



Original Article

## Sulfur doping and its effect on TiO<sub>2</sub> photoactivity

Rungnapa Tongpool\* and Kongthip Setwong

National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency  
Thailand Science Park, Klong 1, Klong Luang, Pathum Thani, 12120, Thailand.

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### Abstract

Sulfur-doped TiO<sub>2</sub> (S-TiO<sub>2</sub>) was prepared by heat treating thiourea with three types of TiO<sub>2</sub>, including commercial P25, C02 and precipitated TiO<sub>2</sub> (pTiO<sub>2</sub>). High S content (1.7 %) in S-doped pTiO<sub>2</sub> (S-pTiO<sub>2</sub>) was achieved using relatively low amount of S precursor (S:Ti atomic ratio = 6%). Incorporation of S in TiO<sub>2</sub> structure was influenced by polarity of an individual host and sulfur solution. Water can be used to prepare S-doped P25 (S-P25) but ethanol was suitable to prepare S-doped C02 (S-C02). Hydrophilicity of TiO<sub>2</sub> and degraded solution played important role in photocatalytic activity. The doping of S either increased or decreased the photocatalytic activity of TiO<sub>2</sub>, depending on the total effects arisen after doping, including the increase of surface area, the extension of the absorption range, the decrease of hole mobility and the blocking of the active sites by the unknown coating layers on the S-doped particles. In this work, S doping improved only the photocatalytic activity of C02 under the sunlight but lessened the activity of P25 and had no effect on pTiO<sub>2</sub>.

**Keywords:** photocatalysis, S-TiO<sub>2</sub>, hydrophilic, preparation, nitrite

### 1. Introduction

TiO<sub>2</sub> has been considered as a safe, efficient and economical photocatalyst for chemical and organic degradation. Unfortunately, TiO<sub>2</sub> has wide band gap and thus it only absorbs and shows photocatalytic activity under UV light which is only 3-4% of the whole solar energy. There were attempts to improve photocatalytic activity by extending the absorption range to visible light region using metallic (Xu *et al.*, 2002, Zhang and Yu, 2005, Chang *et al.*, 2006, Ge *et al.*, 2006) and nonmetallic dopants (Burda *et al.*, 2003, Ohno *et al.*, 2004, Ho *et al.*, 2006, Katoh *et al.*, 2006, Yin *et al.*, 2006). Ohno *et al.* (Ohno *et al.*, 2004) used thiourea as a sulfur precursor which was heat treated with titanium isopropoxide. They reported that the obtained S-doped TiO<sub>2</sub> containing S cation absorbed visible light more strongly than those containing N, C and S anion. It has been reported that metal-doped materials were suffered from thermal instability and the metal sites acted as electron traps (Demeestere *et al.*,

2005). The co-doping of metal and sulfur on TiO<sub>2</sub> showed an improvement of photocatalytic activity under visible light. Fe<sup>3+</sup>, Zn<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> co-doped TiO<sub>2</sub> showed 35% increase of photoactivity toward phenol degradation under visible light (Srinivasan *et al.*, 2006). Ag, C and S co-doped TiO<sub>2</sub> degraded acetaldehyde ten times faster in visible light and 3 times faster in UV light illuminations compared to the undoped (Hamal and Klabunde, 2007). Fe<sup>3+</sup>, N and S co-doped TiO<sub>2</sub> showed higher photodegradation toward 2-propanol than the undoped, N and S-doped TiO<sub>2</sub> (Ohno *et al.*, 2006).

There was no report on the optimization of S-doping process for commercial and synthesized TiO<sub>2</sub> in terms of solvent type and concentration of S precursor. Most photocatalytic applications are outdoor, using sunlight as an energy source but no work compared the photocatalytic activity of the S-doped and the undoped TiO<sub>2</sub> under the UV light and sunlight which includes UV, visible and IR rays.

In this paper the preparation of S-TiO<sub>2</sub> was optimized to achieve high S content while necessary amount of S was used. The effects of solvent and precursor concentration in the doping process were studied. Three kinds of TiO<sub>2</sub> powder were used; P25, C02 and pTiO<sub>2</sub>. The powders are

\*Corresponding author.

Email address: [rungnapt@mtec.or.th](mailto:rungnapt@mtec.or.th)

different in crystallinity, particle size and surface area. The photocatalytic activity of the S-doped and undoped TiO<sub>2</sub> were studied via nitrite degradation under the UV and sunlight.

## 2. Experimental procedure

### 2.1 Materials preparation

The pTiO<sub>2</sub> was obtained from hydrolysis reaction of tetraisopropyl orthotitanate (Ti(OiPr)<sub>4</sub>, Fluka) and calcination at 450°C for 1 h. Two types of commercial TiO<sub>2</sub>, P25 (J.J. Degussa) and C02 (Smith supply, Thailand, no. 02), were also used. The S-pTiO<sub>2</sub> was prepared by mixing Ti(OiPr)<sub>4</sub> with 0.012 M thiourea (99%, Asia Pacific Specialty Chemicals Limited) solution in ethanol. The atomic ratios of S:Ti were 6 and 10%. The S-P25 and S-C02 were obtained from mixing the respective TiO<sub>2</sub> powder with 0.012 and 0.060 M thiourea solution, having ethanol and water as solvents. The atomic ratios of S:Ti were 6%. All the mixtures were stirred for 1 hr and then evaporated and calcined at 450°C for 1 h. The doped samples of 0.4 g were washed with 10 ml distilled water for 8 times before further used.

### 2.2 Analysis and characterization

Structural properties of the samples were obtained by an X-ray diffractometer (XRD, JEOL JDX-3530). Scanning electron microscope (JSM5410) with INCA 300 energy-dispersive spectrometer (EDS) was used to determine atomic contents of S compared to Ti in the samples. Surface area of the samples was obtained by BET surface area analysis using surface area analyzer (Micromeritics FlowSorb II 2300) and the method followed ISO 9277. Transmission electron microscopy (TEM) was carried out with transmission electron microscope (JEOL JEM 1220) with an accelerating of 200 keV.

### 2.3 Photocatalytic activity

TiO<sub>2</sub> samples were added to 0.5 ppm NaNO<sub>2</sub> aqueous solution to obtain TiO<sub>2</sub> suspension concentration of 0.001 g cm<sup>-3</sup>. Before irradiation, the suspensions were stirred for 30

min to ensure equilibration of nitrite over the TiO<sub>2</sub> samples. Then, they were exposed to the sunlight (light intensity =126,018±1386 lux, measured by Lux meter, HIOKI 3423) during the midday for 3 min and to the UV light of 365 nm (UVP Inc., UVLS 26 EL, 6 Watt) for 30 min in the distance of 25 cm from the UV lamp. The suspensions were stirred during the irradiation. Then, the suspensions were centrifuged and the clear solutions were analyzed by standard N-(1-naphthyl) ethylene diamine hydrochloride colorimetric method. Absorbance of the solution was measured using UV-Visible spectrometer (JASCO V-530) at 540 nm. Nitrite was degraded to nitrate after irradiation (Navio *et al.*, 1998) and its degradation was determined according to equation (1);

$$n = (c_0 - c) / c_0 * 100 \quad (1)$$

where  $n$  is % degradation,  $c_0$  and  $c$  are the concentrations of nitrite solutions before and after irradiation, respectively.

### 2.4 Nitrite adsorption on TiO<sub>2</sub> samples

TiO<sub>2</sub> samples were added to 0.5 ppm NaNO<sub>2</sub> aqueous solution to obtain TiO<sub>2</sub> suspension concentration of 0.001 g cm<sup>-3</sup>. The suspensions were stirred for 30 min and then centrifuged to obtain the clear solutions. Then nitrite concentrations in the obtained solutions were analyzed as 2.3 and compared with that in the nitrite solution stirred without TiO<sub>2</sub> samples.

### 2.5 UV-vis spectral response of TiO<sub>2</sub> and S-TiO<sub>2</sub>

TiO<sub>2</sub> samples were added to 0.5 ppm NaNO<sub>2</sub> aqueous solution to obtain TiO<sub>2</sub> suspension concentration of 0.001 g cm<sup>-3</sup>. The suspensions were stirred for 30 min and then the UV-Vis absorbance of the suspensions was studied using UV-Visible spectrometer (JASCO V-530) and 0.5 ppm NaNO<sub>2</sub> solution as a blank.

## 3. Results and Discussion

### 3.1 Materials characterisation

The S atomic contents (compared to Ti) in the doped

Table 1. Sulfur contents in the doped samples after washing.

Sample	S:Ti ratio (%)	Thiourea concentration (M)	Solvent of thiourea	S content (%) after washing
S-pTiO <sub>2</sub>	6	0.012	ethanol	1.67± 0.42 1.52± 0.25
	10	0.012	ethanol	
S-P25	6	0.012	ethanol	0.42± 0.19 0.49± 0.10 0.43 ±0.11
	6	0.060	ethanol	
	6	0.060	water	
S-C02	6	0.060	ethanol	0.46 ±0.12 0.09± 0.04
	6	0.060	water	

samples, prepared by various conditions, were shown in Table 1. They are the average of three values of measurement. The S contents in the S-pTiO<sub>2</sub> were found to be 1.7 and 1.5% for the S:Ti ratios of 6 and 10%, respectively. This indicates the limit of S incorporation in pTiO<sub>2</sub> structure by this doping method to be 1.7%. Ohno (Ohno *et al.*, 2004) and Tachikawa groups (Tachikawa *et al.*, 2004) used relatively high S:Ti ratio of 4:1 (400%) and thiourea concentration of 1.4 M to obtain the same S content. The surface area of S-pTiO<sub>2</sub> prepared by our group was 157 m<sup>2</sup> g<sup>-1</sup>, twice as much as those reported by Tachikawa *et al.* which was 76 m<sup>2</sup> g<sup>-1</sup>. The S-pTiO<sub>2</sub> prepared by S:Ti ratio of 6% was further studied.

In the preparation of S-P25, the S:Ti ratio of 6% gave the S contents of 0.4-0.5% for both thiourea concentrations (0.012 and 0.060 M) and for both solvents (water and ethanol). Thus water was used for S-P25 preparation for economical and environmental reasons. The S-C02 prepared by ethanol showed the same S content (0.5%) as S-P25 but those prepared by water showed very low S content (0.1%). Therefore S-C02 was prepared using ethanol as thiourea solvent.

The S-pTiO<sub>2</sub> showed the S content 3-4 times higher than S-P25 and S-C02. This is because the precursors of the former (Ti(OiPr)<sub>4</sub> and thiourea) were mixed in a molecular level while the precursors of the latter two (P25, C02 and thiourea) were in the form of relatively big particles and agglomerates and thus the dopant cannot easily be incorporated.

It can be seen from Figure 1 that the C02 powder was not wet by water as much as by ethanol. The contact angle between the water drop and C02 powder was wide while there was no contact angle between the ethanol drop and C02 powder as ethanol was totally absorbed. As a result, the reaction between C02 and thiourea aqueous solution was more difficult than that in ethanol solution. The contact angle of the water drop on P25 was smaller than that on C02 and the surface area of the former was much higher than the latter (Table 2). Therefore the S incorporation with P25 was easier than that with C02. The C02, P25 and pTiO<sub>2</sub> powders were wet by ethanol but hardly wet by water, implying that the TiO<sub>2</sub> samples have polarity closer to ethanol than to water.

It was shown in Table 2 that S-pTiO<sub>2</sub> has smaller particle size and larger surface area than pTiO<sub>2</sub>. This is prob-

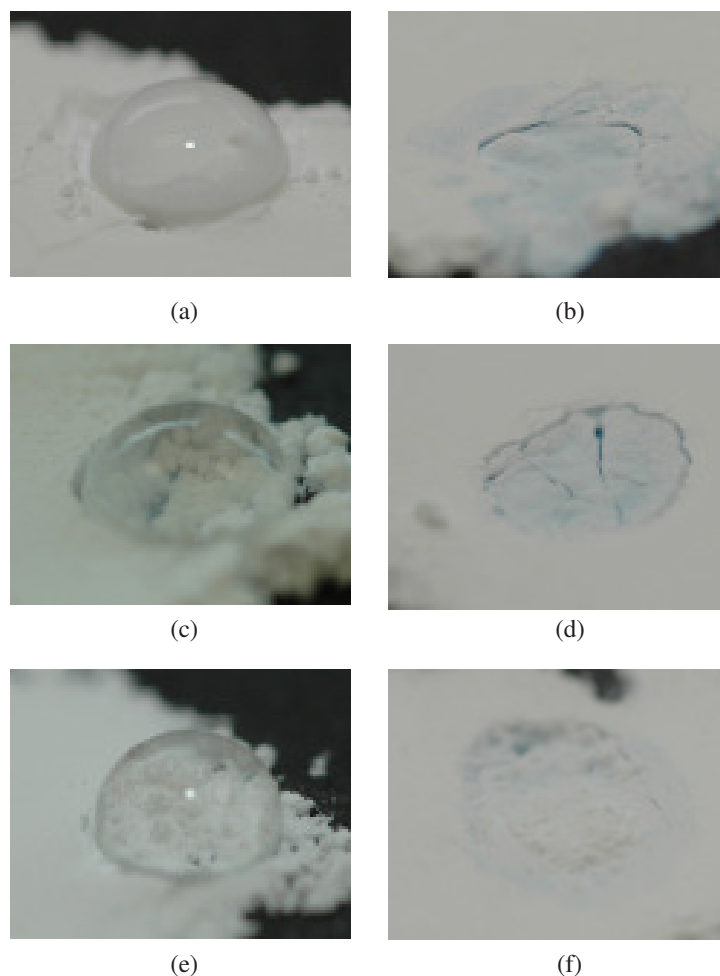


Figure 1. Drops of (a) water on C02 powder, (b) ethanol on C02 powder (c) water on P25 powder, (d) ethanol on P25 powder (e) water on pTiO<sub>2</sub> powder and (f) ethanol on pTiO<sub>2</sub> powder.

Table 2. Particle size, surface area of the undoped and S-doped samples.

samples	size (nm)	surface area ( $\text{m}^2 \text{g}^{-1}$ )
pTiO <sub>2</sub>	11.1 ± 5.5	126.1 ± 1.1
P25	22.5 ± 6.4	54.3 ± 1.5
C02	71 ± 53.5	11.8 ± 0.4
6% S-TiO <sub>2</sub>	9.8 ± 2.3	156.8 ± 0.8
6% S-P25	23.2 ± 6.7	51.4 ± 0.8
6% S-C02	74.8 ± 20.3	18.23 ± 0.5

ably because the S ions incorporated in the TiO<sub>2</sub> lattice structure, inhibiting the grain growth. The surface area of the S-C02 and S-P25 were not much changed compared to the undoped powder but the unknown coating layers were clearly seen on their particles as shown in Figure 2. Shi *et al.* (Shi *et al.*, 2006) also found the unknown coating layer on the synthesised particles and suggested that it might be a labile layer of solvent. In this work, the S-P25 particles were prepared using water as a solvent for thiourea and it is unlikely that the unknown coating layer was water. As the layer is too thin to be characterized by high resolution TEM, we suspected that it was likely to be a carbon layer.

All the S-doped samples showed the same phases as shown in Figure 3. The pTiO<sub>2</sub> and S-pTiO<sub>2</sub> contained anatase and small amount of brookite. The P25 and S-P25 were consisted of anatase and small amount of rutile. The C02 and S-C02 were well crystalline and totally anatase.

Adsorption of nitrite solution on the photocatalyst would influence the photocatalytic activity. However we did not found the adsorption of 0.5 ppm nitrite solution on the TiO<sub>2</sub> samples.

### 3.2 Photocatalytic activity measurement

Photocatalytic activities of the samples exposed to UV and sunlight are shown in Figures 4 and 5, respectively. It can be seen that nitrite was degraded rapidly in the presence of the TiO<sub>2</sub> samples. This is because when TiO<sub>2</sub> was irradiated, photogenerated holes and electrons were produced. Hole was transferred to the particle surface and then reacted with adsorbed H<sub>2</sub>O or OH<sup>-</sup>, producing hydroxyl radical, OH which subsequently oxidized nitrite ion (Navío *et al.*, 1998 and Xu *et al.*, 2002).

The degradation under the sunlight was much faster than that under the UV as a result of high photon flux of the former. The photon flux not only produces photogenerated holes and electrons but also desorbs adsorbed O<sub>2</sub> at oxygen vacancy defect sites, creating active site for water dissociation (Thompson and Yates, 2006).

P25 showed the highest activity although the surface area was much lower than pTiO<sub>2</sub> and S-pTiO<sub>2</sub>. It can be seen from Fig. 1 that the contact angle of the water drop on P25 was smaller than that on pTiO<sub>2</sub>, indicating that the former

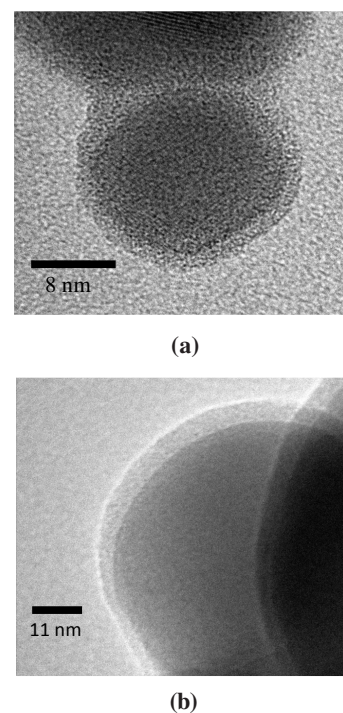


Figure 2. TEM micrographs show unknown coating layers on (a) S-P25 and (b) S-C02 particles.

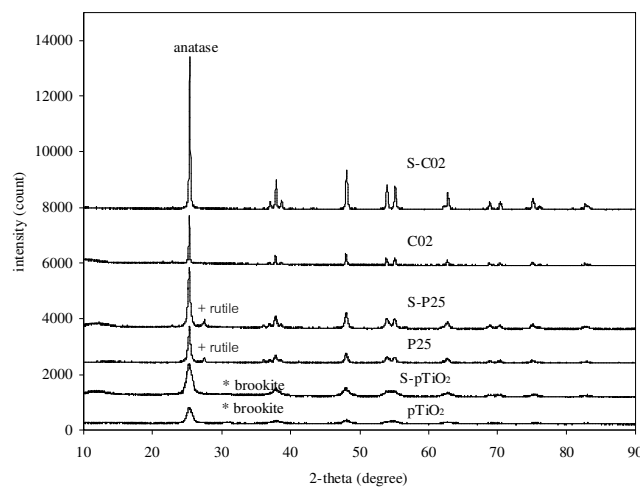


Figure 3. XRD of the doped and undoped samples.

was more hydrophilic than the latter. This might facilitate photodegradation on P25 surface. S-P25 showed lower activity than P25. This is probably because of two reasons. First the coating layer on S-P25 particles (Figure 2) blocked the active sites from interacting with nitrite ions. Second, the S-doping sites have more negative potentials than the rest. Therefore the photogenerated hole being transferred to the surface was deeply trapped at the doping sites, resulting in the decrease of hole mobility (Tachikawa *et al.*, 2004) and thus nitrite degradation.

Under the UV light, C02 showed slightly higher

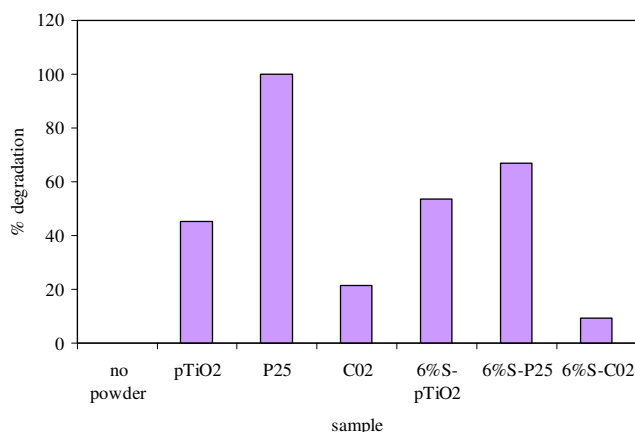


Figure 4. Degradation of nitrite solution under 30-min UV exposure.

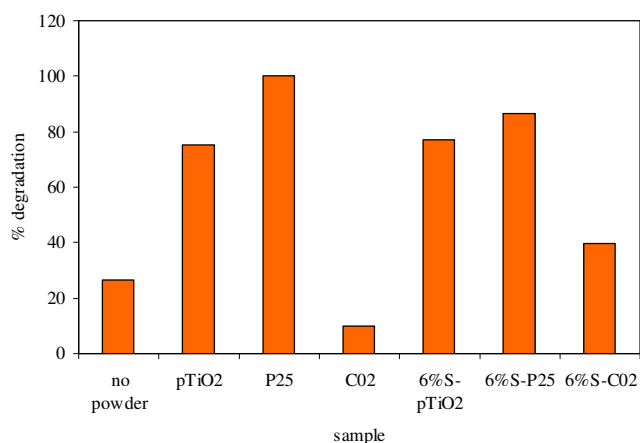


Figure 5. Degradation of nitrite solution under 3-min sunlight exposure (light intensity =  $126,018 \pm 1386$  lux).

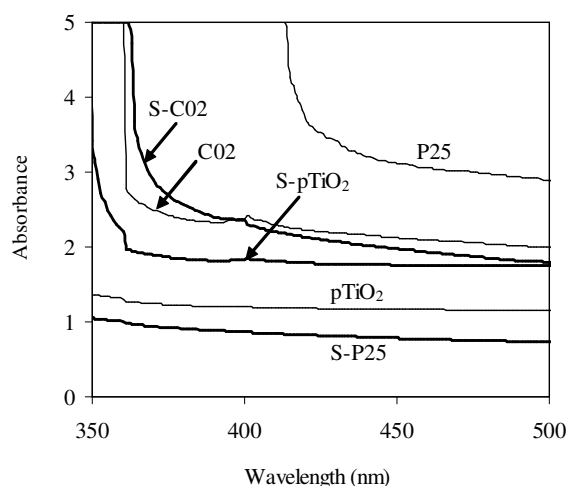


Figure 6. UV-vis absorption spectra of TiO<sub>2</sub> and S-TiO<sub>2</sub> samples.

activity than S-C02. The reasons for this were already explained as above. However, under the sunlight the C02 was less active than S-C02. We can see that under the sunlight,

nitrite degradation in the presence of C02 was lower than that without any powder and this is the results of shielding effect from C02 (Ukaji *et al.*, 2007). This shielding effect was confirmed by the fact that the activity difference between C02 and the others under the sunlight was more than that under the UV light. Since light absorption was the main problem for photocatalytic activity of C02 under the sunlight and it was found that S-C02 was more active than the undoped, it can be concluded that the absorption range of C02 was extended by S doping. Figure 6 confirms the slight red-shift in the absorption region of S-C02.

The activities of S-pTiO<sub>2</sub> and pTiO<sub>2</sub> were nearly the same although the surface area of the former was higher than the latter. This is probably because the decrease of hole mobility by S-doping sites canceled out the surface area effect.

#### 4. Conclusions

High S content in S-pTiO<sub>2</sub> was achieved using low amount of S precursor. Hydrophilicity of photocatalysts and thiourea solvents played important role in S incorporation in TiO<sub>2</sub> structure and photocatalytic activity. Water can be used to prepare S-P5 but cannot be used to prepare S-C02. Ethanol was more appropriate. The doping of S showed good and bad results on photocatalytic activity. It extended the absorption range to visible region and inhibited the grain growth, resulting in the increase of surface area. The unknown coating layer was found on the S-doped particles which might block the active sites. The holes were trapped at the S-doping sites, leading to the decrease of hole mobility. Therefore the doping of S either increased or decreased the photocatalytic activity depending on the sum of all effects in each TiO<sub>2</sub> sample. In this work, S doping improved only the photocatalytic activity of C02 under the sunlight but lessened the activity of P25 and had no effect on pTiO<sub>2</sub>.

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