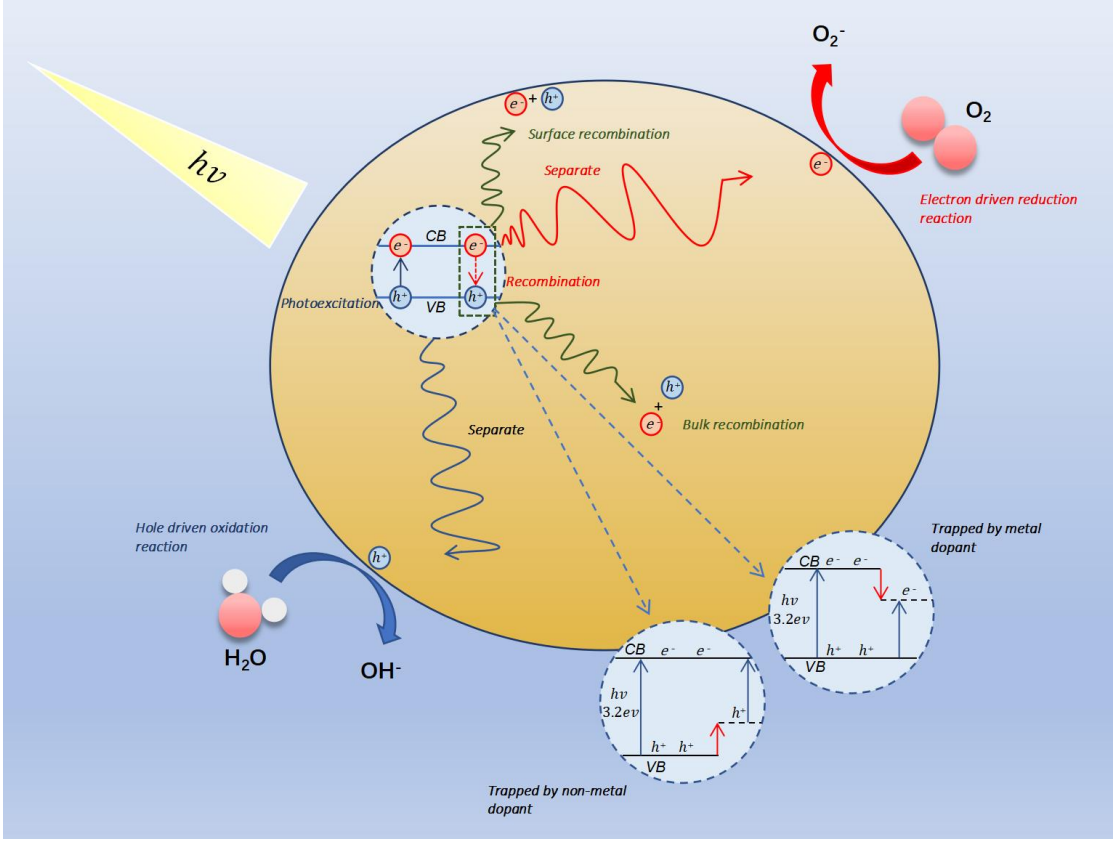

Fig 2. Schematic illustration of basic mechanism of photocatalysis.

3. Factors affecting the photocatalytic activity

The photocatalytic performance affected by intrinsic and extrinsic factors **(Fig. 3)**. Intrinsic factors affecting the photocatalytic ability and VOC degradation has been briefly discussed below [63-65].

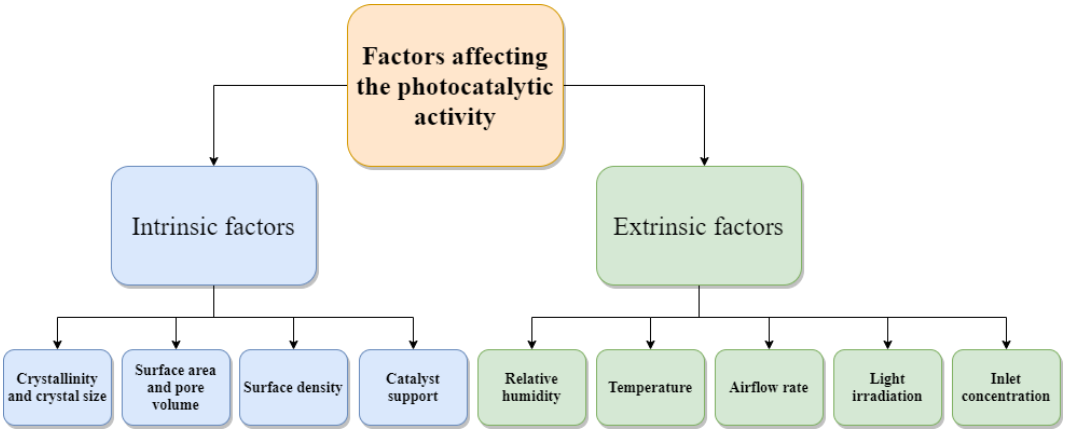

Fig 3. Illustration of factors affecting the photocatalytic activity.

3.1 Influence of catalyst characteristics (intrinsic factors) on VOCs degradation

3.1.1 Crystallinity and crystal size

The presence of defects in crystal lattice and impurities in the catalyst accelerates the recombination process. To improve the efficiency of photocatalysis, the design and research of high bulk crystallinity have received extensive attention [66].

Leite et al. [67]claimed that the property of high crystallinity has advantages over disordered polymers in photocatalytic applications. Pleskunov et al. [68]used a single-step plasma-based technique to synthesize $Ta_3N_yO_x$ nanoparticles(NPs) with controllable crystallinity. In the visible light range, $Ta_3N_yO_x$ exhibits plasmonic and photoluminescent properties. Katsuki et al. [69]found that α-Fe_2O_3 NPs with high crystallinity are more efficient in PCO. A similar finding was also reported by Li et al. [70], they found that the nanorod-shaped photoactive COF containing benzothiadiazole and triazine with good crystallinity exhibited excellent comprehensive performance and good cycle performance in the photocatalytic oxidation reaction. Curtis et al. [71]used the two-temperature method to prepare mesoporous silicon NPs. The initial temperature of the reaction is 650℃ and lasted for 0.5h, and then in the second heating process at 100°C, 200°C and 300°C for 6h. They found that the mesoporous silicon NPs prepared at 300°C have the best photocatalytic performance because of the higher crystallinity of catalyst. Li et al. [72]and Zhang et al. [73] pointed out that synthesizing a new heterogeneous photocatalyst has uniform crystal size and high crystallinity. These advantages accelerate the separation and transfer efficiency of electron-hole pairs.

Besides crystallinity, crystal size also affects photocatalytic activity. Alonso-Tellez et al. [74] found that the smaller crystal size of UV100 is the main reason why it is superior to P25 in terms of photocatalytic oxidation. Generally speaking, higher crystallinity and smaller crystal size can promote the reaction rate.

3.1.2 Surface area

Surface area is an important structural feature of photocatalysts, which has a great influence on photocatalysis [75]. The larger surface area, the more accessible active sites, and the higher the photocatalytic efficiency [76].

Hajaghazadeh et al. [77]found that under steady-state conditions, the conversion rate of methyl

ethyl ketone (MEK) using PC500 catalyst was higher than that of PC50 and P25. The experimental results show that the lower surface area of PC50 and P25 makes the activity decrease over time. However, PC500 has a high surface area, and its positive impact offsets the negative impact of electron and holes on rapid recombination. This finding was also reported by Monteiro's group. During the degradation of perchloroethylene by P25 and PC500, it was also noticed that the surface area has a greater impact on the conversion of pollutants [78]. Liu et al. [79] found that Ag-ZnO NPs have super high photocatalytic efficiency compared with pure ZnO. Researchers speculate that it may be because the Ag NPs are uniformly distributed and have a large specific surface area. Similar results were also reflected in another experiment. Rajca's group tested the removal efficiency of organic substances in the photocatalytic process of commercial nano-catalysts with different accessible surface areas. The results show that because P90 has a larger surface area, the photocatalytic efficiency of P90 is higher than P25 [80].

3.1.3 Pore volume and porosity

In addition to the surface area, another structural feature pore volume of the photocatalyst also has a profound effect on the catalytic efficiency[74]. Chen et al.[81]designed Pt nanoclusters similar to 1.8 nm. The catalytic performance of C/Pt@TiO_2-3% containing 0.54 wt% Pt is greatly improved because of its maximum total pore volume and the average pore diameter is approximately 3 nm. In addition, the mesoporous structure also helps to expose more active sites of the nano-catalyst to promote surface reactions [81].

While achieving porous structure, crystallinity will not be lost. Therefore, the general view is that porous structure is more important catalyst characteristics than crystallinity [62].

Porous materials with superior performance are very suitable for capturing aromatic VOCs in ambient air. In recent years, due to high porosity and strong customization, metal organic frameworks (MOFs) have been studied extensively [82-86]. MOFs are rich in organic contents, which makes them have superior inherent advantages in adsorbing aromatic VOCs [87].

Xie et al. [87]designed and synthesized two MOFs, among which $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(BDB)_6]$ (BUT-66) shows superior adsorption performance of benzene. Single-crystal structure analysis shows that the small hydrophobic pores and the small interaction between the adsorption sites make BUT-66 have the high performance of capturing benzene. Wu et al. [88] used lab-on-fiber technology and nanotechnology to monitor surface nano-functionalization of VOC adsorption/desorption in zeolitic imidazole frameworks (ZIF)-8. The high porosity plays an important role in VOC sensors. This finding was also reported by Wang et al. [89]They found that the shape and size of the porous Co_3O_4 derived from Co-MOF would significantly affect its sensing performance. Besides, the more NPs on the surface, the better the VOC sensing performance. Yu et al. [90] proposed a two-step method to prepare In/Ni MOF-derived mesoporous In_2O_3-NiO composites with a nanosheet hollow sphere (NHS) structure. They observed that mesoporous In_2O_3-NiO NHS has a high porosity, this advantage provides sufficient permeation pathways for VOC, a large number of active sites, and the capacity to capture VOC.

Table 1 Summary of different photocatalysts affect the photoactivity

Photocatalyst	Surface area	Pore volume	Compound	Photo activity	Ref.
TiO_2 USprec	326 m^2/g	0.484 cm^3/g	Benzyl alcohol	Conversion 61%	91
P25	-	-	Benzyl alcohol	Conversion 100%	91
Brookite/anatase TiO_2/g-C_3N_4	37.1 m^2/g	0.2 cm^3/g	Phenol	Degradation rate 5-fold increase over CN	92
CN	45.8 m^2/g	0.29 cm^3/g	Phenol	-	92
Ti^{3+}doped TiO_2/SiO_2	300 m^2/g	0.35 cm^3/g	Methyl orange	31.5%	93
TiO_2	56.8 m^2/g	-	Methyl orange	8%	93
TiO_2/SiO_2	228 m^2/g	0.27 cm^3/g	Methyl orange	16.6%	93

3.1.4 Surface density

Surface density is a key factor as increasing the thickness of the nano-catalyst coating can increase the surface area of the catalyst and reduce competitive adsorption between reactants, thereby increasing the removal rate and the degree of mineralization of the catalyst [94].

Singh et al. [95] used atomic layer deposition method coating TiO_2 on fibrous nanosilica (KCC-1). They observed that the KCC-1/TiO_2 catalyst coated with TiO_2 NPs has a more uniform coating, a higher loading of TiO_2, a smaller loss of surface area, and higher active site accessibility than traditional silica catalysts. Wang et al. [96]confined the dense Au nanoparticles to a bowl-shaped TiO_2 nanoarray doped with N. By adjusting the absorption of light by TiO_2 and fully overlapping the plasma band of Au NPs, the photocatalytic efficiency is greatly improved. Roldan et al. [97]researched a new type of nanostructured coating system, which includes a layer of SiO_2 and a layer of dense anatase TiO_2 doped with Ag NPs. The photocatalytic activity has been improved All in all, increasing the surface density of the nano-catalyst can greatly increase the conversion of VOCs. However, an excessive amount of catalyst will result in a decrease in catalytic efficiency.

3.1.5 Support material

Fixing the nano photocatalyst on a suitable carrier material can reduce their aggregation of the NPs, thereby increasing the catalytic efficiency, adsorption capacity and prolonging the effective life of the photocatalyst [62]. In recent years, engineered carbon has been applied to catalyst support due to its high surface area, porous structure, high-performance adsorption of VOCs [21]. Activated carbon (AC) has been applied to the adsorption and recovery of most VOCs. However, AC has some shortcomings that affect its ability to adsorb VOCs: AC is an inherently non-polar adsorbent, which will hinder the adsorption of hydrophilic particles [22]. Furthermore, the porous structure of activated

carbon is microporous (pore size < 2nm), which makes it difficult for molecules with larger molecular diameters to enter the pores. Furthermore, due to the strong diffusion resistance due to irregular pore structure, the adsorption equilibrium is prolonged due to the disordered pores possessed by AC. Zhang et al. [98] prepared a new nano-β-FeOOH/Fe_3O_4/biochar composite material. Through XPS characterization, it is proved that there are Fe-OC bonds between β-FeOOH and biochar. These bonds facilitated the transfer of photo-generated electrons. The connection promotes the rapid interface transfer of light energy electrons between biochar and β-FeOOH. Zhang et al.[99] prepared N-doped nano-TiO_2-carbon fiber composite material. After TiO_2 NPs are irradiated by microwaves, they generate a large number of hydroxyl adsorption sites. Due to the interface formed between TiO_2 and carbon fiber, this carbon fiber composite material can effectively catalyze the oxidation reaction of phenol. Graphene has the characteristics of inhibiting the annihilation of electrons and holes and exhibits excellent photoactivity, so it is widely used in photocatalysis[100-102]. Saima et al.[103] used graphene oxide(GO) as the support material and randomly dispersed TiO_2 and NiO NPS on it. The GO provides fast electronic conductivity and strong oxidation characteristics, which facilitates the separation of carriers.

As can be seen, the support material of the nano-catalyst will affect the removal of VOCs. In short, a suitable carrier can effectively increase the accessible surface area, mechanical strength and stability of the nano-catalyst.

3.2 Effects of environmental conditions (external factors) on POC of VOCs

The multi-factor synergistic mechanism of photocatalytic degradation of VOCs by adsorption is controlled by two aspects: thermodynamics and dynamics. Considering the complexity of the environment, we briefly review the effects of humidity, airflow rate, light irradiation, concentration of pollutants and temperature on the photocatalytic degradation of VOCs **(Fig. 4)**. The factors influencing the comprehensive adsorption and photocatalysis capability of modified NMs are discussed in **Table 2**.

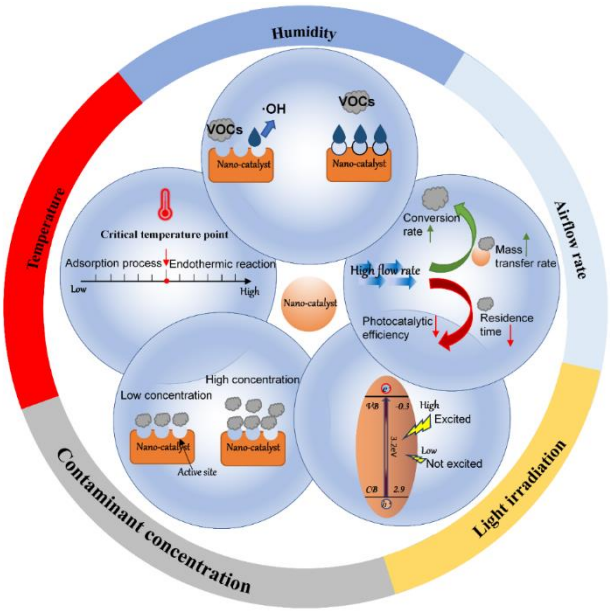

Fig 4. Illustration of external factors and mechanism of action.

3.2.1 Relative humidity and temperature

Water vapor plays a double-sided role in the process of photocatalysis of VOCs and their adsorption onto/interactions with modified NMs [104, 105]. As a polar molecule, water can provide hydroxyl radicals, which is conducive to the adsorption of more hydrophilic VOCs molecules onto the photocatalyst surface through hydrogen bonds. However, if the moisture content is too high, it will compete with VOCs for the adsorption sites. For some pollutants, the presence of moisture can promote mineralization of the pollutants, but excessive moisture will be adsorbed onto the active sites of the catalyst, thereby reducing the catalytic efficiency of the catalyst [106]. Regarding air humidity, modification of the nano-catalyst can reduce the degree of competition between water molecules and VOCs; for example, doped TiO_2 has a higher catalytic efficiency than undoped TiO_2 because the introduction of dopants resulting in more oxidant [107-111].

Temperature is another key factor affecting photocatalysis. In the adsorption process of VOCs onto the photocatalytic material, low temperature is conducive to adsorption processes dominated by exothermic reactions, but it reduces the diffusion rate of adsorbate molecules. Huang et al. [112] pointed out that the efficiency of PCO of formaldehyde is higher at 60°C than at 30°C. This phenomenon shows that higher temperature promotes the photocatalytic process. At lower temperatures, the VOC adsorption process is dominant, and the rate is higher than the photocatalytic oxidation rate[113].

3.2.2 Airflow rate and contaminant concentration

The airflow rate affects the photocatalytic oxidation process of VOCs, and similar to temperature bring advantages and disadvantages. Increasing the airflow rate will increase the transfer rate of VOCs and increase the conversion rate of pollutants. On the contrary, too high air flow rate will reduce the residence time of VOCs and thus reduce the photodegradation efficiency [114-116]. Therefore, optimizing the air flow rate is essential: low air flow rate can increase the residence

time of VOCs so that they can be fully adsorbed on the catalyst surface. Under high flow rates, the residence time is reduced so the removal rate will be reduced. Thus, flow rate should be optimized for each catalyst-VOC pair to determine the optimal flow rate and maximize the PCO efficiency.

The adsorption capacity of the catalyst is related to the number of active sites. When the concentration of VOCs is low (located in the appropriate range) and the adsorption capacity can meet the adsorption demand, the removal efficiency will be improved. Since the by-products produced by catalysis compete for adsorption sites, PCO is more suitable for the degradation of low concentration pollutants [117, 118]. An area for future development is a means to remove the by-products from the adsorption sites, or to ensure they have a lower binding affinity for the sites than the target VOC pollutants.

3.2.3 Light irradiation

It is worth mentioning that light irradiation (wavelength and intensity of light) has a greater impact on the photocatalytic process than adsorption process. On the one hand, the wavelength of light is related to Eg and the energy of the band gap photon. If Eg is too low (less than the energy band of the catalyst) so that the electrons will not be excited and the oxidation process of VOCs on the catalyst surface is difficult to occur. On the other hand, under low light intensity conditions, the light intensity is related to the photocatalytic rate, and as the light intensity increases, the rate and light intensity show a power-law relationship [119]. However, in PCO, the energy loss caused by light reflection and transmission is inevitable. Therefore, researchers have used modification methods such as doping, use of compound semiconductor, and surface modification to use energy as much as possible [106, 120-122].

300 Table 2 The key factors affecting VOC photocatalytic performances.

Factors	VOCs	Humidity	Temperature	Airflow rate	Light	Inlet concentration	Removal effificiency	Ref.
Humidity	MEK	0% 20% 40% 60 ± 1%	23 ± 1 °C	0.015 m^3/min	UV	2.65 ± 0.3 mg/m^3	41% 46% 44% 41%	[123]
	2-ethyl-1-hexanol	20% 50% 80%	-	-	visible light	0.1 ppm	89% 85% 70%	[124]
Temperature	toluene	-	155-160 °C 220-230 °C	30,000mL/g h	650mW/cm^2	200ppm	40-50% 90-95%	[125]
	toluene	-	130°C 180°C	40,000mL/g h	-	-	18-20% 57-60%	[126]
Airflow rate	acetaldehyde	20 ± 1%	25°C	20L/min 40L/min	UV lamps	15 ppm	35-40% 20%	[127]
Light	MEK	0%	23 ± 1 °C 24 ± 2 °C	0.015 m^3/min	UV visible light	2.65 ± 0.3 mg/m^3	60-70% 40-50%	[123]
	1-propanol	10%	30 °C	320 mL/min	1.0 mW/cm^2 2.0 mW/cm^2 3.0 mW/cm^2	400 ppm	45% 55% 65%	[110]
Inlet concentration	toluene	-	-	-	visible light	115 ppm 230 ppm 460 ppm 690 ppm	100% 100% 87.1% 65.5%	[128]

301

4. Surface modification of nano-catalysts as a means to increase PCO efficiency for VOCs

The intrinsic properties of the nanomaterial photocatalysts and the extrinsic factors effecting nano-catalysts have significant role on photocatalytic efficiency. Surface modification methods investigated to date include surface doping, the structure of surface heterojunctions, utilizing a supported co-catalyst, increasing the surface area, and ensuring high reaction surface exposure **(Fig. 5)**. These are discussed below.

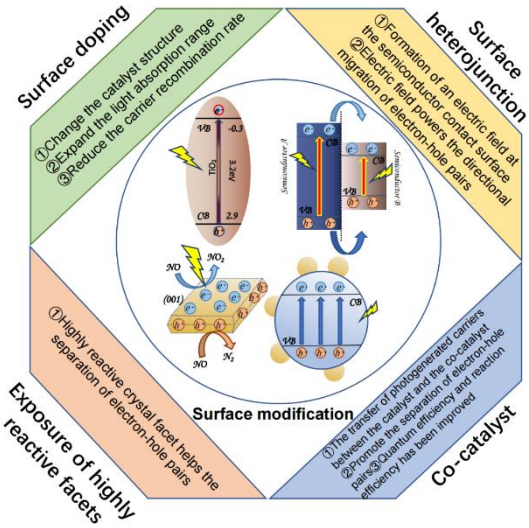

Fig 5. Schematic illustration of different surface modification methods effect on photocatalytic efficiency.

4.1 Surface doping

Surface doping can introduce electrons into the band gap of semiconductor, causing an optical response, which in turn produces a significant redshift. This two-step light excitation process excited by low-energy visible photons promote the visible light activity of the semiconductor [129]. By doping with metal elements, Fang et al. [130] found that surface doping significantly improves the catalytic efficiency of the catalyst for refractory benzene. However, the lattice defects caused by doping can not only serve as the transfer medium of the interface charge but also become the complex center of electron-hole pairs, reducing the catalytic activity [129, 131]. In addition to a single doped metal or non-metal element, co-doping between metal ions, non-metal elements, or between metal ions and non-metal elements can also effectively extend the wavelength of the photocatalyst excitation light.

4.1.1 Metal doping

At present, the research on doping of metal elements mainly includes noble metals, transition metals and rare earth metals. However, noble metals cannot be widely used in practice due to their high cost and scarcity of raw materials. Exploring the effects of different metal doping on photoactivity, optimal doping dose and preparing nano-catalysts with the best benefits and efficiency has become the focus of current research **(Fig. 6)**.

Generally, the preparation method of the doped catalyst will produce different crystal properties

and change the morphology of the photocatalyst. The mechanism behind metal doping can be summarized as follows: (1) Noble metals have anti-oxidation and corrosion resistance properties even in humid air. Under the action of noble metal NPs, the recombination of carriers is reduced, which increases the photoactivity on the surface of the photocatalyst. (2) The type and doping amount of transition metals are two key factors that affect the PCO. If the doping amount is at the optimal value, the dopant can accelerate the separation of carriers. When the optimal value is exceeded, the dopant may become a recombination center, reducing the photocatalytic efficiency. (3) Rare earth metals have incomplete 4f and empty 5d orbitals, which can promote photocatalytic reactions.

Noble metal elements such as platinum (Pt) [132], palladium (Pd) [133], ruthenium (Ru) [134], silver (Ag) [135]. Because of noble metals, the recombination of carriers is reduced, which improve the photoactivity of the catalyst [136]. In fact, the doping of noble metal NPs forms a medium for capturing and transferring electrons on the nano-catalyst surface [137]. Meng et al.[138] doped Pd/$PdCl_2$ onto the surface of the nano-catalyst Bi_2WO_6 by photoreduction method. Compared with TiO_2, the catalyst degrades phenol more efficiently. The researchers concluded that it may be due to the dual factors of the plasmon resonance and the suppression of photo-generated carrier recombination. Xue et al[139]. modified TiO_2 doped with Ag and Ag_2O. The efficiency of this catalyst to degrade toluene is 50%, which is about 9.7 times higher than TiO_2.

Transition metal doping can significantly extend visible light excitation, and more susceptible to doping by other transition metals because of the lower energy required for the substitution process. Thus, there has been extensive research on transition metal doping, such as manganese (Mn) [140, 141], iron (Fe) [142-144], copper (Cu) [145], vanadium (V) [146, 147], and nickel (Ni) [148]. Afif et al. [149]successfully synthesized a highly active Mn-doped Ag_3PO_4 photocatalyst using the co-precipitation method. Mn doping suppressed hydroxyl defects and oxygen vacancies, increased the atomic ratio of oxygen to silver, and improved the photocatalytic performance under visible light irradiation. Patrick et al. [150] found that the photochemical properties of the Mn complex reached or approached the performance of Ru and Ir noble metal catalysts in terms of photon absorption. Devaraji group [151]incorporated V into the TiO_2 crystal lattice to make $Ti_{0.98}V_{0.02}O_2$. Compared with pure TiO_2, this catalyst embodies the quantum transition of benzene oxidation, highlighting the importance of V doping for benzene oxidation. Stucchi et al. [152] used Mn to replace noble metals such as Au and Ag. Through experiments, it was found that TiO_2 doped with 20% Mn under visible light exposure for 24 h, the degradation efficiency of ethanol reached 35%, which is the peak degradation efficiency. The suppression of the defect sites on the catalyst surface and the reduction of electrons compound with holes that may be the reasons for the excellent photocatalytic activity. Li et al. [153] prepared Co-doped TiO_2 nanorod array (Co-TiO_2 @Ti(H_2)) with good stability, and the energy barrier for desorption can be effectively reduced by introducing Co with abundant oxygen vacancies. Sajjad et al.[154] used Si and Ti to modify the magnetic Fe_3O_4 NPs. It was found that the photodegradation effect was in the order of Ti modified Fe_3O_4>Si modified Fe_3O_4>Fe_3O_4.

366 There are 17 kinds of lanthanides, collectively referred to as rare earth metals. Kumar et al. [39]
367 found that lanthanide ion dopants are beneficial to the optical properties of ZnO structure.
368 Parameters such as material properties and pollutant degradation reaction conditions have influence
369 on the performance of ZnO. Xiao et al. [155]found that Ce-doped TiO_2 shows the advantages of
370 stability and higher surface area. Notable, the adsorption capacity of VOCs is also greatly enhanced.
371 The same result also appeared in other experiments. Wang et al. [156] synthesized Ce-doped MoS_2
372 nanocomposite by hydrothermal method. Under visible light irradiation, it exhibits excellent
373 photocatalytic activity.
374 It is worth noting that different cationic dopants have individual effects on the nano-catalyst.
375 Generally speaking, metal doping will produce different properties and also affect the morphology
376 of the nano-catalyst. The lattice defects caused by doping may become the recombination center of
377 carriers, thereby reducing the catalytic activity. Therefore, searching for the optimal amount of
378 doping is still the focus of future work.

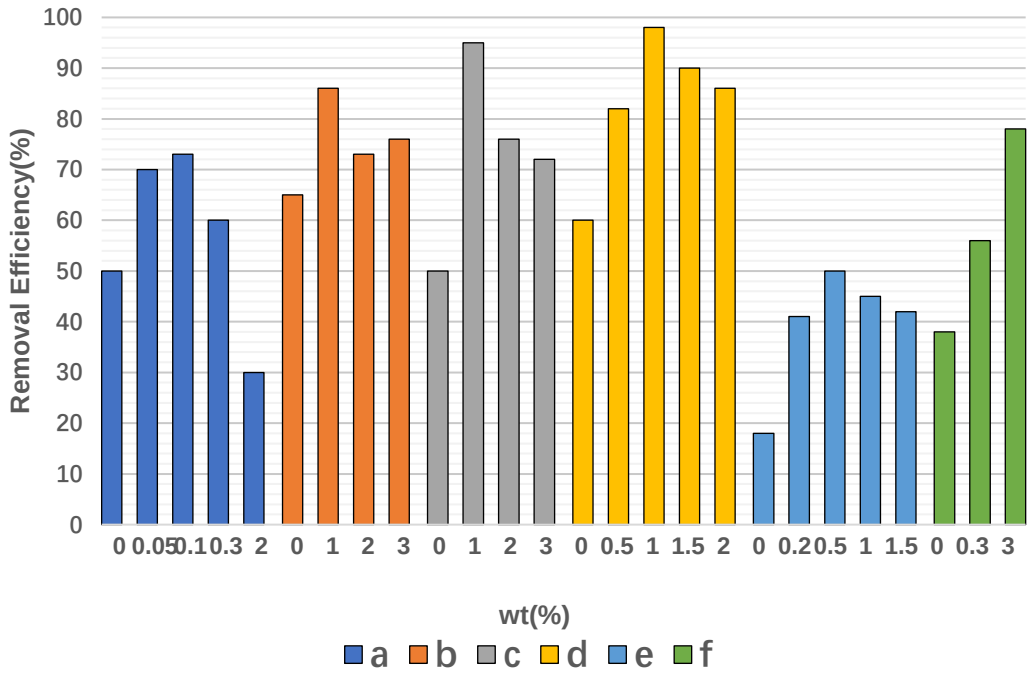

Fig 6. The effect of different doping amounts on the degradation of VOCs by photocatalyst. (a) acetaminophen, Sb-doped TiO_2 [157]. (b) 4-chlorophenol, W-doped TiO_2 [158]. (c) 4-chlorophenol, Mo-doped TiO_2 [158]. (d) 2,4-dichlorophenol, Ce-doped CuMgAl [159]. (e) MEK, Ce-TiO_2 [160]. (f) acetaldehyde, Cr-TiO_2 [161].

4.1.2 Non-metal doping

Non-metal doping such as nitrogen (N) [162-166], carbon (C) [167-169], sulfur (S) [170-173], boron (B) [174, 175]and fluorine (F) [176] has been extensively evaluated previously. In non-metal doping, dopants can change the morphology and improve photoactive performance of the catalyst. Because the doped state is close to the edge of VB and is not used as a carrier, the role of the recombination center will be weakened. When the oxygen atom is replaced by other non-metal element atoms, the top energy level of the VB of the oxide will increase, and the semiconductor band gap will be narrowed, thereby extending the excitation wavelength to improve catalytic efficiency.

Table 3 summarizes metal and non-metal doped photocatalysts synthesized to improve photocatalytic degradation performance. A conclusion can be drawn that after doping, the catalytic efficiency of the catalyst has been improved.

Table 3. Summary of metal and non-metal doped photocatalysts.

Contaminant	Photocatalyst	Dopant	Efficiency before doping	Efficiency after doping	Ref.
Toluene	TiO_2	Ag/Ag_2O	7.5%	23.3%	[139]
Benzene	OMS-2	Mg	68.4%	97.2%	[130]
Benzene	TiO_2	V	0.3%	12.7%	[151]
Benzene	$Ti_{0.98}V_{0.02}O_2$	Au	9%	18%	[151]
Acetaldehyde	TiO_2	F	77.3%	81%	[177]
Acetaldehyde	TiO_2	N	77.3%	92.1%	[177]
Ethylbenzene	TiO_2	N	33%	38%	[178]

Awin et al.[179] pointed out that the N-doped TiO_2 on the Si-OCN support exhibited excellent adsorption properties and high catalytic activity under visible light. Sun et al.[180] developed C-doped and oxygen vacancies Bi_2WO_6 nanospheres mediated by graphene oxide. C-doping can change the band gap structure and can also promote light absorption. This is because carbon doping in the catalyst acts as an acceptor and electron channel to promote the separation of carriers and the production of active substances. Diao et al.[181] synthesized F-doped TiO_2 by hydrothermal method and used EPR measurements to prove that F-doped TiO_2 has superior degradability to formaldehyde due to the participation of superoxide radical and hydroxyl radical in the process of oxidizing formaldehyde into CO_2 and H_2O. Ramacharyulu et al. [182]noted that compared with undoped TiO_2, S-doped TiO_2 had a lower band gap value and better photocatalytic activity. Among various doping materials, non-metallic element doping has been tested to be a better way to improve PCO activity[183, 184].

4.2 Structure of surface heterojunction

When two semiconductors with similar characteristics are in contact, an electric field is formed at the contact interface. The electric field provides the driving force for the directional migration of electron-hole pairs between different semiconductors, which can promote the effective separation. This promotes the oxidation-reduction reaction of the nano-catalyst, which in turn facilitates the degradation of VOC. In heterojunction photocatalysis, photogenerated electrons generally migrate from a semiconductor with a higher CB energy level, and a photogenerated hole will migrate from a semiconductor with a lower VB energy level. The mechanism of surface heterojunction is that a well-defined junction can effectively promote charge transfer and hinder the recombination of electrons and holes. Thus nano-catalysts shows high activity and stability.

Table 4 shows surface heterojunction effect photoactivity. Obviously, the formation of heterojunction promotes the degradation efficiency of pollutants.

Table 4. Heterostructure and degradation efficiency of photocatalyst.

Heterostructure	Photocatalyst	Efficiency before	Efficiency after	Ref.
Z-Scheme	$LaFeO_3$/g-C_3N_4	37%	100%	[185]
Z-Scheme	Au-TiO_2@NH_2-UiO-66	10%	85%	[186]
S-scheme	Cu_2S/SnO_2	17.9	67.2%	[187]

Dai et al. [188] used a new hydroxylation method to coat BiOI on the TiO_2 wall to form the p-n junction of the BiOI/TiO_2 nanotube array **(Fig. 7A)**. They found the photo-electrocatalytic degradation efficiency of BiOI/TiO_2 was increased by 3 times. Guo et al. [189] successfully prepared an Ag/Ag_2O/$PbBiO_2Br$ photocatalyst with a broader spectral response through a series of plasma p-n heterojunctions. Researchers have observed significantly accelerated charge separation, and the degradation efficiency of pollutants has also been significantly improved **(Fig. 7B)**. Huang et al. [190] developed the p-n junction BiOI@$Bi_{12}O_{17}Cl_2$ heterostructure by depositing BiOI nanosheets in situ. Due to charge induction, BiOI@$Bi_{12}O_{17}Cl_2$ forms a unique front-side coupling heterostructure. Compared with the pure sample, the obtained BiOI@$Bi_{12}O_{17}Cl_2$ heterostructure can significantly enhance the catalytic performance and degradation of 2,4-Dichlorophenol. Anum et al.[191] studied a new type heterojunction of Al_2O_3 and GO. FTIR examination showed that the density of hydroxyl on the surface of pure Al_2O_3 was lower, but after adding GO, the density increased **(Fig. 7C)**. The reason may be related to the interaction between hydroxyl and light-generated holes, which promotes electron transfer and inhibits the recombination of carriers. Because of GO, the recombination of electron-hole pairs is reduced. Through the study of activity, it was found that 15.0% GO/Al_2O_3 exhibits superior photocatalytic performance. In another study, the same result was observed[192]. Wu et al. [185] constructed a new p-type $LaFeO_3$ microspheres coated with n-type nano-scale graphite carbon nitride nanosheets. The interface effect of charge carriers is separated and transferred more effectively through solid p-n heterojunction. Yao et al.[193] prepared p-n heterojunction of Bi_2MoO_6/BiOBr which can promote the photocatalysis. In addition the UV-vis absorption edge of the BMOBB-2(The mole ratio of $Na_2MoO_4 \cdot 2H_2O$ to Bi $(NO_3)_3 \cdot 5H_2O$ is set as 5%) sample has a significant red shift, which is related to the better visible light response of Bi_2MoO_6**(Fig. 7D)**. Due to the strong interaction between BiOBr and Bi_2MoO_6, the binding energy changes in the XPS spectrum. It can be seen that there are carrier transfer and chemical bonds at the heterojunction interface between BiOBr and Bi_2MoO_6**(Fig. 7E)**. Another study concluded that the Z-type heterojunction is the main reason for improving the photocatalytic performance of Ag_3PO_4/Ag/MoS_2/TiO_2 composites[194].Wang et al.[195] developed an electrochemically self-doped WO_3/TiO_2 nanotube–composite film by doping oxygen vacancies into heterojunctions for photocatalytic degradation of exhaust gas. Ding et al.[196] synthesized a CoO@TiO_2/MXene hybrid with a double heterojunction structure. EPR measurements prove that $SO_4^{\cdot-}$, $\cdot O_2^-$ and $^1O_2$ are the main reactive species involved in the photocatalytic degradation of phenol **(Fig. 8)**.

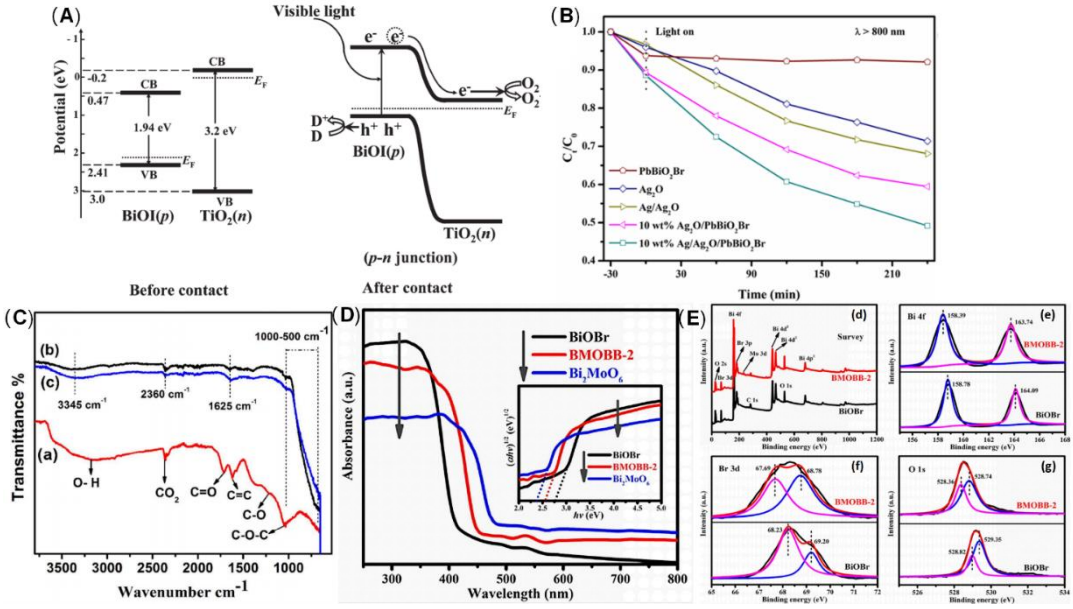

Fig 7. (A) Schematic diagrams ofthe energy bands of p-BiOI and n-TiO_2 before light irradiation and formation of a p–n junction under visible light irradiation. Adapted with permission from ref.[188]. Copyright 2011, American Chemical Society. (B) Photocatalytic degradation of tetracycline with obtained samples under NIR light (λ>800nm). Adapted with permission from ref.[189]. Copyright 2019, Elsevier. (C) FTIR spectra of various samples; (a) pure GO (b) pure γ-Al_2O_3 (c) 10.0% GO/Al_2O_3 composite. Adapted with permission from ref.[191]. Copyright 2018, American Chemical Society. (D) UV-vis diffuse reflectance spectra (DRS). Adapted with permission from ref.[193]. Copyright 2021, Elsevier. (E) (d) XPS survey spectra and high resolution XPS spectra of (e) Bi 4f, (f) Br 3d, (g) O 1 s of BiOBr and BMOBB-2. Adapted with permission from ref.[193]. Copyright 2021, Elsevier.

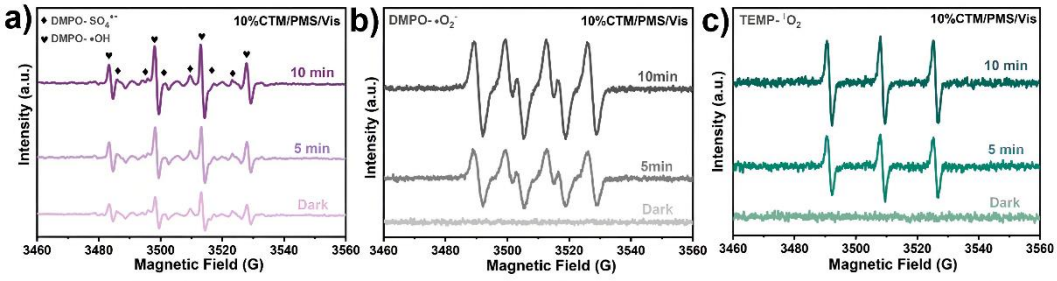

Fig 8. EPR spectra of 10%CTM/PMS/Vis system for (a) 5,5-Dimethyl-1-pyrroline N-oxide (DMPO)- •OH and DMPO- $SO_4^{\bullet-}$, (b) DMPO- $O_2^{\bullet-}$ and (c) TEMP- $^1O_2$. Adapted with permission from ref.[196]. Copyright 2021, Elsevier.

4.3 Supported co-catalyst

The electron-hole transfer between co-catalyst and semiconductor not only accelerates the separation of carriers but also realizes the spatial separation of oxidation and reduction reactions so that both quantum efficiency and reaction efficiency are improved. In addition, the co-catalyst also has abundant surface active sites, which can cut back the overpotential of the surface reaction, thereby increasing the surface reaction rate.

Wang et al. [197] found that WSe_2/g-C_3N_4 prepared with WSe_2 as a co-catalyst both promotes light absorption and improves charge transfer efficiency. Peng et al. [161] by comparing the amount of co-catalyst, found that the Cr_xO co-catalyst (3wt%) is beneficial to improve the removal efficiency of acetaldehyde. Shen et al. [198] used the organic molecule oxamide (OA) as a co-catalyst to prepare modified TiO_2 samples through wet chemical methods to enhance electron-hole separation and photocatalytic H-2 precipitation on TiO_2. Bai et al. [199] found that MoS_2 as a TiO_2 co-catalyst has the following characteristics: (1) No noble metals; (2) High charge transport mobility; (3) Many active sites.

4.4 Exposure of highly reactive facets

Crystals have different optical and electronic structures, so the crystals have unique properties, such as adsorption, high activity and selectivity. The crystal facet can also promote the separation of electrons and holes. Furthermore, the reactivity physical and chemical properties of surface facets are also critical to determine its workability [200].

Liang et al. [201] prepared a high proportion of active (002) crystal planes (>90%) and high specific surface area ultra-thin WO_3 nanosheets, which improved the performance of the catalyst to degrade pollutants. Yu et al. [202] synthesized TiO_2 nanosheets. The exposed (001) crystal facets are beneficial for the reduction of NO_x. The NO conversion rate of the hydrothermal method prepared TiO_2 sheets is higher than the conversion rate of commercial P25 and TiO_2 particles synthesized by the sol-gel method. Li et al.[203] prepared Z-scheme rGO/Bi_2S_3-BiOBr heterojunction which has adjustable exposed BiOBr (102) crystal facet. The optimized catalyst has the best photocatalytic oxidation performance in a single system, and the degradation efficiency of 2-nitrophenol reaches 92%. In different photocatalytic applications, the crystal facets promote the separation of carriers, exposing the highly reactive facets to improve the activity of the catalyst has become a promising method.

5. Summary and outlook

Rapid economic development has posed serious environment and health problems coming from VOCs. They come from a wide range of sources and can cause diseases and even carcinogenesis in the human body. In addition, under light exposure, VOCs generate photochemical smog, and certain halogenated hydrocarbons can cause the destruction of the ozone layer. Up to date, photocatalysis is being recognized as an effective and clean treatment method for VOC removal as it operates at room-temperature, produce no secondary pollution, and have high removal activity. Furthermore, the photocatalytic efficiency has been greatly improved by surface modification of the nano-catalysts.

In this work, we reviewed the influence mechanism of the intrinsic and extrinsic factors of nano-catalysts on the catalytic degradation of VOCs. In addition, four nano-catalyst surface modification strategies are also discussed: surface doping, surface heterojunction, co-catalyst and exposure of highly reactive crystal facets. And analyze and evaluate these four methods respectively.

From what was discussed, the following conclusions can be drawn: (1) By understanding the

basic principles of photocatalysis, it was found that surface modification of the photocatalyst can reduce the recombination of the carrier and improve the photoactivity of the nano-catalyst. (2) The morphology of the catalyst affects the adsorption of VOCs, and the high surface area and porous structure are conducive to the adsorption of VOCs. (3) Temperature and humidity will seriously affect the adsorption of VOC. Low temperature is conducive to adsorption processes dominated by exothermic reactions. High humidity will reduce the adsorption capacity of VOCs. However, photocatalysis also has shortcomings: (1) The photocatalysis is limited to the treatment of low concentrations of pollutants. (2) The performance of the photocatalyst is affected by internal and external factors. (3) The lattice defects caused by doping can reduce the catalytic activity. Therefore, there is often an optimal amount of doping.

Based on our current knowledge about the limitations of PCO technology in removing VOCs, we can make some suggestions for future research **(Fig. 9)** :(1) Improve the electronic and chemical properties of the nano-catalyst to improve its photocatalytic activity, adsorption of VOCs and resistance to deactivation. (2) Explore more stable and more efficient photocatalyst materials, combining different strategies such as facets, heterojunctions and co-catalysts. (3) Photocatalysts with the visible light response show enormous promise and should be widely researched. (4) More attention should be paid to development of synthesis methods that contribute to electron trapping mechanism, efficient structures and production methods. (5) Increase the rate of adsorption and reduce the competitive adsorption behavior of by-products.

We hope that the presented overview can provide key research progress in the field of photocatalysis of the modified NMs, and expect to making greater progress in the design of nano-catalysts in the near future.

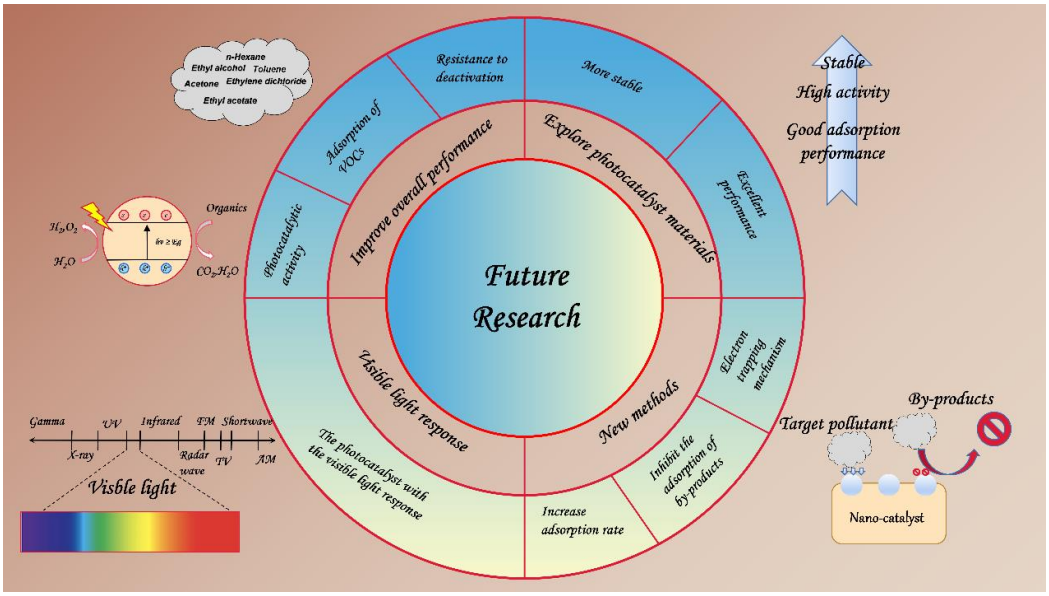

Fig 9. Prospects for future research.

Author contributions

Weichen Zhao: Writing - Original Draft, Visualization, Conceptualization. Muhammad Adeel: Writing - Review & Editing, Conceptualization. Peng Zhang, Pingfan Zhou, Lli Huang, Yongwen Zhao, Muhammad Arslan Ahmad, Noman Shakoor, Benzhen Lou, Yaqi Jiang, Iseult Lynch: Writing - Review & Editing. Yukui Rui: Writing - Review & Editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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