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Review on heterophase/homophase junctions for efficient photocatalysis: The case of phase transition construction

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ABSTRACT

Semiconductor photocatalysts are extensively applied in environmental treatment and energy conversion. However, one of their major disadvantages is their relatively low photocatalytic performance owing to the recombination of generated electron-hole pairs. The presence of the phase junction is an effective way to promote the photocatalytic activity by increasing the separation efficiency of the electron-hole pairs. Accordingly, extensive research has been conducted on the design of phase junctions of photocatalysts to improve their charge transfer properties and efficiencies. Therefore, for the design of an appropriate phase junction and the understanding of the mechanism of electron-hole separation, the development of the photocatalytic phase junction, including the preparation methods of the heterogeneous materials, is tremendously important and helpful. Herein, the commonly used, externally induced phase transformation fabrication techniques and the primary components of the semiconductors are reviewed. Future directions will still focus on the design and optimization of the phase junction of photocatalytic materials according to the phase transition with higher efficiencies for broadband responses and solar energy utilization. Additionally, the most popular phase transformation fabrication techniques of phase junctions are briefly reviewed from the application viewpoint.

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1. Introduction

The efficient utilization of solar energy is a frontier research field in the 21st century with intense competition in various countries. Accordingly, photocatalysis is a very attractive

approach used for the utilization of solar energy [1–4]. Given that photocatalytic materials are usually faced with various problems, including narrow spectral responses, low-quantum efficiency, poor stability, and recycling difficulties [2,5–7], considerable strides ought to be expended to achieve the

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desired environmental treatment and the production of clean and sustainable energy. The latter could be achieved by converting solar energy efficiently on a large scale and at a low cost utilizing multiple methodologies, including photocatalytic pollutant degradation [8–12], photocatalytic water splitting [13–18], and generation of valuable chemical fuels from photocatalytic CO₂ reduction [19–21]. Therefore, the development of photocatalytic materials with wide spectral responses (corresponding solar spectrum), increased activity, and increased light stability plays key roles in improving the utilization efficiency of solar energy, and in the expansion of the use of photocatalysis.

At present, semiconductors that are used as photocatalysts mainly include metal oxides (TiO₂ [22] and ZnO [23]), noble metal compounds (Ag₃PO₄ [24] and AgCO₃ [25]), sulfides (CdS [26] and ZnS [27]), nonmetallic elementary substances (elemental phosphorus [28,29] and S₈ [30]), and polymers (g-C₃N₄ [31]). This particular area has become a hot-spot research area in recent years. Among these types of semiconductors, metal oxides generally have a wide bandgap and can only use the sun's ultraviolet light radiation, thus limiting their efficiency. Noble metal compounds are not suitable for large-scale applications because of their high cost. Sulfides or nonmetallic elements are prone to photo-corrosion and have poor stability. Additionally, the photo-generated electron and hole recombination rates of the polymers are high. The maximum energy conversion from solar energy is in the range of 1%–5% and does not meet the commercial requirement ($\geq 10\%$) [32]. Development of highly active, stable, and inexpensive photocatalytic materials is a core task associated with the improvement of solar energy efficiency. Visible light absorption can be improved by doping or by surface modifications, but the photo-induced electron and hole recombination is still a serious issue in a single semiconductor. In addition, a single semiconductor cannot have a narrower bandgap, a negative conduction band, and a more positive

valence band at the same time. Correspondingly, the heterophase/homophase junction is the most commonly used way to improve the photocatalytic performance in semiconductors. It improves the photocatalytic activity in two ways: one is to widen the photoresponse range of the semiconductor materials, and the other is to improve the efficiency of the separated photogenerated electrons from holes.

2. Advantages and challenges of heterophase/homophase junction in photocatalysts

The construction of the phase junction is one of the methods used to effectively improve the photocatalytic activity and ameliorate the aforementioned problems associated with these materials. These materials can be classified (a) into three types (I, II, and III) [33] according to the relative position of the two semiconductor bands, and (b) into the p-n type and Z scheme [34–36] according to the different electron transfer pathways, as shown in Fig. 1. When different semiconductors, such as the p-type (holes being the majority charge carriers) or n-type (electrons being the majority charge carriers), come into close contact, a junction will be formed, and a potential difference will be established on both sides of the junction owing to the differences in their respective energy bands and other properties. The existence of the space potential difference can make the photo-generating carrier inject charged particles from one semiconductor energy level to another semiconductor energy level, thus facilitating the separation of electrons and holes, and improving the efficiency of photocatalysis [4,37]. Considering the p-n junction as an example, when the two types of carriers coexist in the two regions, a thin p-n junction is formed at their boundary layer. Owing to the high concentration of holes in the p-type region and electrons in the n-type region, diffusion drives the motion of electrons and holes toward the junction. A spatially charged

Fig. 1. Schematic representation of five types of heterojunction systems.

region is formed near the boundary of the p-n junction. The p-type region has a negative charge, while the n-type region has a positive charge, thereby forming a strong local electric field across the junction. Subject to the local electric field of the junction, charge accumulates at both ends of the junction to form a potential difference, which can then be used as a driving force to effectively separate the photo-induced charges [38–40].

In most cases, the construction of the phase junction requires special preparation technology and a good lattice mismatch [41–45]. Additionally, the nanosized semiconductor requirements for lattice matching are not stringent, and the nano-heterojunction interface, in conjunction with more reliable material selections and preparation methods, is extensively used. Nano-heterojunction materials have the advantage of the small sizes and particle confined effects combined with the characteristics of fast moving carriers, which can lead to unique properties that single-component nanomaterials or body phase heterojunctions do not have [46–48]. Nanocrystalline heterostructures are generally designed and used. For example, semiconductor nanocarbon and nanometal heterostructures can facilitate the rapid transfer of photogenerated electrons [49]. Therefore, considerable efforts have been expended in recent years on the design and fabrication of nanophase junctions for improving the photocatalytic activity. Although the heterojunction has an excellent performance, it is not composed of a single element, and its construction is based on a step-by-step reaction process. First, it is necessary to synthesize the two components of the heterojunction separately. The heterojunction is formed subsequently by using a second binding process. The reaction is complex, time consuming, and not environmentally friendly. Compared to the heterojunction, the homogenous junction is constructed with the same material, and based on the established phase transition, it can also achieve a highly efficient separation of photogenerated carriers. Homogenization does not require the introduction of other elements and has, thus, attracted considerable attention [50–52]. However, the formation of the homojunction is very difficult. Most of the homojunction structures are formed by semiconductors with different crystal phases in the phase transition process, such as anatase/rutile TiO_2 , α/β phase Ga_2O_3 , or hexagonal/cubic CdS . Because of the similar chemical compositions, the band structures of these semiconductor materials cannot be easily modified. Therefore, only a few studies exist in the literature on the homojunction of homocrystalline materials.

Despite the existence of several review papers on phase junctions, such as semiconductor/semiconductor junctions, semiconductor/metal junctions, semiconductor/nonmetal junctions, and surface heterojunctions [4,14–15,47,53–59], an extensive review of the rational designs of phase junctions using fabrication methods, based on externally induced phase transitions, is still necessary to provide readers with an understanding of the current developments in this dynamic research field. In this study, the current research status is discussed in relation to the progress of low-cost applications

with the efficient use of constructed nanophase junctions in photocatalysis.

3. Fabrication strategies of heterophase/homophase junction photocatalysts

As mentioned above, the creation of heterophase/homophase structures on the photocatalysts plays important roles in their photocatalytic activities [60,61]. From the viewpoint of the structural origin, the heterojunctions/homojunctions can be categorized into the composite phase (consisted of two or three different phases), the in-situ growth composite phase, and the phase-, facet- and van der Waals type junctions of a single substance. The junctions of a single substance can be constructed from different crystalline phases of the same chemical composition, like anatase/rutile TiO_2 [62], α/β - Bi_2O_3 [63], and the α/γ - Bi_2O_3 homojunction [64], whereby different crystal facets of the single same semiconductor [65,66] are stacked on a layer-by-layer basis on two-dimensional materials [67,68].

3.1. Heterophase junctions of two or three different phases

Based on the recombination processes in different semiconductors that aim to the formation of heterophase junction structures, the optical absorption threshold can be effectively expanded, and the separation efficiency of the photogenerated carriers can be improved. Semiconductor recombination can transfer photogenerated electrons from the conduction band with a higher conductance to the band with a lower conductance so that the electrons and holes cannot be recombined, thus improving the photocatalytic activity of the photocatalyst. Numerous techniques have been developed to establish nanostructured heterophase junctions as well as the heterogeneous photoelectrodes using facile, low-cost, and energy-efficient methods, such as hydrothermal/solvothermal methods, electrochemical deposition, chemical bath deposition, sol-gel processes, and chemical precipitation [69–101]. Previously, we reviewed some typical heterophase junctions [9], such as TiO_2 -based, Ag-based [100], ZnO-based, and metal-sulfide-based heterophase junctions. Additionally, many heterojunction semiconductors have been studied by combining two semiconductor types, as shown in Table 1. For example, in the CdS-TiO_2 composite photocatalyst [103,104], the composite CdS is excited by visible light to produce photogenerated electrons and holes. Because the lower energy level of the conduction band of CdS is higher than that of TiO_2 , the photogenerated electrons will be transmitted to the conduction band of TiO_2 through the two-phase interface, and the photogenerated holes will be left on the CdS , thus realizing the spatial separation of the positions of the photogenerated charges. Two of the most important issues in the system are lattice matching and contact tightness. Chen et al. [104] found that the CdS-TiO_2 obtained using a single-step method can result in a better interfacial contact performance than the two-step method. Thus, higher photocatalytic activity was obtained. Inserting narrow bandgap semiconductors between layers of inorganic layered

Table 1

Typical nano-heterophase junctions of photocatalysts.

Nano-hetero-phase junctions	Production of H ₂ from water splitting	Generation of C _x H _y O _z from CO ₂ reduction	Photocatalytic degradation of pollutions
p-n type	Cu ₂ S/CdS [69], MoS ₂ /CdS [70], CuO/ZnO [71]	CuO/TiO _{2-x} N [84], CuInS ₂ /TiO ₂ [85]	Ag ₂ O and NaTaO ₃ [92], CuInSe ₂ /ZnO [93], BiOI/ZnO [94]
Z scheme	WO ₃ /g-C ₃ N ₄ [72], ZnO/Cd/CdS [73], g-C ₃ N ₄ /Au/CdS [74], CdS/SiC [75]	Ag ₃ PO ₄ /Ag/g-C ₃ N ₄ [86], Fe ₂ V ₄ O ₁₃ /RGO/CdS [87], TaON/Ag/Ru BLRu' [88]	Ag ₂ CrO ₄ /GO [95], C ₃ N ₄ /TiO ₂ [96]
Type I	TiO ₂ /CuO [76], CdSe/CdS [77], MoS ₂ /g-C ₃ N ₄ [78], CdS/ZnS [79]	Bi ₂ S ₃ /CdS [89]	Sb ₂ S ₃ /TiO ₂ [97], TiO ₂ /CuO [98]
Type II	g-C ₃ N ₄ /g-C ₃ N ₄ [80], g-C ₃ N ₄ /polypyrrole [81], g-C ₃ N ₄ /SrTiO ₃ [82], CdS/g-C ₃ N ₄ [83]	ZnO/g-C ₃ N ₄ [90], Cu ₂ O/TiO ₂ [91]	Bi ₂ WO ₆ /WO ₃ [99], BiOI/SnS ₂ [100], BiOI/ZnTiO ₃ [101]

materials, such as CdS into H₄NbO₁₇, H₂Ti₄O₉, KTiNbO₅, or microporous/mesoporous materials, can also realize the close contact of the catalyst interface and the directional transfer of charge, thus improving the effect of the photocatalytic charge separation.

3.2. In situ growth of phase junction

The properties of the phase junction interface determine the resistance of electron transfer. The ohmic contact can change the path of the electron transfer by optimizing the preparation or treatment conditions. Compared to this particular phase junction, the conductor transfer electron method is more powerful and can form a more reliable ohmic contact. In situ growth of phase junctions of semiconductor heterophase/homophase structures can be controlled by the microstructural or surface morphologies, as shown in Fig. 2. The motion patterns of the electrons and holes generated by photoexcitation are dependent on the crystallization and surface state of the materials [105–108]. For a single semiconductor, the microstructure or surface morphologies of the crystal can be controlled effectively, and the photoelectron and hole pairs can be separated along the internal or surface directions, thereby allowing the quantification of the photocatalytic activity.

In fact, for a semiconductor material, there are usually different crystal forms, and the transition requires time if the re-

action needs to be controlled at the time at which the phase transition occurs. A semiconductor material with a mixed phase can be obtained. It is worth noting that the band-edge positions of different crystal phases of uniform materials usually change slightly because of the changes of the crystal lattice parameters. Therefore, "in situ junctions" can be produced by controlling the formation of different crystalline phases in the same substance. The most successful example of this theory is the formation of a surface heterogeneous junction between TiO₂ anatase and rutile [57], which is further demonstrated by the α/β Ga₂O₃ surface junction [109].

The formation of "in situ junctions" can be achieved by controlling the surface morphology of the semiconductor. The ability of the surface to regulate the electrons and holes will change owing to the arrangement of atoms, the state of the surface bonding, and the coordination condition. In other words, the density of electron states on different surfaces is not the same. Therefore, the generated electric potentials on adjacent crystal planes (surfaces) that drive the electrons and holes in the direction of the junction also vary. Accordingly, this can also achieve an effective spatial charge separation.

The methods described above mainly aim at the enhancement of the ability of photocharged migration on the surface of the catalyst. The actual acceleration point of the catalytic reaction should be the acceleration of the surface chemical reaction. Therefore, almost all of the above "in situ junctions" can be formed by combining homogenous and other (different) phases, or different homogenous surfaces. To improve the catalytic efficiency, it is necessary to accelerate the rate of the interfacial chemical reaction. As mentioned earlier, the reaction rate has increased to a new value by the introduction of sacrificial agents in the solution (loading Pt nanoparticles by the addition of chloroplatinic acid for hydrogen production). Correspondingly, it is necessary to introduce the co-catalyst by constructing the "in situ Schottky junction" [111,112]. Precious metal nanoparticles have a lower superpotential. Accordingly, the overpotential required for hydrogen production can be reduced. Owing to the existence of the Schottky barrier, a single electron is transferred from the semiconductor to the metal nanoparticle, but cannot be recombined with photogenerated holes. The metal nanoparticles can act as the capture center of the electron, and the photogenerated charge is thus spatially separated [112].

Fig. 2. Nanoscale heterogeneity. (a) Mixed type, (b) Laminated type, (c) Core-shell type, (d) Coaxial type, (e) Surface dispersion type. Reprinted with permission from Ref. [110]. Copyright 2009 China National Knowledge Internet.

3.3. In situ phase transformation (close interface)

The regulation and control of the crystal type includes two aspects: one of them is the achievement of the mixed crystal for the enhanced charge separation, and the other is the identification of the temperature-dependence law or the externally induced synthesis of the phase transition. Numerous facile, low-cost, and energy efficient techniques of phase transformations, such as ion doping [113,114], oxide regulations [115,116], wet chemical or solution-phase methods [117–120], pressure-induced phase transitions [121,122], calcination-induced phase transitions [123–125], self-induced self-surface phase junctions [126,127], pulse laser irradiation or UV/ozone-assistants [128,129], mechanical alloying [130], molten salt auxiliary [131], and electrochemistry methods [132,133], have been extensively developed to fabricate heterojunctions/homojunctions. A large number of experimental studies have defined some of these laws that possess increased significance for the rational design of the crystal structure, the guidance of the synthesis, and the optimization of the catalytic performance of the catalyst [134].

3.3.1. Anionic and cationic regulations

Introducing a small number of anions into the semiconductor photocatalyst will influence the phase transition of undoped semiconductors. For example, the introduction of small, low-valence anions (such as Cl^- , F^-) can promote the formation of the rutile phase in TiO_2 . However, the introduction of high-valence anions (such as PO_4^{3-} and SO_4^{2-}) with large radii is not conducive to the transformation of anatase to rutile [135,136]. The percentage of anatase in the surface region can

increase from 2% to 75% with the increase of the content of SO_4^{2-} in TiO_2 from 0 to 3 wt%. In other words, smaller anionic valency makes the formation of rutile titanium dioxide more favorable. This also explains why the sulfuric acid process cannot easily generate rutile products, while the chlorination process can be easily executed in an industrial setting. In effect, when the doped ion radius is greater than or less than the Ti^{4+} radius, the doped ion enters the TiO_2 matrix and generates lattice defects that improve the lattice energy. This energy should be released before the phase transition, which makes the anatase TiO_2 more stable. Accordingly, this leads to the increase of the anatase-rutile phase transition temperature. However, it is worth noting that different phase structures of TiO_2 - SO_4^{2-} samples can be obtained by this method at the same increased temperature (Fig. 3), thus resulting in activities that are six times higher than those of P25 in the photocatalytic H_2 production of the reformation of methanol. In the chart on the right part of Fig. 3, small anatase particles were well dispersed on the large rutile particles to construct an intimate anatase-rutile phase junction, which is conducive to the efficient charge transfer.

The anions NO_3^- , HCO_3^- , PO_4^{3-} , SiO_3^{2-} , and MoO_4^{2-} can be utilized to regulate the anatase-rutile phase of TiO_2 [137]. Larger anions are more favorable to the formation of anatase-type titanium dioxide. Experiments by Devi et al. [138] confirmed that only anatase exists at 700 °C for TiO_2 doped Mo^{6+} , and the rutile phase appears at 700 °C for doped Mn^{2+} . This may be owing to the fact that the doping of high-valence ions (Mo^{6+}) makes the Fermi energy level drift upward, raises the surface barrier, narrows the charge region, and ensures an effective separation of the photogenerated electrons and holes

Fig. 3. (a) Overall photocatalytic activity of H_2 production and (b) surface-specific photocatalytic activity of H_2 production of Pt/P25, Pt/P25- H_2O -700, and Pt/P25- $x\%\text{SO}_4^{2-}$ -700. The solid line in (b) indicates the surface area of the samples. (c) CO selectivities of Pt/P25, Pt/P25- H_2O -700, and Pt/P25- $x\%\text{SO}_4^{2-}$ -700 catalysts. (d) TEM image of typical agglomerates of nanoparticles, (e) fast Fourier transform of the HRTEM image, (f) HRTEM image and colorization of anatase (A, blue) and rutile (R, red) by reverse FFT based on the respective anatase and rutile spots observed in (e) (for interpretation of the references to different colors in this figure, the reader is referred to the web version of this article). Reprinted with permission from Refs. [136] and [119]. Copyright 2012 Royal Society of Chemistry, Copyright 2014 Elsevier.

in the presence of a strong electric field, thus enhancing the photodegradation effect. Liu et al. [119] found that N^{3-} doping can promote the formation of the rutile phase to form heterojunctions, reduce the bandgap of the TiO_2 semiconductor, and expand the irradiation light from ultraviolet to visible light. Tian et al. [139] has studied the effect of S^{2-} doping on the ratio of anatase to rutile. The results show that the higher the S^{2-} doping is, the higher the ratio of anatase to rutile is, which is more favorable to the photocatalytic activity. Pichavant et al. [140] obtained the interfaced anatase-rutile photocatalysts by thermohydrolysis using very low levels (less than 0.5%) of $Sn(IV)$ that acted as a rutile phase promoter, as shown in Fig. 3. This process is much more direct than the coprecipitation of the amorphous product and is followed by the hydrothermal treatment process.

The $Sn(IV)$ content can accurately control the anatase-rutile ratio and the nanoparticles obtained (diameters of 10 nm) exhibit epitaxial relationships between the anatase (200) and rutile (210) planes, thus building porous submicronic composite agglomerates with increased specific surface area (200 m^2/g). Su et al. [141] modified the Bi atoms on the $BiVO_4$ surface by ZnO coating and etching treatments. Based on this coating process, the Zn doping on the surface lowered the Fermi level of $BiVO_4$ and a $BiVO_4/Zn:BiVO_4$ homojunction with a type II band alignment was formed. The construction of the $BiVO_4$ homojunction improved the charge transfer process and avoided the surface electron trapping, thereby exhibiting an enhanced PEC performance. Therefore, anionic and cationic doping can effectively regulate the phase transition and improve the photocatalytic activity of semiconductor photocatalysts.

3.3.2. Oxide regulations

Introducing oxide in the photocatalyst can also regulate its phase transition and influence the photocatalytic activity. Jung et al. [142] showed that the addition of Al_2O_3 into TiO_2 for the thorough transformation of anatase-rutile types has an obvious inhibitory effect, the calcining temperature is as high as 800 $^{\circ}C$, and anatase TiO_2 is still the main crystal structure with a specific spatial extent regarding the rutile phase. Li et al. [143] found that the addition of Nd_2O_3 has an effect on the surface

phase of TiO_2 and on the photocatalytic activity studied by UV Raman spectroscopy. They showed that the amount of Nd_2O_3 that was well dispersed onto the surface of $Nd-TiO_2$ particles had a higher surface area and a wider optical response, and could tune the crystalline phase and composition of $Nd-TiO_2$ calcined by high temperatures, inhibit the crystal size agglomeration, and transform the anatase phase to the rutile phase. Additionally, $Nd-TiO_2$ nanoparticles are more reactive in the photocatalytic degradation of RhB. Nonmetal oxide, such as SiO_2 , can also regulate and effectively control the crystal type and the grain growth of TiO_2 and improve the catalytic performance. SiO_2 composite particles can effectively improve the lifetime of TiO_2 catalysts, and the TiO_2-SiO_2 composite has a larger specific surface area and is more acidic than TiO_2 . The superior photocatalytic performance may be attributed to the bridging oxygen structures of $Ti-O-Si$ from TiO_2 and SiO_2 . This led to increased specific surface area and surface defects, which is advantageous to the photogenerated electron-hole separation, and promoted the photocatalytic reaction [144,145]. Furthermore, $Ti-O-Si$ effectively inhibited the thorough phase transition of anatase to rutile, increased the stability of anatase, and prevented the accumulation of the TiO_2 grain growth [146]. Periyat et al. [115] studied different silicon contents on the effect of the stability of the TiO_2 anatase type. When the mass fraction of SiO_2 was 15%, rutile appeared and was maintained up to a calcined temperature of 1000 $^{\circ}C$.

3.3.3. Soft-chemical-route-induced phase junctions

Soft chemical route uses the circuitous steps to prepare the nanomaterials based on a slow reaction process in the presence of mild reaction conditions. Common soft chemical methods include the sol-gel, hydrothermal, microemulsion, low-temperature solution phase, vapor deposition, precursor, microwave-assisted synthesis methods, and others. Sun et al. [58] successfully prepared $\alpha/\gamma-Bi_2O_3$ homojunctions via a hydrothermal method that exhibited a synergetic effect on the photocatalytic activity. The diffuse reflectance and impedance spectra determined the homojunction between the $\alpha-Bi_2O_3$ and $\gamma-Bi_2O_3$. Based on these, they pointed out the mechanism of the charge transfer and the separation on the interface of $\alpha/\gamma-Bi_2O_3$. Bera et al. [147] and Shi et al. [59] also successfully

Fig. 4. (a) Photocatalytic mechanism and (b) the HRTEM images of the $\alpha/\beta-Bi_2O_3$ photocatalyst. Reprinted with permission from Ref. [59]. Copyright 2017 Elsevier.

synthesized the α/β - Bi_2O_3 homojunction photocatalyst with the use of novel solvothermal-calcination or one-pot hydrothermal methods. Correspondingly, the material exhibited exceptional and synergistic photocatalytic activity and a fairly stable performance for the removal of 17 α -ethinylestradiol and rhodamine B from aqueous solutions. Fig. 4 shows a possible photocatalytic mechanism and a clear phase junction between α - Bi_2O_3 and β - Bi_2O_3 . It suggests that the approach is practicable toward the design and construction of heterogeneous photocatalysts. Because of the different electronic structures of the layered 2H/1T-MoS₂ with the semiconducting 2H (trigonal prismatic D3h) phase and the 1T (octahedral Oh) metallic phase, Wu et al. [148] reported earth-abundant 1T-MoS₂ and graphitic C₃N₄ heterojunctions formed by a facile hydrothermal method in thioacetamide and molybdenum pentachloride. These allowed faster photogeneration of electrons for a drastically improved photocatalytic hydrogen evolution activity compared to that of the 2H counterpart (Fig. 5). Furthermore, mixed-phase TiO₂ powders with controllable anatase/rutile ratios could be easily controlled by the hydrothermal or solvothermal method, such as the pH [149,150], solvent type [151], and precursor [152]. For instance, Li et al. [149] reported anatase and rutile mixed-phase TiO₂ photocatalysts by the tartaric acid as a phase regulator in the hydrothermal environment and found that the heterojunction catalyst with an anatase to rutile content ratio of 77% to 23% exhibited the highest photocatalytic activity. Li et al. [152] also prepared under controlled conditions a pure phase and mixtures of four TiO₂ poly-

morphs (anatase, rutile, brookite, and TiO₂(B)) based on hydrothermal reactions in an acidic potassium titanate solution as the precursor. In Fig. 6, the acid concentrations of the HCl, HNO₃, and H₂SO₄ solutions can change the compositions of the mixed-phase anatase/TiO₂(B), rutile/brookite, and TiO₂(B)/rutile/brookite hierarchical nanostructures. Accordingly, the samples with 59% anatase were obtained and led to the highest photocatalytic activity, which was 1.43 times that of P25. Similarly, Sun et al. [153] fabricated the heterostructured Bi₂O₂CO₃/Bi₂O₄ photocatalysts by a facile one-pot hydrothermal method, where Bi₂O₄ nanorods and particles were deposited on the surfaces of the Bi₂O₂CO₃ plates, and the material exhibited remarkably enhanced activity compared to Bi₂O₂CO₃ and Bi₂O₄.

3.3.4. Controlling calcination-induced phase junctions

When the semiconductors were heated, the atoms or ions in the lattices vibrated violently and broke away from the original lattice to form new nuclei. They gradually grew by accepting diffused material flow. The main factors that affected semiconductor phase transitions were the crystal structure, internal defects, morphology (particle size, porosity, and surface condition), energy state of components, as well as the heating temperature, time, and atmosphere. According to this phenomenon, a theoretical model of semiconductor phase transition is proposed to construct the heterojunction, as shown in Fig. 7 [123]. Herein, owing to the control of thermodynamics and phase transition kinetics, the phase transition of semiconduc-

Fig. 5. (a) Photocatalytic hydrogen production rates for g-C₃N₄ and 0.20 wt% 2H-MoS₂@g-C₃N₄ nanosheets and 0.20 wt% 1T-MoS₂@g-C₃N₄ nanosheets; (b) Stability test outcomes of 0.20 wt% 1T-MoS₂@g-C₃N₄ nanosheets over a period of 12 h in 4 h cycles; (c) Schematics showing the synthetic process of the 1T-MoS₂@g-C₃N₄ nanosheets. Reprinted with permission from Ref. [148]. Copyright 2017 Royal Society of Chemistry.

Fig. 6. (a) Phase diagram of TiO_2 samples prepared in HCl , HNO_3 , and H_2SO_4 solutions based on hydrothermal reactions; (b) Photocatalytic activities of the samples with different anatase contents and P25 for MB decomposition. Reprinted with permission from Ref. [152]. Copyright 2012 Royal Society of Chemistry.

Fig. 7. Theoretical model of semiconductor phase transition explaining the construction of heterojunctions.

tors usually occurs in a step-by-step manner. When the temperature of the system rises to Temp. 1, the first phase transition takes place in the semiconductor. By controlling the phase transition rate, a two-phase coexistence system can be obtained. Because the phase transition occurs within itself, phases 1 and 2 can generate close contact heterostructures, and the heterostructures of the crystal phase 2/crystal phase 3 or crystal phase 3/crystal phase 4 may also be formed. Once the appropriate amount of heterogeneous phase structure is successfully constructed, a potential difference may exist between the two types of semiconductor crystal phases with energy

level matching, which will establish an internal electric field, accelerate the separation of photogenerated electrons and holes, and improve the activity and stability of the photocatalytic reaction.

For instance, our group constructed binary [123,124] and ternary [154,155] semiconductor phase formation systems with heterogeneous phase junctions based on thermodynamics and phase transformation kinetics, and found the regulation of the crystal phase interface on photoelectrons (e^-) and holes (h^+). Thereinto, the phase transition law of Ag_2CO_3 was found, and the mechanism of phase transition was established to construct $\text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O}$. Thus, the silver-based photocatalyst was obtained with high-stability and high-photocatalytic efficiency, which established Ag_2CO_3 as a hotspot photocatalyst in recent years. Thermogravimetric analyses in Fig. 8a show that the weightlessness in the temperature range of 180 to 250 °C corresponds to the phase transition of $\text{Ag}_2\text{CO}_3 \rightarrow \text{Ag}_2\text{O}$. Meanwhile, the Ag_2O phase was stable in the temperature range of 250 to 300 °C, and the $\text{Ag}_2\text{O} \rightarrow \text{Ag}$ phase transition corresponded to the temperature range of 300 to 425 °C. Fig. 8b shows that the

Fig. 8. (a, b) TG curves of Ag_2CO_3 in air atmosphere; (c) Schematic of the $\text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O}$ heterostructure according to the Ag_2CO_3 phase transition; (d) Photograph showing the color changes of different samples; (e) Energy-level structure of $\text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O}$; (f) Electron and hole transfer model diagram showing the surface plasmon resonance effect. Reprinted with permission from Refs. [123,124]. Copyright 2014 Wiley and 2016 Elsevier.

production of the Ag_2CO_3 phase transition was completely dependent on Ag_2O at 210 °C and occurred over a period of 22 min. The Ag_2CO_3 surface began to change into Ag_2O when it was heated, and the new phase of Ag_2O was wrapped on the Ag_2CO_3 surface, which prevented the escape of CO_2 and the Ag_2O crystal growth and reduced the phase transition rate. The existence of the $\text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O}$ heterocrystalline interface was confirmed by HRTEM. Therefore, the core-shell structure of $\text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O}$ at different phase contents could be prepared by accurately controlling the heating parameters of Ag_2CO_3 . The calculation of electronegativity proved that the constructed $\text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O}$ had a matching energy level structure (Fig. 8e) that can generate an internal electric field. With the use of visible light irradiation, the photogenerated holes of Ag_2CO_3 could easily migrate to the Ag_2O valence band, while the electron of Ag_2O could move to the conduction band of Ag_2CO_3 , thereby accelerating the separation of h^+ and e^- . Based on the surface plasmon resonance effect of precious metals (Fig. 8e), Au, Ag, Au, and Pt nanoparticles were deposited on the heterogeneous boundary plane and the activity of photocatalytic reaction was further improved [154].

The $\text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O}$ heterojunction interface has increased the photocatalytic degradation efficiency for organic pollutants, such as dyes, phenol, bisphenol A, and others. In the presence of visible light irradiation, the photocatalytic activity of the highly concentrated methyl orange dye can be completely degraded with mineralization. The efficiency of $\text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O}$ is 67 times and 31 times higher than those of Ag_2CO_3 and Ag_2O , respectively, and is much higher than that of the novel Ag_3PO_4 photocatalyst [24]. A silver-based photocatalyst is used as a noble metal photocatalyst and has a high cost in engineering applications. Additionally, the silver ion of the binary heterojunction photocatalyst may be reduced to a simple mass by the photogenerated electrons produced by itself during the reaction process. Accordingly, the active component may be lost. Meanwhile, a $\text{Zn}_3(\text{VO}_4)_2/\text{Zn}_2\text{V}_2\text{O}_7/\text{ZnO}$ ternary and cheap zinc vanadate photocatalyst system has been developed [155] whose photocatalytic activity was much higher than that of the $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ precursor synthesized with the use of the

microwave hydrothermal synthesis and the $\text{Zn}_2\text{V}_2\text{O}_7$ monoclinic system calcined at 800 °C. The thermodynamic calculation shows that $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ is a step-by-step phase transition material ($\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O} \rightarrow \text{Zn}_3(\text{VO}_4)_2/\text{Zn}_2\text{V}_2\text{O}_7/\text{ZnO} \rightarrow \text{Zn}_2\text{V}_2\text{O}_7$), as shown in Fig. 9a. The double Z-scheme mechanism in Fig. 9b shows the nontraditional transport of photo-induced h^+ and e^- for the efficient removal of the pollutants.

Based on this principle, more types of bismuth-based heterogeneous phase junction catalysts were developed with increased photocatalytic performance, such as $\text{BiOI}/\text{Bi}_5\text{O}_7\text{I}$, $\text{Bi}_5\text{O}_7\text{I}/\text{Bi}_2\text{O}_3$, $\text{BiOBr}/\text{Bi}_{24}\text{O}_{31}\text{Br}$, and $\text{Bi}_{24}\text{O}_{31}\text{Br}/\alpha\text{-Bi}_2\text{O}_3$ [156–158]. Other thermodynamically unstable substances, such as other series of heterogeneous photocatalysts of silver-based semiconductors, bismuth oxyhalides, bismuth oxide, and bismuth carbonate, were systematically investigated by other groups [116,159–162]. For example, Huang et al. [164] prepared three-dimensional hierarchical bismuth oxyiodides with an in situ phase transformation process based on a controlled calcination strategy. Accordingly, BiOI microspheres were used as a self-sacrificed template for the construction of the phase junctions, while the formation diagram of the hierarchical $\text{Bi}_4\text{O}_5\text{I}_2\text{-Bi}_5\text{O}_7\text{I}$ hetero architecture was obtained as shown in Fig. 10. The authors confirmed that the activity order was $\text{Bi}_4\text{O}_5\text{I}_2\text{-Bi}_5\text{O}_7\text{I} > \text{Bi}_4\text{O}_5\text{I}_2 > \text{Bi}_5\text{O}_7\text{I} > \text{BiOI}$, which ascribed to the efficient charge separation and transfer that originated from band alignment of the as-formed phase junction. Hou et al. [165] prepared an $\alpha\text{-}\beta$ phase Bi_2O_3 nanowire heterojunction by a facile hydrothermal that was responsive to visible light, and the following heat treatment process and the reaction temperature could readily tailor the ratio of the monoclinic $\alpha\text{-Bi}_2\text{O}_3$ and the tetragonal $\beta\text{-Bi}_2\text{O}_3$, and adjust the morphology from two-dimensional $\beta\text{-Bi}_2\text{O}_3$ sheets to the $\alpha\text{-}\beta\text{-Bi}_2\text{O}_3$ nanowire junction. The $\alpha\text{-}\beta\text{-Bi}_2\text{O}_3$ heterojunction had an exceptional photocatalytic performance compared to that of the $\beta\text{-Bi}_2\text{O}_3$ sheets in the degradation of rhodamine B and methyl orange in the presence of visible light irradiation that was attributed to the efficient charge separation and transfer. Bian et al. [126] fabricated $\beta\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{2.33}/\text{Bi}_2\text{O}_2\text{CO}_3$ ternary composites based on the self-integration of the slow, thermal decomposi-

Fig. 9. (a) Construction of the $\text{Zn}_3(\text{VO}_4)_2/\text{Zn}_2\text{V}_2\text{O}_7/\text{ZnO}$ ternary heterojunction according to the thermal analysis of $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$; (b) Possible photocatalytic process of organic pollutants over the $\text{Zn}_3(\text{VO}_4)_2/\text{Zn}_2\text{V}_2\text{O}_7/\text{ZnO}$ system. Reprinted with permission from Ref. [155]. Copyright 2018 Elsevier.

Fig. 10. Photodegradation efficiency of (a) RhB and (b) BPA over calcinated BiOI at different temperatures; (c) Formation diagram of the hierarchical architectures; (d) $\text{Bi}_4\text{O}_5\text{I}_2$ - $\text{Bi}_5\text{O}_7\text{I}$ phase junction. Reprinted with permission from Ref. [164]. Copyright 2017 Elsevier.

tion of $\text{Bi}_2\text{O}_2\text{CO}_3$. Equivalently, $\text{Bi}_2\text{O}_2\text{CO}_3 \rightarrow \beta\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{2.33}@\text{Bi}_2\text{O}_2\text{CO}_3$ (300 °C) $\rightarrow \beta\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{2.33}$ (320 °C) $\rightarrow \beta\text{-Bi}_2\text{O}_3$ (350 °C). It was found that $\beta\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{2.33}@\text{Bi}_2\text{O}_2\text{CO}_3$ had a well-matched bandgap and displayed superior photocatalytic performance compared to $\text{Bi}_2\text{O}_2\text{CO}_3$.

In addition, other heterogeneous phase junction catalysts were evaluated. For example, Zeng et al. [166] constructed a $\text{Sr}_2\text{Ta}_2\text{O}_{7-x}\text{N}_x/\text{SrTaO}_2\text{N}$ heterostructured photocatalyst in situ using hydrothermally prepared $\text{Sr}_2\text{Ta}_2\text{O}_7$ nanosheets in the atmosphere of NH_3 , thereby achieving a well-matched band structure. In the photocatalytic hydrogen evolution, the $\text{Sr}_2\text{Ta}_2\text{O}_{7-x}\text{N}_x/\text{SrTaO}_2\text{N}$ heterostructured photocatalyst yielded the highest rate with $\text{Sr}_2\text{Ta}_2\text{O}_{7-x}\text{N}_x$ and pure SrTaO_2N using similar reaction conditions. Wang et al. [109] first investigated the α - β Ga_2O_3 phase junction by phase transformation at elevated temperatures from 673 to 1073 K. Furthermore, they demonstrated that in photocatalytic water splitting, the Ga_2O_3 phase junction calcined at a temperature range of 863–893 K had a much higher activity than the pure α phase (673 to 773 K) or the β phase (973 to 1073 K) of Ga_2O_3 .

On the basis of phase transitions, the mechanism of phase transition and the co-doping of elements used to improve pho-

tocatalytic performance were further explored. For example, Ti_2CN was used for the first time as a raw material, and C-N self-doping was realized at the same time by the precise control of the O_2 atmosphere, heating time, and temperature, in the reactions relevant to the formation of the crystal phase of anatase and rutile TiO_2 [167]. The photoelectron spectra indicated that C and N were doped in the process of the phase transition. It was further proved that C-N/ TiO_2 could be prepared with different C and N contents based on the accurate control of the heating temperature, time, and atmosphere of Ti_2CN . C-N codoping can form impurity energy levels, reduce the gap of TiO_2 , accelerate the separation of h^+ and e^- , and improve the absorption ability. Additionally, the preparation of P and WO_3 co-doped TiO_2 can significantly inhibit the photogenerated electron and hole recombination [168]. Zhu et al. [169] investigated the effects of heat treatment on the anatase-rutile phase transformation and the photocatalytic activity of Sn-doped TiO_2 nanomaterials. It is found that at 350 °C, 1% Sn doping led to the highest degradation rate, while at 500 °C and 650 °C, 5% Sn doping led to the best photocatalytic activity. The relationship between the regulation of heterogeneous phase junctions and the physical properties of the compounds, such as the crystal structure, morphology, ionic radius, and decomposition kinet-

ics, were also investigated. Therefore, the highly efficient heterojunction photocatalyst was synthesized by the phase transformation kinetics method of heating and self-transformation. This constitutes the technological innovation of the preparation process of the heterojunction photocatalyst, whereby the quality of the photocatalyst has been improved.

3.3.5. Self-surface phase junctions of crystal plane

In a photocatalytic reaction on the surface of a semiconductor, it is essential to achieve an effective transfer and spatial separation of the photoinduced charges on the surface of the photocatalyst [170]. Thereinto, the surface phase junctions and the aligned built-in electric fields can drive the charge separation and transfer [171–173]. The outcome of this process is the formation of two spatially separated surface locations that boost the targeted chemical reaction. Therefore, the self-surface phase junction of a single semiconductor underlines the role of the built-in electric field in conducting the semiconductor carriers to the surface redox reaction sites.

Using effective detection technology, Li et al. [57] developed ultraviolet (UV) Raman spectroscopy in the study of the surface properties of the TiO_2 catalyst, which has recently proved to be a powerful tool in determining the variation of the surface phase structure. Because UV Raman spectroscopy can be more sensitive to the surface phase, it can overcome the interference of fluorescence and strengthen the Raman signals at short wavelengths. Li's group [143] also investigated the influence of Nd_2O_3 on the surface phase of TiO_2 using UV Raman spectroscopy and showed that the coexistence of anatase and rutile in the surface region of Nd-TiO_2 determined the optimal activity. UV Raman spectra certainly justified the fact that the surface ion SO_4^{2-} could restrain the surface phase transformation at elevated temperatures [145].

Based on the hydrothermal treatment strategy in the HNO_3 solution using titanate nanotube as a precursor, Huang et al. [174] synthesized the highly active TiO_2 photocatalysts of the anatase-brookite and anatase-rutile surface phase junction. The surface heterophase junctions of TiO_2 could suppress the recombination of photoinduced charge carriers. Additionally, TiO_2 consisted of 72.9 wt% anatase, 24.6 wt% brookite, and 2.5 wt% rutile, and exhibited a higher photocatalytic activity owing to the H_2 yield than that of P25 using the same reaction conditions ($179 \mu\text{mol h}^{-1} \text{g}^{-1}$ vs. $45.3 \mu\text{mol h}^{-1} \text{g}^{-1}$).

According to the density functional theory (DFT), Yu et al. [172] calculated the density of states on different crystal planes of anatase TiO_2 . It was found that the (001) and the (101) planes can form heterojunctions of crystal planes and promote the separation and transfer of photogenerated electrons and holes (Fig. 11(a)). The results of the photocatalytic reduction of CH_4 by CO_2 show that when the ratio of the (101) and (001) surfaces exposed to TiO_2 is close to 1:1 (optimum ratio), the photogenerated electrons gathered on the (101) plane could participate in the reduction reaction, while holes gathered on the (001) plane could participate in the oxidation reduction. The formation rate of CH_4 reached $1.35 \mu\text{mol h}^{-1} \text{g}^{-1}$ and increased 21 times.

In recent years, Li et al. [175] also indicated that the pho-

Fig. 11. (a) Spatial separation of redox sites of the exposed (101) and (001) facets on TiO_2 ; (b) Charge separation on the (001) facet of Cu_2O parallel to the light irradiation direction; SEM images of (c) Au-deposited ($\text{Cu}_2\text{O}/\text{Au}$) and (d) dual co-catalyst deposited ($\text{Cu}_2\text{O}/\text{Au}/\text{MnO}_x$) Cu_2O crystals prepared via photodeposition with the use of asymmetric illumination; SPVM images of (e) Au-deposited and (f) dual co-catalyst-deposited Cu_2O crystals obtained with the use of asymmetric illumination. Reprinted with permission from Refs. [60,61]. Copyright 2014 American Chemical Society and 2018 Nature.

to-induced surface potential changes (SPV) could be imaged directly to assess the localized spatial charge separation behavior across the spatially varying charge regions at the surfaces of the photocatalysts. The same authors were able to identify complex charge separation and transfer processes that have been revealed in many other photocatalysts [176,177]. For instance, single cubic Cu_2O crystals were prepared to reveal the influence of the intrinsic asymmetric built-in electric field on charge separation by localized SPV measurements [61]. The (001) facet was exposed to the light direction (Fig. 11(b)), and the charge separation was driven by the built-in electric field with a SPV of 20 mV. The quantitative results showed that the photogenerated charge separation was highly dependent on the length of Cu_2O (i.e., the particle size), whereby holes moved toward the illuminated facet, and electrons moved toward the shadow facet. It can be deduced that the heterojunction of the crystal plane of cubic Cu_2O particles under asymmetric illumination was important in the photocatalyst system. The spatially separated electrons and holes were available for surface redox reactions of trivalent Au^{3+} reduction and Mn^{2+} oxidation, as shown by Fig. 11(c) and (d), whereby the shadow facets included the deposition of Au particles and the illuminated facets contained the MnO_x agglomerates. The charge separation behavior was also further confirmed by SPV, as shown in Fig.

Fig. 12. SEM images of BiVO₄ with and without the deposition of single metal/oxide. (a) BiVO₄, (b) Au/BiVO₄, (c) Pt/BiVO₄, (d) Ag/BiVO₄, (e) MnO_x/BiVO₄, (f) PbO₂/BiVO₄. The contents of the deposited metals/metal oxides are all 5 wt%. Scale bar, 500 nm. Reprinted with permission from Ref. [176]. Copyright 2013 Nature.

11(e) and (f).

Similarly, in Fig. 12, also shown are the spatial separations of the photogenerated electrons and holes on the (010) and (110) crystal facets of BiVO₄ [60,168,177]. The reduction reaction of the photogenerated electrons and the oxidation reaction of the photogenerated holes can occur on the (010) and (110) facets of BiVO₄ and correspond to the selective deposition of the Pt and MnO_x cocatalysts. These results demonstrate that a material with appropriate self-phase-junction of crystal planes is vitally important in the photocatalytic system. This also provides guidance in designing different, high-energy crystal planes for efficient charge separation and redox reactions in energy and in environmental photocatalysis.

3.3.6. Other assistant-driven phase junctions

To-this-date, other empirical and experimental methods have also been reported for the construction of phase junctions, such as electrochemistry, pulse laser irradiation or UV/ozone-driving, mechanical alloying, and pressure-induced phase transitions. Using electrochemical methods, Liang et al. [179] prepared a mixture of anatase and rutile phases with TiO₂ nanotubes. These nanotubes were synthesized with the

anodic oxidation method and exhibited high-photocatalytic activity for the degradation of 2,3-dichlorophenol in an aqueous solution. Sreekantan et al. [132] prepared anatase-rutile TiO₂ nanotubes using the titanium foil anodization method in an electrochemical bath of 1 mol/L glycerol with 0.5 wt% NH₄F at a pH of 6. Furthermore, it was shown that the anodization voltage could influence the morphology of the anodized and well-aligned growing titanium with pit-like oxide. Ren et al. [133] reported a one-step electrochemical oxidation method which only required a few minutes to prepare mixed-phase TiO₂ porous films with oriented rutile. In the synthetic process, the additive amount of HCl or HF in the electrolyte could regulate the orientation as well as the rutile nanocrystallites with a large specific surface area. The obtained tailor-oriented TiO₂ porous films could produce an enlarged photocurrent based on the treatment of HF which was used as an additive compared to the photocurrent from randomly oriented TiO₂ films. Additionally, the synergistic effects of orientation led to a film arrangement with increased exposure of the rutile (101) facets, while the F impurity of the surface showed improved photocatalytic and photoelectrochemical performances. Lv et al. [180] fabricated an α - β phase junction in Bi₄V₂O₁₁ nanofibers based on the electrospinning retardation effect (electrospinning with subsequent calcination), which could transform the α -Bi₄V₂O₁₁ in β -Bi₄V₂O₁₁ and construct an α - β Bi₄V₂O₁₁ phase junction with a well-defined type-II band alignment, as shown in Fig. 13. The α - β phase junction on the Bi₄V₂O₁₁ nanofibers achieved an outstanding photocatalytic activity used in the removal of Cr(VI) and MB with the concurrent use of nitrogen fixation.

Several other studies focused on the phases that are naturally induced by extra pressure, induced phase transitions, wire explosion processes, or UV or pulse laser irradiations, in materials such as Nb-doped TiO₂ [140] and RbPbCl₃ [141]. Lu et al. [140] reported enhanced electron transport in Nb-doped TiO₂ nanoparticles based on pressure-induced phase transitions. The electron transport in semiconductors was related to the packing factor of the pressure-induced conductivity evolution. Huang et al. [141] also studied the generation of new pressure-induced phase transitions and their photocatalytic properties in RbPbCl₃ using calculations based on fundamental principles. Accordingly, they predicted four new phases, in-

Fig. 13. Formation process and fast separation and transfer of photogenerated carriers on the α - β phase junction structure of the Bi₄V₂O₁₁ nanofibers. Reprinted with permission from Ref. [180]. Copyright 2018 ACS.

cluding $P4/mmm$, $C2mm$, $I4mm$, and Cm , for $RbPbCl_3$, whereby the electronic structural properties could be modulated by pressure at specific phases. Accordingly, the same authors showed that the $C2mm$, $I4mm$, and Cm phases were promising candidates in photocatalytic water splitting.

Based on the wire explosion process, Ranjan et al. [181] synthesized mixed phases for TiO_2 nanoparticles of anatase and rutile in an oxygen atmosphere at a specific pressure. The phase and morphology of TiO_2 nanoparticles were governed by the ratio of the stored quantity in the capacitor and the sublimation quantity of the wire. Additionally, the increase of the ratio and the decrease of the oxygen pressure could promote the enhancement of the rutile content. At the two extreme concentration conditions of 300 and 400 mg/L, it exhibited an excellent performance in the photocatalytic removal of methylene blue.

In addition, Zhang et al. [128] reported a UV/ozone-assisted method to prepare mesoporous TiO_2 with controlled phase composition at temperatures as low as 100 °C. The exposure time can potentially adjust and control the mixture of the crystalline mesoporous anatase and rutile phases. Choi et al. [129] introduced a facile crystalline phase control method of electrospinning and pulse laser irradiation in liquid to prepare the mixed anatase and rutile phases of TiO_2 nanofibers to achieve enhanced photochemical responses and photocatalytic activities in the decomposition of methylene blue. Similarly, Russo et al. [182] studied the phase transformation of TiO_2 nanoparticles governed by the femtosecond laser ablation of P25 in aqueous solutions and the deposition on FTO conductive substrates. It was then found that the prolongation of the ablation time of the TiO_2 dispersion could widen the bandgap. In other words, it is highly desirable to develop a new, low-cost and effective preparation method for the advancement of phase junctions.

4. Applications of heterophase/homophase junction photocatalysts

4.1. Photocatalytic H_2 evolution

Photocatalytic splitting of water is used to produce hydrogen and is considered as one of the most challenging reactions for the preparation of fuel by solar energy. As the understand-

ing of the mechanisms of operation of semiconductor photocatalysts and co-catalysts continues to improve, research progress will continue to be accomplished in the field of photocatalysis. Li et al. [183] prepared a composite $Sr_2TiO_4/SrTiO_3(La,Cr)$ heterojunction photocatalyst using a simple, in situ, polymerized complex method. Well defined heterojunctions were formed by matching the lattice fringes of $SrTiO_3(La,Cr)$ and $Sr_2TiO_4(La,Cr)$ based on microscopic observations. The absorption spectroscopy and Mott-Schottky plots revealed the band structure of the composite $Sr_2TiO_4/SrTiO_3(La,Cr)$, and the facts that the photogenerated electrons migrated from $SrTiO_3(La,Cr)$ to $Sr_2TiO_4(La,Cr)$ and holes tended to move from $Sr_2TiO_4(La,Cr)$ to $SrTiO_3(La,Cr)$ driven by a minor potential difference. These findings indicated the superior photocatalytic activity of photocatalytic H_2 production (Fig. 14). A time-resolved FT-IR spectroscopic study confirmed the long-lived electrons and the facilitated charge transfer and separation. Li et al. [184] studied the integration of the nanorod photocatalyst with the hexagonal@cubic CdS core@ shell for highly active production of H_2 with unprecedented stability by taking into consideration advantages of core-shell structures in reference to the surface passivation. This shortened the electron diffusion length, increased light absorption, and enhanced the tunneling of charge carriers. The entire process was based on a highly effective, low-cost strategy of the one-pot hydrothermal method, i.e., the direct treatment of cadmium nitrate and thiourea precursor solution at a specific temperature with a variable Cd/S precursor molar ratio and reaction time (Fig. 15).

Liu et al. [185] also prepared CuO_x/TiO_2 photocatalysts which employed TiO_2 with different phase structures, and $CuO_x/P25$ with the largest population of Cu_2O -anatase TiO_2 heterojunction. These compounds exhibited the highest photocatalytic production of H_2 . Similarly, Devaraji et al. [186] also synthesized two-dimensional mixed phase leaf- $Ti_{1-x}Cu_xO_2$ sheets. The synthesis was based on a natural leaf template, and the incorporation of Cu ions (1 wt%) into the leaf- TiO_2 lattice using a deposition-precipitation method, and was followed by a calcination process. Two-dimensional mixed-phase leaf- $Ti_{1-x}Cu_xO_2$ sheet calcination at 750 °C led to the highest hydrogen yield. This was mainly attributed to surface-phase junctions, disordering mesoporosity, 2D sheet morphology, and

Fig. 14. Schematic band structure and photocatalytic H_2 production activities of La and Cr codoped $Sr_2TiO_4/SrTiO_3$ and its mechanism for H_2 production in the presence of visible light irradiation. Reprinted with permission from Ref. [183]. Copyright 2013 RSC.

Fig. 15. Formation process and the photocatalytic H_2 production activity at different conditions pertaining to the nanorod photocatalyst with the hexagonal@cubic CdS core@ shell. Reprinted with permission from Ref. [184]. Copyright 2016 Wiley.

fast charge carriers. Xu et al. [187] constructed a bi-phasic (anatase/rutile) nanocomposite TiO_2 nanofiber photocatalyst with a direct Z scheme which attained an enhanced photocatalytic H_2 production activity. A novel anatase/rutile TiO_2 photoelectrode with hydrogenated heterophase interface structures was also found, and was synthesized by the hydrothermal synthesis-hydrogenation-branching growth method [188]. The superior photoelectrochemical (PEC) performance was attributed to the matching energy levels between anatase-branches and the hydrogenated rutile-nanorod, and to the new energy levels of oxygen vacancy and Ti-OH . Qiu et al. [189] constructed TiO_2 hierarchical architecture assembled by nanowires with anatase/ $\text{TiO}_2(\text{B})$ phase junctions using a hydrothermal process which was followed by calcination. The optimum calcination treatment at 450°C yielded the best photocatalytic hydrogen production activity. Wang et al. [80] constructed the isotype C_3N_4 /sulfur-mediated C_3N_4 heterojunctions of polymeric carbon nitride between two different crystal phases of a single substance (known as crystal-phase heterojunctions) by combining bulk C_3N_4 and the molecularly engineered heptazine

tectons in a sulfur medium (sulfur-mediated C_3N_4 can adjust its packing structure and electronic band structure). As shown in Fig. 16, such polymeric isotype heterojunctions show significant enhancements in the activities and durabilities of the H_2 evolution reactions. This was attributed to the promoted exciton dissociation and charge separation from the band offsets.

4.2. Photocatalytic CO_2 reduction

The photocatalytic reduction of CO_2 is the conversion of the C=O double bonds from linear CO_2 molecules to C-O single bonds through renewable solar energy, and the use of new catalysts, thereby producing methane, methanol, or olefin, and other products. This can create new chemical supplies to replace the current dependence on oil, coal, and natural gas, and provide an economical and environmentally friendly CO_2 utilization process. For example, small metal particle-coated p-Si electrodes (Cu, Ag, or Au) were prepared for the photoelectrochemical reduction of CO_2 [190]. These particles had high photovoltages of ca. 0.5 V and were used as effective electrodes for

Fig. 16. Organic heterojunction and stability test of the evolution of H_2 between C_3N_4 /sulfur-mediated C_3N_4 photocatalysts in the presence of visible-light irradiation. Reprinted with permission from Ref. [80]. Copyright 2012 Wiley.

Fig. 17. Photocatalytic mechanism of the $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$. Reprinted with permission from Ref. [86]. Copyright 2015 ACS.

the photoelectrochemical reduction of CO_2 . He et al. [86] prepared $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{g-C}_3\text{N}_4$ in situ using $\text{g-C}_3\text{N}_4$, AgNO_3 , and Na_2HPO_4 as raw materials. The photogenerated electrons of Ag_3PO_4 and photogenerated holes of $\text{g-C}_3\text{N}_4$ could transfer to Ag for the recombination (Fig. 17). In this way, the photogenerated electrons could catalyze the reduction of CO_2 at the high position of the $\text{g-C}_3\text{N}_4$ conduction band, and result in higher activities. The rate of preparation of $\text{C}_x\text{H}_y\text{O}_z$ was as high as $57.5 \mu\text{mol h}^{-1} \text{g}^{-1}$, and was 6.1 and 10.4 times higher than $\text{g-C}_3\text{N}_4$ and P25, respectively.

Wang et al. [191] designed hierarchical $\text{In}_2\text{S}_3\text{-CdIn}_2\text{S}_4$ heterostructured nanotubes based on a novel self-template strategy, including sequential anion- and cation-exchange reactions (Fig. 18a). These nanotubes can be efficient and stable photocatalysts for visible light and CO_2 reduction owing to the separation and migration of the photoinduced charge carriers, the adsorption and concentration of CO_2 molecules, and the abundant number of active sites for surface redox reactions in the hierarchical heterostructured nanotubes. Similarly, the same authors [192] also constructed the sandwich-like $\text{ZnIn}_2\text{S}_4\text{-In}_2\text{O}_3$ hierarchical tubular heterostructures based on (a) the thermal annealing treatment of the in-MIL-68 prism precursor, and (b) the subsequent hydrothermal reaction on the surfaces of the as-derived In_2O_3 tubes (Fig. 18b) (growing ZnIn_2S_4 nanosheets on both the inner and outer surfaces of the In_2O_3 microtubes) where the optimized $\text{ZnIn}_2\text{S}_4\text{-In}_2\text{O}_3$ exhibited an outstanding performance for CO_2 reduction ($3075 \mu\text{mol h}^{-1} \text{g}^{-1}$) and in-

creased stability.

4.3. Photocatalytic degradation

Hou et al. [193] constructed bismuth oxychloride microflower/nanosheet homojunctions via a solvent-free route for the first time with the controlled reaction temperature owing to some microflowers merging into large nanosheets at $T > 120^\circ\text{C}$ (Fig. 19). The increased photoactivity of the homojunction sample was attributed to the considerable differences in sizes and the exposed facets between the microflowers and the nanosheets. This allowed the determination of the increased specific surface area and the differences in their energy band levels. Furthermore, Hao et al. [194] fabricated an n-n type bismuth oxychloride ($\text{BiOCl}/\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$) homogeneous phase junction by facilely manipulating the basicity in a one-pot hydrothermal process. The $\text{BiOCl}/\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ phase junctions showed a much higher photocatalytic activity than the single BiOCl and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ toward the degradation of industrial contaminants in the presence of simulated solar light that was attributed to the efficient separation and transfer of photo-induced carriers because of the junction interface between BiOCl and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$.

Kondamareddy et al. [195] synthesized TiO_2 -anatase/rutile heterojunctions by incorporating tungsten (W^{6+}) ions into the lattice of pure anatase TiO_2 nanoparticles with ultra-trace concentrations (ppm) using a simple one-step hydrothermal method. The enhancement of the photocatalytic activity under visible light irradiation for the degradation of rhodamine B was assigned to the impurity energy levels of the W^{6+} ions, oxygen vacancies, and the anatase-rutile heterojunction. Gao et al. [196] also investigated the effects of the C and Y doping and annealing temperatures on the structural and optical properties and photocatalytic activity of mixed phase TiO_2 . It was found that C and Y doping can broaden the absorption spectrum of TiO_2 , increase the specific surface area, and enhance the photocatalytic activity. Makal et al. [197] studied (a) TiO_2 nanowires with different phases using the hydrothermal technique, e.g., $\text{TiO}_2\text{-B}$, anatase, and rutile, and (b) the subsequent thermal annealing process in vacuum at different temperatures, and investigated their photocatalytic performance. The $\text{TiO}_2\text{-B}/\text{anatase}$ heterostructured nanowires by partial phase transformation at 700°C showed enhanced photocatalytic ca-

Fig. 18. Schematic illustration of the synthetic process of hierarchical (a) $\text{In}_2\text{S}_3\text{-CdIn}_2\text{S}_4$ and (b) $\text{ZnIn}_2\text{S}_4\text{-In}_2\text{O}_3$ heterostructures. Reprinted with permission from Refs. [191,192]. Copyright 2017, 2018 ACS.

Fig. 19. Formation and growth process, energy band levels, and photogenerated charge carrier transfer pathways of BiOCl microflower/nanosheet homojunctions. Reprinted with permission from Ref. [193]. Copyright 2018 Wiley.

capacity because of their broad optical band gaps.

Jo et al. [198] fabricated a unique Janus $\text{Ag}_2\text{O}/\text{Ag}_2\text{CO}_3$ heterojunction photocatalyst with improved photocatalytic properties using in situ phase transformation, and Zhao et al. [199] reported $\text{Ag}_2\text{O}/\text{Ag}_2\text{CO}_3$ 3D hollow flower-like hierarchical microspheres, which exhibited improved photocatalytic performance and stability compared to those of bare Ag_2CO_3 . Wang et al. [200] fabricated $\text{TiO}_2(\text{B})/\text{anatase}$ heterophase junctions in nanowires via a surface-preferred phase transformation process, i.e., a three-step synthesis method, including hydrothermal treatment, H^+ exchange, and annealing. The optimized structure with 24% $\text{TiO}_2(\text{B})$ in the bulk and 100% anatase on the surface led to an enhanced photocatalytic activity (Fig. 20).

Samsudin et al. [201] fabricated bluish-gray hydrogenated TiO_2 by hydrogenating it at constant temperature and pressure with controlled hydrogenation duration. They demonstrated that the photocatalytic activity was attributed to the increased oxygen vacancies and Ti^{3+} for solar light absorption, while the extended hydrogenation duration caused decreases in the activity owing to the excessive catalyst growth and loss in the total surface area. Li et al. [202] studied the charge transfer at an anatase/rutile TiO_2 phase junction using time-resolved photoluminescence spectroscopy, and found that the charge separation at the anatase/rutile phase junction reduced the microsecond time scale photoluminescence decay rate for the charge carriers because of the slower electron-hole recombination

Fig. 20. Formation and growth process of the phase transformation (a) on the surface, (b) in the bulk, and (c) at the surface-preferred phase junction at 600 °C. Reprinted with permission from Ref. [200]. Copyright 2018 Elsevier.

(Fig. 21). Moro et al. [203] studied the mesoporous and nanocrystalline titanium dioxide by a possible synergism between TiO_2 and carbon nanotubes under hydrothermal conditions. Based on this study, they showed that the addition of a small amount of MWCNTs further increased the photoactivity of the nanocrystalline titania for the degradation of 4-nitrophenol.

Because of the different band structures of g- C_3N_4 prepared separately from urea and thiourea using the same thermal conditions, Dong et al. [204] prepared a novel layered g- C_3N_4 /g- C_3N_4 metal-free isotype heterojunction in situ with molecular composite precursors, which exhibited significantly enhanced photocatalytic activity for visible light for the removal

of NO from air. This was directly ascribed to an efficient charge separation and transfer across the heterojunction interface and to the prolonged lifetime of charge carriers, as indicated in Fig. 22. Meanwhile, Liu et al. [205] studied an amorphous/crystalline g- C_3N_4 homojunction with a matched energy level structure via a two-step polymerization of melem on the surface of crystalline g- C_3N_4 (as seeds). They also optimized the ratio of crystalline g- C_3N_4 in the homojunction that resulted in a superior photocatalytic performance for the degradation of organic pollutants under visible light irradiation. The synthetic process and photocatalytic degradation of RhB of composites are shown in Fig. 23.

Fig. 21. PL decays of TiO_2 samples with different phase compositions at the excitation source of 340 nm, and charge transfer and recombination at anatase/rutile phase junction. Reprinted with permission from Ref. [202]. Copyright 2016 Elsevier.

Fig. 22. Charge transfer, visible-light photocatalytic performance, and in situ formation process of the CN-T/CN-U isotype heterojunction. Reprinted with permission from Ref. [204]. Copyright 2013 ACS.

Fig. 23. Preparation process and photocatalytic degradation of RhB of amorphous/crystalline g-C₃N₄ composites. Reprinted with permission from Ref. [205]. Copyright 2018 RSC.

5. Conclusions and perspectives

Highly efficient photocatalysts are required to maximize the solar spectrum usage that ultimately leads to an effective separation of photo-generated electron-hole pairs. The separated electron-hole pairs can be transferred to the surface of the catalysts and react with substrates. Nanocrystalline heterojunction photocatalytic materials, including semiconductor/semiconductor, semiconductor/metal, semiconductor/nonmetal, and surface heterojunctions, have successfully achieved the effective separation and long-term stability of

carriers.

With respect to Table 2, we discussed the general strategies and recent progress with the use of efficient techniques for the construction of phase junctions for the development of highly efficient and stable photocatalysts, including: (1) the addition of a suitable amount of anions or positive ions (such as Cl⁻, F⁻, PO₄³⁻, SO₄²⁻, and Mo⁶⁺) to regulate the phase transition on undoped semiconductor photocatalysts, (2) the implementation of oxide regulation in the phase transition process of the photocatalysts to improve the photocatalytic activity of the phase junction, (3) the induction of phase junctions with the soft chemical route to achieve exceptional and synergistic photo-

Table 2 Comparison of the typical heterojunctions based on an externally driven phase transformation.

Formation technique	Types	Preparation	Improved performance	Proposed reasons
Anionic and cationic regulations	Mo ⁶⁺ , Mn ²⁺ , Cl ⁻ , F ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , PO ₄ ³⁻ , SiO ₃ ²⁻ , and MoO ₄ ²⁻	Regulation of the composition of anatase-rutile phase of TiO ₂	Higher activities than that of industrial P25 in the photocatalytic H ₂ production	Effective separation of the photogenerated electron-hole pair
Oxide regulations	Al ₂ O ₃ , Nd ₂ O ₃ , SiO ₂	Anatase-rutile type	Promotion of the degradation of RhB	Prevention of the accumulation of TiO ₂ grain growth
Soft chemical route	α-/γ-Bi ₂ O ₃ homojunction, α-/β-Bi ₂ O ₃ homojunction, 2H/1T-MoS ₂ /C ₃ N ₄ , mixed-phase TiO ₂ , TiO ₂ (B)/rutile/rookite, Bi ₂ O ₂ CO ₃ /Bi ₂ O ₄	A one-pot hydrothermal method or a novel solvothermal calcination method	Exceptional and synergistic photocatalytic activity	Enhanced separation of photogenerated electron and hole pairs
Control of calcination	Ag ₂ CO ₃ @Ag ₂ O, BiOI/Bi ₅ O ₇ I, Bi ₅ O ₇ I/Bi ₂ O ₃ , BiOBr/Bi ₂ O ₃ , Bi ₂ O ₃ /α-Bi ₂ O ₃ , β-Bi ₂ O ₃ /Bi ₂ O ₃ @Bi ₂ O ₂ CO ₃ , Zn ₃ (VO ₄) ₂ /Zn ₂ V ₂ O ₇ /ZnO, Sr ₂ Ta ₂ O _{7-x} N _x /SrTaO ₂ N, α-β Ga ₂ O ₃	Control of heating temperature, time, and atmosphere	Higher photocatalytic activity than single primitive sample	Energy level matching and an internal electric field accelerate the separation of photogenerated carriers
Self-surface phase junctions of crystal plane	(101) and (001) surfaces of TiO ₂ , (001) facet of cubic Cu ₂ O, (010) and (110) crystal facets of BiVO ₄	Design of a single crystal semiconductor	Improved CO ₂ reduction and H ₂ production rate	Spatial separation of photogenerated electrons and holes on different crystal facets
Electro-chemistry	α-β Bi ₄ V ₂ O ₁₁ , mixed-phase TiO ₂	Anodic oxidation or one-step electrochemical oxidation	Outstanding photocatalytic activity in the removal of Cr(VI) and MB, and nitrogen fixation	Well-established type-II band alignment
Pressure induction	Nb-doped TiO ₂	Extra pressure	Promotion of photocatalytic water splitting	Enhanced electron transport

catalytic activity, (4) the control of calcination-induced phase junctions based on the control of the phase transition rate and time, (5) the creation of self-surface phase junctions of the crystal plane to improve the separation and transportation of the electron-hole pairs, (6) the use of other assistant-driven phase junctions, such as pulse laser irradiation, UV/ozone, and electrochemistry methods, for the enhancement of the utilization of sunlight and the improvement of the separation/transportation of the carriers. The efficient techniques in this field associated with phase transitions provided a promising route to the preparation of the phase junctions and to the enhancement of the photocatalytic efficiencies.

The factors that affect the performance of photocatalysts are very complex. Accordingly, the photocatalytic activity was not only influenced by its phase structure, but also by its surface chemical properties. These factors introduced many difficulties in the interpretation of nanocrystalline heterostructures with the use of the traditional solid band theory. Therefore, the research of phase junction photocatalytic materials at the nanometer scale may be focused on the following aspects: (1) development of simple, cheap, large-scale, and pollution-free preparation technologies of phase transitions, to regulate the energy band structure of the nanoscale heterojunction and to improve the matching degree of the energy band; (2) design of a suitable preparation method to construct a novel and efficient heterogeneous structure type according to the properties and the final structure of the related semiconductors; (3) fabrication of nano-heterojunction photocatalytic materials in devices and application to the actual photocatalysis control process. It is necessary to use the effective in situ and transient technologies to study the actual charge transfer of nanocrystalline het-

erostructures for the establishment of a suitable theory for nanocrystalline heterostructures.

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Graphical Abstract

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Review on heterophase/homophase junctions for efficient photocatalysis: The case of phase transition construction

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Applications of the low-cost and efficient phase junction pathway for the construction of nanophase junctions in photocatalysis.

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异质/同质相结高效光催化的研究进展：以相变构建为例

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摘要: 半导体光催化剂在环境处理和能量转换方面有着巨大的应用潜力, 但由于电子-空穴对的复合作用, 半导体光催化剂的光催化性能较低。相结的存在是提高电子-空穴分离效率及光催化活性的有效途径, 对相结设计的深入研究是提高电荷转移性能和效率的有效手段。因此, 相结光催化技术的发展, 对于设计一个良好的相结和了解电子-空穴分离机理具有重要的意义。

通常, 相结的构建需要特殊的制备技术以及良好的晶格匹配。纳米异质结材料结合快速转移载流子的特点, 具有小尺寸效应和颗粒限域效应的优点, 且具有单组分纳米材料或体相异质结不具有的独特特性。纳米晶异质结可以促进光生电子的快速转移, 根据两种半导体带的相对位置, 异质结可分为I型、II型和III型, 根据不同的电子转移途径可分为p-n型和Z-型。当p型半导体(空穴为多数电荷载流子)或n型半导体(电子为多数电荷载流子)密切接触时, 由于能带和其它性质的差异, 会形成结, 并在结的两侧形成空间电位差。空间电位差的存在可以使产生光生载流子从一个半导体能级注入到另一个半导体能级, 从而促进电子和空穴的分离, 提高光催化效率。以p-n结为例, 当它们在这两个区域共存时, 它们的边界层形成一个薄的p-n结。由于p型区空穴浓度高, n型区电子浓度高, 结处存在电子和空穴的扩散现象。在p-n结边界附近形成空间电荷区, 从而在结内形成强的局域电场。在结的局部电场作用下, 电荷在结两端累积形成电位差, 后者作为驱动力可以有效地分离光生电荷。

近年来, 人们在纳米相结的设计和制备上做了大量工作以提高光催化剂活性。虽然异质结具有优良的性能, 但异质结的成分和元素并不是单一的, 它的形成也不是一步反应。首先, 需要分别合成异质结的两个成分, 反应复杂, 耗时, 不环保。与异质结相比, 同一材料通过相变构建的结也能实现光生载流子的高效分离。同质化不需要引入其它要素, 因此引起了大量关注。在相变过程中, 大多数均由不同晶相的半导体形成, 如锐钛矿型/金红石型TiO₂, α - β 相Ga₂O₃或六方/立方CdS。由于化学成分相同, 半导体材料的能带结构不易改变。因此, 对同晶材料的同质结研究较少。虽然已有几篇关于异质相结的综述论文, 但通过对外部诱导相变法制备相结的回顾, 仍可为读者提供有关该领域研究进展的新的认识。本文对低成本、高效率的相变思路在光催化领域中的应用进行了简要的总结, 并对其在光催化领域中的应用前景进行了展望。

关键词: 相变; 相结; 光催化; 有效电子转移

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