CHAPTER 6

ENHANCING PHOTOOXIDATION OF Ag_2S SENSITIZER ON GRAPHENE–TiO_2 COMPOSITE FILMS FOR FORMALDEHYDE REMOVAL

6.1 Introduction

TiO_2 photocatalysts coupled with narrow band width semiconductors such as CdS (2.4 eV), CdSe (1.7 eV), $InVO_4$ (2.0 eV) and Bi_2S_3 (1.3 eV) have been synthesized (Bessekhouad et al., 2004; Ho and Yu, 2006; Min et al., 2012; Zyoud et al., 2010). Ag_2S is a good candidate sensitizer to enhance the photoexcitation of TiO_2 in the visible light region because it has a narrow semiconductor band gap around 1.0 eV (Nevesa et al., 2009). However, there are few reports on the preparation of Ag_2S–TiO_2. Ag_2S–coupled TiO_2 nanoparticles have been prepared using peroxo titanic acid (PTA) solution and the reaction between silver acetate (AgAc) and thiourea for TiO_2 and Ag_2S synthesis, respectively (Xie et al., 2010). Silver nitrated ($AgNO_3$) and sodium sulfide pentahydrate ($Na_2S{\cdot}5H_2O$) have been used as starting materials for Ag_2S and porous Ag_2S–TiO_2 synthesis (Zhu et al., 2012b).

Recently, a co–adsorbent of TiO_2 photocatalysts using graphene, has been intensively studied to enhance the photocatalytic activity of TiO_2. Graphene, which is a two–dimensional structure of sp^2 carbon atoms, shows outstanding properties such as high surface area (theoretical surface about 2600 m^2g^{-1}) (Zhang et al., 2010b), good thermal stability and conductivity. The results of photocatalytic experiments have shown that graphene–TiO_2 (GR–TiO_2) photocatalysts exhibit higher photocatalytic activity than pure TiO_2 (Zhang et al., 2010a). The effects of graphene on TiO_2 photocatalysts are described as follows: reduced band gap of TiO_2 by the formation of Ti–O–C bonds, increased adsorption capacity and efficient charge separation (Low and Boonamnuayvitaya, 2013b; Wang and Zhang, 2011).

In this work, a facilitated method for graphene/Ag_2S–TiO_2 (GR/Ag_2S–TiO_2) photocatalyst preparation at a relatively low temperature was proposed. The obtained Ag_2S–TiO_2 was mixed with graphene oxide. The graphene oxide/Ag_2S–TiO_2 composite was further converted to GR/Ag_2–TiO_2 via UV–assisted photocatalytic reduction (Williams et al., 2008). The GR/Ag_2S–TiO_2 sol was coated on a glass substrate for formaldehyde (HCHO) removal. The efficiencies of HCHO degradation were investigated in the presence of GR/Ag_2S–TiO_2 photocatalyst films under UV and visible light irradiation.

6.2 Results and discussion

6.2.1 Characterization

Figure 6.1 shows the XRD diffraction patterns of the as–prepared Ag_2S, TiO_2, GR–TiO_2, Ag_2S–TiO_2 and GR/Ag_2S–TiO_2 photocatalysts. The Ag_2S sensitizer showed XRD peaks at 28.9°, 31.5°, 33.6°, 34.4°, 36.8°, 40.7° and 43.4°corresponding to acanthite Ag_2S phase (JCPDS 14–0072), as shown in Figure 6.1 (a). The average crystal size of Ag_2S sensitizer calculated by Scherrer's equation is about 8.3 nm. This result confirms that Ag_2S was successfully synthesized by the chemical reaction between silver acetate and thiourea solution. In Figure 6.1 (b), the XRD peaks of TiO_2 at 25.3°, 37.9°, 48.1°, 54.5° and 62.8° were indexed to the anatase phase (JCPDS 21–1272) with an average crystal size of 15.0 nm. In the case of Ag_2S–TiO_2 and GR/Ag_2S–TiO_2, the diffraction peaks of the Ag_2S sensitizer including TiO_2 were clearly observed. The experimental results verify that the GR/Ag_2S–TiO_2 photocatalyst was successfully synthesized.

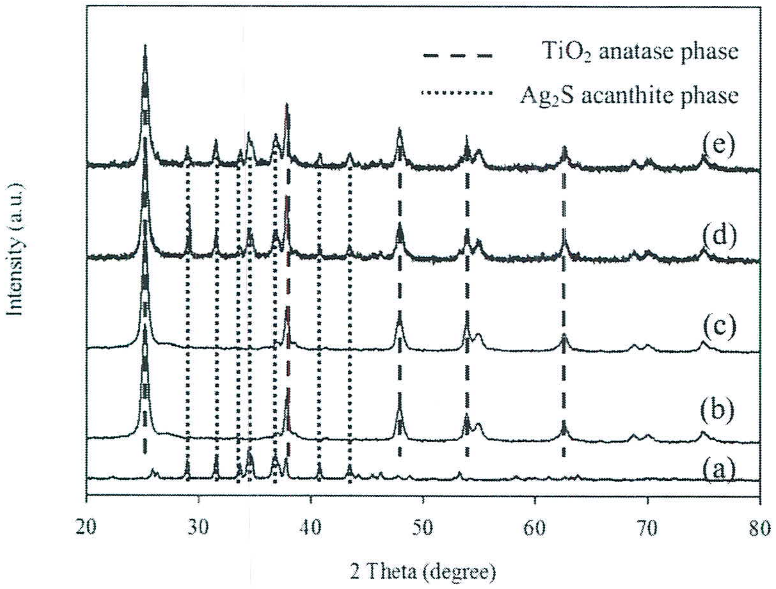

Figure 6.1 XRD diffraction patterns of prepared catalysts (a) Ag_2S sensitizer, (b) TiO_2, (c) GR–TiO_2, (d) Ag_2S–TiO_2 and (e) GR/Ag_2S–TiO_2 photocatalysts.

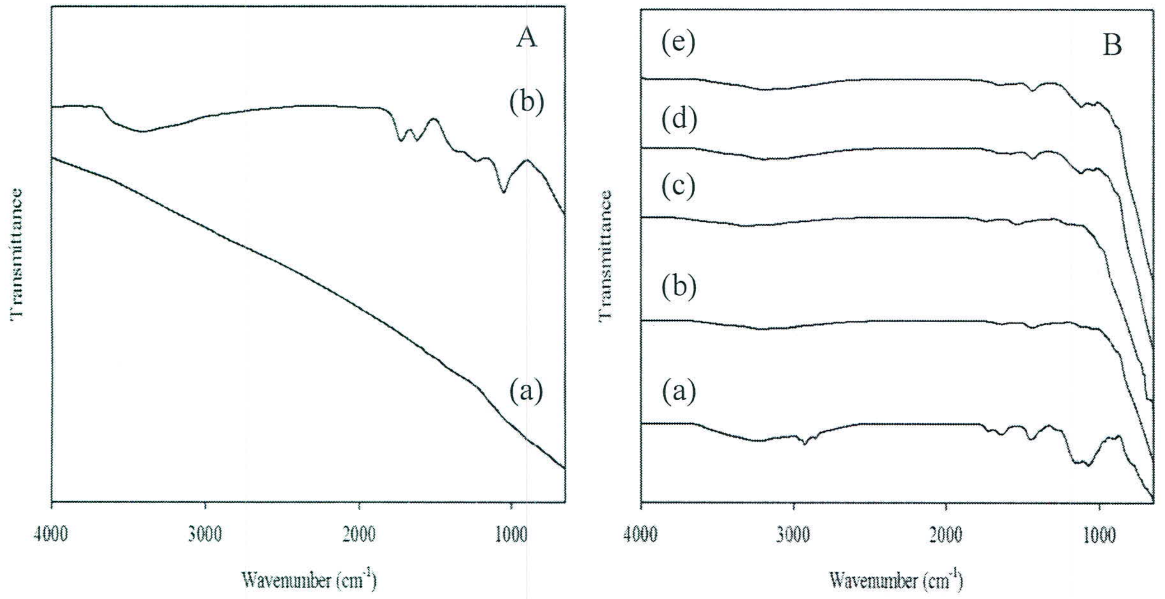

Figure 6.2 FTIR spectra of A(a) graphite, A(b) graphene oxide, B(a) Ag_2S, B(b) TiO_2, B(c) GR–TiO_2, B(d) Ag_2S–TiO_2 and B(e) GR/Ag_2S–TiO_2.

Figure 6.2 (A) shows the FTIR spectra of graphite (a) and graphene oxide (b). It is obvious that Hummer's method is an effective method for graphene oxide preparation. The signal of organic function groups can be observed at 3000, 1700, 1226, 1071 and 1390 cm^{-1} corresponding to O–H, C–O (epoxy), C=O, C–O (alkoxy) and O=C–O groups, respectively. Figure 6.2 (B) demonstrates the FTIR spectra of Ag_2S, TiO_2, GR–TiO_2, Ag_2S–TiO_2 and GR/Ag_2S–TiO_2. The broad peaks at 3000–3600 and 1665 cm^{-1} found in all samples can be assigned to the vibration of OH groups in adsorbed water. In the case of the TiO_2 composite, the signal of OH groups was also considered to indicate the formation of Ti–OH. The Ag_2S sensitizer shows many organic functional groups. The peak at around 3260 and 1440 cm^{-1} can be assigned as to carboxylic groups. The peak of $-CH_3$ group was also observed around 2950 cm^{-1}. The formation of Ag_2S is presented as follows (Xie et al., 2010):

$$2CH_2COOAg + (NH_2)_2CS + 2H_2O \longrightarrow Ag_2S + 2NH_3 + CO_2 + 2CH_3COOH \tag{6.1}$$

Therefore, it was noted that the peaks of O=C–O and $-CH_3$ are from a carboxylic acid which is a by-product of Ag_2S preparation. In addition, the strong peaks at 1390–1260 and 1150–910 cm^{-1} can be assigned as residual thiourea. Generally, excessive thiourea added to synthesize the Ag_2S sensitizer can be degraded to sulfur dioxide (H_2S) by heating, as shown in Equation 6.2 (Xie et al., 2010).

$$(NH_2)_2CS + 2H_2O \longrightarrow 2NH_3 + H_2S + CO_2 \tag{6.2}$$

In the case of GR/Ag_2S–TiO_2 and GR–TiO_2, the signals of C–O (epoxy), C=O, C–O (alkoxy) and O=C–O groups on the graphene oxide disappear after UV-assisted photocatalytic reduction of graphene oxide. This result indicates that UV-assisted photocatalytic reduction of graphene oxide is an effective method to convert graphene oxide to graphene.

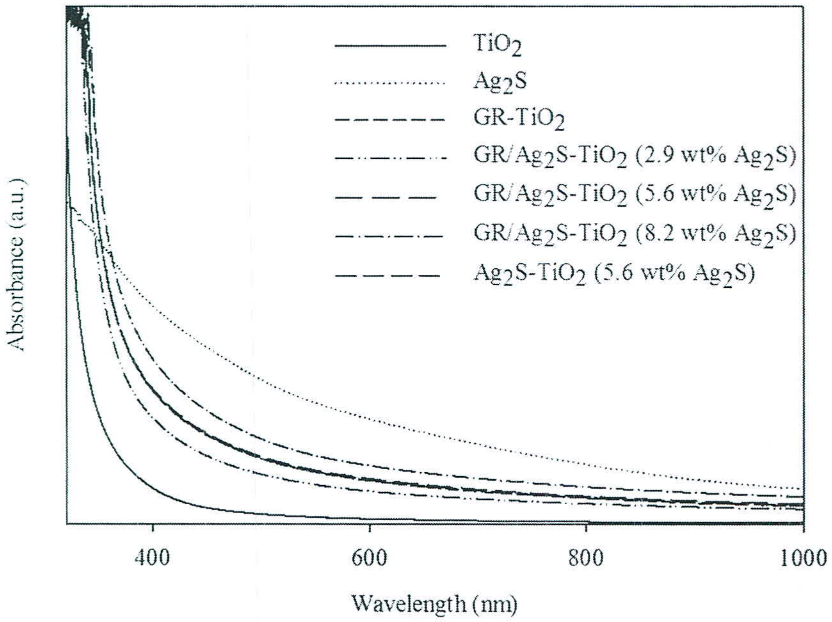

Figure 6.3 UV-vis adsorption spectra of prepared photocatalysts.

Figure 6.3 shows the UV-vis absorption spectra of the as-prepared photocatalysts. The Ag_2S sensitizer exhibited strong absorption properties in the visible light region because of its low band gap energy. GR–TiO_2, Ag_2S–TiO_2 and GR/Ag_2S–TiO_2 showed more UV-vis absorption in comparison with that of TiO_2. In addition, the absorption property of GR/Ag_2S–TiO_2 increased with increasing Ag_2S content in GR–TiO_2. The band gap energy of catalysts can be estimated by the Kubelka–Munk function (Zhang et al., 2010b).

Table 6.1 indicates that the band gap energy of TiO_2 decreased by adding graphene and Ag_2S sensitizer. In our previous report, the decrease in the band gap energy of GR–TiO_2 was attributed to the formation of Ti–O–C bonds (Low and Boonamnuayvitaya, 2013b). Furthermore, in this work, it was noted that the reduced band gap of Ag_2S–TiO_2 was the primary result of greater absorption by the Ag_2S sensitizer. The extendable photoresponse under visible light irradiation was attributed to the photoexcitation of Ag_2S. Therefore, the reduced band gap of the GR/Ag_2S–TiO_2 photocatalyst is the effect of the formation of Ti–O–C bonds (graphene) and the excellent visible light absorption of the Ag_2S sensitizer.

Table 6.1 Estimated band gap energy of photocatalysts.

Sample	Estimated band gap energy* (eV)
TiO_2	3.31
Ag_2S	1.35
GR–TiO_2 (1:50)	3.17
GR/Ag_2S–TiO_2 (2.9 wt% Ag_2S)	3.05
GR/Ag_2S–TiO_2 (5.6 wt% Ag_2S)	3.15
GR/Ag_2S–TiO_2 (8.2 wt% Ag_2S)	3.17
Ag_2S–TiO_2 (5.6 wt% Ag_2S)	3.16

* Estimated band gap energy of the catalyst was calculated using the Kubelka–Munk function.

6.2.2 Photocatalytic activity

Figure 6.4 shows the photocatalytic degradation of HCHO in the presence of the catalysts. Under UV and visible light irradiation GR/Ag_2S–TiO_2, GR–TiO_2 and Ag_2S–TiO_2 showed larger photocatalytic activities than those of pure TiO_2 and Ag_2S.

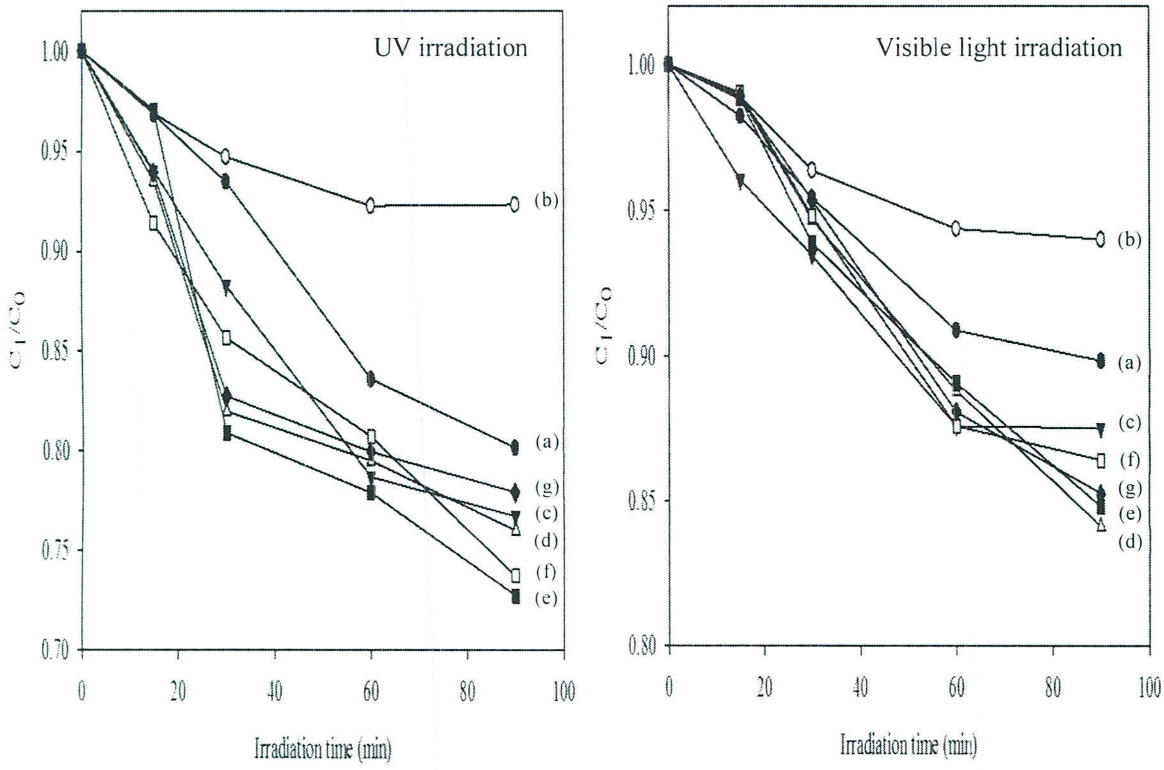

Figure 6.4 Photocatalytic degradation of HCHO in the presence of (a) TiO_2, (b) Ag_2S, (c) GR–TiO_2, (d) GR/Ag_2S–TiO_2 (2.9 wt% Ag_2S), (e) GR/Ag_2S–TiO_2 (5.6 wt% Ag_2S), (f) GR/Ag_2S–TiO_2 (8.2 wt% Ag_2S) and (g) Ag_2S–TiO_2 (5.6 wt% Ag_2S).

Furthermore, the GR/Ag_2S–TiO_2 photocatalyst series exhibited better photocatalytic degradation of HCHO in comparison with those of GR–TiO_2 and Ag_2S–TiO_2. The increase in photocatalytic activity could be attributed to the synergistic effects of graphene and Ag_2S. The order of HCHO degradation efficiency under visible light irradiation was as follows: GR/Ag_2S–TiO_2 (5.6 wt% Ag_2S) > GR/Ag_2S–TiO_2 (2.9 wt% Ag_2S) ≈ GR/Ag_2S–TiO_2 (8.2 wt% Ag_2S) > Ag_2S–TiO_2 (5.6 wt% Ag_2S) > GR–TiO_2 > TiO_2 > Ag_2S. In addition, the excessive Ag_2S added to GR–TiO_2 led to a decrease in photocatalytic activity of GR/Ag_2S–TiO_2 owing to light obstruction of Ag_2S.

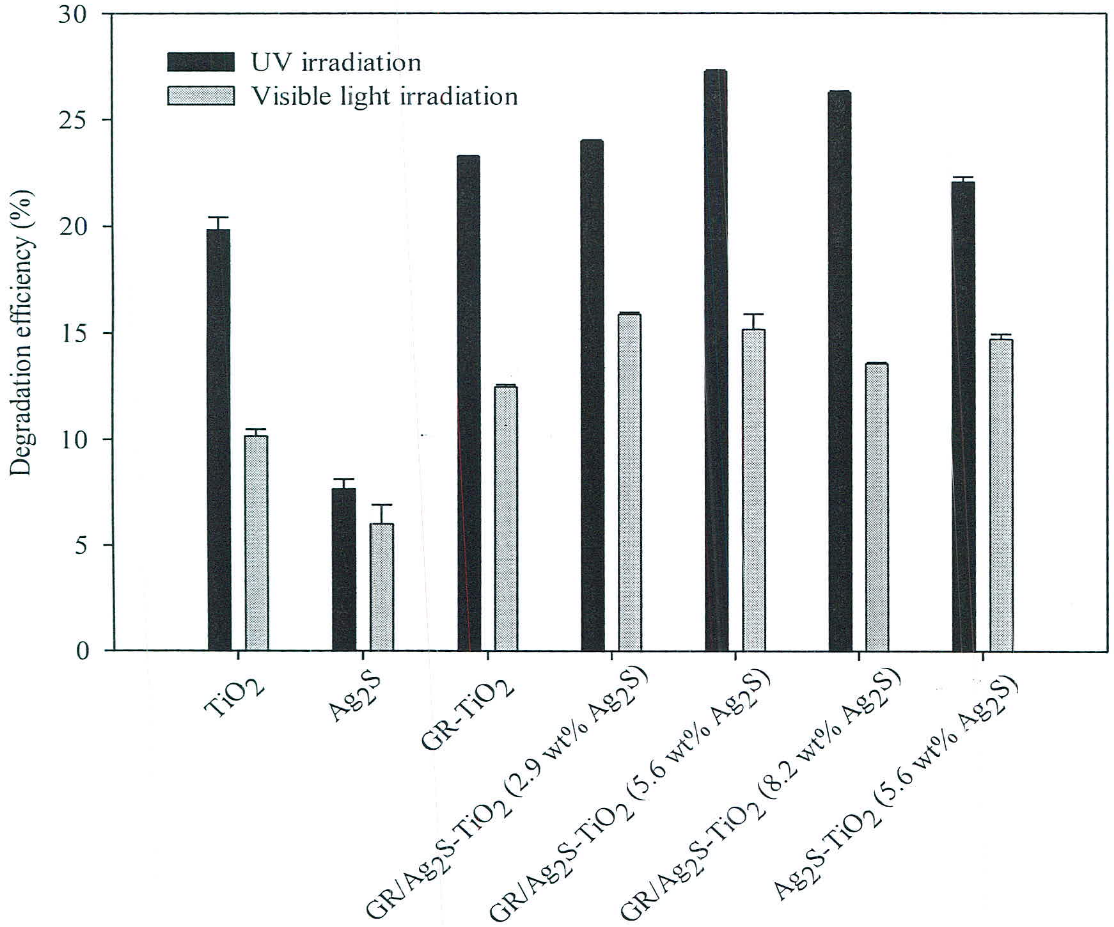

Figure 6.5 Degradation of HCHO in the presence of catalysts under UV and visible light irradiation.

GR/Ag_2S–TiO_2 composites show larger degradation efficiencies in comparison with that of GR–TiO_2, Ag_2S–TiO_2, TiO_2 and Ag_2S as shown in Figure 6.5. From Figure 6.5, it can be concluded that the optimal amount of Ag_2S added to GR–TiO_2 is in the range of 2.9–5.6 wt% Ag_2S. In order to understand the enhanced photocatalytic activity of graphene and/or the Ag_2S sensitizer on TiO_2 photocatalysts, the mechanism of TiO_2, graphene and/or Ag_2S sensitizer interactions are discussed below. The photoexcitation and photodegradation mechanism of TiO_2 photocatalyst for HCHO removal is generally written as shown in Equation (6.3)–(6.8) (Ao et al., 2004 and Kaewtip et al., 2012a).

$$\mathrm{TiO_2 + hv \longrightarrow TiO_2\ (h^+) + TiO_2\ (e^-)} \tag{6.3}$$

$$\mathrm{O_2 + e^- \longrightarrow {}^{\bullet}O_2^-} \tag{6.4}$$

$$\mathrm{2O_2^- + 2H_2O \longrightarrow 2H_2O_2 + O_2} \tag{6.5}$$

$$\mathrm{H_2O_2 + e^- \longrightarrow {}^{\bullet}OH + OH^-} \tag{6.6}$$

$$\mathrm{h^+ + Ti{-}OH^- \longrightarrow Ti{-}{}^{\bullet}OH} \tag{6.7}$$

$$\mathrm{{}^{\bullet}OH\ or\ {}^{\bullet}O_2^- + HCHO \longrightarrow CO_2 + H_2O} \tag{6.8}$$

The electron in the valence band (VB) of the TiO_2 photocatalyst can be excited to the conduction band (CB) by a photoexcitation process, leading to the generation of electron–hole pairs. Oxygen molecules, including adsorbed water molecules, on the surface of TiO_2 further react with electron–hole pairs, resulting in highly active oxidizing agents such as hydroxyl ($^{\bullet}OH$) and superoxide ($^{\bullet}O_2^-$) radicals. The photoexcitation process of Ag_2S is also reported to have the same mechanism as that of TiO_2 as shown in Equations (6.9)–(6.10).

$$\mathrm{Ag_2S + hv \longrightarrow Ag_2S\ (h^+) + Ag_2S\ (e^-)} \tag{6.9}$$

$$\mathrm{Ag_2S\ (h^+) + H_2O \longrightarrow Ag_2S + OH^{\bullet} + H^+} \tag{6.10}$$

Therefore, the decrease in the HCHO concentration in the presence of Ag_2S could be attributed to the reaction between OH radicals and HCHO. The excited electron from the valence band of Ag_2S not only reacts with adsorbed water molecules, but also migrates to the conduction band of the TiO_2 photocatalyst, as shown in Equation (6.11).

$$\mathrm{Ag_2S\ (h^+, e^-){-}TiO_2 \longrightarrow Ag_2S\ (h^+){-}TiO_2\ (e^-)} \tag{6.11}$$

The migration of an excited electron from the conduction band of Ag_2S to the conduction band of TiO_2 leads to an increase in the production of oxidizing agents and the prevention of charge recombination. Thus, the additional photoexcitation and photooxidation processes of Ag_2S the Ag_2S–TiO_2 photocatalyst system was considered as a major role for enhancing the photocatalytic activity of TiO_2. The photoexcitation mechanism of the Ag_2S–TiO_2 system is shown in Figure 6.6 (a).

Based on the previous work, the effect of graphene on TiO_2 photocatalysts is attributed to the reduced band gap energy of TiO_2, the prevention of charge recombination and the modified adsorption properties. A reduction in the band gap energy of TiO_2 by adding graphene can be observed from the estimated band gap energy, as shown in Table 6.1. This phenomenon is usually referred to as the formation of Ti–O–C bonds. The photocurrent generation of TiO_2 under UV and visible light irradiation is about 2.90 and 2.30 $\mu A\ cm^{-2}$. For GR–TiO_2, the photocurrent generation under UV and visible light irradiation is about 4.33 and 2.98 $\mu A\ cm^{-2}$, respectively (Low and Boonamnuayvitaya, 2013b).

It is obvious that GR–TiO_2 performs photocurrent generation about 1.5 and 1.3 times better than that of pure TiO_2. The excited electrons from the valence band of TiO_2 can move to graphene because of the high conductivity of graphene due to its π–π conjugated system. In addition, π–π conjugated system of graphene not only improves the photocatalytic activity by preventing the charge recombination but also enhances the adsorption capability. The adsorption efficiency of TiO_2 increases from 9.1 to 11.0 $mg_{(HCHO)}\ g^{-1}$ by adding graphene (Low and Boonamnuayvitaya, 2013a). A schematic mechanism of GR–TiO_2 photoexcitation is shown in Figure 6.6 (b).

In the case of the GR/Ag_2S–TiO_2 photocatalyst, the photoexcitation and photooxidation of the HCHO removal processes were enhanced with the synergistic effect of graphene and the Ag_2S sensitizer. The reaction mechanism is proposed as shown in Figure 6.6 (c). The photocatalytic activity of GR/Ag_2S–TiO_2 is influenced by the large photoresponse of Ag_2S sensitizer owing to the low band gap energy of Ag_2S, together with the formation of $OH^{\bullet}$ (Equation (6.10)). The excited electron of Ag_2S can also move to the conduction band of TiO_2 (Equation (6.11)) and further produce $^{\bullet}OH$ and $^{\bullet}O_2^-$ radicals. The charge recombination of TiO_2 can be suppressed by the rapid electron transfer process due to the high electrical conductivity of graphene.

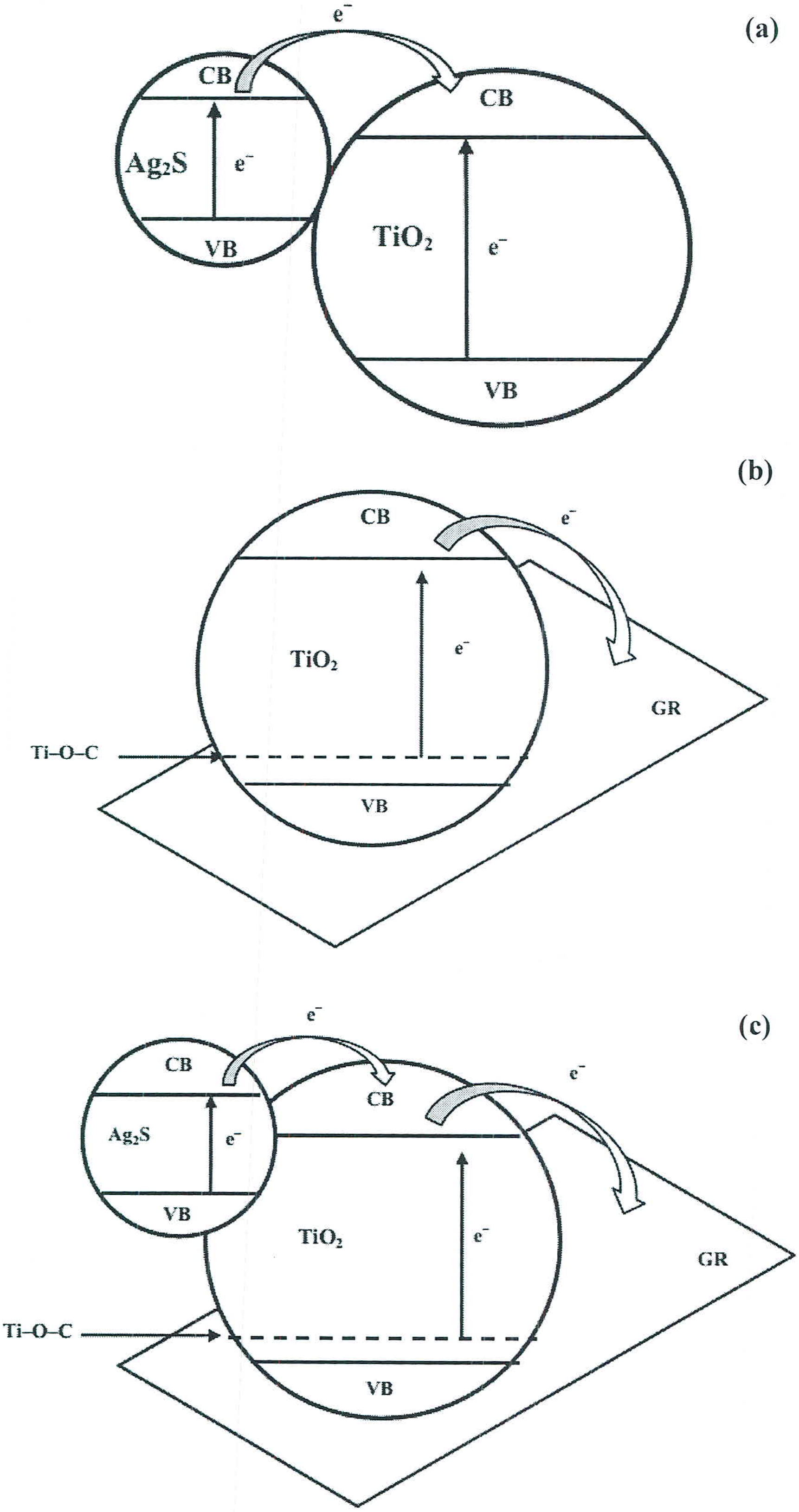

Figure 6.6 Schematic mechanism of photoexcitation of (a) Ag_2S–TiO_2, (b) GR–TiO_2 and (c) GR/Ag_2S–TiO_2 photocatalyst.

6.3 Conclusions

In this work, the preparation of Ag_2S sensitizer using the reaction of silver acetate and thiourea was successfully applied to synthesize the GR/Ag_2S–TiO_2 photocatalyst. The GR/Ag_2S–TiO_2 composite showed larger degradation efficiency in comparison with that of TiO_2, GR–TiO_2 and Ag_2S–TiO_2. The photoresponse in the visible light region was attributed to Ag_2S sensitizer and the formation of Ti–O–C bonds. The increase in the HCHO degradation efficiency in the presence of the Ag_2S sensitizer may be attributed to the formation of hydroxyl radicals from Ag_2S (h^+). The increase in the photocatalytic activity of GR/Ag_2S–TiO_2 may be attributed to the decrease in band gap energy of TiO_2, the extension of photoresponse in the visible light region and prevention of charge recombination. However, the excessive Ag_2S added to GR–TiO_2, decreases the photodegradation efficiency of GR/Ag_2S–TiO_2 owing to light obstruction. Therefore, the recommended amount of the Ag_2S sensitizer added to GR–TiO_2 is about 2.9–5.6 wt% Ag_2S in order to reach the highest photocatalytic activity under UV and visible light irradiation.