

Research Article

Stannic Oxide-Titanium Dioxide Coupled Semiconductor Photocatalyst Loaded with Polyaniline for Enhanced Photocatalytic Oxidation of 1-Octene

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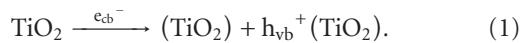
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Stannic oxide-titanium dioxide ($\text{SnO}_2\text{-TiO}_2$) coupled semiconductor photocatalyst loaded with polyaniline (PANI), a conducting polymer, possesses a high photocatalytic activity in oxidation of 1-octene to 1,2-epoxyoctane with aqueous hydrogen peroxide. The photocatalyst was prepared by impregnation of SnO_2 and followed by attachment of PANI onto a TiO_2 powder to give sample PANI- $\text{SnO}_2\text{-TiO}_2$. The electrical conductivity of the system becomes high in the presence of PANI. Enhanced photocatalytic activity was observed in the case of PANI- $\text{SnO}_2\text{-TiO}_2$ compared to PANI- TiO_2 , $\text{SnO}_2\text{-TiO}_2$, and TiO_2 . A higher photocatalytic activity in the oxidation of 1-octene on PANI- $\text{SnO}_2\text{-TiO}_2$ than $\text{SnO}_2\text{-TiO}_2$, PANI- TiO_2 , and TiO_2 can be considered as an evidence of enhanced charge separation of PANI- $\text{SnO}_2\text{-TiO}_2$ photocatalyst as confirmed by photoluminescence spectroscopy. It suggests that photojected electrons are tunneled from TiO_2 to SnO_2 and then to PANI in order to allow wider separation of excited carriers.

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1. INTRODUCTION

Photocatalysis over titanium dioxide (TiO_2) is initiated by the absorption of a photon with energy equal to or greater than the band gap of TiO_2 (3.2 eV), producing electron-hole (e^-/h^+) pairs [1]:



Consequently, following irradiation, the TiO_2 particle can act as either an electron donor or acceptor for molecules in the surrounding media. However, the photoinduced charge separation in bare TiO_2 particles has a very short lifetime because of charge recombination. Therefore, it is important to prevent electron-hole recombination before a designated chemical reaction occurs on the TiO_2 surface. TiO_2 and high-recombination rate of the photogenerated electron-hole pairs hinders its further application in industry. Having recognized that charge separation is a major problem, numerous efforts have been attempted to improve its photocatalytic activity by modifying the surface or bulk properties of TiO_2 , such as deposition of metals, doping, surface chelation, and coupling of two semiconductors [2–4]. Among the coupled semiconductor photocatalysts, many efforts have been

devoted to the $\text{SnO}_2\text{-TiO}_2$ system [5, 6]. Here, $\text{SnO}_2\text{-TiO}_2$ coupled semiconductor photocatalyst loaded with PANI, a conducting polymer, has been studied as photocatalyst in the oxidation of 1-octene with aqueous hydrogen peroxide. One expects that the attachment of polyaniline (PANI) on the surface of $\text{SnO}_2\text{-TiO}_2$ composite will reduce the electron-hole recombination during the photocatalytic oxidation of 1-octene due to PANI's electrical conductive properties.

2. EXPERIMENTAL

2.1. Preparation of photocatalysts

2.1.1. PANI- TiO_2

Preparation of PANI- TiO_2 was done by using 360 μl of aniline which is dissolved in 20 ml distilled water containing 3 ml 30% hydrochloric acid. The solution was precooled at 4°C and 2 g of anatase TiO_2 was added, and the suspension was stirred for 30 minutes and allowed to stand for further period of 60 minutes. Then, 4 ml of potassium persulphate as initiator was added in the solution and stirred thoroughly until we can see green pale color. The resultant

product obtained was filtered, wash thoroughly with water, and dried till it shows constant weight at 60°C. The polymer prepared in such manner is commonly termed as PANI-HCl (Emeraldine-salt). The amount of PANI in PANI-TiO₂ was *ca.* 2 wt% as analyzed by thermogravimetry analyzer.

2.1.2. SnO₂-TiO₂

Here, 0.285 g stannous chloride was added to 10 ml methanol. Then, 3 g of anatase TiO₂ was mixed into the solution and stirred for 6 hours until the solvent is completely dry. The sample was calcined at 500°C for 4 hours. The sample was labeled as SnO₂-TiO₂. The molar amount of SnO₂ in 1 g TiO₂ was 500 μmol.

2.1.3. PANI-SnO₂-TiO₂

Stannic oxide-titanium dioxide (SnO₂-TiO₂) coupled semiconductor photocatalyst loaded with polyaniline (PANI) was prepared in two steps by a procedure similar to that preparation of SnO₂-TiO₂ and PANI-TiO₂. First, stannous chloride was impregnated into TiO₂ to give sample SnO₂-TiO₂ (see Section 2.1.2). In the second step, PANI was attached on the surface of SnO₂-TiO₂ particle (see Section 2.1.1). This modified SnO₂-TiO₂ is called PANI-SnO₂-TiO₂.

2.2. Characterizations

The physical characteristics of TiO₂, SnO₂-TiO₂, and PANI-SnO₂-TiO₂ particles are experimentally studied by X-ray diffraction (XRD), UV-Vis diffuse reflectance (UV-Vis DR), scanning electron microscopy (SEM), photoluminescence spectroscopy, and electrical conductivity analysis techniques. Electrical conductivity was carried by an impedance analyzer. Pellets of 2–4 mm thick were prepared by placing sufficient amount of sample (50 mg) in a steel die measuring 13 mm in diameter, and a pressure of 5 tons were applied and held for 30 seconds. The electric properties of the pellet prepared were measured by AC impedance spectroscopy using frequency response analyzer (Autolab POST AT 30) in the frequency range from 0.01 Hz to 1 MHz with an applied voltage of 10 mV. The impedance data were fitted by GPES software. Luminescence spectra were recorded on Perkin-Elmer LS 55 spectrometer. About 0.04 g of the sample was placed on a sample holder. After locating and locking sample holder in a proper place in the analyzer, samples were measured in the emission λ (wavelength) scale of 200–900 nm at excitation $\lambda = 333$ nm.

2.3. Photocatalytic oxidation of 1-octene

Photocatalytic reactions were carried out in Pyrex glass tubes ($\phi = 10$ mm) that contained photocatalyst powder (50 mg), 1-octene (0.85 ml) and 30% hydrogen peroxide (1.5 ml). In this experiment, H₂O₂ was added in the photocatalytic reaction system because it has been reported that photocatalytic oxidation of some compounds is activated by addition of H₂O₂ [7]. During the photocatalytic reaction, the photocatalyst particles were suspended in the solution using a

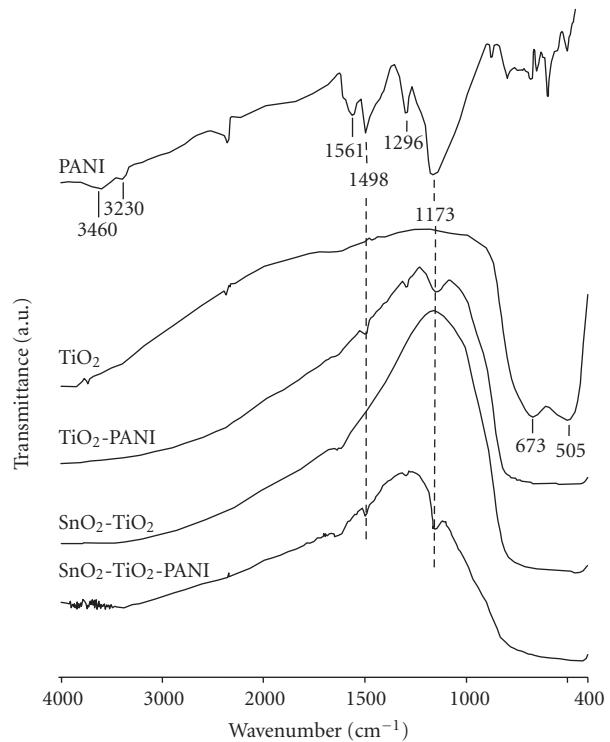


FIGURE 1: IR spectra of photocatalysts.

magnetic stirrer. The suspension was photoirradiated using a 450-Watt Hanovia high-pressure mercury-vapor lamp (Ace Glass Co., Vineland, NJ). The light source was placed 8 cm away from the reactor. The temperature of the reactor solutions was maintained at 4°C throughout the experiments by using a water circulation system equipped with chiller. The photocatalytic reactions were carried out for 20 hours. The products were analyzed with a gas-liquid chromatograph (ThermoFinnigan Trace GC). The products were identified by coinjecting the corresponding authentic samples into the columns.

3. RESULTS AND DISCUSSION

3.1. Physical properties

The XRD patterns of TiO₂, PANI-TiO₂, and SnO₂-TiO₂ (data not shown) demonstrated that all the modified catalysts possess a similar crystalline structure which is corresponded to anatase phase of TiO₂. Figure 1 shows the FTIR spectra of PANI, TiO₂, TiO₂-PANI, SnO₂-TiO₂, and PANI-SnO₂-TiO₂. The broad peaks around 500–680 cm⁻¹ of TiO₂, TiO₂-PANI, SnO₂-TiO₂, and PANI-SnO₂-TiO₂ are due to the Ti-O bond in the TiO₂. The peak at 673 cm⁻¹ refers to symmetric O-Ti-O stretch while 505 cm⁻¹ is due to the vibration of Ti-O bend. As shown in Figure 1, the main characteristic peaks of PANI are assigned as follows: the band at 3460 and 3230 cm⁻¹ can be attributed to the free (nonhydrogen bonded) N-H stretching vibration and hydrogen-bonded N-H bond between amine and imine sites, C=N

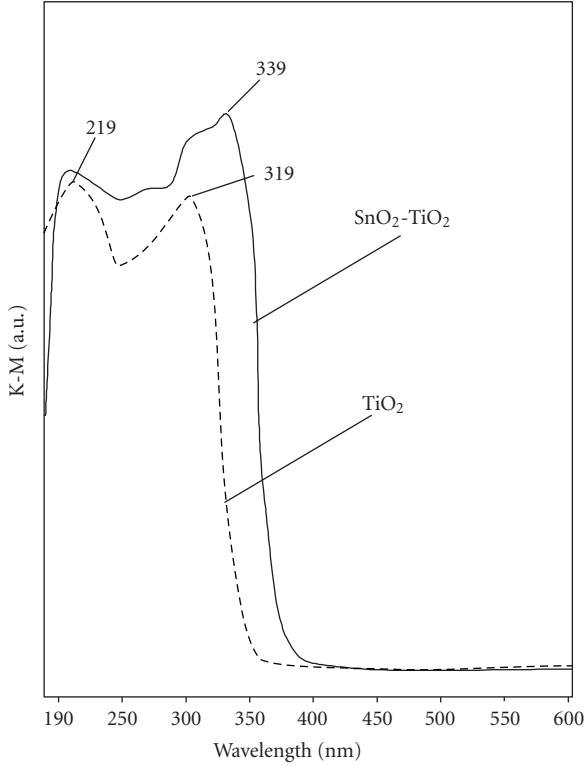


FIGURE 2: UV-Vis DR spectra of photocatalysts in the range of wavelength from 190 to 600 nm.

and C=C stretching modes for the quinonoid and benzenoid units occur at 1561 and 1498 cm^{-1} , the band at 1296 cm^{-1} has been attributed to C–N stretching mode for benzenoid unit, while the strong band at 1173 cm^{-1} was considered to be a measure of the degree of electron delocalization and thus it is a characteristic peak of PANI conductivity [8]. The peaks at 1173 and 1498 cm^{-1} were observed in $\text{TiO}_2\text{-PANI}$ and $\text{PANI-SnO}_2\text{-TiO}_2$ samples thereby endorsing the presence of PANI in the $\text{TiO}_2\text{-PANI}$ and $\text{PANI-SnO}_2\text{-TiO}_2$. However, the others low-intense PANI's peaks were not observed in PANI-TiO_2 and $\text{PANI-SnO}_2\text{-TiO}_2$ since the amount of PANI was only *ca.* 2 wt% in these samples as analyzed by thermogravimetry analyzer.

The UV-Vis spectra of TiO_2 , PANI-TiO_2 , and $\text{SnO}_2\text{-TiO}_2$ are shown in Figures 2 and 3. As revealed in Figure 2, the band in the range of 200–240 nm is attributed to a charge-transfer of the tetrahedral titanium sites between O^{2-} and the central Ti(IV) atoms, while octahedral Ti was reported appear at around 260–330 nm [9]. The UV-Vis spectrum of $\text{SnO}_2\text{-TiO}_2$ (see Figure 3), on the other hand, shows absorption at higher wavelengths (339 nm) due to the presence of hexa-coordinated Sn species or polymeric Sn–O–Sn units [10].

It is generally known that the peak of PANI could be observed in the range of wavelength from 400 to 1400 nm. As shown in Figure 3, PANI-TiO_2 and $\text{PANI-SnO}_2\text{-TiO}_2$ samples show two characteristic absorptions peaks at 428 and

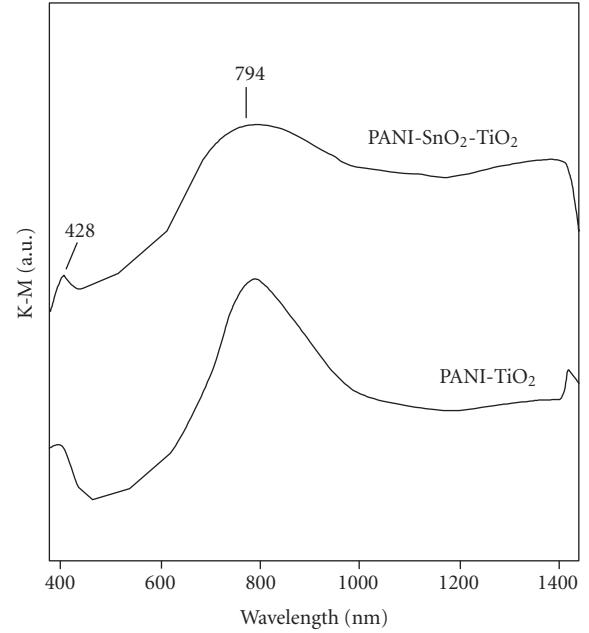


FIGURE 3: UV-Vis DR spectra of photocatalysts in the range of wavelength from 400 to 1400 nm.

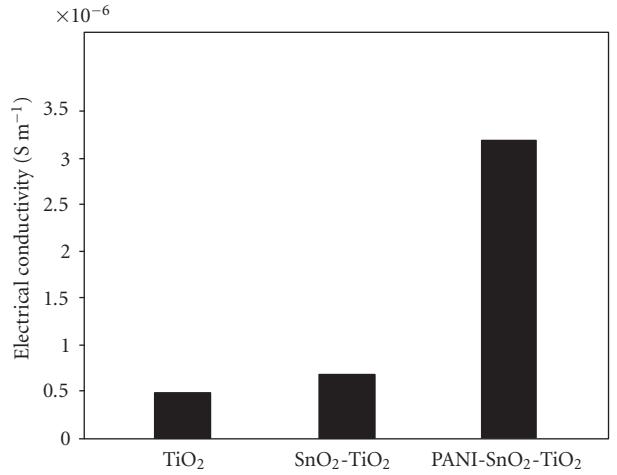


FIGURE 4: Electrical conductivity of photocatalysts.

794 nm. These peaks originate from the charged cationic species known as polarons [11, 12].

Considering that PANI is a conducting polymer, it is of interest to check the electrical conductivity of $\text{PANI-SnO}_2\text{-TiO}_2$. The electrical conductivity of TiO_2 and $\text{SnO}_2\text{-TiO}_2$ were increased significantly due to the presence of PANI in the composite (see Figure 4). Electrical transfer is obviously associated with the PANI attached on the surface of $\text{PANI-SnO}_2\text{-TiO}_2$. However, the electrical conductivity of $\text{PANI-SnO}_2\text{-TiO}_2$ is much lower compared than the result observed by Bian and Xue for PANI attached on the surface of TiO_2 [13]. They observed that the electrical conductivity was 0.5 S cm^{-1} . Our observations are different because

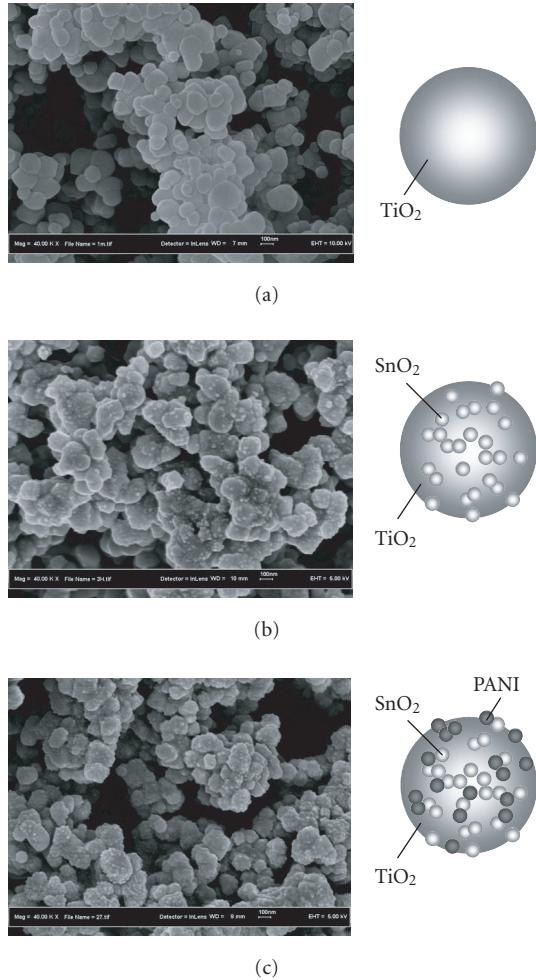


FIGURE 5: SEM photographs of (a) TiO_2 , (b) $\text{SnO}_2\text{-TiO}_2$, and (c) $\text{PANI-SnO}_2\text{-TiO}_2$.

the amount of PANI attached on the TiO_2 particles differs from those used by Bian and Xue. The amount of PANI reported by Bian and Xue was 60 wt%. Instead, we decreased the PANI content thirty fold. Clearly these changes influence the electrical conductivity of $\text{PANI-SnO}_2\text{-TiO}_2$. One expects that by using a large amount PANI, the surface of TiO_2 particle is covered by PANI. In this study, the amount of PANI in $\text{PANI-SnO}_2\text{-TiO}_2$ was only *ca.* 2 wt% as analyzed by thermogravimetry analyzer, so that TiO_2 particle is only covered by PANI with a lower coverage compared to those previously reported [13]. Since the photocatalytic reaction is occurred on the surface TiO_2 , it is necessary to use a small amount of PANI to avoid coating TiO_2 with PANI.

Figure 5 shows the SEM photographs of TiO_2 , $\text{SnO}_2\text{-TiO}_2$, and $\text{PANI-SnO}_2\text{-TiO}_2$. It reveals the difference in surface morphology among the samples. It is clearly observed the existence of SnO_2 nanoparticles attached on the surface of $\text{SnO}_2\text{-TiO}_2$. SEM photographs of $\text{SnO}_2\text{-TiO}_2$ (see Figure 5(b)) and $\text{PANI-SnO}_2\text{-TiO}_2$ (see Figure 5(c)) shows that the amount of particles sticking on the surface of $\text{PANI-SnO}_2\text{-TiO}_2$ is higher than those

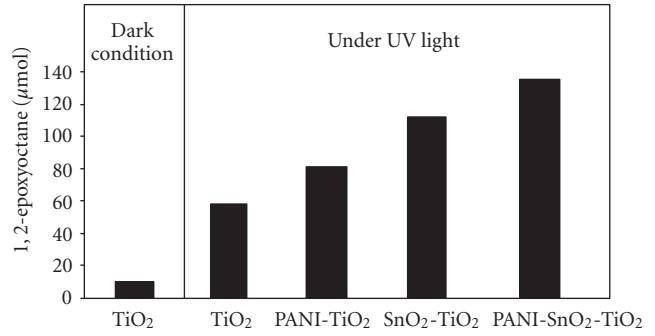


FIGURE 6: The photocatalytic epoxidation of 1-octene over $\text{PANI-SnO}_2\text{-TiO}_2$, $\text{SnO}_2\text{-TiO}_2$, PANI-TiO_2 , and TiO_2 . All reactions were carried out at 4°C under dark and UV light irradiation conditions.

of $\text{SnO}_2\text{-TiO}_2$ confirming the existence of PANI in $\text{PANI-SnO}_2\text{-TiO}_2$. However, SnO_2 and PANI particles are very difficult to distinguish in $\text{PANI-SnO}_2\text{-TiO}_2$ since their size and shape are almost similar. Based on the above results, it can be concluded that PANI is successfully attached on the surface of TiO_2 and $\text{SnO}_2\text{-TiO}_2$.

3.2. Photocatalytic activity and radiative recombination process

Gas chromatography analyses indicated that 1,2-epoxyoctane was the sole product, and other expected by-products, such as 2-octanone, 1-octanol, 2-octanol, or 1,2-octanediol, were not detected. As shown in Figure 6, a considerable increase in 1,2-epoxyoctane yield was observed when the reaction was carried out under UV irradiation, suggesting that the photocatalytic action was occurred on the surface of TiO_2 . A similar trend was also observed when the surface of TiO_2 was attached with SnO_2 , and PANI. It is observed that the photocatalytic activity in decreasing order of the yield of 1,2-epoxyoctane as the following: $\text{PANI-SnO}_2\text{-TiO}_2 > \text{SnO}_2\text{-TiO}_2 > \text{PANI-TiO}_2 > \text{TiO}_2$. The most active photocatalyst, $\text{PANI-SnO}_2\text{-TiO}_2$, combined three materials, PANI, SnO_2 and TiO_2 which complemented each other in photocatalytic reaction as described below.

Semiconductors such as TiO_2 and SnO_2 can be excited by photons with appropriate energy to produce the photogenerated electron or hole pairs [1]. It was reported that the high photocatalytic activity arose from the increase in the reaction efficiency due to the electron transfer from TiO_2 to SnO_2 . The valence band (VB) edge of SnO_2 (+3.67 V) is much lower than that of TiO_2 (+2.87 V) [1, 6]. Since holes move in the opposite direction from the electrons, they can be trapped in the TiO_2 . As such, charge separation is increased so recombination is reduced. In order to confirm this argument, the photoluminescence (PL) experiments were carried out.

The PL emission spectra have been widely used to investigate the efficiency of charge carrier trapping, immigration, and transfer, and to understand the fate of e^-/h^+ pairs in semiconductor particles [14]. As depicted in Figure 7, it is observed that the maximum of the PL emission peaks of

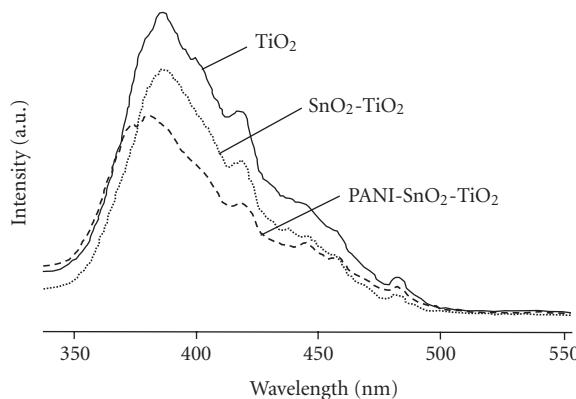


FIGURE 7: Photoluminescence (PL) spectra of photocatalysts.

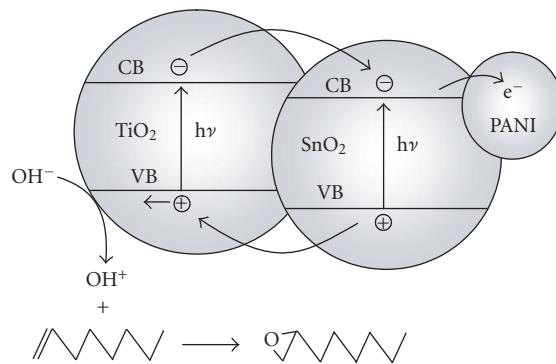


FIGURE 8: The proposed mechanism of photocatalytic epoxidation of 1-octene over PANI-SnO₂-TiO₂.

the pure TiO₂ and SnO₂-TiO₂ occurred at 385 nm, while the maximal emission for the PANI-SnO₂-TiO₂ appeared at 380 nm. One suggests that the interaction between the conjugated polymer chains and the surface of the TiO₂ particles played a key role in the resulting blue shift [15]. Compared with the spectrum of TiO₂, it is found that the intensity of the PL spectra of the PANI-SnO₂-TiO₂ and SnO₂-TiO₂ in the same range of wavelength are much lower than that of pure TiO₂. This indicates the decrease of the radiative recombination process in these samples. The intensity of the PL spectra in decreasing order as the following: TiO₂ > SnO₂-TiO₂ > PANI-SnO₂-TiO₂ (see Figure 7). On the basis of these results, a model of the mechanism of photocatalytic epoxidation of 1-octene using PANI-SnO₂-TiO₂ system is proposed (see Figure 8). By attaching SnO₂ and PANI on the surface of TiO₂, it is possible to drive the photogenerated electrons farther away from the TiO₂, thereby achieving more efficient charge separation in these semiconductor particles. As a result, a more active photocatalyst is obtained.

4. CONCLUSION

An enhancement of the photocatalytic activity of the SnO₂-TiO₂ coupled semiconductor photocatalyst loaded with polyaniline (PANI), a conducting polymer, has been

confirmed in the oxidation of 1-octene to 1,2-epoxyoctane with aqueous hydrogen peroxide. A higher photocatalytic activity in the oxidation of 1-octene on PANI-SnO₂-TiO₂ than PANI-TiO₂, SnO₂-TiO₂, and TiO₂ can be considered as an evidence of enhanced charge separation of PANI-SnO₂-TiO₂ photocatalyst as confirmed by photoluminescence spectroscopy. It suggests that photojected electrons are tunneled from TiO₂ to SnO₂ and then to PANI in order to allow wider separation of excited carriers.

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REFERENCES

- [1] A. L. Linsebigler, G. Lu, and J. T. Yates Jr., "Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results," *Chemical Reviews*, vol. 95, no. 3, pp. 735–758, 1995.
- [2] M.-W. Xu, S.-J. Bao, and X.-G. Zhang, "Enhanced photocatalytic activity of magnetic TiO₂ photocatalyst by silver deposition," *Materials Letters*, vol. 59, no. 17, pp. 2194–2198, 2005.
- [3] D. Chatterjee and A. Mahata, "Visible light induced photodegradation of organic pollutants on dye adsorbed TiO₂ surface," *Journal of Photochemistry and Photobiology A*, vol. 153, no. 1-3, pp. 199–204, 2002.
- [4] H. Tada, Y. Kubo, M. Akazawa, and S. Ito, "Promoting effect of SiO_x monolayer coverage of TiO₂ on the photoinduced oxidation of cationic surfactants," *Langmuir*, vol. 14, no. 11, pp. 2936–2939, 1998.
- [5] S. Pilkenton and D. Rafty, "Solid-state NMR studies of the adsorption and photooxidation of ethanol on mixed TiO₂-SnO₂ photocatalysts," *Solid State Nuclear Magnetic Resonance*, vol. 24, no. 4, pp. 236–253, 2003.
- [6] P. V. Kamat and K. Vinodgopal, "Environmental photochemistry with semiconductor nanoparticles," *Molecular and Supramolecular Photochemistry*, vol. 2, pp. 307–350, 1998.
- [7] J. Fernández, J. Kiwi, J. Baeza, J. Freer, C. Lizama, and H. D. Mansilla, "Orange II photocatalysis on immobilised TiO₂: effect of the pH and H₂O₂," *Applied Catalysis B*, vol. 48, no. 3, pp. 205–211, 2004.
- [8] S. Quillard, G. Louarn, S. Lefrant, and A. G. McDiarmid, "Vibrational analysis of polyaniline: a comparative study of leucoemeraldine, emeraldine, and pernigraniline bases," *Physical Review B*, vol. 50, no. 17, pp. 12496–12508, 1994.
- [9] H. Nur, N. Y. Hau, I. I. Misnon, H. Hamdan, and M. N. M. Muhib, "Hydrophobic fluorinated TiO₂-ZrO₂ as catalyst in epoxidation of 1-octene with aqueous hydrogen peroxide," *Materials Letters*, vol. 60, no. 17-18, pp. 2274–2277, 2006.
- [10] N. K. Mal, A. Bhaumik, R. Kumar, and A. V. Ramaswamy, "Sn-ZSM-12, a new, large pore MTW type tin-silicate molecular sieve: synthesis, characterization and catalytic properties in oxidation reactions," *Catalysis Letters*, vol. 33, no. 3-4, pp. 387–394, 1995.
- [11] L. Zhang and M. Wan, "Polyaniline/TiO₂ composite nanotubes," *Journal of Physical Chemistry B*, vol. 107, no. 28, pp. 6748–6753, 2003.

- [12] H. Xia and Q. Wang, "Preparation of conductive polyaniline/nanosilica particle composites through ultrasonic irradiation," *Journal of Applied Polymer Science*, vol. 87, no. 11, pp. 1811–1817, 2003.
- [13] C. Bian and G. Xue, "Nanocomposites based on rutile-TiO₂ and polyaniline," *Materials Letters*, vol. 61, no. 6, pp. 1299–1302, 2007.
- [14] H. Yamashita, Y. Ichihashi, S. G. Zhang, et al., "Photocatalytic decomposition of NO at 275 K on titanium oxide catalysts anchored within zeolite cavities and framework," *Applied Surface Science*, vol. 121-122, pp. 305–309, 1997.
- [15] J. B. Lagowski, "Ab initio investigation of conformational and excitation energies of phenylene vinylene oligomers," *Journal of Molecular Structure: THEOCHEM*, vol. 589-590, pp. 125–137, 2002.

