

Mineral-Supported Photocatalysts

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Although they are of significant importance for environmental applications, the industrialization of photocatalytic techniques still faces many difficulties, and the most urgent concern is cost control. Natural minerals possess abundant chemical inertia and cost-efficiency, which is suitable for hybridizing with various effective photocatalysts. The use of natural minerals in photocatalytic systems can not only significantly decrease the pure photocatalyst dosage but can also produce a favorable synergistic effect between photocatalyst and mineral substrate. Owing to their unique structures, large surface area, and negatively charged surface, silicate minerals could enhance the adsorption capacity, reduce particle aggregation, and promote photogenerated electron-hole pair separation for hybrid photocatalysts. Moreover, controlling the morphology and structure properties of these materials could have a great influence on their light-harvesting ability and photocatalytic activity. Composed of silica and alumina or magnesia, some silicate minerals possess unique orderly organized porous or layered structures, which are proper templates to modify the photocatalyst framework. The non-silicate minerals (referred to carbonate and carbon-based minerals, sulfate, and sulfide minerals and other special minerals) can function not only as catalyst supports but also as photocatalysts after special modification due to their unique chemical formula and impurities. The dye-sensitized minerals, as another natural mineral application in photocatalysis, are proved to be superior photocatalysts for hydrogen evolution and wastewater treatment.

Keywords: photocatalysis ; photocatalysts ; natural mineral photocatalytic supports ; synergistic effect ; wastewater treatment ; dye photodegradation ; composite photocatalysts

1. Introduction

As environmental pollution issues have taken place more and more frequently in recent years, sustainable development has become the leading target of energy and environmental policy-making worldwide, determining the public concern for scientific research. Since the TiO_2 -based water-splitting phenomenon was discovered by Fujishima and Honda in 1972, photocatalysis has stepped onto the solar energy conversion stage ^[1]. Many researchers have verified the extensive potential of TiO_2 in the photodegrading of different pollutants, such as bisphenol A ^[2], tetracycline ^[3], gaseous formaldehyde ^[4], *S. aureus* ^[5], etc. As a result, photocatalysis is widely regarded as the most promising route to solve both the energy and pollution crises. Several common photocatalysts have been found to possess excellent photocatalytic performance for the degradation of toxic dye and organic pollutants, including ZnO ^{[6][7]}, In_2O_3 ^[8], $\text{g-C}_3\text{N}_4$ ^[9], BiOBr ^[10], etc.

However, large-scale industrial applications of pure photocatalysts often suffer several key issues: (1) small specific surface area and resultant poor adsorptive ability; (2) easy photo-generated electron-hole recombination and resultant low quantum efficiency; (3) difficult solid-liquid separation and photocatalyst recycling; and (4) high cost. For example, CdS has superior visible-light absorption and photocatalytic activity ^[11], while it suffers severe photo-corrosion issues and easily causes secondary pollution problems. Although TiO_2 has stable and superb photocatalytic performance, it is only UV-light responsive and hard to recycle ^[12]. Additionally, self-aggregation and high photogenerated electron-hole recombination rates are the other common issues that the purest photocatalysts encounter. Researchers have been trying many different modification strategies to address these problems. So far, several modification strategies have been developed to control the photocatalyst morphology and suppress photo-induced charge carrier recombination, including heterojunction design, noble-metal deposition, support composites, etc. ^{[13][14][15]}. Among these modification strategies, the support composite is the most promising method to overcome the photocatalyst recycling difficulty and thus realize the industrialization of photocatalysts. Common photocatalyst support materials are carbon nanotubes, mesoporous carbon, graphene graphite, zeolite, etc. While these carbon materials generally exhibit more regular morphology and better electrical properties, they are not the ideal support candidates for photocatalyst industrial development considering their cost and recycling issues. Natural minerals are generally defined as abundant natural resources on earth that are obtained directly from nature. Compared with other support materials, natural minerals are well known as suitable photocatalyst support candidates for the following reasons: (1) They are environmentally friendly, low cost, chemical

resistant, mechanically stable, easily available, and do not cause secondary pollution to the environment; (2) natural minerals have the characteristics of a large specific surface area, providing more active centers and adsorbing pollutants to concentrate catalysis; (3) natural minerals are also excellent photocatalysts, such as ilmenite and pyrite, which play a good role in the degradation of water pollutants. More importantly, the combination of photocatalysts and natural minerals has become one of the most valuable modification strategies due to the vast availability and cost-effectiveness of natural minerals.

2. Photocatalyst Modification Methods

Essentially, photocatalysis is a particular catalysis type involving light absorption by several specific active species [16]. For example, a novel inorganic–organic TiO_2 -g- C_3N_4 composite could be excited under visible light ($\lambda \geq 400 \text{ nm}$) irradiation, activating the electron (e^-) transfer from the valence band (VB) to the conduction band (CB) [17]. In this case, the photo-induced holes of TiO_2 could be attracted to the facet-coupled interface between TiO_2 and g- C_3N_4 due to the internal static electric fields of TiO_2 , and then transferred to VB of g- C_3N_4 , oxidizing RhB directly. Meanwhile, the photo-induced electrons of g- C_3N_4 transfer to TiO_2 due to the higher CB potential, reacting with the adsorbed O_2 into superoxide radicals ($\bullet\text{O}_2^{-1}$).

2.1. Ion Doping

Doping is one of the most frequently applied methods to effectively extend the light absorption range of semiconductors via directly altering the bandgap structure [18]. Generally, TiO_2 photocatalysts could be doped with metal and non-metal dopants to enhance their photocatalytic activity [19][20][21]. For example, cobalt-doped TiO_2 samples synthesized via one-step hydrothermal method varied the cobalt dopant concentration from 0.1% to 3.0% to expand its optical response to the visible light region [22]. The photocatalytic phenol degradation reaction reached the highest degradation rate (81.72%) when the cobalt-doped amount was fixed at 0.3%. First principle calculation results indicate the density of the impurity state strengthens with increased dopant concentration, which is beneficial for the visible light absorption range extension and the enhancement of its photocatalytic efficiency. Additionally, the doped ions can also act as shallow traps to promote photoinduced electron-hole separation. However, when the doping concentration exceeds by too much, these doped ions are contrarily exchanged into photo-excited electron-hole recombination centers. Another work found that nitrogen ions could substitute the oxygen lattice of the TiO_2 matrix, therefore narrowing the band gap and shifting the absorption edge to the visible light region [23]. The BET surface areas of N- TiO_2 and N- TiO_2/C nanocomposite were calculated to be 101.4 and 131.6 m^2/g , higher than that of TiO_2 (87.7 m^2/g).

In order to process acidic gas pollution such as CO_2 and NO_x , special ions, namely alkali or alkaline earth metal ions, are incorporated into photocatalysts for better acidic gas adsorption capacity. For example, alkali (Na, K, Rb, and Cs) or alkaline earth metals (Mg, Ca, Sr, and Ba) were selected to modify anatase TiO_2 photocatalyst and investigate their effect on low-temperature NO_x trapping efficiency [24]. It was proved that the NO_x storage capacity is positively related to the amount of the modified metal species, and Cs- TiO_2 and Ba- TiO_2 have similar capacities (179 and 187 $\mu\text{mol}\cdot\text{g}^{-1}$, respectively), which is higher than that of conventional NO_x -trapping catalysts. According to in situ diffuse reflectance infrared Fourier transfer (DRIFT) spectra results, adsorbed NO_x species were trapped on the Ti sites of alkaline earth-doped TiO_2 and the alkali sites of alkali-doped TiO_2 , while NO_x trapped on Ti sites was found to be more efficient than on other sites for its excellent photocatalytic oxidation ability.

2.2. Noble-Metal Deposition

Coupling with one or more noble metal nanoparticles, such as Pt, Au, Ag, and Pd, is another well-developed surface modification approach. First of all, the noble metal nanoparticles function as electron traps and realize the rapid electron migration from photocatalyst to metal nanoparticles through the Schottky barrier formed at the interface between the semiconductor and the noble metals. The surface plasma resonance properties of noble metals can promote photocatalyst excitation under visible light and thus facilitate interfacial electron transfer [25]. Furthermore, the Fermi levels of the noble metal nanoparticles are generally lower than the CB of TiO_2 ; therefore, the band gap structure could be modified. For instance, four noble metals (Pt, Pd, Ag, and Au) were loaded onto the TiO_2 surface, and it was found that photoactivity of the noble metal-deposited TiO_2 increased with the amount of noble metals [26]. Among these metals, 0.2 wt% Ag-deposited TiO_2 exhibited the highest phenol degradation rate ($0.51 \mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$) under 60 min visible light irradiation, which is five times that of pure TiO_2 . It is pointed out that Ag nanoparticles are deposited on the {101} crystal facet of anatase TiO_2 according to TEM analysis, which results in decreasing photoinduced electron-hole recombination and visible light absorption extension via acting as electron traps and the surface plasma resonance effect.

2.3. Heterojunction Design

Heterojunction construction is one of the most commonly applied and effective surface modification approaches, coming from the combination of two or more semiconductors with different VB and CB positions and the resultant narrower band gap structure. The referred heterojunction is the type-II heterojunction and could be classified into four types such as the conventional type-II heterojunction, P–N junction, surface heterojunction and direct Z-scheme heterojunction, depending on the charge carrier separation mechanism [27]. Generally, the photocatalytic activity of TiO₂ could be enhanced by designing a heterojunction structure with several oxides and non-oxide materials [28][29][30]. For example, g-C₃N₄/TiO₂ heterojunction composite was synthesized via the in situ hydrothermal method, and the obtained band gap energy was proved to be 2.8 eV compared with 3.0 eV of TiO₂ [31]. The g-C₃N₄/TiO₂ sample with a mass ratio of 1:4 exhibited the maximum hydrogen evolution rate (1041 $\mu\text{mol}/(\text{g}\cdot\text{h})$) under visible light irradiation, which could be attributed to the heterojunction formation and its spatial charge separation effect. The XPS valence spectra results confirm the interaction between g-C₃N₄ and TiO₂ as type-II heterojunction, and the mechanism for photocatalytic performance improvement is explained such that the electron migration from VB of g-C₃N₄ to CB of TiO₂ via C–O–Ti bonding can offer electrons more photocatalytic reaction time. TiO₂ is known as a typical n-type semiconductor and can be used to construct p–n heterojunctions by combining it with a p-type semiconductor. As a result, BiOI was selected to couple with TiO₂, and it was found that the 20% BiOI/TiO₂ heterostructure achieved the highest phenol conversion efficiency (13.5%) and the best selectivity (92.1%) [32]. The enhanced photocatalytic performance is ascribed to a narrower band gap and efficient photoinduced electron-hole separation due to the p–n heterojunction structure as well as more exposed reactive facets.

2.4. Support Material Combination

Over the past decade, loading the well-developed photocatalysts onto special supporting materials with unique chemical properties or morphology has become more popular. Compared with photocatalyst modification methods such as ion doping, support material combinations have different characteristics in promoting photocatalysts. Support material generally only influences the photocatalytic reaction rate instead of the reaction process. On the one hand, when deposited onto the surface of minerals, the aggregation of photocatalysts could be greatly meliorated, which considerably decreases the chance of photo-generated electron-hole recombination [33][34]. For example, the addition of reduced graphene oxide into the titanium oxide matrix could hinder the agglomeration of photocatalyst nanoparticles and efficiently promote photoinduced electron-hole immigration [35]. On the other hand, the combination of minerals and photocatalysts could obtain better adsorptive ability, which is favorable for the concentration of pollutants near the photocatalysts and shortens the transfer route of photo-induced charge carriers. With high specific surface area and porosity, porous diatomite could cooperate with silver phosphate to harvest visible light and adsorb dye molecules [36]. In many cases, minerals have some active species that function differently in photocatalytic reaction systems. Some active species in minerals could be combined with photocatalysts and modify the crystalline and electronic structure of photocatalysts, similar to the mechanism of ion doping and heterojunction construction. While other active species could act as the separation center of photo-induced electron and hole pairs and vary the transfer route of the charge carriers. The most promising directions in recent decades are more postulates of mineral support influences and further elucidations of the known influences.

3. Natural Carbonate or Carbon-Based Mineral-Supported Photocatalysts

3.1. Calcite-Supported Photocatalysts

As the most stable polymorph of calcium carbonate, calcite is extremely common in sedimentary, metamorphic, and igneous rocks throughout the world and is thus considered a rock-forming carbonate mineral. In 2019, Belhouchet et al. made full use of the natural Algerian shale abundantly existing in northeastern Algeria and North Africa to search for highly efficient photocatalytic material [37]. The study results revealed that the natural mineral mainly consisted of calcite coated with TiO₂ by the sol-gel method, and the composite CAL30 sample, had the largest pore volume, higher specific surface area, and, therefore, the best photocatalytic activity. It was analyzed that this calcite/TiO₂ system followed a pseudo-first-order kinetic model from the photocatalytic experiment results. The introduction of the mineral into CAL30 sample could suppress the electron-hole recombination and reach a close tetracycline degradation performance (the rate constant $k = 2 \times 10^{-2} \text{ min}^{-1}$) of pure TiO₂, saving 70% of the TiO₂ amount.

Additionally, limestone and marble generally make up the Earth's crust, a significant part with primary constituent as calcite, and serve as one of the largest carbon storages on this planet. Generally speaking, limestone as sedimentary carbonate rock is often formed by the skeletal fragments of marine organisms and the chemical precipitation of calcium carbonate. Because of the water solubility, weak acid properties, and wide distribution, limestone is usually used as a

building material, white pigment, and product filler [38]. However, regardless of whether it is a building material or wall painting material, limestone always encounters a cleaning problem. As a result, self-cleaning technology design is put forward to solve this issue economically and efficiently. In 2017, N. Fadhilah could successfully synthesize super-hydrophilic self-cleaning limestone coating paint with TiO_2 nanoparticles modified by dispersant polyethylene glycol 6000 (PEG6000) [39]. This new paint with the composition of TiO_2 :PEG600 as 1:6 could achieve the highest self-cleaning ability (83.1%) with water contact angles of 7° . Up to 2019, Mohsen et al. prepared $\text{CaCO}_3/\text{TiO}_2$ nanostructures with high surface area, mesoporous structure, and lower band gap energy of 2.05 eV by the precipitation method [40]. Thus, the $\text{CaCO}_3/\text{TiO}_2$ nanocomposite showed photocatalytic desulfurization of 95% dibenzothiophene under 550 Watt linear halogen lamp illumination and in the presence of H_2O_2 and acetic acid.

Often referred to as magnesium-rich limestone, dolomite is known as an anhydrous carbonate mineral composed of calcium magnesium carbonate and crystallizes in the trigonal-rhombohedral system. With the ideal formula $\text{CaMg}(\text{CO}_3)_2$, dolomite has double carbonate-containing alternating planes of Ca^{2+} and Mg^{2+} ions. In 2019, Belarbi et al. calcined dolomite under 800°C and then modified it by $\text{Ca}(\text{NO}_3)_2$ to obtain the dolomite-based catalyst CaD800, which could degrade 95% pentachlorophenol under UV light irradiation after only 1 h [41].

3.2. Other Carbon Material-Supported Photocatalysts

Apart from graphene, other carbon materials with specific morphology are also excellent candidates for photocatalyst support, such as carbon quantum dots, carbon nanotubes, carbon nanofibers, etc. [42]. Similar to graphene, these carbon nanomaterials also possess superior mechanical and electrical properties. In one benzene mineralization study, carbon nanotubes were combined with TiO_2 by the wet impregnation method. Carbon nanotubes as support could provide a stable electron reservoir and efficient electron transfer route. Moreover, the existence of carbon nanotubes effectively suppresses the agglomeration of TiO_2 particles, and thus more reactive sites could be exposed. Compared with the bare TiO_2 , the enhanced photocatalytic performance of TiO_2/CNT composite was proved to come from tight interfacial contact between carbon nanotubes and TiO_2 . Due to all these factors, the conversion efficiency from benzene to CO_2 over TiO_2/CNT is much higher than P25, a kind of commercial TiO_2 [43].

4. Natural Sulfate or Sulfide Mineral—Supported Photocatalysts

4.1. Gypsum-Supported Photocatalysts

As the most common sulfate mineral, gypsum is a soft calcium sulfate dihydrate compound that is often used as a fertilizer and as the main constituent in many forms of plaster, blackboard, and drywall. Generally, gypsum deposited from lake, sea, and hot springs crystallizes as a translucent crystal of selenite and forms as an evaporite mineral and hydration product of anhydrite. The previous research mainly focuses on assembling efficient photocatalytic additives with commercial gypsum to develop self-cleaning building materials and exploring their photodegradation efficiency on various pollutants. A novel $\text{BiOCl}_x\text{Br}_{1-x}/\text{gypsum}$ heterojunction composite was constructed as a self-cleaning surface for building material [44]. The photocatalytic activity results showed that the as-obtained hybrid material could mineralize RhB in 4 min and the recalcitrant Naphthalene contamination in 20 min under visible light irradiation. Additionally, it could maintain superior photocatalytic activity and efficiency for at least 7 months. Janus et al. incorporated N, C co-modified TiO_2 into commercial gypsum to obtain a self-cleaning property and exhibit obvious dye removal capacity [45]. They found that N, C- TiO_2 photocatalyst functioned as the void space fillers in gypsum matrix could reduce gypsum particle size and over 10% mass content of N, C- TiO_2 additive into gypsum causes a considerable decrease of the compressive strength value, pore volume, and specific surface area. The obtained N, C- $\text{TiO}_2/\text{gypsum}$ sample treated at 300°C exhibited 85% and 70% degradation of azo dye Remazol red 198 after 15 h of UV and visible light irradiation, respectively. V. Binas et al. fabricated photocatalytic cement-based coating mixed with Mn-doped TiO_2 and compared the influence of different supporting materials on the photocatalytic activity against NO air pollutants [46]. The substrate materials displayed a slight difference in photocatalytic degradation efficiency, and the mixture of Mn-doped TiO_2 composite coating influenced its surface area and porosity.

4.2. Pyrite-Supported Photocatalysts

As a naturally n-type semiconductor material, pyrite is a brass-yellow sulfide mineral with metallic luster and chemical formula of FeS_2 . Considering its broad existence in igneous, metamorphic, and sedimentary rocks worldwide, pyrite is widely regarded as a promising candidate for wastewater treatment. Diao et al. employed pyrite as a photocatalyst for the degradation of malachite green (MG) and Cr(VI) reduction [47]. Pyrite photocatalysts showed removal efficiency of MG and Cr(VI) reached 96.2% and 53.1%, respectively, from their mixture solution after 120 min UV light irradiation, which is better than that determined for individual separated solutions. They suggested that the presence of malachite green could

accelerate Cr(VI) reduction and vice versa, which is attributed to the synergistic effect in the MG and Cr(VI) coexistence system. They also found that the dissolved oxygen could remarkably promote MG degradation efficiency and Cr(VI) reduction that is mainly controlled by direct electrons of pyrite. Furthermore, natural pyrite could be applied to inactivate *Escherichia coli* in the presence of citrate and EDTA as chelating agents [48]. These chelating agents would increase the iron solubility and reduce the oxidation of the pyrite surface, which promotes the photo-Fenton process and the *E. coli* inactivation rate. Additionally, natural pyrite could be transformed structurally into a Z-scheme FeS₂/Fe₂O₃ composite via the heat treatment method, and the synergistic effects between FeS₂ and Fe₂O₃ have a remarkable positive influence on its photocatalytic activity [49]. It was proved that the as-obtained composite exhibits increased photocatalytic degradation efficiency from 36% to 65% with the presence of 30 mg/L Cr(VI), and the addition of Cr(VI) ions can also be almost reduced. That is related to the fact that Cr(VI) could capture the electrons and thus improve photo-induced electron-hole pair separation efficiency. These findings make natural pyrite suitable for designing a low-cost and efficient photocatalyst for wastewater treatment and environmental applications.

5. Natural Special Mineral-Based Photocatalysts

5.1. Ilmenite-Based Photocatalysts

As a wide-bandgap anti-ferromagnetic semiconductor, ilmenite is known as a titanium–iron oxide mineral with the idealized chemical formula FeTiO₃, containing around 40–60% of TiO₂. Generally, pure ilmenite has a rhombohedral crystal structure with the hexagonal packing of the oxygen atoms with cations occupying two-thirds of the octahedral positions, where Fe and Ti occupy alternating layers [50]. Due to its chemical composition and unique properties, ilmenite is always considered the most suitable natural precursor of photocatalyst TiO₂. A. Simpraditpan et al. explored the effect of calcination temperature on the properties of titanate nanofibers originated from natural ilmenite minerals and concluded that the temperature increase could result in the phase transformation from thermodynamically metastable anatase phase to the most stable rutile phase with increasing the crystallite size [51]. They found that the nanofibers calcined at high temperatures of 600–1000 °C were mixtures of three crystalline phases, e.g., anatase, rutile, and Fe₂O₃. Moreover, increasing the calcination temperature induces the increase of crystallite sizes, therefore leading to the absorption edge of the as-synthesized sample shifts to the visible light region. Among these samples, the nanofibers calcined at 400 °C for 2 h exhibited the best photocatalytic activity, even higher than the commercial TiO₂. Shao et al. synthesized iron-doped TiO₂ nanorods from raw ilmenite ore via a direct acid leaching method. They found that the band gap energy decreased from 2.94 eV to 2.49 eV with higher iron concentration, as compared with 3.02 eV of bare rutile TiO₂ [52]. The optimal amount of iron dopant was reported to be 1.69%, leading to the best photogenerated charge carrier separation efficiency. Another study showed that iron species from natural ilmenite minerals could be converted into Fe₃O₄ in addition to titania phases, providing magnetic recyclability of the photocatalyst under an external magnetic field [53]. This composite was characterized to be composed of face-centered cubic Fe₃O₄ and body-centered tetragonal anatase TiO₂ with superparamagnetic behavior and strong visible-light absorption ability. It could be separated and recycled quickly and easily due to the magnetization effect of Fe₃O₄ core. Moreover, superoxide radicals were proved to be the main active species of the Rhodamine B degradation process. Xia et al. introduced persulfate into the natural ilmenite reaction system to achieve efficient *E. coli* inactivation under visible light irradiation [54].

5.2. Monazite-Supported Photocatalysts

A monazite is a group of monoclinic phosphate and arsenate minerals that contains one or several kinds of rare-earth metals. Monazite (Ce), as a thorium-bearing mineral, was selected as TiO₂ substrate for its minor radioactivity and its interior framework of a composite on which TiO₂ grew by forming Ti–O–Ce microstructure [55]. TiO₂ embedded in monazite became a kind of radiation-sensitive photocatalyst, and the degradation principle was similar to photocatalysis in that the band gap of TiO₂ is activated by γ-ray irradiation. It was revealed that the radiations of thorium nuclides in TiO₂/monazite composite endowed energy to trigger TiO₂ excitation, existent cerium ions in monazite served as energy absorber with charge separator, and the TiO₂/CeO₂ structure could provide a unique electron transfer process which is beneficial to separate the charge-carriers more efficiently and thus improve catalytic activity in dark conditions. Furthermore, radioluminescence (RL) is the phenomenon by which luminescence is produced in a material by the bombardment of α-particles, γ-rays, or β-particles. It was proposed that radio-sensitive Ce could produce interior UV because of RL and TiO₂ were excited by RL. This self-activated photocatalytic behavior was similar to the heterojunction reaction mechanism and inner electric field established within TiO₂ semiconductor and CeO₂ due to Fermi level equilibrium and could transfer electron-hole pairs more effectively.

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