

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



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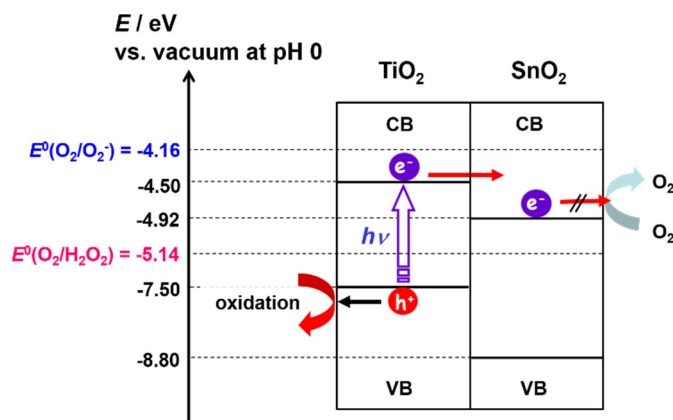
1. Introduction

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 degradations 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.



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

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).

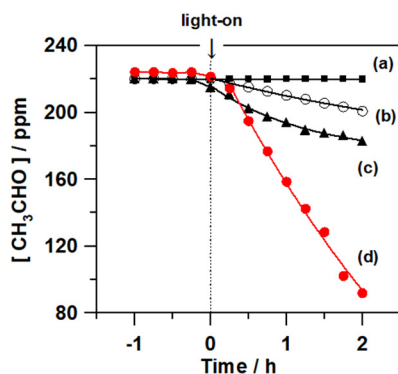


Figure 1. Time courses of decomposition of CH₃CHO upon illumination in the presence of SnO₂/SL-glass (a), TiO₂/quartz (b), TiO₂/SnO₂/SL-glass (c), and pat-TiO₂/SnO₂/SL-glass (d). The figure is taken from ref. [26].

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. However, the conduction band (CB) minimum of SnO₂ 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).



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 TiO₂ film-coated FTO (TiO₂/FTO) electrodes in argon-bubbled and aerated electrolyte solutions (Figure 2a). In the LSV for TiO₂/FTO, the cathodic current flows at $E < -0.4$ V regardless of the absence and presence of O₂, and the current is ascribable to the reduction of TiO₂ [27]. On the other hand, in the LSV for FTO with O₂, the current-onset potential shifts to approximately 0 V with the magnitude of current drastically increased, while no current is observed without O₂. 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 O₂ 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 SnO₂), whereas TiO₂ is electrocatalytically inactive for ORR. The electrons in the CB of SnO₂ also has a potential sufficient to proceed two-electron ORR (Equation (2), Scheme 1). Thus, another reason for the effective SnO₂-TiO₂ coupling effect is ascribable to the electrocatalytic activity of SnO₂ for two-electron ORR. On the basis of this scheme, the photocatalytic activity of pat-TiO₂/SnO₂/SL-glass much higher than that of nonpatterned sample is rationalized in terms of the balanced areas of the surfaces where oxidation (TiO₂) and reduction (SnO₂) sites occur in the former system.

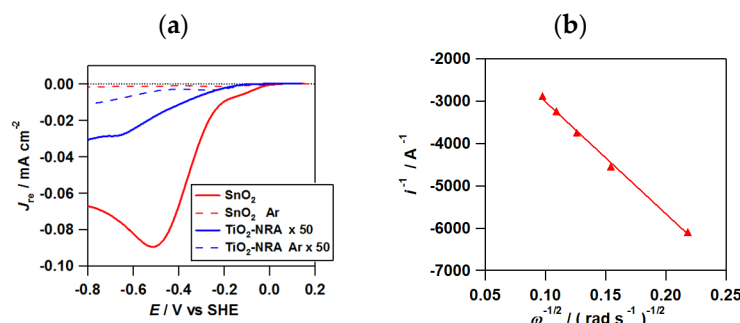


Figure 2. (a) Linear sweep voltammogram obtained with the TiO₂/FTO and FTO electrodes in argon gas-bubbled and aerated 0.1 M NaClO₄ electrolyte solution (pH 5.70) with a potential sweep rate of 20 mVs^{−1}. J_{re} expresses the current density per real surface area of the electrode. (b) Koutecky–Levich 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 SnO₂-TiO₂ nanohybrid system [16]. The effective charge separation can arise from the smooth interfacial electron transfer from TiO₂ to SnO₂-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 SnO₂-NR. This nanoscale band engineering presents a novel methodology for the effective charge separation to enhance the activity of the nanohybrid photocatalysts.

SnO₂ NRs were grown from rutile TiO₂ seed nanocrystals in an alkaline SnCl₄ 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 TiO₂ 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° , and 52.46° 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 $\text{SnO}_2\text{-NR}/\text{TiO}_2$ (Figure 3d) shows an SnO_2 (110) lattice fringe parallel to its growth direction. Clearly, $\text{SnO}_2\text{-NRs}$ 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].

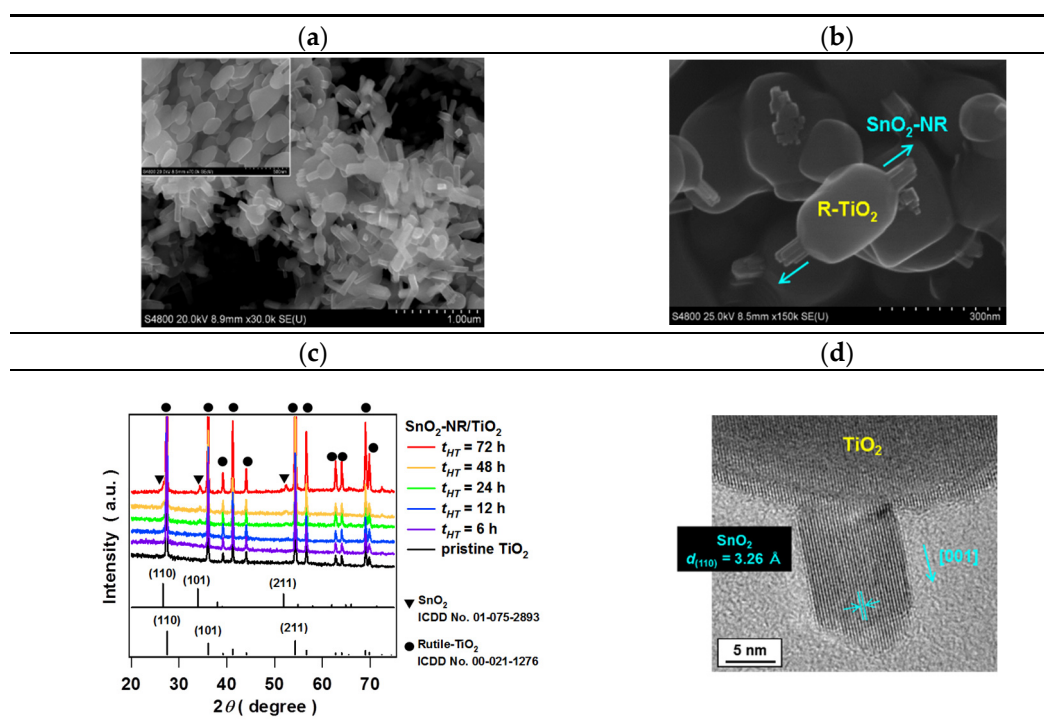
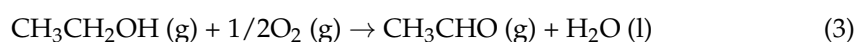


Figure 3. Low (a) and high (b) magnification SEM images for $\text{SnO}_2\text{-NR}/\text{TiO}_2$ ($t_{\text{HT}} = 72$ h). The inset in (a) shows SEM image for pristine rutile TiO_2 . (c) XRD patterns for $\text{SnO}_2\text{-NR}/\text{TiO}_2$, and pristine TiO_2 for comparison. (d) HR-TEM image for $\text{SnO}_2\text{-NR}/\text{TiO}_2$. 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 $\text{SnO}_2\text{-NR}$ grown in the [001] direction from the rutile TiO_2 surface having a heteroepitaxial relation of $\text{SnO}_2\{001\}/\text{TiO}_2\{001\}$ ($\text{SnO}_2\text{-NR}\#\text{TiO}_2$). Previously, oriented SnO_2 nanowire arrays were formed on rutile $\text{TiO}_2(001)$ 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 $\text{PdCl}_2\text{-CuCl}_2$ catalyst at ~ 1 MPa and ~ 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].



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 SnO₂ are denoted as x_{SnO_2} and l_{NR} , respectively. UV-irradiation of TiO₂ produces acetaldehyde of which amount increases with an increase in irradiation time, while SnO₂ is completely inert. Rutile TiO₂ shows much higher photocatalytic activity than anatase TiO₂, and the former activity is further enhanced by mixing with 10.0 mass% SnO₂. Strikingly, SnO₂-NR#TiO₂ ($l_{\text{NR}} = 61.4$ 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 TiO₂ and SnO₂, whereas no reaction proceeded in the dark or under UV-light irradiation without O₂. The apparent quantum yield or external quantum yield (ϕ_{ex}) defined by Equation (4) reached 25.6% at $\lambda_{\text{ex}} = 365$ nm in the SnO₂-NR#TiO₂ system.

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

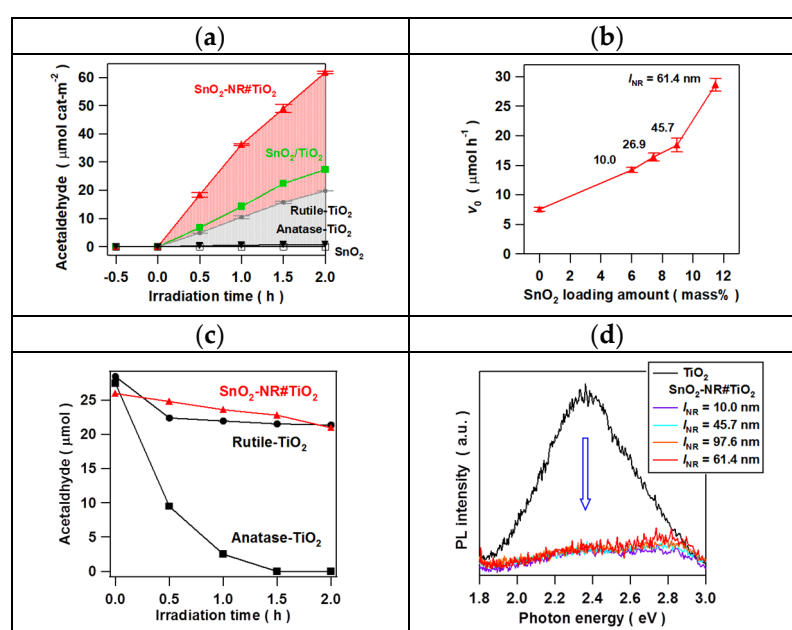


Figure 4. (a) Time courses for gas-phase photocatalytic oxidations of ethanol to acetaldehyde under UV-light irradiation ($\lambda_{\text{ex}} > 300$ nm). The amount of acetaldehyde is normalized by the specific surface area of the photocatalyst. (b) Relation between the photocatalytic activity and SnO₂ loading amount. The corresponding SnO₂-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 SnO₂-NR#TiO₂ ($l_{\text{NR}} = 61.4$ nm) system, and anatase and rutile TiO₂ system for comparison. (d) PL spectra for authentic rutile TiO₂ and SnO₂-NR#TiO₂ with varying mean SnO₂-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 TiO₂ photocatalytic oxidation of ethanol to acetaldehyde ($< \sim 10\%$) [34,36]. These findings evince the importance of the junction state between SnO₂ and TiO₂ for the activity in the hybrid photocatalyst.

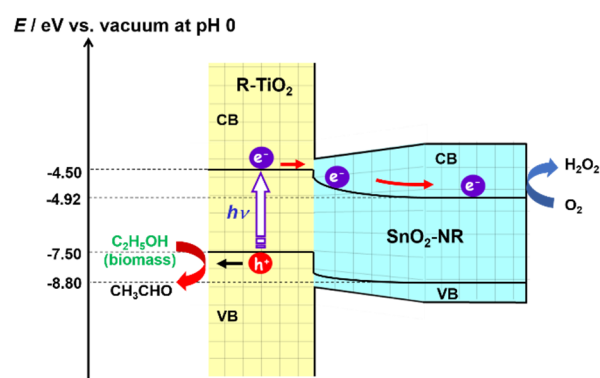
Further, the initial photocatalytic activity of SnO₂-NR#TiO₂ ($v_0/\text{mol h}^{-1}$) increases with an increase in x_{SnO_2} (Figure 4b). In addition, there is a clear trend that the photocatalytic activity increases with increasing l_{NR} . On the other hand, there is linear relations between the amount of acetaldehyde produced and the amount of ethanol consumed in the SnO₂-NR#TiO₂ and unmodified rutile TiO₂ systems. The selectivity was calculated from the slope in the SnO₂-NR#TiO₂ ($l_{\text{NR}} = 61.4$ nm) system to be $\sim 100\%$. The photocatalytic decomposition of acetaldehyde was further examined with SnO₂-NR#TiO₂, anatase and rutile TiO₂ particles. Rutile TiO₂ and SnO₂-NR#TiO₂ exhibit much lower photocatalytic activity than anatase TiO₂ (Figure 4c). Ethanol oxidation has so far been reported for the photocatalysts of anatase TiO₂ 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 $\text{SnO}_2\text{-NR}\#\text{TiO}_2$ 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 $\text{SnO}_2\text{-NR}\#\text{TiO}_2$, the emission band extremely weakens. In addition, selective TiO_2 excitation of $\text{SnO}_2\text{-NR}\#\text{TiO}_2$ in AgNO_3 aqueous solution led to preferential deposition of Ag NPs on $\text{SnO}_2\text{-NR}$ [26]. Evidently, UV-light irradiation of $\text{SnO}_2\text{-NR}\#\text{TiO}_2$ induces smooth interfacial electron transfer from TiO_2 to $\text{SnO}_2\text{-NR}$ followed by the effective charge separation through the high-quality heterojunction.

The $\text{SnO}_2(110)$ d -spacing in the NR was determined as a function of the distance from the interface with TiO_2 (d_{FIF}) from the HR-TEM analysis [16]. The a -axis length calculated from the (110) d -spacing gradually increased with an increase in d_{FIF} from 4.52 Å at $d_{\text{FIF}} = 1$ nm to 4.73 Å at $d_{\text{FIF}} = 75$ 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 $\text{SnO}_2\text{-NR}$ from the root to the tip. Density functional theory (DFT) simulations were performed for model slabs of the $\text{SnO}_2\text{-NR}$ 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 $\text{Al}_2\text{O}_3(0001)$ substrate, the interfacial tensile strain generated in the SnO_2 lattice conversely lowers the band gap [42].

The action mechanism of $\text{SnO}_2\text{-NR}\#\text{TiO}_2$ 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. $\text{SnO}_2\text{-NRs}$ are grown on rutile TiO_2 with a heteroepitaxial relation of $\text{SnO}_2\{001\}/\text{TiO}_2\{001\}$ by the present hydrothermal reaction. The positive a -axis mismatch generates a compressive strain in the $\text{SnO}_2\text{-NR}$ near the interface to induce the continuous increase in the a -axis length extending over 60 nm towards the $\text{SnO}_2[001]$ direction from the root to the tip. As a result, a downward band bending is formed in the interior of the $\text{SnO}_2\text{-NR}$. UV-light irradiation of $\text{SnO}_2\text{-NR}\#\text{TiO}_2$ 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 $\text{SnO}_2\text{-NR}$ 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 $\text{SnO}_2\text{-NR}$. The CB-electrons in the $\text{SnO}_2\text{-NR}$ have sufficient energy to cause a two-electron oxygen reduction reaction ($E^0(\text{O}_2/\text{H}_2\text{O}_2) = -5.14$ 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, $\cdot\text{OH}_s$) 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 $\text{SnO}_2\text{-NR}\#\text{TiO}_2$ photocatalytic reaction system, the highly selective and efficient oxidation of ethanol to acetaldehyde proceed.



Scheme 2. A proposed action mechanism of the $\text{SnO}_2\text{-NR}\#\text{R-TiO}_2$ -photocatalyst in the oxidation of ethanol to acetaldehyde. The scheme is taken from ref. [16].

4. Atom-Level Homojunction Effect

4.1. $\text{SnO}_2\text{-TiO}_2$ Homojunction Systems

In the as-grown $\text{SnO}_2\text{-NR}\#\text{TiO}_2$, the apparent single $\text{SnO}_2\text{-NR}$ is actually composed of a bundle of thin SnO_2 NRs. This section discusses the effect of the formation of homojunction between the thin SnO_2 NRs on the photocatalytic activity [17]. The photocatalytic activity-heating temperature (T_c) curve in the $\text{SnO}_2\text{-NR}\#\text{TiO}_2$ system shows a volcano-shaped profile with the maximum activity at $T_c = 500^\circ\text{C}$. The increase in the photocatalytic activity by the heating at $T_c = 500^\circ\text{C}$ results from the high electron mobility in the SnO_2 NRs with the fusion of the thin SnO_2 NRs.

SEM observation was carried out for $\text{SnO}_2\text{-NR}\#\text{TiO}_2$ prepared at varying T_c in air for 1 h (Figure 5a,b). As-grown $\text{SnO}_2\text{-NR}\#\text{TiO}_2$ consists of a bundle of thin SnO_2 NRs. The heat treatment at 500°C induces fusion of the bundle forming a monolithic SnO_2 NR.

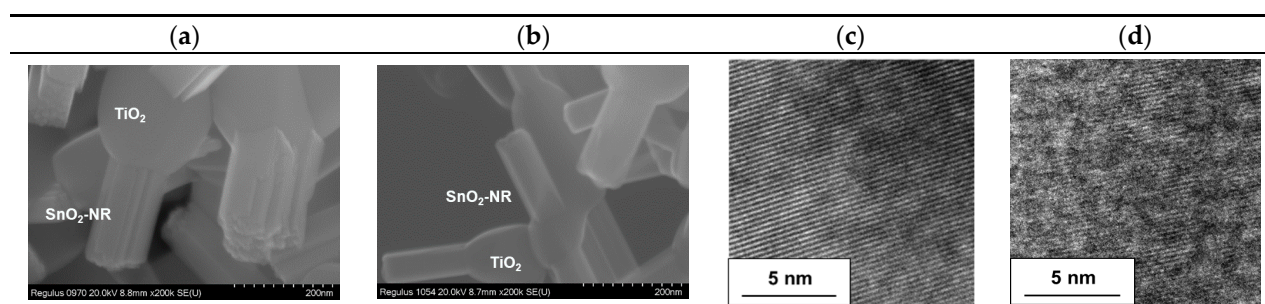


Figure 5. SEM images of $\text{SnO}_2\text{-NR}\#\text{TiO}_2$: (a) as-grown (b) $T_c = 500^\circ\text{C}$. HR-TEM image of the $\text{SnO}_2\text{-NR}$ moiety of $\text{SnO}_2\text{-NR}\#\text{TiO}_2$: (c) $T_c = 500^\circ\text{C}$, (d) $T_c = 700^\circ\text{C}$. The figure is taken from ref. [17].

Further, the HR-TEM image shows that the SnO_2 moiety of $\text{SnO}_2\text{-NR}\#\text{TiO}_2$ ($T_c = 500^\circ\text{C}$) 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 SnO_2 NRs (Figure 5d).

The specific surface area (S_{BET}) of $\text{SnO}_2\text{-NR}\#\text{TiO}_2$ was measured by Brunauer–Emmett–Teller method. As a result of an increase in T_c , the S_{BET} gradually decreases with fusion of the bundle of thin SnO_2 NRs (Figure 6a). In addition, the crystallite size of SnO_2 (D) was estimated using the Scherrer equation from the full-width at half maximum of the $\text{SnO}_2(110)$ diffraction peak. In the plot of D versus T_c , the D value of ~ 25 nm for the as-grown sample increases with an increase in T_c , going through a maximum of ~ 80 nm at $T_c = 500^\circ\text{C}$ to steeply decrease above 600°C (Figure 6a). Clearly, the growth of crystallites with increasing T_c at $\leq 500^\circ\text{C}$ increases the D value, which then decreases due to the segmentation at $T_c \geq 600^\circ\text{C}$.

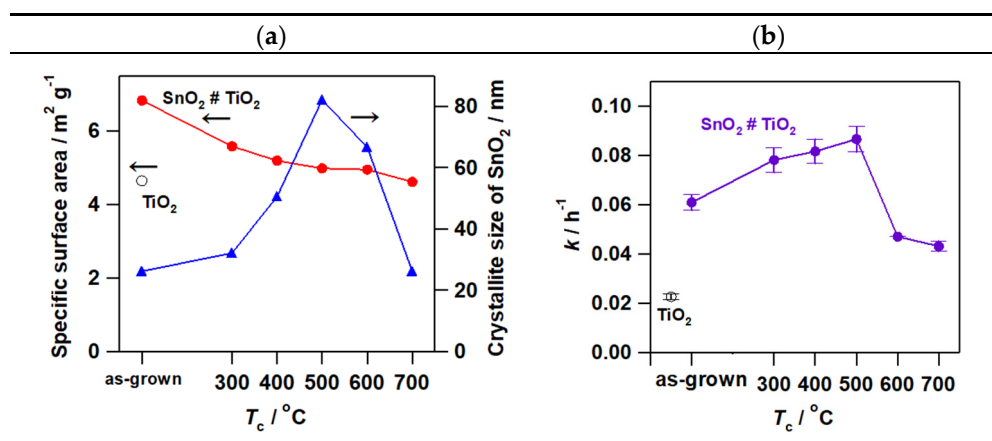


Figure 6. (a) Plots of specific surface area and SnO₂ crystallite size as a function of heating temperature (T_c). (b) Relation between the photocatalytic activity and T_c . The figure is taken from ref. [17].

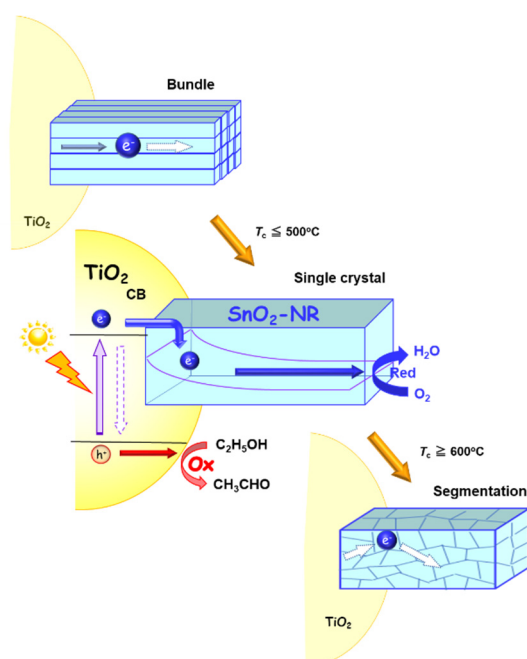
The T_c -dependence of the photocatalytic activity for the gas-phase oxidation of ethanol to acetaldehyde was studied. The reaction apparently follows the first-order rate law in every system, and the pseudo-first-order rate constant (k) was calculated from the plots of $\ln [C_0/(C_0-C)]$ versus t , 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 SnO₂ NRs (Scheme 3) [17]. As explained in Section 3, SnO₂-NR#TiO₂ can work as an excellent charge separator owing to the smooth interfacial electron transfer from TiO₂ to SnO₂ through the high-quality interface and the subsequent electron transport in the SnO₂-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 SnO₂ 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 SnO₂ crystal, which is also evidence of the presence of the hetero-epitaxial junction-induced lattice distortion in the SnO₂ NR. The many boundaries generated in the SnO₂ 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 $^{\circ}\text{C}$.

Zeng and co-workers constructed a branched rutile TiO₂ 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 TiO₂ NR and the branch by HR-TEM. The sample prepared at $t_{\text{CBD}} = 36$ h exhibits a high level of photocatalytic activity for gas-phase decomposition of benzene under UV-light irradiation ($200 \text{ nm} < \lambda_{\text{ex}} < 400 \text{ nm}$). 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 TiO₂ 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.



Scheme 3. Heating effect of the $\text{SnO}_2\text{-NR}/\text{TiO}_2$ photocatalyzed on the oxidation of ethanol to acetaldehyde.

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 $\text{Bi}_4\text{V}_2\text{O}_{11}$ 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 ($\lambda_{\text{ex}} = 254 \text{ nm}$). 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

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 ($300\text{ nm} < \lambda_{\text{ex}}$). 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 hetero-epitaxial 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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