Synthesis and characterization of visible light active S-doped TiO$_2$ nanophotocatalyst

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ABSTRACT: S-doped and baremesoporous TiO$_2$ were prepared using titaniumtetraisopropoxideand thiocarbamide as raw materials. Prepared materials were characterized by means of fourier transform infrared spectroscopy FT-IR, thermogravimetry-differential scanning calorimetry (TG-DSC), X-ray diffraction (XRD), UV–Vis absorption spectroscopy, Brunauer–Emmett–Teller (BET) specific surface area and Barrett–Joyner–Halenda (BJH) pore size distribution analyses, scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX). The band gap of S-doped was estimated from UV-Vis spectroscopy data to be 2.8 eV. The specific surface area of S-doped TiO$_2$ nanoparticles obtained via the BET method, calculated to be 181.3 m$^2$/g and its pore size distribution curve revealed that the average diameter of the pores is 12.3 nm using BJH method. Photocatalytic efficiency of synthesized S-doped mesoporous TiO$_2$ was tested for degradation of Congoredazo dye under ultraviolet and visible lights. The results revealed that the S-doped mesoporous TiO$_2$ is the most effective under visible light in comparison with bare one.

Keywords: Band gap; Congored; Mesoporous; Photocatalyst; S-doped; TiO$_2$.

INTRODUCTION

Titanium dioxide (TiO$_2$) is highlighted as an important semiconductor photocatalyst because of its superior characters such as exceptional optoelectronic property, strong oxidizing power, chemical stability, low cost, and so on [1, 2]. However, the photocatalytic activity of TiO$_2$ is not high enough to be suitable for commercial application. One major restriction in utilizing of this semiconductor is related to its wide band gap energy, causing TiO$_2$ not be able to generate photoexcited electrons and holes to promote red-ox reactions unless it is irradiated by ultraviolet light [3]. Another drawback of this semiconductor is a fast recombination of its photogenerated charges (electrons and holes) which decrease photocatalytic efficiency of TiO$_2$.

In recent years, many efforts have been directed toward shifting the optical sensitivity of the TiO$_2$ from UV to the visible-light spectrum for the efficient use of solar radiation or artificial visible light [4]. It is generally agreed that the presence of metal or nonmetal dopants into TiO$_2$ lattice increases the photocatalytic activity of the mater under visible light irradiation [5-7]. On the other side, producing porous TiO$_2$ samples with large surface area can improve its photocatalytic properties by means of reducing the recombination rate of photo induced electron-hole pairs. This is due to their faster arrival to the reaction site of the surface and efficient charge separation which increases the lifetime of the charge carriers and enhances the photocatalytic efficiency [8].

The doping of non-metal elements such as N,F, S and P in TiO$_2$ lattice can lower its band gap and shift its optical response to the visible light region [9, 10]. Ohno et al. reported that S cation-doped TiO$_2$ powder absorbed visible light more strongly than N, C and the S anion-doped TiO$_2$ powders also showed photocatalytic activity under visible light [11]. However, sulfur doping TiO$_2$ has small specific surface area and low adsorption capability, which results in poor photocatalytic efficiency when the contaminant
The concentration is low [12]. The pending problem is how to improve the visible light photocatalytic efficiency of doping TiO$_2$ towards low concentration solution, because some contaminants are harmful to people, animals and plants even at low concentration.

In this work S-doped mesoporous TiO$_2$ and a bare mesoporous TiO$_2$ were prepared using a simple sol-gel method. The photocatalytic efficiency of synthesized nonmaterial was tested for degradation of Congoredazo dye under ultraviolet and visible lights.

**EXPERIMENTAL**

**Materials and Apparatus**

All the raw materials used in this work were bought from Merck company. Spectroscopic analyses of mesoporous bare TiO$_2$ and S-doped TiO$_2$ were performed using Bruker-Eqinox 55 FT-IR spectrometer. Powder phase identification was performed by X-ray diffraction (XRD) obtained on Philips X-pert diffractometer using Cu Kα line (λ=1.54056Å) radiation, working with voltage and current of 40 kV and 40 mA. UV-vis spectrophotometer (Shimadzu UV 2100) was applied for the study of photodegradation reactions. Brunauer–Emmett–Teller (BET) specific surface area and Barret–Joyner–Halenda (BJH) pore size distribution of the S-doped TiO$_2$ nanoparticles was determined through nitrogen adsorption (Quantachrome NOVA 2200 e). The morphology of the prepared photocatalysts was investigated by scanning electron microscopy (SEM, Philips XL30). Oxford INCA energy-dispersive X-ray (EDX) was used to analyze the elemental constituents of S-doped TiO$_2$ nanoparticles.

**Preparation of S-doped TiO$_2$ and bare mesoporous TiO$_2$ nanoparticles**

Preparation of the S-doped TiO$_2$ nanoparticles was started by dissolving 3g of triblock copolymer EO$_{20}$PO$_{70}$EO$_{20}$ (P123) and a proper amount of thiourea in 170 mL of absolute ethanol under vigorous stirring. Another solution by mixing 0.02 mol of titanium tetraisopropoxide (Ti(OCH$_3$)$_2$)$_2$) (TTIP), 0.01 mol of acetylacetone, and 30 mL of ethanol was prepared then mixed with the first solution. The produced mixture was stirred for 2h. The produced dispersion was treated by HCl and pH adjusted to 1.5. The mixture was hydrolyzed in this acidic medium under 3h gentle stirring. After that, the solution was aged for 48 h to obtain a gel and then dried at 100°C for 24h. Finally, it calcined at 450°C for 1h.

Bare mesoporous TiO$_2$ was prepared by triblock copolymer EO$_{20}$PO$_{70}$EO$_{20}$ (P123) surfactant and titanium tetraisopropoxide as starting materials. 3 g of Pluronic P-123 was dissolved in 200 mL ethanol. The resulting solution was stirred for 1 h. Then 0.02 mol of titanium tetraisopropoxide under vigorous stirring was added to above clear solution. The mixture was maintained in a beaker for 5 h under gentle stirring. After that, the mixture was dried at 100°C for 32h to obtain a gel, and then calcined at 500°C for 1h.

**RESULTS AND DISCUSSION**

**Characterization of the photocatalysts**

Fig. 1 a and b exhibits FT-IR spectrum of the S-doped TiO$_2$ photocatalyst, before and after calcination. FT-IR spectrum of the S-doped TiO$_2$ before calcination (spectrum a) shows a broad peak at 3000–3600 cm$^{-1}$, which is assigned to the fundamental stretching vibration of hydroxyl groups (free or bonded) [13]. This is further confirmed by the weak band at about 1615 cm$^{-1}$ [14], which is as a result of bending vibration of coordinated H$_2$O as well as Ti–OH. The bending vibrational mode of water may appear as shoulders on the spectrum, as in 2800 cm$^{-1}$ [15]. It was reported that the vibration of the Ti–Oh bonds in the
TiO$_2$ lattice may be located at 500 and 430 cm$^{-1}$[13]. Other peaks are attributed to the P-123 surfactant. After calcinations (spectrum b), the absorption feature due to P-123 is almost removed, as evidenced by the significantly reduced characteristic bands at 2850, 2940 and 1080 cm$^{-1}$[16]. In the curve b, appearing shoulder at 1030 cm$^{-1}$ should be related to Ti–O–S, suggesting a conjugation effect between the S and Ti–O bonds. This finding is in accordance with Liu et al. report [17].

Differential thermal and thermogravimetric curves of the S-doped TiO$_2$ powder before the calculation are shown in Fig. 2. According to Thermogravimetry (TG) analysis, the weight loss consists of some distinct steps.

The first stage of weight loss corresponds to removal of physically absorbed water up to 100°C. The second step is regarding to evolution of CO$_2$ and carbonylsulfide at 140°C which reach the maximum rate

![FT-IR spectrum](image1)

**Fig. 1:** FT-IR spectrum of the S-doped TiO$_2$ photocatalyst, before (a) and (b) after calcinations.

![Thermogravimetry-differential scanning calorimetry (TG-DSC) curves](image2)

**Fig. 2:** Thermogravimetry-differential scanning calorimetry (TG-DSC) curves of the S-doped TiO$_2$ before calcination.
at 170°C and 180°C, respectively [18]. Also, Release of ammonia has been reported to occur from 170°C to 185°C. The significant exothermic peak in DSC curve at around 320°C corresponds to oxidation of NH₃ into N₂O and H₂O [18]. Finally, a weak thermal effect at 400–500 °C is accompanied by a diffuse exothermal peak at around 450 °C in the DSC curve which confirms the crystallization of the amorphous phase to anatase. The gel–crystalline conversion temperature has been reported to be 350–500 °C for TiO₂ prepared by the sol–gel method [19]. However, direct observation of the exothermic effect in the DSC curve has been difficult, probably because the crystallization temperature is usually close to the decomposition temperatures of residual surfactant, which are demonstrated as endothermic effects [8].

The crystalline structure of S-doped and bare TiO₂ nanoparticles was investigated by X-ray diffraction (XRD) measurements. The XRD patterns obtained from these samples are shown in Fig. 3. The X-ray diffraction results of samples indicated that both of S-doped and bare TiO₂ nanoparticles exhibited anatase phase of TiO₂ and doping with sulfur does not change the crystal structure of TiO₂. The average crystallite size of bare TiO₂ and S-doped TiO₂ samples were calculated by Scherrer’s equation to be 28.32 and 23.81 nm, respectively.

SEM images of S-doped TiO₂ and bare TiO₂ nanoparticles were presented in Fig. 4a and b. According to SEM images, the samples are granular and the obtained S-doped TiO₂ nanoparticles are approximately 10 nm in diameter. Combined with the result of XRD, it is obvious that the agglomeration was significant for bare TiO₂ compared to S-doped TiO₂. So, S-doping can reduce the agglomerate size of TiO₂. EDX analysis of S-doped sample (Fig. 5) exhibits that the prepared matter is composed of a small amount of sulfur element.

The optical band gap (Eg) in a semiconductor was determined by plotting (ahv)¹/m versus photon energy (hv) where a represents optical absorption coefficient and m represents the nature of transition. Now, m may have different values, such as 1/2, 2, 3/2 or 3 for allowed direct and indirect; and forbidden direct and indirect
transitions, respectively [20, 21]. The plots of $(ahv)^{1/2}$ for allowed indirect transitions of prepared S-doped TiO$_2$ (b) sample dispersed in ethanol versus photon energy are shown in Fig. 6. According to Fig. 6, the extrapolated optical absorption gap of S-doped TiO$_2$ is found to be 2.8 eV at room temperature. The visible light absorbance of S-doped TiO$_2$ is of great significance for its practical application point of view. The estimated indirect band gap of the S-doped TiO$_2$ reveals 0.5 eV red shift from value reported in literature for bare TiO$_2$ [22, 23]. This phenomenon could be related to the mixing of the 3p states of sulfur with TiO$_2$ valence band (VB) causing an increase of (VB) width [17]. In the bare TiO$_2$ crystal, the valence band (VB) and conduction band (CB) consisted of the Ti3d and O2p orbits. The Ti3d orbit was split in two part ($t_2g$ and $e_g$) states [20]. According to Umebayashi et al. obtained results, when TiO$_2$ was doped with sulfur, the 3p states of sulfur were somewhat delocalized. They also reported that the mixing of the 3p states with (VB) increased the width of the (VB) itself. So, sulfur doping makes TiO$_2$ band gap to be narrowing [21, 23].

Fig. 7 shows the pore size distribution curve of S-doped TiO$_2$ nanoparticles calculated from a desorption branch of the nitrogen isotherm obtained by BJH (Barrett-Joyner-Halenda) method and its corresponding nitrogen adsorption-desorption isotherms (inset). According to inset of Fig. 7, isotherm is of type IV which proves the presence of mesopores within the synthesized sample [24]. The specific surface area of prepared material calculated to be 181.3 m$^2$/g using the BET method and Pore size distribution curve of the mater obtained via BJH method revealed that the average diameter of the pores is 12.3 nm.

**Photocatalytic activity performance**

In photocatalytic experiments, 100 ml aqueous solution of Congored (5 ppm) containing 0.05 g of photocatalyst was taken in the glass vessel under visible or ultraviolet light irradiation. The good visible light response of S-doped TiO$_2$ and its strong adsorption capability due to mesoporosity result a
catalyst with improved photocatalytic activity. Photocatalytic degradation of Congored causes its absorption bands to decrease with time, indicating the destruction of its chemical structure. Decrease of Congored concentration in photocatalytic systems was monitored by measuring the absorbance of the samples via UV-Vis spectrophotometer in different intervals. Fig. 8a and b shows changes of the UV-Vis absorption spectrum of Congored after adsorption of dye on S-doped TiO$_2$ at dark and during photocatalysis under ultraviolet and visible lights. It is observed that the intensity of the visible light chromophore band of Congo red, $\lambda = 497$ decreased as time passed and disappeared after 5 min of irradiation under either ultraviolet or visible light sources. Moreover, according to Fig. 8, visible light chromophore band of Congored undergoes a remarkable red shift during the course of photocatalytic degradation. This phenomenon is due to aggregation of Congored molecules in acidic conditions which is in accordance with our former reports [25]. Experiments had shown that Congored molecules exhibit an aggregate feature in acidic aqueous solutions with a red shift compared to monomer in UV-Vis absorption spectra due to dimmer molecules [25]. So, it is obvious that S-doping could enhance the surface acidity of TiO$_2$. These acidic sites could act as an electron acceptor, which would enhance the separation of the photo-generated charge carriers and improve the photocatalytic performance. This result is in accordance with Fengyu et al. findings [26].

Fig. 9 shows photocatalytic efficiency of S-doped TiO$_2$ and bare TiO$_2$ for removal of dye solution as a function of time at $\lambda = 497$ nm under ultraviolet and visible lights. The efficiency or degree of photodecolorization $(X)$ is given by: $X = (C_0 - C)/C_0$, where $C_0$ is the initial concentration of dye, and $C$ is the concentration of dye at time $T$. The photocatalytic experiments using S-doped TiO$_2$ nanoparticles exhibited that not only sulfur modification makes the prepared photocatalyst to be active under visible light, but also more sensitive to ultraviolet light.

**CONCLUSION**

This research demonstrates the possibility of preparation of sol–gel mesoporous S-doped TiO$_2$ using titaniumtetraisopropoxide, thiocarbamide and pluronic P123 surfactant as raw materials. S-doped TiO$_2$ prepared by this method has a highly crystalline single anatase phase and exhibits a high degree of mesoporosity that corresponds to a large surface area resulting good photocatalytic properties. S- doping could lower the band gap of TiO$_2$ by the presence of an impurity state of S3p on the upper edge of TiO$_2$ valence band. So that, the optical band gap of prepared S-doped TiO$_2$ estimated to be 2.8 eV that shows a large red shift compared to bare type. The prepared S-doped TiO$_2$ has good photocatalytic properties towards Congoredazo dye either under ultraviolet or visible light sources due to its anatase phase, narrowing of the band gap, acidic surface sites and large surface area.

![Fig. 6: (ahv)$^{1/2}$ as a function of photon energy for prepared the S-doped TiO$_2$ sample dispersed in ethanol.](image-url)
Fig. 7: Pore size distribution curve of the S-doped TiO$_2$ nanoparticles - Inset: N$_2$ adsorption–desorption isotherm.

Fig. 8: Changes of UV-Vis spectrum of Congored in aqueous S-doped TiO$_2$ nanoparticles dispersion irradiated with a 30 W UV-C lamp light (a) and with two 18 W Osram lamps (b) as a function of time.

Fig. 9: Variation of photocatalytic activity of S-doped TiO$_2$ nanoparticles under ultraviolet and visible lights in comparison with bare TiO$_2$. 

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