Coupling of W-Doped SnO₂ and TiO₂ for Efficient Visible-Light Photocatalysis

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Five mol % tungsten-doped tin oxide (W₀.₀₅Sn₀.₉₅O₂, TTO5) was prepared by co-precipitation of SnCl₄·5H₂O and WCl₆, followed by calcination at 1000 °C. The as-prepared TTO5 was in the pure cassiterite phase with a particle size of ~50 nm and optical bandgap of 2.51 eV. Herein it was applied for the formation of TTO5/TiO₂ heterojunctions by covering the TTO5 surface with TiO₂ by sol-gel method. Under visible-light irradiation (λ ≥ 420 nm), TTO5/TiO₂ showed a significantly high photocatalytic activity in removing gaseous 2-propanol (IP) and evolving CO₂. It is deduced that its high visible-light activity is caused by inter-semiconductor hole-transfer between the valence band (VB) of TTO5 and TiO₂, since the TTO5 nanoparticle (NP) exhibits the absorption edge at ~450 nm and its VB level is located more positive side than that of TiO₂. The evidence for the hole-transport mechanism between TTO5 and TiO₂ was also investigated by monitoring the hole-scavenging reaction with 1,4-terephthalic acid (TA).

Key Words : Tungsten-doped tin oxide, Heterojunction, WₓSn₁₋ₓO₂/TiO₂, Visible-light, Photocatalyst

Introduction

Photocatalytic removal of volatile organic compounds in air and aqueous solution has attracted extensive attentions for the last few decades.¹-⁴ Even though TiO₂ has been known as the most efficient photocatalyst, however, TiO₂ can only utilize the photons in UV region (λ < 380 nm) due to its wide bandgap (Eg = 3.2 eV), which limits its practical applications in sun light or indoor.⁵-⁹ Therefore, the design of new photocatalysts working under visible-light is necessary in order to utilize the major portion of the solar spectrum.

Thus far, several strategies have been attempted in designing visible-light photocatalysts, such as lowering the conduction band (CB) of TiO₂ by doping transition metal ions¹⁰-¹³ and elevating the valence band (VB) by substituting anions to the oxygen site of TiO₂.¹⁴-¹⁷ Another noticeable strategy in designing visible-light photocatalysts is coupling the narrow bandgap semiconductors to the TiO₂.¹⁸-²⁷ On the basis of relative energy band location between the sensitizers and TiO₂, used as main photocatalyst, the heterojunction structure can be classified as two kinds. First, if sensitizer CB is positioned more positive side than that of TiO₂, the heterojunction can be classified as Type-A heterojunction, the photo-induced electrons of the sensitizer can be transferred to TiO₂ CB, and these electrons can be used for the chemical reactions. Metal calceinimide quantum dot-deposited or molecular dye-anchored TiO₂ systems will be the typical examples of Type-A heterojunction.¹⁸-²² Second, if the VB level of sensitizer is located more positive side than that of TiO₂, as shown in Scheme 1(a), the holes induced in the sensitizer VB under visible-light irradiation can be transferred to that of TiO₂.

This is classified as “Type- B heterojunction”,²³-²⁷ in which the photocatalytic reaction takes place on the basis of inter-semiconductor hole transfer mechanism. Considering the powerful oxidative ability of the holes in the VB of TiO₂, efficient and complete oxidation of organic compounds is expected with this heterojunction system under visible-light. SnO₂ (3.5 eV vs. NHE) is considered to be an appropriate candidate for the construction of Type-B heterojunction structure, since the VB of SnO₂ (+3.5 V vs. NHE) has been reported to be located considerably more positive side than that of TiO₂ (+2.7 V vs. NHE),²⁸,²⁹ but its wide bandgap (Eg) of 3.5 eV does not allow utilization of visible-light. Herein, we doped the W ions into the crystal lattice of SnO₂, and

Scheme 1. Energy band diagram describing the photo-generated charge transport in the TTO5/TiO₂ heterojunction under visible-light irradiation (a), and preparation strategy of TTO5/TiO₂ (b).

† This paper is to commemorate Professor Myung Soo Kim’s honourable retirement.
successfully lowered the conduction band position of SnO\textsubscript{2}. Thus the prepared tungsten-doped tin oxide (W\textsubscript{x}Sn\textsubscript{1-x}O\textsubscript{2}, TTO) can absorb the considerable portion of visible light. In this work, we prepared the several composites between W\textsubscript{0.05}Sn\textsubscript{0.95}O\textsubscript{2} (TTO5) nanoparticle (NP) and TiO\textsubscript{2} by sol-gel method. The visible-light photocatalytic mechanism as well as the photocatalytic behavior of TTO5/TiO\textsubscript{2} composites in decomposing gaseous IP was rigorously investigated.

**Experimental**

**Preparation of Tungsten Doped Tin Oxides (TTOs).** TTO NPs were synthesized by co-precipitation and subsequent calcination process.\textsuperscript{30} In typical synthesis of 5 mol \% W-doped SnO\textsubscript{2}, TTO5, 9.5 mmol of tin(IV) chloride pentahydrate (SnCl\textsubscript{4}·5H\textsubscript{2}O, Aldrich) and the stoichiometric amount of tungsten(IV) chloride (WCl\textsubscript{6}, Aldrich) were dissolved in 50 mL anhydrous ethanol. After vigorous stirring for 1 h, aqueous ammonia solution (NH\textsubscript{4}OH, 30 wt \% aqueous solution) was slowly added to obtain pH 7.5. The solution was then precipitated, and the collected precipitate was washed with de-ionized water for several times. It was then dried overnight in air at 60 °C, followed by calcination at 1000 °C for 3 h.

**Preparation of TTO5/TiO\textsubscript{2} Heterojunction.** For the formation of TTO5/TiO\textsubscript{2} heterojunction structures, 3.56 g titanium isopropoxide (97\%, Aldrich) was stabilized in a mixed solution of 30 mL ethanol, 1 mL concentrated nitric acid, and 1 mL water. The mixed Ti-precursor solution was gently stirred for 1 h for the stabilization. The stoichiometric amount of TTO5 NP was then added to this solution. Typically, in preparing the composite consisting of 3 wt \% TTO5 and 97 wt \% TiO\textsubscript{2} (3/97 TTO5/TiO\textsubscript{2}), 30 mg TTO5 NP pre-suspended in 10 mL ethanol was added to the Ti-precursor solution and gently stirred overnight. The sample was then dried at 90 °C for 24 h, and subsequently heat-treated at 300 °C for 3 h.

**Characterization.** X-ray diffraction (XRD) patterns were obtained for the powder samples by using a Rigaku Multi-flex diffractometer with monochromatic light-intensity Cu K\textsubscript{α} radiation. XRD scanning was performed under ambient conditions over 20 region of 20-70° at a rate of 2°/min (40 kV, 20 mA). UV-visible diffuse reflectance spectra were acquired by a Perkin-Elmer Lambda 40 spectrophotometer. BaSO\textsubscript{4} was used as the reflectance standard. SEM image was observed by Field emission scanning electron microscope (FE-SEM, Hitachi S-4500). Transmission electron microscope (TEM) images were obtained by a JOEL JEM 2100F operated at 200 kV, 1 mg of powder samples were dispersed in 50 mL of ethanol, and a drop of the suspension was then spread on a holey amorphous carbon coated Ni grid (JEOL Ltd.).

**Evaluation of Photocatalytic Activity.** The visible-light photocatalytic efficiencies of the photocatalytic samples were estimated by monitoring the evolved amount of CO\textsubscript{2} by decomposing 2-propanol (IP) in gas phase. An aqueous suspension containing 8.0 mg of photocatalytic sample was spread on a 2.5 × 2.5 cm\textsuperscript{2} Pyrex glass in a film form and subsequently dried at room temperature. The gas reactor system used for this photocatalytic activity has been described elsewhere.\textsuperscript{31} The net volume of the gas-tight reactor was 200 mL, and the photocatalytic film was located at the center of the reactor. The entire area of the photocatalytic film (2.5 cm × 2.5 cm) was irradiated by a 300 W Xe lamp through a UV cut-off filter (λ < 422 nm, ZUL0422 Asahi Co.) and a water filter to cut-off IR. After evacuation of the reactor, 1.6 μL of the IP diluted in water (IP:H\textsubscript{2}O = 1:9 in volume) was injected into the reactor. The initial concentration of gaseous IP in the reactor was maintained at 117 ppm in volume (ppmv). Thus the ultimate concentration of CO\textsubscript{2} evolved, with all of the IP decomposed, will be 351 ppmv, as shown in the following equation:

\[
2(CH\textsubscript{3})\textsubscript{2}CHOH(g) + 9O\textsubscript{2}(g) \rightarrow 6CO\textsubscript{2}(g) + 8H\textsubscript{2}O(g) \quad (1)
\]

The total pressure of the reactor was then adjusted to 750 Torr by adding oxygen gas. Under this condition, the IP and H\textsubscript{2}O remained in the vapor phase. After a certain irradiation interval, 0.5 mL of the gas in the reactor was automatically picked up and sent to a gas chromatograph (Agilent Technologies, Model 6890N) using an auto sampling valve system. For CO\textsubscript{2} detection, a methanizer was installed between the GC column outlet and the FID detector.

**Results and Discussion**

TTO particles in different W-doping levels were prepared by co-precipitation of SnCl\textsubscript{4}·5H\textsubscript{2}O and WCl\textsubscript{6}, followed by calcination at 1000 °C for 3 h. X-ray diffraction patterns in Figure 1(a) show that the pure cassiterite phase (JCPDS, No. 77-0450) can be retained up to 5 mol \% W ion incorporation, whereas further incorporation leads to formation of the impurity phase, inherent from the orthorhombic SnWO\textsubscript{4} phase (JCPDS, No. 29-1354). It is suggested that only a limited amount of W ions can be doped into the SnO\textsubscript{2} lattice and the maximum doping level is 5 mol \%. Hence, 5 mol \% W-doped SnO\textsubscript{2} (W\textsubscript{0.05}Sn\textsubscript{0.95}O\textsubscript{2}, TTO5) was prepared and utilized in fabricating the coupled structure with TiO\textsubscript{2} in this work. In TTO structure, the W\textsuperscript{6+} ions replace the Sn\textsuperscript{4+} in the SnO\textsubscript{2} lattice.\textsuperscript{32} Thus in the energy band structure of TTO they form the interbands, originating from W 5d and 6s, below the CB of SnO\textsubscript{2}, as shown in Scheme 1(a).

UV-visible diffuse reflectance spectrum of TTO5 in Figure 2(a) shows that the absorption band edge is ~450 nm. The bandgap of the prepared TTO5 was determined by the following equation.

\[
\alpha h\nu = A(h\nu - E_g)^n \quad (2)
\]

where \(\alpha\), \(h\nu\), \(A\), and \(E_g\) are the optical absorption coefficient, the photon energy, proportionality constant, and band gap, respectively.\textsuperscript{33} In this equation, \(n\) decides the type of the transition in a semiconductor (\(n = 1\), direct absorption; \(n = 4\), indirect absorption). By applying \(n = 1\), the direct bandgap of the prepared TTO5 was determined from the plot of \((\alpha h\nu)^2\) vs. \(h\nu\), as shown in the inset of Figure 2. By extra-
polating the straight line to the x-axis in this plot, \( E_g \) of the TTO5 was estimated to 2.51 eV.

The SEM image in Figure 3(a) indicates that the as-prepared TTO5 is moderately monodispersed with a size of 50-60 nm. Figure 3(b) exhibits the TEM image of a single TTO5 NP and its dotted area was further magnified, as shown in Figure 3(c). The uniform fringe patterns observed over the whole area suggest that the individual particle is a single crystal. The spacing of the fringe patterns was measured to be 0.335 nm, corresponding to \( d_{110} \) of the cassiterite SnO\(_2\) phase.

Scheme 1(b) describes the preparation strategy of TTO5/TiO\(_2\) coupled structure derived from sol-gel method. Figure 1(b) shows the XRD patterns of the pure TTO5, TiO\(_2\), and TTO5/TiO\(_2\) composites in different compositions. The diffraction peaks at 25.36\(^\circ\), 37.90\(^\circ\), 48.15\(^\circ\), 54.05\(^\circ\), 55.20\(^\circ\), 62.86\(^\circ\) and 75.27\(^\circ\) corresponding to (101), (004), (200), (105), (211), (204) and (215) peaks, respectively, of the anatase TiO\(_2\) (JCPDS, No. 73-1764), clearly indicating that the sol-gel processed TiO\(_2\) has been sufficiently crystallized. XRD

Figure 1. XRD patterns of the bare SnO\(_2\) and several W\(_x\)Sn\(_{1-x}\)O\(_2\) (TTO) in different doping levels (a), and those of TiO\(_2\), TTO5, and several TTO5/TiO\(_2\) composites (b).

Figure 2. UV-visible diffuse reflectance spectrum of TTO5 obtained at absorbance mode (a), and those spectra for TiO\(_2\), SnO\(_2\), 1/99 TTO5/TiO\(_2\), 3/99 TTO5/TiO\(_2\), 5/95 TTO5/TiO\(_2\), TTO5 obtained at reflectance mode (b). The plot of \((\alpha hv)^2\) vs. \((hv)\) for TTO5 is shown in the inset of a.

Figure 3. SEM images of TTO5 NPs (a). TEM image of a TTO5 NP (b), and high resolution image taken over the dotted area in b (c).
patterns of the several TTO5/TiO2 composites also indicate no presence of other impurity peaks, suggesting that there was no chemical reaction occurred between TTO5 and TiO2 during the heat-treatment at 300°C. UV-visible diffuse reflectance spectra of the TTO5/TiO2 in several compositions are shown in Figure 2(b). Since TTO5 reveals significant absorption toward the photons shorter than 450 nm, TTO5/TiO2 composites can also show appreciable absorption in the visible region, and its absorbance gradually increases with increase of TTO5 content. The TEM image of the 3/97 TTO5/TiO2 is shown in Figure 4(a). The TTO5 NP with a size of ~50 nm was fully covered with TiO2. Figure 4(b) is a high-magnification image focusing the interface between TiO2 and TTO5. The sharp interface without any gap or interface clearly indicates that the TiO2 is tightly bound to the TTO5.

Photocatalytic activities of the bare TTO5, TiO2, and several TTO5/TiO2 composites in decomposing gaseous IP were evaluated under visible-light irradiation ($\lambda \geq 420$ nm). It is well known that the photocatalytic reaction proceeds through the oxidation of IP to acetone and it is then fully mineralized to CO2. Figure 5(a) describes the photocatalytic removal of IP with several photocatalytic samples as a function of visible-light irradiation time. The TTO5/TiO2 composites exhibit remarkably higher catalytic activity than the bare TTO5 or TiO2. Especially, the 3/97 TTO5/TiO2 exhibited the highest photocatalytic activity: About 72% of IP was removed in 2 h irradiation, whereas 5.7% and 3.5% was removed with Degussa P25 and bare TTO5, respectively.

The photocatalytic activity was also evaluated, according to the amount of CO2 evolved under visible-light irradiation. The 3/97 TTO5/TiO2 composite also demonstrated the highest photocatalytic activity in evolving CO2 among the several composites in different compositions, as shown in Figure 5(b). The amount of CO2 evolved in 2 h is 6.9 ppmv, which is 6.2 times that of Degussa P25 TiO2 and 15.1 times that of the bare TTO5. Noticeably, its photocatalytic efficiency reaches to 80.2% that of the typical N-doped TiO2, as illustrated in Figure 6.

It is deduced that the high visible-light photocatalytic activity of TTO/TiO2 is caused by the relative energy band location between these two semiconductors. As shown in Scheme 1(a), the VB position of TTO5 is located more positive side, compared with that of TiO2. Under visible-light irradiation, the electrons in the VB of TTO5 are excited to its CB. Thereby, the holes in the TTO5 VB can be transferred to the VB of TiO2. By this inter-semiconductor hole-transport mechanism, holes are generated on the TiO2 VB, resultanty producing the •OH radicals by the Eqs. (3)
and (4).

\[
(H_2O)_{ads} + h^+ \rightarrow H^+ + \cdot OH \quad (3)
\]
\[
(OH^-)_{ads} + h^+ \rightarrow \cdot OH \quad (4)
\]

As a result, the generated \(\cdot OH\) radicals can completely decompose the organic compounds to \(CO_2\) and \(H_2O\).

In order to support the hole transfer mechanism, the presence of \(\cdot OH\) radicals in the TiO\(_2\) side of the TTO5/TiO\(_2\) during the visible-light irradiation was monitored. That is, 20 mg TTO5, TiO\(_2\) or 3/97 TTO5/TiO\(_2\) was suspended in 50 mL aqueous solution containing 0.01 M NaOH and 3 mM 1,4-terephthalic acid (TA). Before exposure to the visible-light, the suspension was stirred in dark for 30 min. Five mL of the solution was then taken after 2 h irradiation for the fluorescence measurement. It is well known that \(\cdot OH\) radical reacts with TA in basic solution and generates 2-hydroxyterephthalic acid (TAOH), which emits the unique fluorescence peak at 426 nm.\(^{34,35}\)

Bare TiO\(_2\) suspended in TA solution did not show no fluorescence peak under visible-light (\(\lambda \geq 420\) nm) irradiation, as shown in Figure 7. Only a small amount of \(\cdot OH\) radical was formed with the bare TTO5, even though TTO5 can be sensitized by visible-light. This will be caused by the fast recombination of electron-hole pairs in the TTO5 NP. Contrarily, the TTO5/TiO\(_2\) shows the intense characteristic fluorescence peak. This clearly indicates that lots of holes are formed at the TiO\(_2\) side and that they have been transported from the TTO5 VB by the inter-semiconductor hole-transport mechanism.

**Conclusion**

About 50 nm-sized TTO5 NP was successfully prepared by co-precipitation and subsequent heat-treatment at 1000 °C. The 5 mol % doping of W ion in the lattice site of SnO\(_2\) reduced the band gap of SnO\(_2\) from 3.5 to 2.51 eV. The coupled structure of TTO5 and TiO\(_2\) exhibited a significantly enhanced visible-light photocatalytic activity. In evolving CO\(_2\) from the gaseous IP with 3/97 TTO5/TiO\(_2\), the amount of CO\(_2\) evolved in 2 h was 6.9 ppmv, which is 6.2 times that of Degussa P25 TiO\(_2\) and 80.2% that of the typical N-doped TiO\(_2\). The significantly high activity of TTO5/TiO\(_2\) is considered to be caused by the inter-semiconductor hole-transport mechanism. The evidence for the hole-transport between TTO5 and TiO\(_2\) was also investigated by monitoring the OH radicals in TiO\(_2\) side during the visible-light irradiation using 3 mM TA. It was monitored that the 3/97 TTO5/TiO\(_2\) composite converted TA to TAOH with high rate, indicative of hole-transport between TTO5 and TiO\(_2\).

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**References**