Synthesis, Characterization of Cu, S doped TiO₂ and Its Photocatalytic Activity for Degradation of Remazol Black B

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Article Info

Abstract

Copper and sulfur modified TiO_2 (Cu-S-TiO₂) photocatalyst was successfully synthesized using $TiCl_4$, $Cu(NO_3)_2.3H_2O$ and H_2SO_4 as precursors by the sol-gel method andcalcination at 450°C for 4 hours. The synthesized photocatalyst was characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS), Diffuse Reflectance Spectroscopy (DRS), Brunauer Emmett Teller (BET) method. The XRD results showed that the Cu-S-TiO₂ photocatalyst had an anatase phase with a crystal grain size of 17.54 nm. However, the SEM image of the modified TiO₂ showed inhomogeneous phase due to the crystal clustering of imperfect homogenization during the synthesis and sintering processes. The patterns of EDSof Cu-S-TiO₂depicted the elements of Ti, O, Cu and S with doping of Cu and S c.a. 7 and 1%, respectively. Analysis using DRS UV-Vis showed Cu-S-TiO₂ was able to shift the absorption of the TiO₂ photocatalyst wavelength to the visible region with a band energy gap of 1.9 eV. The BET analysis results showed that the specific surface area (S_{BET}), pore volume (V_p) and average pore volume radius (D_p) were measured from large Cu-S-TiO₂, therefore Cu-S-TiO₂ had good physicochemical and photocatalytic properties. The photocatalytic activity of 0.1 g Cu-S-TiO₂ with 15 Watt tungsten light irradiation for 4 h was able to degrade 50 mL remazol black B 10 mg/L c.a. 92.60 %.

1. Introduction

One potential method for treating organic waste is by photocatalysis. Photocatalyst material when subjected to the appropriate photon energy will produce electrons in the conduction band and holes in the valence band. The electrons can reduce heavy metals, while the holes can oxidize organic compounds [1]. Semiconductor of titanium dioxide is widely used as a photocatalyst because it is nontoxic, inexpensive, and has a high catalytic activity [2]. TiO₂ appears in 3 different polymorphic forms, namely rutile, anatase, and brookite. Two TiO₂ crystal structures, rutile and anatase, are most commonly used in photocatalysis. The structure of the two crystals is distinguished by octahedron distortion and the octahedron chain arrangement pattern. This difference in lattice structure causes differences in density and electronic band structure between the two forms of TiO₂ [3]. TiO₂ has a large band energy of 3.2 eV which is the absolute difference between the conduction band energy and the position of the valence band energy level. This indicates that h^+ on the surface of TiO₂ is a strong oxidizing species so that it can oxidize other chemical species that have smaller redox potentials including H_2O

molecules which will produce hydroxyl radicals. The hydroxyl radical has a potential of 2.8 Vat pH 1 so that it can oxidize organic substances which mostly have a smaller redox potential [4]. However TiO₂ has a band gap of 3.2 eV (anatase) which can only be applied under UV light (λ <387 nm). Research on the modification of TiO₂ which aims to expand the absorption of wavelengths so that it can be applied to visible light is being developed, among others, by the combination of sensitized dye [5, 6], doping of transition metals [7] and insertion of precious metals [8]. Doping transition metals and non-metals in TiO₂ can modify its electronic structure effectively and be able to shift its absorption at lower energy levels [9]. In this study, synthesis of Cu and S-modified TiO₂ (Cu-S-TiO₂) for degradation of remazol black B was applied to the visible light region [10, 11]. The synergy effect of S and Cu doped on TiO₂ has a higher activity compared to bare TiO₂ in degrading organic compounds [12, 13].

In this study, the sol gel method was used which is one method that is often used to synthesize TiO₂ doped with metals and non-metals. This method allows to control several parameters with a relatively slow reaction process, including homogeneity of composition, grain

size, particle morphology and porosity [14, 15, 16]. The process of sol gel generally includes the hydrolysis stage of a metal alkoxide or precursor alkoxide, usually in alcohol, so that the hydroxide is obtained, then proceed with the condensation process, so that the sol is formed. Removal of solvent by heating gives a gel and then xerogel. Cu-S-TiO₂ powder was obtained as a result of calcination [17, 18, 19]. Synthesized Cu-S-TiO₂ powder was carried out by characterization and photocatalytic activity test for degradation of remazol black B.

2. Experimental Details

2.1. Synthesis of Cu-S-TiO₂

Synthesis of Cu-S-TiO₂ was done by addition of 2-propanol dropwise into 10 mL TiCl₄ until total volume of 100 mL (d=1.73 g/cm³) to form a clear yellow solution. The solution was stirred for 30 min at room temperature. Then, gradually adding with NH₄OH solution until pH 3-4, then stirred for 1 h until white solution was obtained. After that, solution containing 7.7 g Cu(NO₃)₂.3H₂O and 4.9 mL H₂SO₄ (98%, density=1.84g/cm³) as dopants was added dropwise with stirring for 6 h until a green solution was formed, and finally a green Cu-S-TiO₂ gel was formed. The gel was left for for 3 days and dried in oven at 80-100 ℃ for 24 h so that xerogel of Cu-S-TiO₂ was obtained, then calcined at 450 ℃ for 4 hours. The product was greenish Cu-S-TiO₂ powder. All chemicals were puchased from Merck.

2.2. Characterization of Cu-S-TiO₂

Synthesized Cu-S-TiO₂ was characterized using X-Ray Diffraction Instrument (XRD) (Shimadzu 7000), Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS), UV-Visible Diffuse Reflectance Spectrophotometer, Instrument Quantachrome Novawin version 11.0 for BET test.

2.3. Photocatalytic process of sample solution

The photocatalyst process was carried out at a room temperature in a static cylindric flask reactor by soaking 0.1 g Cu-S-TiO₂ into a sample solution of 50 mL remazol black B 10 mg/L, then the reactor was irradiated with a 15 Watt tungsten lamp (Philips) at a distance of 20 cm for varied times of 1, 2, 3, 4 h. The remaining remazol black B, further, was measured using UV-Vis spectrophotometer (PG Instruments Limited Model T60U). The percentage of degradation was calculated using the following equation:

$$Degradation\ (\%) = \frac{Co - Ct}{Co} \times 100\ \%$$

Where *Co* and *Ct* are initial sample concentration and sample concentration after photocatalysis process, respectively.

3. Results and Discussion

3.1. XRD characterization of Cu-S-TiO₂

X-ray diffractogram results were analyzed using the Match! Application. and compared it with the data in JCPDS to know the shape of the crystal and the constituent compounds formed from the synthesized Cu-S-TiO₂. Fig. 1 shows the XRD diffractogram of Cu-S-TiO₂.
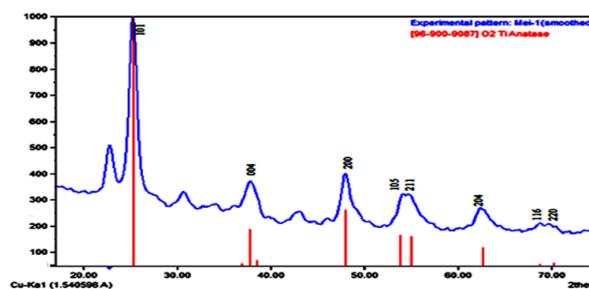
Figure 1. XRD patterns of Synthesized Cu-S-TiO₂.

Analysis results of Match! application there is a red line which is a specific peak that refers to the anatase TiO₂ database (entry # 96-900-9087). Based on the picture shows that the crystal structure formed is anatase TiO₂ which is characterized by the presence of peaks that correspond to the anatase TiO₂ database in the Match! Application. The diffractogram results then were matched with the data contained in (JCPDS 21-1272) as showed X-ray diffraction patterns from samples of nanocrystalline anatase structures confirmed by (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 1 1) with the main peak at 2θ = 25.28. The average nanoparticle size is estimated from the Scherrer equation on anatase peak diffraction (1 0 1). The size of the crystal sample isdetermined quantitatively using Scherrer method with the equation:

$$D = \frac{k \times \lambda}{\beta \times cos\,\theta}$$

Where k is a constant of 0.89; λ is the wavelength of the X-ray source (in this case Cu kα is 0.15418 nm), and β is half width of the diffraction peak (FWHM) in radians. The β value used in this case is the maximum peak value possessed by the anatase peak at 2θ of 25.28° which is equal to 0.48505° and obtained a crystal size of 17.54 nm.The small size of the crystal can expand the catalyst surface so that its performance becomes more effective. The diffractogram shows the peaks at 2θ of 22.835, 30.728, and 42.926° was also formed and estimated as S6, SO₃ and CuO from the Match! Database. The diffractogram are mapped to the data base in JCPDS 74-1654, 73-2169, and 78-0428. The emergence of these peaks indicates that some of the dopants were not completely dispersed in the crystal lattice structure of TiO₂ either at substantional or interstitial position but the dopants were only embeded on the TiO2 surface. The synthesis process which could not create a great homogeneity allows the added dopants not to be all dispersed. The calcination environment, rich in oxygen, formed some of the dopants were not in the atom forms but also in the form of their oxides, namely SO₃ and CuO.

3.2. SEM-EDS characterization of Cu-S-TiO₂

SEM images of synthesized Cu-S-TiO₂ are shown in Fig. 3. Fig. 2. The surface SEM image at a 1000x magnification only shows the presence of many chunks in same surface with different intensity and dimension indicating the presence of different matter that is supposed as the dopants on the TiO₂ surface. At 5000x magnification the visible surface is bumpy and uneven with many cavities, making it possible to assist in trapping the target compounds on the surface of the photocatalyst so as to facilitate the photocatalyst to oxidize or reduce the compounds. Whereas, at 15,000x magnification can be seen the morphology of the material surface is viewed not homogeneous. The matter may form clusters due to imperfect homogenization during synthesis and sintering processes. Next characterization

by EDS informs elemental composition of the surface that is as shown in fig. 3 as well.

a.

b.

c.
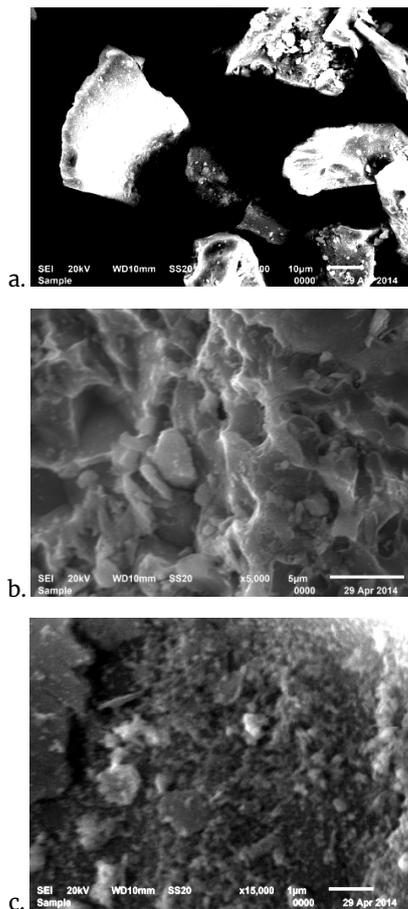
Figure 2. SEM images of Cu–S–TiO$_2$ at magnifiications of a. 1000x; b. 5000x; c.15000x.
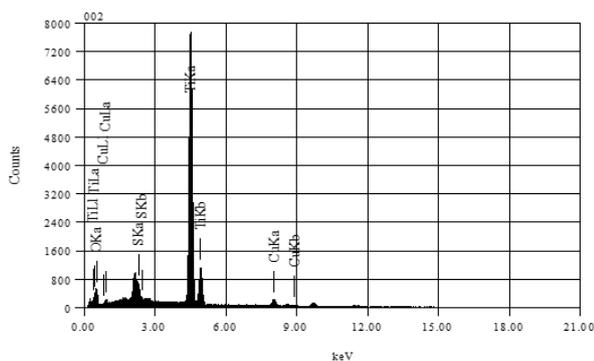
Figure 3. EDSprofile of synthesized Cu–S–TiO$_2$.

Table 1. Elemental composition of Cu–S–TiO$_2$ measured by EDS.

Element	Atom (%)
O	25.62
S	1.03
Ti	66.42
Cu	6.93

Based on the EDS pattern of Cu–S–TiO$_2$ photocatalyst as seen in Fig. 3 and Table 1, the synthesized photocatalyst composed of several elements, namely oxygen (O), sulfur (S), titanium (Ti) and copper (Cu). So that from these results proved that in the synthesis process, Cl$^-$ which binds to Ti^{4+} was substituted all by the alkoxide group ($-OCH(CH_3)_2$) from isopropanol to form titanium (IV) isopropoxide and HCl gas. Then the aging and calcination processes carried out was able to remove the Cl component so that the synthesized photocatalyst had no impurity. The percentages of each dopant were 1% and 7% for sulfur (S) and copper (Cu) elements, respectively from total mass.

3.3. Characterization of Cu–S–TiO$_2$ photocatalyst using Diffuse UV–Visible Reflectance Spectrophotometer.

Characterization using a UV-Vis diffuse reflectance spectrophotometer aims to determine the band gap energy. The analysis using diffuse UV-Vis reflectance spectrophotometer are shown in Fig. 4 as the following:
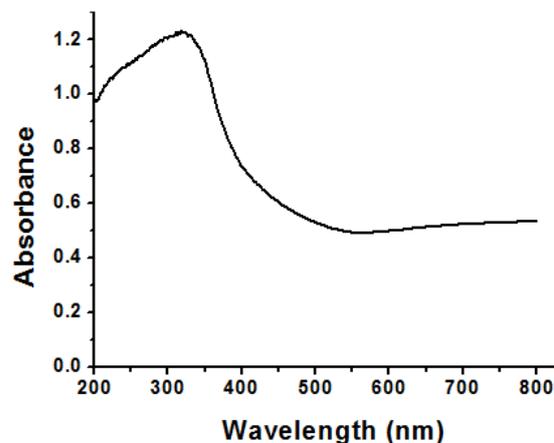
Figure 4. Variation of absorbance with wavelength of Cu–S–TiO$_2$ measured using UV-Vis diffuse reflectance spectrophotometer.

Based on the spectrum in Fig. 4 shows that the presence of Cu and S doping was able to shift the absorption of the TiO$_2$ photocatalyst wavelength at the visible light as evidenced by the absorption (absorbance> 0.4) at wavelengths above 400 nm and an increase in absorption in the wavelength region of 700 nm. The value of band gap energy generated from the doping process can be estimated by Kubelka-Mulk equation by processing sample reflectance data from the analysis results. The band gap energy value is obtained by extension of the line from the maximum slope of the graph from the relationship between $[F(R)h\nu]^n$ and $h\nu$ at $[F(R)h\nu]^n = 0$ in Fig. 5, then the band gap energy value found is 1.9 eV. Therefore, it is proven that the doping can reduce the band gap energy of TiO$_2$ which generally has a band gap of 3.2 eV. The smaller the band gap energy value, the smaller the energy required by the photocatalyst to excite electrons from the valence band to the conduction band. This is very beneficial in photocatalyst applications because it is able to work at wavelength with a wider range of visible light region. Curve of $[F(R)h\nu]^{1/2}$ vs $h\nu$ for determination of band gap as shown in Fig. 5 below:
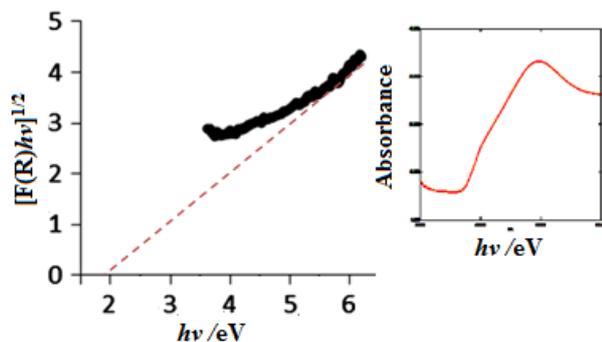
Figure 5. Curve of $[F(R)hv]^{1/2}$ vs hv for determination of band gap.

Doping either metal or non metal occupying the constitutional and interstitial sides of the TiO_2 crystal lattice provides changes to the electronic band structure [15]. The size of Cu^{2+} ion (0.87 Å) is not much different from Ti^{4+} (0.75 Å) so that it is possible to dope Cu into the crystal lattice which can then distort the crystal structure of TiO_2 [16]. Copper doping which is on the constitutional side of the TiO_2 crystal lattice will produce a band gap energy level under the TiO_2 conduction band whereas if it is in the interstitial position it will produce a band gap energy between the valence band and the conduction band [2]. The presence of dopant sulfur will replace O atoms in TiO_2. This substitution produces a mixture of p orbitals from S and O atoms which causes a rise in the valence band so that a smaller band gap value is obtained [10]. The change in band gap energy in the synthesized Cu-S TiO_2 indicates that some of the dopants are dispersed into the TiO_2 crystal lattice.

3.4. BET Analysis

The results of BET analysis of Cu-S-TiO_2 photocatalyst had a specific surface area (S_{BET}) of $85.737 m^2/g$, pore volume (V_p) of $0.1137 cc/g$ and radius of average pore volume (D_p) of $1060,100$ Å, thus the modified photocatalyst had physicochemical properties and can be used as a photocatalyst material.

3.5. Test of photocatalytic activity of Cu-S-TiO_2 on degradation of Remazol Black B

Before the photocatalytic activity tests using Cu-S-TiO_2, 50 mL remazol black B 10 mg/L solution was irradiated using 15 Watt tungsten lamp at a distance of 20 cm for 4 h and the concentration reduced c.a. 9.09 % due to the oxidation process by the irradiation. Then, solution of 50 mL remazol black B 10 mg/L was evaluated by addition with 0.1 g of Cu-S-TiO_2 photocatalyst for 4 h, which could reduce the concentration of 16.36% due to adsorption process of the photocatalyst. Fig. 6 shows the decrease of the absorbance of remazol black B obtained by both irradiation and photocatalyst Cu-S-TiO_2 without irradiation.
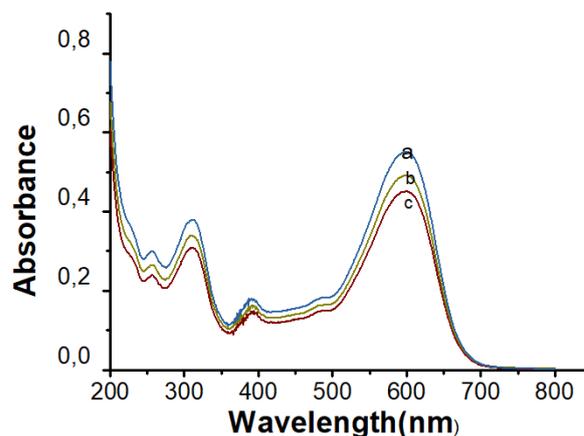
Figure 6. UV-Vis spectra of remazol black B (a) at initial, (b) after irradiation with tungsten lamp 15 Watt for 4 h without photocatalyst, (c) after addition with 0.1 g Cu-S-TiO_2 for 4 h without irradiation.

From the results of remazol black B analysed using UV-Vis spectrophotometer before and after contacted with modified photocatalys as depicted in Fig. 7 below.
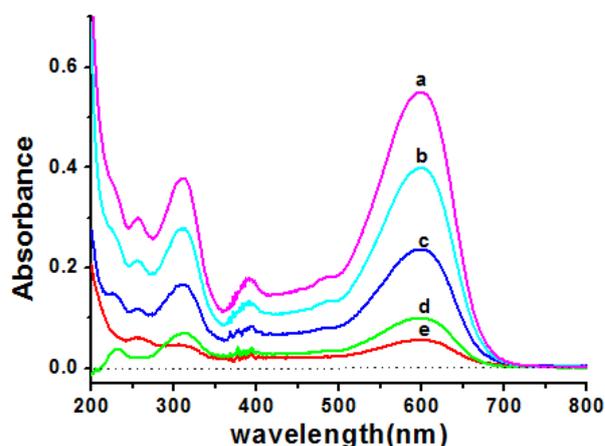
Figure 7. UV-Vis spectra of remazol black B before and after contacted with modified photocatalyst of Cu-S-TiO_2 for (a) 0, (b) 1,(c) 2, (d) 3, and (e) 4 h under tungsten lamp irradiation.

From UV-Vis spectra, it can be seen that the longer the photocatalytic process increases the degradation of remazol black B from 1; 2; 3 and 4 hours with degradation percentages of 24.54; 55.86; 84.32; and 92.60%, respectively. The results also shows that the photocatalyst activity in degrading remazol black B decreases with increasing time of photocatalysis.

4. Conclusion

Modified Cu and S doped TiO_2 had been synthesized by sol-gel and calcination methods using precursors $TiCl_4$, $Cu(NO_3)_2.3H_2O$ and H_2SO_4. The resulting Cu-S-TiO_2 had an anatase phase with a crystal size of 17.54 nm. The doped copper and sulfur of 7 and 1% respectively, was able to shift the wavelength absorption of the TiO_2 photocatalyst towards the visible region with a band gap energy of 1.9 eV. BET analysis of Cu-S-TiO_2 gave large specific surface area, pore volume, and a measured radius of the average pore volume, consequently the synthesized Cu-S-TiO_2 had good physicochemical and photocatalytic properties. The photocatalytic activity test results of Cu-S-TiO_2 were able to degrade remazol black B.

Acknowledgements

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