

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

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

4 Weichen Zhao<sup>a†</sup>, Muhammad Adeel<sup>b†</sup>, Peng Zhang<sup>c,d</sup>, Pingfan Zhou<sup>a</sup>, Lili Huang<sup>f</sup>, Yongwen  
5 Zhao<sup>f</sup>, Muhammad Arslan Ahmad<sup>e</sup>, Noman Shakoor<sup>a</sup>, Benzhen Lou<sup>a</sup>, Yaqi Jiang<sup>a</sup>, Iseult  
6 Lynch<sup>e</sup>, Yukui Rui<sup>a,g,h\*</sup>

7 <sup>a</sup> Beijing Key Laboratory of Farmland Soil Pollution Prevention and Remediation, College of  
8 Resources and Environmental Sciences, China Agricultural University, Beijing 100193, China

9 <sup>b</sup> BNU-HKUST Laboratory of Green Innovation, Advanced Institute of Natural Sciences,  
10 Beijing Normal University at Zhuhai 519087, China

11 <sup>c</sup> School of Geography, Earth and Environmental Sciences, University of Birmingham,  
12 Edgbaston, Birmingham B15 2TT, United Kingdom.

13 <sup>d</sup> Department of Environmental Science and Engineering, University of Science and  
14 Technology of China, Hefei 230026, China

15 <sup>e</sup> Shenzhen Key Laboratory of Marine Bioresource and Eco-environmental science, College of  
16 Life Sciences and Oceanography, Shenzhen University, Shenzhen 518060, China

17 <sup>f</sup>Jiaer Chen Academician Workstation, Jinan Huaxin Automation Engineering Co., Ltd. ,  
18 Xincheng Road, Shanghe County, Jinan, Shandong, China

19 <sup>g</sup> China Agricultural University Professor Workstation of Yuhuangmiao Town, Shanghe  
20 County, Jinan, Shandong, China

21 <sup>h</sup> China Agricultural University Professor Workstation of Sunji Town, Shanghe County,  
22 Shanghe County, Jinan, Shandong, China

23 \*Corresponding author: Yukui Rui: [ruiyukui@163.com](mailto:ruiyukui@163.com)

24 †These authors contributed equally in this work.

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37 **Abstract**

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

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

52

53 **1.Introduction**

54 Air quality has received a widespread attention due to its injurious effects on living organism.  
55 Industries, such as petroleum refining <sup>1</sup>, chemical production <sup>2</sup>, synthetic resin <sup>3</sup>, clothing dyeing <sup>4-  
56 6</sup>, leather processing <sup>7</sup>, pharmaceutical industry <sup>2, 8</sup>, insecticide production <sup>9</sup>, coating and adhesive  
57 manufacturing <sup>10</sup>, spraying <sup>11</sup>, printing <sup>4, 12</sup>, electronic component manufacturing <sup>2, 5, 13</sup> releasing  
58 significant amount of volatile organic compound (VOC) which ultimately effects the air quality (**Fig.  
59 1**). Due to easy diffusivity, toxicity and volatility, VOCs can cause irreversible damage to human  
60 health <sup>14-16</sup>. The adverse effects of VOCs on human health include not only acute irritation to the  
61 eyes and lung but also chronic diseases such as asthma, gastrointestinal diseases, cardiovascular  
62 diseases and cancer <sup>17-20</sup>.

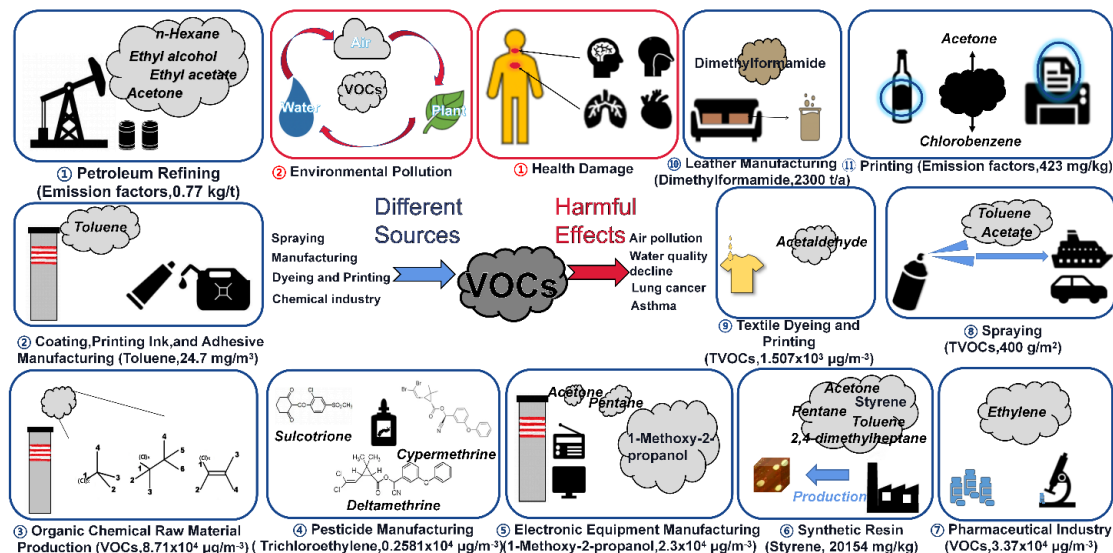
63 To overcome devastating effects of VOCs, several efficient purification techniques of VOCs  
64 has been developed. Such as incineration, condensation, adsorption, photocatalytic oxidation (PCO),  
65 ozone-catalytic oxidation and membrane separation <sup>21</sup>. Comparing with these techniques,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

70 Commonly used photocatalysts material for purification of VOCs includes TiO<sub>2</sub>, ZnO, WO<sub>3</sub>,  
71 V<sub>2</sub>O<sub>5</sub>, ZnS and CdS <sup>23-25</sup>. To date, nanotechnology has made exponential progress <sup>26-28</sup>.  
72 Nanomaterials (NMs) are widely used in the field of environmental remediation <sup>29</sup>. Nowadays, TiO<sub>2</sub>  
73 has a large number of applications photocatalysis <sup>30-33</sup>, due to its high photocatalytic efficiency,  
74 stability under extreme conditions, and suitable edge potential to act as active centers for catalytic  
75 reactions <sup>34-36</sup>. However, the performance of these nano-catalyst is not efficient. For example,  
76 compared with other semiconductor materials, TiO<sub>2</sub> has a wider band gap and higher carrier  
77 recombination rate which limit the photocatalytic process to the UV region of the spectrum <sup>31, 37</sup>.

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

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

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



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

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

97 **2. Mechanism behind photocatalytic oxidation of VOCs**

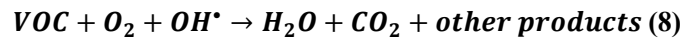
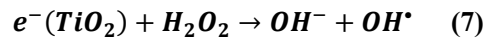
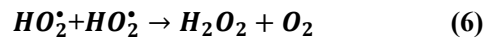
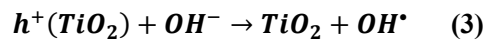
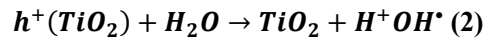
98 The photocatalytic reaction is a complex process, which begins with the absorption of a large  
 99 amount of visible light on the surface of the material. When the energy of the absorbed photon is  
 100 not less than the energy of the semiconductor band gap photon ( $E_g$ ), the electrons existing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



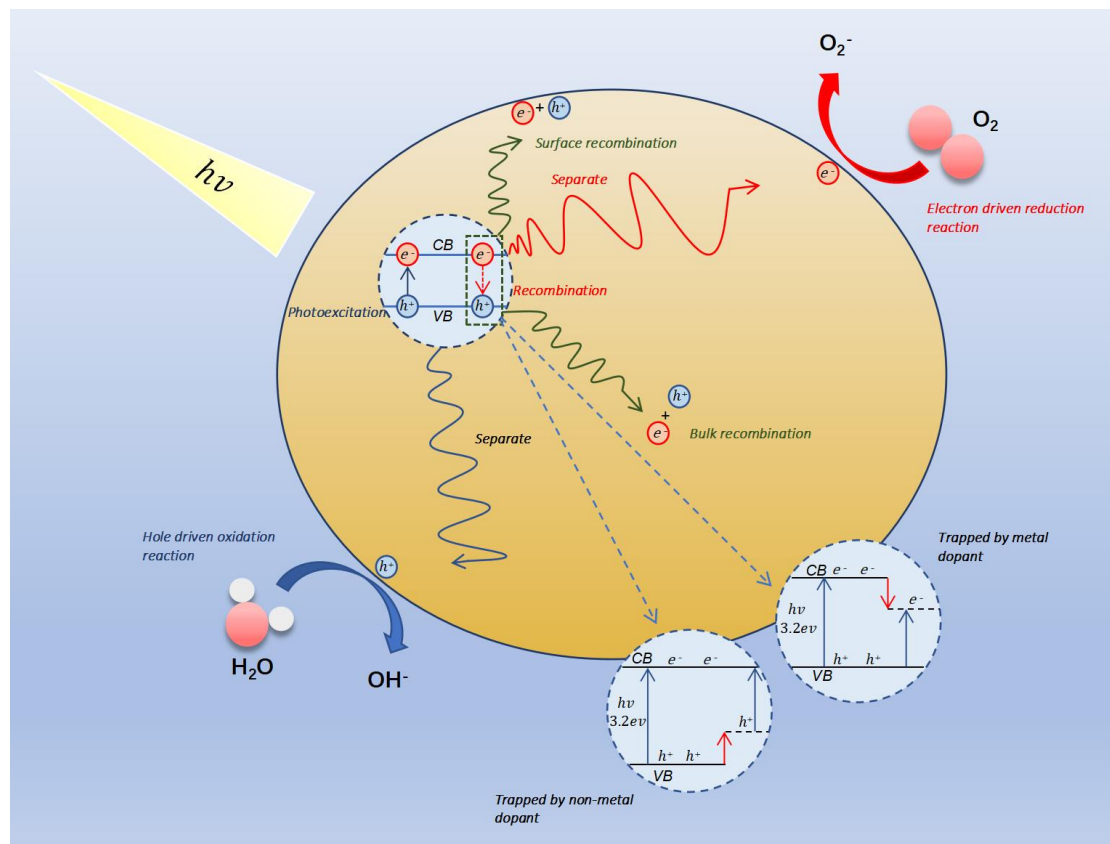
105 There are three possible processes for electrons and holes :(1) Separate and move to the surface  
 106 of the material to have an opportunity to participate in redox reaction (2) Trapped by defect sites.  
 107 (3) Recombine and release energy. However, the second and the third process do not promote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

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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.

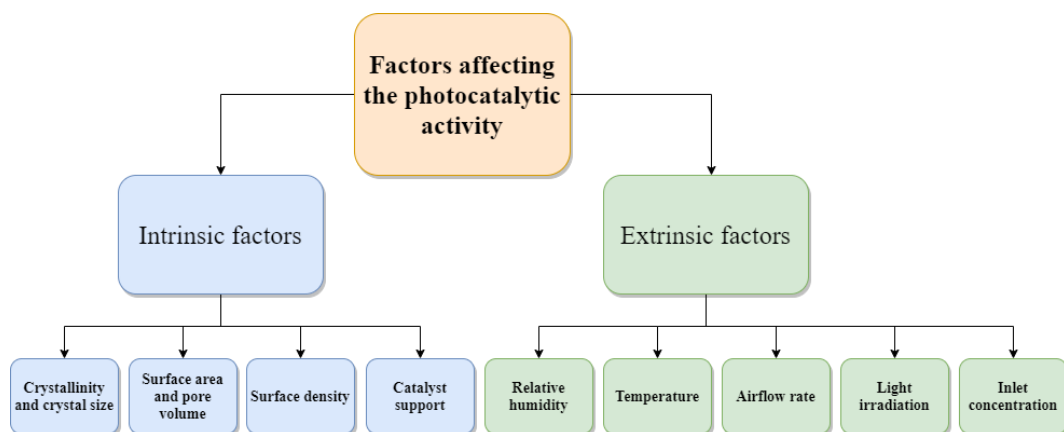


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**Fig 2. Schematic illustration of basic mechanism of photocatalysis.**

### 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.



135  
136 **Fig 3. Illustration of factors affecting the photocatalytic activity.**

137 **3.1 Influence of catalyst characteristics (intrinsic factors) on VOCs degradation**

138 **3.1.1 Crystallinity and crystal size**

139 The presence of defects in crystal lattice and impurities in the catalyst accelerates the  
140 recombination process. To improve the efficiency of photocatalysis, the design and research of high  
141 bulk crystallinity have received extensive attention <sup>66</sup>.

142 Leite et al. <sup>67</sup>claimed that the property of high crystallinity has advantages over disordered  
143 polymers in photocatalytic applications. Pleskunov et al. <sup>68</sup>used a single-step plasma-based  
144 technique to synthesize Ta<sub>3</sub>N<sub>y</sub>O<sub>x</sub> nanoparticles(NPs) with controllable crystallinity. In the visible  
145 light range, Ta<sub>3</sub>N<sub>y</sub>O<sub>x</sub> exhibits plasmonic and photoluminescent properties. Katsuki et al. <sup>69</sup>found that  
146 α-Fe<sub>2</sub>O<sub>3</sub> NPs with high crystallinity are more efficient in PCO. A similar finding was also reported  
147 by Li et al. <sup>70</sup>, they found that the nanorod-shaped photoactive COF containing benzothiadiazole  
148 and triazine with good crystallinity exhibited excellent comprehensive performance and good cycle  
149 performance in the photocatalytic oxidation reaction. Curtis et al. <sup>71</sup>used the two-temperature  
150 method to prepare mesoporous silicon NPs. The initial temperature of the reaction is 650°C and  
151 lasted for 0.5h, and then in the second heating process at 100°C, 200°C and 300°C for 6h. They  
152 found that the mesoporous silicon NPs prepared at 300°C have the best photocatalytic performance  
153 because of the higher crystallinity of catalyst. Li et al. <sup>72</sup>and Zhang et al. <sup>73</sup> pointed out that  
154 synthesizing a new heterogeneous photocatalyst has uniform crystal size and high crystallinity.  
155 These advantages accelerate the separation and transfer efficiency of electron-hole pairs.

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

160 **3.1.2 Surface area**

161 Surface area is an important structural feature of photocatalysts, which has a great influence on  
162 photocatalysis <sup>75</sup>. The larger surface area, the more accessible active sites, and the higher the  
163 photocatalytic efficiency <sup>76</sup>.

164 Hajaghadzadeh et al. <sup>77</sup>found that under steady-state conditions, the conversion rate of methyl

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

### 177 **3.1.3 Pore volume and porosity**

178 In addition to the surface area, another structural feature pore volume of the photocatalyst also  
179 has a profound effect on the catalytic efficiency<sup>74</sup>. Chen et al.<sup>81</sup> designed Pt nanoclusters similar to  
180 1.8 nm. The catalytic performance of C/Pt@TiO<sub>2</sub>-3% containing 0.54 wt% Pt is greatly improved  
181 because of its maximum total pore volume and the average pore diameter is approximately 3 nm. In  
182 addition, the mesoporous structure also helps to expose more active sites of the nano-catalyst to  
183 promote surface reactions <sup>81</sup>.

184 While achieving porous structure, crystallinity will not be lost. Therefore, the general view is  
185 that porous structure is more important catalyst characteristics than crystallinity <sup>62</sup>.

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

190 Xie et al. <sup>87</sup> designed and synthesized two MOFs, among which [Zr<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(BDB)<sub>6</sub>]  
191 (BUT-66) shows superior adsorption performance of benzene. Single-crystal structure analysis  
192 shows that the small hydrophobic pores and the small interaction between the adsorption sites make  
193 BUT-66 have the high performance of capturing benzene. Wu et al. <sup>88</sup> used lab-on-fiber technology  
194 and nanotechnology to monitor surface nano-functionalization of VOC adsorption/desorption in  
195 zeolitic imidazole frameworks (ZIF)-8. The high porosity plays an important role in VOC sensors.  
196 This finding was also reported by Wang et al. <sup>89</sup> They found that the shape and size of the porous  
197 Co<sub>3</sub>O<sub>4</sub> derived from Co-MOF would significantly affect its sensing performance. Besides, the more  
198 NPs on the surface, the better the VOC sensing performance. Yu et al. <sup>90</sup> proposed a two-step method  
199 to prepare In/Ni MOF-derived mesoporous In<sub>2</sub>O<sub>3</sub>-NiO composites with a nanosheet hollow sphere  
200 (NHS) structure. They observed that mesoporous In<sub>2</sub>O<sub>3</sub>-NiO NHS has a high porosity, this  
201 advantage provides sufficient permeation pathways for VOC, a large number of active sites, and the  
202 capacity to capture VOC.



203 Table 1 Summary of different photocatalysts affect the photoactivity

Photocatalyst	Surface area	Pore volume	Compound	Photo activity	Ref.
TiO <sub>2</sub> USprec	326 m <sup>2</sup> /g	0.484 cm <sup>3</sup> /g	Benzyl alcohol	Conversion 61%	91
P25	-	-	Benzyl alcohol	Conversion 100%	91
Brookite/anatase TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	37.1 m <sup>2</sup> /g	0.2 cm <sup>3</sup> /g	Phenol	Degradation rate 5-fold increase over CN	92
CN	45.8 m <sup>2</sup> /g	0.29 cm <sup>3</sup> /g	Phenol	-	92
Ti <sup>3+</sup> doped TiO <sub>2</sub> /SiO <sub>2</sub>	300 m <sup>2</sup> /g	0.35 cm <sup>3</sup> /g	Methyl orange	31.5%	93
TiO <sub>2</sub>	56.8 m <sup>2</sup> /g	-	Methyl orange	8%	93
TiO <sub>2</sub> /SiO <sub>2</sub>	228 m <sup>2</sup> /g	0.27 cm <sup>3</sup> /g	Methyl orange	16.6%	93

204

205 **3.1.4 Surface density**

206 Surface density is a key factor as increasing the thickness of the nano-catalyst coating can  
 207 increase the surface area of the catalyst and reduce competitive adsorption between reactants,  
 208 thereby increasing the removal rate and the degree of mineralization of the catalyst <sup>94</sup>.

209 Singh et al. <sup>95</sup> used atomic layer deposition method coating TiO<sub>2</sub> on fibrous nanosilica (KCC-  
 210 1). They observed that the KCC-1/TiO<sub>2</sub> catalyst coated with TiO<sub>2</sub> NPs has a more uniform coating,  
 211 a higher loading of TiO<sub>2</sub>, a smaller loss of surface area, and higher active site accessibility than  
 212 traditional silica catalysts. Wang et al. <sup>96</sup> confined the dense Au nanoparticles to a bowl-shaped TiO<sub>2</sub>  
 213 nanoarray doped with N. By adjusting the absorption of light by TiO<sub>2</sub> and fully overlapping the  
 214 plasma band of Au NPs, the photocatalytic efficiency is greatly improved. Roldan et al. <sup>97</sup> researched  
 215 a new type of nanostructured coating system, which includes a layer of SiO<sub>2</sub> and a layer of dense  
 216 anatase TiO<sub>2</sub> doped with Ag NPs. The photocatalytic activity has been improved All in all,  
 217 increasing the surface density of the nano-catalyst can greatly increase the conversion of VOCs.  
 218 However, an excessive amount of catalyst will result in a decrease in catalytic efficiency.

219 **3.1.5 Support material**

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

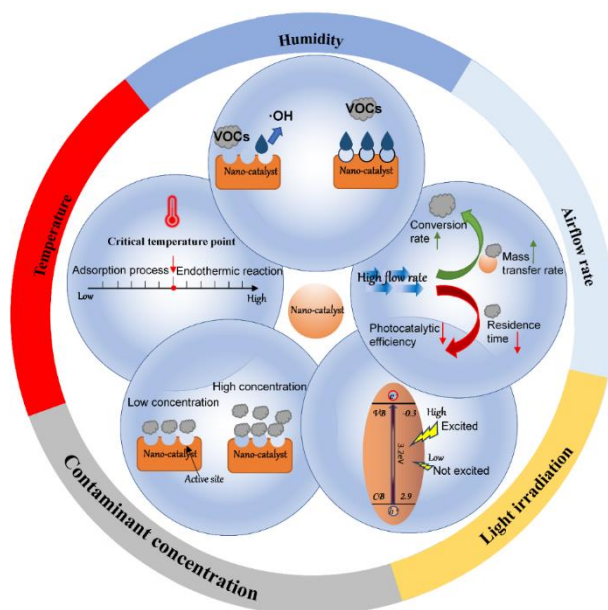
227 carbon is microporous (pore size < 2nm), which makes it difficult for molecules with larger  
228 molecular diameters to enter the pores. Furthermore, due to the strong diffusion resistance due to  
229 irregular pore structure, the adsorption equilibrium is prolonged due to the disordered pores  
230 possessed by AC. Zhang et al.<sup>98</sup> prepared a new nano- $\beta$ -FeOOH/Fe<sub>3</sub>O<sub>4</sub>/biochar composite material.  
231 Through XPS characterization, it is proved that there are Fe-OC bonds between  $\beta$ -FeOOH and  
232 biochar. These bonds facilitated the transfer of photo-generated electrons. The connection promotes  
233 the rapid interface transfer of light energy electrons between biochar and  $\beta$ -FeOOH. Zhang et al.<sup>99</sup>  
234 prepared N-doped nano-TiO<sub>2</sub>-carbon fiber composite material. After TiO<sub>2</sub> NPs are irradiated by  
235 microwaves, they generate a large number of hydroxyl adsorption sites. Due to the interface formed  
236 between TiO<sub>2</sub> and carbon fiber, this carbon fiber composite material can effectively catalyze the  
237 oxidation reaction of phenol. Graphene has the characteristics of inhibiting the annihilation of  
238 electrons and holes and exhibits excellent photoactivity, so it is widely used in photocatalysis<sup>100-102</sup>.  
239 Saima et al.<sup>103</sup> used graphene oxide(GO) as the support material and randomly dispersed TiO<sub>2</sub> and  
240 NiO NPS on it. The GO provides fast electronic conductivity and strong oxidation characteristics,  
241 which facilitates the separation of carriers.

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

### 245 **3.2 Effects of environmental conditions (external factors) on POC of VOCs**

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

252



**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<sup>104, 105</sup>. 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<sup>106</sup>. Regarding air humidity, modification of the nano-catalyst can reduce the degree of competition between water molecules and VOCs; for example, doped TiO<sub>2</sub> has a higher catalytic efficiency than undoped TiO<sub>2</sub> because the introduction of dopants resulting in more oxidant<sup>107-111</sup>.

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.<sup>112</sup> 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<sup>113</sup>.

### 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<sup>114-116</sup>. Therefore, optimizing the air flow rate is essential: low air flow rate can increase the residence

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

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

### 289 **3.2.3 Light irradiation**

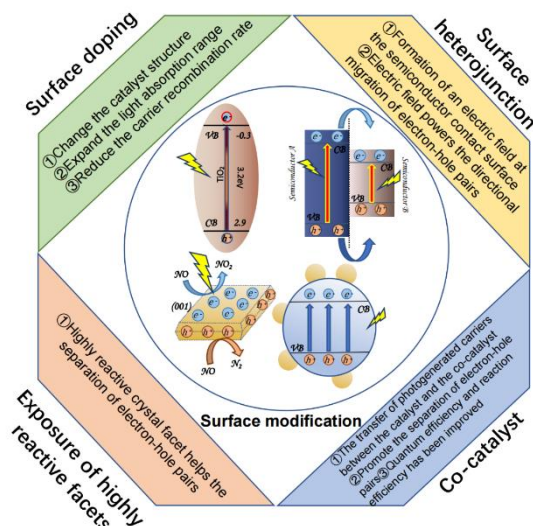
290 It is worth mentioning that light irradiation (wavelength and intensity of light) has a greater  
291 impact on the photocatalytic process than adsorption process. On the one hand, the wavelength of  
292 light is related to  $E_g$  and the energy of the band gap photon. If  $E_g$  is too low (less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

300 Table 2 The key factors affecting VOC photocatalytic performances.

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

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

303 The intrinsic properties of the nanomaterial photocatalysts and the extrinsic factors effecting  
304 nano-catalysts have significant role on photocatalytic efficiency. Surface modification methods  
305 investigated to date include surface doping, the structure of surface heterojunctions, utilizing a  
306 supported co-catalyst, increasing the surface area, and ensuring high reaction surface exposure (**Fig.**  
307 **5**). These are discussed below.



308

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

311 **4.1 Surface doping**

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

321 **4.1.1 Metal doping**

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

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

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

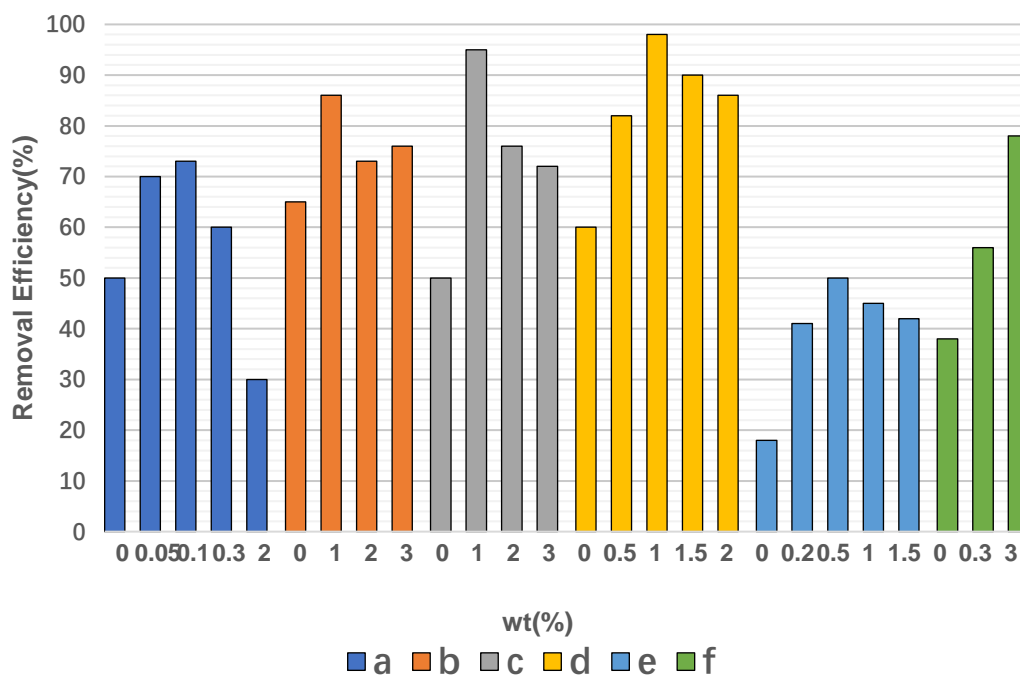
337 Noble metal elements such as platinum (Pt)<sup>132</sup>, palladium (Pd)<sup>133</sup>, ruthenium (Ru)<sup>134</sup>, silver  
338 (Ag)<sup>135</sup>. Because of noble metals, the recombination of carriers is reduced, which improve the  
339 photoactivity of the catalyst<sup>136</sup>. In fact, the doping of noble metal NPs forms a medium for capturing  
340 and transferring electrons on the nano-catalyst surface<sup>137</sup>. Meng et al.<sup>138</sup> doped Pd/PdCl<sub>2</sub> onto the  
341 surface of the nano-catalyst Bi<sub>2</sub>WO<sub>6</sub> by photoreduction method. Compared with TiO<sub>2</sub>, the catalyst  
342 degrades phenol more efficiently. The researchers concluded that it may be due to the dual factors  
343 of the plasmon resonance and the suppression of photo-generated carrier recombination. Xue et al.<sup>139</sup>,  
344 modified TiO<sub>2</sub> doped with Ag and Ag<sub>2</sub>O. The efficiency of this catalyst to degrade toluene is 50%,  
345 which is about 9.7 times higher than TiO<sub>2</sub>.

346 Transition metal doping can significantly extend visible light excitation, and more susceptible  
347 to doping by other transition metals because of the lower energy required for the substitution process.  
348 Thus, there has been extensive research on transition metal doping, such as manganese (Mn)<sup>140, 141</sup>,  
349 iron (Fe)<sup>142-144</sup>, copper (Cu)<sup>145</sup>, vanadium (V)<sup>146, 147</sup>, and nickel (Ni)<sup>148</sup>. Afif et al.<sup>149</sup> successfully  
350 synthesized a highly active Mn-doped Ag<sub>3</sub>PO<sub>4</sub> photocatalyst using the co-precipitation method. Mn  
351 doping suppressed hydroxyl defects and oxygen vacancies, increased the atomic ratio of oxygen to  
352 silver, and improved the photocatalytic performance under visible light irradiation. Patrick et al.<sup>150</sup>  
353 found that the photochemical properties of the Mn complex reached or approached the performance  
354 of Ru and Ir noble metal catalysts in terms of photon absorption. Devaraji group<sup>151</sup> incorporated V  
355 into the TiO<sub>2</sub> crystal lattice to make Ti<sub>0.98</sub>V<sub>0.02</sub>O<sub>2</sub>. Compared with pure TiO<sub>2</sub>, this catalyst embodies  
356 the quantum transition of benzene oxidation, highlighting the importance of V doping for benzene  
357 oxidation. Stucchi et al.<sup>152</sup> used Mn to replace noble metals such as Au and Ag. Through  
358 experiments, it was found that TiO<sub>2</sub> doped with 20% Mn under visible light exposure for 24 h, the  
359 degradation efficiency of ethanol reached 35%, which is the peak degradation efficiency. The  
360 suppression of the defect sites on the catalyst surface and the reduction of electrons compound with  
361 holes that may be the reasons for the excellent photocatalytic activity. Li et al.<sup>153</sup> prepared Co-doped  
362 TiO<sub>2</sub> nanorod array (Co-TiO<sub>2</sub> @Ti(H<sub>2</sub>)) with good stability, and the energy barrier for desorption  
363 can be effectively reduced by introducing Co with abundant oxygen vacancies. Sajjad et al.<sup>154</sup> used  
364 Si and Ti to modify the magnetic Fe<sub>3</sub>O<sub>4</sub> NPs. It was found that the photodegradation effect was in  
365 the order of Ti modified Fe<sub>3</sub>O<sub>4</sub>>Si modified Fe<sub>3</sub>O<sub>4</sub>>Fe<sub>3</sub>O<sub>4</sub>.

366           There are 17 kinds of lanthanides, collectively referred to as rare earth metals. Kumar et al. <sup>39</sup>  
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. <sup>155</sup>found that Ce-doped TiO<sub>2</sub> 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. <sup>156</sup> synthesized Ce-doped MoS<sub>2</sub>  
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.





379

380 **Fig 6. The effect of different doping amounts on the degradation of VOCs by photocatalyst.**

381 **(a) acetaminophen, Sb-doped TiO<sub>2</sub><sup>157</sup>. (b) 4-chlorophenol, W-doped TiO<sub>2</sub><sup>158</sup>. (c) 4-**

382 **chlorophenol, Mo-doped TiO<sub>2</sub><sup>158</sup>. (d) 2,4-dichlorophenol, Ce-doped CuMgAl<sup>159</sup>. (e) MEK,**

383 **Ce-TiO<sub>2</sub><sup>160</sup>. (f) acetaldehyde, Cr-TiO<sub>2</sub><sup>161</sup>.**

384

#### 385 4.1.2 Non-metal doping

386 Non-metal doping such as nitrogen (N)<sup>162-166</sup>, carbon (C)<sup>167-169</sup>, sulfur (S)<sup>170-173</sup>, boron (B)<sup>174,</sup>

387 <sup>175</sup>and fluorine (F)<sup>176</sup> has been extensively evaluated previously. In non-metal doping, dopants can

388 change the morphology and improve photoactive performance of the catalyst. Because the doped

389 state is close to the edge of VB and is not used as a carrier, the role of the recombination center will

390 be weakened. When the oxygen atom is replaced by other non-metal element atoms, the top energy

391 level of the VB of the oxide will increase, and the semiconductor band gap will be narrowed, thereby

392 extending the excitation wavelength to improve catalytic efficiency.

393 Table 3 summarizes metal and non-metal doped photocatalysts synthesized to improve

394 photocatalytic degradation performance. A conclusion can be drawn that after doping, the catalytic

395 efficiency of the catalyst has been improved.

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

Contaminant	Photocatalyst	Dopant	Efficiency before doping	Efficiency after doping	Ref.
Toluene	TiO <sub>2</sub>	Ag/Ag <sub>2</sub> O	7.5%	23.3%	139
Benzene	OMS-2	Mg	68.4%	97.2%	130
Benzene	TiO <sub>2</sub>	V	0.3%	12.7%	151
Benzene	Ti <sub>0.98</sub> V <sub>0.02</sub> O <sub>2</sub>	Au	9%	18%	151
Acetaldehyde	TiO <sub>2</sub>	F	77.3%	81%	177
Acetaldehyde	TiO <sub>2</sub>	N	77.3%	92.1%	177
Ethylbenzene	TiO <sub>2</sub>	N	33%	38%	178

404 Awin et al.<sup>179</sup> pointed out that the N-doped TiO<sub>2</sub> on the Si-OCN support exhibited excellent  
 405 adsorption properties and high catalytic activity under visible light. Sun et al.<sup>180</sup> developed C-doped  
 406 and oxygen vacancies Bi<sub>2</sub>WO<sub>6</sub> nanospheres mediated by graphene oxide. C-doping can change the  
 407 band gap structure and can also promote light absorption. This is because carbon doping in the  
 408 catalyst acts as an acceptor and electron channel to promote the separation of carriers and the  
 409 production of active substances. Diao et al.<sup>181</sup> synthesized F-doped TiO<sub>2</sub> by hydrothermal method  
 410 and used EPR measurements to prove that F-doped TiO<sub>2</sub> has superior degradability to formaldehyde  
 411 due to the participation of superoxide radical and hydroxyl radical in the process of oxidizing  
 412 formaldehyde into CO<sub>2</sub> and H<sub>2</sub>O. Ramacharyulu et al.<sup>182</sup> noted that compared with undoped TiO<sub>2</sub>,  
 413 S-doped TiO<sub>2</sub> had a lower band gap value and better photocatalytic activity. Among various doping  
 414 materials, non-metallic element doping has been tested to be a better way to improve PCO activity<sup>183</sup>,  
 415 <sup>184</sup>.

#### 416 4.2 Structure of surface heterojunction

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

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

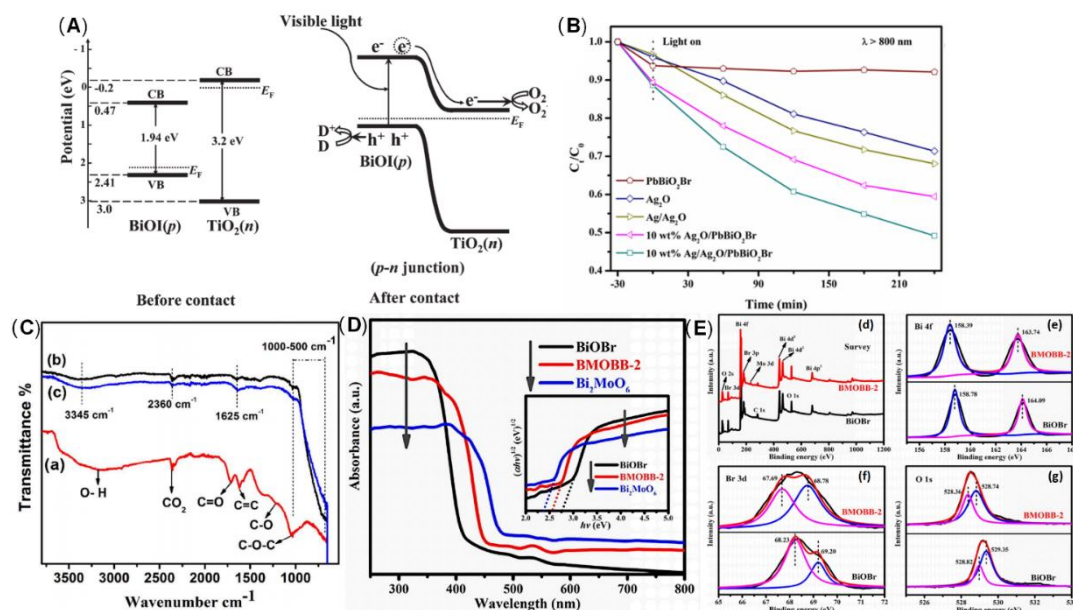
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432 Table 4. Heterostructure and degradation efficiency of photocatalyst.

Heterostructure	Photocatalyst	Efficiency before	Efficiency after	Ref.
Z-Scheme	LaFeO <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	37%	100%	185
Z-Scheme	Au-TiO <sub>2</sub> @NH <sub>2</sub> - UiO-66	10%	85%	186
S-scheme	Cu <sub>2</sub> S/SnO <sub>2</sub>	17.9	67.2%	187

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434 Dai et al.<sup>188</sup> used a new hydroxylation method to coat BiOI on the TiO<sub>2</sub> wall to form the p-n  
435 junction of the BiOI/TiO<sub>2</sub> nanotube array (**Fig. 7A**). They found the photo-electrocatalytic  
436 degradation efficiency of BiOI/TiO<sub>2</sub> was increased by 3 times. Guo et al.<sup>189</sup> successfully prepared  
437 an Ag/Ag<sub>2</sub>O/PbBiO<sub>2</sub>Br photocatalyst with a broader spectral response through a series of plasma p-  
438 n heterojunctions. Researchers have observed significantly accelerated charge separation, and the  
439 degradation efficiency of pollutants has also been significantly improved (**Fig. 7B**). Huang et al.<sup>190</sup>  
440 developed the p-n junction BiOI@Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub> heterostructure by depositing BiOI nanosheets in situ.  
441 Due to charge induction, BiOI@Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub> forms a unique front-side coupling heterostructure.  
442 Compared with the pure sample, the obtained BiOI@Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub> heterostructure can significantly  
443 enhance the catalytic performance and degradation of 2,4-Dichlorophenol. Anum et al.<sup>191</sup> studied a  
444 new type heterojunction of Al<sub>2</sub>O<sub>3</sub> and GO. FTIR examination showed that the density of hydroxyl  
445 on the surface of pure Al<sub>2</sub>O<sub>3</sub> was lower, but after adding GO, the density increased (**Fig. 7C**). The  
446 reason may be related to the interaction between hydroxyl and light-generated holes, which  
447 promotes electron transfer and inhibits the recombination of carriers. Because of GO, the  
448 recombination of electron-hole pairs is reduced. Through the study of activity, it was found that  
449 15.0% GO/Al<sub>2</sub>O<sub>3</sub> exhibits superior photocatalytic performance. In another study, the same result  
450 was observed<sup>192</sup>. Wu et al.<sup>185</sup> constructed a new p-type LaFeO<sub>3</sub> microspheres coated with n-type  
451 nano-scale graphite carbon nitride nanosheets. The interface effect of charge carriers is separated  
452 and transferred more effectively through solid p-n heterojunction. Yao et al.<sup>193</sup> prepared p-n  
453 heterojunction of Bi<sub>2</sub>MoO<sub>6</sub>/BiOBr which can promote the photocatalysis. In addition the UV-vis  
454 absorption edge of the BMOBB-2(The mole ratio of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O to Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O is set as  
455 5%) sample has a significant red shift, which is related to the better visible light response of  
456 Bi<sub>2</sub>MoO<sub>6</sub>(**Fig. 7D**). Due to the strong interaction between BiOBr and Bi<sub>2</sub>MoO<sub>6</sub>, the binding energy  
457 changes in the XPS spectrum. It can be seen that there are carrier transfer and chemical bonds at the  
458 heterojunction interface between BiOBr and Bi<sub>2</sub>MoO<sub>6</sub>(**Fig. 7E**). Another study concluded that the  
459 Z-type heterojunction is the main reason for improving the photocatalytic performance of  
460 Ag<sub>3</sub>PO<sub>4</sub>/Ag/MoS<sub>2</sub>/TiO<sub>2</sub> composites<sup>194</sup>. Wang et al.<sup>195</sup> developed an electrochemically self-doped  
461 WO<sub>3</sub>/TiO<sub>2</sub> nanotube-composite film by doping oxygen vacancies into heterojunctions for  
462 photocatalytic degradation of exhaust gas. Ding et al.<sup>196</sup> synthesized a CoO@TiO<sub>2</sub>/MXene hybrid  
463 with a double heterojunction structure. EPR measurements prove that SO<sub>4</sub><sup>-</sup>, ·O<sub>2</sub><sup>-</sup> and <sup>1</sup>O<sub>2</sub> are the  
464 main reactive species involved in the photocatalytic degradation of phenol (**Fig. 8**).



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**Fig 7. (A) Schematic diagrams of the energy bands of p-BiOI and n-TiO<sub>2</sub> before light irradiation and formation of a p-n junction under visible light irradiation. Adapted with permission from ref.<sup>188</sup>. Copyright 2011, American Chemical Society. (B) Photocatalytic degradation of tetracycline with obtained samples under NIR light ( $\lambda > 800\text{ nm}$ ). Adapted with permission from ref.<sup>189</sup>. Copyright 2019, Elsevier. (C) FTIR spectra of various samples; (a) pure GO (b) pure  $\gamma\text{-Al}_2\text{O}_3$  (c) 10.0% GO/ $\text{Al}_2\text{O}_3$  composite. Adapted with permission from ref.<sup>191</sup>. Copyright 2018, American Chemical Society. (D) UV-vis diffuse reflectance spectra (DRS). Adapted with permission from ref.<sup>193</sup>. Copyright 2021, Elsevier. (E) (d) XPS survey spectra and high resolution XPS spectra of (e) Bi 4f, (f) Br 3d, (g) O 1s of BiOBr and BMOBB-2. Adapted with permission from ref.<sup>193</sup>. Copyright 2021, Elsevier.**

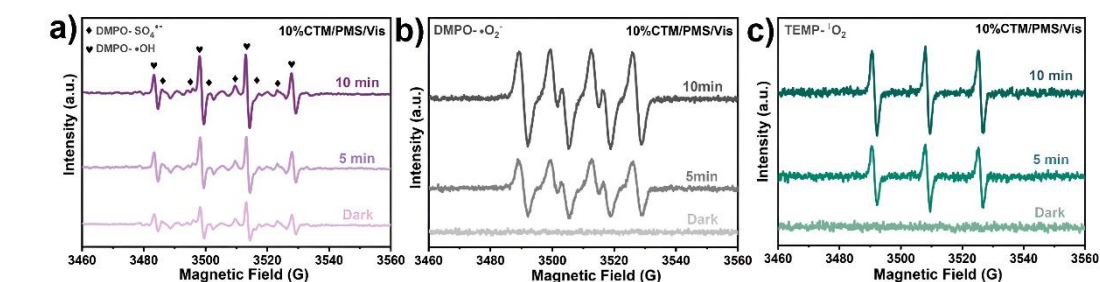
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**Fig 8. EPR spectra of 10%CTM/PMS/Vis system for (a) 5,5-Dimethyl-1-pyrroline N-oxide (DMPO)-  $\bullet\text{OH}$  and DMPO-  $\text{SO}_4^{\bullet-}$ , (b) DMPO-  $\text{O}_2^{\bullet-}$  and (c) TEMP-  $^1\text{O}_2$ . Adapted with permission from ref.<sup>196</sup>. Copyright 2021, Elsevier.**

#### 4.3 Supported co-catalyst

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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.

486 Wang et al.<sup>197</sup> found that WSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> prepared with WSe<sub>2</sub> as a co-catalyst both promotes  
487 light absorption and improves charge transfer efficiency. Peng et al.<sup>161</sup> by comparing the amount of  
488 co-catalyst, found that the Cr<sub>x</sub>O co-catalyst (3wt%) is beneficial to improve the removal efficiency  
489 of acetaldehyde. Shen et al.<sup>198</sup> used the organic molecule oxamide (OA) as a co-catalyst to prepare  
490 modified TiO<sub>2</sub> samples through wet chemical methods to enhance electron-hole separation and  
491 photocatalytic H<sub>2</sub> precipitation on TiO<sub>2</sub>. Bai et al.<sup>199</sup> found that MoS<sub>2</sub> as a TiO<sub>2</sub> co-catalyst has the  
492 following characteristics: (1) No noble metals; (2) High charge transport mobility; (3) Many active  
493 sites.

#### 494 **4.4 Exposure of highly reactive facets**

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

499 Liang et al.<sup>201</sup> prepared a high proportion of active (002) crystal planes (>90%) and high  
500 specific surface area ultra-thin WO<sub>3</sub> nanosheets, which improved the performance of the catalyst to  
501 degrade pollutants. Yu et al.<sup>202</sup> synthesized TiO<sub>2</sub> nanosheets. The exposed (001) crystal facets are  
502 beneficial for the reduction of NO<sub>x</sub>. The NO conversion rate of the hydrothermal method prepared  
503 TiO<sub>2</sub> sheets is higher than the conversion rate of commercial P25 and TiO<sub>2</sub> particles synthesized by  
504 the sol-gel method. Li et al.<sup>203</sup> prepared Z-scheme rGO/Bi<sub>2</sub>S<sub>3</sub>-BiOBr heterojunction which has  
505 adjustable exposed BiOBr (102) crystal facet. The optimized catalyst has the best photocatalytic  
506 oxidation performance in a single system, and the degradation efficiency of 2-nitrophenol reaches  
507 92%. In different photocatalytic applications, the crystal facets promote the separation of carriers,  
508 exposing the highly reactive facets to improve the activity of the catalyst has become a promising  
509 method.

#### 510 **5. Summary and outlook**

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

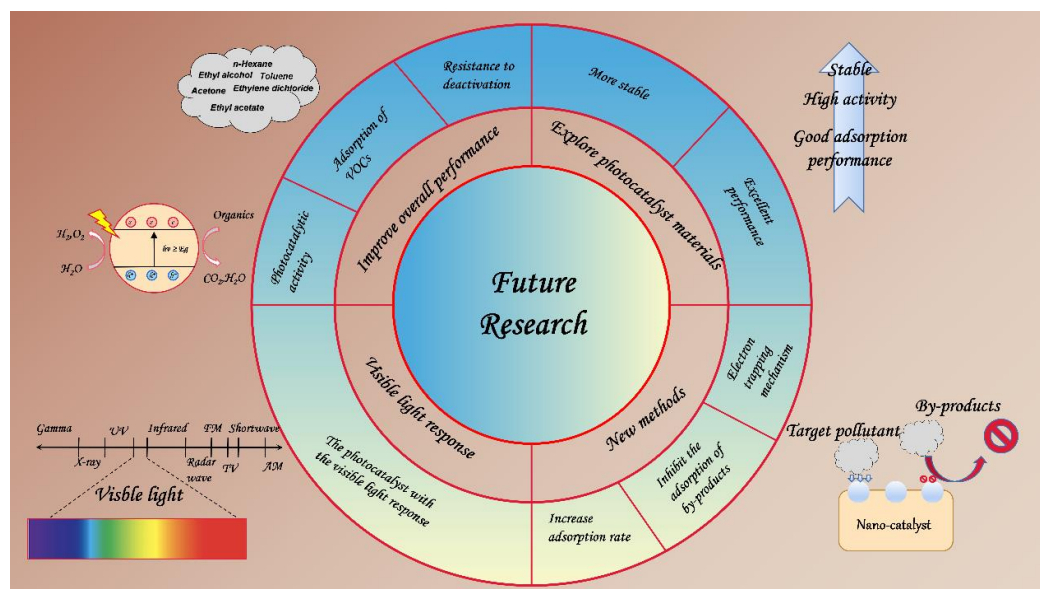
519 In this work, we reviewed the influence mechanism of the intrinsic and extrinsic factors of  
520 nano-catalysts on the catalytic degradation of VOCs. In addition, four nano-catalyst surface  
521 modification strategies are also discussed: surface doping, surface heterojunction, co-catalyst and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

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

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

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

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



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**Fig 9. Prospects for future research.**

548 **Author contributions**

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

553 **Declaration of Competing Interest**

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

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