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Recent advances in TiO₂ modification for improvement in photocatalytic purification of indoor VOCs

 Lian Yu, *^a Yajing Duan,^a Dabin Wang,^b Zhen Liang,^c Cunzhen Liang^a and Yafei Wang^a

TiO₂-based photocatalytic oxidation technology has been widely used for the purification of indoor VOCs. However, the fast recombination rates of photoexcited charge carriers and wide energy band gaps have limited the practical application of TiO₂-based photocatalysts. Therefore, developing highly efficient catalysts is crucial for efficiently separating charge carriers and hindering their recombination, fully utilizing visible light. There are four main methods to improve TiO₂ photocatalytic activity: increasing e⁻-h⁺ separation rates and decreasing e⁻-h⁺ recombination rates, increasing visible light photocatalytic activity, increasing surface-active sites, and increasing physicochemical stability. Metal and non-metal doping, coupling of different semiconductors, surface and interface design, and TiO₂ immobilization are usually used to enhance the photocatalytic activity of TiO₂. This review aims to improve photocatalytic purification efficiency for indoor VOCs, and may provide new insights and guidance for the design of novel photocatalysts based on the intrinsic characteristics of VOCs, such as high volatility, low molecular weight, low polarity, high hydrophobicity, strong chemical activity and high toxicity.

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1. Introduction

Nowadays, most people spend more than 80% of their time in indoors, such as in the office, home, shopping centre or car, so indoor air quality has attracted extensive attention. Many kinds of volatile organic compounds (VOCs) have been detected in indoor air, including aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated hydrocarbons, ketones, and aldehydes.¹ The main sources of VOCs can be classified into three kinds: endogenous sources, reaction products from the indoor environment, and outdoor sources. Endogenous sources consist mainly of permanent and occasional sources. Permanent sources include releases from building materials, adhesives, laminated materials, plywood, insulators, and paints.² The occasional sources can be attributed to human activities, such as the use of different disinfection products, cleaning, cooking and personal care. Smoking was an important source of indoor VOCs, and more than 78 kinds of compounds (such as polycyclic aromatic hydrocarbons, aromatics, carbonyls, and quinones) were detected in cigarette gases.³ Human metabolism was regarded as an endogenous source of indoor VOCs:

199 kinds of VOCs have been identified in human breath, such as isoprene and acetone.⁴ Apart from direct emission of VOCs from indoor sources, the products from gas-phase reactions indoors were also sources of indoor VOCs. Outdoor air pollutants were derived mainly from road traffic, industry, and the combustion of fossil fuels.⁵ In addition, natural sources can also release VOCs (such as biological VOCs, from metabolic reactions of vegetation) to the outdoor atmosphere.⁶

The concentration of indoor VOCs depended strongly on the existence of emission sources and conditions of ventilation. The concentrations of indoor single VOCs were generally below 15 ppb, and most were below 1.5 ppb.⁷ Most VOCs were toxic, and some were carcinogenic, teratogenic or mutagenic. Long-term exposure to VOCs can cause chronic diseases, such as inflammation of the nasal passages and throat, dizziness, and headaches, and they can even cause cancer.⁸ Exposure to low concentrations can cause damage to the prior respiratory system,⁹ while exposure to high concentrations can depress the central nervous system.¹⁰ Benzene and toluene can cause myelodysplastic syndrome.⁹ Formaldehyde can cause immune dysfunction and intellectual decline, and it may even cause colon cancer, nasopharyngeal cancer, leukemia and brain tumors.¹¹ Currently, millions of people are suffering from the effects of poor indoor air quality; VOCs are the main source of indoor air pollution, and billions of dollars are lost worldwide each year.¹² It is essential to find an efficient and feasible method to remove VOCs from the indoor environment. In general, three kinds of methods were proposed to remove VOCs

^aDepartment of Environmental Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, PR China. E-mail: yulian@bipt.edu.cn

^bLaboratory of Quality & Safety Risk Assessment for Tobacco, Ministry of Agriculture, Tobacco Research Institute of Chinese Academy of Agricultural Sciences, Qingdao, 266101, PR China

^cCollege of Fisheries, Southwest University, Chongqing, 402460, PR China


from indoor air: source control, ventilation, and air cleaning.¹³ Source control was usually uncontrollable, and increased ventilation may transport other outdoor pollutants to the indoor environment. Therefore, air cleaning was considered the most feasible method to remove VOCs from indoor air.

Many efficient and feasible air cleaning technologies for indoor VOC removal have been developed, such as adsorption,¹⁴ membrane separation,¹⁵ microbial routes,¹⁶ catalytic combustion,¹⁷ thermal catalysis,¹⁸ non-thermal plasmas¹⁹ and photocatalysis.²⁰ However, all these methods showed significant limitations for practical application, and it was difficult for these methods to achieve efficient and safe purification for indoor VOCs. Adsorption consumed low energy, but the adsorbents required frequent regeneration, and the adsorbed VOCs may be released to the environment again during adsorbent regeneration.²¹ The cost of membrane separation was high, and there existed the problem of membrane fouling. The microbial route required large-scale facilities to carry out the process. Catalytic combustion, thermal catalysis, and non-thermal plasmas were effective, but they consumed a lot of energy.²² Photocatalysis usually occurred at room temperature and atmospheric pressure, so it was theoretically, technically and economically competitive with other techniques.²³ In the middle of the 1990s, photocatalysis was first used for air purification in Japan.²⁴ The photocatalysts commonly used in photocatalytic oxidation (PCO) were metal oxides or sulfides, such as TiO₂, ZnO, SnO₂, ZrO₂, CeO₂, WO₃, Al₂O₃, Fe₂O₃, ZnS and CdS.²⁵

Due to its high photocatalytic activity, non-selectivity in oxidation reactions, easy synthesis and immobilization on support materials, high stability, colorlessness, non-toxicity, as well as cheapness, TiO₂ was most commonly used for indoor air purification.²⁶ TiO₂-based photocatalytic technology solved three main problems in indoor VOC purification: insufficient adsorption, incomplete oxidation, and high costs for treatment. However, there were some drawbacks for TiO₂, such as a high charge carrier recombination rate and inefficient utilization of visible light, low adsorption capacity for VOCs, the production of hazardous intermediate products, and deactivation of photocatalysts, and many strategies have been used to overcome the defects of TiO₂: for example, ion doping, the formation of oxygen vacancies, the construction of heterojunctions and homojunctions, surface halogenation, facet engineering, specific surface area and pore structure modulation.

Because of the inefficient utilization of visible light, photogenerated electrons from the valence band of TiO₂ can only be induced under ultraviolet (UV) light irradiation, and many researchers have tried to develop novel TiO₂-based catalysts with low band gaps, using methods such as metal and non-metal doping, and coupling with different semiconductors.²⁷ Although they can improve the absorption of visible light, the dopants may act as recombination centers for photoinduced electrons and holes.²⁸ Oxygen vacancies and active facets were beneficial to activate VOC molecules, and surface halogenation adjusted the performance of the TiO₂ surface and promoted VOC adsorption.²⁹ The larger pore structure was favourable for mass transfer, and the larger specific surface area could provide

more active sites.³⁰ The crystallinity, crystal size, porosity, surface area, surface morphology, energy band structure and adsorption performance were also adjusted to enhance the photocatalytic activity of TiO₂.³¹ The photocatalytic purification of indoor VOCs involved the following main steps: diffusion, external and internal mass transfer, adsorption of VOCs on the surface of the photocatalysts, VOC degradation, desorption of products, and transfer of products to the airflow. Methods for TiO₂ modification which can enhance the efficiency of the above steps can also improve photocatalytic purification performance for indoor VOCs.

In the past two decades, TiO₂-based photocatalytic oxidation for the removal of indoor VOCs has attracted extensive interest, and some reviews have been published.^{8,22,26,27,31–33} As far as we know, there have only been a few reviews which comprehensively and thoroughly summarized methods for improving the photocatalytic purification performance of indoor VOCs from the perspective of TiO₂ modification.^{3,27,32} The methods of TiO₂ modification to improve removal efficiency for indoor VOCs focused mainly on an increase in e⁻-h⁺ separation rates and a decrease in e⁻-h⁺ recombination rates, an increase in visible light photocatalytic activity, an increase in surface-active sites, and an increase of physicochemical stability. In this review, five kinds of modification methods are summarized for improving indoor VOCs photocatalytic degradation based on promoting charge carrier separation and visible light absorption for TiO₂-based photocatalysts: (1) metal doping and surface loading; (2) non-metal doping; (3) metal and non-metal co-doping; (4) surface and interface design; (5) immobilization of photocatalysts. This review will aid a deep understanding of recent advances in the application of TiO₂-based photocatalytic technology for the purification of indoor VOCs at ambient temperature, especially for aromatic hydrocarbons and aldehydes. It will also provide new insights and guidance for the design of efficient photocatalysts based on the intrinsic characteristics of pollutants.

2. Metal doping and surface deposition

Both metal and non-metal doping can induce new doping levels inside the TiO₂ band gap; they can change its electronic structure, thus reducing its high band-gap energy (Fig. 1). The photocatalytic performance depended strongly on the chemical nature and concentration of dopants, catalyst preparation, and thermal treatment method.²⁷ Under visible light irradiation, photoinduced electrons from the TiO₂ valence band can be transferred to the doping levels inside the TiO₂ band gap.³⁵ Metal doping can introduce additional states near the TiO₂ conduction band by substituting metal ions of Ti⁴⁺; electrons are transferred from the TiO₂ conduction band to the doping states; at the same time, they can be also excited from the TiO₂ valence band to the doping states by photons whose energy is less than 3.2 eV, which can lower the band gap of TiO₂.³⁶ Metal ion doping influences TiO₂ photocatalysis according to the following principles:³⁷ (1) an improvement in the separation of



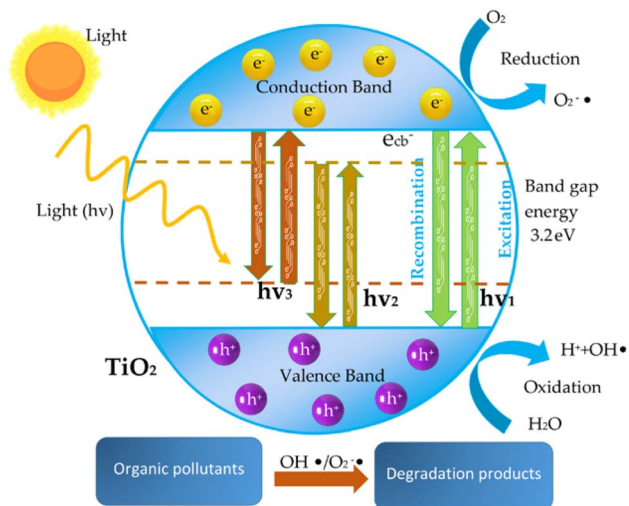


Fig. 1 Mechanism of TiO_2 photocatalysis— $h\nu_1$: pure TiO_2 ; $h\nu_2$: metal-doped TiO_2 , and $h\nu_3$: non-metal-doped TiO_2 .³⁴ Reprinted with permission from ref. 34 Copyright 2023, MDPI.

electrons and holes by selective trapping; (2) extension of optical absorption to the visible light range; (3) a decrease in the carrier lifespan due to acting as recombination centers.

Noble metals (such as gold and silver) depend mainly on surface electron trap and plasmon resonance effects; rare earth elements (such as cerium and lanthanum) with 4f orbitals can introduce impurity levels into the band gap of TiO_2 and also hinder recombination of electrons and holes; and transition metals (such as iron and chromium) can change the band gap by forming impurity levels. Precious metals are costly, but the catalysts showed strong photocatalytic activity; rare earth elements showed selectivity for specific pollutants; transition metals are cheap, but they may introduce recombination centers. The visible light photocatalytic efficiency of metal-doped TiO_2 not only rested with a red shift of the absorption spectra but also depended on the generated and recombined rates of electrons and holes. Even though metal doping can extend optical absorption to the visible light range, the photocatalytic activity decreased significantly in the UV region.³⁸ Commonly used metal dopants, such as noble metals, rare earth metals, transition metals, and their properties are discussed in following sections.

2.1. Noble metal deposition

Unlike most metals, noble metals showed high stability in corrosion and oxidation conditions in humid air. There existed localized surface plasmon resonance (LSPR) for noble metals, which enabled efficient visible light harvesting, plasmon resonance energy transfer (PRET), the generation of hot electrons and holes, scattering, and the photothermal heating effect (Fig. 2).³⁹ Deposition of noble metals onto TiO_2 was favorable for efficient light-harvesting and absorption, and it could effectively hinder charge carrier recombination due to the Schottky barrier generated at the interface of the metal and TiO_2 junction.⁴⁰ LSPR excitation can generate LSPR-excited charge carriers under visible light, then charge carriers are transferred at the metal–semiconductor interface, and energetic hot electrons are directly injected into the CB of the adjacent semiconductor (Fig. 2(a)). LSPR excitation can lead to the formation of intense electric fields near the surface of noble metals, and the electric fields can improve light absorption by the nearby semiconductor (Fig. 2(b)). After energy absorption from light by noble metals, resonant energy can be transferred to the adjacent semiconductor through dipole–dipole coupling, leading to the production of charge carriers near and below the semiconductor band edge (Fig. 2(c)).⁴⁰

Noble metals, like Pd,⁴² Pt,⁴⁰ Au,⁴³ Ag,⁴⁴ Ru,⁴⁵ and Ir,⁴⁶ can expand the optical absorption of TiO_2 to the visible light range. Au and Ag were the most widely used for improving visible light photocatalytic degradation efficiency of TiO_2 for VOCs, such as formaldehyde, methanol, ethylene, and many other VOCs.³⁹ The SPR effect promoted the photocatalytic activity of plasmonic Au/ TiO_2 ; hot electrons (SPR state) from Au directly injected into the TiO_2 conduction band can reduce O_2 (an electron acceptor) to form O_2^- at the interface of TiO_2 and Au; at the same time, $\text{Au}^{\delta+}$ cations (from SPR) can migrate to the interface of TiO_2 and Au to facilitate formaldehyde oxidation decomposition (particularly for formate and carbonate) and form OH^\bullet via H_2O oxidation.

Au/ TiO_2 was used for formaldehyde oxidation, under visible light irradiation, and the photocatalytic degradation efficiency of formaldehyde was about 83.3% over 1.07% Au/ TiO_2 , while formaldehyde conversion decreased to 22.3% over 0.2% Au/ TiO_2 .⁴³ In wet air (44% RH), 83.3% of formaldehyde was completely removed under visible light, while in dry air, the

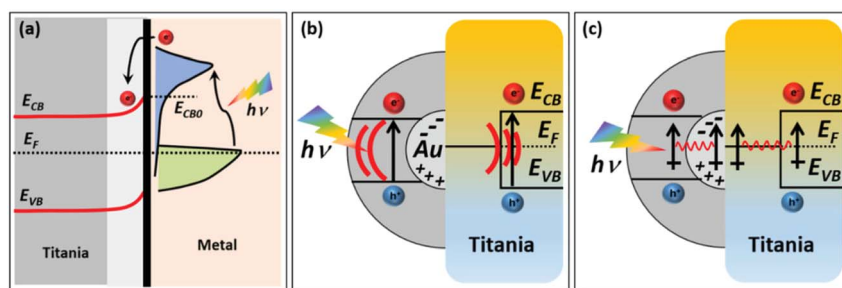


Fig. 2 Schematic of the energy transfer processes at the metal–semiconductor interface by LSPR excitation: (a) hot-electron generation and transfer to the semiconductor CB, (b) enhancement of absorption near-field EM, and (c) energy transfer by plasmon resonance.³⁹ Reprinted with permission from ref. 39 Copyright 2022, John Wiley and Sons.



catalyst was inactive, so moisture is indispensable for the decomposition of carbonate and could promote the oxidation of dioxymethylene to formate; visible light could accelerate formate oxidation to carbonate and its further decomposition, which were the rate-determining steps.⁴³ Ag species were deposited onto titania nanotubes (TNTs), and metallic Ag could be easily converted to Ag₂O; surface oxygen and Ag₂O species were responsible for the production of ROSSs; metallic Ag could generate hot electrons under visible light irradiation; toluene (30 ppm) could be effectively decomposed (~83.3%) and mineralized (~70.7%) in 3 h under UV-visible light irradiation; an appropriate Ag/Ag₂O ratio on TNT film was crucial for improving photocatalytic performance.⁴⁴

Deposition of noble metals can also relieve the deactivation of photocatalysts: the deposition of Pd could effectively remove the inherent -OH groups on the surface of TiO₂, which notably promoted O₂ activation, thus accelerating the degradation of toluene and xylenes and producing aromatic aldehydes and ring-opening products, avoiding the formation of methylphenolics, which could lead to the deactivation of catalysts.⁴² Pd/TiO₂ (1 wt%) showed excellent performance for the photocatalytic degradation of toluene under UV light, and the production of toxic methylphenols was suppressed compared with pure TiO₂.⁴² Pd/TiO₂ (1 wt%) was used for the photocatalytic oxidation of benzene in air; metallic (Pd⁰) and oxidized (PdO_x) palladium could form on the TiO₂ surface; in addition to increase the photocatalytic activity for oxidation of benzene, Pd nanoparticles could also suppress the production of CO and other intermediates during the photocatalytic reaction process and increase air purification efficiency.⁴⁷ The photocatalytic oxidation of toluene over Pd/TiO₂-N mainly followed the process: toluene → benzyl alcohol → benzaldehyde → benzoic acid → maleate, short-chain carboxylate and aldehyde/ketone (acetone) → CO₂ and H₂O, as shown in Fig. 3.⁴¹

2.2. Rare earth metals

Rare earth metals contain 17 kinds of chemical elements, Sc, Y and 15 lanthanides, where these elements possess incomplete 4f orbitals and empty 5d orbitals. Doping TiO₂ with rare earth

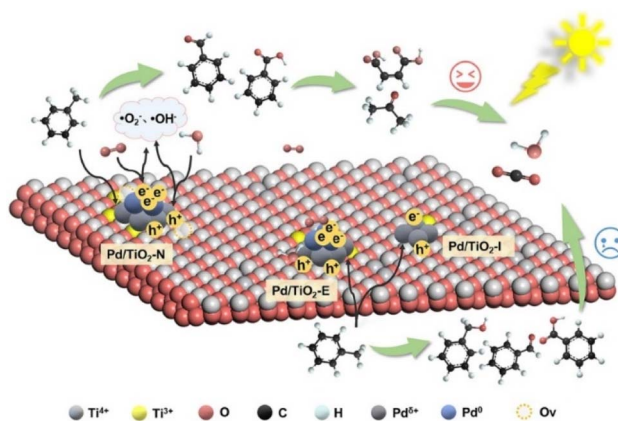


Fig. 3 The reaction pathway of toluene photocatalytic oxidation over Pd/TiO₂ catalysts.⁴¹ Reprinted with permission from ref. 41 Copyright 2023, Elsevier.

cations can increase light absorption, modifying the phase structure, morphology and surface area of the catalysts. Additionally, doping with rare earth ions can hinder the phase change from anatase to rutile.⁴⁹ Recently, doping with lanthanide group metals has attracted more and more attention. For Nd-doped TiO₂, the substitutional incorporation of Nd³⁺ distorted the TiO₂ lattice because of the significantly larger Nd³⁺ ionic radius (0.983 Å) than that of Ti⁴⁺ ion (0.605 Å), and Ti⁴⁺ ions replacing Nd³⁺ in the neodymium oxides lattice produced a Ti–O–Nd bond.⁵⁰ As a result, the lattice crystallite size of TiO₂ decreased, and some defects formed in the TiO₂ crystallite. An optimum content of dopant (1 mol%) was crucial to improve the photocatalytic activity of Nd-doped TiO₂. The interaction of Nd ions and Ti⁴⁺ can generate Ti³⁺ ions, inhibiting the recombination of photoinduced electrons and holes.⁵⁰

It was indicated that doping with rare earth metal ions could improve the adsorption capacity of TiO₂ for organic pollutants (Fig. 4),⁵¹ and the incorporation of lanthanide ions (like La³⁺, Nd³⁺, Eu³⁺, Pr³⁺, and Sm³⁺) into the TiO₂ lattice could facilitate the chemical and physical adsorption of organic pollutants on the surface of the catalysts, thus improving TiO₂ photocatalytic activity.⁵² TiO₂ modified with Er single atoms and Er³⁺ ions showed high adsorption capacity and strong ability to generate ROSSs. The catalysts showed excellent performance for the photocatalytic degradation of *o*-xylene and acetaldehyde, and were more inclined to produce intermediates and simplify degradation reactions instead of the generation of CO₂ when they were used for the photocatalytic degradation of an *o*-xylene–acetaldehyde mixture.⁵³

2.3. Transition metals

The most commonly used transition metals were Mn,⁵⁵ Fe,⁵⁵ Cu,⁵⁶ V,⁵⁷ Cr,⁵⁸ Co⁵⁹ and Ni.⁶⁰ Doping with transition metals can

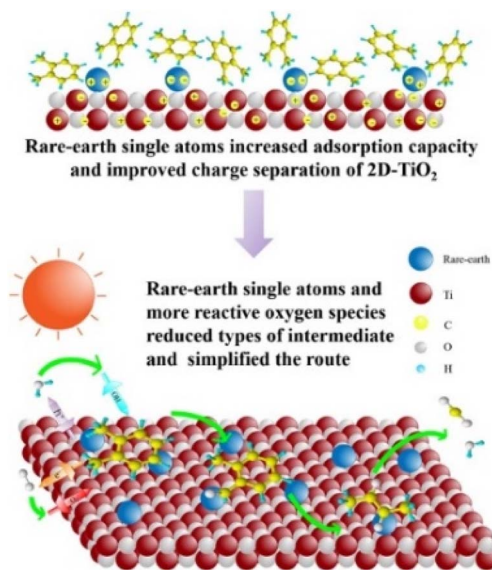


Fig. 4 Schematic of and charge separation of TiO₂ modified with rare-earth single atoms and *o*-xylene adsorption and photocatalytic degradation process over modified TiO₂.⁴⁸ Reprinted with permission from ref. 48 Copyright 2022, Elsevier.



reduce the energy band gap, and hinder recombination of electrons and holes.⁵⁵ For transition metals, the type and amount were two key parameters affecting the photocatalytic reaction. When the amount of metal dopants was kept at the optimum level, the dopants could serve as a bridge for charge carriers, which promoted the separation of electrons and holes, but, when the amount of dopants was above the optimum level, they might have distorted the crystallinity of the catalysts and become recombination centers for photogenerated charge carriers.⁵⁵ After doping beyond the optimum amount of transition metals (Cu, Ni, Mn, Co, and Fe), the catalyst surface area decreased, because they might have blocked TiO₂ pores or induced the agglomeration of particles.

M-modified TiO₂ (where M = Fe, Cu, Co, Zn and Ni) showed notably higher photocatalytic activity than pure TiO₂ under both UV and visible light irradiation; Cu/TiO₂ showed the best performance, where Cu species were uniformly dispersed on the surface of TiO₂ and existed as both oxidized Cu²⁺ and reduced Cu⁰/Cu⁺, where the ratio of Cu⁰/Cu⁺ to Cu²⁺ decreased during

the photocatalysis process, due to the transfer of photogenerated electrons and holes under UV or visible light.⁶¹ CuO_x clusters were loaded onto the surface of TiO₂; Cu dopants could substitute Ti⁴⁺ ions; and some defects were produced in the TiO₂ lattice *via* the formation of Cu–O–Ti bonds; Cu²⁺ and Cu⁺ in CuO_x clusters/TiO₂ showed high redox reversibility, which greatly promoted the separation of holes and electrons, thus enhancing the photocatalytic oxidation efficiency of HCHO under visible light; the introduction of H₂O greatly promoted HCHO oxidation, and [•]OH played a critical role in formate decomposition, rather than [•]O₂⁻.⁵⁶

The position of the TiO₂ VB and CB edges can be adjusted by Fe and Cu doping (Fig. 6).⁵⁴ After Cu⁺ and Fe³⁺/Fe²⁺ doping, the wavelength at the tangential point of the extrapolated slope increased from 410 nm to 780 nm and 500 nm, which can be attributed to the absorption of Cu₂O and iron oxides; for Cu⁺ and Fe³⁺/Fe²⁺ co-doping, these peaks were slightly reduced and blue-shifted (Fig. 5(a)). The band gaps of TiO₂, 10CuTiO₂, 10FeTiO₂, and 5Cu5FeTiO₂ were 2.91, 2.89, 2.38, and 2.48 eV,

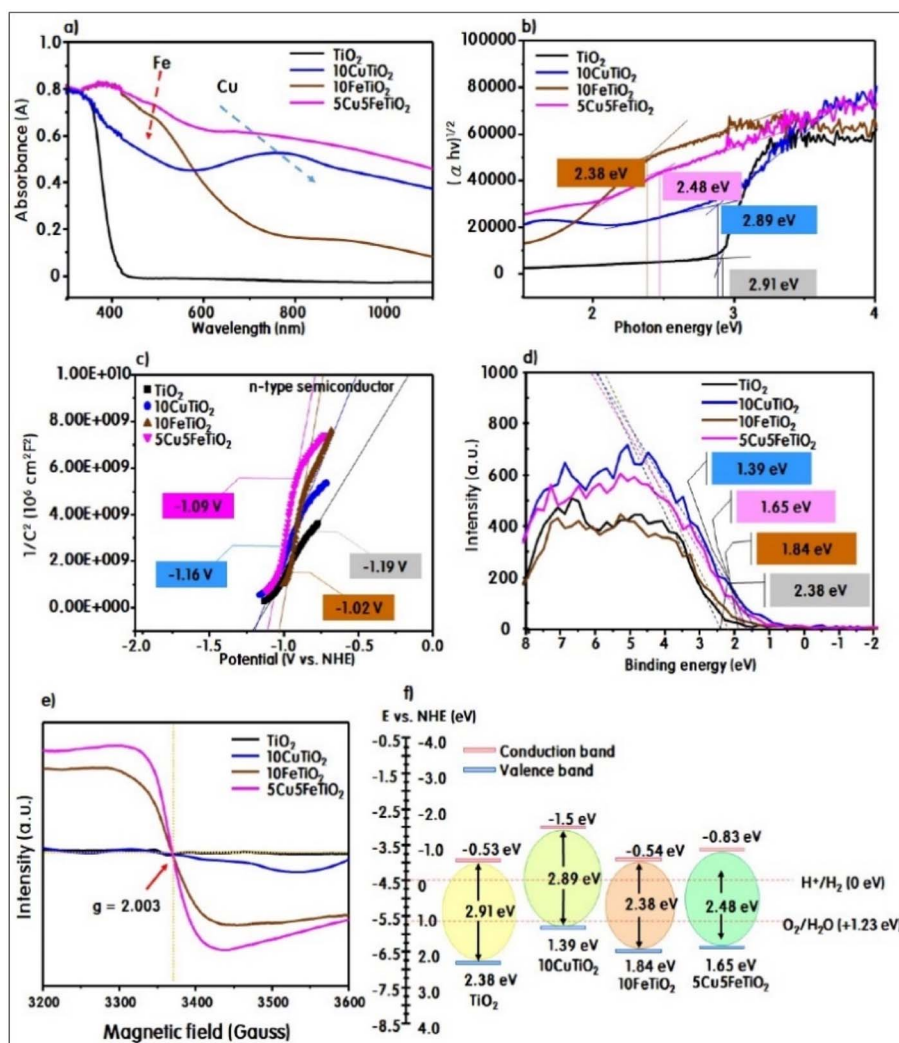


Fig. 5 DRS UV-visible absorption spectra (a), Tauc plots (b), Mott–Schottky plots (c), XPS-VB curves (d), EPR curves (e), energy diagrams of the catalyst (f) based on VBM, CBM, and band gaps.⁵⁴ Reprinted with permission from ref. 54 Copyright 2024, Elsevier.



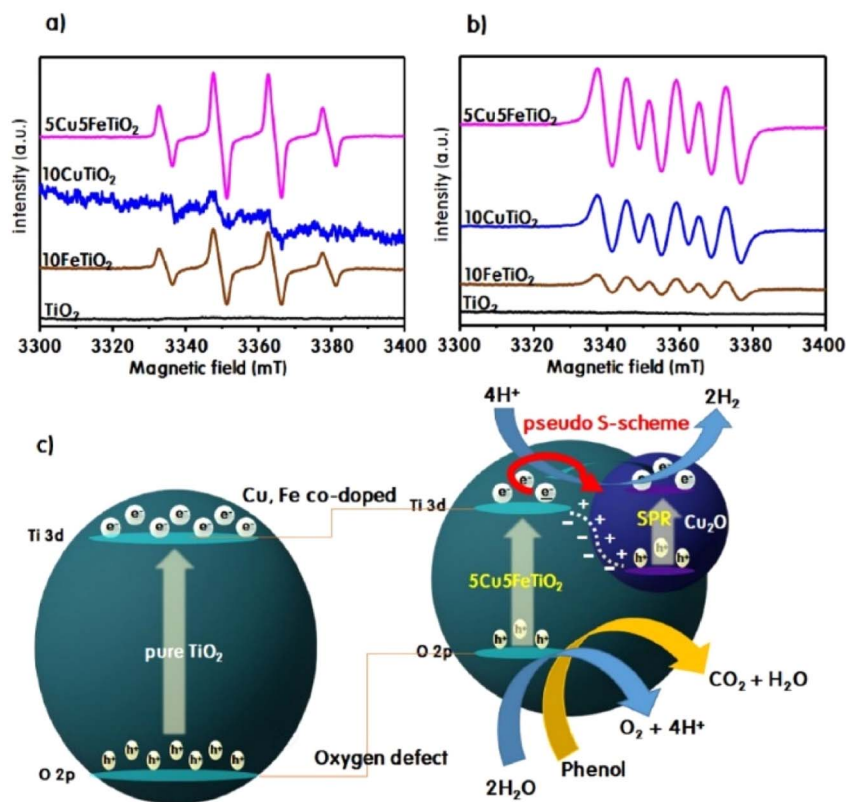


Fig. 6 DMPO- \cdot OH (a) and \cdot O $_2^-$ (b) radical ESR trapping signals under light irradiation of each sample, and charge transfer and reaction mechanism over 5Cu5FeTiO $_2$ (c).⁵⁴ Reprinted with permission from ref. 54 Copyright 2024, Elsevier.

respectively (Fig. 5(b)).⁵⁴ The Mott–Schottky curves exhibited a positive slope; Cu-doped regions facilitated electron transfer, while Fe-doped regions enhanced hole transfer, which inhibited electron–hole recombination and promoted the formation of ROS (Fig. 5(c)). From XPS-VBM (valence band maximum) and EPR analysis (Fig. 5(d and e)), the co-doping of Cu⁺ and Fe³⁺/Fe²⁺ into the TiO $_2$ lattice promoted the formation of oxygen vacancies through interaction with the electronic structure, which further enhanced the catalytic performance.⁵⁴ Compared to pure TiO $_2$, the insertion of Cu⁺ shifted the VBM energy level upward, while the insertion of Fe³⁺/Fe²⁺ shifted the CBM (conduction band maximum) energy level downward (Fig. 5(f)), which resulted in a reduced band gap; as for Cu⁺ and Fe³⁺/Fe²⁺ co-doping, both VBM and CBM levels decreased, resulting in a significant reduction in the band gap.⁵⁴ 5Cu5FeTiO $_2$ showed much stronger signals for both DMPO- \cdot OH and DMPO- \cdot O $_2^-$, suggesting that phenol oxidation was efficient (Fig. 6(a and b)), indicating a synergistic effect between copper and iron.

3. Non-metal doping of TiO $_2$

Anions can substitute oxygen in the TiO $_2$ lattice; the TiO $_2$ band gap can be narrowed by doping with non-metal (anions) rather than cations; and non-metal dopants form new states close to the valence band, which lowers the TiO $_2$ band gap.⁶⁴ Among non-metal dopants, N,⁶⁵ C,⁶⁶ S,⁶⁷ B,⁶⁸ and F,⁶⁹ showed promising results for improving TiO $_2$ photocatalytic activity. N and C

doped TiO $_2$ showed excellent visible light photocatalytic activity compared to other anion dopants.⁶⁴ Compared with N and S doping, the states in the band gap of TiO $_2$ were the deepest for C doping (Fig. 7(a and b)).⁶² S-doped TiO $_2$ was extensively investigated and used for VOC purification, introducing S into the TiO $_2$ lattice. The S $_{3p}$ states and O $_{2p}$ of TiO $_2$ can mix, increasing valence bandwidth, and narrowing the TiO $_2$ band gap (Fig. 7(c)). Fig. 8(a and b) illustrates the dopant sites in the structure of a 2 \times 2 \times 1 supercell consisting of 24 Ti $_8$ O $_{16}$ atoms based on the lattice constants.⁶³ A number of physical methods or chemical methods, such as sol–gel, hydrolysis, microemulsion, and hydrothermal methods, have been used for the preparation of TiO $_2$ doped with non-metals. N, C, S doping along with non-metal co-doped TiO $_2$ are reviewed in the following sections.

3.1. N doping

N doping attracted extensive attention because it could narrow the TiO $_2$ band gap by creating intra-band-gap states above the VB; electrons could be excited from N impurity levels to the TiO $_2$ CB by N doping, thus enabling visible light absorption.⁷⁰ The atomic radius of N is comparable to that of oxygen, and the ionization potential of N is low; therefore, N was prone to enter the TiO $_2$ lattice.⁷² Generally, doping with a non-metal whose electronegativity is lower than that of oxygen into the TiO $_2$ lattice can shift the 2p-orbital levels of the VB upward and narrow the band gap. N incorporated into the TiO $_2$ lattice



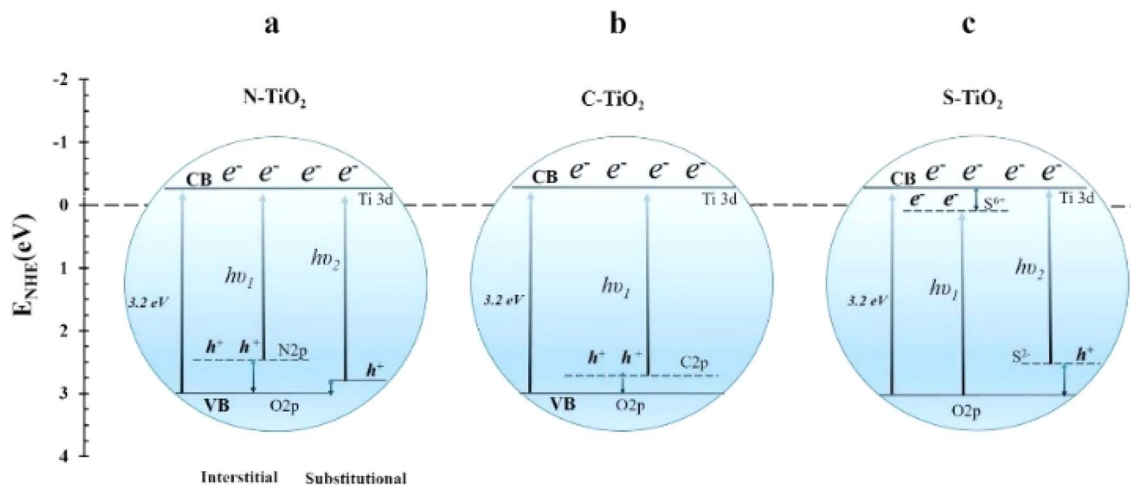


Fig. 7 Schematic of energy levels for (a) N-doped TiO₂, (b) C-doped TiO₂, (c) S-doped TiO₂.⁶² Reprinted with permission from ref. 62 Copyright 2018, Elsevier.

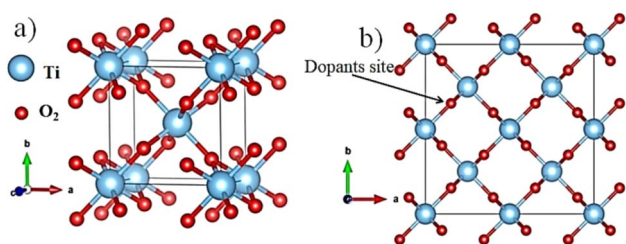


Fig. 8 (a) Crystal structure of rutile TiO₂ and (b) 2 × 2 × 1 supercell of rutile TiO₂.⁶³ Reprinted with permission from ref. 63 Copyright 2025, Springer Nature.

structure can exist as N³⁻ anions in the form of interstitial states and substitutional states. For substitutional N, the N atom replaced an O atom in the lattice, and the energy of the 2p orbital of N is higher than that of O, thus forming a new impurity level above the top of the valence band or mixing with the 2p orbital of O to shift the valence band upward, significantly enhancing the absorption of visible light. For interstitial N, the N atom is located in the interstitial space of

the TiO₂ lattice, and it will also introduce a new energy level into the band gap (usually below the bottom of the conduction band), which could reduce the energy required for electron transition and broaden the light response range. Furthermore, interstitial N often works together with oxygen vacancies, which may be more conducive to charge separation. Substitutional N and interstitial N were the origin of visible light photocatalytic activity for TiO₂ (Fig. 9).⁷⁰ The schematics of the electronic band of TiO₂ doped with substitutional N and interstitial N can be seen in Fig. 10.⁷³ Furthermore, N doping changed the hardness, elastic modulus, refraction index and electrical conductivity of TiO₂.⁶⁴

After baking in an ammonia atmosphere, the binding energy of Ti_{2p} for N-TiO₂ shifted to a lower value, because the electronegativity of N was lower than that of O, after doping TiO₂ with N, and Ti⁴⁺ was situated in a chemical environment with greater electron cloud density.⁷² As for the electronic band structure of N-TiO₂, the highest localized states (acceptor levels) for substitutional and interstitial N were 0.14 eV and 0.73 eV above the VB (Fig. 7(a and c)).⁶² For N-TiO₂, three peaks at 396.1 eV, 400 eV, 403.6 eV can be ascribed to N_{1s}. The first peak (396.1 eV) of N_{1s} can be ascribed to substitutional N dopants. The second peak (400 eV) can be ascribed to interstitial N dopants. The third peak (403.6 eV) can be ascribed to NO_x species.⁷² N doping can promote the formation of oxygen vacancies in the TiO₂ lattice, since three oxygen atoms can be replaced by two nitrogen atoms to maintain electro-neutrality.⁷⁴ The number of surface oxygen vacancies of N-TiO₂ were greater than that of pure TiO₂, and oxygen vacancies could activate O₂ to generate [•]O₂⁻. Furthermore, the N-TiO₂ hydroxyl level was stronger than that of pure TiO₂.⁷²

Various N-doped TiO₂ were used to photodegrade gaseous formaldehyde,⁷⁵ acetaldehyde,⁷⁶ acetone,⁷⁷ ethylbenzene⁷⁸ and toluene,⁷⁹ and the photocatalytic activity of photocatalysts under visible light was significantly improved. N-TiO₂ began to deactivate during the photocatalytic reaction. A TiO₂ amorphous layer over N-TiO₂ can improve the photocatalytic stability

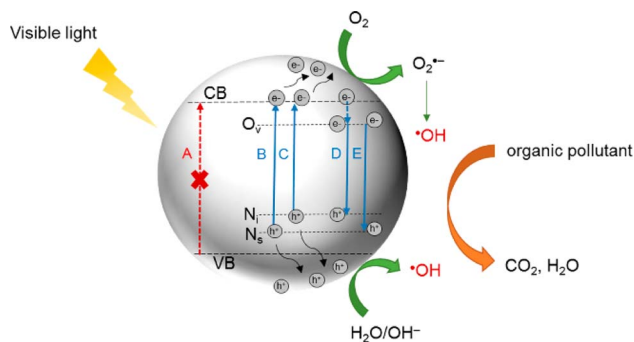


Fig. 9 Effect of N doping on the band structure and visible light photocatalytic activity of TiO₂.⁷⁰ Reprinted with permission from ref. 70 Copyright 2021, MDPI.



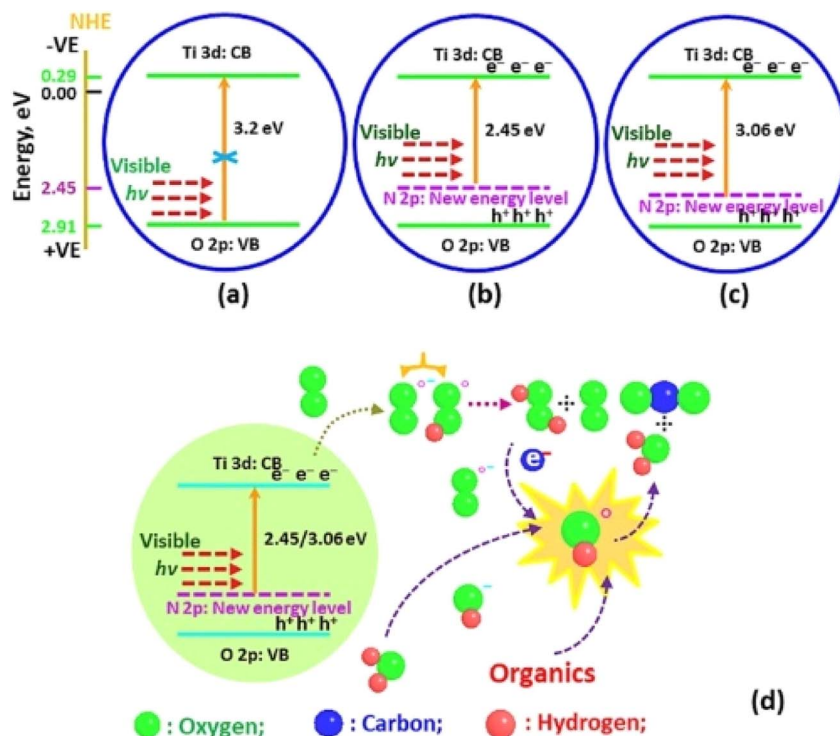


Fig. 10 Energy band gaps of (a) pure TiO₂, (b) N-TiO₂ (interstitial doping), (c) N-TiO₂ (substitutional doping) and (d) the formation mechanism of reactive species during photocatalysis.⁷¹ Reprinted with permission from ref. 71 Copyright 2023, Elsevier.

of the photocatalyst, amorphous TiO₂ can capture photogenerated e⁻-h⁺ pairs and adsorb O₂, inhibiting the oxidation of lattice nitrogen.⁷⁶

3.2. C doping

For C-doped TiO₂, the lattice oxygen atoms of TiO₂ were partially substituted by carbon atoms. C doping led to the appearance of new impurity energy levels above the VB, which could narrow the band gap, and electrons from the impurity levels were transferred to the TiO₂ CB (Fig. 11),⁷⁰ which led to absorption of light with wavelengths below 535 nm.⁸⁰ The impurity levels of C-doped TiO₂ shifted upward as the carbon concentration increased, and photogenerated holes showed

higher oxidative potential with an increase in carbon concentration.⁸¹ The photocatalytic activity increased with an increase in the electronegativity of the dopant element; C doping was unfavorable for ethylene adsorption, but favorable for ·OH formation; ethylene was selectively oxidized to CO₂ by C-doped TiO₂ without deactivation.⁸¹ It was unclear whether the type of carbon doping was interstitial or substitutional; the peak at 280.65 eV (C_{1s} characteristic peak) can be attributed to the Ti-C bond or substitutional carbon doped into the TiO₂ lattice, suggesting the existence of C doping; multiple carbon species, such as carbonate species, substitutional carbon and interstitial carbon, may exist in the lattice of TiO₂ spheres.⁸⁰ Furthermore, carbon doping can increase TiO₂ conductivity, accelerating charge transfer from TiO₂ to adsorbed VOC molecules.⁷⁰ Carbon doping may stabilize anatase TiO₂ and enhance the adsorption capacity of a catalyst for VOCs; C-doped TiO₂ spheres showed superior photocatalytic activity to P25.⁸⁰

Density functional theory (DFT) calculation was used to study the structural, optical and electronic characteristics of C-doped TiO₂; the substitution of O atoms by C atoms was thermodynamically more favorable, and the substitution was independent of preparation conditions; the impurity levels in the TiO₂ band gap could reduce the gap energy (E_g), thus enhancing the absorbance of visible light.⁸² An O atom substituted by a C atom led to great distortion in the structural arrangement around the dopants, changing the electronic and optical properties of TiO₂; a reduction of 0.3 eV was achieved for the band gap.⁸² The newly formed electronic levels above the TiO₂ VB were responsible for the narrowed band gap of C-doped TiO₂.

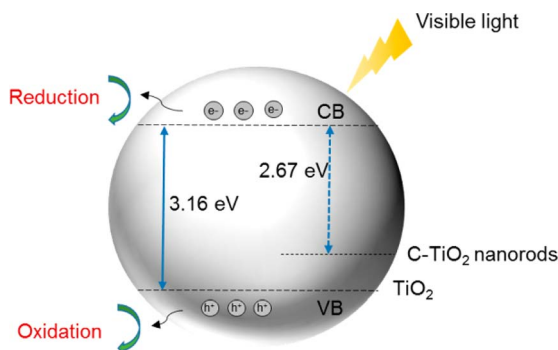


Fig. 11 Schematic of the photocatalytic mechanism of C-doped TiO₂ nanorods with visible light.⁷⁰ Reprinted with permission from ref. 70 Copyright 2021, MDPI.



However, lattice defects may form during the process of C doping, which can serve as recombination centers for charge carriers, so it was critical to choose appropriate methods to reduce the amount of TiO₂ lattice defects.

3.3. S doping

S_{3p} states mixing with O_{2p} states of TiO₂ can increase the width of the VB, and incorporating S into TiO₂ lattice can narrow the band gap.⁶³ The valent states of dopant atoms significantly affected the positions of photogenerated electrons and holes. S⁴⁺/S⁶⁺ cations can substitute Ti⁴⁺, while the S²⁻ anion can replace lattice oxygen (Fig. 12).⁶⁷ Cationic S doping can improve charge separation⁸³ and extend the TiO₂ absorption spectrum region to visible light,⁸⁴ so cationic S doping was a facile method to improve TiO₂ photocatalytic activity. The ion atomic radius of Ti⁴⁺ (0.64 Å) is significantly greater than that of S⁶⁺ (0.29 Å), so S⁶⁺ substituting for Ti⁴⁺ may decrease the TiO₂ crystal size.⁶⁷ After substitution of S⁶⁺ for Ti⁴⁺, S_{3s} orbitals created states which were above the O_{2p} orbitals of the TiO₂ VB, while S_{3p} orbitals contributed to the lowered TiO₂ CB.⁶³ Anionic S doping was more difficult to realize than cationic S, because the S²⁻ ionic radius (1.7 Å) is notably larger than that of O²⁻ (1.22 Å).⁸³ Therefore, a Ti-S bond required higher formation energy than a Ti-O bond.

Some other researchers reported that TiO₂ doping by replacing Ti with S⁴⁺ and S⁶⁺ was unfavorable for TiO₂ bulk but favorable for the TiO₂ surface; the reports of strong absorption of visible light by S-doped TiO₂ may be ascribed to other impurities, such as N, C or Ti³⁺.⁸⁴ Novel theoretical models were used to analyze S⁴⁺ and S⁶⁺ doping in different surface and bulk positions of TiO₂. S preserved its typical coordination geometries in S-doped TiO₂: a trigonal pyramid for S⁴⁺ but a tetrahedron for S⁶⁺. For S⁴⁺-doped TiO₂, the band gap decreased from 3.22 eV to 2.65 eV, while for S⁶⁺-doped TiO₂, the band gap decreased from 3.22 eV to 2.96 eV. The maximum amount of S⁶⁺ was observed with the ratio S⁶⁺/S⁴⁺ being about 5.61 with 9% S atoms, indicating that S in the catalyst was in the form of cations; the presence of S⁶⁺ in TiO₂ improved visible light photocatalytic activity and reduced the band-gap energy; in

addition, S⁶⁺/S⁴⁺ can act as an electron capture agent, improving the electrical conductivity of the photocatalyst and accelerating the transfer of electrons and holes; compared with pure TiO₂, S-doped TiO₂ showed improved photoactivity for acetaldehyde degradation under visible-light irradiation.⁸⁵

Thiourea and CS₂ were used as sulfur precursors, and cationic S and anionic S were doped into the TiO₂ lattice. As for the cationic precursor, Ti⁴⁺ can be substituted by S⁶⁺, forming a Ti-O-S bond. The charges between sulfur and oxygen atoms should maintain a balance; therefore, the created hydroxide eventually neutralized the extra positive charges. For the anionic precursor, an O-Ti-S bond appeared in S-TiO₂, and O atoms in the O-Ti-O network were partially replaced by S atoms; it was noted that anionic S²⁻ existed mainly in the lattice of TiO₂, while cationic S, such as SO₄²⁻, was mainly chemisorbed on the TiO₂ surface due to the calcination process.⁶³ S-doped TiO₂ using thiourea (S²⁻) as the source shifted the absorption to the visible spectrum region and enabled photocatalytic activity under visible light; compared with TiO₂, S-doped TiO₂ was significantly more active for acetaldehyde degradation under visible light irradiation.⁸⁶

4. Metal and non-metal co-doping

Metal and non-metal co-doping was considered a way to solve the problems existing in single-doped TiO₂. Doping metal and non-metal into the TiO₂ lattice can produce doping energy levels in the TiO₂ band gap (Fig. 13). As for doping, metal components usually substituted Ti sites in the TiO₂ lattice to form dopant levels near the CB, while non-metal components usually formed new dopant levels close to the TiO₂ VB, which reduced the band gap and led to the absorption of visible light; co-doping of TiO₂ showed lower band-gap energy values than single-doped TiO₂; and the synergistic effects of metal and non-metal co-doping also promoted the separation of electrons and holes.²⁷ Furthermore, co-doping can decrease crystallite size and increase the specific surface area of TiO₂.⁸⁷ It was crucial to find appropriate dopants and the optimum amounts of dopants. TiO₂ co-doped with metal/metal, metal/non-metal and non-metal/non-metal are discussed in the following sections.

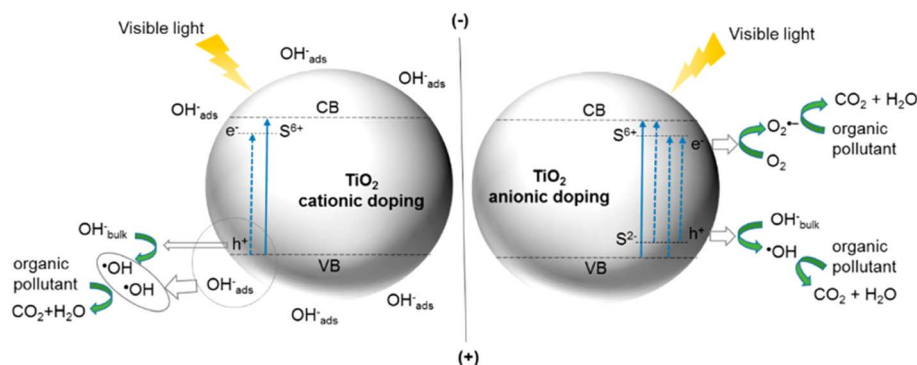


Fig. 12 Schematic of the PCO mechanism of TiO₂ doped with cationic and anionic S.⁷⁰ Reprinted with permission from ref. 70 Copyright 2021, MDPI.



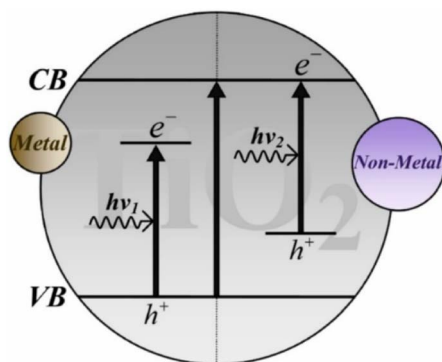


Fig. 13 The mechanism of TiO₂ photocatalysts co-doped by metal and non-metal dopants.²⁷ Reprinted with permission from ref. 27 Copyright 2024, Elsevier.

4.1. Metal co-doping

The doping mechanism and physiochemical properties of TiO₂ doped with two different metals have not yet been investigated in depth. New energy levels were formed in Mn/FeTNT@Ti-500 due to doping with Fe²⁺, Fe³⁺, Mn²⁺ and Mn³⁺ ions. The trapped states involving Fe³⁺/Fe²⁺ formed below the conduction band, while Fe³⁺/Fe⁴⁺ trapped states formed above the valence band.⁸⁸ As shown in Fig. 14, Mn³⁺/Mn²⁺ also acted as an electron trap site, while the Fe³⁺/Fe⁴⁺ site above the TiO₂ valence band acted as a hole trapping site. These trapped holes were immediately released because of the reduction of unstable Fe⁴⁺ to stable Fe³⁺ ions; thereafter, these holes migrated to the surface and oxidized adsorbed H₂O molecules.⁸⁸ As the standard redox potential for Cu²⁺/Cu⁺ (0.17 V) is lower than that for Fe³⁺/Fe²⁺ (0.77 V), Cu⁺ can easily reduce Fe³⁺ to Fe²⁺; therefore, Fe²⁺ can be regenerated on the TiO₂ surface (Fig. 15), promoting Cu²⁺/Cu⁺ and Fe³⁺/Fe²⁺ cycles and further promoting ROS generation.⁸⁹

The Ag⁺ ion radius (1.26 Å) is much bigger than that of Ti⁴⁺ (0.74 Å). The ion radius of V⁴⁺ (0.72 Å) is similar to that of Ti⁴⁺ (0.74 Å); therefore, V⁴⁺ can substitute Ti⁴⁺ and form a Ti–O–V bond in the TiO₂ lattice. Both Ag⁺ and V⁴⁺ can be incorporated into the TiO₂ lattice, which may reduce Ti⁴⁺ to Ti³⁺.

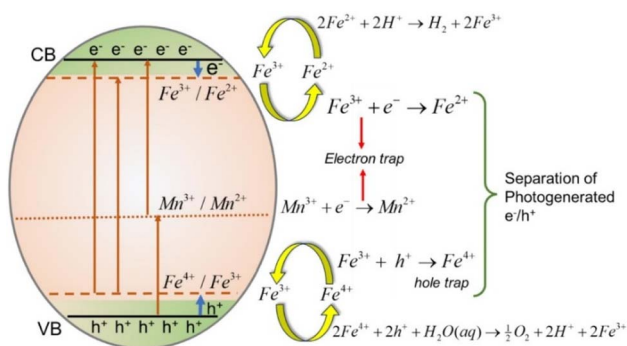


Fig. 14 Schematics of the charge transfer process of photocarriers in a Mn/Fe-TNT@Ti-500 photocatalyst.⁸⁸ Reprinted with permission from ref. 88 Copyright 2024, Elsevier.

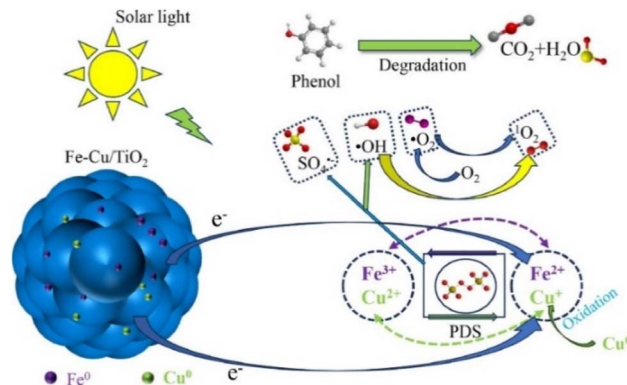


Fig. 15 Mechanistic diagram of the synergistic degradation of phenol by Fe–Cu/TiO₂ composites.⁸⁹ Reprinted with permission from ref. 89 Copyright 2024, Elsevier.

Consequently, the ratio of Ti³⁺/Ti⁴⁺ for TiO₂ co-doped with Ag and V was higher than that for V or Ag singly-doped TiO₂, Ag and V co-doping promoted doping into the TiO₂ lattice, which was favorable for oxygen vacancy formation in TiO₂ (or Ti³⁺ formation). The incorporation of Ti³⁺ and V⁴⁺ into the TiO₂ lattice can act as intermediate agents for internal electron transfer; the Ag₂O band-gap energy (1.3 eV) was lower than that of V₂O₅ (2.3 eV); and the energy needed for internal electron transfer for Ag–TiO₂ was lower than that for V–TiO₂.⁸⁷ In addition, many different Fermi levels existed for metallic Ag; Ag can facilitate internal electron transfer by Ag₂O; V can facilitate internal electron transfer in the TiO₂ lattice; and they can also facilitate exterior electron transfer among Ag, Ag₂O and TiO₂ in Ag–TiO₂.⁸⁷ Furthermore, Ag, Ag₂O, and V₂O₅ agglomeration could be hindered in Ag and V co-doped TiO₂.⁸⁷

For Ag-doped TiO₂/PU, the removal efficiency and degree of mineralization of *n*-hexane were 87.2% and 92.1%, while the removal efficiency and degree of mineralization of *n*-butyl acetate were 90.1% and 94.3%. For V-doped TiO₂/PU, the removal efficiency and degree of mineralization of *n*-hexane were 82.6% and 91.1%, while the removal efficiency and degree of mineralization of *n*-butyl acetate were 84.7% and 92.7%. For Ag and V co-doped TiO₂/PU, the removal efficiency and degree of mineralization of *n*-hexane were 93.7% and 93.2%, while the removal efficiency and degree of mineralization of *n*-butyl acetate were 95.5% and 96.2%.⁸⁷ Ag@V–TiO₂/PU showed advantages of both Ag and V, and exhibited excellent photocatalytic degradation performance for a hexane and butyl acetate mixture.⁸⁷

Bi and Zn co-doped TiO₂ was used for the photocatalytic degradation of toluene, and moderate Bi–Zn co-doping levels were significantly favorable for toluene photodegradation under visible light irradiation.⁹⁰ Doping Bi into the TiO₂ lattice can generate a new doped energy level below the TiO₂ CB edge, and electrons excited from the TiO₂ VB to Bi orbitals led to a decrease in the band gap. Zn²⁺ was not incorporated into the TiO₂ lattice and formed ZnO crystallites, which were distributed mainly on the interface of TiO₂, and it acted as a mediator for interfacial charge transfer and hindered electron–hole



recombination. These synergistic effects were responsible for enhanced photocatalytic performance. Under visible light irradiation, electrons were excited at the TiO₂ (R) VB and transferred to the Bi energy level; then they shifted to the CB of TiO₂ (R) (−0.48 eV vs. SHE), ZnO (−0.15 eV) and TiO₂ (A) (−0.13 eV); electrons transferred along the gradient of the CB edge potential (Fig. 15).⁹⁵ Toluene degradation efficiencies over TiBi_{1.9%}O₂ and TiBi_{1.9%}Zn_{1%}O₂ were 51% and 93%, much higher than the 25% for TiO₂.⁹⁰

4.2. Non-metal co-doping

C and N co-doped TiO₂ combined the advantages of C-doped and N-doped TiO₂. The incorporated C atoms can form carbonaceous species I, which can serve as photosensitizer (C*).⁷⁰ After excitation of carbonaceous species I, electrons were injected into the TiO₂ CB; these electrons could be further transferred to O₂ adsorbed on the TiO₂ surface, forming [•]O₂[−], which could subsequently generate H₂O₂ and [•]OH, combining with [•]OH, and participating in pollutant degradation (Fig. 16).⁷⁰ C doping can also enhance the adsorption capacity of TiO₂ for pollutants. N doping can create an intra-band-gap state (IB) above the VB, narrowing the band gap.⁷⁰ The synergistic effect of N and C co-doping can further decrease the band-gap energy of C,N-co-doped TiO₂ to 2.80 eV. C and N can be co-doped into TiO₂ by various carbon and nitrogen sources, such as ETA, DEA and TELA. The N 1s peak in the range of ca. 396–402 eV can be ascribed to the existence of O–Ti–N bonds, suggesting the incorporation of substitutional N into the TiO₂ lattice.⁷⁰ The peaks from 284.6 to 289.6 eV were attributed to the existence of carbon; the peaks at 285.9–286.7 eV and 288.5–288.7 eV were mainly attributed to C–O and C=O bonds; the peaks at 288.0–288.9 eV could be ascribed to Ti–O–C bonds.⁷⁰

N and S co-doping can reduce the band gap of TiO₂ because of the generation of additional impurity levels.⁶⁴ N doping can form a delocalized state in the TiO₂ band gap, which increases visible light absorption. S doping facilitates the adsorption of organic species onto the surface of N and S co-doped TiO₂. The improved photocatalytic degradation efficiency can be ascribed to the following reasons:⁷⁴ (1) inhibition of the recombination of electron–hole pairs; (2) the generation of impure electronic

states narrowing the band gap; (3) interfacial bonding; (4) defective sites; (5) a change in textural characteristics. Thiourea was usually used as an S source, and urea and ammonium nitrate were usually used as an N source; some chemical reagents can be used as both N and S source, such as ammonium sulfate and ammonium thiocyanate.⁷⁰ N and F co-doped TiO₂ was also used for the degradation of gaseous ethylbenzene; N doping promoted the generation of [•]O₂[−] over TiO₂ oxygen vacancy sites under visible light irradiation; F doping can generate new active sites and facilitate the generation of [•]OH; conversion rates of ethylbenzene for undoped, N-doped, and N and F co-doped TiO₂ were 0%, 13.5%, and 17.0%, respectively, under visible light.⁹¹

Tri-doping was an efficient method to improve TiO₂ visible light photocatalytic activity. C, N, and S co-doping can form new impurity levels, including N_{2p}, S_{2p} and C_{1s} (Fig. 17); the carbon atom served as a photosensitizer under visible light irradiation, while N and S doping led to a mixture of N_{2p} and S_{2p} orbitals with O_{2p} orbitals in TiO₂;⁷⁰ and the band gap was narrowed compared to pure TiO₂. In the XPS spectra for N, S and C tri-doped TiO₂, N can be ascribed to Ti–O–N and Ti–N bonds, S can be mainly ascribed to the Ti–O–S bond, and C can be attributed to the Ti–O–C bond.⁹² C,N,S-tri-doped TiO₂ nano-sheets exposing {001} facets exhibited excellent photocatalytic activity.⁹³

4.3. Metal and non-metal co-doping

Metal and nonmetal co-doping combined the advantages and overcame some drawbacks of single doping. The synergistic effects of metal and non-metal co-doping facilitated the separation of electrons and holes, and enhanced the visible light photocatalytic activity of TiO₂. Metal dopants were easy to substitute for Ti sites in the TiO₂ lattice to generate dopant levels near the CB, and metal ions could act as a mediator for interfacial charge transfer and hinder electron–hole pair recombination due to the enhancement in quantum efficiency for co-doped TiO₂.⁹⁰ Non-metal dopants potentially formed new levels close to the VB, which reduced the band gap and led to the absorption of visible light. Non-metal and transition metal co-doping was a feasible method to improve TiO₂ photocatalytic

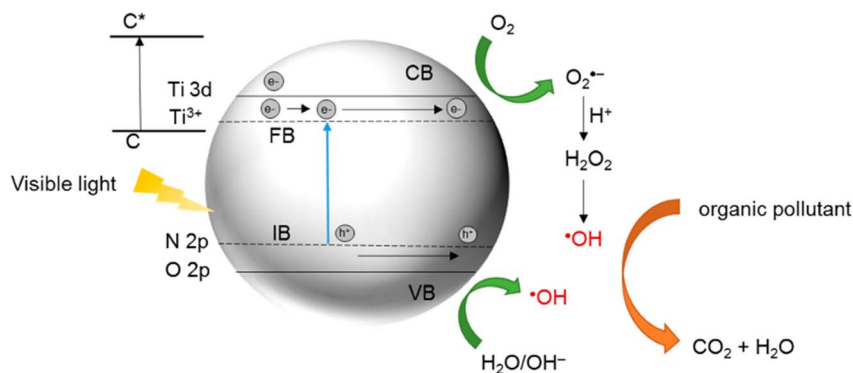


Fig. 16 Schematic of the mechanism for C,N-co-doped TiO₂ photocatalysis under visible light.⁷⁰ Reprinted with permission from ref. 70 Copyright 2021, MDPI.



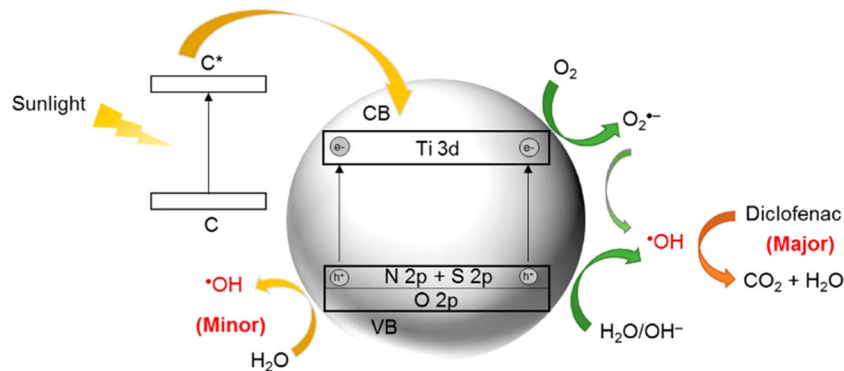


Fig. 17 Schematic for the improvement of photocatalytic activity over C,S,N-tri-doped TiO_2 .⁷⁰ Reprinted with permission from ref. 70 Copyright 2021, MDPI.

activity. Fe, Zn, Cu, Cr combined with N co-doped TiO_2 showed improved photocatalytic activity under visible light.⁹⁶ The photocatalytic activity of N-doped TiO_2 could be further enhanced by W^{4+} (Fig. 18) or Fe^{3+} co-doping. Photogenerated holes can oxidize the lattice nitrogen of N-doped TiO_2 , and nitrogen is gradually lost; however, Fe-ion doping could improve the stability of N-doped TiO_2 .⁹⁷ Furthermore, N and Fe co-doping could hinder the transformation of anatase to rutile. The removal efficiency of *p*-nitrophenol for Fe-doped, N-doped, and Fe and N co-doped TiO_2 were about 47%, 41%, and 67%, respectively.⁹⁷

Different preparation methods may dope ions into different positions of the TiO_2 crystal lattice.⁹⁸ The position and structure of dopant elements significantly affected the electronic, optical, structural characteristics of TiO_2 .⁷³ Based on the doping sites and relative positions of the dopants, the network of Fe and N co-doped TiO_2 was modeled with three configurations (Fig. 19).⁹⁴ In Model A, Fe atoms and N atoms were doped at Ti and N sites, and the distance between Fe atoms and N atoms was 1.739 Å. In Model B, Ti atoms were replaced by Fe atoms, O atoms were replaced by N atoms, and the distance between Fe atoms and N atoms was 7.805 Å. In Model C, two N atoms (at a distance of 2.21 Å) were inserted at the interstitial sites, Fe was located at the Ti site of a $3 \times 2 \times 1$ supercell, and DFT calculation was applied to study the influence of dopant location on

band structure and the enhancement of visible light absorption of mono-doped and co-doped TiO_2 .⁹⁴ After iron oxide was loaded into N-doped TiO_2 , the heterogeneous electrons transferred from $\text{TiO}_{2-x}\text{N}_y$ to Fe_2O_3 , promoting the effective separation of photoinduced electrons and holes; furthermore, the electrons can be excited and transferred by various pathways from the VB to the CB after co-doping, enhancing the visible light photocatalytic activity of N/Fe co-doped TiO_2 .⁷³ However, a negative effect on photocatalytic activity for TiO_2 co-doping with Fe was also observed, which could be due to the formation of anion vacancies in co-doped TiO_2 for charge compensation.

5. Surface and interface design

Photodegradation reactions occurred on the catalyst surface, and the surface and interface structure and properties of catalysts (like crystallite size, crystalline phases, pore structure, specific surface area, active sites and adsorption performance) greatly influenced heterogeneous photocatalytic reactions. The interface structure influenced interfacial charge transfer and recombination; furthermore, the surface structure affected the generation of reactive radicals, so they significantly affected the removal efficiency of gaseous VOCs.²⁶ Interfacial charge separation and transfer occurred at the interface of semiconductors

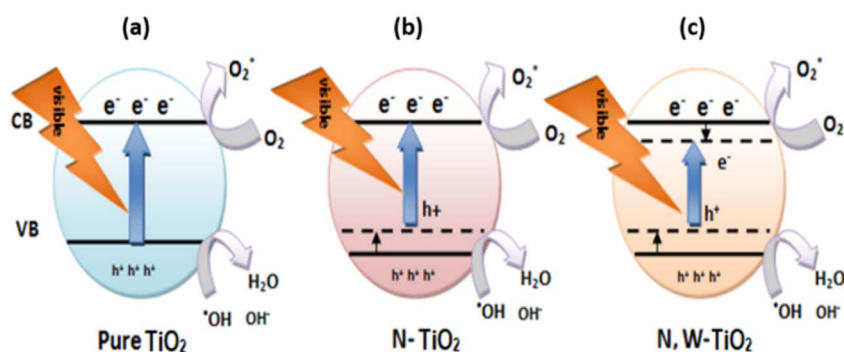


Fig. 18 Proposed pathway for photocatalytic degradation over (a) undoped TiO_2 ; (b) TiO_2 doped with N; (c) TiO_2 co-doped with N and W.⁹⁵ Reprinted with permission from ref. 95 Copyright 2022, MDPI.



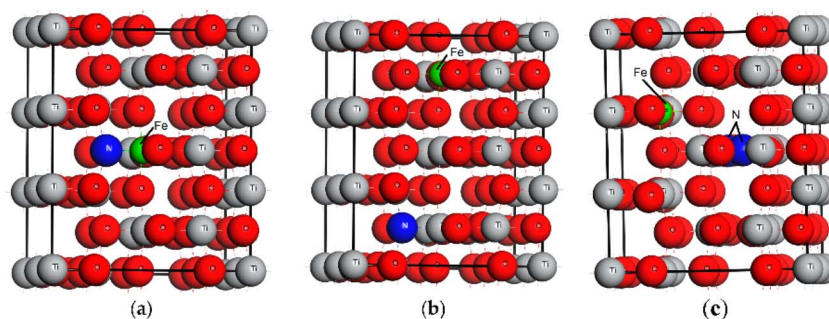


Fig. 19 Relative positions of Fe and N dopants in the TiO_2 lattice: Model A (a), Model B (b), and Model C (c).⁹⁴ Reprinted with permission from ref. 94 Copyright 2018, MDPI.

and organic compounds; interfacial charges may directly oxidize or reduce VOCs or form reactive oxidants like superoxides and hydroxyl radicals.⁹⁹ The surface and interface design of TiO_2 can promote charge carrier separation, hinder charge carrier recombination and shift the optical absorption to visible light.

5.1. Construction of oxygen vacancy

The loss of lattice oxygen led to the generation of oxygen vacancies (OVs), which could increase active sites; the TiO_2 lattice OVs can be seen in Fig. 20.¹⁰² After doping with Ni^{2+} , two Ti atoms were substituted by two Ni atoms to keep the concentration of Ni similar to the experimental doped concentration of Ni (Fig. 20). It was reported that the insertion of one OV subsequently introduced two Ti^{3+} defects into the Ni-doped TiO_2 supercell.¹⁰⁰ At present, many methods have been used to construct OVs, such as ultraviolet induction,¹⁰³ laser ablation,¹⁰⁴ annealing,¹⁰¹ reductant addition,¹⁰⁵ and doping.¹⁰⁶ OVs significantly influence the photocatalytic degradation of VOCs. Firstly, OVs could influence mobility of surface lattice oxygen and provide coordinated sites for molecule activation, thus activating the gas molecules.¹⁰⁷ Secondly, surface OVs can capture electrons or holes and facilitate the transfer of charge carriers to the adsorbate, thus greatly influencing the dynamics of charge carrier transfer. Thirdly, oxygen defects generally adjusted the

electronic state *via* local electrons and the coordination structure of the adsorbate *via* hanging bonds,¹⁰¹ promoting charge carrier transport, and hindering the recombination of electrons and holes.¹⁰⁷ Fourthly, OVs over the TiO_2 surface provided the primary adsorption sites for VOC molecules,¹⁰⁸ improving the adsorption capacity of TiO_2 for VOCs.

OVs can reduce the adsorption energy and activation barrier of O_2 , which is beneficial for the formation of $\cdot\text{O}_2^-$; OVs can also promote the disintegration of H_2O to $\cdot\text{OH}$.¹⁰⁹ However, O_2 and H_2O molecules can be easily adsorbed on the surface of OV sites, so the structural stability of surface OVs was poor. Constructing subsurface defects and decorating metal nanoparticles were used to improve the stability of surface OVs.⁶² OVs created on the surface of TiO_2 facilitated the incorporation of O atoms from O_2 into phenol, because OVs could effectively suppress the single-electron reduction of O_2 to form $\cdot\text{O}_2^-$, and promote the two-electron reduction process instead, which was typically associated with the generation of H_2O_2 ; and the generated H_2O_2 could (in some cases) provide additional $\cdot\text{OH}$ to drive the benzene hydroxylation reaction (Fig. 21).¹⁰¹

Annealing temperature was used to adjust the concentration of surface OVs, and photocurrent and photoluminescence measurements suggested that the existence of interfacial OVs promoted interfacial electron transfer; surface OVs promoted the adsorption and activation of toluene and O_2 , facilitating the formation of intermediates and enhancing the mineralization efficiency for toluene.¹¹⁰ Ru/TiO_x with abundant OVs showed

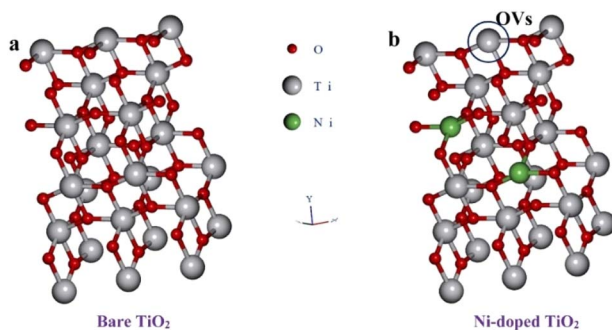


Fig. 20 Anatase TiO_2 (101) supercell ($2 \times 2 \times 1$) models for (a) pure TiO_2 (16Ti and 32O atoms) and (b) Ni-doped TiO_2 (14Ti, 31O and 2Ni atoms).¹⁰⁰ Reprinted with permission from ref. 100 Copyright 2025, Elsevier.

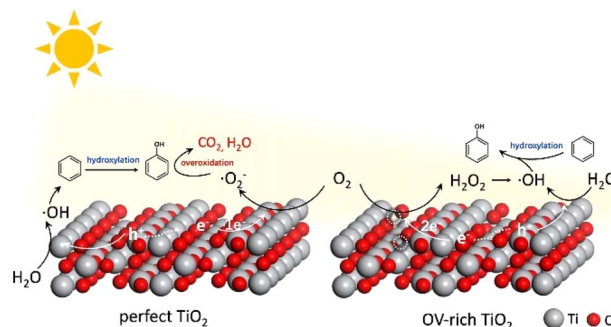


Fig. 21 Potential reaction pathways for the photocatalytic oxidation of benzene to phenol over pristine TiO_2 and OV-rich TiO_2 .¹⁰¹ Reprinted with permission from ref. 101 Copyright 2025, John Wiley and Sons.



excellent catalytic performance for 1,2-DCE and toluene oxidation; Ru/TiO_x greatly inhibited the formation of intermediate byproducts and Cl₂; most OVs of Ru/TiO_x were still retained after use; and the catalysts with OVs were more suitable and promising for the oxidative removal of multicomponent VOCs.¹⁰⁷ However, surface OVs in TiO₂ can also serve as electron and hole recombination centers, which is adverse for photocatalysis.¹¹¹

5.2. Facet engineering

Different lattice planes of TiO₂ showed different activities; exposing different facets could influence VOC degradation paths, and exposing highly active facets could enhance photocatalytic activity.⁴² The design of a facet was a feasible method to improve TiO₂ photocatalytic activity. Although the role of the facets was controversial, some studies indicated that exposing particular facets can enhance the selectivity of VOC photocatalytic degradation, and partial facets showed higher adsorption capacity for VOC molecules.²⁹ Anatase nanosheets, such as rectangular, octahedral, and decahedral shape structures, exposed different ratios of (001), (101) and (100) facets; the exposed facets affected their photocatalytic activity, especially in terms of mineralization efficiency and degradation pathways.¹¹⁴

Experiments combining computational methods were used to study the attack on the phenyl ring by [•]OH and [•]O₂⁻: the increased distance of adjacent sites was favorable to facilitate the attack by [•]O₂⁻ on the para position; so the surface structure may significantly influence the formation of products.¹¹⁴ Different TiO₂ nanostructures, such as nanotubes, nanorods,

nanofibers, nanospheres, and nanosheets with different exposed facets, were produced and showed different photocatalytic activity for VOC degradation.¹¹⁸ The respective functions of different crystal facets were explored in the reaction, as shown in Fig. 22(a–e). Photodeposited Au particles generated by AuCl₄⁻ reduction were distributed mainly on the (101) facet; while the photodeposited MnO_x formed by Mn²⁺ oxidation was predominantly distributed on the (001) facet, indicating that the photogenerated electrons tended to accumulate on the (101) facet, causing a reduction reaction; whereas photogenerated holes migrated preferentially to the (001) facet, causing an oxidation reaction; therefore, *p*-xylene was activated mainly on the (001) facet, while O₂ was activated predominantly on the (101) facet (Fig. 22(f)).¹¹²

Crystal planes with higher stability were preferentially exposed. TiO₂ with particular facets exposed can be achieved by reducing the surface energy. It had been proved that the anatase TiO₂ (001) facet showed higher photoreactivity. F-capping could induce the growth of a TiO₂ crystal along a specific axis, which led to the formation of particularly reactive (001) facets in anatase TiO₂. TiO₂ surface termination with F atoms led to the exposure of more (001) facets, and the percentage of (001) facets could be predicted if *c* values were provided.¹¹⁵ Adsorbed HF can create additional energy bands in the primordial band gap of pure anatase TiO₂, such as Ti³⁺ d-bands, narrowing the band gap.¹¹⁶ The residual fluoride adsorbed on the TiO₂ surface can form bonds with Ti atoms, improving the adsorption performance for O₂ and promoting charge carrier separation: the adsorption capacity of TiO₂ (001) facets for phenol was 1.68 times that of polycrystalline TiO₂, and the oxidation rate on the

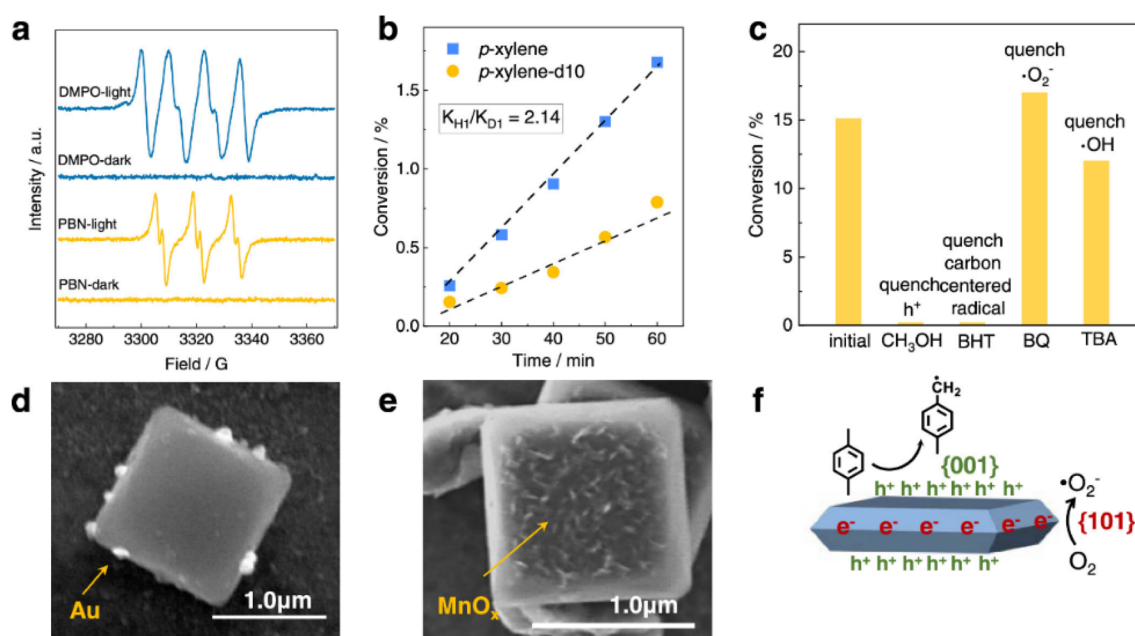


Fig. 22 (a) *In situ* EPR spectra of [•]O₂⁻ and carbon-centered radicals on (001)-exposed TiO₂. (b) KIE experiments of *p*-xylene photooxidation on (001)-exposed TiO₂. (c) The conversion of *p*-xylene in the presence of O₂ with the addition of scavengers contrasted to the general condition. SEM images of *in situ* photodeposited Au (d) and MnO_x (e) on TiO₂. (f) Schematic diagram of charge distribution on TiO₂ under irradiation.¹¹² Reprinted with permission from ref. 112 Copyright 2024, American Chemical Society.



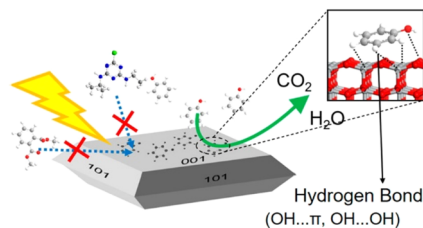


Fig. 23 Schematic diagram of phenol photocatalytic oxidation on 001-MI-TiO₂.¹¹³ Reprinted with permission from ref. 113 Copyright 2020, American Chemical Society.

TiO₂ (001) facet was 12.93 times that of polycrystalline TiO₂.¹¹⁷ The significantly increased removal of phenol could be ascribed to enhanced adsorption and photocatalytic performance (Fig. 23).¹¹³

5.3. Pore structure and specific surface area

The specific surface and pore structure significantly influenced photocatalytic activity, and the design of the specific surface area and pore structure of TiO₂ was a feasible method to enhance VOC photocatalytic degradation efficiency. There were many methods for preparing photocatalysts with high specific surface area and ideal pore structure, such as the hydrothermal method,¹²⁰ template method,¹²¹ and anodic oxidation method,¹²² and the template method was the most widely used. Pore structures, like macropores and mesopores, can hinder the agglomeration of photocatalysts and facilitate mass transfer, which can facilitate VOC molecules to make adequate contact with photocatalysts. Furthermore, the pore structure can also shorten the transmission distance of charge carriers, which is favorable for the separation of electrons and holes. Mesoporous TiO₂ was used for the photocatalytic degradation of xylenes: compared to TiO₂ nanoparticles, mesoporous TiO₂ showed better photocatalytic activity and stability.¹²³ The preparation route for a hierarchical flower-like Ag₃PO₄/TiO₂ heterojunction can be seen in Fig. 24. 0D/3D hierarchical Ag₃PO₄/TiO₂ showed excellent photocatalytic performance under solar light irradiation, which could be due to its unique hierarchical porous

structure, suitable size of Ag₃PO₄, the formation of type-II heterojunctions, and the high separation efficiency of photo-induced carriers.¹¹⁹

Generally, photocatalysts with larger specific surface areas provided more active sites, generating more active free radicals, which can decompose interacted VOC molecules. Specific surface area was related to the mean particle size of TiO₂: the particle size significantly affected TiO₂ photocatalytic performance, the specific surface area of TiO₂ nanoparticles was three times that of P25, and they showed excellent photocatalytic degradation efficiency. Trimesoyl chloride-melamine copolymer and TiO₂ nanocomposites were applied for the photocatalytic degradation of gas-phase benzene under visible light; the amide bonds of TMP decreased the size of TiO₂ nanoparticles, thus increasing the specific surface area of the photocatalysts, and the degradation efficiency for (TMP)-TiO₂, unmodified TiO₂ and P25 were 100%, 19% and 23.6%, respectively.¹²⁴ Titania microballs with different exposed facets (Fig. 25) composed of faceted nanoparticles were used for various photocatalytic applications, because of their high activity for both reduction and oxidation reactions and large size (favourable for recycling and commercialization).¹²⁰ The enhanced photocatalytic activity could be ascribed to mesoporous structure, higher specific surface area, extended light absorption and shortened mass transfer distance due to a thinner hollow shell structure with abundant pore channels.

5.4. Surface halogenation

Surface halogenation was related to the incorporation of halogens (F, Cl, Br, I) onto the surface of the photocatalyst to improve surface properties. The introduced H₂O molecules interacted with holes to generate [•]OH; at the same time, H₂O molecules would compete for adsorption sites with VOC molecules, which was adverse for VOC degradation.²⁹ Surface halogenation could adjust the surface hydrophilicity of photocatalysts. Surface fluorination was favorable for the generation of free [•]OH, although surface fluorination was adverse for TiO₂ to adsorb acetaldehyde; it would enhance the first-order rate constant for CO₂ production by 2.5 times.¹²⁵

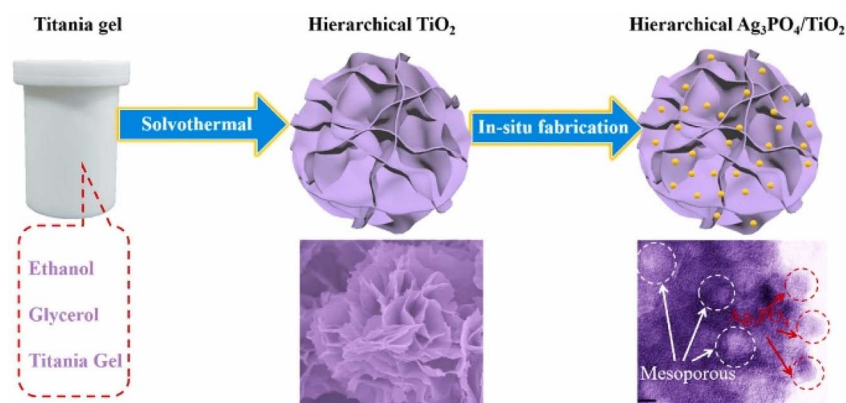


Fig. 24 Schematic of the prepared hierarchical flower-like Ag₃PO₄/TiO₂ heterojunction.¹¹⁹ Reprinted with permission from ref. 119 Copyright 2022, Elsevier.



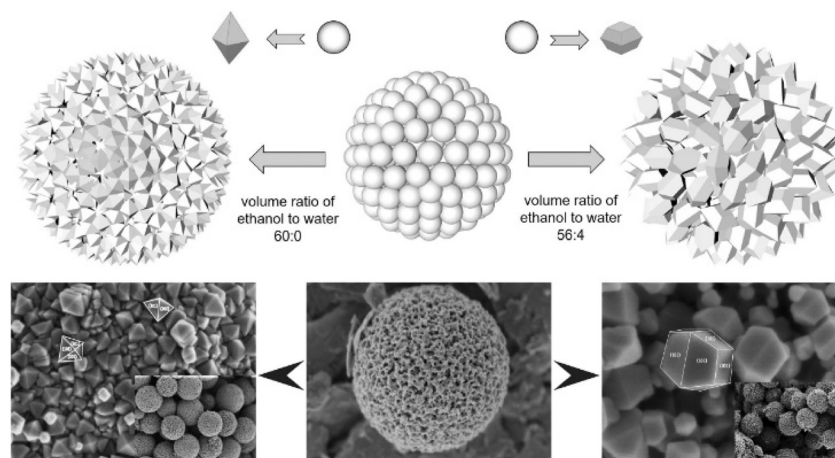


Fig. 25 (Top) Schematic illustration for the formation of a mesoporous microball composed of faceted anatase nanocrystals; (Bottom) respective FE-SEM images.¹²⁰ Reprinted with permission from ref. 120 Copyright 2024, Elsevier.

Surface-fluorination can also stabilize the (001) facets and promote the formation of anatase TiO₂ nanosheets.¹²⁶

As shown in Fig. 26, the O₂ adsorption energy, E_{ads} , for photocatalysts can be ordered as follows: TiO₂ (−0.346 eV) < F-TiO₂ (−0.607 eV) < TiO_{2-x} (−1.928 eV) < F-TiO_{2-x}(OV) (−1.956 eV) < F-TiO_{2-x}(FD) (−2.431 eV), indicating that F-TiO_{2-x} had the strongest O₂ adsorption capacity, and both F and OVs were favourable for oxygen adsorption. The ordered ability of O₂ molecules to accept electrons was: F-TiO₂ (0.03 eV) < TiO₂ (−0.11 eV) < F-TiO_{2-x}(OV) (−0.37 eV) < F-TiO_{2-x}(FD) (−0.40 eV) < TiO_{2-x} (−0.57 eV). Although the electron transfer ability and activation of O₂ molecules over F-TiO_{2-x} were lower than those of TiO_{2-x}, F-TiO_{2-x} (with more F-substituted oxygen sites and OVs) could adsorb more O₂ molecules, which could increase the generation of [•]O₂[−] and ¹O₂.²⁹ After TiO₂ fluorination, the adsorption capacity for toluene was enhanced by about two times under three different humidity conditions.²⁹ The total photocatalytic activity would also eventually be increased.

Many different explanations have been proposed to explain the surface fluorination mechanism to improve photocatalytic activity. Some studies proved that more [•]OH can be produced over surface-fluorinated TiO₂.¹²⁷ However, some studies proposed that surface fluorination can form Ti-F bonds on the TiO₂ surface, which can hinder the recombination of photogenerated electrons and holes.⁶⁹ F-modified TiO₂ was prepared *via* a plasma method; lattice F, ≡Ti-F bonds, and oxygen defects were found in F-doped TiO₂; ≡Ti-F bonds can efficiently facilitate the separation of electrons and holes, boost the production of [•]O₂[−] and [•]OH, and the band gap for treated TiO₂ can be reduced to 2.78 eV after lattice F doping.¹²⁸ However, excessive fluorination induced structural defects, which can serve as recombination centers for electrons and holes and hinder the transfer of interfacial electrons.

Besides surface fluorination, chlorination, bromination and iodination can also affect the photocatalytic activity of TiO₂. Three halogen hydric acids (HF, HCl and HBr) were used to

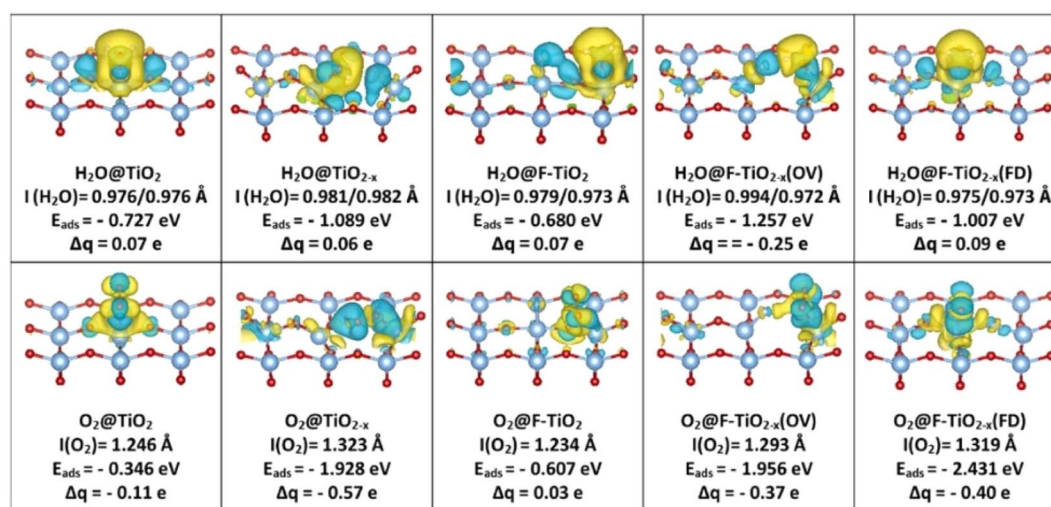


Fig. 26 Calculated adsorption and activation of O₂ and H₂O molecules on fluorinated TiO₂.²⁹ Reprinted with permission from ref. 29 Copyright 2022, Elsevier.



synthesize mesoporous TiO₂ nanosheets.¹²⁹ F, Cl or Br species on the surface of TiO₂ were confirmed by XPS; the kinds of halogenated acid affected the composition of crystalline phases: 100% anatase for TiO₂-I(HF), anatase/rutile phases for TiO₂-I(HCl), anatase/brookite phases for TiO₂-I(HBr).¹²⁹ Surface halogenation can narrow the band gap and lead to a red shift of the absorption edge, from 395 nm to 517 nm; with an increase in Br doping content, the band gap of Br-TiO₂ hollow spheres reduced from 2.85 eV to 1.75 eV; doping with an appropriate content of Br significantly improved the photocatalytic activity.¹³⁰ All in all, appropriate surface halogenation can improve TiO₂ photocatalytic activity.

5.5. Construction of a heterojunction

A heterojunction semiconductor can be obtained by coupling a semiconductor with another material, such as noble metals or other semiconductors. Many semiconductors have been used for the construction of heterojunctions, such as CdS,¹³³ ZnO,¹³⁴ SnO₂,¹³⁵ WO₃,¹³⁶ and SiO₂.¹³⁷ The energetic positions of the CB and VB edges of selected semiconductors vs. some standard half-reaction potentials can be seen in Fig. 27. The heterojunction can significantly facilitate the separation of photogenerated carriers, hinder carrier recombination, and extend the absorption threshold into the visible light region, which can be ascribed to the effective matching of the energy band structure.¹³¹ The two (or more) semiconductors of the heterojunction can form inherent electric fields, leading to a shift in individual Fermi level, and it finally settled at a uniform value.⁵¹ According to the types of semiconductors, the heterojunctions can be divided into p-p, p-n and n-n heterojunctions. The Fermi levels for p-type and n-type semiconductors were close to the VB and CB, respectively. Hole transfer occurred in p-p heterojunctions; the hole depletion layer was generated on one side, and the hole accumulation layer was generated on the other side, until the Fermi energy levels were equal,¹³⁸ building an internal electric field. Due to different potentials, electron transfer proceeded until the Fermi energy level reached equilibrium,¹³⁹ and p-n

heterojunctions can generate a built-in electric field, promoting charge separation (Fig. 28). After the Fermi energy level of an n-n semiconductor reached equilibrium through electron transfer, the Z-scheme mechanism would finally occur in photocatalysis.¹⁴⁰

There have been many methods for heterojunction preparation, such as the *in situ* hydrothermal method,¹⁴¹ *in situ* deposition,¹⁴² co-precipitation,¹⁴³ *in situ* calcination,¹⁴⁴ chemical vapor deposition,¹⁴⁵ and ball milling.¹⁴⁶ The lattice parameters and tetragonal structures of SnO₂ were similar to those of TiO₂; photoinduced electrons can transfer from TiO₂ to the SnO₂ CB; holes can transfer in the reverse direction; the TiO₂/SnO₂ heterojunction promoted charge carrier separation and suppressed their recombination.¹³⁵ Because the band gap of SnO₂ was larger than that of TiO₂, the light absorption spectra of the SnO₂/TiO₂ heterojunction led to a blue shift compared with TiO₂. The improved photocatalytic activity for the SnO₂/TiO₂ heterojunction could be due to the coexistence of rutile and anatase phases, reduced band-gap energy, increased active sites, and suitable content of OH⁻ groups on the SnO₂/TiO₂ surface.¹⁴⁷ After selective oxidation of toluene to benzaldehyde by S-scheme TiO₂/Bi₂WO₆ under visible light irradiation, the composites exhibited excellent photocatalytic performance: the benzaldehyde production rate was 1725.41 μmol g⁻¹ h⁻¹, 2.31 and 1.91 times higher than that of TiO₂ and Bi₂WO₆, respectively, where the excellent performance can be ascribed to the formation of a heterojunction by loading TiO₂ nanoparticles, improving the separation efficiency of photogenerated carriers.¹⁴⁸ For CdS-TiO₂, photogenerated electrons can transfer from the CdS CB to TiO₂ due to the less positive CB of CdS, while photogenerated holes of the TiO₂ VB can accumulate in the CdS VB and form a hole center, effectively reducing the charge carrier recombination rate, further improving the photocatalytic degradation efficiency for benzene.¹³³

TiO₂ and NH₂-MIL-125 could be excited under UV light, and the photoinduced electrons migrated to the NH₂-MIL-125 VB through interactions between TiO₂ and NH₂-MIL-125; then the

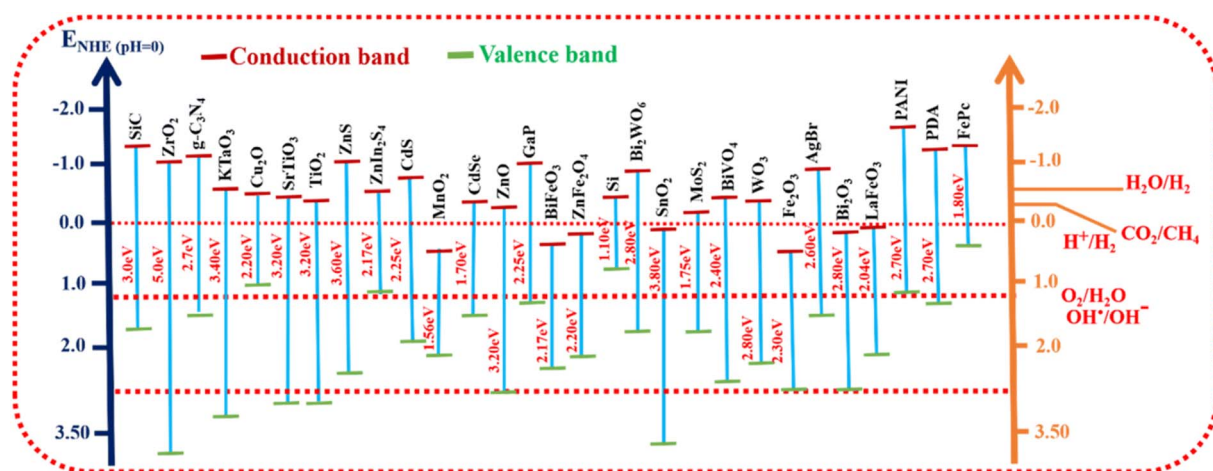


Fig. 27 Energy positions of the CB and VB edges of specific semiconductors vs. different standard half-reaction potentials.¹³¹ Reprinted with permission from ref. 131 Copyright 2024, Royal Society of Chemistry.



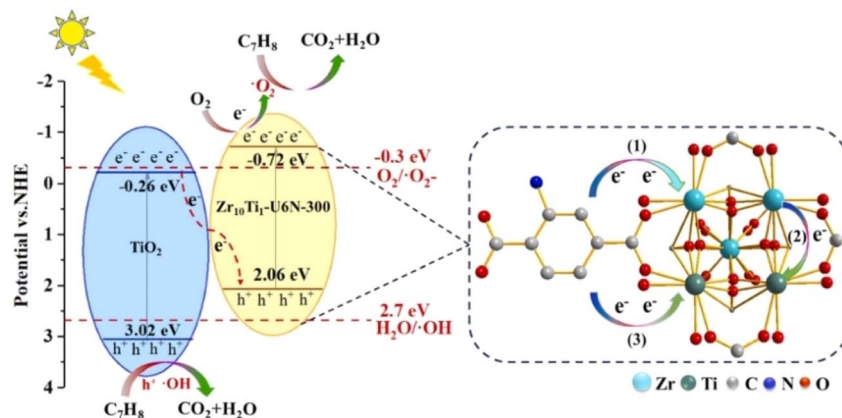


Fig. 28 Reaction mechanism for toluene photocatalytic oxidation over $Zr_{10}Ti_1-U_6N-300@TiO_2$.¹³² Reprinted with permission from ref. 132 Copyright 2025, Elsevier.

generated electrons migrated from the VB to the CB, while the holes remained at the TiO_2 VB, and the heterojunction interface provided an efficient electron transfer pathway.¹⁴⁹ The CB/VB of TiO_2 was $-0.24/2.86$ eV, while that for $NH_2-MIL-125$ was $-0.72/1.75$ eV, which, combined with the standard redox potentials of $OH^-/^{\bullet}OH$ (2.7 V vs. NHE) and $O_2/^{\bullet}O_2^-$ (-0.3 V vs. NHE) couples, meant that only holes from the TiO_2 VB could react with H_2O molecules to produce $^{\bullet}OH$.¹⁴⁹ While only electrons from the $NH_2-MIL-125$ CB could react with the adsorbed O_2 molecules to generate $^{\bullet}O_2^-$, HCHO was oxidized to H_2O and CO_2 by these ROSs.¹⁴⁹ However, there were several setbacks hindering the application of heterojunctions, such as different lattice structure constants or atomic thermal expansivity, which can lead to distortion of the interfacial lattice, where lattice distortion can promote the recombination of the charge carriers.¹⁵⁰

5.6. Construction of a homojunction

Homojunction photocatalysts were prepared from materials with the same chemical composition but various band structures or crystal phases, where various band potential values of components formed a spatial charge layer at the homojunction interface.¹⁵⁰ Similar to heterojunctions, the construction of homojunctions can change the relative position of the energy band, the built-in electric field can transfer photogenerated carriers to the reverse direction, and the matching chemical and electronic structure of homojunctions are favorable for the separation and transfer of carriers (Fig. 29).¹⁵³ There was virtually no mismatch in homojunction lattices, and the same components on both sides of the homojunction interface could also avoid a discontinuity of band bonding.¹⁵⁰ Generally, homojunction photocatalysts are divided into two types: p-n junctions and n-n junctions. TiO_2 -based homojunctions could be constructed in many different forms, like different dimensions (nanoparticles, nanobelts, nanosheets), crystal phases (anatase, rutile and brookite), crystal facets or morphologies, which can exhibit beneficial synergistic effects in the photocatalytic reaction.

TiO_2 -based homojunctions were commonly constructed by merging TiO_2 with different crystal phases, and the electron

bridge between different TiO_2 polymorphs can facilitate electron transfer;¹⁵⁵ therefore, the electrons generated on anatase CB jumped easily to less positive rutile, hindering the recombination of electrons and holes in anatase sites.¹⁵⁶ Fig. 30 shows the band gap energies of anatase, rutile, and brookite TiO_2 , with mixed phases showing better photocatalytic activity than TiO_2 with a pure anatase phase. For mixed-phase TiO_2 , the oxidation and reduction processes could be accelerated, because the oxidation process was limited in the anatase structure and the reduction process was limited in the rutile structure. The increased activity can be generally attributed to the interaction of the two forms, so this mixed phase with interfacial electron trapping sites can enhance the photocatalytic activity of TiO_2 .¹⁵¹

Homojunctions with various dimensions, morphologies or facets, like quantum dots (0D)/nanosheets (2D), and nanobelts (1D)/nanosheets (2D), were prepared.¹⁵⁰ TiO_2 QDs were loaded onto the surface of TiO_2 nanoparticles; the electrons were redistributed at the interface of TiO_2 QDs and TiO_2 nanoparticles, which facilitated hole accumulation on the side of TiO_2 QDs, while electrons accumulated at TiO_2 nanoparticles, notably promoting charge separation and interfacial transfer; TiO_2 QDs and adjacent TiO_2 nanoparticles generated

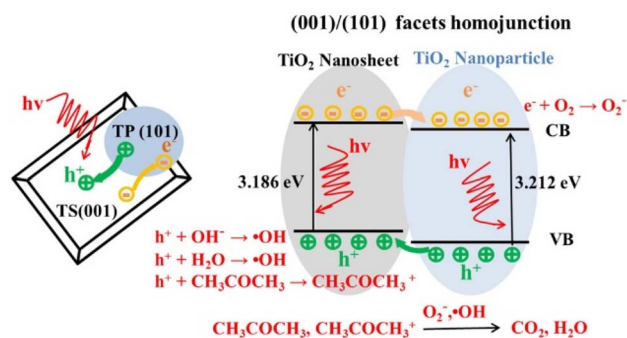


Fig. 29 Illustration of the synergistic effect of the homojunction of anatase TiO_2 nanoparticles (TP) with dominant (101) facets and nanosheets (TS) with dominant (001) facets.¹⁵³ Reprinted with permission from ref. 153 Copyright 2019, Elsevier.



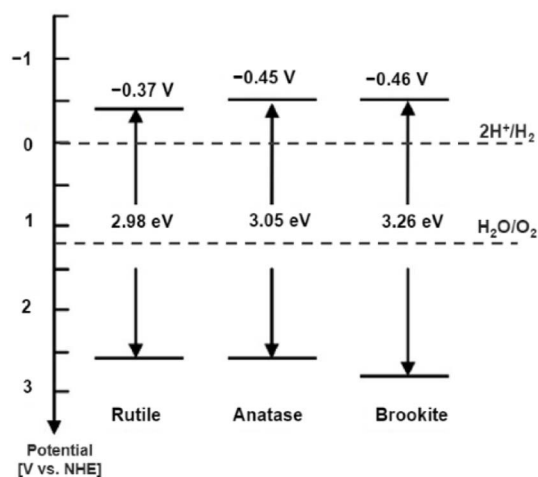


Fig. 30 Band-gap energies, VB, and CB for anatase, rutile, and brookite on the potential scale (V) versus the normal hydrogen electrode (NHE).¹⁵¹ Reprinted with permission from ref. 151 Copyright 2023, MDPI.

a quantum-scale catalytic area, which significantly increased the toluene mineralization efficiency to 95.8% over QD-loaded TiO₂.¹⁵⁷ For a rutile TiO₂ nanorod@nanoparticle homojunction, the CB of the rutile TiO₂ nanoparticle could be elevated *via* a quantum effect, and absolute charge separation could be realized through long-distance transfer of electrons along the single-crystalline nanorod.¹⁵⁸ Moreover, nanoparticles embedded onto a nanorod roughened the smooth surface,

promoting light absorption and generating more charge carriers. The nanorod@nanoparticle homojunction showed notably enhanced photocatalytic performance for benzene decomposition—the CO₂ yield was 10 times that of a nanorod array—where the enhanced photocatalytic activity could be attributed to higher photo-to-electron conversion efficiency and effective charge separation.¹⁵⁸ When microporous TiO₂ was loaded onto the surface of anatase TiO₂, the homojunction notably enhanced photogenerated carrier separation efficiency; it could also form microporous structures and an enlarged surface area, favorable for the concentration of toluene and intermediates near the photocatalytic sites; and the toluene mineralization efficiencies of the homojunction were 1.78 and 2.12 times higher than those of microporous TiO₂ and anatase TiO₂.¹⁵⁹

The concept of a facet heterojunction was also proposed, indicating that the energy band structures and band edge locations were different for different facets (3.18 eV for the (001) facet, 3.22 eV for the (101) facet, and 3.23 eV for the (010) facet) (Fig. 31); therefore, different facets can be used to form surface heterojunctions.¹¹⁷ The crystals with (001) and (010) facets exposed were favorable for a photo-oxidative reaction due to the high density of Ti_{5c} sites, and the crystals with (101) and (010) facets exposed were favorable for a photo-reductive reaction because of the higher energy of electrons at the CB minimum, as shown in Fig. 29 and 32. Anatase TiO₂ nanoparticles predominantly exposing (101) facets (TP) were loaded onto anatase TiO₂ nanosheets predominantly exposing (001) facets (TS) to form a TP/TS junction (Fig. 33).¹⁵³ TEM images of TP/TS

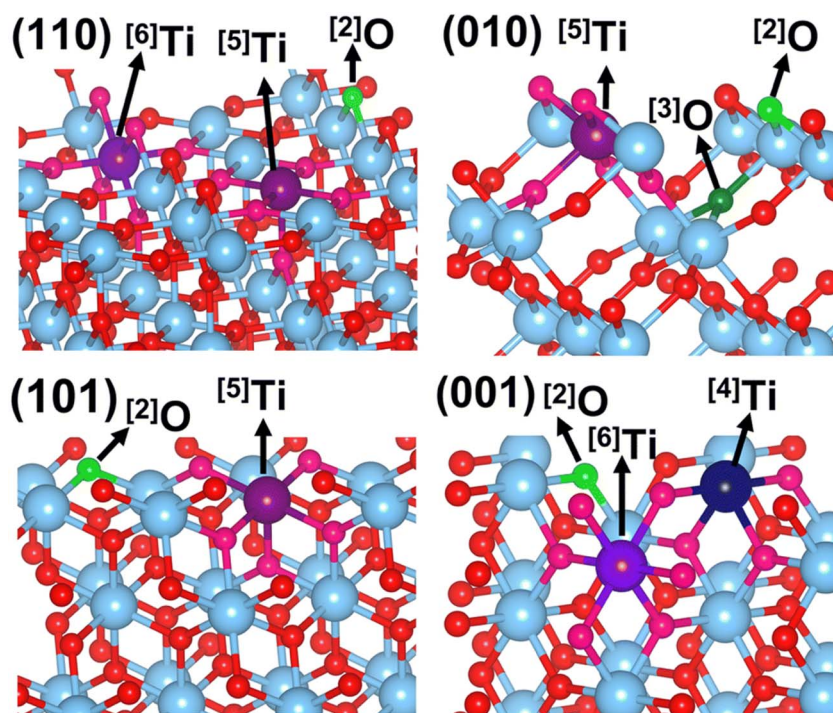


Fig. 31 Rutile (110), (010), (101), and (001) facets and surface atom coordination (bright green [2]O, dark green [3]O, and dark blue [4]Ti, dark purple [5]Ti, light purple [6]Ti) on each. Red atoms are O and light blue are Ti.¹⁵² Reprinted with permission from ref. 152 Copyright 2023, Royal Society of Chemistry.



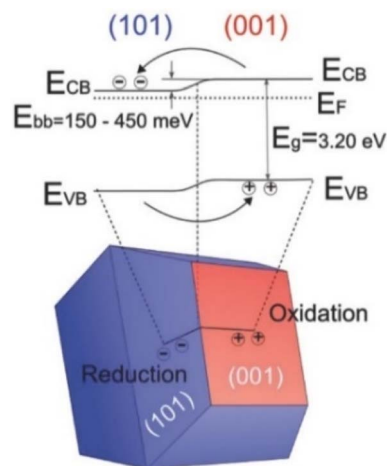


Fig. 32 Interfacial band bending and charge carrier spatial separation over anatase crystallites with both (001) and (101) facets exposed.¹⁵⁴ Reprinted with permission from ref. 154 Copyright 2018, John Wiley and Sons.

(2.5%), TP/TS (5%) and TP/TS (10%) can be seen in Fig. 33. For a TP/TS homojunction, holes in the VB of TiO₂ nanoparticles transferred to the VB of TiO₂ nanosheets, while electrons from the CB of TiO₂ nanosheets transferred to the CB of TiO₂ nanoparticles; during acetone degradation over optimized TP/TS (5%), CO₂ production rates were 5.4, 4.0 and 3.3 times higher than those over TP, TS and P25.¹⁵³

6. Immobilization of photocatalysts

6.1. Immobilization method

For the practical application of photocatalysis for VOC degradation, the photocatalysts should be immobilized onto supports, and it was found that TiO₂ film showed higher catalytic activity than most TiO₂ powders. The main functions of loading photocatalysts onto supports were as follows: (1) enhancing dispersion and specific surface area; (2) facilitating photogenerated carrier separation; (3) strengthening light absorption capacity; (4) improving stability and recyclability; (5) simplifying recovery and practical application; (6) synergistic catalytic effect with photocatalysts. Various methods were applied for TiO₂ immobilization, like sol-gel, chemical/physical vapor deposition, electrophoretic deposition, and thermal spraying; then the photocatalyst layer was usually treated under high-temperature calcination to obtain TiO₂ with high crystallinity and be strongly adhered on supports.¹⁶⁷

Immobilization methods can be divided into two types. The first was to treat photocatalyst powders *via* directly dip-coating or sintering (sometimes called wash-coating).¹⁶⁸ The other method was to load TiO₂ film onto the supports with various methods, like sol-gel, chemical vapor deposition (CVD), metal-organic CVD (MOCVD), and spray coating.¹⁶⁹ Thermal treatments were technically simple, but there was a significant barrier to practical preparation for scaled-up reactors, since they consumed abundant energy, which may increase the overall cost. The successful exploitation of a room-temperature

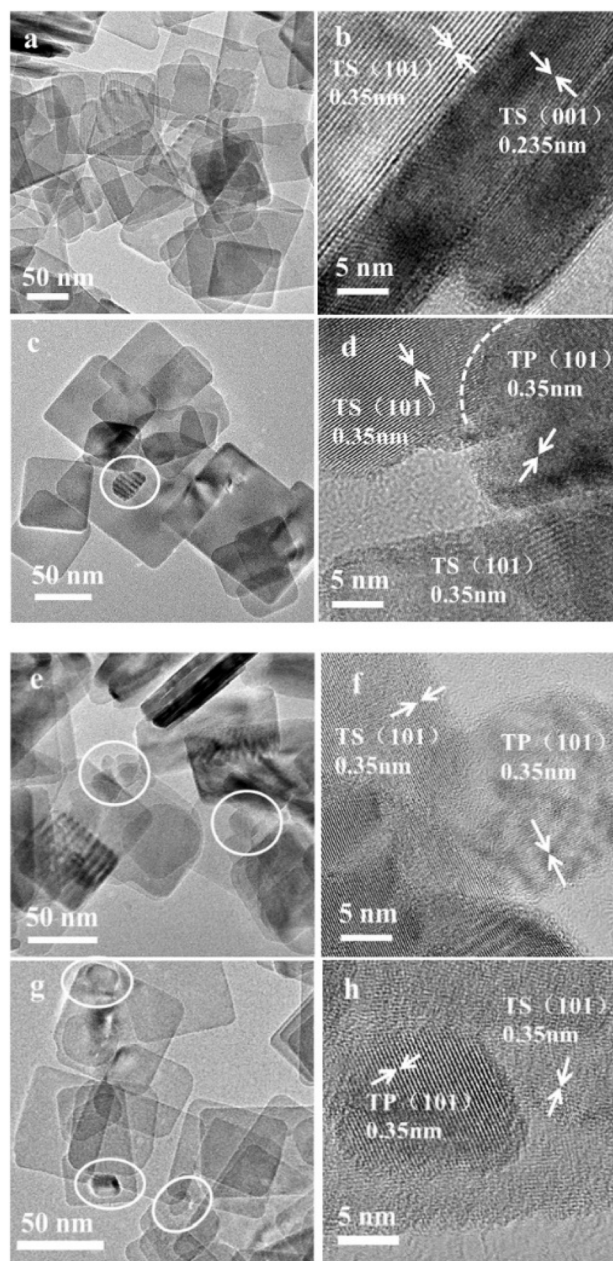


Fig. 33 TEM and HRTEM of TiO₂ homojunction with different ratios of TP/TS: TS (a and b), TP/TS (2.5%) (c and d), TP/TS (5%) (e and f), TP/TS (10%) (g and h).¹⁵³ Reprinted with permission from ref. 153 Copyright 2019, Elsevier.

immobilization method would be a breakthrough in promoting practical applications of photocatalysts.¹⁶⁷ A desirable immobilization method should possess the following characteristics: (1) durable and stable immobilization; (2) sufficient contact between photocatalyst and pollutant; (3) non-selectivity for various substrates; and (4) suitability and effectiveness for large-scale application.⁶³ Choosing an appropriate preparation and immobilization method to immobilize the photocatalyst is very important for improving photocatalytic efficiency.

Sol-gel was a wet-chemical method, where precursors were suspended in liquid phase, then put under gel conditions until



the photocatalyst film (sol-gel) became dehydrated.³⁵ Various methods have been used to load precursor solution on supports to form the photocatalyst film. Drying time was required to remove the solvent, and then the photocatalyst was substantially loaded on the support after densification and shrinkage, when thermal treatment was necessary to densify the photocatalyst layer. Vanadium and nitrogen co-doped TiO₂ was loaded on the honeycomb ceramics of continuous-flow photocatalytic degradation reactors, and the introduction of V/N dopants narrowed the band gap and widened the light absorption range of TiO₂, resulting in continuous and nearly-complete toluene photocatalytic degradation, where the degradation efficiency for toluene gas could reach 97.8%.¹⁷⁰

The chemical vapor deposition technique was also used to prepare TiO₂ film. The precursors were transformed into vapor and injected into a chamber, where an anatase TiO₂ layer was loaded onto the substrate by the corresponding reaction, and they were used for the photocatalytic degradation of benzene.¹⁷¹ TiO₂ thin films with specific crystal structure, high crystallinity, high porosity and high surface area can be obtained using this method. Physical vapor deposition was a simple and eco-friendly method to immobilize TiO₂ onto supports, because it required no harsh chemicals or residual solvents. Molecules from a target material were ejected onto substrates to form TiO₂ thin film, and films prepared by physical vapor deposition exhibited improved photocatalytic activity compared to conventional TiO₂ films.¹⁷²

Electrochemical deposition was a feasible method, in which the main ions in an electrolyte could participate in an electrochemical reaction under particular conditions to load target products onto the gap of a photonic crystal which was used as an electrode.¹⁷³ The gap of the template could be filled with parent material, and the exact reverse replica could be easily obtained from the original opal template.¹⁷³ Electrochemical deposition was also used for coating a photocatalyst, where a three-dimensional polymer, SU8, was used as a template, and a sol-gel of TiO₂ fully filled the polymer template through electrochemical deposition, so a photonic crystal with reversed structure could be obtained.¹⁷⁴ Electrophoresis was a suitable method for covering a variety of materials on electrically conductive surfaces with two electrodes, where the powder was used as the solvent solution for depositing photocatalysts. Additives (like acetylacetone and isopropanol) were usually applied to improve the conductivity of the suspension, which could make the consequent coating more uniform and stable.

Spray-coating and dip-coating were simple and low-cost methods used for coating photocatalysts. Initially, photocatalysts were dispersed in a suitable solvent, such as methanol or ethanol, which were then sprayed on the substrate, and the photocatalysts were immobilized onto the substrate after solvent evaporation. Aerosol-assisted technologies, like spray atomization (SA), spray gun (SG) and spray-drying (SD), were applied for TiO₂ deposition onto fibrous filter media. A TiO₂ layer deposited by SG and SA methods showed excellent photocatalytic performance for the degradation of toluene, while a TiO₂ layer deposited by SD showed poor photocatalytic performance and stability.¹⁷⁵ TiO₂ was dispersed in ethanol

solvent to form a slurry, and then sprayed onto a glass plate by an aero spray, and TiO₂ immobilization could be achieved after drying at room temperature.⁴⁵ In some research, additional chemical binders were also used to strongly and uniformly immobilize the photocatalysts onto the substrate.⁴⁶ However, the photocatalytic activity may decrease because of the reduced available surface area caused by chemical binders. Thermal spraying can quickly immobilize photocatalysts onto substrates, but a higher temperature used for spraying may change the photocatalyst crystal structure and finally decrease its photocatalytic activity.

Interfacial polymerization was also used for immobilizing photocatalysts onto the substrate. The interfacial polymerization reaction was usually carried out between two different monomers (water hating and water loving) at the oil-water interface. Nylon/TiO₂ was immobilized onto polysiloxane-coated paper *via* interfacial polymerization.¹⁶⁶ Tetraethyl orthosilicate and 3-aminopropyltrimethoxysilane (as silane coupling agent) were used to synthesize polysiloxane-coated paper, and cationic TiO₂ was combined with anionic polysiloxane-coated paper *via* electrostatic interactions. The paper showed excellent degradation performance for acetaldehyde, and the structure of photocatalyst layer remained unchanged for 240 h under UV light illumination.¹⁶⁶

6.2. Substrate type

The type of substrate influenced PCO performance, where the low adsorption capacity of TiO₂ could be improved by constructing composites with substrates, and VOCs could be adsorbed on the substrates, forming a high-concentration environment of VOCs around the loaded TiO₂, enhancing the photocatalytic reaction rate.¹⁷¹ The physical and chemical characteristics of the substrates should be stable in photochemical oxidation reactions, and the surface area of the substrates should be high enough to load photocatalysts. Other essential characteristics of the substrates were sufficient adhesion to TiO₂ particles, strong adsorbability with VOCs, and resistance to sintering temperature. Various materials, like activated carbon fibers,¹⁷⁷ carbon nanotubes,¹⁷⁸ glass,⁸⁴ glass fibers,¹⁷⁹ fiberglass fibers,¹⁸⁰ polymeric materials,¹⁶⁸ zeolites,¹⁷⁶ and stainless steel,¹⁸¹ have been used as substrates (Table 1).

Activated carbon with high porosity can create a high specific surface area and improve the photocatalytic activity of hybrid photocatalysts. Carbonized cotton fibers (CCFs) showed great resistance to corrosion and temperature, and the conductivity and strength of CCFs were high enough for photocatalysis, so they were alternative supports for TiO₂.¹⁷⁷ When nanostructured TiO₂ was immobilized on ACFs, TiO₂/ACFF was used for toluene degradation, and the removal efficiency increased from 41% (for TiO₂ power) to 97% (for TiO₂/ACFF), which could be ascribed to hindered electron-hole pair recombination and reduced band-gap energy by ACF.¹⁸²

Glass and silica substrates were transparent, and were widely used for the immobilization of photocatalysts. Furthermore, glass fibers were simpler to treat than other supports due to their high flexibility; when Fe-doped TiO₂ was immobilized on



**Table 1** Different deposition methods and types of support for photocatalyst preparation

| VOCs | Immobilization method | Features | Photocatalyst/support | Removal efficiency | Reference |
|------------------|---------------------------------------|---|--|---|-----------|
| Benzene | Dip coating | The loading amount can be flexibly controlled to promote interface contact and retain carrier structure, but the active component was unevenly distributed, and the loading amount was limited | g-C ₃ N ₅ -coupled TiO ₂ /ceramic balls | 93.9% (1 ppm, UV light, 20 min) | 160 |
| Toluene | Physical coating | Retaining the intrinsic properties of the material, flexible and controllable, low cost, but poor stability, and uneven contact | Anatase and bronze phase TiO ₂ /stainless steel disk | 97% (100 ppm, UV light, 60 min) | 161 |
| Acetaldehyde | Drop casting | Little interference with material properties, controllable load and thickness, strong substrate compatibility, but weak binding force and poor uniformity | Mesoporous TiO ₂ /dry glass slides | 82% (77 ppm, UV light, 250 mL min ⁻¹) | 162 |
| Toluene | Step-by-step electrospinning–spraying | The multi-level structure optimizes mass transfer and light utilization, flexible regulation of load, balance of activity and stability, but a risk of interface bonding and high cost | TiO ₂ /non-woven fabrics | 93% (78 ppm, UV light, 240 min) | 163 |
| HCHO | Pulp coating | Intrinsic properties of the catalyst were retained, the load was flexibly controlled, substrate compatibility was strong, but the binding force was weak, so it easily fell off, and the distribution uniformity was poor | Na/@TiO ₂ (B)-O _v /filter membrane | 80% (65 ppm, visible light, 100 mL min ⁻¹) | 164 |
| <i>m</i> -Xylene | Solvent deposition | Simple operation, needs no thermal treatment, can form on any complex substrate, but high cost of the precursor and not suitable for large-scale preparation | TiO ₂ /glass plate | ~96.0% (1000 ppm, UV light, cyclic 200 mL min ⁻¹) | 165 |
| Acetaldehyde | Interfacial polymerization | No usage of binding agent, regulated interface structure, stable structure, but high cost | TiO ₂ /nylon film | ~100% (250 ppm, UV light, 240 min) | 166 |

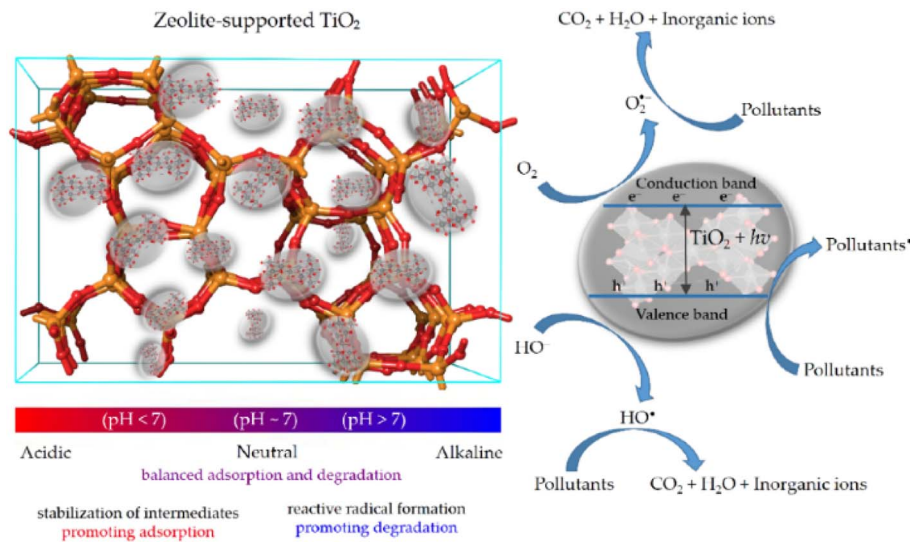


Fig. 34 Schematic illustration of photocatalysis mechanism for TiO_2 -zeolite composite.¹⁷⁶ Reprinted with permission from ref. 176 Copyright 2025, MDPI.

glass fiber, it showed excellent VOC photocatalytic removal efficiency under both UV light and visible light irradiation.¹⁷⁹ TiO_2 was immobilized on fiberglass fibers (FGFs), TiO_2 /FGFs showed hydrophilic characteristics and higher adsorption ability for polar VOCs than for non-polar VOCs under the same RH levels, which enhanced photocatalytic oxidation efficiency for VOCs.¹⁸⁰ TiO_2 was immobilized onto porous polyurethane and used for the photocatalytic removal of toluene with visible light, where immobilization improved both the photocatalytic oxidation and adsorption performance of TiO_2 .¹⁷⁰

Zeolites with high surface area, a crystalline framework, and well-defined pore structure showed selective adsorption of organic and inorganic pollutants, which could effectively concentrate them near photocatalytic sites of TiO_2 , and the reaction efficiency was significantly increased *via* a “pre-concentration effect”, where the pollutants were more easily available for photocatalytic degradation, and zeolite-supported TiO_2 composites promoted the formation of ROS, such as $\cdot\text{OH}$, which were crucial for the degradation of organic pollutants (Fig. 34).¹⁷⁶ Functional substrates were also used for immobilizing photocatalysts, such as metal-organic frameworks (MOFs), where MOF substrates could work as photosensitizers to realize efficient light harvesting and provide more active sites for photocatalysis, thus improving VOC photodegradation.¹³²

7. Summary and perspectives

TiO_2 -based photocatalytic oxidation technology is promising for the purification of indoor VOCs, which could effectively degrade VOCs to CO_2 and H_2O at room temperature, and the development of a high-efficiency photocatalyst is crucial for this technology. However, limitations, like fast recombination of charge carriers, low quantum efficiency, poor visible light photocatalytic activity, and catalyst deactivation, have limited their

practical application. This review has thoroughly summarized the methods for improving the photocatalytic purification of indoor VOCs from the perspective of TiO_2 modification, based on some intrinsic characteristics of VOCs, such as metal and non-metal doping, coupling of different semiconductors, surface/interface design, and TiO_2 immobilization.

Future trends in PCO purification for indoor VOCs include the development of highly stable and efficient photocatalysts, hydrophobic photocatalysts to hinder the negative effects of water vapor on PCO, novel PCO reactors with a UV-LED source, hybrid technologies (such as photothermal and photoelectric catalysis), catalysts and equipment for VOC degradation in scale-up. Furthermore, under actual conditions, such as a mixture of VOCs, sub-ppm levels of VOCs and high moisture content, the performance and economy of the novel air purification units should also be critically evaluated. This review could offer guidance for the development of TiO_2 -based photocatalysts for the efficient purification of indoor VOCs.

Author contributions

Lian Yu: investigation, methodology, formal analysis, supervision, writing – review & editing. Yajing Duan: writing – review & editing. Dabin Wang: investigation, methodology, formal analysis, validation, review & editing. Zhen Liang: formal analysis, writing – review & editing. Cunzhen Liang: project administration, resources, supervision, visualization. Yafei Wang: project administration, resources, validation, visualization.

Conflicts of interest

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



Data availability

There is no additional data associated with this article.

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