Review

Heterostructured Nanoscale Photocatalysts via Colloidal Chemistry for Pollutant Degradation

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Abstract: With the further acceleration in the industrialization process, organic pollutants and gas pollution in the environment have posed severe threats to human health. It has been a global challenge regarding achieving an efficient solution to pollutant degradation. In such a context, photocatalysts have attracted researchers’ attention for their simplicity, efficiency, cleanliness and low cost. However, the single photocatalyst is facing a research bottleneck owing to its narrow light absorption spectrum and high photocarrier recombination rate. Given that heterojunctions can achieve efficient separation of photogenerated carriers in space, constructing heterostructured photocatalysts has become the most perspective method to improve the performance of photocatalysts. Furthermore, nanoparticles prepared through colloidal chemistry have the characteristics of high dispersion, stability and adsorption, further enhancing the degradation efficiency of heterostructured photocatalysts. This article reviews the primary methods for preparing heterostructured photocatalysts through colloidal chemistry, classifies the heterojunction types by transport routes of photogenerated carriers and summarizes the recent progress of heterostructured photocatalysts in pollutant degradation. To implement environmental remediation, it is crucial to explore economical and efficient photocatalysts for practical applications. It is hoped that this review will stimulate further exploration of colloidal heterostructured photocatalysts for pollutant degradation.

Keywords: photocatalyst; contamination treatment; heterojunction; colloidal chemistry

1. Introduction

The continuous consumption of non-renewable fossil fuels brings the problem of environmental pollution into sharp focus. Human activities, based on fossil fuels for life and production, will produce a wide range of gas pollutants and water pollutants. Long-term exposure to various pollutants is detrimental to human health and other living organisms [1–3]. Degrading pollutants from the environment has become a global challenge. To achieve this goal, biocatalysis, photocatalysis, electrocatalysis and other technologies have been widely studied and applied. Among all these technologies, photocatalysis has become a preferred candidate for environmental remediation, especially pollutant degradation, with its characteristics of being simple, safe, clean and cost-effective, and it can be thoroughly degraded without secondary pollution [4].

The critical issue for the industrialization of photocatalytic technology lies in improving the spectral response range and catalytic effect of photocatalysts. Research on the modification of photocatalysts mainly includes: (1) the optimization and modification of...
single semiconductor photocatalysts and (2) composite semiconductors containing heterojunctions [5]. The single semiconductor photocatalyst represented by TiO$_2$ proposes and implements strategies such as doping [6,7], photosensitization [8–10] and deposition of precious metal [11–14]. However, the shortcoming of low light utilization has not been improved, so has the problem of high recombination rate. Therefore, the construction of heterojunctions is considered a potential and effective way to improve photocatalyst performance. The separation of photolithography can be inhibited, meanwhile the higher utilization rate of visible light can be obtained through semiconductors with different energy levels [4].

According to the generation and transport of carriers, heterojunctions can be divided into conventional and advanced types. Considering the relative position of energy levels between semiconductors, conventional heterojunctions can be classified as: straddling gap (type-I), staggered gap (type-II) and broken gap (type-III) [15]. In order to solve the inherent defect of redox capacity in the conventional heterojunction, the idea of p-n heterojunctions is proposed, which are comprised of p-type and n-type. Later, inspired by the natural photosynthesis of plants, the researchers propose the Z-scheme heterojunctions, which further improve the photocatalyst performance [16,17]. Therefore, the heterostructured nanoscale photocatalyst is considered a potential candidate to make up for its shortcoming in the degradation of pollutants.

In general, powdered nanoscale photocatalysts are favored in photocatalysis. Their high specific surface area brings more active sites, as well as the reduction in the charge migration pathway, thereby improving the recombination of carriers. However, the powdered nanoscale photocatalyst has an inevitable tendency to recombine, which largely obscures the original active sites [18]. Moreover, the recovery operation of powdered nanoparticles is complex and easy to lose, resulting in the occurrence of secondary pollution. In the past few years, researchers have solved the problem of powder photocatalyst agglomeration by preparing heterostructure nanoscale photocatalysts with colloidal chemistry. The synthesis methods of photocatalysts have also evolved from direct synthesis to fixed photocatalysts based on aerogel frames. The main preparation methods, types and main degradation contaminants of colloidal heterojunction catalysts are shown in Figure 1. This article summarizes colloidal heterostructure nanoscale photocatalysts for pollutant degradation and introduces the mainstream colloidal synthesis methods of heterostructured nanoscale photocatalysts. The design and latest progress of various heterostructured nanoscale photocatalysts are reviewed. In particular, this review focuses on four typical and exceptional heterojunctions: type-I, type-II, p-n heterojunctions and Z-scheme heterojunctions and discusses the application of various heterostructured photocatalysts in pollutant degradation. At the end of this paper, a critical evaluation of colloidal heterostructured photocatalysts is proposed, as well, the challenges in this field are presented.

2. Colloidal Synthesis of Nanoscale Photocatalysts

Since the crystal and band structures of each semiconductor are different, many factors need to be taken into account when designing and manufacturing colloidal heterostructured photocatalysts. Maximizing the advantages of different semiconductors within heterojunctions is a bottleneck in applying colloid chemistry to photocatalyst preparations. The sol–gel method is the most widely used through colloidal chemistry in the direct synthesis of photocatalysts. With the further research of the photocatalysts and progress in material preparation technologies, the assembly method based on nanoscale units has significantly broadened the scope of colloid chemistry applications in photocatalysts.
Figure 1. The preparation methods, types and main degradation contaminants of colloidal heterojunction catalysts.

2.1. Sol–Gel Method

The sol–gel method, a simple and economical method, has been widely used in conjunction with the solvothermal method, which gives materials significant surface properties. This method makes up for the vacancy in the synthesis of nanoparticles at low temperatures and can obtain high-purity and homogeneous metal oxides, mainly Si and Ti [4]. The synthesis method of solid materials from the colloidal solution is called the sol–gel method. Colloidal solutions are generally aqueous phases with solid particles suspended or solvents with solid particles dispersed.

B. Palanisamy et al. [19] prepared a Fe$_2$O$_3$/TiO$_2$ heterostructured photocatalyst to degrade 4-chlorophenol with the sol–gel method. The synthetic procedure is illustrated in Figure 2a. Firstly, precursors for Ti$^{4+}$ and Fe$^{3+}$ are synthesized from titanium isopropoxy ferric nitrate nanoscale hydrates. The above nanoscale hydrates and Pluronic P123 are dissolved in ethanol, and then the pH is maintained at around 10. Mixed mesoporous oxides are synthesized by controlling different molar ratios of Fe(NO$_3$)$_3$·9H$_2$O to Ti(OiPr)$_4$ for mesoporous Fe$_2$O$_3$/TiO$_2$. The Fe$_2$O$_3$/TiO$_2$ mesoporous composite oxide is composited through experiments to find the appropriate molar ratio and keep the molar ratio unchanged. The resultant precipitate is centrifuged to remove the template residue and grounded after drying to obtain the final product.
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Figure 2. (a) Schematic flow chart for the preparation of mesoporous Fe$_2$O$_3$/TiO$_2$ by sol–gel method; (b) SEM images of different mass fractions of Fe$_2$O$_3$; (c) plausible mechanism for the degradation of 4-chlorophenol in TiO$_2$ and Fe$_2$O$_3$/TiO$_2$; (d) photocatalytic degradation of 4-chlorophenol using meso-TiO$_2$, mesoporous Fe$_2$O$_3$/TiO$_2$ (10, 30, 50, 70 and 90 wt.% Fe$_2$O$_3$) and meso-Fe$_2$O$_3$ catalysts. Reprinted with permission from Ref. [19]. Copyright 2013, Elsevier.

The crystal growth characteristics of Fe doped TiO$_2$ remain unchanged in Figure 2b. However, the presence of Fe is beneficial for reducing the agglomeration of particles, which can increase the active sites of photocatalysts and improve the catalytic performance. From the degradation mechanism of 4-chlorophenol in Figure 2c, the visible light absorptivity of the prepared mesoporous Fe$_2$O$_3$/TiO$_2$ photocatalyst is significantly improved. The incorporation of Fe reduces the forbidden bandwidth between the conduction and valence band. It adds a new absorption band increasing the visible light absorption rate, thus improving the photocatalyst activity. When visible light is incident, the stimulated electrons leave the valence band leaving holes, and the excited electrons in the forbidden band produce Fe$^{3+}$ transfer electrons, triggering an effective reduction reaction. The holes cause 4-chlorophenol to convert into carbon dioxide and water, and an oxidation reaction occurs. The higher valence band potential provides the photocatalyst with strong oxidizing ability, and carriers can also achieve effective spatial separation.
The degradation progress is reflected by detecting total organic carbon (TOC) in the pollution source and examining the activity of the photocatalyst. The degradation of 4-chlorophenol by photocatalyst with different mole ratios is shown in Figure 2d. From the reduction in TOC, we can see that meso-TiO$_2$ and meso-Fe$_2$O$_3$ have little effect on the degradation of 4-chlorophenol. When Fe is doped into a TiO$_2$ lattice to form a heterogeneous structure, the activity of the photocatalyst is significantly improved. The degradation of 4-chlorophenol by photocatalysts with different Fe/Ti ratios shows a similar trend over time, but meso30-Fe$_2$O$_3$/TiO$_2$ degradation is more radical, and the degradation rate can reach 100%. These results are in accordance with the predicted mechanism, suggesting that the formation of heterojunctions can decrease the bandgap width and the absorption rate of visible light, thus improving the photocatalytic performance.

Recently, applying the sol–gel method in the preparation of heterojunctions has been extensively studied. Carina et al. [20] prepared a TiO$_2$/ZnO/Bi$_2$O$_3$ (TZB) nanofiber photocatalyst using a sol–gel in collaboration with the electrospinning method. The reduction efficiency of NO by TZB is higher than that by commercial TiO$_2$ because the difference in energy band position leads to the shortening of the energy gap and the decrease in recombination rate of photogenerated electron-hole pairs. Thamaraiselvi K et al. [21] synthesized SrTiO$_3$-BiOBr heterojunction composite photocatalysts with a combination of the sol–gel route with impregnation and precipitation methods. The synthesized photocatalysts exhibit higher activity by virtue of the lowest recombination rate and the lowest electron transfer resistance.

2.2. Immobilizing Photocatalysts in Aerogel Frameworks

Photocatalysts prepared by direct synthesis have been widely studied and applied. However, the direct synthesis method still suffers from complicated preparation steps and few types of photocatalysts, which have been the critical problems restricting its industrialization. To solve the above shortcomings and enrich the types of colloid heterojunction photocatalysts, the aerogel framework has given researchers new preparation ideas. A hypothesis is proposed to immobilize photocatalysts in the prepared aerogel framework to form composite photocatalysts, which not only have the functions of aerogel frame and photocatalyst but also specific effects on the activity and morphology of the photocatalyst. At present, aerogel frameworks used in research mainly include SiO$_2$, graphene-based and polymer aerogel [18]. Among them, the SiO$_2$ aerogel framework is the most widely used aerogel framework with good transparency and mature sol–gel technology. With the deepening research on graphene, the graphene-based aerogel framework has become increasingly prominent as a photocatalyst framework. Graphene has many excellent properties. The higher specific surface area provides more active sites, the good conductivity accelerates electron transfer and its black body enhances the absorption of visible light. These characteristics can widen the bandgap and make Fermi energy levels more dispersed, providing theoretical support for the modification of photocatalysts.

Yang et al. [22] prepared a sheet–sheet NiAl-LDH/g-C$_3$N$_4$ heterojunction with graphene aerogel base, which possesses high photocatalytic activity for CO reduction. The g-C$_3$N$_4$(CN) nanosheets are derived from urea pyrolysis, and the two-dimensional flower-like NiAl-LDH(NALDH) nanosheets are further added with NH$_4$F. The above two nanosheets are hydrothermally constructed to build a NiAl-LDH/g-C$_3$N$_4$/GA hybrid heterojunction system, as shown in Figure 3a. Scanning electron microscopy (SEM) of the prepared photocatalyst shows that the nanosheet is ultrasonically stripped into smaller pieces, and the heterojunction formed in the hydrothermal process also exhibits a curly folded layer structure, which provides the basis for assembling the NALDH/CN framework and shorten the distance of charge transmission. Therefore, the transfer and separation of photocarriers and the adsorption and transfer of reactants are accelerated, hence improving the activity of the photocatalyst.
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Figure 3. (a) Synthetic process for NALDH/CN/GA hybrid; (b) CO and CH$_4$ average gas production rates over all synthesized photocatalysts; (c) schematic diagram of possible photocatalytic mechanism for NALDH/CN/GA. Reproduced with permission; (d) the possible pathways of the CO$_2$ photocatalytic reduction, where * indicates the adsorbed state. Reprinted with permission from Ref. [22]. Copyright 2022, Elsevier.

The photocatalyst activity is reflected by the detection of reduction products (mainly CO). As shown in Figure 3b, only when the heterojunction is formed between NALDH and CN can the CO yield significantly increase. After GA is introduced, the charge transfer of the heterogeneous interface is further promoted, and the CO yield rate reaches its highest. The team also tested the stability of NALDH/CN/GA-20 and found that it retains more than 90% of its photocatalytic activity after more than 100 repeating experiments. The FT-IR spectra further prove the high stability of the structure. It is found that the interfacial interaction between NALDH/CN and GA is enhanced through the surface photo-voltage spectra. The enhancement of the photogenerated electron capture ability of the photocatalyst reduces the recombination rate of photocarriers and improves the...
utilization rate of photoelectrons and the photocatalytic activity. In order to elucidate the type of heterojunction and the mechanism of CO reduction, the team extrapolates the Mott-Schottky method to indicate the type of semiconductor and band position in a group of valence band XPS-(VB-XPS). Through calculation, the NALDH/CN/GA-20 photocatalyst belongs to the staggered gap heterojunction, and its energy band diagram is shown in Figure 3c. Based on the photocatalytic mechanism of type-II heterojunction, the team propose as conjecture the CO reduction route, as shown in Figure 3d.

Wang et al. [23] made an innovative attempt to prepare photocatalysts with ice templates and calcination. The graphene aerogel is loaded with g-C$_3$N$_4$/TiO$_2$, and the obtained g-C$_3$N$_4$/TiO$_2$@C aerogel is used for hydrogen peroxide activation. The specific surface area of the photocatalyst is increased by the layered mesoporous design. Meanwhile, separation of the photogenerated electron-hole is accelerated by g-C$_3$N$_4$/TiO$_2$ heterojunctions, providing the photocatalyst with a favorable photocatalytic performance and a high efficiency for NO removal, up to 90.7%. CN/TiO@C-3 has been verified to possess good stability and repeatability in NO removal, which gives it potential for industrialization. Based on similar studies, Liu et al. [24] modified g-C$_3$N$_4$ nanosheets with 0D silver metavanadate quantum dots via electrostatic interaction. Constructing heterojunctions improves the separation rate of photogenerated electron-holes, as well as the stability of the photocatalyst.

In addition to the two synthetic methods of heterostructured photocatalysts mainly using colloidal chemistry, there are some other preparation methods involving colloidal chemistry, as shown in Table 1. Particularly, researchers usually do not adopt a single synthesis method, but combine several methods in practical research.

### Table 1. Frequently used methods preparing heterostructured photocatalyst through colloidal chemistry.

| Kind                                           | Method                        | Features                                                                 |
|------------------------------------------------|-------------------------------|--------------------------------------------------------------------------|
| Direct synthesis                               | Sol–gel method                | High homogeneity and high specific surface area; highly dispersed metal components; controllable synthesis process; controllable composition of the material |
|                                                | Assembly method               | Cheap for mass production; fast, simple and convenient; no cleanroom facility needed; unable to fabricate very complex structures; difficult to control over crystal orientation |
|                                                | Template method               | Simple synthesis process; capable of mass production; easy to control the size, shape and dispersion of materials; especially suitable for the synthesis of one-dimensional materials and structures |
| Immobilizing photocatalysts in aerogel frameworks | Graphene-based aerogel framework | Frequently use the hydrothermal method; energy-consuming; difficult for large-scale production |
|                                                | Polymer aerogel framework     | Easy to load catalyst; high mechanical strength; convenient synthesis; low cost |

3. Different Heterojunctions for Pollutant Degradation

The contact of two semiconductors with different band structures forms the interface region, which is called the heterojunction. Since Fermi energy levels representing carrier concentrations vary for different semiconductors, carriers will transfer between two semiconductors when they contact each other. According to the transfer characteristics of photogenerated electrons and holes at the heterojunction interface, the researchers divide heterojunction into such types: type-I, type-II, p-n and Z-scheme. Although carrier transfer characteristics vary, the photocatalytic degradation of pollutants via semiconductors involves at least five steps, as shown in Figure 4: (1) light absorption of semiconductors; (2) generation of the photogenerated carriers; (3) migration and recombination of photogenerated carriers; (4) adsorption of pollutants and desorption of products and (5) redox reactions.
reaction on the semiconductor surface. In this section, we summarize the research progress of these four different types of heterojunctions.

Figure 4. Schematic and flowchart representation of steps involved in heterogeneous photocatalysis. Reprinted with permission from authors Reprinted with permission from Ref. [25]. Copyright 2017, Elsevier.

3.1. Straddling Gap Heterojunctions

Type-I and type-II both belong to the traditional heterojunctions. Due to the different relative positions of the two semiconductor bands, the photogenerated carrier transmission routes are different, so the characteristics of the redox reaction are different [26]. Generally, the heterojunction formed by the conduction band energy level of semiconductor II (SC II) is lower than that of semiconductor I (SC I) and the valence band is higher than that of SC I and is called a straddling gap (type-I) heterostructured photocatalyst. After light absorption, the photogenerated carriers will accumulate on SC II, and the corresponding photocatalytic redox reaction will also take place on SC II with lower redox potential. The transfer routes of conventional heterojunctions are shown in Figure 5.
Chen et al. [28] prepared a chromium-modified Bi$_4$Ti$_3$O$_{12}$ photocatalyst for pollutant degradation of organic pollutants owing to its excellent photocatalytic activity and stability. However, the high rate of recombination between photogenerated carriers has a negative effect on its photocatalytic activity, so it is necessary to enhance its absorption of light and ensure the separation of photogenerated carriers by doping chromium without changing the crystal structure. Chen applied a novel low-temperature sol–gel hydrothermal technique to reduce the reaction temperature to 160 °C, ensuring crystal perfection while improving the absorbance of Bi$_4$Ti$_3$O$_{12}$ in the visible region. The degradation of methyl orange (MO) in the aqueous solution by photocatalyst varies with the increase in Cr content. The addition of Cr can effectively improve the degradation ability of the photocatalyst to MO, but meanwhile leads to the accumulation of particles and reduces the surface activity of the photocatalyst. Moreover, the degradation of MO by the Cr-modified Bi$_4$Ti$_3$O$_{12}$ photocatalyst is only three times above that without Cr-modified Bi$_4$Ti$_3$O$_{12}$, so it is still challenging to satisfy the requirements of commercial application.

In 2017, Li et al. [29] prepared the LaFe$_{1-x}$Mn$_x$O$_3$/Attapulgite (ATP) nanocomposite photocatalyst, combining the sol–gel method and co-deposition method. It is applied to the photocatalytic NO reduction at low temperatures with specific selectivity. While regulating the amount of Mn deposition to form heterojunctions, they find that the photocatalyst has the highest activity when x = 0.6, and the conversion of NO is up to 85%. As shown in Figure 6a, the NO conversion rate with different Mn-deposition is tested. It is found that both the photocatalytic activity and stability are improved with the increase in Mn-deposition. However, the NO conversion sharply decreases when x > 0.6, which indicates that excessive LaMnO$_3$ deposition may hinder the light absorption or heterojunction formation, thus reducing the catalytic efficiency. By calculating the bandgap of LaMnO$_3$ and predicting the bandgap structure of LaFe$_{1-x}$Mn$_x$O$_3$, the team proposed a photosensitive catalytic mechanism for NO, as shown in Figure 6b. The LaMnO$_3$/ATP nanocomposite photocatalyst exhibits remarkable room temperature catalytic performance, which broadens its application prospect. Huang et al. [30] successfully prepared different heterojunctions in Bi$_2$O$_3$/La$_2$O$_3$/g-C$_3$N$_4$. The results show that the type-II heterojunction has higher catalytic activity and more types of pollutants for degradation. It indicates that the low separation efficiency of photogenerated hole-electron pairs will limit the development of type-I heterojunctions.
Due to the defects of the type-I heterojunctions, there is little research on type-I heterostructured photocatalysts. In Table 2, we present the degradation of pollutants by photocatalysts based on type-I heterojunctions.

### Table 2. Degradation of pollutants by photocatalyst based on type-I heterojunction.

| Photocatalyst          | Pollutant | Effect                                                                 | Ref. |
|------------------------|-----------|------------------------------------------------------------------------|------|
| InVO₄/N-TiO₂            | 4-NP      | Present a reduction in 4-NP of 89% at a time of 90 min for all materials.| [31] |
| ZrO₂/TiO₂              | Oily wastewater | Exhibit adsorption–photodegradation of 95%, respectively within 300 min for oily wastewater at 100 ppm | [32] |
| BiₓOᵧIₓ/g-C₃N₄        | MO        | Present almost 98% decomposition of MO molecules                       | [30] |
| TiO₂@nanosheet SnS₂     | RhB       | The highest photocatalytic activity for RhB                             | [33] |
| CoWO₄/g-C₃N₄           | MB        | The highest photocatalytic efficiency up to 94.5% after 100 min         | [34] |
| BiₓTi₂₋ₓCrₓO₁₂         | MO        | Show the highest ~91% of MO degradation                                | [28] |

#### 3.2. Staggered Gap Heterojunctions

For type-I heterojunctions with the straddling gap, the photogenerated hole–electron pairs cannot be effectively separated, which significantly limits the redox ability. The structure of type-II is different from the type-I heterojunction, and both the conduction and valance band of SC I are higher than those of SC II, as shown in Figure 7. Therefore, under the excitation of light, the photogenerated holes migrate to the vacancy in the valence band of SC I, and the photogenerated electrons migrate to the conduction band of SC II, facilitating the spatial separation of photogenerated carriers [15,27]. Because of the photogenerated carriers’ transfer characteristics, the type-II heterostructured photocatalyst exhibits a more comprehensive light absorption range, a quicker transfer rate of mass and stronger photocatalytic activity.

Liu et al. [35] prepared a heterostructured photocatalyst via a simple sol–gel method for visible light degradation of formaldehyde. They added waste zeolite to assist the adsorption of formaldehyde gas on the basis of previous studies. Sols were prepared by dispersing photocatalysts in HCl solution. Then, they combined the above sol and waste zeolite via the sol–gel method to achieve photocatalysts. As shown in the TEM images (Figure 8a), the samples exhibit a polycrystalline structure in the selected region, suggesting that the heterostructure of the sample has an intense quantum confinement effect. The effect may be beneficial for the improvement of the photocatalytic activity. According to the simulation experiment, the efficiency of the degrading formaldehyde is related to the proportion of 110, up to 90%. Cyclic tests of formaldehyde photodegradation...
further investigate the durability of 90% I-WZ coatings. As shown in Figure 8b–d, the photocatalytic activity retains over 95% after four cycles. The performance of the newly prepared g-C3N4-TiO2/spent zeolite coating is significantly improved, and its reaction rate is 2.3 times that of commercial TiO2 (P25) in formaldehyde degradation applications. This study also demonstrates the possibility of photocatalyst coatings for formaldehyde with interior lighting.

![Type-II heterojunction](image)

**Figure 7.** Schematic illustrations of the migration of charge carriers for conventional heterostructured photocatalysts under visible-light irradiation: type-II. Reprinted with permission from authors. Reprinted with permission from Ref. [27]. Copyright 2021, Elsevier.

![SEM images and EIS plots](image)

**Figure 8.** (a) TEM image, high-resolution TEM image and SAED pattern of i10 samples; (b) the time dependence of formaldehyde degradation; (c) conversions and rate constants and (d) the cycling tests of 90% I-WZ for four cycles of photodegradation. Reprinted with permission from authors. Reprinted with permission from Ref. [35]. Copyright 2019, Elsevier.

Wang et al. [36] studied ternary heterostructured photocatalysts and prepared a ZnIn2S4@SiO2@TiO2 photocatalyst in a combination with sol–gel and solvothermal meth-
ods. The ternary heterojunction is formed by uniformly dispersing SiO$_2$@TiO$_2$ nanoparticles on a prefabricated 2D layered flower-like ZnIn$_2$S$_4$, as shown in Figure 9a. According to the transient photocurrent response and the variation in EIS of the heterojunctions in Figure 9b,c, it can be determined that the electron transfer rate at the semiconductor interface is enhanced, indicating that the heterojunction improves the utilization of photo-generated carriers. The photocatalytic experiments also confirm this speculation. According to the theoretical model established in the study (Figure 9d), the heterojunction formed between SiO$_2$@TiO$_2$ and ZnIn$_2$S$_4$ is characterized by a staggered gap, which effectively decreases the recombination probability of photocatalytic carriers and enhances the degradation rate of the MB dye stuff up to 99.7%.

More research on type-II heterojunctions is briefly shown in Table 3. Although type-II heterojunctions overcome the disadvantage of low hole–electron pair separation rate, its further application is still challenged. The redox reactions occur on the semiconductor with low reduction potential and low oxidation potential, respectively, which greatly limit the redox ability of the type-II heterostructured photocatalyst. In addition, the migration of hole to the hole-rich VB of the semiconductor and electron to the electron-rich conduction band (CB) of the semiconductor is difficult because of the electrostatic repulsion. Therefore, it is still necessary to develop a more efficient heterojunction to overcome these shortcomings, to be further applied in pollutant degradation.

Figure 9. (a) The illustration of the procedure for preparation of the ZIS@SiO$_2$@TiO$_2$ photocatalyst; (b) the EIS Nyquist plots of the SiO$_2$, TiO$_2$, SiO$_2$@TiO$_2$, ZnIn$_2$S$_4$ and ZIS@SiO$_2$@TiO$_2$ composites; (c) the transient photocurrent responses and (d) the schematic of the Charge-Carrier migration process in the ZIS@SiO$_2$@TiO$_2$ heterostructure for H$_2$ production synchronously with organic pollutant degradation under simulated sunlight irradiation. Reprinted with permission from authors Reprinted with permission from Ref. [36]. Copyright 2020, American Chemical Society.
Table 3. Degradation of pollutants by photocatalysts based on type-II heterojunctions.

| Photocatalyst         | Pollutant | Effect                                                                 | Ref.  |
|-----------------------|-----------|------------------------------------------------------------------------|-------|
| g-C₃N₄/Ag₃PO₄/SrAl₂O₄| RhB       | Present the RhB degradation rates of 94.75%; the overall loss of photoactivity from the first to the fourth run, 8.15% | [37]  |
| g-C₃N₄/BiPO₄          | TC        | Decompose 97% TC after 120 min illumination                            | [38]  |
| TiO₂/ZrTiO₄/SiO₂      | RhB       | Show excellent adsorption rate (75.6%, 60 min) and photodegradation rate (95%, 90 min) | [39]  |
| ZnO/Bi₂MoO₆           | RhB       | 99.4% degradation of RhB dye at the first run, only a small drop of photoactivity of 7.8% | [40]  |
| CdS@SnO₂              | RhB       | Degraded rhodamine B dye almost completely within 60 min             | [41]  |
| WS₂/g-C₃N₄            | CO        | A methanol productivity of 372.1 µmol h⁻¹ gcat⁻¹                   | [42]  |
| Ag₆Mo₁₀O₃₃/g-C₃N₄    | MO        | The RhB or MB degradation efficiency reaches 100% after 60 min of irradiation | [43]  |
| TiO₂/g-C₃N₄           | N₂O       | The N₂O decomposition reaches 1.2 h⁻¹                             | [44]  |
| g-C₃N₄/BiOClₓBr₁₋ₓ   | RhB       | Complete photodecomposition of RhB in 60 min under visible light exposure | [45]  |
| TiO₂/SiO₂/g-C₃N₄     | Phenol    | Exhibit the degradation of phenol (98.5%), reduction of Cr⁶⁺ (97%) and photocatalytic hydrogen evolution (572.6 µmol h⁻¹ g⁻¹) | [46]  |
| Ag₁₀Si₄O₁₃/TiO₂       | MB        | The rate of MB decomposition followed a pseudo-first-order kinetic profile (98.2% within 35 min) | [47]  |
| 3D g-C₃N₄/TiO₂        | Phenol    | The maximum removal rate of phenol reaches 30.8%, and remains at about 16.0% after 90 h | [48]  |

3.3. p-n Heterojunctions

The emergence of p-n heterojunctions solves the above problems. The p-n heterojunction can enhance the photocatalyst efficiency by accelerating the transfer of the photogenerated carriers, which is the influence of the built-in electric field [49]. The p-n heterojunction is composed of two independent semiconductors, namely, the p-type semiconductor with more holes and the n-type semiconductor with more electrons. When p and n-type semiconductors are in contact with each other, due to the concentration difference between electrons and holes, electrons diffuse to the p-type, meanwhile holes diffuse to the n-type until the Fermi energy level of the structure is balanced. The immovable charged particles of the two semiconductors form a region of space charge at the heterojunction, resulting in a built-in electric field owing to the interaction between positive and negative charges (from the positively charged n region to the negatively charged p region). As shown in Figure 10, when the bandgap of the built-in electric field is smaller than the incident light energy, the semiconductor is excited to produce electrons and holes. With the built-in electric field, the n-type semiconductor attracts electrons, and the p-type semiconductor attracts holes, realizing the separation of photocatalyst carriers. Moreover, the CB and VB of the n-type semiconductor are lower than those of the p-type semiconductor, which is beneficial to the separation of photocarriers [4,15]. In conclusion, under the synergistic effect of the built-in electric field and band arrangement, the separation of carriers is realized to the greatest extent without decreasing the redox capacity, which integrates the advantages of the first two types [50].
which play a crucial role in ATZ photodegradation as ROS scavengers. Combined with the process in Vis/TLFO/PMS is given in Figure 11d.

Guo et al. [51] synthesized rGO/SnO2 p-n heterojunction aerogels via the sol–gel method for phenol detection. The heterojunction aerogel formed by p-type graphene and n-type tin dioxide nanoparticles improves the low conductivity of metal oxide semiconductors and the low specific surface area of graphene composites, effectively improving the sensitivity of gas sensors. Meanwhile, the aerogel possesses excellent high-temperature stability. According to the detection results of phenol gas by rGO/SnO2 heterojunction aerogels, it is found that the optimal mass ratio of SnO2 and rGO is 7.5:1. With the above mass ratio, the sensitivity of the gas sensor hardly changes after repeated testing, showing good repeatability and stability. The gas selectivity of rGO/SnO2 heterojunction aerogel is also tested, and the gas sensor shows better baseline stability, proving the relative selectivity to phenol.

Wei et al. [52] developed a core-shell TiO2@LaFeO3 (TLFO) heterojunction nanosphere photocatalyst via the carbon-sphere-templated and sol–gel method and employed peroxomonosulfate (PMS) to initiate the reaction for atrazine removal. Compared with the LFO heterojunction synthesized by predecessors, the core-shell structure improves mass transfer and charge separation efficiency by expanding the surface area and improving the light efficiency at the same mass. The synthesis process of the TLFO hollow core-shell structure is shown in Figure 11a. The TLFO nanospheres are obtained with the deposition of LFO. TEM images of TLFO verify the formation of the structure and the stability of the hollow structure after repeated cycling. By comparing the photocatalytic degradation performance of 2-chloro-4-methylamino-6-isopropylamine-s-triazine (ATZ) in different systems and under different conditions, as shown in Figure 11b,c, ATZ can be completely removed by the reaction initiated by adding PMS, which confirms the synergistic effect of the Vis/PMS/TLFO system. In order to further explore the optimal degradation effect of the system on ATZ, the team changed the photocatalyst dose, PMS concentration, initial pH value, coexisting ions and other parameters to observe the change in degradation efficiency. They propose a hypothesis of a photocatalytic mechanism and verify it by EPR spectroscopy. The incident light causes the system to produce a variety of free radicals, which play a crucial role in ATZ photodegradation as ROS scavengers. Combined with the Mott-Schottky measurement, the band structure diagram of the TLFO and ROS generation process in Vis/TLFO/PMS is given in Figure 11d.
In order to accelerate the separation of BiOBr carriers, Qu et al. [53] prepared a polyimide aerogel/BiOBr p-n type heterojunction via the water bath method. The polyimide aerogel not only retains the advantages of polyimide’s adjustable band gap and high stability but also possesses stronger adsorption capacity due to its larger specific surface area and abundant pore structure, which can better capture pollutants. The p-n heterojunction formed between polyimide and BiOBr can effectively inhibit the recombination of photogenerated carriers and significantly improve the degradation efficiency of organic contaminants. To further improve the interfacial properties of p-n heterojunctions, a colloidal quantum dot treated with a low-temperature solution is developed [54]. Moreover, a conjugated polyelectrolyte polymer film is added between PbS colloidal quantum dots (CQD) and ZnO layers to enhance the built-in electric field and charge selectivity of the heterojunction, which has the potential to improve the photocatalyst performance. In recent years, increasing research has been conducted on p-n heterostructured photocatalysts in degrading pollutants, and some of them are showed in Table 4.
Table 4. Degradation of pollutants by photocatalysts based on p-n heterojunctions.

| Photocatalyst          | Pollutant | Effect                                                                 | Ref. |
|------------------------|-----------|----------------------------------------------------------------------|------|
| CsPbBr$_3$ QDs@2D Cu-TCPP | CO$_2$    | An evolution yield of 287.08 mmol g$^{-1}$ during 4 h reaction with high CO selectivity (99%) | [55] |
| MgAl$_2$O$_4$/CeO$_2$/Mn$_3$O$_4$ | MB       | The degradation percentage is up to 94.5%, and maintains 81.8% after the fifth repetition | [56] |
| Cu$_2$O@H NbWO$_6$ | MB        | The degradation rate of the composite is nearly 90.0% in 120 min     | [57] |
| Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ | RhB      | The percentage degradation of RhB after 30 min of photocatalysis reaches 99.5% | [58] |
| ZnSe·xN$_2$H$_4$/GS | MB        | The percentage degradation of MB after 4.5 h reaches 62.8%     | [59] |
| BiOI/TiO$_2$ | MO        | The percentage degradation of MB is 92%, and the rate constant of MO decomposition is about 0.015 | [60] |
| GN/ZnSe | MO        | The bleaching of MO reaches 71.50% after 7 h                     | [61] |
| CuBi$_2$O$_4$/Bi$_2$MoO$_6$ | E. coli  | Completely inactivate E. coli cells within 4 h                       | [62] |

3.4. Direct Z-Scheme Heterojunctions

Although the above three types of heterojunctions effectively inhibit the photocatalyst carrying recombination, the redox ability is limited due to the low reduction and oxidation potential. Bard et al. [63] proposed the idea of Z-scheme heterojunctions by simulating natural photosynthesis in 1979. They found that it had overwhelming advantages, including the maximization of system redox capacity, the widening of visible light absorption and the photogenerated electron–hole separation. According to electronic media, Z-scheme photocatalysts can be divided into three types: conventional Z-scheme heterojunctions, all solid Z-scheme heterojunctions and direct Z-scheme heterojunctions [64–66]. Reversible redox ion pairs are the common medium of the conventional Z-scheme, and the ion pairs tend to exist in the form of the liquid phase, so this scheme is also called the liquid phase Z-scheme. Tada et al. firstly implemented the all-solid Z-scheme using solid materials such as precious metals or carbon-based materials as the charge transfer media. Although it possesses the advantages of light absorption range, strong redox potential, and separation of reduction and oxidation active sites, some problems exist: (1) the existence of the medium increases the charge transfer route and manufacturing cost of the system; (2) the conventional Z-scheme is limited to solution and is sensitive to pH and (3) the all solid Z-scheme means that the system exist in both liquid and gas phases, so the particle growth is difficult to control [67]. Therefore, the direct Z-scheme without charge transfer media has attracted more and more attention. In this part, the direct Z scheme is mainly discussed.

In order to solve the problem that traditional wastewater plants could not effectively degrade ibuprofen, Ashutosh K et al. [68] developed a type of direct Z-scheme heterojunction that can be directly recycled, which solves the inherent problems of type-II heterojunctions and made up for the recycling and complex synthesis process of g-C$_3$N$_4$/TiO$_2$ developed by predecessors. The team introduces Fe$_3$O$_4$@SiO$_2$ nanoparticles with magnetic properties and synthesizes g-C$_3$N$_4$/TiO$_2$/FeO@SiO$_2$ (gCTFS) heterojunctions via a simple sol–gel method with only a few ultra-thin g-C$_3$N$_4$ nanosheets. To remove the impurities in the synthesis process and achieve better photocatalytic efficiency, the team researched the IBU removal at different calcination temperatures, as shown in Figure 12a. It was found that gCTFS calcined at 500 °C has the best degradation effect of IBU. Through the XRD diffraction diagram shown in Figure 12b, it was found that gCTFS-500 has the highest crystallinity and the strongest intensity of its plane diffraction peak. This also indicates that the variation trend of photocatalytic removal efficiency is consistent with the crystallinity of the sample. High-resolution transmission electron microscopy (HRTEM) is applied to measure the gCTFS-500, as shown in Figure 11c, which further verifies the high crystallinity of the gCTFS heterojunction. It is confirmed that the charge transfer mechanism is Z-scheme rather than type-II by •OH radical trapping tests. The gCTFS heterojunction has the advantages of high photocatalytic performance, recyclability and good stability.
However, the disadvantage of low light absorption rate still exists, which may affect its practical application in environmental remediation.

Li et al. [69] prepared a Z-scheme heterostructure of nitrogen-doped carbon quantum dots (N-CQDs)-modified PrFeO₃/palygorskite (Pal) for photocatalytic reduction in NOₓ. As shown in Figure 13a–c, increasing the doping amount of N-CQDs significantly improves the NOₓ conversion rate. However, excessive N-CQDs also reduce the NOₓ loading rate, and the optimal doping amount is 5 wt.%. The reason may be that excessive N-CQDs deposition on the surface of the heterojunction affects the wider absorption of the heterojunction, thus reducing the photocatalytic activity. The conversion rate of 5 wt.% N-CQDs/PrFeO₃/Pal to NOₓ can still reach 89% after six cycles of testing, indicating the good stability of the catalyst. Li et al. [70] applied a freeze-drying technology to prepare photocatalysts and synthesized a porous In₂O₃/In₂S₃ heterostructure with a three-dimensional structure, achieving the efficient photocatalytic degradation of RhB. According to the comparative analysis of the degradation process, the high photocatalytic ability of the photocatalyst is mainly attributed to: (1) the formation of heterojunctions inhibiting the electron–hole recombination; (2) the layered porous structure increasing the specific surface area and reaction sites and (3) the three-dimensional structure promoting the mass
transfer. The team also tests the repeatability and degradability of the 3DHPS \( \text{In}_2\text{O}_3/\text{In}_2\text{S}_3 \) heterojunction. As shown in Figure 13d–f, the \( \text{In}_2\text{O}_3/\text{In}_2\text{S}_3 \) heterojunction exhibits good recycling performance, making it possible to achieve practical applications.

Figure 13. (a) \( \text{NO}_x \) conversion of N-CQDs/PrFeO\(_3\)/Pal with various amounts of N-CODs; (b) and 5 wt.% N-CQDs/PrFeO\(_3\)/Pal after six lamp-on/off tests and (c) the schematic for photo-SCR of \( \text{NO}_x \).
over the N-CQDs/PrFeO$_3$/Pal catalyst. Reprinted with permission from authors Reprinted with permission from Ref. [69]. Copyright 2018, American Chemical Society. (d) Degradation profiles of RhB over 3DHPS In$_2$O$_3$, In$_2$O$_3$/In$_2$S$_3$-1, In$_2$O$_3$/In$_2$S$_3$-2, In$_2$O$_3$/In$_2$S$_3$-3 and In$_2$O$_3$/In$_2$S$_3$ nanoparticles, respectively; (e) the cycling test and reusability of 3DHPS In$_2$O$_3$/In$_2$S$_3$-2 under visible-light irradiation and (f) the sedimentation property of 3DHPS In$_2$O$_3$/In$_2$S$_3$-2. Reprinted with permission from authors Reprinted with permission from Ref. [70]. Copyright 2019, American Chemical Society.

In order to improve pollutant adsorption, Zhang et al. [65] proposed a novel direct Z-scheme by combining 3D g-C$_3$N$_4$-ZnO with graphene aerogel. The photocatalyst is prepared by the hydrothermal method, self-assembly method and cold drying method. It realizes the efficient degradation of RhB, methyl orange and other organic dyes. In recent years, researchers have no longer been satisfied with the development of a single Z-scheme heterojunction, and new double Z-scheme photocatalytic systems are gradually being designed and prepared. Yao et al. [71] paid more attention to the design of a novel double-Z-scheme and prepared the black phosphorus quantum dots (BPQDs)/g-C$_3$N$_4$/BiFeO$_3$ photocatalyst by a sol–gel method, which significantly improves its degradation ability and stability, demonstrating a new direction to the design of Z-scheme heterojunctions. In Table 5, we have summarized recent research on Z-scheme heterojunctions.

**Table 5. Degradation of pollutants by photocatalyst based on p-n heterojunction.**

| Photocatalyst                  | Pollutant | Effect                                      | Ref. |
|-------------------------------|-----------|---------------------------------------------|------|
| g-C$_3$N$_4$/Bi$_2$WO$_6$      | MB        | The photodegradation efficiency of the 2% CNQD/BWO composites was 82.0%, and achieved 71.8% after the 4th cycle | [72] |
| g-C$_3$N$_4$/3DOM-WO$_3$       | CO$_2$    | The formation rate of CO product is 48.7 µmol g$^{-1}$ h$^{-1}$ | [73] |
| CuBi$_2$O$_4$/BiVO$_4$         | Phenol    | 95% phenol degradation under visible-light irradiation within 3 h | [74] |
| Ag$_3$PO$_4$/Fe$_3$O$_4$/MP     | TC, p-CP  | The catalytic activity of the catalyst over eight experimental runs was above 76% | [75] |
| WO$_3$/K NbO$_3$               | R bB, MB  | In the RhB degradation the efficiencies were 76% after 20 min reaction; in the MB degradation the efficiencies were 45.3% after 20 min reaction | [76] |
| Pt/TiO$_2$/Nb$_2$O$_5$         | DCF, KTF  | The optimal photocatalyst showed a DCF and KTF mineralization rate of 0.0555 and 0.0746 min$^{-1}$, respectively | [77] |
| g-C$_3$N$_4$/Gr-CNTs/TiO$_2$   | Phenol    | Phenol removal over g-C$_3$N$_4$/Gr-CNTs/TiO$_2$ reached up to 90% within 120 min | [78] |
| AgI/ BiOBr                     | CIP       | A rapid degradation ability for CIP with a removal efficiency of 90.9% in 1 h | [79] |
| Ag$_5$CrO$_4$-GO              | MB, RhB, MO | MB, RhB and MO could be completely degraded within 15, 28 and 40 min, respectively | [80] |

4. Conclusions

In the past few decades, heterostructured photocatalysts have shown a bright application prospect in pollutant degradation and environmental remediation due to their superior efficiency and activity, ecological friendliness and recyclability. Type-I possesses high redox capacity, but its recombination cannot be effectively inhibited due to the transfer of photogenerated carriers to the same semiconductor. Although type-II solves the problem of low photogenerated electron–hole separation rate in type-I, the redox ability is limited due to the low redox potential. The p-n heterojunction effectively inhibits the photogenerated carrier’s recombination due to its built-in electric field, but it has the disadvantage of low redox ability and limited degradation ability to pollutants. Therefore, the Z-scheme heterojunction with high photogenerated electron–hole separation rate, high redox capacity and wide visible-light absorption is considered the most promising photocatalyst system.
5. Prospects

In this review, the application of heterojunctions in pollutant degradation over the years is discussed, including the degradation efficiency, the stability and the possibility of further improvement of photocatalyst. In order to realize the industrialization and commercialization of heterostructured photocatalysts in pollutant degradation, future research on efficient heterostructured photocatalysts should focus on the following aspects:

1) The preparation of heterostructured photocatalysts should ensure that the process is simple, efficient, economically and environmentally-friendly. Meanwhile, accurate control of heterojunction morphology, contact interface, crystallization and layered assembly should be achieved. With the further development of nanomaterials and colloidal chemistry, it is possible to make further progress in the preparation of heterostructured photocatalysts.

2) Research on photogenerated electron and hole migration in heterostructured photocatalysts to confirm the formation of different heterojunctions should be perfected. At present, there are still gaps in studies that can directly explain the electron and hole migration at the cross-section of heterojunctions, and only a limited number of characteristics can confirm their spatial separation.

3) It is essential to develop novel materials for the preparation of heterostructured photocatalysts, mainly those with appropriate bandgap structure, high visible-light absorption region, high optical stability and other characteristics. Advanced materials with high catalytic and economic efficiency are of paramount importance in the practical application of heterostructured photocatalysts.

In this review, the preparations, characterizations and applications of several heterojunctions for pollutant degradation are briefly introduced. In particular, colloidal chemistry occupies an important position in the morphology, interface and assembly of photocatalysts. Several types of heterostructured photocatalysts introduced in this paper are prepared under the guidance of colloidal chemistry. In order to achieve environmental remediation, it is important to explore advanced and efficient photocatalysts for practical application. It is hoped that this review will stimulate further exploration of colloidal heterogeneous photocatalysts for pollutant degradation.

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Abbreviations

Acronyms of abbreviations used in this review article.

| Abbreviations | Acronyms |
|---------------|----------|
| 0D            | Zero-dimensional |
| 2D            | Two-dimensional  |
| Ti(OiPr)₄     | Titanium(IV) isopropoxide |
| P123          | Polyethylene oxide-polypropylene oxide-polyethylene oxide |
| meso          | Mesoporous |
| GA            | Graphene aerogel |
LDH  Lactate dehydrogenase  
ATP  Attaulgite  
I-WZ  Waste zeolite-type catalysts  
GO  Graphene oxide  
rGO  Reduced graphene oxide  
ROS  Reactive oxygen species  
XPS  X-ray photoelectron spectroscopy  
EIS  Electrochemical impedance spectroscopy  
FT-IR  Fourier transform infrared spectrometer  
SCR  Selective catalytic reduction  
MO  Methyl orange  
MB  Methylene blue  
RhB  Rhodamine b  
CIP  Ciprofloxacin  
4-NP  P-nitrophenol  
p-CP  4-chlorophenol  
TC  Tetracycline  
DCF  Diclofenac  
KTF  Ketoprofen  
E. coli  Escherichia coli  

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