



Synthesis and characterization of S-doped Degussa P25 with application in decolorization of Orange II dye as a model substrate

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ABSTRACT

The commercially available and relatively cheap TiO₂, Degussa P25, was modified and doped with sulfur (using thiourea as a source of sulfur) by simple and effective hydrolysis method at room temperature followed by calcination in the presence of air. S-doped P25 photocatalyst with different TU:P25 mass ratios of 0:1, 0.25:1, 1:1, 3:1 and 5:1 have been prepared and investigated. The photocatalytic activity of the prepared S-doped P25 was examined by photo-decolorization of azo dye Orange II under natural solar light irradiation. X-ray diffraction (XRD), UV–vis spectroscopy, X-ray photoelectron spectra (XPS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to characterize the catalyst. The results showed that the S-doped P25 catalyst at mass ratio of (1:1) and calcinated at 550 °C for 4 h exhibited the highest photocatalytic activity under solar light irradiation; the undoped-P25 photocatalytic activity increased about 23% by doping with sulfur. The XPS and UV–vis spectra results suggest that the crystal lattices of S-doped P25 powder are locally distorted by incorporating S⁶⁺ species into TiO₂ and substitutes for some of the lattice titanium (Ti⁴⁺). The XRD results showed that doped sulfur can retard the grain growth of TiO₂ to some extent. Increasing the TU:P25 ratio up to (1:1) reduced the crystalline size and increased the anatase content. Higher ratios (3:1 and 5:1) have negative effect on the photocatalytic activity of the catalysts. The calcinations temperature for S-doped P25 (1:1) have been also investigated and it was found that calcination at 550 °C is the optimum one. The commendable visible photoactivities of S-doped P25 are predominantly attributed to an improvement in anatase crystallinity, low band gap and low particle size. We suggest that Degussa P25 could be used as a Ti precursor for further improving its activity under natural solar light.

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1. Introduction

Titanium dioxide (TiO₂) is non-toxic, efficient photocatalyst, chemically stable and relatively inexpensive. Although TiO₂ is the most popular photocatalytic material, it has not been applied widely in the field of environmental pollution control under natural solar light. It is active only in the ultraviolet (UV) region because of its wide band gap energy ($E_g = 3.2$ eV) which considerably limits the utilization of natural solar light or artificial visible light. Since UV light accounts for only a fraction <10% of the sun's energy compared to visible light (45%), any shift in the optical response of TiO₂ from the UV to the visible spectral range will have a profound positive effect on the photocatalytic efficiency of the material [1]. It was found that traditional visible light responsive catalysts are unstable under illumination (such as CdS and CdSe) or have low activity (such as WO₃ and Fe₂O₃) [2]. Therefore, modification of TiO₂ to

extend its absorption edge toward the visible light region has been the subject of recent researches.

Several attempts and approaches for TiO₂ modification have already been proposed to lower the band gap energy of crystalline TiO₂, including reduction with hydrogen [3–5] and transition metal doping (using transition metals: Cr, Mn, Mo, Nb, V, Fe) [6–10]. However, reduction with hydrogen and transition metal doping produced only a small change in the TiO₂ band-gap, and the metal-doped materials suffer from thermal instability [11].

Band-gap narrowing by the introduction of non-metal anions (N, C, S, P and F) into TiO₂ was recently found to be efficient to yield catalyst with high catalytic activity under visible light irradiation [12–23]. N-doped and S-doped TiO₂ as active photocatalysts under visible light have been prepared by different methods: hydrolysis of titanium precursors (titanium tetraisopropoxide or tetrachloride) in the presence of thiourea, thioacetamide, and NH₄OH followed by calcination [12,24–26], Gas-phase thin film deposition method [27], atmospheric pressure plasma-enhanced nano-particles synthesis (APPENS) [28], treating anatase in NH₃/Ar atmosphere and sputtering the TiO₂ target in N₂/Ar gas mixture [29].

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However, all the above-mentioned approaches required either a special apparatus for synthesis or tight control of experimental conditions. Furthermore, to prepare the TiO₂ nano-particles, relatively expensive chemicals as a source of titanium are required (e.g. titanium tetraisopropoxide or tetrachloride, titanium(IV) butoxide).

The Degussa P25 have been used by many researchers as a standard reference for comparison with their modified/synthesis TiO₂, the poor activity of the P25 under solar or visible light was dominant in their results. Liu and Chen [24] showed that only 21% phenol removal can be accomplished using P25 under solar irradiation, while 100% phenol removal occurred when S-doped TiO₂ was used. Liu et al. [1] using Degussa P25 could not detect any dye decolorization under solar light. Sathish et al. [30] showed the lower activity of Degussa P25 in the visible region for methylene blue decolorization against the N-doped TiO₂ prepared by thermal decomposition of Ti–melamine complex. Modifying Degussa P25, which is relatively cheap and available commercially, to improve its solar photoactivity is an interesting subject, according to the author's knowledge; very limited attempts were found recently in the literature to improve the Degussa P25 photoactivity. Janus and Morawski [31] modified P25 under elevated pressure in organic solvent atmosphere. They found that the photocatalytic activity of the modified P25 for dye decomposition under UV light irradiation was two times higher than the unmodified P25. Bowering et al. [32] prepared silver modified Degussa P25, by drying dispersions of Degussa P25 from silver nitrite solution, for the photocatalytic removal of nitric oxide under UV illumination. However, in both cases, the photocatalyst activity was tested only under UV light. Recently Rengifo-Herrera et al. [33] prepared N, S co-doped and N-doped Degussa P25 using thiourea and urea as a source of N, C and S. However, they applied ball milling technique in preparation the doped P25 powders. Randeniya et al. [34] also prepared S-doped TiO₂ by ball milling P25 with thiourea for photoelectrochemical hydrogen generation from water.

Therefore, in this work, with the aim of developing a high efficient cost effective solar photocatalyst, the P25 Degussa was doped with sulfur using thiourea as a source of sulfur raw material and applying simple hydrolysis method. The activity was examined by photo-decolorization of azo dye Orange II in aqueous solution under natural solar light. In this study Orange II was selected as a model pollutant, which is an abundant class of synthetic, colored, organic compounds, characterized by the presence of one azo bonds (–N=N–). Based on the results of the photocatalyst characterization and its photoactivity test, the improvement of the photoactivity was also discussed.

2. Experimental

2.1. Preparation of the S-doped P25 photocatalyst

A specific amount of P25 Degussa (1 g) was doped with thiourea (TU) as a source of sulfur raw material by simple hydrolysis method at room temperature. 0.25, 1, 3 and 5 g of thiourea (TU) was used to get mass ratio of TU:P25 = 0.25:1, 1:1, 3:1, and 5:1 respectively. For comparison, the unmodified P25 (TU:P25 = 0:1) was prepared under otherwise the identical conditions, the synthesis steps are summarized in Fig. 1.

2.2. Characterization

The crystalline structure of the photocatalysts was characterized by X-ray powder diffraction (XRD) analysis (RINT Ultima III, Rigaku Co., Japan) using Cu K α radiation at a scan of 4°/min. The acceleration voltage and the applied current were 40 kV and 40 mA, respectively. The mean size of crystallite (D , nm) was calculated

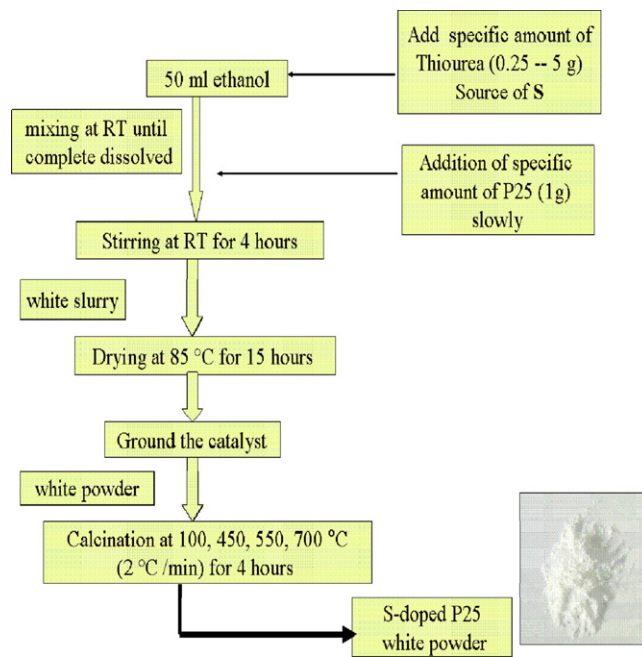


Fig. 1. Preparation of S-doped P25 Degussa photocatalyst.

from full-width at half-maxima (FWHM) of corresponding X-ray diffraction peaks using Scherrer's formula $D = 0.89\lambda / \beta \cos \phi$, where λ is the wavelength of the X-ray radiation ($\lambda = 1.54056$ nm Cu K α), β is the full-width at half-maximum (rad), ϕ is the reflect angle. The content of anatase w_A % was determined according to the following equation [12]: $w_A (\%) = \{I_A / (I_A + 1.265 I_R)\} \times 100$, where I_R and I_A are the intensities of the diffraction peaks of rutile (110) and anatase (101), respectively, obtained from XRD patterns. X-ray photoelectron spectra (XPS) of the TiO₂ powders were measured using Shimadzu ESCA 750 photoelectron spectrometer with an (Mg K α 1253.6 eV), the shift of binding energy due to relative surface charging was corrected using the C1s level at 285 eV as an internal standard. The diffuse reflectance UV–vis spectra were measured with an Ocean Optics high resolution HR4000 USB spectrometer (HR4000 Ocean Optics Inc.) with an extended wavelength range from 190 to 1100 nm. The microstructures of the photocatalyst were observed by a scanning electron microscope (JSM-5310LV, Jeol Co., Japan). Measurements of particle size and distribution were also carried out by transmission electron microscopy (TEM).

2.3. Photocatalytic activity measurement

Solar photocatalytic decolorization of Orange II dye was carried out in 300 ml Pyrex glass beaker. All the reactions were carried out according to the following procedure: 0.5 g of photocatalyst (modified or unmodified P25) was added to 250 ml of aqueous dye (Orange II) solution (10 mg/l). The dye solution was mixed with a magnetic stirrer during the course of the experiment. At the beginning the solution mixture was stirred for 30 min in the dark to ensure establishment of the dye's equilibrium adsorption. Then sun light was allowed to irradiate the reaction mixture, and at regular time intervals, samples were taken from the suspension and the change of Orange II concentration was measured using UV–Vis spectrophotometer (TU-1900 UV spectrometer) at fixed wavelength of 486 nm. For this purpose, the photocatalyst was immediately removed from the sample by filtration, using a 0.45 μ m syringe filter. Solar experiments were carried out from 9:10 a.m. to 5:30 p.m. during the autumn season in Saitama, Japan.

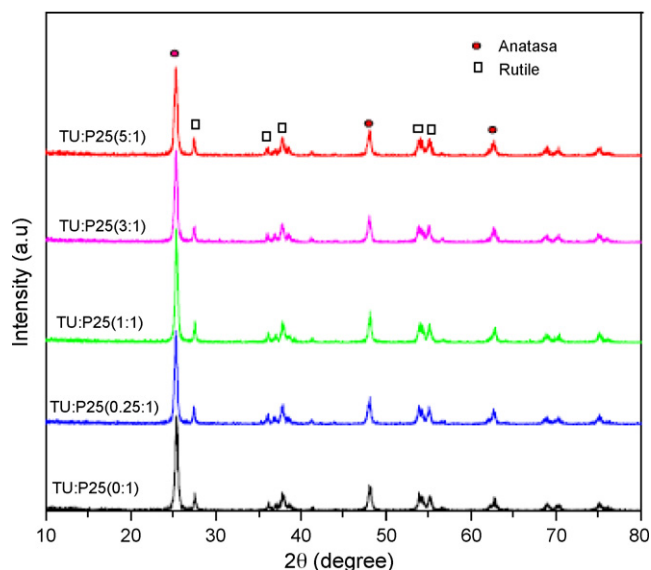


Fig. 2. XRD results for S-doped P25 at different TU:P25 ratios and 550 °C calcination temperature for 4 h.

During the solar experiments, the UV and the visible ranges (illumination) of the solar light intensity were measured by the UV radiometer (UVR-2, TOPCON, with UD-36 (310–400 nm/average 365 nm) detector, Tokyo, Japan) and Illuminance meter (T-10, Konica Minolta), respectively. The accumulated solar energy was calculated by [35]:

$$Q_n = Q_{n-1} + \Delta t I \left(\frac{A}{V} \right), \quad \Delta t = t_n - t_{n-1} \quad (1)$$

Q_n accumulated solar energy per unit of slurry volume (kJ l^{-1}), Δt is the time difference between radiation measurements (h), I is the solar light intensity per unit of irradiation surface area measured during time interval Δt (W m^{-2}), A is the irradiated surface area of the photoreactor (m^2), V is the photoreactor volume (m^3).

3. Results and discussion

3.1. XRD results

The X-ray diffractograms, Fig. 2 for the prepared S-doped P25 photocatalysts at different TU:P25 ratios (0:1, 0.25:1, 1:1, 3:1 and 5:1) showed reflections due to anatase and rutile phases of TiO_2 , and no significant shift of the characteristic peaks of anatase and rutile was observed, also no reflections due to any sulfur containing

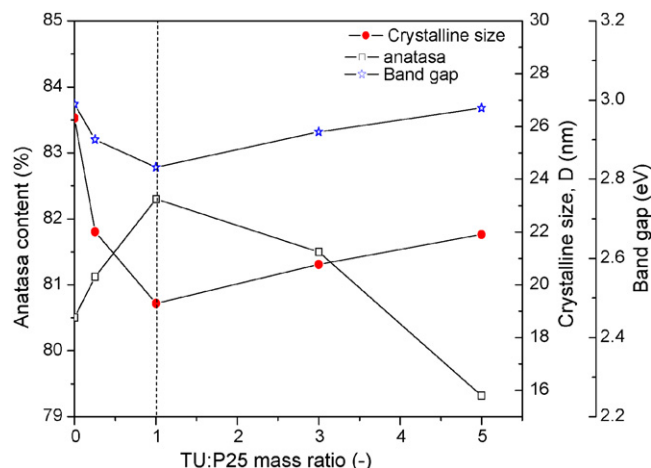


Fig. 3. Influence of the TU:P25 mass ratio on the crystalline size, anatase content and the band gap.

species were observed, this is probably due to the low concentration of such species in the sample. Liu and Chen [24] did not detect any sulfur signal in their XRD results for TU: TiO_2 mass ratio of 3:1, they used TiCl_4 as a source of TiO_2 and applied different preparation method.

It was found from XRD results (Figs. 2 and 3) that using thiourea, as a source of sulfur, slightly reduced the crystalline size and increase the anatase content. S-doped P25 (1:1) calcinated at 550 °C has an approximate crystalline size of 19.32 nm and 82.30% anatase content, while that of the non-doped (0:1) was 26.31 nm and 80.5% anatase content, which means the thiourea can retard the grain growth of TiO_2 to some extent. It has previously been observed that Degussa P25 consists of amorphous material, besides anatase and rutile [36]. It is unsurprising therefore, that an apparent transformation of the amorphous material to anatase, and thus an increase in crystallinity, were observed after calcination. Moreover, some literatures clearly pointed out that the crystallite size of Degussa P25 doped or undoped could be changed after calcination [32,37].

TEM results showing in Fig. 4 confirm the crystalline size. However, interesting results was observed at TU:P25 ratio of 5:1, where the anatase content reduced to 79.33% and the average particle size increased from 19.32 to 21.91 nm. Probably presence of sulfur with relatively high concentration in the sol during synthesis will hinder the structure-directing action by changing the ionic strength of the medium.

Fig. 5 shows XRD pattern of S-doped P25 prepared at TU:P25 of 1 and different calcinations temperatures (100, 550 and 770 °C)

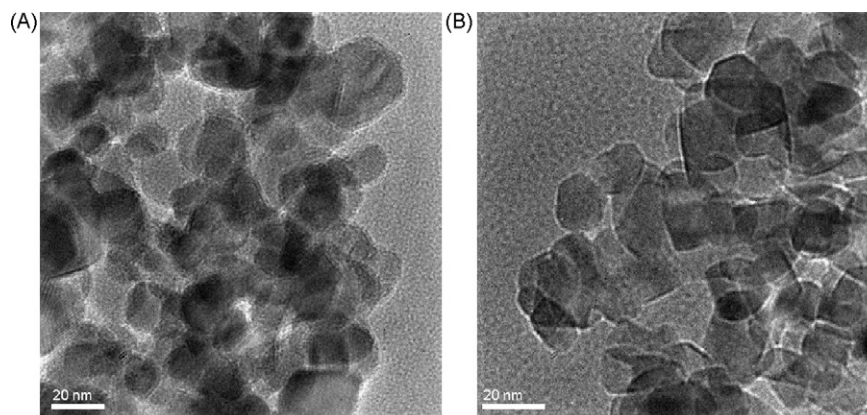


Fig. 4. TEM results for (A) S-doped P25 (1:1) and (B) undoped one (0:1).

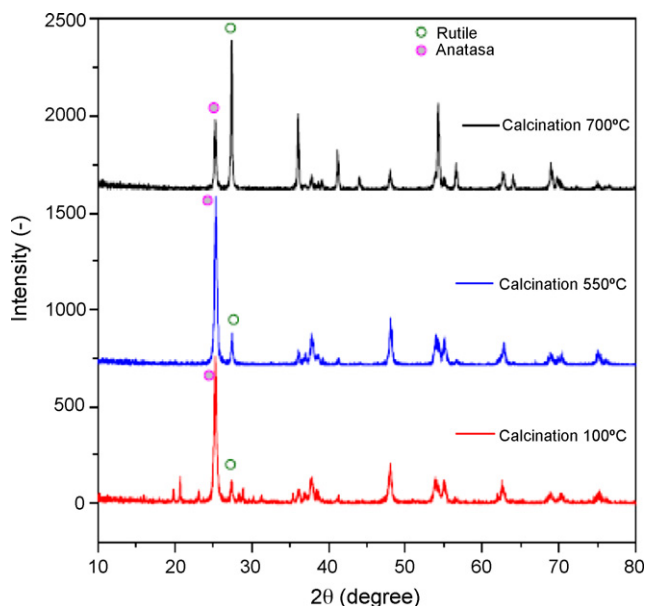


Fig. 5. XRD results for S-doped P25 (1:1) at different calcination temperatures for 4 h.

for 4 h. The patterns apparently revealed the effect of calcination temperature on the phase change of S-doped P25. It is observed that increase of calcination temperature from 100 to 550 °C, the peak intensity of anatase (1 0 1) ($2\theta = 25.3^\circ$) increases and the width of (1 0 1) plane becomes narrow, which is attributed to gradual crystallization of the anatase TiO_2 with temperature rising. The increase of calcination temperature forced condensation of free OH groups on the surface of TiO_2 particles. It increased the crystallinity and also the intensity of diffraction peaks of anatase phase [38]. It should be noted here that because of using Degussa P25 as a source of TiO_2 that has significant anatase peak intensity at (1 0 1), the anatase peak was predominant at 100 °C which is expected result.

Furthermore, observation shows that with increasing the calcination temperature (>550 °C), the peak intensity of rutile steadily becomes stronger. When S-doped P25 was calcinated at 700 °C, the pattern exhibited a major rutile TiO_2 structure indicating significant phase transformation from anatase to rutile at this temperature. An earlier study on the kinetics of the anatase–rutile transformation has shown that the transformation involves an overall contraction or shrinking of the oxygen structure and a co-operative movement of ions. The transformation needs to overcome both strain energy for the oxygen ions to reach their new configuration and the energy necessary to break the Ti–O bonds as the titanium ions redistribute [39]. High activation energy is required for this process (over 420 kJ/mol) and so the phase transition takes place only at high temperatures.

SEM photographs clearly showed that calcination the powder significantly change its microstructure. Surface morphologies of S-doped P25 (TU:P25 = 1:1) before and after calcinations at 550 °C for 4 h in the presence of air, are shown in Fig. 6. The powder before calcination composed of many large particles, in comparison to that after calcinations which looks with less agglomeration. It worth mentioned here that increasing the calcination temperature to a certain limit (550 °C) reduce the crystalline size.

3.2. XPS results

The X-ray photoelectron spectroscopy (XPS) was carried out to determine the chemical composition of the prepared photocatalyst and the valence states of various species present therein. Fig. 7 shows the S2p spectrum of S-doped P25, a strong peak around

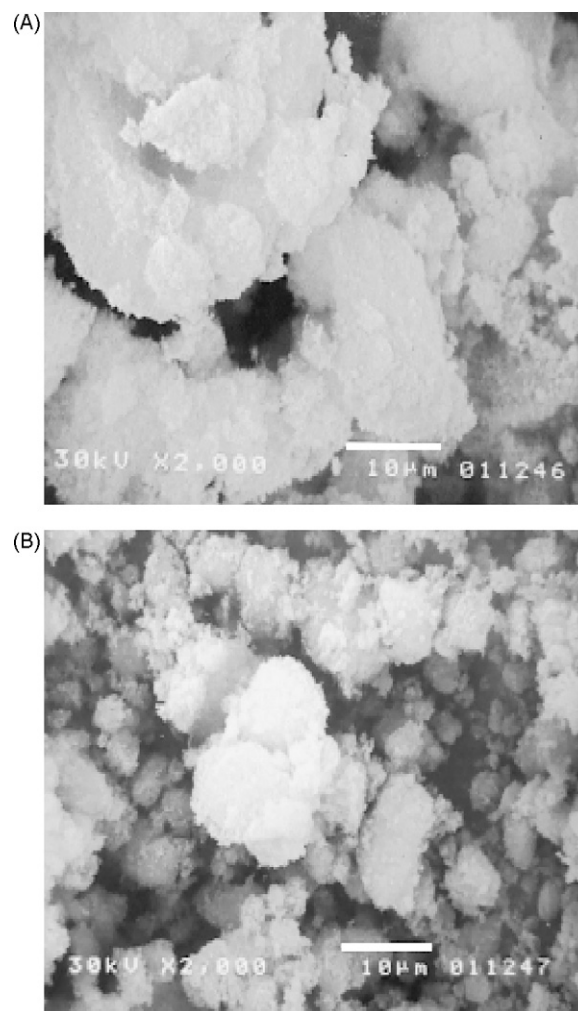


Fig. 6. SEM photographs showing the produced S-doped P25 (1:1) powder. (A) Before calcination and (B) after calcination at 550 °C for 4 h.

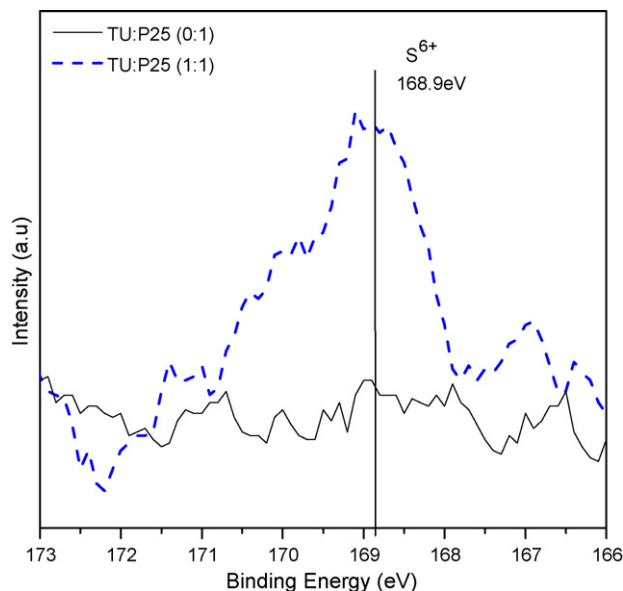


Fig. 7. XPS profiles of S2p spectra for S-doped (1:1) and undoped Degussa P25 photocatalyst after calcination at 550 °C for 4 h in air.

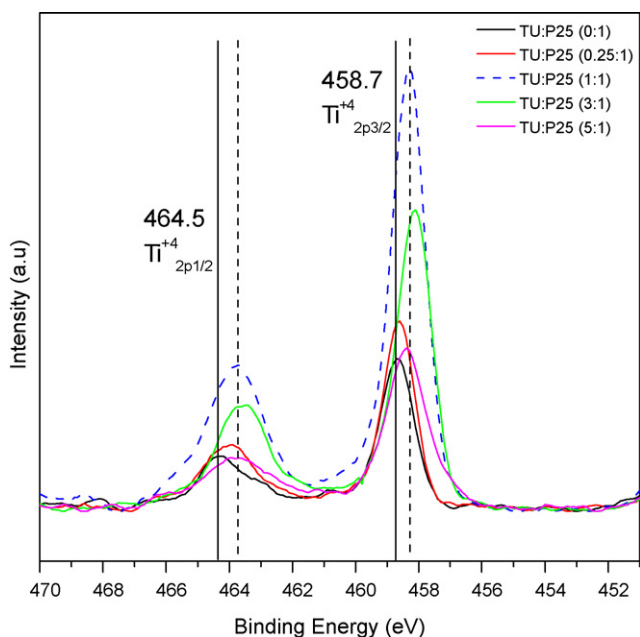


Fig. 8. XPS profiles of Ti2p spectra for S-doped and undoped Degussa P25 photocatalyst after calcination at 550 °C for 4 h in air.

168.9 eV assigned to S^{6+} was observed. This peak was thought to consist of several oxidation states of S atoms such as S^{5+} and S^{4+} states [12,22,40]. Previous study reported that if thiourea was used as sulfur precursors, the substitution of Ti^{4+} by S^{6+} would be more favorable than replacing O^{2-} with S^{2-} [12,22,24].

Ohno et al. [22] prepared S-doped TiO_2 by hydrolysis of titanium isopropoxide blended with thiourea. Their XPS results showed a broad peak, around 168 eV, attributed to S2p. Zaleska et al. [41] observed the strongest peak for 168.8 eV assigned to S^{6+} and another weak one around 169.8 eV in their S-doped TiO_2 . Katoh et al. [42] reported synthesis of new S-containing TiO_2 powders prepared from titanium(III) chloride and ammonium thiocyanate solutions. For S- TiO_2 , the S2p (3/2) peak appeared at around 170 eV, which is attributed to S^{6+} species. Those results are in good agreement with our observation; therefore, it is clear that sulfur was doped mainly as S^{6+} .

It must be mentioned here that when the S-doped sample (at TU:P25 mass ratio of 1:1) was washed with water several times, the intensity and binding energy of S^{6+} remained unchanged significantly. This revealed that doped S was not formed in the form of sulfur oxides on TiO_2 surface [12].

Fig. 8 shows the binding energies of the spin-orbit components (2p 3/2 and 2p 1/2) of Ti2p observed to be at 458.7 and 464.5 eV, respectively, which should be assigned to Ti^{4+} of TiO_2 (corresponding to Ti^{4+} in a tetragonal structure) [24]. It is obvious that the doped sulfur can lead to the peak of Ti2p 1/2 and Ti2p 3/2 shift to the lower binding energy. This may be caused due to the difference of ionization energy of Ti and S [24]. Therefore, it could be concluded that the lattice titanium sites of TiO_2 were substituted by S^{6+} and formed a new band energy structure.

In spite of using thiourea as a source of sulfur, we could not detect a clear peak for N. This can be attributed to the well-known fact that the ion radii of N is larger than that of O [43]. Therefore the N which is located at the position of oxygen is usually not so stable. On the other hand, S-doped TiO_2 is quite stable because ion radii of S^{4+} or S^{6+} is much smaller than that of Ti^{4+} . Furthermore, when N^{3-} replaced with O^{2-} , oxygen defects should be generated in order to neutralize the electricity. Eventually, during calcination S atoms were incorporated into the lattice of TiO_2 and the S-doped

TiO_2 is quite stable. N atoms which are incorporated into the lattice of TiO_2 may be released gradually during calcinations.

Furthermore, interesting XPS results (Figs. 8 and 9) were observed under different TU:P25 ratios (0:1, 0.25:1, 1:1, 1:3, and 1:5), increasing the ratio from 0:1 to 1:1 significantly enhanced the peak intensities of the S-doped P25. However, further increase in the TU:P25 ratio (3:1 to 5:1) reduced the peak intensities and consequently reduced the activities.

Probably the doped sulfur at higher TU:P25 ratios (>3) was formed in the form of sulfur oxide on TiO_2 surface during the hydrolysis process, and most of the sulfur will remove during the calcination process, i.e., higher thiourea (TU) loading could enhance the removal of the sulfur from the sample during the calcinations, which reflected the significant reduction in the intensity of S^{6+} . It seems that there is a limit to the amount of thiourea used for doping Degussa P25, in this work it was 1:1 TU:P25 mass ratio, that resulted in better S-doped P25 performance.

Katoh et al. [42] found in their S- TiO_2 powders, that the peak area of S2p (3/2) increased with increase of ammonium thiocyanate solution. But the content of sulfur was much smaller than the content in the starting materials and most of the sulfur atoms were removed from the TiO_2 surface under calcination. In the same way Zaleska et al. [41] reported that S2p peak increased with increasing amount of thiourea (increasing TU: TiO_2 mass ratio from 0:1 to 0.147:1), and sulfur content in the catalyst was much smaller than might be expected from original sulfur content in the substrates. In the present results (Fig. 9) only increasing the ratio up to 1:1 agrees with their observations. Further work for better understanding this unexpected result is being under way.

3.3. UV-vis results

Fig. 10 shows the diffuse reflectance UV-vis spectra of base P25 and S-doped P25 prepared at different TU:P25 mass ratios (0:1, 0.25:1, 1:1, 3:1 and 5:1). Noticeable shifts of the optical absorption shoulders toward the visible light regions of the solar spectrum were observed for S-doped P25. Notably, this shift towards the longer wavelength originates from the band gap narrowing of P25

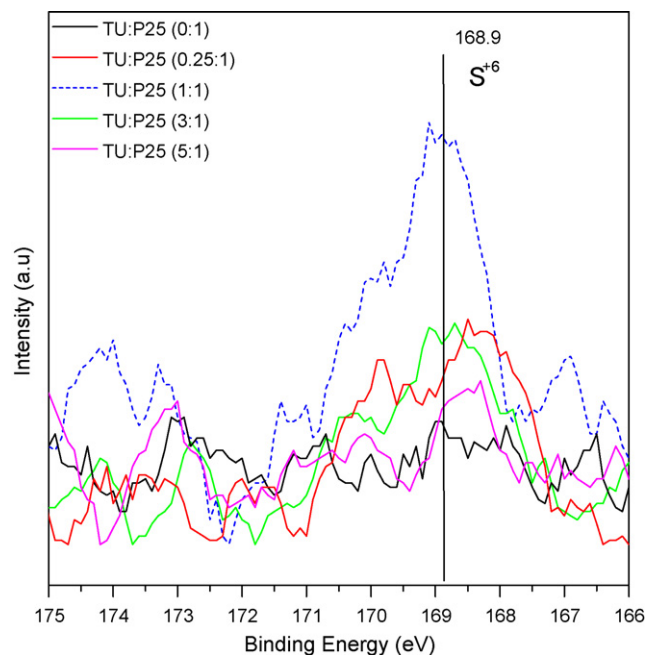


Fig. 9. XPS profiles of S2p spectra for S-doped (at different TU:P25 mass ratios) and undoped Degussa P25 photocatalyst after calcination at 550 °C for 4 h in air.

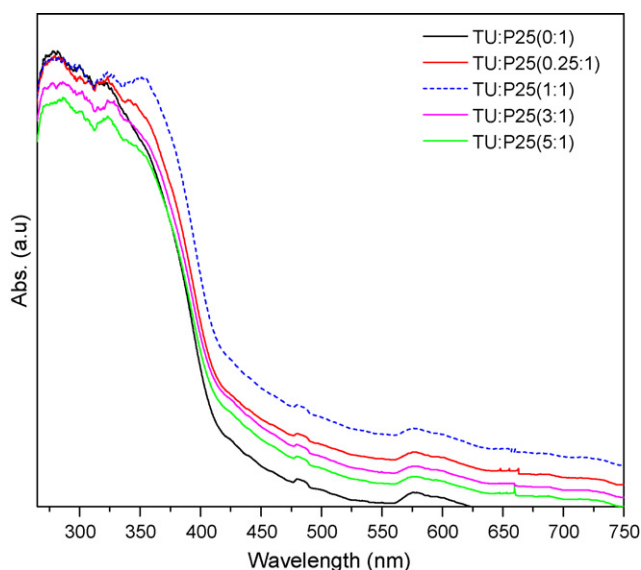


Fig. 10. UV-vis diffuse reflectance spectra of the sulfur doped and undoped-P25 at different TU:P25 ratios.

by sulfur doping [12,44,45], this feature was more evident at TU:P25 ratio of 1:1. The results clearly indicated that increasing the TU:P25 ratio from 0:1 to 1:1, leads to an enhancement in the absorption shifting of the P25. However, further loading (3:1 and 5:1) will decrease the shifting; the spectrum of (5:1) sample is almost identical to that of non-doped P25. Zaleska et al. [41] pointed out that increasing the amount of thiourea during catalyst preparation (increasing the TU:TiO₂ mass ratios from 0:1 to 0.147:1), increased the absorption in the visible region, however, in their work they did not investigate high TU:TiO₂ mass ratios, higher than 0.147.

Estimations of the band-gap energies were obtained from the diffuse reflectance spectra of the doped and undoped-P25 powders. The relation between the absorption coefficient (α) and incident photon energy ($h\nu$) can be written as $\alpha = B_d(h\nu - E_g)^2/\lambda$, where B_d is the absorption constant [46]. Plots of $(A h\nu)^{0.5}$ versus $h\nu$ from the spectral data in Fig. 10 are presented in Fig. 11. Extrapolating the linear part of the curve for the TiO₂ gives direct values of band gap. The linear part of the curve for the undoped-P25 gives a direct

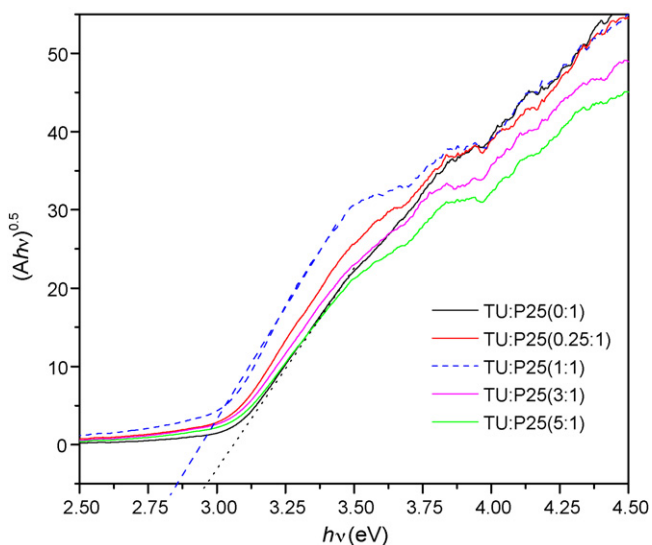


Fig. 11. $(A h\nu)^{0.5}$ vs. $h\nu$ for the doped and undoped-P25 (derived from Fig. 10), showing a linear relation between $(A h\nu)^{0.5}$ and $h\nu$ in the wavelength region of fundamental absorption edge.

Table 1

Estimated apparent first-order rate constant (k_a).

Photocatalyst (TU:P25 mass ratio)	k_a (min ⁻¹)	Correlation coefficient R^2
S-doped P25 (0:1)	0.044	0.99
S-doped P25 (0.25:1)	0.051	0.99
S-doped P25 (1:1)	0.055	0.99
S-doped P25 (5:1)	0.040	0.98

band gap of 2.99 eV, which is very close to the commercial Degussa P25 (3–3.2 eV). The band gap energies of S-doped P25 (0.25:1, 1:1, 3:1 and 5:1) samples were found to be 2.90, 2.83, 2.92 and 2.98 eV, respectively (Fig. 3). The maximum band gap reduction was 0.15 eV for S-doped p25 at 1:1 TU:P25 mass ratio. Probably the distortion of the local lattice of TiO₂ by S⁶⁺ is responsible to the absorption in the visible region and to the shift of the onset of their absorption edge near 400 nm [22,24]. Previous results (Figs. 7 and 8) clearly showed that the crystal lattices of S-doped P25 powder are locally distorted by incorporating S⁶⁺ species into TiO₂ and substitute for some of Ti⁴⁺. It is worth noting to mention here that Ti⁴⁺ which was released from the lattice of TiO₂ may react with O₂ to produce TiO₂ which might be replaced in somewhere in the bulk of TiO₂. Wu et al. [47] claimed that within doping of S atoms (using thiourea as a source of S) into Ti(OBu)₄, Ti atoms firstly bond to S atoms, forming a small amount of TiS₂ nucleus, and then the rest of the Ti atoms begin coordinating with O atoms, forming a large amount of anatase-TiO₂ nucleus surrounding the TiS₂ nucleus. To get a clear conclusion an extensive experiments are required.

Irie et al. [16] reported that the band structure of the N-doped TiO₂ (TiO_{2-x}N_x) with lower values of x (lower N concentration) should differ from that doped with higher x values. Zaleska et al. [41] reported that more thiourea used during photocatalyst preparation resulted in increased band gap. In the present results we noticed that the band gap at 1:1 TU:P25 mass ratio is smaller than that at 5:1.

3.4. Solar photocatalyst activity

To evaluate the photocatalytic activity of S-doped P25 catalysts under natural solar light irradiation, tests were carried out to decolorize and mineralize Orange II dye in an aqueous suspension at an initial Orange II concentration of 10 mg/l. Fig. 12A demonstrates the solar photo-decolorization observed for Orange II in the presence of S-doped P25 and undoped one. During the course of the solar experiments, the total accumulated UV light (350–400 nm) and the total accumulated visible light (400–750 nm) were 0.444 and 68.08 kJ/l, respectively.

A plot of $\ln(C/C_0)$ versus t represents approximate linear straight lines, showing the case of the first-order reaction. The slope of the line equals the apparent first-order rate constant (k_a), the estimated k_a values are summarized in Table 1.

The activity of catalyst was found to be dependent on the doping amount of sulfur. The results in Table 1 showed that the decolorization rate of Orange II dye increased with increasing S content, but decreased at higher levels. The undoped-P25 photocatalytic activity under solar light increased about 23% by doping with TU at mass ration of (1:1), however, it decreased about 12.3% by doping at mass ration of (5:1). It seems too high content of sulfur is harmful for the activity of the prepared photocatalyst. Possibly due to the block of too many TiO₂ active sites. It has been reported that the presence of phosphate ions would absorb strongly on the surface of TiO₂ by a bidentate chelation and reduce the rate of photocatalyzed oxidation of model organic contaminants by as much as 70% [20]. Furthermore, doped sulfur can form a new band above the valence band and narrow the band-gap of the photocatalyst, giving rise to

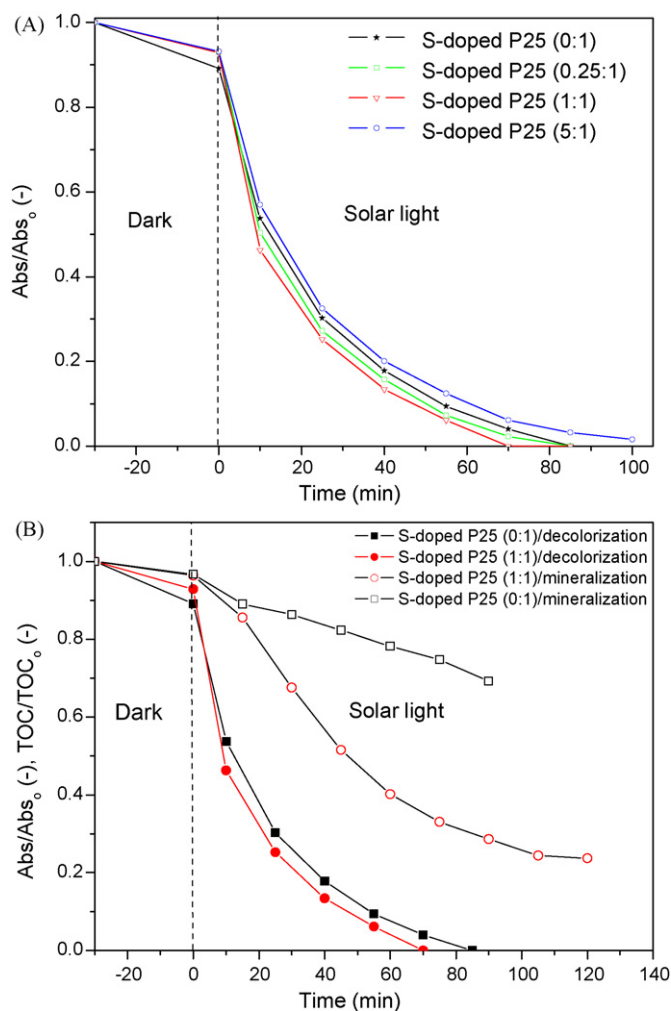


Fig. 12. Effect of the TU:P25 ratios on the solar photoactivity of S-doped P25: (A) decolorization and (B) decolorization and mineralization (Orange II concentration = 10 mg/l).

the absorption edge in the visible light region (previous section, Fig. 10). However, too much of new-generated band-gap structures due to higher sulfur doping could act as recombination centers for electron-hole pairs and consequently reducing the photoactivity of the catalyst. Mineralization of the Orange II dye also has been tested under natural solar light (Fig. 12B). The S-doped P25 photocatalyst at mass ratio of (1:1) shows higher activity than undoped one.

One may raise the doubt of whether it is the photocatalyst that plays the key role in decomposing Orange II dye because the dye can absorb visible light itself. If the decomposition of Orange II dye is due to the light absorbance itself, then the efficiency of the decomposition using a different photocatalysts may not vary so much as shown in Fig. 12A and B.

During all the solar experiments the pH value of the treated solution was varied from 5.7 (at the beginning of the experiment) to about 3.9 (after complete decolorization). It was reported that the value of pH_{pzc} (pH of point zero charge) of P25 is 6.0 [48]. Actually, when pH value of aqueous dye solution is lower than TiO₂ pH_{pzc}, the catalyst surface develops a positive charge and attractive forces between catalyst and dye can promote the adsorption process. Increasing the pH dye solution, leads to the situation where the electrostatic charge on the TiO₂ surface will become less positive or even negative if the point of zero charge is surpassed developing repulsive forces between the catalyst and the dye, thus decreasing

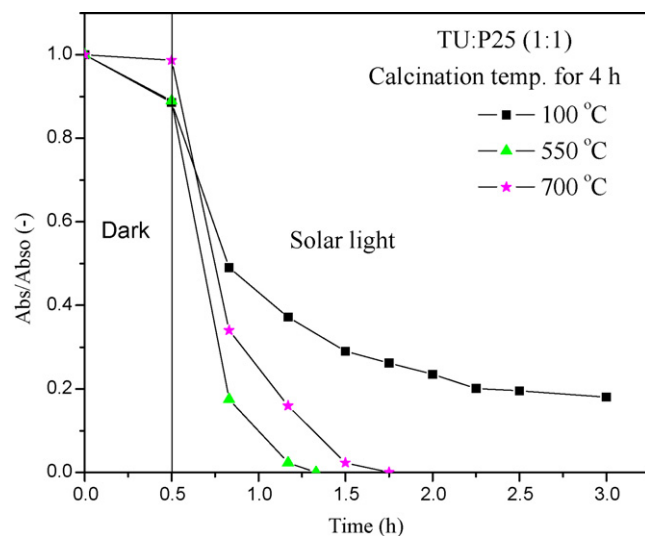


Fig. 13. Effect of the calcination temperature on the Orange II decolorization (Orange II concentration = 10 mg/l, total accumulated UV light intensity (320–400 nm) = 0.916 kJ/l, total accumulated visible light intensity = 101.07 kJ/l).

dye adsorption. Therefore, the pH range of experiments (5.7–3.9) is favorable for adsorption and consequently to the degradation.

The mechanism of photocatalytic decolorization suggests that the dye molecules are first adsorbed on TiO₂ surface then under illumination by UV radiation, one electron is promoted from conduction band to the valence band of the TiO₂ generating e⁻/h⁺ pair. The action of the e⁻/h⁺ pair is terminated by degrading dye molecules into products through intermediate formation and generating heating effect through a complex reaction.

Additional experiments were carried out to test the activity of the S-doped P25 under different calcinations temperatures (Fig. 13). It was found that the calcinations temperature has a significant effect upon the photoactivity of the prepared photocatalyst. The results obtained (Figs. 13 and 14) showed that the decolorization rate of the Orange II has increased 6 times as the calcinations temperature of the S-doped P25 (1:1) increased from 100 to 550 °C, which is attributed to gradual crystallization of the anatase TiO₂

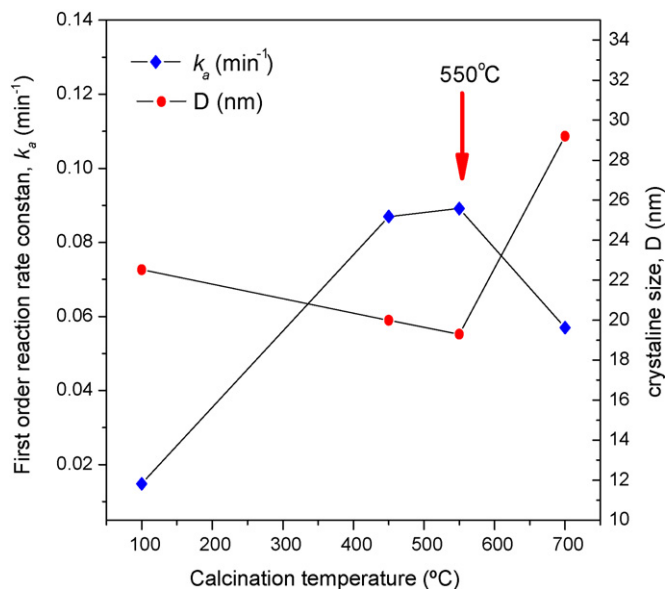


Fig. 14. Effect of the calcination temperature on the reaction rate constant (k_a) and the crystalline size (D).

with temperature rising. However, further increase in the calcinations temperature (to 700 °C) results in an obvious decrease in the activity, which is probably due to the increase of the crystalline size. Its evidence from Fig. 14 that the optimum calcination temperature was 550 °C.

4. Conclusions

The commercially available TiO₂ photocatalyst (Degussa P25) has been doped with sulfur, employing a simple hydrolysis method at room temperature. The synthesized S-doped P25 showed higher activity than the naked P25 under natural solar light. The amount of dopant used during the hydrolysis process clearly affects the physico-chemical properties of S-doped P25 which in turn exhibit a crucial influence on its photocatalytic activity. The maximum activity was observed when the catalyst was obtained by calcinated at 550 °C with mass ratio of TU:P25 = 1:1. The solar decolorization improved by 23%, the band gap reduced to 2.8 eV, the average crystalline size reduced to 19 nm and the anatase content increased from 80.5 to 82.3%, after doping with sulfur at TU:P25 mass ratio of (1:1).

The calcinations temperature has a significant effect upon the photoactivity of the prepared photocatalyst, decolorization rate increased 6 times as the calcinations temperature of the S-doped P25 increased from 100 to 550 °C, while calcination temperature of 700 °C resulted in an obvious decrease in the photoactivity. The XRD and XPS results clearly showed that using thiourea as a source of sulfur can retard the grain growth of TiO₂ to some extent and leads to the substitution of Ti⁴⁺ by S⁶⁺ which is more favorable than replacing O²⁻ with S²⁻. The results suggest that the crystal lattices of S-doped P25 powder are locally distorted by incorporating S⁶⁺ species into TiO₂, forming a new band energy structure, which is responsible to the absorption in the visible region.

Interesting results were observed under different TU:P25 ratios (0:1, 0.25:1, 1:1, 3:1, and 5:1), increasing the ratio from 0:1 to 1:1 significantly enhanced the peak intensities and improved the solar photocatalytic activity of the S-doped P25. However, further increase in the TU:P25 ratio (3:1 to 5:1) reduced the peak intensities and consequently reduced the activities. The solar photoactivities of S-doped P25 are predominantly attributed to an improvement in anatase crystallinity, low band gap and low particle size. The presented results greatly encourage the researchers for further improving and modifying the commercial TiO₂ (Degussa P25) by using it as a Ti precursor rather than the costly chemicals like titanium tetraisopropoxide.

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References

- [1] Y. Liu, X. Chen, J. Li, C. Burda, *Chemosphere* 61 (2005) 11–18.
- [2] K. Kobayakawa, Y. Murakami, Y. Sato, *J. Photochem. Photobiol. A: Chem.* 170 (2005) 177–246.
- [3] I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara, K. Takeuchi, *J. Mol. Catal. A: Chem.* 161 (2000) 205–212.
- [4] C. Kilic, A. Zunger, *Appl. Phys. Lett.* 81 (2002) 73–75.
- [5] R.A. Palmer, T.M. Doan, P.G. Lloyd, B.L. Jarvis, N.U. Ahmed, *Plasma Chem. Plasma Process.* 3 (2002) 335–350.
- [6] S.I. Shah, W. Li, C.P. Huang, O. Jung, C. Ni, *Proc. Natl. Acad. Sci.* 99 (2002) 6482–6486.
- [7] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, *J. Phys. Chem. Solids* 63 (2002) 1909–1920.
- [8] G. Liu, X. Zhang, Y. Xu, X. Niu, L. Zheng, X. Ding, *Chemosphere* 55 (2004) 1287–1291.
- [9] M. Anpo, *Pure Appl. Chem.* 72 (2000) 1787–1792.
- [10] A. Fuerte, M.D. Hernandez-Alonso, A.J. Maira, A. Martinez-Arias, M. Fernandez-Garcia, J.C. Conesa, J. Soria, *Chem. Commun.* (2001) 2718–2719.
- [11] A. Di Paola, S. Ikeda, G. Marci, B. Ohtani, *Int. J. Photoenergy* 3 (2001) 171–176.
- [12] T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, M. Matsumura, *Appl. Catal. A: Gen.* 265 (2004) 115–121.
- [13] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, *Appl. Phys. Lett.* 81 (2002) 454–456.
- [14] R. Gómez, T. López, E. Ortiz-Islas, J. Navarrete, E. Sanchez, F. Tzompanzti, X. Bokhimi, *J. Mol. Catal. A: Chem.* 193 (2003) 217–226.
- [15] S.X. Liu, X.Y. Chen, X. Chen, *Chin. J. Catal.* 27 (2006) 697–702.
- [16] H. Irie, Y. Watanabe, K. Hashimoto, *J. Phys. Chem. B* 107 (2003) 5483–5486.
- [17] H. Irie, Y. Watanabe, K. Hashimoto, *Chem. Lett.* 32 (2003) 772–773.
- [18] S.U.M. Khan, M. Al-Shahry, W.B. Ingler Jr., *Science* 297 (2002) 2243–2245.
- [19] T. Umebayashi, T. Yamaki, S. Tanaka, K. Asai, *Chem. Lett.* 32 (2003) 330–332.
- [20] L. Lin, R.Y. Zheng, J.L. Xie, Y.X. Zhu, Y.C. Xie, *Appl. Catal. B: Environ.* 76 (2007) 196–202.
- [21] I. Justicia, P. Ordejon, G. Canto, *Adv. Mater.* 14 (2002) 1399–1402.
- [22] T. Ohno, T. Mitsui, M. Matsumura, *Chem. Lett.* 32 (2003) 364–366.
- [23] T. Ohno, *Water Sci. Technol.* 49 (2004) 159–163.
- [24] S. Liu, X. Chen, *J. Hazard. Mater.* 152 (2008) 48–55.
- [25] S. Sato, R. Nakamura, S. Abe, *Appl. Catal. A* 284 (2005) 131–137.
- [26] S. Sakthivel, M. Janczarek, H. Kisch, *J. Phys. Chem. B* 108 (2004) 19384–19387.
- [27] V. Pore, M. Heikkilä, M. Ritala, M. Leskela, S. Areva, *J. Photobiol. Photochem. A: Chem.* 177 (2006) 68–75.
- [28] C. Chen, H. Bai, S. Chang, C. Chang, W. Den, *J. Nanopart. Res.* 9 (2007) 365–375.
- [29] R. Asashi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* 293 (2001) 269–271.
- [30] M. Sathish, B. Viswanathan, R.P. Viswanath, *Appl. Catal. B: Environ.* 74 (2007) 307–312.
- [31] M. Janus, A.W. Morawski, *Appl. Catal. B: Environ.* 75 (2007) 118–123.
- [32] N. Bowering, D. Croston, P.G. Harrison, G.S. Walker, *Int. J. Photoenergy* 2007, Article ID90752, (2007) 1–8.
- [33] J.A. Rengifo-Herrera, J. Kiwi, C. Pulgarin, *J. Photochem. Photobiol. A: Chem.* 205 (2009) 109–115.
- [34] L.K. Randeniya, A.B. Murphy, I.C. Plumb, *J. Mater. Sci.* 43 (2008) 1389–1399.
- [35] H.B. Thu, M. Karkmaz, E. Puzenat, C. Guillard, J.M. Herrmann, *Res. Chem. Intermed.* 31 (2005) 449–461.
- [36] R.I. Bickley, T. Gonzalez-Carreno, J.S. Lees, L. Palmisano, R.J.D. Tilley, *J. Solid State Chem.* 92 (1991) 178.
- [37] F.J. Porter, Y.G. Li, K.C. Chan, *J. Mater. Sci.* 34 (1999) 1523–1531.
- [38] N. Venkatachalam, M. Palanichamy, V. Murugesan, *Mater. Chem. Phys.* 104 (2007) 454–459.
- [39] R.D. Shannon, J.A. Pask, *J. Am. Ceram. Soc.* 48 (1965) 391.
- [40] K. Nishijima, T. Kamae, N. Murakami, T. Tsubota, T. Ohno, *Int. J. Photoenergy* 2008, Article ID173943, (2008) 1–7.
- [41] A. Zaleska, P. Górska, J.W. Sobczak, J. Hupka, *Appl. Catal. B: Environ.* 76 (2007) 1–8.
- [42] M. Katoh, H. Amhara, T. Horikawa, T. Tomida, *J. Colloid Interface Sci.* 298 (2006) 805–809.
- [43] R.D. Shannon, *Acta Cryst. A* 32 (1976) 751–767.
- [44] K. Nagaveni, M.S. Hedge, N. Ravishankar, G.N. Subbanna, G. Madras, *Langmuir* 20 (2004) 2900.
- [45] D.B. Hamal, K.J. Klabunde, *J. Colloid Interface Sci.* 311 (2007) 514–522.
- [46] X.H. Wang, J.G. Li, H. Kamiyama, M. Katada, N. Ohashi, Y. Moriyoshi, T. Ishigaki, *J. Am. Chem. Soc.* 127 (2005) 10982–10990.
- [47] X.W. Wu, D.J. Wu, X.J. Liu, *Appl. Phys. A* 97 (2009) 243–248.
- [48] C.G. Silva, W. Wang, J.L. Faria, *J. Photochem. Photobiol. A: Chem.* 181 (2006) 314.