Stannic oxide-titanium dioxide coupled semiconductor photocatalyst loaded with polyaniline for enhanced photocatalytic oxidation of 1-octene

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Stannic oxide-titanium dioxide (SnO$_2$–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-SnO$_2$–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-SnO$_2$–TiO$_2$ compared to PANI-TiO$_2$, SnO$_2$–TiO$_2$, and TiO$_2$. A higher photocatalytic activity in the oxidation of 1-octene on PANI-SnO$_2$–TiO$_2$ than SnO$_2$–TiO$_2$, PANI-TiO$_2$, and TiO$_2$ can be considered as an evidence of enhanced charge separation of PANI-SnO$_2$–TiO$_2$ photocatalyst as confirmed by photoluminescence spectroscopy. It suggests that photoinjected 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]:

$$\text{TiO}_2 \xrightarrow{\hbox{hv}} \text{e}^- + h^+ \text{TiO}_2.$$  (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 SnO$_2$–TiO$_2$ system [5, 6]. Here, SnO$_2$–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 SnO$_2$–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 a 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, washed 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 of stannous chloride was added to 10 ml of 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 GPESS 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 λ = 333 nm.

2.3. Photocatalytic oxidation of 1-octene

Photocatalytic reactions were carried out in Pyrex glass tubes (φ = 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 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 co-injecting 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 bond. 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
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 TiO\(_2\)-PANI and PANI-SnO\(_2\)–TiO\(_2\) samples thereby endorsing the presence of PANI in the TiO\(_2\)-PANI and PANI-SnO\(_2\)–TiO\(_2\). However, the others low-intense PANI’s peaks were not observed in PANI-TiO\(_2\) and PANI-SnO\(_2\)–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 SnO\(_2\)–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 SnO\(_2\)–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 PANI-SnO\(_2\)–TiO\(_2\) samples show two characteristic absorptions peaks at 428 and 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 PANI-SnO\(_2\)–TiO\(_2\). The electrical conductivity of TiO\(_2\) and SnO\(_2\)–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 PANI-SnO\(_2\)–TiO\(_2\). However, the electrical conductivity of PANI-SnO\(_2\)–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) SnO$_2$−TiO$_2$, and (c) PANI−SnO$_2$−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 PANI−SnO$_2$−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 PANI−SnO$_2$−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$_2$, SnO$_2$−TiO$_2$, and PANI−SnO$_2$−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 SnO$_2$−TiO$_2$. SEM photographs of SnO$_2$−TiO$_2$ (see Figure 5(b)) and PANI−SnO$_2$−TiO$_2$ (see Figure 5(c)) shows that the amount of particles sticking on the surface of PANI−SnO$_2$−TiO$_2$ is higher than those of SnO$_2$−TiO$_2$ confirming the existence of PANI in PANI−SnO$_2$−TiO$_2$. However, SnO$_2$ and PANI particles are very difficult to distinguish in PANI−SnO$_2$−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 SnO$_2$−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 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: PANI−SnO$_2$−TiO$_2$ > SnO$_2$−TiO$_2$ > PANI−TiO$_2$ > TiO$_2$. The most active photocatalyst, PANI−SnO$_2$−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, immigation, 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
the pure TiO\(_2\) and SnO\(_2\) occurred at 385 nm, while the maximal emission for the PANI-SnO\(_2\)–TiO\(_2\) appeared at 80 nm. One suggests that the interaction between the conjugated polymer chains and the surface of the TiO\(_2\) particles played a key role in the resulting blue shift [15]. Compared with the spectrum of TiO\(_2\), it is found that the intensity of the PL spectra of the PANI-SnO\(_2\)–TiO\(_2\) and SnO\(_2\)–TiO\(_2\) in the same range of wavelength are much lower than that of pure TiO\(_2\). This indicates the decrease of the radiative recombination process in these samples. The intensity of the PL spectra in decreasing order as the following: TiO\(_2\) > SnO\(_2\)–TiO\(_2\) > PANI-SnO\(_2\)–TiO\(_2\) (see Figure 7). On the basis of these results, a model of the mechanism of photocatalytic epoxidation of 1-octene using PANI-SnO\(_2\)–TiO\(_2\) system is proposed (see Figure 8). By attaching SnO\(_2\) and PANI on the surface of TiO\(_2\), it is possible to drive the photogenerated electrons farther away from the TiO\(_2\), thereby achieving more efficient charge separation in these semiconductor particles. As a result, a more active photocatalyst is obtained.

![Figure 7: Photoluminescence (PL) spectra of photocatalysts.](Image)

![Figure 8: The proposed mechanism of photocatalytic epoxidation of 1-octene over PANI-SnO\(_2\)–TiO\(_2\).](Diagram)

## 4. CONCLUSION

An enhancement of the photocatalytic activity of the SnO\(_2\)–TiO\(_2\) 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-SnO\(_2\)–TiO\(_2\) then PANI-TiO\(_2\), SnO\(_2\)–TiO\(_2\), and TiO\(_2\) can be considered as an evidence of enhanced charge separation of PANI-SnO\(_2\)–TiO\(_2\) photocatalyst as confirmed by photoluminescence spectroscopy. It suggests that photoinjected 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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