Review

Atomic Level Interface Control of SnO₂-TiO₂ Nanohybrids for the Photocatalytic Activity Enhancement

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Abstract: This review article highlights atom-level control of the heterojunction and homojunction in SnO₂-TiO₂ nanohybrids, and the effects on the photocatalytic property. Firstly, a comprehensive description about the origin for the SnO₂-TiO₂ coupling effect on the photocatalytic activity in the conventional SnO₂-TiO₂ system without heteroepitaxial junction is provided. Recently, a bundle of thin SnO₂ nanorods was hetero-epitaxially grown from rutile TiO₂ seed nanocrystals (SnO₂-NR#TiO₂, # denotes heteroepitaxial junction). Secondly, the heterojunction effects of the SnO₂-NR#TiO₂ system on the photocatalytic activity are dealt with. A novel nanoscale band engineering through the atom-level control of the heterojunction between SnO₂ and TiO₂ is presented for the photocatalytic activity enhancement. Thirdly, the homojunction effects of the SnO₂ nanorods on the photocatalytic activity of the SnO₂-NR#TiO₂ system and some other homojunction systems are discussed. Finally, we summarize the conclusions with the possible future subjects and prospects.

Keywords: photocatalyst; nanohybrid; interface; charge separation; TiO₂; SnO₂

1. Introduction

Nanohybrid photocatalysts consisting of metals and semiconductors is the key material for solar-driven chemical transformations [1–5]. The enhancement in the photocatalytic activity stems from the effective interplay between the components depending on the interface quality. Among the nanohybrid photocatalysts, the system consisting of SnO₂ and TiO₂ is the representative one [6]. TiO₂-SnO₂ (or fluorine-doped SnO₂, FTO) is also the basic electrode for various photoelectrochemical devices for solar-to-electric and chemical conversions [7–10]. From a view of practical point, the SnO₂-TiO₂ coupling system is a very promising material owing to the robustness, harmlessness, and inexpensiveness. The remarkable SnO₂-TiO₂ coupling effect on the photocatalytic activity is well recognized for various reactions as reported in recent papers on degradation of phenol [11] and dyes [12–15]. However, the fundamental mechanism has not been fully understood so far. Further, the effects of atomically commensurate junctions in the SnO₂-TiO₂ coupling system on the photocatalytic activity have recently been clarified [16,17]. This article reviews atomic level control of the heterojunction and homojunction in the SnO₂-NR#TiO₂ system, and the effects on the photocatalytic property. Section 2 describes the origin for the remarkable SnO₂-TiO₂ coupling effect on the photocatalytic activity. Section 3 deals with the heterojunction effects of the SnO₂-NR#TiO₂ system on the photocatalytic activity. Section 4 discusses the homojunction effect of the SnO₂-NR#TiO₂ system on the photocatalytic activity. Finally, in Section 5, the conclusions are summarized with the future subjects and prospects. Recently, the research of homojunction photocatalysts including the p-n homojunction type [18–20] and the morphological homojunction type [21–25] is currently in rapid progress. This article would also contribute to the development of the homojunction photocatalysts.
2. Origin for the SnO2-TiO2 Coupling Effect

This section describes the general features of the conventional SnO2-TiO2 nanohybrid photocatalysts without atomically commensurate junction (Scheme 1). The photocatalytic activity of TiO2 can be greatly boosted by coupling with SnO2 for various reactions [11–17]. It is worth noting that the electron acceptor in common with these reactions is molecular oxygen.

As an example, here we take gas-phase decomposition of acetaldehyde by a patterned TiO2/SnO2 bilayer type photocatalyst [26]. Samples nonpatterned and patterned TiO2 films on SnO2/soda lime (SL)-glass are designated as TiO2/SnO2/SL-glass and pat-TiO2/SnO2/SL-glass, respectively. In the pat-TiO2/SnO2/SL-glass, 1 mm wide stripes of TiO2 film regularly appeared on the SnO2/SL-glass substrate in a 1 mm pitch. In this study, acetaldehyde was used as a model for harmful organic gas (Figure 1).

This reaction is categorized as photocatalytic on the basis of the fact that both illumination and TiO2 are needed for the decomposition to occur (a) and a turnover number of $>$10$^3$. The photocatalytic activity of TiO2/SnO2/SL-glass (c) is higher than that of TiO2/quartz (b). However, the rate in the former system decreases with irradiation time, while the rate in the latter system is almost constant. Strikingly, the patterning of the TiO2 film (d) drastically increases the photocatalytic activity without causing the decay. The high photocatalytic activity of the SnO2-TiO2 coupling system partly stems from effective charge separation by the interfacial electron transfer from TiO2 to SnO2, which was substantiated by labeling and visualizing the reduction sites using the Ag photodeposition method [26]. Consequently, SnO2 and TiO2 act as reduction and oxidation sites, respectively, in the SnO2-TiO2 coupling system [26].

Scheme 1. Energy diagram of the SnO2-TiO2 hybrid-photocatalyzed reaction system.

Figure 1. Time courses of decomposition of CH3CHO upon illumination in the presence of SnO2/SL-glass (a), TiO2/quartz (b), TiO2/SnO2/SL-glass (c), and pat-TiO2/SnO2/SL-glass (d). The figure is taken from ref. [26].
system. However, the conduction band (CB) minimum of SnO$_2$ is situated at $-4.92$ eV vs. vacuum at pH 0 [26], which is too low to cause one-electron oxygen reduction reaction (ORR) (Equation (1), Scheme 1).

$$O_2 + e^- \rightarrow O_2^-$$  \hspace{1cm} (1)

To determine the electron number of ORR ($n$), linear sweep voltammograms (LSVs) were measured at electrode potential ($E$ vs. hydrogen electrode potential, SHE) from $-0.8$ V to $+0.2$ V for FTO and TiO$_2$ film-coated FTO (TiO$_2$/FTO) electrodes in argon-bubbled and aerated electrolyte solutions (Figure 2a). In the LSV for TiO$_2$/FTO, the cathodic current flows at $E < -0.4$ V regardless of the absence and presence of O$_2$, and the current is ascribable to the reduction of TiO$_2$ [27]. On the other hand, in the LSV for FTO with O$_2$, the current-onset potential shifts to approximately 0 V with the magnitude of current drastically increased, while no current is observed without O$_2$. The current was measured as a rotating rate of the FTO electrode in aerated electrolyte solution. The Koutecky–Levich plot of the FTO electrode for the current in the presence of O$_2$ at $E = -0.8$ V provides a straight line from the slope of which the $n$ value was calculated to be 1.6 (Figure 2b). This finding indicates that two-electron ORR can partially occur on FTO (or SnO$_2$), whereas TiO$_2$ is electrocatalytically inactive for ORR. The electrons in the CB of SnO$_2$ also has a potential sufficient to proceed two-electron ORR (Equation (2), Scheme 1). Thus, another reason for the effective SnO$_2$-TiO$_2$ coupling effect is ascribable to the electrocatalytic activity of SnO$_2$ for two-electron ORR. On the basis of this scheme, the photocatalytic activity of pat-TiO$_2$/SnO$_2$/SL-glass much higher than that of nonpatterned sample is rationalized in terms of the balanced areas of the surfaces where oxidation (TiO$_2$) and reduction (SnO$_2$) sites occur in the former system.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$  \hspace{1cm} (2)

![Figure 2](image_url)

**Figure 2.** (a) Linear sweep voltammogram obtained with the TiO$_2$/FTO and FTO electrodes in argon gas-bubbled and aerated 0.1 M NaClO$_4$ electrolyte solution (pH 5.70) with a potential sweep rate of 20 mVs$^{-1}$. $j_{dc}$ expresses the current density per real surface area of the electrode. (b) Koutecky-Levich plots of the FTO electrode for the current as $E = -0.8$ V.

### 3. Atom-Level Heterojunction Effect

This section deals with the hetero-epitaxial junction effect on the charge separation and photocatalytic activity of the SnO$_2$-TiO$_2$ nanohybrid system [16]. The effective charge separation can arise from the smooth interfacial electron transfer from TiO$_2$ to SnO$_2$-NR through the high-quality junction and subsequent efficient charge separation due to the lattice strain-induced unidirectional potential gradient of the CB minimum in the SnO$_2$-NR. This nanoscale band engineering presents a novel methodology for the effective charge separation to enhance the activity of the nanohybrid photocatalysts.

SnO$_2$ NRs were grown from rutile TiO$_2$ seed nanocrystals in an alkaline SnCl$_4$ solution by a hydrothermal process for a given time ($t_{HT}$). Low- and high-magnification scanning electron microscopy (SEM) images of the sample prepared at $t_{HT} = 72$ h (Figure 3a,b) shows that NRs are grown from every TiO$_2$ particle with a specific orientation by the hydrothermal reaction. The powder X-ray diffraction (XRD) pattern (Figure 3c) has the
diffraction peaks of rutile TiO$_2$, and after the hydrothermal reaction, new peaks appear at $2\theta = 26.52^\circ$, $34.42^\circ$, and $52.46^\circ$ assigned to the diffraction from the (110), (101), and (211) crystal planes of SnO$_2$, respectively. The high resolution-transmission electron microscopy (HR-TEM) image of SnO$_2$-NR/TiO$_2$ (Figure 3d) shows an SnO$_2$(110) lattice fringe parallel to its growth direction. Clearly, SnO$_2$-NRs grow in the [001] direction from the rutile TiO$_2$ surface. Conversely, the solvothermal preparation of rutile TiO$_2$ nanowire arrays with the [001] orientation on FTO electrode has recently been reported [28].

![Figure 3](image_url)

**Figure 3.** Low (a) and high (b) magnification SEM images for SnO$_2$-NR/TiO$_2$ ($t_{HT} = 72$ h). The inset in (a) shows SEM image for pristine rutile TiO$_2$. (c) XRD patterns for SnO$_2$-NR/TiO$_2$ and pristine TiO$_2$ for comparison. (d) HR-TEM image for SnO$_2$-NR/TiO$_2$. The figure is taken from ref. [16].

In the bulk system, an $a$-axis mismatch of 3.11% is present between SnO$_2$ and rutile TiO$_2$. Surprisingly, a heteroepitaxial junction was formed in the nanoscale system [16] in spite that the formation of heteroepitaxial junction is limited to the systems with the lattice mismatch smaller than 0.1% in the bulk systems [29]. This finding suggests that even if the heteroepitaxial junction cannot be formed in the bulk state, it is possible in the nanoscale [30]. A junction model was presented with the SnO$_2$-NR grown in the [001] direction from the rutile TiO$_2$ surface having a heteroepitaxial relation of SnO$_2$(001)/TiO$_2$(001) (SnO$_2$-NR#TiO$_2$). Previously, oriented SnO$_2$ nanowire arrays were formed on rutile TiO$_2$(001) single crystal by a chemical vapor deposition method [31].

In today’s time, acetaldehyde is industrially produced by the Wacker oxidation of ethylene using a PdCl$_2$-CuCl$_2$ catalyst at $\sim$1 MPa and $\sim$400 K [32], and, then, the development of the green process for the selective synthesis of acetaldehyde from biomass-derived ethanol under mild conditions is very significant (Equation (3)) [33].

$$\text{CH}_3\text{CH}_2\text{OH} (g) + 1/2\text{O}_2 (g) \rightarrow \text{CH}_3\text{CHO} (g) + \text{H}_2\text{O} (l) \quad (3)$$

We have recently found that rutile TiO$_2$ exhibits high photocatalytic activity for the partial oxidation of ethanol to acetaldehyde at ambient temperature and pressure, whereas ethanol is completely oxidized to carbon dioxide in the anatase TiO$_2$ photocatalytic system [34,35].
The photocatalytic activity of various samples was studied for gas-phase oxidation of ethanol to acetaldehyde (Figure 4a). The loading amount and rod length of SnO$_2$ are denoted as $x_{\text{SnO}_2}$ and $l_{\text{NR}}$, respectively. UV-irradiation of TiO$_2$ produces acetaldehyde of which amount increases with an increase in irradiation time, while SnO$_2$ is completely inert. Rutile TiO$_2$ shows much higher photocatalytic activity than anatase TiO$_2$, and the former activity is further enhanced by mixing with 10.0 mass% SnO$_2$. Strikingly, SnO$_2$-NR#TiO$_2$ ($l_{\text{NR}} = 61.4$ nm, $x_{\text{SnO}_2} = 11.0$ mass%) exhibits a high level of photocatalytic activity far exceeding even that of the physical mixture of rutile TiO$_2$ and SnO$_2$, whereas no reaction proceeded in the dark or under UV-light irradiation without O$_2$. The apparent quantum yield or external quantum yield ($\phi_{\text{ex}}$) defined by Equation (4) reached 25.6% at $\lambda_{\text{ex}} = 365$ nm in the SnO$_2$-NR#TiO$_2$ system.

$$\phi_{\text{ex}} (%) = \frac{2 \times \text{(number of acetaldehyde molecules)}}{\text{number of incident photons}} \times 100 \quad (4)$$

Figure 4. (a) Time courses for gas-phase photocatalytic oxidations of ethanol to acetaldehyde under UV-light irradiation ($\lambda_{\text{ex}} > 300$ nm). The amount of acetaldehyde is normalized by the specific surface area of the photocatalyst. (b) Relation between the photocatalytic activity and SnO$_2$ loading amount. The corresponding SnO$_2$-NR length is shown in the figure. (c) Time courses for gas-phase photocatalytic decomposition of acetaldehyde under UV-light irradiation ($\lambda_{\text{ex}} > 300$ nm) in the SnO$_2$-NR#TiO$_2$ ($l_{\text{NR}} = 61.4$ nm) system, and anatase and rutile TiO$_2$ system for comparison. (d) PL spectra for authentic rutile TiO$_2$ and SnO$_2$-NR#TiO$_2$ with varying mean SnO$_2$-NR length under irradiation of light with wavelength of 340 nm at 77 K. The figure is taken from ref. [16].

This value surpasses the values reported for the TiO$_2$ photocatalytic oxidation of ethanol to acetaldehyde (<10%) [34,36]. These findings evince the importance of the junction state between SnO$_2$ and TiO$_2$ for the activity in the hybrid photocatalyst.

Further, the initial photocatalytic activity of SnO$_2$-NR#TiO$_2$ ($v_0$/mol h$^{-1}$) increases with an increase in $x_{\text{SnO}_2}$ (Figure 4b). In addition, there is a clear trend that the photocatalytic activity increases with increasing $l_{\text{NR}}$. On the other hand, there is linear relations between the amount of acetaldehyde produced and the amount of ethanol consumed in the SnO$_2$-NR#TiO$_2$ and unmodified rutile TiO$_2$ systems. The selectivity was calculated from the slope in the SnO$_2$-NR#TiO$_2$ ($l_{\text{NR}} = 61.4$ nm) system to be ~100%. The photocatalytic decomposition of acetaldehyde was further examined with SnO$_2$-NR#TiO$_2$, anatase and rutile TiO$_2$ particles. Rutile TiO$_2$ and SnO$_2$-NR#TiO$_2$ exhibit much lower photocatalytic activity than anatase TiO$_2$ (Figure 4c). Ethanol oxidation has so far been reported for the photocatalysts of anatase TiO$_2$ and P-25 (anatase-rutile mixture). These studies reported...
that ethanol undergoes complete oxidation to carbon dioxide, and the selectivity to acetaldehyde is lower than 50% [34,37–39]. Therefore, the high selectivity in the rutile TiO$_2$ and SnO$_2$-NR#TiO$_2$ systems results from the suppression of the ethanol overoxidation.

The insight into the charge separation in the hybrid photocatalysts can be gained by photoluminescence (PL) measurements [40]. TiO$_2$ has a broad PL band arising from the emission from vacancy levels around 520 nm (Figure 4d) [41]. In the spectra for SnO$_2$-NR#TiO$_2$, the emission band extremely weakens. In addition, selective TiO$_2$ excitation of SnO$_2$-NR#TiO$_2$ in AgNO$_3$ aqueous solution led to preferential deposition of Ag NPs on SnO$_2$-NR [26]. Evidently, UV-light irradiation of SnO$_2$-NR#TiO$_2$ induces smooth interfacial electron transfer from TiO$_2$ to SnO$_2$-NR followed by the effective charge separation through the high-quality heterojunction.

The SnO$_2$(110) $d$-spacing in the NR was determined as a function of the distance from the interface with TiO$_2$ ($d_{\text{eff}}$) from the HR-TEM analysis [16]. The $a$-axis length calculated from the (110) $d$-spacing gradually increased with an increase in $d_{\text{eff}}$ from 4.52 Å at $d_{\text{eff}} = 1$ nm to 4.73 Å at $d_{\text{eff}} = 75$ nm, which is equal to the value for bulk SnO$_2$. The formation of the heteroepitaxial junction causes the shrinkage of the $a$-axis near the interface to relax in the [001] direction of SnO$_2$-NR from the root to the tip. Density functional theory (DFT) simulations were performed for model slabs of the SnO$_2$-NR hetero-epitaxially grown from TiO$_2$. The energy diagram created by using the calculated values qualitatively reproduced the increase in the band gap with decreasing rod length. More importantly, the energy diagram showed that a significant downward bending in the CB minimum potential is induced in the direction from the root to the tip of SnO$_2$ NR. A recent paper has reported that in the SnO$_2$ thin film epitaxially grown on the Al$_2$O$_3$(0001) substrate, the interfacial tensile strain generated in the SnO$_2$ lattice conversely lowers the band gap [42].

The action mechanism of SnO$_2$-NR#TiO$_2$ in the photocatalytic gas-phase selective oxidation of ethanol to acetaldehyde can be explained on the basis of the energy diagram in Scheme 2, where the energy levels are shown with respect to the vacuum level (at pH 0). The flat band potentials of rutile TiO$_2$ and SnO$_2$ electrodes were previously determined to be $-4.50$ V [43] and $-4.92$ V [26] by the Mott–Schottky plots. SnO$_2$-NRs are grown on rutile TiO$_2$ with a heteroepitaxial relation of SnO$_2$(001)/TiO$_2$(001) by the present hydrothermal reaction. The positive $a$-axis mismatch generates a compressive strain in the SnO$_2$-NR near the interface to induce the continuous increase in the $a$-axis length extending over 60 nm towards the SnO$_2$(001) direction from the root to the tip. As a result, a downward band bending is formed in the interior of the SnO$_2$-NR. UV-light irradiation of SnO$_2$-NR#TiO$_2$ promotes the electrons in the VB of TiO$_2$ to the CB. The excited electrons in the CB with $E_{\text{CBM}} = -4.50$ eV are smoothly transferred to the CB of SnO$_2$-NR with the $E_{\text{CBM}} = -4.92$ eV through the atomically commensurate interface, while the holes are left in the VB of TiO$_2$ because the VB maximum of SnO$_2$ is located much lower with respect to that of TiO$_2$. In addition, the electrons can be separated from the VB-holes in TiO$_2$ due to the unidirectional downward potential gradient in the CB minimum in the SnO$_2$-NR. The CB-electrons in the SnO$_2$-NR have sufficient energy to cause a two-electron oxygen reduction reaction ($E^{\text{e}}(\text{O}_2/\text{H}_2\text{O}_2) = -5.14$ V), while the VB-holes in TiO$_2$ selectively oxidize ethanol to acetaldehyde because of the suppression of the overoxidation. The enhancement of the photocatalytic activity with increasing rod length can be rationalized in terms of the long-range charge separation. The groups of Majima and Choi have recently shown that the reactive oxygen species photogenerated on rutile TiO$_2$ are the surface bound OH radicals (or surface trapped holes, $\cdot\text{OH}$) limiting the oxidation mainly to the surface, whereas the oxidation on anatase TiO$_2$ can occur at the place far away from the surface in the former system because of the diffusion of OH radicals from the surface (or free OH radicals) [44]. Further, we have found that the adsorption of acetaldehyde on rutile TiO$_2$ is suppressed in the presence of adsorbed water [45]. Consequently, in the present SnO$_2$-NR#TiO$_2$ photocatalytic reaction system, the highly selective and efficient oxidation of ethanol to acetaldehyde proceed.
we have found that the adsorption of acetaldehyde on rutile TiO₂ is suppressed in the catalytic reaction system, the highly selective and efficient oxidation of ethanol to acetaldehyde. The scheme is taken from ref. [16].

4. Atom-Level Homojunction Effect

4.1. SnO₂-TiO₂ Homojunction Systems

In the as-grown SnO₂-NR#TiO₂, the apparent single SnO₂-NR is actually composed of a bundle of thin SnO₂ NRs. This section discusses the effect of the formation of homojunction between the thin SnO₂ NRs on the photocatalytic activity [17]. The photocatalytic activity-heating temperature (Tc) curve in the SnO₂-NR#TiO₂ system shows a volcano-shaped profile with the maximum activity at Tc = 500 °C. The increase in the photocatalytic activity by the heating at Tc = 500 °C results from the high electron mobility in the SnO₂ NRs with the fusion of the thin SnO₂ NRs.

SEM observation was carried out for SnO₂-NR#TiO₂ prepared at varying Tc in air for 1 h (Figure 5a,b). As-grown SnO₂-NR#TiO₂ consists of a bundle of thin SnO₂ NRs. The heat treatment at 500 °C induces fusion of the bundle forming a monolithic SnO₂ NR.

Further, the HR-TEM image shows that the SnO₂ moiety of SnO₂-NR#TiO₂ (Tc = 500 °C) has good crystallinity (Figure 5c). On the other hand, heating at 700 °C causes many disjuncture in the lattice fringe due to the fine segmentation of the SnO₂ NRs (Figure 5d).

The specific surface area (S_{BET}) of SnO₂-NR#TiO₂ was measured by Brunauer–Emmett–Teller method. As a result of an increase in Tc, the S_{BET} gradually decreases with fusion of the bundle of thin SnO₂ NRs (Figure 5a). In addition, the crystallite size of SnO₂ (D) was estimated using the Scherrer equation from the full-width at half maximum of the SnO₂(110) diffraction peak. In the plot of D versus Tc, the D value of ~25 nm for the as-grown sample increases with an increase in Tc, going through a maximum of ~80 nm at Tc = 500 °C to steeply decrease above 600 °C (Figure 5a). Clearly, the growth of crystallites with increasing Tc at ≤500 °C increases the D value, which then decreases due to the segmentation at Tc ≥ 600 °C.

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**Figure 5.** SEM images of SnO₂-NR#TiO₂: (a) as-grown (b) Tc = 500 °C. HR-TEM image of the SnO₂-NR moiety of SnO₂-NR#TiO₂: (c) Tc = 500 °C, (d) Tc = 700 °C. The figure is taken from ref. [17].
The $T_c$-dependence of the photocatalytic activity for the gas-phase oxidation of ethanol to acetaldehyde was studied. The reaction apparently follows the first-order rate law in every system, and the pseudo-first-order rate constant ($k$) was calculated from the plots of ln $[C_0/(C_0-C)]$ versus $t$, where $C_0$ and $C$ are the initial concentration of EtOH and the concentration of acetaldehyde at the irradiation time $t$, respectively. The plot of $k$ vs. $T_c$ exhibits a volcano-shaped curve with the peak at $T_c = 500 \, ^\circ\text{C}$ (Figure 6b), which well resembles the $D-T_c$ one (Figure 6a).

The heating effect on the photocatalytic activity can be explained in terms of the change in the homojunction state in the SnO$_2$ NRs (Scheme 3) [17]. As explained in Section 3, SnO$_2$-NR#TiO$_2$ can work as an excellent charge separator owing to the smooth interfacial electron transfer from TiO$_2$ to SnO$_2$ through the high-quality interface and the subsequent electron transport in the SnO$_2$-NR from the interface to the tip by the assistance of the lattice strain-induced unidirectional potential gradient in the CB [16]. In this case, the heat treatment at $T_c \leq 500 \, ^\circ\text{C}$ causes the fusion of the bundle of the SnO$_2$ NRs to decrease the resistance for the electron transport and enhance the charge separation. At $T_c \geq 600 \, ^\circ\text{C}$, the heat treatment incurs the segmentation of the SnO$_2$ crystal, which is also evidence of the presence of the hetero-epitaxial junction-induced lattice distortion in the SnO$_2$ NR. The many boundaries generated in the SnO$_2$ NR would scatter electrons to interfere with the electron transport or charge separation. As a result of the balance between them, there exists an optimum heating temperature around 500 °C.

Zeng and co-workers constructed a branched rutile TiO$_2$ NR array on FTO substrate using a two-step route involving a hydrothermal synthesis and a chemical bath deposition [22]. In this method, the length of the branches was controlled by the chemical bath deposition time ($t_{CBD}$). A coherent interface was observed between the TiO$_2$ NR and the branch by HR-TEM. The sample prepared at $t_{CBD} = 36$ h exhibits a high level of photocatalytic activity for gas-phase decomposition of benzene under UV-light irradiation (200 nm $< \lambda_{ex} < 400$ nm). The striking photocatalytic activity was ascribable to the branch-to-NR interfacial electron transfer and subsequent charge separation due to the smooth electron transport along the single-crystal TiO$_2$ NR.

4.2. Other Homojunction Systems

Among various homojunction systems, those with the formation of coherent interface confirmed are only limited. In addition to those, the works on the homojunction between the identical crystals with only different morphologies are described in this section.
Zou and co-workers prepared a homojunction system consisting of n-type oxygen-defected TiO$_2$ and p-type titanium-defected TiO$_2$ by a multi-step process involving liquid-phase synthesis and calcination [18]. The formation of a somewhat atomically commensurate interface was confirmed by HR-TEM observation. PL and electrochemical impedance spectroscopy (EIS) analyses indicated that effective charge separation occurs in this system. Consequently, Pt nanoparticle-loaded p-n homojunction TiO$_2$ (Pt/p-n homojunction TiO$_2$) showed higher photocatalytic activity than Pt/p-TiO$_2$ and Pt/n-TiO$_2$ by factors of 2.3 and 10.8, respectively, for H$_2$ generation from a methanol aqueous solution under UV-light irradiation. The simultaneous interfacial electron transfer from p-type TiO$_2$ to n-type TiO$_2$ and hole transfer in the opposite direction were assumed.

Chen, Zhou, and co-workers prepared p-n Bi$_4$V$_2$O$_{11}$ homojunction through Bi$^{5+}$ self-doping (Bi$^{5+}$-BVO) [19]. Electrochemical analysis of the Bi$^{5+}$-BVO electrode showed a p-n junction character, while a nondoped BVO electrode has an n-type character. PL, EIS, and time-resolved fluorescence decay spectroscopy indicated that the p-n homojunction suppresses the electron-hole recombination. Bi$^{5+}$-BVO exhibited significantly larger photocatalytic activity than nondoped BVO for Cr(VI) reduction in the presence of citric acid under visible-light irradiation. The high photocatalytic activity was ascribable to the effective charge separation through the p-n junction although no information about the interface at an atomic level was provided.

Lyu and co-workers fabricated a homojunction between anatase TiO$_2$ nanoparticles (NPs) and a microporous anatase TiO$_2$ layer by a two-step process involving vapor-induced hydrothermal synthesis and subsequent photothermocatalytic treatment [23]. No information about the junction state was provided; however, the homojunction sample provided significantly higher mineralization efficiency in the gas-phase decomposition of toluene than microporous and nonporous TiO$_2$ NPs under UV-light irradiation ($\lambda_{\text{ex}} = 254$ nm). On the basis of the data on surface photovoltage spectroscopy (SPS) measurements, the remarkable photocatalytic activity of the homojunction system was ascribable to effective charge separation in addition to the large specific surface area.

Yang and co-workers proposed a p-n TiO$_2$ homojunction involving amorphous and anatase TiO$_2$ prepared by controlling the heating temperature ($T_c$) of the latter around 350 °C [20]. The structure of the interface between amorphous and anatase TiO$_2$ was shown...
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at an atomic level resolution. The homojunction sample showed photocatalytic activity significantly larger than amorphous TiO$_2$ and anatase TiO$_2$, but the reason remains unclear.

Ren, Li, and co-workers formed a homojunction between anatase TiO$_2$ nanosheets (NSs) and anatase TiO$_2$ NPs by a two-step process involving vapor-induced hydrothermal synthesis and subsequent photothermocatalytic treatment [25]. HR-TEM image showed that the anatase TiO$_2$ NS and NPs possess dominant [001] and [101] facets although the junction state is unclear. The homojunction sample afforded much higher photocatalytic activity than TiO$_2$ NSs and NPs for gas-phase decomposition of acetone under UV-light irradiation (300 nm < $\lambda_{ex}$). The reduction and oxidation reactions were reported to primarily occur on the [001] and [101] facets, respectively, in faceted anatase TiO$_2$ photocatalyst. The authors proposed a crystal facet-induced charge separation mechanism to explain the high photocatalytic activity.

5. Conclusions and Future Prospects

Most importantly, this review article points to the general possibility of the heteroepitaxial junction formation between the components of the nanoscale hybrids even if it is inhibited in the bulk state because of significant lattice mismatch. This is also valid for the SnO$_2$-TiO$_2$ coupling system with an $a$-axis mismatch over 3%.

The improvement in the photocatalytic activity of TiO$_2$ by the hybridization with SnO$_2$ for the oxidative reactions originates from the charge separation because of the interfacial electron transfer from TiO$_2$ to SnO$_2$ and the electrocatalytic activity of SnO$_2$ for two-electron ORR. A novel nanoscale band engineering of heteronanostructured photocatalysts for the charge separation and activity enhancement is presented in a hybrid consisting of SnO$_2$ NR and TiO$_2$ with heteroepitaxial junction (SnO$_2$-NR#TiO$_2$). In addition, fusion of the homojunctions between a bundle of thin SnO$_2$ NRs in SnO$_2$-NR#TiO$_2$ further increases the photocatalytic activity due to the lowering in the resistance of the electron transport in the SnO$_2$ NR. In this manner, the enhancement in the photocatalytic activity of the SnO$_2$-TiO$_2$ nanohybrid can be achieved through the atomic-level control of the heterojunction and homojunction.

SnO$_2$-NR#TiO$_2$ has wide and high potentials as the photocatalytic for various reactions, and the exploitation should be a coming subject. In addition, they only respond to UV-light, and the visible-light response is of crucial importance for the effective utilization of the sunlight as the driving force. A promising approach to achieve this is the surface modification by plasmonic metals such Au [46] and Ag [47,48]. Finally, the development of various nanohybrids with atomically commensurate junctions other than the SnO$_2$-NR#TiO$_2$ system can bring wide and fruitful applications.

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