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

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#### 37 Abstract

Surface modification of nano-catalyst got significant attention due its outstanding 38 photocatalytic performance with minimum secondary pollution. Photocatalytic oxidation (PCO) is 39 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 review study summarizes the recent reports of nano-catalyst surface modification technology, 43 including overcoming the internal and external limitations of nano-catalyst, and improving the 44 45 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 46 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 catalyst performance should be managed and paid more attention. 49

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

51 compounds; Surface chemistry;

#### 53 1.Introduction

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

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 <sup>21</sup>. 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<sup>22</sup>. 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.

70 Commonly used photocatalysts material for purification of VOCs includes TiO<sub>2</sub>, ZnO, WO<sub>3</sub>, V2O5, ZnS and CdS <sup>23-25</sup>. To date, nanotechnology has made exponential progress <sup>26-28</sup>. 71 Nanomaterials (NMs) are widely used in the field of environmental remediation <sup>29</sup>. Nowadays, TiO<sub>2</sub> 72 73 has a large number of applications photocatalysis <sup>30-33</sup>, due to its high photocatalytic efficiency, stability under extreme conditions, and suitable edge potential to act as active centers for catalytic 74 reactions <sup>34-36</sup>. However, the performance of these nano-catalyst is not efficient. For example, 75 compared with other semiconductor materials, TiO2 has a wider band gap and higher carrier 76 recombination rate which limit the photocatalytic process to the UV region of the spectrum <sup>31, 37</sup>. 77

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 <sup>38-42</sup>.

Previously published articles give a detailed introduction to the processes for modification of various nano-catalysts <sup>43-46</sup>. 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 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.



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Fig 1. Illustration of industries releasing VOCs in air, concentration obtained from <sup>47-57</sup>.

#### 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 <sup>58</sup>. The following uses TiO<sub>2</sub> as an example to analyze the electrons and holes generation process:

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

105 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. 106 (3) Recombine and release energy. However, the second and the third process do not promote the 107 photocatalytic reaction, and only the first process can drive reduction and oxidation <sup>59</sup>. Before 108 driving the redox reaction, the charge needs to undergo separation, thermalization, trapping, 109 recombination, and transport <sup>60</sup> (Fig. 2). Interfacial charge transfer may directly eliminate VOCs 110 through oxidation or generate hydroxyl radicals and superoxides <sup>61</sup>. The process can be depicted as 111 follows equations (2)-(8) <sup>62</sup>: 112

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- 119  $h^+(TiO_2) + H_2O \rightarrow TiO_2 + H^+OH^{\bullet}(2)$
- 120  $h^+(TiO_2) + OH^- \rightarrow TiO_2 + OH^{\bullet}$  (3)
- 121  $e^{-}(TiO_2) + O_2 \rightarrow TiO_2 + O_2^{\bullet-}$  (4)
- $\mathbf{0}_{2}^{\bullet-} + \mathbf{H}^{+} \to \mathbf{H}_{2}^{\bullet}$
- 123  $HO_2^{\bullet}+HO_2^{\bullet} \rightarrow H_2O_2+O_2 \qquad (6)$

124 
$$e^{-}(TiO_2) + H_2O_2 \rightarrow OH^- + OH^{\bullet}$$
(7)

- 125  $VOC + O_2 + OH^{\bullet} \rightarrow H_2O + CO_2 + other \ products \ (8)$
- 126 Current model is difficult to explain due to the complex charge transfer process. Understanding

(5)

127 the underlying mechanisms, will help us to find new photocatalysts for application in VOCs

128 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
 <sup>63-65</sup>.





Fig 3. Illustration of factors affecting the photocatalytic activity.

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>.

Leite et al. <sup>67</sup>claimed that the property of high crystallinity has advantages over disordered 142 polymers in photocatalytic applications. Pleskunov et al. <sup>68</sup>used a single-step plasma-based 143 technique to synthesize Ta<sub>3</sub>N<sub>y</sub>O<sub>x</sub> nanoparticles(NPs) with controllable crystallinity. In the visible 144 light range,  $Ta_3N_vO_x$  exhibits plasmonic and photoluminescent properties. Katsuki et al. <sup>69</sup> found that 145 α-Fe<sub>2</sub>O<sub>3</sub> NPs with high crystallinity are more efficient in PCO. A similar finding was also reported 146 147 by Li et al. <sup>70</sup>, they found that the nanorod-shaped photoactive COF containing benzothiadiazole and triazine with good crystallinity exhibited excellent comprehensive performance and good cycle 148 performance in the photocatalytic oxidation reaction. Curtis et al. <sup>71</sup>used the two-temperature 149 method to prepare mesoporous silicon NPs. The initial temperature of the reaction is 650°C and 150 lasted for 0.5h, and then in the second heating process at 100°C, 200°C and 300°C for 6h. They 151 found that the mesoporous silicon NPs prepared at 300°C have the best photocatalytic performance 152 153 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.

Besides crystallinity, crystal size also affects photocatalytic activity. Alonso-Tellez et al. <sup>74</sup> 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.

#### 160 3.1.2 Surface area

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

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Hajaghazadeh 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 results show that the lower surface area of PC50 and P25 makes the activity decrease over time. 166 However, PC500 has a high surface area, and its positive impact offsets the negative impact of 167 electron and holes on rapid recombination. This finding was also reported by Monteiro's group. 168 During the degradation of perchloroethylene by P25 and PC500, it was also noticed that the surface 169 170 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 may be because the Ag NPs are uniformly distributed and have a large specific surface area. Similar 172 173 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

In addition to the surface area, another structural feature pore volume of the photocatalyst also has a profound effect on the catalytic efficiency<sup>74</sup>. Chen et al.<sup>81</sup>designed Pt nanoclusters similar to 1.8 nm. The catalytic performance of C/Pt@TiO<sub>2</sub>-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 <sup>81</sup>.

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

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 <sup>82-86</sup>. MOFs are rich in organic contents, which makes them have superior inherent advantages in adsorbing aromatic VOCs <sup>87</sup>.

Xie et al. <sup>87</sup>designed and synthesized two MOFs, among which  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(BDB)_6]$ 190 (BUT-66) shows superior adsorption performance of benzene. Single-crystal structure analysis 191 192 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. <sup>88</sup> used lab-on-fiber technology 193 194 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. 195 This finding was also reported by Wang et al. <sup>89</sup>They found that the shape and size of the porous 196 197 Co<sub>3</sub>O<sub>4</sub> 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. <sup>90</sup> proposed a two-step method 198 199 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 capacity to capture VOC. 202

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

203 Table 1 Summary of different photocatalysts affect the photoactivity

#### 205 **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 <sup>94</sup>.

Singh et al. <sup>95</sup> used atomic layer deposition method coating TiO<sub>2</sub> on fibrous nanosilica (KCC-209 1). They observed that the KCC-1/TiO<sub>2</sub> catalyst coated with TiO<sub>2</sub> NPs has a more uniform coating, 210 a higher loading of TiO<sub>2</sub>, a smaller loss of surface area, and higher active site accessibility than 211 212 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 plasma band of Au NPs, the photocatalytic efficiency is greatly improved. Roldan et al. 97 researched 214 215 a new type of nanostructured coating system, which includes a layer of SiO<sub>2</sub> and a layer of dense anatase TiO<sub>2</sub> doped with Ag NPs. The photocatalytic activity has been improved All in all, 216 217 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. 218

#### 219 **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 <sup>62</sup>. In recent years, engineered carbon has been applied to catalyst support due to its high surface area, porous structure, high-performance adsorption of VOCs <sup>21</sup>. 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 <sup>22</sup>. Furthermore, the porous structure of activated

carbon is microporous (pore size < 2nm), which makes it difficult for molecules with larger 227 molecular diameters to enter the pores. Furthermore, due to the strong diffusion resistance due to 228 irregular pore structure, the adsorption equilibrium is prolonged due to the disordered pores 229 possessed by AC. Zhang et al. <sup>98</sup> prepared a new nano-β-FeOOH/Fe<sub>3</sub>O<sub>4</sub>/biochar composite material. 230 231 Through XPS characterization, it is proved that there are Fe-OC bonds between β-FeOOH and 232 biochar. These bonds facilitated the transfer of photo-generated electrons. The connection promotes the rapid interface transfer of light energy electrons between biochar and  $\beta$ -FeOOH. Zhang et al.<sup>99</sup> 233 prepared N-doped nano-TiO<sub>2</sub>-carbon fiber composite material. After TiO<sub>2</sub> NPs are irradiated by 234 235 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>. Saima et al.<sup>103</sup> used graphene oxide(GO) as the support material and randomly dispersed TiO<sub>2</sub> and 239 240 NiO NPS on it. The GO provides fast electronic conductivity and strong oxidation characteristics, 241 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.

245 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**

256 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 257 hydroxyl radicals, which is conducive to the adsorption of more hydrophilic VOCs molecules onto 258 259 the photocatalyst surface through hydrogen bonds. However, if the moisture content is too high, it 260 will compete with VOCs for the adsorption sites. For some pollutants, the presence of moisture can 261 promote mineralization of the pollutants, but excessive moisture will be adsorbed onto the active 262 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 263 molecules and VOCs; for example, doped TiO<sub>2</sub> has a higher catalytic efficiency than undoped TiO<sub>2</sub> 264 because the introduction of dopants resulting in more oxidant <sup>107-111</sup>. 265

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>.

#### 273 **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 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 <sup>117, 118</sup>. 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.

#### 289 3.2.3 Light irradiation

290 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 291 292 light is related to Eg and the energy of the band gap photon. If Eg 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 reflection and transmission is inevitable. Therefore, researchers have used modification methods 297 298 such as doping, use of compound semiconductor, and surface modification to use energy as much as possible 106, 120-122. 299

Factors	VOCs	Humidity	Temperatur	Airflow rate	Light	Inlet concentration	<b>Removal effificiency</b>	Ref.
			e					
Humidity	MEK	0% 20% 40% 60 + 1%	23 ± 1 °C	0.015 m <sup>3</sup> /min	UV	$2.65\pm0.3\ mg/m^3$	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 <sup>2</sup>	200ppm	40-50% 90-95%	125
	toluene	-	130°C 180°C	40,000mL/g h	-	-	18-20% 57-60%	126
Airflow rate	acetaldehyde	$20 \pm 1\%$	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 <sup>3</sup> /min	UV visible light	$2.65\pm0.3\ mg/m^3$	60-70% 40-50%	123
	1-propanol	10%	30 °C	320 mL/min	1.0 mW/cm <sup>2</sup> 2.0 mW/cm <sup>2</sup> 3.0 mW/cm <sup>2</sup>	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

Table 2 The key factors affecting VOC photocatalytic performances.

#### **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.



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

#### 311 4.1 Surface doping

312 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 313 by low-energy visible photons promote the visible light activity of the semiconductor <sup>129</sup>. By doping 314 with metal elements, Fang et al. <sup>130</sup> found that surface doping significantly improves the catalytic 315 efficiency of the catalyst for refractory benzene. However, the lattice defects caused by doping can 316 317 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 <sup>129, 131</sup>. In addition to a single doped metal or non-318 metal element, co-doping between metal ions, non-metal elements, or between metal ions and non-319 320 metal elements can also effectively extend the wavelength of the photocatalyst excitation light.

321 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).

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 summarized as follows: (1) Noble metals have anti-oxidation and corrosion resistance properties 329 even in humid air. Under the action of noble metal NPs, the recombination of carriers is reduced, 330 which increases the photoactivity on the surface of the photocatalyst. (2) The type and doping 331 amount of transition metals are two key factors that affect the PCO. If the doping amount is at the 332 333 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. (3) Rare earth metals have incomplete 4f and empty 5d orbitals, which can promote photocatalytic 335 336 reactions.

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

Transition metal doping can significantly extend visible light excitation, and more susceptible 346 to doping by other transition metals because of the lower energy required for the substitution process. 347 Thus, there has been extensive research on transition metal doping, such as manganese (Mn) <sup>140, 141</sup>, 348 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 349 350 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 silver, and improved the photocatalytic performance under visible light irradiation. Patrick et al. <sup>150</sup> 352 353 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 <sup>151</sup>incorporated V 354 355 into the TiO<sub>2</sub> crystal lattice to make  $Ti_{0.98}V_{0.02}O_2$ . Compared with pure TiO<sub>2</sub>, this catalyst embodies the quantum transition of benzene oxidation, highlighting the importance of V doping for benzene 356 357 oxidation. Stucchi et al. <sup>152</sup> used Mn to replace noble metals such as Au and Ag. Through experiments, it was found that TiO<sub>2</sub> doped with 20% Mn under visible light exposure for 24 h, the 358 degradation efficiency of ethanol reached 35%, which is the peak degradation efficiency. The 359 360 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. <sup>153</sup> prepared Co-doped 361 362 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 can be effectively reduced by introducing Co with abundant oxygen vacancies. Sajjad et al.<sup>154</sup> used 363 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 364 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>. 365

There are 17 kinds of lanthanides, collectively referred to as rare earth metals. Kumar et al. <sup>39</sup> 366 found that lanthanide ion dopants are beneficial to the optical properties of ZnO structure. 367 Parameters such as material properties and pollutant degradation reaction conditions have influence 368 on the performance of ZnO. Xiao et al. <sup>155</sup>found that Ce-doped TiO<sub>2</sub> shows the advantages of 369 370 stability and higher surface area. Notable, the adsorption capacity of VOCs is also greatly enhanced. The same result also appeared in other experiments. Wang et al. <sup>156</sup> synthesized Ce-doped MoS<sub>2</sub> 371 nanocomposite by hydrothermal method. Under visible light irradiation, it exhibits excellent 372 photocatalytic activity. 373

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.

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-

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>.

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#### 385 4.1.2 Non-metal doping

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>,
<sup>175</sup>and fluorine (F) <sup>176</sup> 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.

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

Contaminant	Photocatalyst	Dopant	Efficiency before	Efficiency after	Ref.
			doping	doping	
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	$Ti_{0.98}V_{0.02}O_2$	Au	9%	18%	151
Acetaldehyde	TiO <sub>2</sub>	F	77.3%	81%	177
Acetaldehyde	TiO <sub>2</sub>	Ν	77.3%	92.1%	177
Ethylbenzene	TiO <sub>2</sub>	Ν	33%	38%	178

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

#### 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 from a semiconductor with a higher CB energy level, and a photogenerated hole will migrate from 422 423 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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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-TiO2@NH2-	10%	85%	186
	UiO-66			
S-scheme	$Cu_2S/SnO_2$	17.9	67.2%	187

432 Table 4. Heterostructure and degradation efficiency of photocatalyst.

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 434 junction of the BiOI/TiO<sub>2</sub> nanotube array (Fig. 7A). They found the photo-electrocatalytic 435 degradation efficiency of BiOI/TiO2 was increased by 3 times. Guo et al. <sup>189</sup> successfully prepared 436 an Ag/Ag<sub>2</sub>O/PbBiO<sub>2</sub>Br photocatalyst with a broader spectral response through a series of plasma p-437 n heterojunctions. Researchers have observed significantly accelerated charge separation, and the 438 439 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. Due to charge induction, BiOI@Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub> forms a unique front-side coupling heterostructure. 441 442 Compared with the pure sample, the obtained BiOI@Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub> heterostructure can significantly enhance the catalytic performance and degradation of 2,4-Dichlorophenol. Anum et al.<sup>191</sup> studied a 443 444 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  $Al_2O_3$  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 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 450 nano-scale graphite carbon nitride nanosheets. The interface effect of charge carriers is separated 451 and transferred more effectively through solid p-n heterojunction. Yao et al.<sup>193</sup> prepared p-n 452 heterojunction of Bi2MoO6/BiOBr which can promote the photocatalysis. In addition the UV-vis 453 454 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 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 456 457 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  $Bi_2MoO_6$ (Fig. 7E). Another study concluded that the Z-type heterojunction is the main reason for improving the photocatalytic performance of 459 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 460 461 WO<sub>3</sub>/TiO<sub>2</sub> nanotube-composite film by doping oxygen vacancies into heterojunctions for photocatalytic degradation of exhaust gas. Ding et al.<sup>196</sup> synthesized a CoO@TiO2/MXene hybrid 462 with a double heterojunction structure. EPR measurements prove that  $SO_4^{-1}$ ,  $O_2^{-1}$  and  $^1O_2$  are the 463 464 main reactive species involved in the photocatalytic degradation of phenol (Fig. 8).



466 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 467 permission from ref.<sup>188</sup>. Copyright 2011, American Chemical Society. (B) Photocatalytic 468 degradation of tetracycline with obtained samples under NIR light ( $\lambda$ >800nm). Adapted with 469 permission from ref.<sup>189</sup>. Copyright 2019, Elsevier. (C) FTIR spectra of various samples; (a) 470 pure GO (b) pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (c) 10.0% GO/Al<sub>2</sub>O<sub>3</sub> composite. Adapted with permission from 471 ref.<sup>191</sup>. Copyright 2018, American Chemical Society. (D) UV-vis diffuse reflectance spectra 472 (DRS). Adapted with permission from ref.<sup>193</sup>. Copyright 2021, Elsevier. (E) (d) XPS survey 473 spectra and high resolution XPS spectra of (e) Bi 4f, (f) Br 3d, (g) O 1 s of BiOBr and 474 BMOBB-2. Adapted with permission from ref.<sup>193</sup>. Copyright 2021, Elsevier. 475



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477 Fig 8. EPR spectra of 10%CTM/PMS/Vis system for (a) 5,5-Dimethyl-1-pyrroline N-oxide 478 (DMPO)-  $\cdot$ OH and DMPO- SO<sub>4</sub>-, (b) DMPO- O<sub>2</sub>- and (c) TEMP- <sup>1</sup>O<sub>2</sub>. Adapted with 479 permission from ref.<sup>196</sup>. Copyright 2021, Elsevier.

480 **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. <sup>197</sup> found that  $WSe_2/g-C_3N_4$  prepared with  $WSe_2$  as a co-catalyst both promotes 486 light absorption and improves charge transfer efficiency. Peng et al. <sup>161</sup> by comparing the amount of 487 co-catalyst, found that the Cr<sub>x</sub>O co-catalyst (3wt%) is beneficial to improve the removal efficiency 488 of acetaldehyde. Shen et al. <sup>198</sup> used the organic molecule oxamide (OA) as a co-catalyst to prepare 489 490 modified TiO<sub>2</sub> samples through wet chemical methods to enhance electron-hole separation and 491 photocatalytic H-2 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 following characteristics: (1) No noble metals; (2) High charge transport mobility; (3) Many active 492 493 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>.

Liang et al. <sup>201</sup> prepared a high proportion of active (002) crystal planes (>90%) and high 499 specific surface area ultra-thin WO<sub>3</sub> nanosheets, which improved the performance of the catalyst to 500 degrade pollutants. Yu et al. <sup>202</sup> synthesized TiO<sub>2</sub> nanosheets. The exposed (001) crystal facets are 501 502 beneficial for the reduction of NO<sub>x</sub>. The NO conversion rate of the hydrothermal method prepared 503  $TiO_2$  sheets is higher than the conversion rate of commercial P25 and TiO<sub>2</sub> particles synthesized by 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 504 505 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 from VOCs. They come from a wide range of sources and can cause diseases and even 512 513 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 it operates at room-temperature, produce no secondary pollution, and have high removal activity. 516 517 Furthermore, the photocatalytic efficiency has been greatly improved by surface modification of the 518 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 524 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 525 morphology of the catalyst affects the adsorption of VOCs, and the high surface area and porous 526 structure are conducive to the adsorption of VOCs. (3) Temperature and humidity will seriously 527 affect the adsorption of VOC. Low temperature is conducive to adsorption processes dominated by 528 529 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 concentrations of pollutants. (2) The performance of the photocatalyst is affected by internal and 531 532 external factors. (3) The lattice defects caused by doping can reduce the catalytic activity. Therefore, 533 there is often an optimal amount of doping.

Based on our current knowledge about the limitations of PCO technology in removing VOCs, 534 535 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 536 resistance to deactivation. (2) Explore more stable and more efficient photocatalyst materials, 537 combining different strategies such as facets, heterojunctions and co-catalysts. (3) Photocatalysts 538 539 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 mechanism, efficient structures and production methods. (5) Increase the rate of adsorption and 541 542 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.



Fig 9. Prospects for future research.

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- 551 Zhao, Muhammad Arslan Ahmad, Noman Shakoor, Benzhen Lou, Yaqi Jiang, Iseult Lynch: Writing
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#### 553 Declaration of Competing Interest

- 554 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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#### 561 References

- 5621.P. Amoatey, H. Omidvarborna, M. S. Baawain and A. Al-Mamun, Emissions and exposure563assessments of SOX, NOX, PM10/2.5 and trace metals from oil industries: A review study (2000-5642018), Process Saf. Environ. Protect., 2019, **123**, 215-228.
- 5652.B. B. Huang, C. Lei, C. H. Wei and G. M. Zeng, Chlorinated volatile organic compounds (Cl-VOCs)566in environment sources, potential human health impacts, and current remediation567technologies, Environ. Int., 2014, **71**, 118-138.
- S. B. Ge, N. L. Ma, S. C. Jiang, Y. S. Ok, S. S. Lam, C. Li, S. Q. Shi, X. Nie, Y. Qiu, D. L. Li, Q. D. Wu,
   D. C. W. Tsang, W. X. Peng and C. Sonne, Processed Bamboo as a Novel Formaldehyde-Free
   High-Performance Furniture Biocomposite, *ACS Appl. Mater. Interfaces*, 2020, **12**, 30824-30832.
- 4. H. K. Yuan, J. Ren, X. H. Ma and Z. L. Xu, Dehydration of ethyl acetate aqueous solution by
  pervaporation using PVA/PAN hollow fiber composite membrane, *Desalination*, 2011, 280,
  252-258.
- P. I. Beamer, C. E. Luik, L. Abrell, S. Campos, M. E. Martinez and A. E. Saez, Concentration of Trichloroethylene in Breast Milk and Household Water from Nogales, Arizona, *Environ. Sci. Technol.*, 2012, **46**, 9055-9061.
- 6. R. Baran, Kaminska, II, A. Srebowata and S. Dzwigaj, Selective hydrodechlorination of 1,2dichloroethane on NiSiBEA zeolite catalyst: Influence of the preparation procedure on a high
  dispersion of Ni centers, *Microporous Mesoporous Mat.*, 2013, **169**, 120-127.
- 5807.Y. C. Chien, Variations in amounts and potential sources of volatile organic chemicals in new581cars, *Sci. Total Environ.*, 2007, **382**, 228-239.
- 5828.M. R. Gwinn, D. O. Johns, T. F. Bateson and K. Z. Guyton, A review of the genotoxicity of 1,2-583dichloroethane (EDC), Mutation Research-Reviews in Mutation Research, 2011, 727, 42-53.
- 9. B. C. McDonald, J. A. de Gouw, J. B. Gilman, S. H. Jathar, A. Akherati, C. D. Cappa, J. L. Jimenez,
  J. Lee-Taylor, P. L. Hayes, S. A. McKeen, Y. Y. Cui, S.-W. Kim, D. R. Gentner, G. Isaacman-VanWertz,
  A. H. Goldstein, R. A. Harley, G. J. Frost, J. M. Roberts, T. B. Ryerson and M. Trainer, Volatile
  chemical products emerging as largest petrochemical source of urban organic emissions, *Science*, 2018, **359**, 760-764.
- Z. M. Zhong, Q. E. Sha, J. Y. Zheng, Z. B. Yuan, Z. J. Gao, J. M. Ou, Z. Y. Zheng, C. Li and Z. J. Huang,
   Sector-based VOCs emission factors and source profiles for the surface coating industry in the
   Pearl River Delta region of China, *Sci. Total Environ.*, 2017, **583**, 19-28.
- J. L. Jiang, X. S. Ding, A. Tasoglou, H. Huber, A. D. Shah, N. Jung and B. E. Boor, Real-Time
   Measurements of Botanical Disinfectant Emissions, Transformations, and Multiphase
   Inhalation Exposures in Buildings, *Environ. Sci. Technol. Lett.*, 2021, **8**, 558-566.
- 595 12. X. H. Zhang, Q. L. Liu, Y. Xiong, A. M. Zhu, Y. Chen and Q. G. Zhang, Pervaporation dehydration
  596 of ethyl acetate/ethanol/water azeotrope using chitosan/poly (vinyl pyrrolidone) blend
  597 membranes, J. Membr. Sci., 2009, **327**, 274-280.

- 59813.R. J. Keith, J. L. Fetterman, O. A. Orimoloye, Z. Dardari, P. K. Lorkiewicz, N. M. Hamburg, A. P.599DeFilippis, M. J. Blaha and A. Bhatnagar, Characterization of Volatile Organic Compound600Metabolites in Cigarette Smokers, Electronic Nicotine Device Users, Dual Users, and Nonusers601of Tobacco, Nicotine Tob. Res., 2020, **22**, 264-272.
- 60214.Z. Zhang, Z. Jiang and W. Shangguan, Low-temperature catalysis for VOCs removal in603technology and application: A state-of-the-art review, Catalysis Today, 2016, 264, 270-278.
- 60415.C. He, J. Cheng, X. Zhang, M. Douthwaite, S. Pattisson and Z. Hao, Recent Advances in the605Catalytic Oxidation of Volatile Organic Compounds: A Review Based on Pollutant Sorts and606Sources, Chem. Rev., 2019, **119**, 4471-4568.
- 60716.U. Poschl and M. Shiraiwa, Multiphase Chemistry at the Atmosphere-Biosphere Interface608Influencing Climate and Public Health in the Anthropocene, Chem. Rev., 2015, **115**, 4440-4475.
- 609 17. C. P. Weisel, Assessing exposure to air toxics relative to asthma, *Environmental Health* 610 *Perspectives*, 2002, **110**, 527-537.
- 5. Weichenthal, R. Kulka, P. Belisle, L. Joseph, A. Dubeau, C. Martin, D. Wang and R. Dales,
  Personal exposure to specific volatile organic compounds and acute changes in lung function
  and heart rate variability among urban cyclists, *Environ. Res.*, 2012, **118**, 118-123.
- 614 19. R. Xiao, J. Mo, Y. Zhang and D. Gao, An in-situ thermally regenerated air purifier for indoor 615 formaldehyde removal, *Indoor Air*, 2018, **28**, 266-275.
- 61620.K. Rumchev, J. Spickett, M. Bulsara, M. Phillips and S. Stick, Association of domestic exposure617to volatile organic compounds with asthma in young children, *Thorax*, 2004, **59**, 746-751.
- K. Zhang, B. Gao, A. E. Creamer, C. Cao and Y. Li, Adsorption of VOCs onto engineered carbon
  materials: A review, *Journal of Hazardous Materials*, 2017, **338**, 102-123.
- W. X. Zou, B. Gao, Y. S. Ok and L. Dong, Integrated adsorption and photocatalytic degradation
  of volatile organic compounds (VOCs) using carbon-based nanocomposites: A critical review, *Chemosphere*, 2019, **218**, 845-859.
- 623 23. U. I. Gaya and A. H. Abdullah, Heterogeneous photocatalytic degradation of organic
  624 contaminants over titanium dioxide: A review of fundamentals, progress and problems, J.
  625 Photochem. Photobiol. C-Photochem. Rev., 2008, 9, 1-12.
- 626 24. M. Tahir, S. Tasleem and B. Tahir, Recent development in band engineering of binary
  627 semiconductor materials for solar driven photocatalytic hydrogen production, *Int. J. Hydrog.*628 *Energy*, 2020, **45**, 15985-16038.
- T. K. Tseng, Y. S. Lin, Y. J. Chen and H. Chu, A Review of Photocatalysts Prepared by Sol-Gel
  Method for VOCs Removal, *Int. J. Mol. Sci.*, 2010, **11**, 2336-2361.
- 631 26. M. Adeel, N. Shakoor, T. Hussain, I. Azeem, P. F. Zhou, P. Zhang, Y. Hao, J. Rinklebe and Y. K. Rui,
  632 Bio-interaction of nano and bulk lanthanum and ytterbium oxides in soil system: Biochemical,
  633 genetic, and histopathological effects on Eisenia fetida, *Journal of Hazardous Materials*, 2021,
  634 415.
- R. K. Huang, C. Y. Cao, J. Liu, L. R. Zheng, Q. H. Zhang, L. Gu, L. Jiang and W. G. Song, Integration
  of Metal Single Atoms on Hierarchical Porous Nitrogen-Doped Carbon for Highly Efficient
  Hydrogenation of Large-Sized Molecules in the Pharmaceutical Industry, *ACS Appl. Mater. Interfaces*, 2020, **12**, 17651-17658.
- K. L. Zhao, Y. L. Song, W. G. Song, W. Liang, X. Y. Jiang, Z. Y. Tang, H. X. Xu, Z. X. Wei, Y. Q. Liu, M.
  H. Liu, L. Jiang, X. H. Bao, L. J. Wan and C. L. Bai, Progress of nanoscience in China, *Frontiers of Physics*, 2014, **9**, 257-288.
- M. M. Rui, C. X. Ma, J. C. White, Y. Hao, Y. Y. Wang, X. L. Tang, J. Yang, F. P. Jiang, A. Ali, Y. K. Rui,
  W. D. Cao, G. C. Chen and B. S. Xing, Metal oxide nanoparticles alter peanut (Arachis hypogaea
  bysiological response and reduce nutritional quality: a life cycle study, *Environ. Sci.-Nano*,
  2018, **5**, 2088-2102.
- 646 30. C. Santhosh, V. Velmurugan, G. Jacob, S. K. Jeong, A. N. Grace and A. Bhatnagar, Role of
  647 nanomaterials in water treatment applications: A review, *Chemical Engineering Journal*, 2016,
  648 **306**, 1116-1137.
- 549 31. D. S. Selishchev, T. N. Filippov, M. N. Lyulyukin and D. V. Kozlov, Uranyl-modified TiO2 for
  550 complete photocatalytic oxidation of volatile organic compounds under UV and visible light,
  651 *Chemical Engineering Journal*, 2019, **370**, 1440-1449.
- 65232.X. Liu, J. locozzia, Y. Wang, X. Cui, Y. Chen, S. Zhao, Z. Li and Z. Lin, Noble metal-metal oxide653nanohybrids with tailored nanostructures for efficient solar energy conversion, photocatalysis654and environmental remediation, *Energy & Environmental Science*, 2017, **10**, 402-434.

- G55 33. Q. K. Shen, C. Y. Cao, R. K. Huang, L. Zhu, X. Zhou, Q. H. Zhang, L. Gu and W. G. Song, Single
  G56 Chromium Atoms Supported on Titanium Dioxide Nanoparticles for Synergic Catalytic Methane
  G57 Conversion under Mild Conditions, *Angew. Chem.-Int. Edit.*, 2020, 59, 1216-1219.
- A. Suligoj, U. L. Stanger, A. Ristic, M. Mazaj, D. Verhovsek and N. N. Tusar, TiO2-SiO2 films from
  organic-free colloidal TiO2 anatase nanoparticles as photocatalyst for removal of volatile
  organic compounds from indoor air, *Applied Catalysis B-Environmental*, 2016, **184**, 119-131.
- S. Suarez, I. Jansson, B. Ohtani and B. Sanchez, From titania nanoparticles to decahedral
  anatase particles: Photocatalytic activity of TiO2/zeolite hybrids for VOCs oxidation, *Catalysis Today*, 2019, **326**, 2-7.
- 664 36. C. Karthikeyan, P. Arunachalam, K. Ramachandran, A. M. Al-Mayouf and S. Karuppuchamy,
  665 Recent advances in semiconductor metal oxides with enhanced methods for solar
  666 photocatalytic applications, *J. Alloy. Compd.*, 2020, **828**, 15.
- 37. Z. Shayegan, C. S. Lee and F. Haghighat, TiO2 photocatalyst for removal of volatile organic
  compounds in gas phase A review, *Chemical Engineering Journal*, 2018, **334**, 2408-2439.
- 38. Z. J. Zhu, Q. Zhang, X. Xiao, F. Q. Sun, X. X. Zuo and J. M. Nan, Dual-iodine-doped BiOIO3: Bulk
  and surface co-modification for enhanced visible-light photocatalytic removal of bisphenol AF,
  671 *Chemical Engineering Journal*, 2021, **404**, 13.
- S. G. Kumar and R. Kavitha, Lanthanide ions doped ZnO based photocatalysts, *Sep. Purif. Technol.*, 2021, **274**, 33.
- 67440.K. Li, S. Zhang, Y. Li, J. Fan and K. Lv, MXenes as noble-metal-alternative co-catalysts in675photocatalysis, Chinese Journal of Catalysis, 2021, 42, 3-14.
- M. Malakootian, A. Nasiri and M. A. Gharaghani, Photocatalytic degradation of ciprofloxacin
  antibiotic by TiO2 nanoparticles immobilized on a glass plate, *Chemical Engineering Communications*, 2020, **207**, 56-72.
- H. Zangeneh, A. A. L. Zinatizadeh, M. Habibi, M. Akia and M. H. Isa, Photocatalytic oxidation of
  organic dyes and pollutants in wastewater using different modified titanium dioxides: A
  comparative review, J. Ind. Eng. Chem., 2015, 26, 1-36.
- 43. Q. Guo, C. Y. Zhou, Z. B. Ma and X. M. Yang, Fundamentals of TiO2 Photocatalysis: Concepts,
  Mechanisms, and Challenges, *Adv. Mater.*, 2019, **31**, 26.
- 44. H. Yi, L. Qin, D. L. Huang, G. M. Zeng, C. Lai, X. G. Liu, B. S. Li, H. Wang, C. Y. Zhou, F. L. Huang,
  S. Y. Liu and X. Y. Guo, Nano-structured bismuth tungstate with controlled morphology:
  Fabrication, modification, environmental application and mechanism insight, *Chemical Engineering Journal*, 2019, **358**, 480-496.
- 68845.C. P. Xu, P. R. Anusuyadevi, C. Aymonier, R. Luque and S. Marre, Nanostructured materials for689photocatalysis, Chem. Soc. Rev., 2019, 48, 3868-3902.
- 46. B. S. Li, C. Lai, G. M. Zeng, D. L. Huang, L. Qin, M. M. Zhang, M. Cheng, X. G. Liu, H. Yi, C. Y. Zhou,
  F. L. Huang, S. Y. Liu and Y. K. Fu, Black Phosphorus, a Rising Star 2D Nanomaterial in the PostGraphene Era: Synthesis, Properties, Modifications, and Photocatalysis Applications, *Small*,
  2019, **15**.
- 694 47. G. Liu, W. Xi, X. You, Y. Zhi, C. Li and Iop, Sanya, PEOPLES R CHINA, 2018.
- 69548.U. B. Celebi and N. Vardar, Investigation of VOC emissions from indoor and outdoor painting696processes in shipyards, Atmospheric Environment, 2008, 42, 5685-5695.
- H. Wang, L. Nie, J. Li, Y. Wang, G. Wang, J. Wang and Z. Hao, Characterization and assessment
  of volatile organic compounds (VOCs) emissions from typical industries, *Chinese Science Bulletin*, 2013, **58**, 724-730.
- K. Yang, C. Wang, S. Xue, W. Li, J. Liu and L. Li, The identification, health risks and olfactory
   effects assessment of VOCs released from the wastewater storage tank in a pesticide plant,
   *Ecotoxicology and Environmental Safety*, 2019, **184**.
- 51. S. M. T. Sendesi, Y. Noh, M. Nuruddin, B. E. Boor, J. A. Howarter, J. P. Youngblood, C. T. Jafvert
  and A. J. Whelton, An emerging mobile air pollution source: outdoor plastic liner
  manufacturing sites discharge VOCs into urban and rural areas, *Environmental Science- Processes & Impacts*, 2020, 22, 1828-1841.
- Y. Liu, F. Han, W. Liu, X. Cui, X. Luan and Z. Cui, Process-based volatile organic compound emission inventory establishment method for the petroleum refining industry, *J. Clean Prod.*, 2020, 263.
- 71053.X. Zhang, D. Wang, Y. Liu, Y. Cui, Z. Xue, Z. Gao and J. Du, Characteristics and ozone formation711potential of volatile organic compounds in emissions from a typical Chinese coking plant,

- 712 *Journal of Environmental Sciences*, 2020, **95**, 183-189.
- 54. Q. Li, G. Su, C. Li, M. Wang, L. Tan, L. Gao, M. Wu and Q. Wang, Emission profiles, ozone
  formation potential and health-risk assessment of volatile organic compounds in rubber
  footwear industries in China, *Journal of Hazardous Materials*, 2019, **375**, 52-60.
- 55. C. T. Chang and K. L. Lin, Assessment of the strategies for reducing VOCs emission from polyurea-formaldehyde resin synthetic fiber leather industry in Taiwan, *Resources Conservation and Recycling*, 2006, 46, 321-334.
- 56. N. Cheng, D. Jing, C. Zhang, Z. Chen, W. Li, S. Li and Q. Wang, Process-based VOCs source
  profiles and contributions to ozone formation and carcinogenic risk in a typical chemical
  synthesis pharmaceutical industry in China, *Sci. Total Environ.*, 2021, **752**.
- Final Strain Stra
- 72558.H. H. Chen, C. E. Nanayakkara and V. H. Grassian, Titanium Dioxide Photocatalysis in726Atmospheric Chemistry, *Chem. Rev.*, 2012, **112**, 5919-5948.
- 727 59. Q. Guo, C. Zhou, Z. Ma, Z. Ren, H. Fan and X. Yang, Elementary photocatalytic chemistry on
  728 TiO2 surfaces, *Chem. Soc. Rev.*, 2016, **45**, 3701-3730.
- M. A. Henderson, A surface science perspective on TiO2 photocatalysis, *Surf. Sci. Rep.*, 2011,
  66, 185-297.
- 5. H. Zhan, Y. Yang, X. C. Gao, H. B. Yu, S. S. Yang, D. D. Zhu and Y. Li, Rapid degradation of toxic toluene using novel mesoporous SiO2 doped TiO2 nanofibers, *Catalysis Today*, 2014, **225**, 10-17.
- A. H. Mamaghani, F. Haghighat and C. S. Lee, Photocatalytic oxidation technology for indoor
  environment air purification: The state-of-the-art, *Applied Catalysis B-Environmental*, 2017,
  203, 247-269.
- A. Bazyari, A. A. Khodadadi, A. H. Mamaghani, J. Beheshtian, L. T. Thompson and Y. Mortazavi,
  Microporous titania-silica nanocomposite catalyst-adsorbent for ultra-deep oxidative
  desulfurization, *Applied Catalysis B-Environmental*, 2016, **180**, 65-77.
- V. Puddu, H. Choi, D. D. Dionysiou and G. L. Puma, TiO2 photocatalyst for indoor air remediation:
  Influence of crystallinity, crystal phase, and UV radiation intensity on trichloroethylene
  degradation, *Applied Catalysis B-Environmental*, 2010, **94**, 211-218.
- 74365.Z. Long, Q. Li, T. Wei, G. Zhang and Z. Ren, Historical development and prospects of744photocatalysts for pollutant removal in water, *Journal of Hazardous Materials*, 2020, **395**.
- S. Wang, Q. Sun, W. Chen, Y. Q. Tang, B. Aguila, Y. X. Pan, A. M. Zheng, Z. Y. Yang, L. Wojtas, S.
  Q. Ma and F. S. Xiao, Programming Covalent Organic Frameworks for Photocatalysis: Investigation of Chemical and Structural Variations, *Matter*, 2020, 2, 416-427.
- R. O. Da Silva, R. H. Goncalves, D. G. Stroppa, A. J. Ramirez and E. R. Leite, Synthesis of recrystallized anatase TiO2 mesocrystals with Wulff shape assisted by oriented attachment, *Nanoscale*, 2011, **3**, 1910-1916.
- 68. P. Pleskunov, T. Kosutova, M. Vaidulych, D. Nikitin, Z. Krtous, S. Ali-Ogly, K. Kishenina, R.
  752 Tafiichuk, H. Biederman, I. Gordeev, J. Drewes, I. Barg, F. Faupel, M. Cieslar, R. Yatskiv, Y. Pihosh,
  753 V. Nandal, K. Seki, K. Domen and A. Choukourov, The sputter-based synthesis of tantalum
  754 oxynitride nanoparticles with architecture and bandgap controlled by design, *Appl. Surf. Sci.*,
  755 2021, 559.
- 756 69. T. Katsuki, Z. N. Zahran, K. Tanaka, T. Eo, E. A. Mohamed, Y. Tsubonouchi, M. R. Berber and M.
  757 Yagi, Facile Fabrication of a Highly Crystalline and Well-Interconnected Hematite Nanoparticle
  758 Photoanode for Efficient Visible-Light-Driven Water Oxidation, ACS Appl. Mater. Interfaces,
  759 2021, 13, 39282-39290.
- 760
  70. Q. Li, J. Wang, Y. Z. Zhang, L. Ricardez-Sandoval, G. Y. Bai and X. W. Lan, Structural and
  761 Morphological Engineering of Benzothiadiazole-Based Covalent Organic Frameworks for
  762 Visible Light-Driven Oxidative Coupling of Amines, ACS Appl. Mater. Interfaces, 2021, 13,
  763 39291-39303.
- 764 71. I. S. Curtis, R. J. Wills and M. Dasog, Photocatalytic hydrogen generation using mesoporous
  765 silicon nanoparticles: influence of magnesiothermic reduction conditions and nanoparticle
  766 aging on the catalytic activity, *Nanoscale*, 2021, **13**, 2685-2692.
- 767 72. Q. L. Li, T. Song, Y. P. Zhang, Q. Wang and Y. Yang, Boosting Photocatalytic Activity and Stability
   768 of Lead-Free Cs3Bi2Br9 Perovskite Nanocrystals via In Situ Growth on Monolayer 2D Ti3C2Tx

- 769 MXene for C-H Bond Oxidation, ACS Appl. Mater. Interfaces, 2021, **13**, 27323-27333.
- 770 73. Y. H. Zhang, G. D. Shen, C. H. Sheng, F. Zhang and W. Fan, The effect of piezo-photocatalysis on
  771 enhancing the charge carrier separation in BaTiO3/KNbO3 heterostructure photocatalyst, *Appl.*772 Surf. Sci., 2021, 562, 12.
- 773 74. A. Alonso-Tellez, R. Masson, D. Robert, N. Keller and V. Keller, Comparison of Hombikat UV100
  774 and P25 TiO2 performance in gas-phase photocatalytic oxidation reactions, *Journal of*775 *Photochemistry and Photobiology a-Chemistry*, 2012, **250**, 58-65.
- 776 75. K. Nakata and A. Fujishima, TiO2 photocatalysis: Design and applications, *J. Photochem.*777 *Photobiol. C-Photochem. Rev.*, 2012, **13**, 169-189.
- 778 76. M. Xiao, Z. L. Wang, M. Q. Lyu, B. Luo, S. C. Wang, G. Liu, H. M. Cheng and L. Z. Wang, Hollow
  779 Nanostructures for Photocatalysis: Advantages and Challenges, *Adv. Mater.*, 2019, **31**, 23.
- 780
  77. M. Hajaghazadeh, V. Vaiano, D. Sannino, H. Kakooei, R. Sotudeh-Gharebagh and P. Ciambelli,
  781 Heterogeneous photocatalytic oxidation of methyl ethyl ketone under UV-A light in an LED782 fluidized bed reactor, *Catalysis Today*, 2014, **230**, 79-84.
- 78. J. Taranto, D. Frochot and P. Pichat, Photocatalytic Treatment of Air: Comparison of Various
  784 TiO2, Coating Methods, and Supports Using Methanol or n-Octane as Test Pollutant, *Industrial*785 & Engineering Chemistry Research, 2009, 48, 6229-6236.
- 786
  79. Y. T. Liu, Q. P. Zhang, M. Xu, H. Yuan, Y. Chen, J. X. Zhang, K. Y. Luo, J. Q. Zhang and B. A. You,
  787 Novel and efficient synthesis of Ag-ZnO nanoparticles for the sunlight-induced photocatalytic
  788 degradation, *Appl. Surf. Sci.*, 2019, **476**, 632-640.
- 789 80. M. Rajca, NOM (HA and FA) Reduction in Water Using Nano Titanium Dioxide Photocatalysts
  790 (P25 and P90) and Membranes, *Catalysts*, 2020, **10**, 13.
- N. Chen, Q. N. Gong, F. Wang, J. Ren, R. X. Wang and W. Z. Jiao, N-doped porous carbonstabilized Pt in hollow nano-TiO2 with enhanced photocatalytic activity, *Int. J. Hydrog. Energy*,
  2020, **45**, 24779-24791.
- W.-H. Li, K. Ding, H.-R. Tian, M.-S. Yao, B. Nath, W.-H. Deng, Y. Wang and G. Xu, Conductive
  Metal-Organic Framework Nanowire Array Electrodes for High-Performance Solid-State
  Supercapacitors, Advanced Functional Materials, 2017, 27.
- 797 83. S. Wang, C. M. McGuirk, A. d'Aquino, J. A. Mason and C. A. Mirkin, Metal-Organic Framework
  798 Nanoparticles, *Adv. Mater.*, 2018, **30**.
- 79984.Y. Zhang, X. Feng, S. Yuan, J. Zhou and B. Wang, Challenges and recent advances in MOF-800polymer composite membranes for gas separation, *Inorg. Chem. Front.*, 2016, **3**, 896-909.
- 85. Y. B. Dou, J. Zhou, A. Zhou, J. R. Li and Z. R. Nie, Visible-light responsive MOF encapsulation of
  noble-metal-sensitized semiconductors for high-performance photoelectrochemical water
  splitting, *J. Mater. Chem. A*, 2017, **5**, 19491-19498.
- 804 86. W. L. Xue, L. Wang, Y. K. Li, H. Chen, K. X. Fu, F. Zhang, T. He, Y. H. Deng, J. R. Li and C. Q. Wan,
  805 Reticular Chemistry for Ionic Liquid-Functionalized Metal-Organic Frameworks with High
  806 Selectivity for CO2, Acs Sustainable Chemistry & Engineering, 2020, 8, 18558-18567.
- 807 87. L.-H. Xie, X.-M. Liu, T. He and J.-R. Li, Metal-Organic Frameworks for the Capture of Trace
  808 Aromatic Volatile Organic Compounds, *Chem*, 2018, 4, 1911-1927.
- 809
  88. J. Y. Wu, C. L. Tang, W. Y. Zhang, X. X. Ma, S. W. Qu, K. X. Chen, T. Hao and S. Chiang, Lab on optical fiber: surface nano-functionalization for real-time monitoring of VOC adsorption/desorption in metal-organic frameworks, *Nanophotonics*, 2021, **10**, 2705-2716.
- 89. M. J. Wang, Z. R. Shen, X. D. Zhao, F. P. Duanmu, H. J. Yu and H. M. Ji, Rational shape control of
  porous Co3O4 assemblies derived from MOF and their structural effects on n-butanol sensing,
  Journal of Hazardous Materials, 2019, **371**, 352-361.
- 90. Q. Yu, R. R. Jin, L. P. Zhao, T. S. Wang, F. M. Liu, X. Yan, C. G. Wang, P. Sun and G. Y. Lu, MOFB16 Derived Mesoporous and Hierarchical Hollow-Structured In2O3-NiO Composites for Enhanced
  817 Triethylamine Sensing, *Acs Sensors*, 2021, **6**, 3451-3461.
- 81891.D. A. Giannakoudakis, A. Qayyum, D. Lomot, M. O. Besenhard, D. Lisovytskiy, T. J. Bandosz and819J. C. Colmenares, Boosting the Photoactivity of Grafted Titania: Ultrasound-Driven Synthesis of820a Multi-Phase Heterogeneous Nano-Architected Photocatalyst, Advanced Functional Materials,8212021, **31**.
- B22 92. H. Wei, W. A. McMaster, J. Z. Y. Tan, D. H. Chen and R. A. Caruso, Tricomponent brookite/anatase TiO2/g-C3N4 heterojunction in mesoporous hollow microspheres for enhanced visible-light photocatalysis, *J. Mater. Chem. A*, 2018, **6**, 7236-7245.
- 93. M. Q. Hu, Y. Cao, Z. Z. Li, S. L. Yang and Z. P. Xing, Ti3+ self-doped mesoporous black TiO2/SiO2

826 nanocomposite as remarkable visible light photocatalyst, Appl. Surf. Sci., 2017, 426, 734-744. 827 94. N. Quici, M. L. Vera, H. Choi, G. L. Puma, D. D. Dionysiou, M. I. Litter and H. Destaillats, Effect of 828 key parameters on the photocatalytic oxidation of toluene at low concentrations in air under 829 254+185 nm UV irradiation, Applied Catalysis B-Environmental, 2010, 95, 312-319. 830 95. R. Singh, R. Bapat, L. J. Qin, H. Feng and V. Polshettiwar, Atomic Layer Deposited (ALD) TiO2 on 831 Fibrous Nano-Silica (KCC-1) for Photocatalysis: Nanoparticle Formation and Size Quantization 832 Effect, Acs Catalysis, 2016, 6, 2770-2784. 833 96. X. N. Wang, R. Long, D. Liu, D. Yang, C. M. Wang and Y. J. Xiong, Enhanced full-spectrum water 834 splitting by confining plasmonic Au nanoparticles in N-doped TiO2 bowl nanoarrays, Nano 835 Energy, 2016, 24, 87-93. 836 97. M. V. Roldan, P. de Ona, Y. Castro, A. Duran, P. Faccendini, C. Lagier, R. Grau and N. S. Pellegri, 837 Photocatalytic and biocidal activities of novel coating systems of mesoporous and dense TiO2-838 anatase containing silver nanoparticles, Materials Science & Engineering C-Materials for 839 *Biological Applications*, 2014, **43**, 630-640. 840 98. Z. Zhang, G. H. Wang, W. B. Li, L. D. Zhang, B. W. Guo, L. Ding and X. C. Li, Photocatalytic Activity 841 of Magnetic Nano-beta-FeOOH/Fe3O4/Biochar Composites for the Enhanced Degradation of 842 Methyl Orange Under Visible Light, Nanomaterials, 2021, 11. 843 99. J. J. Zhang, Y. X. Li, L. Li, W. L. Li and C. F. Yang, Dual Functional N-Doped TiO2-Carbon Composite 844 Fibers for Efficient Removal of Water Pollutants, Acs Sustainable Chemistry & Engineering, 2018, 845 **6**, 12893-12905. 846 100. S. Shamaila, A. K. L. Sajjad, A. Quart ul, S. Shaheen, A. Iqbal, S. Noor, G. Sughra and U. Ali, A 847 cost effective and eco-friendly green route for fabrication of efficient graphene nanosheets 848 photocatalyst, J. Environ. Chem. Eng., 2017, 5, 5770-5776. 849 101. S. Noor, S. Sajjad, S. A. K. Leghari, C. Flox, T. Kallio, E. I. Kauppinen and S. Ahmad, Electronic 850 transitions of SWCNTs in comparison to GO on Mn3O4/TiO2 nanocomposites for hydrogen 851 energy generation and solar photocatalysis, New Journal of Chemistry, 2021, 45, 2431-2442. 852 102. Z. Yousaf, S. Sajjad, S. A. K. Leghari, M. Mehboob, A. Kanwal and B. Uzair, Interfacial charge 853 transfer via 2D-NiO and 2D-graphene nanosheets combination for significant visible 854 photocatalysis, Journal of Solid State Chemistry, 2020, 291. 855 103. S. Noor, S. Sajjad, S. A. K. Leghari and M. C. Long, Energy harvesting for electrochemical OER 856 and solar photocatalysis via dual functional GO/TiO2-NiO nanocomposite, J. Clean Prod., 2020, 857 277. 858 104. F. Fresno, M. D. Hernandez-Alonso, D. Tudela, J. M. Coronado and J. Soria, Photocatalytic 859 degradation of toluene over doped and coupled (Ti,M)O-2 (M = Sn or Zr) nanocrystalline oxides: 860 Influence of the heteroatom distribution on deactivation, Applied Catalysis B-Environmental, 861 2008, **84**, 598-606. 862 105. M. Takeuchi, J. Deguchi, S. Sakai and M. Anpo, Effect of H2O vapor addition on the 863 photocatalytic oxidation of ethanol, acetaldehyde and acetic acid in the gas phase on TiO2 864 semiconductor powders, Applied Catalysis B-Environmental, 2010, 96, 218-223. 865 106. M. J. Munoz-Batista, A. Kubacka, M. Natividad Gomez-Cerezo, D. Tudela and M. Fernandez-866 Garcia, Sunlight-driven toluene photo-elimination using CeO2-TiO2 composite systems: A 867 kinetic study, Applied Catalysis B-Environmental, 2013, 140, 626-635. 107. 868 N. Bouazza, M. A. Lillo-Rodenas and A. Linares-Solano, Photocatalytic activity of TiO2-based 869 materials for the oxidation of propene and benzene at low concentration in presence of 870 humidity, Applied Catalysis B-Environmental, 2008, 84, 691-698. 871 108. H. Einaga, S. Futamura and T. Ibusuki, Heterogeneous photocatalytic oxidation of benzene, 872 toluene, cyclohexene and cyclohexane in humidified air: comparison of decomposition 873 behavior on photoirradiated TiO2 catalyst, Applied Catalysis B-Environmental, 2002, 38, 215-874 225. 875 109. T. Guo, Z. Bai, C. Wu and T. Zhu, Influence of relative humidity on the photocatalytic oxidation 876 (PCO) of toluene by TiO2 loaded on activated carbon fibers: PCO rate and intermediates 877 accumulation, Applied Catalysis B-Environmental, 2008, 79, 171-178. 878 110. G. Vincent, P. M. Marquaire and O. Zahraa, Photocatalytic degradation of gaseous 1-propanol 879 using an annular reactor: Kinetic modelling and pathways, Journal of Hazardous Materials, 880 2009, **161**, 1173-1181. 881 111. R. A. R. Monteiro, A. M. T. Silva, J. R. M. Angelo, G. V. Silva, A. M. Mendes, R. A. R. Boaventura 882 and V. J. P. Vilar, Photocatalytic oxidation of gaseous perchloroethylene over TiO2 based paint,

883		Journal of Photochemistry and Photobiology a-Chemistry, 2015, <b>311</b> , 41-52.
884	112.	Y. Huang, H. Hu, S. Wang, MS. Balogun, H. Ji and Y. Tong, Low concentration nitric acid facilitate
885		rapid electron-hole separation in vacancy-rich bismuth oxylodide for photo-thermo-synergistic
886		oxidation of formaldehyde. Applied Catalysis B-Environmental. 2017. <b>218</b> , 700-708.
887	113	Y Tao C-Y Wu and D W Mazyck Removal of methanol from nuln and naner mills using
888	115.	combined activated carbon adcorntion and nhotocatalytic regeneration. <i>Chemosphere</i> 2006
000		combined activated carbon adsorption and photocatalytic regeneration, chemosphere, 2000,
009		
890	114.	B. M. da Costa Filho, A. L. P. Araujo, G. V. Silva, R. A. R. Boaventura, M. M. Dias, J. C. B. Lopes
891		and V. J. P. Vilar, Intensification of heterogeneous TiO2 photocatalysis using an innovative
892		micro-meso-structured-photoreactor for n-decane oxidation at gas phase, Chemical
893		Engineering Journal, 2017, <b>310</b> , 331-341.
894	115.	Z. Han, VW. Chang, X. Wang, TT. Lim and L. Hildemann, Experimental study on visible-light
895		induced photocatalytic oxidation of gaseous formaldehyde by polyester fiber supported
896		photocatalysts, Chemical Engineering Journal, 2013, <b>218</b> , 9-18.
897	116.	M. Hussain, N. Russo and G. Saracco, Photocatalytic abatement of VOCs by novel optimized
898		TiO2 nanoparticles. <i>Chemical Engineering Journal</i> , 2011, <b>166</b> , 138-149.
899	117	E Moulis and L Krysa. Photocatalytic degradation of several VOCs (n-becane in-butyl acetate
900	/.	and toluene) on TiO2 layer in a closed-loon reactor. Catalysis Today, 2013, <b>209</b> , 153-158
001	110	L Zhong E Haghighat C S Log and N Lakdawala Derformance of ultraviolet nhotocatalutic
002	110.	L. Zhong, F. Hagnighat, CS. Lee and N. Lakuawala, Performance of ultraviolet photocalalytic
902		oxidation for indoor air applications: Systematic experimental evaluation, <i>Journal of Hazardous</i>
903		Materials, 2013, <b>261</b> , 130-138.
904	119.	Y. X. Deng, Developing a Langmuir-type excitation equilibrium equation to describe the effect
905		of light intensity on the kinetics of the photocatalytic oxidation, <i>Chemical Engineering Journal</i> ,
906		2018, <b>337</b> , 220-227.
907	120.	L. Pinho, M. Rojas and M. J. Mosquera, Ag-SiO2-TiO2 nanocomposite coatings with enhanced
908		photoactivity for self-cleaning application on building materials, Applied Catalysis B-
909		Environmental, 2015, <b>178</b> , 144-154.
910	121.	S. Sun, J. Ding, J. Bao, C. Gao, Z. Qi, X. Yang, B. He and C. Li, Photocatalytic degradation of
911		gaseous toluene on Fe-TiO2 under visible light irradiation: A study on the structure, activity
912		and deactivation mechanism Appl Surf Sci 2012 <b>258</b> 5031-5037
913	122	R Daghrir P Drogui and D Robert Modified TiO2 For Environmental Photocatalytic
Q1/	122.	Applications: A Review Industrial & Engineering Chemistry Research 2013 52 3581-3509
015	172	7 Shavogan E Haghighat and C S Loo Carbon doned TiO2 film to enhance visible and LIV light
915	125.	2. Shayegan, F. Hagnighat and C. S. Lee, Carbon-uopeu HOZ hint to emiance visible and OV light
910		cham Firm 2020 0 14
917		Chem. Eng., 2020, <b>8</b> , 14.
918	124.	HH. Chun and WK. Jo, Adsorption and photocatalysis of 2-ethyl-1-nexanol over graphene
919		oxide-TiO2 hybrids post-treated under various thermal conditions, Applied Catalysis B-
920		Environmental, 2016, <b>180</b> , 740-750.
921	125.	E. Q. Yu, J. Chen and H. P. Jia, Enhanced light-driven photothermocatalytic activity on selectively
922		dissolved LaTi1-xMnxO3+delta perovskites by photoactivation, Journal of Hazardous Materials,
923		2020, <b>399</b> , 11.
924	126.	Y. Zhang, Y. X. Liu, S. H. Xie, H. B. Huang, G. S. Guo, H. X. Dai and J. G. Deng, Supported ceria-
925		modified silver catalysts with high activity and stability for toluene removal, Environ. Int., 2019,
926		<b>128</b> . 335-342.
927	127	E Montecchio M II Babler and K Engvall Development of an irradiation and kinetic model
928	127.	for LIV processes in volatile organic compounds abatement applications. <i>Chemical Engineering</i>
020		Journal 2018 2/18 560-582
020	170	M L Tian E Lian O E Kn V L Cup and V D Cup Supergetic effect of titanium diovide ultraleng
950	120.	W. J. Hall, F. Llao, Q. F. Ke, F. J. Guo allu F. P. Guo, Synergetic effect of inaliant dioxide unitationg
931		nanotibers and activated carbon fibers on adsorption and photodegradation of toluene,
932		Chemical Engineering Journal, 2017, <b>328</b> , 962-976.
933	129.	X. Li, J. G. Yu, J. X. Low, Y. P. Fang, J. Xiao and X. B. Chen, Engineering heterogeneous
934		semiconductors for solar water splitting, J. Mater. Chem. A, 2015, <b>3</b> , 2485-2534.
935	130.	S. M. Fang, Y. Z. Li, Y. Yang, J. Chen, H. H. Liu and X. J. Zhao, Mg-doped OMS-2 nanorods: a highly
936		efficient catalyst for purification of volatile organic compounds with full solar spectrum
937		irradiation, Environ. SciNano, 2017, 4, 1798-1807.
938	131.	X. Li, J. Q. Wen, J. X. Low, Y. P. Fang and J. G. Yu, Design and fabrication of semiconductor
939		photocatalyst for photocatalytic reduction of CO2 to solar fuel, Science China-Materials, 2014,

940		<b>57</b> , 70-100.
941	132.	F. Zhang, Y. Zhu, Q. Lin, L. Zhang, X. Zhang and H. Wang, Noble-metal single-atoms in
942		thermocatalysis, electrocatalysis, and photocatalysis, Energy & Environmental Science, 2021,
943		<b>14</b> , 2954-3009.
944	133.	C. H. Nguyen, C. C. Fu and R. S. Juang, Degradation of methylene blue and methyl orange by
945		palladium-doped TiO2 photocatalysis for water reuse: Efficiency and degradation pathways, J.
946		Clean Prod., 2018, <b>202</b> , 413-427.
947	134.	P. Garcia-Ramirez, E. Ramirez-Morales, J. C. S. Cortazar, I. Sires and S. Silva-Martinez, Influence
948		of ruthenium doping on UV- and visible-light photoelectrocatalytic color removal from dve
949		solutions using a TiO2 nanotube array photoanode. <i>Chemosphere</i> , 2021, <b>267</b> , 10.
950	135.	M. Perez-Gonzalez and S. A. Tomas. Surface chemistry of TiO2-ZnO thin films doped with Ag.
951		Its role on the photocatalytic degradation of methylene blue. <i>Catalysis Today</i> , 2021, <b>360</b> , 129-
952		137.
953	136	A P Manuel and K Shankar Hot Electrons in TiO2-Noble Metal Nano-Heteroiunctions:
954	100.	Fundamental Science and Applications in Photocatalysis Nanomaterials 2021 <b>11</b> 55
955	137	S I Mogal V G Gandhi M Mishra S Trinathi T Shrinathi P A Joshi and D O Shah Single-
956	157.	Stan Synthesis of Silver-Doned Titanium Diovide: Influence of Silver on Structural Textural and
957		Photocatalytic Properties Inductrial & Engineering Chemistry Research 2014 53 5749-5758
058	120	Y C Mong H N Oin and Z S Zhang New insight into the enhanced visible light driven
930	150.	nbotocatalytic activity of Dd/DdCl2 donod Di2W/QC photocatalytic Journal of Collaid and
959		Interface Science 2018 E12 977 800
900	120	Milefule Science, 2010, <b>313</b> , 677-650.
901	139.	X. L. Xue, X. Y. Chen and X. W. Gong, Fast electron transfer and eminanced visible light
902		photocatalytic activity of silver and Ag2O co-doped titalium dioxide with the doping of
903		electron mediator for removing gaseous toluene, <i>Materials Science in Semiconductor</i>
964	1.40	Processing, 2021, <b>132</b> .
965	140.	C. V. Reddy, I. N. Reddy, B. Akkinepally, V. V. N. Harish, K. R. Reddy and S. Jaesool, Min-doped
966		2rO2 nanoparticles prepared by a template-free method for electrochemical energy storage
967		and abatement of dye degradation, <i>Ceram. Int.</i> , 2019, <b>45</b> , 15298-15306.
968	141.	I. Isuzuki, R. L. He, A. Dodd and M. Saunders, Challenges in Determining the Location of
969		Dopants, to Study the Influence of Metal Doping on the Photocatalytic Activities of ZnO
970		Nanopowders, Nanomaterials, 2019, <b>9</b> .
971	142.	X. Wang, M. Hong, F. Zhang, Z. Zhuang and Y. Yu, Recyclable Nanoscale Zero Valent Iron Doped
972		g-C3N4/MoS2 for Efficient Photocatalysis of RhB and Cr(VI) Driven by Visible Light, Acs
973		Sustainable Chemistry & Engineering, 2016, 4, 4055-4062.
974	143.	P. K. Boruah, B. Sharma, I. Karbhal, M. V. Shelke and M. R. Das, Ammonia-modified graphene
975		sheets decorated with magnetic Fe3O4 nanoparticles for the photocatalytic and photo-Fenton
976		degradation of phenolic compounds under sunlight irradiation, Journal of Hazardous Materials,
977		2017, <b>325</b> , 90-100.
978	144.	H. R. Rajabi, O. Khani, M. Shamsipur and V. Vatanpour, High-performance pure and Fe3+-ion
979		doped ZnS quantum dots as green nanophotocatalysts for the removal of malachite green
980		under UV-light irradiation, <i>Journal of Hazardous Materials</i> , 2013, <b>250</b> , 370-378.
981	145.	J. N. Qu, Y. Du, P. H. Ji, Z. F. Li, N. Jiang, X. Y. Sun, L. Xue, H. Y. Li and G. L. Sun, Fe, Cu co-doped
982		BiOBr with improved photocatalytic ability of pollutants degradation, J. Alloy. Compd., 2021,
983		<b>881</b> , 10.
984	146.	H. Bantawal, U. S. Shenoy and D. K. Bhat, Vanadium-Doped SrTiO3 Nanocubes: Insight into role
985		of vanadium in improving the photocatalytic activity, <i>Appl. Surf. Sci.</i> , 2020, <b>513</b> , 7.
986	147.	T. Wang, X. Q. Liu, D. L. Han, C. C. Ma, M. B. Wei, P. W. Huo and Y. S. Yan, Biomass derived the
987		V-doped carbon/Bi2O3 composite for efficient photocatalysts, Environ. Res., 2020, 182, 9.
988	148.	I. N. Reddy, C. V. Reddy, J. Shim, B. Akkinepally, M. Y. Cho, K. Yoo and D. Kim, Excellent visible-
989		light driven photocatalyst of (Al, Ni) co-doped ZnO structures for organic dye degradation,
990		Catalysis Today, 2020, <b>340</b> , 277-285.
991	149.	M. Afif, U. Sulaeman, A. Riapanitra, R. Andreas and S. Yin, Use of Mn doping to suppress defect
992		sites in Ag3PO4: Applications in photocatalysis, Appl. Surf. Sci., 2019, 466, 352-357.
993	150.	P. Herr, C. Kerzig, C. B. Larsen, D. Haussinger and O. S. Wenger, Manganese(i) complexes with
994		metal-to-ligand charge transfer luminescence and photoreactivity, Nat. Chem., DOI:
995		10.1038/s41557-021-00744-9, 8.
996	151.	P. Devaraji, N. K. Sathu and C. S. Gopinath, Ambient Oxidation of Benzene to Phenol by

- 997 Photocatalysis on Au/Ti0.98V0.02O2: Role of Holes, Acs Catalysis, 2014, 4, 2844-2853. 998 152. M. Stucchi, D. C. Boffito, E. Pargoletti, G. Cerrato, C. L. Bianchi and G. Cappelletti, Nano-MnO2 999 Decoration of TiO2 Microparticles to Promote Gaseous Ethanol Visible Photoremoval, 1000 Nanomaterials, 2018, 8. 1001 153. R. C. Li, B. H. Hu, T. W. Yu, Z. P. Shao, Y. Wang and S. Q. Song, New TiO2-Based Oxide for 1002 Catalyzing Alkaline Hydrogen Evolution Reaction with Noble Metal-Like Performance, Small 1003 Methods, 2021, 5, 9. 1004 154. S. Shamaila, T. Bano and A. K. L. Sajjad, Efficient visible light magnetic modified iron oxide 1005 photocatalysts, Ceram. Int., 2017, 43, 14672-14677. 1006 155. J. R. Xiao, T. Y. Peng, R. Li, Z. H. Peng and C. H. Yan, Preparation, phase transformation and 1007 photocatalytic activities of cerium-doped mesoporous titania nanoparticles, Journal of Solid 1008 State Chemistry, 2006, 179, 1161-1170. H. G. Wang, F. F. Wen, X. Y. Li, X. R. Gan, Y. N. Yang, P. Chen and Y. Zhang, Cerium-doped MoS2 1009 156. 1010 nanostructures: Efficient visible photocatalysis for Cr(VI) removal, Sep. Purif. Technol., 2016, 1011 170, 190-198. 1012 157. H. Gandelman, A. L. da Silva, B. Ramos and D. Gouvea, Interface excess on Sb-doped TiO2 1013 photocatalysts and its influence on photocatalytic activity, Ceram. Int., 2021, 47, 619-625. 1014 158. O. Aviles-Garcia, J. Espino-Valencia, R. Romero, J. L. Rico-Cerda, M. Arroyo-Albiter and R. 1015 Natividad, W and Mo doped TiO2: Synthesis, characterization and photocatalytic activity, Fuel, 1016 2017, 198, 31-41. 1017 159. K. Goswami and R. Ananthakrishnan, Ce-Doped CuMgAl Oxide as a Redox Couple Mediated 1018 Catalyst for Visible Light Aided Photooxidation of Organic Pollutants, Acs Applied Nano 1019 Materials, 2019, 2, 6030-6039. 1020 160. Z. Shayegan, F. Haghighat and C. S. Lee, Surface fluorinated Ce-doped TiO2 nanostructure 1021 photocatalyst: A trap and remove strategy to enhance the VOC removal from indoor air 1022 environment, Chemical Engineering Journal, 2020, 401. 1023 161. X. F. Peng, C. H. Wang, Y. Y. Li, H. Ma, F. Yu, G. S. Che, J. Y. Yan, X. T. Zhang and Y. C. Liu, Revisiting 1024 cocatalyst/TiO2 photocatalyst in blue light photothermalcatalysis, Catalysis Today, 2019, 335, 1025 286-293. 1026 162. Y. Huang, Z. Guo, H. Liu, S. Zhang, P. Wang, J. Lu and Y. Tong, Heterojunction Architecture of N-1027 Doped WO3 Nanobundles with Ce2S3 Nanodots Hybridized on a Carbon Textile Enables a 1028 Highly Efficient Flexible Photocatalyst, Advanced Functional Materials, 2019, 29. 1029 163. H. Che, G. Che, P. Zhou, C. Liu, H. Dong, C. Li, N. Song and C. Li, Nitrogen doped carbon ribbons 1030 modified g-C3N4 for markedly enhanced photocatalytic H-2-production in visible to near-1031 infrared region, Chemical Engineering Journal, 2020, 382. 1032 164. S. Wu, H. Hu, Y. Lin, J. Zhang and Y. H. Hu, Visible light photocatalytic degradation of tetracycline 1033 over TiO2, Chemical Engineering Journal, 2020, 382. 1034 165. G. S. Jamila, S. Sajjad, S. A. K. Leghari and M. Long, Nitrogen doped carbon quantum dots and 1035 GO modified WO3 nanosheets combination as an effective visible photo catalyst, Journal of 1036 Hazardous Materials, 2020, 382. 1037 166. G. S. Jamila, S. Sajjad, S. A. K. Leghari and T. Mahmood, Role of nitrogen doped carbon quantum 1038 dots on CuO nano-leaves as solar induced photo catalyst, Journal of Physics and Chemistry of 1039 Solids, 2020, **138**. 1040 167. J. Lu, Y. Wang, J. Huang, J. Fei, L. Cao and C. Li, In situ synthesis of mesoporous C-doped TiO2 1041 single crystal with oxygen vacancy and its enhanced sunlight photocatalytic properties, Dyes 1042 and Pigments, 2017, 144, 203-211. 1043 168. J. Matos, J. Ocares-Riquelme, P. S. Poon, R. Montana, X. Garcia, K. Campos, J. C. Hernandez-1044 Garrido and M. M. Titirici, C-doped anatase TiO2: Adsorption kinetics and photocatalytic 1045 degradation of methylene blue and phenol, and correlations with DFT estimations, Journal of 1046 Colloid and Interface Science, 2019, 547, 14-29. 1047 169. S. Wang, X. Zhang, S. Li, Y. Fang, L. Pan and J.-J. Zou, C-doped ZnO ball-in-ball hollow 1048 microspheres for efficient photocatalytic and photoelectrochemical applications, Journal of 1049 Hazardous Materials, 2017, 331, 235-245. 1050 170. Z. Ma, Y. Li, Y. Lv, R. Sa, Q. Li and K. Wu, Synergistic Effect of Doping and Compositing on 1051 Photocatalytic Efficiency: A Case Study of La2Ti2O7, ACS Appl. Mater. Interfaces, 2018, 10, 1052 39327-39335.
- 1053 171. C. Feng, L. Tang, Y. Deng, G. Zeng, J. Wang, Y. Liu, Z. Chen, J. Yu and J. Wang, Enhancing optical

1054		absorption and charge transfer: Synthesis of S-doped h-BN with tunable band structures for
1055		metal-free visible-light-driven photocatalysis, Applied Catalysis B-Environmental, 2019, 256.
1056	172.	M. A. Baghchesara, H. R. Azimi, A. G. Shiravizadeh, M. A. M. Teridi and R. Yousefi, Improving
1057		the intrinsic properties of rGO sheets by S-doping and the effects of rGO improvements on the
1058		photocatalytic performance of Cu3Se2/rGO nanocomposites, Appl. Surf. Sci., 2019, 466, 401-
1059		410.
1060	173.	R. Wang, D. Li, H. Wang, C. Liu and L. Xu, Preparation, Characterization, and Performance
1061		Analysis of S-Doped Bi2MoO6 Nanosheets, Nanomaterials, 2019, 9.
1062	174.	Y. Shi, G. Zhan, H. Li, X. Wang, X. Liu, L. Shi, K. Wei, C. Ling, Z. Li, H. Wang, C. Mao, X. Liu and L.
1063		Zhang, Simultaneous Manipulation of Bulk Excitons and Surface Defects for Ultrastable and
1064		Highly Selective CO2 Photoreduction, Adv. Mater., 2021, DOI: 10.1002/adma.202100143.
1065	175.	Y. Dong, D. Xu, Q. Wang, G. Zhang, Q. Zhang, Z. Zhang, L. Lv, Y. Xia, Z. Ren and P. Wang, Tailoring
1066		the electronic structure of ultrathin 2D Bi3O4Cl sheets by boron doping for enhanced visible
1067		light environmental remediation, Appl. Surf. Sci., 2021, 542.
1068	176.	Q. Wang, B. Rhimi, H. Wang and C. Y. Wang, Efficient photocatalytic degradation of gaseous
1069		toluene over F-doped TiO2/exfoliated bentonite, Appl. Surf. Sci., 2020, 530, 12.
1070	177.	A. Khalilzadeh and S. Fatemi, Spouted bed reactor for VOC removal by modified nano-TiO2
1071		photocatalytic particles, Chemical Engineering Research & Design, 2016, 115, 241-250.
1072	178.	M. Kamaei, H. Rashedi, S. M. M. Dastgheib and S. Tasharrofi, Comparing Photocatalytic
1073		Degradation of Gaseous Ethylbenzene Using N-doped and Pure TiO2 Nano-Catalysts Coated on
1074		Glass Beads under Both UV and Visible Light Irradiation, Catalysts, 2018, 8.
1075	179.	E. W. Awin, A. Lale, K. C. H. Kumar, S. Bernard and R. Kumar, Disordered mesoporous polymer
1076		derived N-doped TiO2/Si-O-C-N nanocomposites with nanoscaled heterojunctions towards
1077		enhanced adsorption and harnessing of visible light, Appl. Surf. Sci., 2020, 508.
1078	180.	M. L. Sun, X. A. Dong, B. Lei, J. Y. Li, P. Chen, Y. X. Zhang and F. Dong, Graphene oxide mediated
1079		co-generation of C-doping and oxygen defects in Bi2WO6 nanosheets: a combined DRIFTS and
1080		DFT investigation, Nanoscale, 2019, <b>11</b> , 20562-20570.
1081	181.	W. Y. Diao, J. Y. Xu, X. Rao and Y. P. Zhang, Facile Synthesis of Fluorine Doped Rutile TiO2
1082		Nanorod Arrays for Photocatalytic Removal of Formaldehyde, Catalysis Letters, DOI:
1083		10.1007/s10562-021-03700-x.
1084	182.	P. Ramacharyulu, J. P. Kumar, G. K. Prasad and B. Sreedhar, Sulphur doped nano TiO2: Synthesis,
1085		characterization and photocatalytic degradation of a toxic chemical in presence of sunlight,
1086		Materials Chemistry and Physics, 2014, <b>148</b> , 692-698.
1087	183.	R. Asahi, T. Morikawa, H. Irie and T. Ohwaki, Nitrogen-Doped Titanium Dioxide as Visible-Light-
1088		Sensitive Photocatalyst: Designs, Developments, and Prospects, Chem. Rev., 2014, 114, 9824-
1089		9852.
1090	184.	S. L. Yang, L. Peng, P. P. Huang, X. S. Wang, Y. B. Sun, C. Y. Cao and W. G. Song, Nitrogen,
1091		Phosphorus, and Sulfur Co-Doped Hollow Carbon Shell as Superior Metal-Free Catalyst for
1092		Selective Oxidation of Aromatic Alkanes, Angew. ChemInt. Edit., 2016, 55, 4016-4020.
1093	185.	Y. Wu, H. Wang, W. Tu, Y. Liu, Y. Z. Tan, X. Z. Yuan and J. W. Chew, Quasi-polymeric construction
1094		of stable perovskite-type LaFeO3/g-C3N4 heterostructured photocatalyst for improved Z-
1095		scheme photocatalytic activity via solid p-n heterojunction interfacial effect, Journal of
1096		Hazardous Materials, 2018, <b>347</b> , 412-422.
1097	186.	H. L. Liu, X. Y. Chang, X. X. Liu, G. Y. Li, W. P. Zhang and T. C. An, Boosting the photocatalytic
1098		degradation of ethyl acetate by a Z-scheme Au-TiO2@NH2-UiO-66 heterojunction with
1099		ultrafine Au as an electron mediator, <i>Environ. SciNano</i> , 2021, <b>8</b> , 2542-2553.
1100	187.	A. Enesca and L. Isac, Photocatalytic Activity of Cu2S/WO3 and Cu2S/SnO2 Heterostructures
1101		for Indoor Air Treatment, Materials, 2021, <b>14</b> .
1102	188.	G. P. Dai, J. G. Yu and G. Liu, Synthesis and Enhanced Visible-Light Photoelectrocatalytic Activity
1103		of p-n Junction BiOI/TiO2 Nanotube Arrays, Journal of Physical Chemistry C, 2011, 115, 7339-
1104		7346.
1105	189.	H. Guo, C. G. Niu, D. W. Huang, N. Tang, C. Liang, L. Zhang, X. J. Wen, Y. Yang, W. J. Wang and G.
1106		M. Zeng, Integrating the plasmonic effect and p-n heterojunction into a novel
1107		Ag/Ag2O/PbBiO2Br photocatalyst: Broadened light absorption and accelerated charge
1108		separation co-mediated highly efficient visible/NIR light photocatalysis, Chemical Engineering
1109		Journal, 2019, <b>360</b> , 349-363.
1110	190.	H. W. Huang, K. Xiao, Y. He, T. R. Zhang, F. Dong, X. Du and Y. H. Zhang, In situ assembly of

- 1111BiOl@Bi12O17Cl2 p-n junction: charge induced unique front-lateral surfaces coupling1112heterostructure with high exposure of BiOl {001} active facets for robust and nonselective1113photocatalysis, Applied Catalysis B-Environmental, 2016, **199**, 75-86.
- 1114 191. A. Iqbal, S. Sajjad and S. A. K. Leghari, Low Cost Graphene Oxide Modified Alumina
  1115 Nanocomposite as Solar Light Induced Photocatalyst, *Acs Applied Nano Materials*, 2018, 1,
  1116 4612-4621.
- 1117 192. S. Sajjad, M. Khan, S. A. K. Leghari, N. A. Ryma and S. A. Farooqi, Potential visible WO3/GO
  1118 composite photocatalyst, *International Journal of Applied Ceramic Technology*, 2019, 16, 12181127.
- 1120193.Z. Y. Yao, H. J. Sun, S. B. Xiao, Y. L. Hu, X. F. Liu and Y. Zhang, Synergetic piezo-photocatalytic1121effect in a Bi2MoO6/BiOBr composite for decomposing organic pollutants, *Appl. Surf. Sci.*, 2021,1122560.
- 1123 194. J. Q. Pan, C. Y. Chi, M. Z. You, Z. Y. Jiang, W. J. Zhao, M. Zhu, C. S. Song, Y. Y. Zheng and C. R. Li,
  1124 The three dimensional Z-scheme Ag3PO4/Ag/MoS2/TiO2 nano-heterojunction and its sunlight
  1125 photocatalytic performance enhancement, *Materials Letters*, 2018, 227, 205-208.
- 1126 195. X. G. Wang, M. H. Sun, M. Murugananthan, Y. R. Zhang and L. Z. Zhang, Electrochemically self1127 doped WO3/TiO2 nanotubes for photocatalytic degradation of volatile organic compounds,
  1128 Applied Catalysis B-Environmental, 2020, 260, 11.
- 1129196.M. M. Ding, W. Ao, H. Xu, W. Chen, L. Tao, Z. Shen, H. H. Liu, C. H. Lu and Z. L. Xie, Facile1130construction of dual heterojunction CoO@TiO2/MXene hybrid with efficient and stable1131catalytic activity for phenol degradation with peroxymonosulfate under visible light irradiation,1132Journal of Hazardous Materials, 2021, 420.
- 1133197.W. J. Wang, W. Q. Gu, G. Y. Li, H. J. Xie, P. K. Wong and T. C. An, Few-layered tungsten selenide1134as a co-catalyst for visible-light-driven photocatalytic production of hydrogen peroxide for1135bacterial inactivation, *Environ. Sci.-Nano*, 2020, **7**, 3877-3887.
- 1136 198. J. Shen, R. Wang, Q. Q. Liu, X. F. Yang, H. Tang and J. Yang, Accelerating photocatalytic hydrogen
  evolution and pollutant degradation by coupling organic co-catalysts with TiO2, *Chinese Journal*of Catalysis, 2019, 40, 380-389.
- 1139 199. S. Bai, L. M. Wang, X. Y. Chen, J. T. Du and Y. J. Xiong, Chemically exfoliated metallic MoS2
  1140 nanosheets: A promising supporting co-catalyst for enhancing the photocatalytic performance
  1141 of TiO2 nanocrystals, *Nano Res.*, 2015, **8**, 175-183.
- 1142200.L. Q. Ye, Y. R. Su, X. L. Jin, H. Q. Xie and C. Zhang, Recent advances in BiOX (X = Cl, Br and I)1143photocatalysts: synthesis, modification, facet effects and mechanisms, *Environ. Sci.-Nano*, 2014,11441, 90-112.
- 1145201.Y. Liang, Y. Yang, C. W. Zou, K. Xu, X. F. Luo, T. Luo, J. Y. Li, Q. Yang, P. Y. Shi and C. L. Yuan, 2D1146ultra-thin WO3 nanosheets with dominant {002} crystal facets for high-performance xylene1147sensing and methyl orange photocatalytic degradation, J. Alloy. Compd., 2019, **783**, 848-854.
- 1148 202. J. C. C. Yu, V. H. Nguyen, J. Lasek and J. C. S. Wu, Titania nanosheet photocatalysts with dominantly exposed (001) reactive facets for photocatalytic NOx abatement, *Applied Catalysis*1150 *B-Environmental*, 2017, **219**, 391-400.
- 1151203.H. Li, F. Deng, Y. Zheng, L. Hua, C. H. Qu and X. B. Luo, Visible-light-driven Z-scheme rGO/Bi2S3-1152BiOBr heterojunctions with tunable exposed BiOBr (102) facets for efficient synchronous1153photocatalytic degradation of 2-nitrophenol and Cr(vi) reduction, *Environ. Sci.-Nano*, 2019, **6**,11543670-3683.
- 1155