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# A comparative run for visible-light-driven photocatalytic activity of anionic and cationic S-doped TiO<sub>2</sub> photocatalysts: A case study of possible sulfur doping through chemical protocol



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## ABSTRACT

Photocatalytic degradation of pollutant molecules delivered great challenges for sustainable development of green energy in the field of environmental science. For this purpose, growing interests have been made to witness the fast development of new photocatalysts with improved catalytic efficiency and to monitor the reaction mechanism at the atomic and molecular levels. Therefore, doping of semiconductor metal oxide (e.g. TiO<sub>2</sub>) with main group elements, especially with sulfur atoms (S), has gained much interest due to the introduction of a localized band between the conduction bands (CB) and valence bands (VB) that increase the absorbance in the visible light region. More interestingly, photocatalytic practices of the S-doped TiO<sub>2</sub> material are of pronounced significance due to photon-to-carrier conversion ability of S-doping beneath the band gap energy region of pure TiO<sub>2</sub>. Therefore, visible-light-activated S-doped TiO<sub>2</sub> photocatalysts were prepared via template free and low-temperature oxidant peroxide method (OPM) assisted hydrothermal treatments. Experimental findings have revealed the successful incorporation of sulfur atoms into TiO<sub>2</sub> crystal lattice and, as a result, substitution of Ti<sup>4+</sup> by S<sup>6+</sup> to form Ti-O-S bonds for cationic S-doping was observed. Whereas, in the case of anionic S-doping, substitution of  $S^{2-}$  by  $O^{2-}$  to form O–Ti–S bonds was achieved. More evidence was observed for the presence of chemisorbed sulfate groups on the surface of S-doped TiO<sub>2</sub> samples and inhibition of crystallite size growth by S-doping, and obviously, upsurge the absorbance in the visible light region. The photocatalytic activity of as-prepared 1-D nanorods shaped photocatalysts and the mechanism involved for the photodegradation of organic molecules (methyl orange and phenol) under visible-light irradiation were investigated by adding different scavengers into the system solution to capture active species. It was found that in cationic S-doped TiO<sub>2</sub> photocatalysts, chemisorbed hydroxyls (OH<sub>ads-</sub>) and photoinduced holes (h<sup>+</sup>) played a major role in photocatalysis. Whereas, in the case of anionic S-doped TiO<sub>2</sub> photocatalysts, electrons (e<sup>-</sup>) and photoinduced holes (h<sup>+</sup>) played the nearly equal role in photocatalysis.

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### 1. Introduction

In recent decades, development of one-dimensional (1-D) metal oxide semiconductor photocatalysts has been one of a promising subject for environmental remediation due to their unique stability, high reactivity, thermodynamic and transport properties [1]. Therefore, efforts have been made to prepare semiconductor materials specifically TiO<sub>2</sub> (titanium dioxide) in nanorods shape due to its high specific surface area, enhanced properties, easy acceptance,

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splitting to create hydrogen, and waste water purification etc. [2]. Another characteristic feature of TiO<sub>2</sub> is its ability to hold on the higher absorption of hydroxyl groups on the surface and facilitate the destruction of pollutants molecules (organic and inorganic) in an aqueous medium by interacting with the adsorbed hydroxyl groups [3]. However, intrinsic flaws of the TiO<sub>2</sub> limit the advantages of these unique properties as a photocatalyst due to its large band gap needs ultraviolet radiation to excite electron-hole pairs and a higher rate of recombination for photogenerated electron-hole pairs [4]. More importantly, the adsorption capacity of TiO<sub>2</sub> lies in the range of 4.8-63.5 mg/g deprived of photocatalytic reduction due to performed reaction conditions [2]. This may result in the inferior pollutants destruction efficiencies and feebler reproducibility due

cheap, and widespread applications in solar energy cells water

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to the fast ruination of the active surface area by self-aggregation [5,6]. Furthermore, the greater adsorption capacity is desired for TiO<sub>2</sub> to add its application range deprived of photocatalytic reduction [7]. Therefore, efforts have been focused to overcome these deficiencies by tweaking the band gap of TiO<sub>2</sub> to prolong the light absorption response in the visible-light region and to enhance the separation efficiency of photoinduced charge carriers. For this purpose, considerable research has been focused on doping TiO<sub>2</sub> crystal structure with either metal or nonmetal elements [8,9], loading noble metals [10,11] and coupling with narrow band gap semiconductors [12,13].

One of the important aspects of the photocatalytic activity of non-metal doped TiO<sub>2</sub> is to understand the keen relationship between the origins of absorption shift due to doping on the photocatalytic chemistry. First time, Asahi et al. assumed that N-doping creates a rise in valence band due to delocalized coupling between the orbital of O 2p and N 2p [14]. Whereas, in the recent reports, it has been proposed that a mid-gap level is generated above the valence band due to dopant atom orbitals [15]. Therefore, to understand the photocatalytic chemistry, these distinguished views are very important to elaborate for initiation of catalytic oxidation of pollutant degradation pathway on the surface of TiO<sub>2</sub>. As an overall lowering of oxidizing power for the generation of photoinduced holes on the surface of the pristine catalyst due to rising of valence band energy level, there should be possible interfere with the photocatalytic degradation reaction. On the other hand, the role of the chemically active and low energy hole (h<sup>+</sup>) trap is unclear due to isolated mid-gap level as compared to the core-valence band holes [16]. It is expected that absorption-excitation process in the low energy edge would probably direct the generation of such hole trapped. Nonetheless, these low energy holes trapped could also migrate towards the dopant center after UV excitation. Therefore, it is apparent that expected excitation over pristine TiO<sub>2</sub> might have lower oxidation potential due to rapid trapping and constraint of high charge mobility. Whereas, we might observe a wavelength dependence on the photocatalytic chemistry due to adsorbed substrates oxidation of pollutant molecules via competitive charge migration within the crystal lattice of TiO<sub>2</sub> [17].

In details, S-doping into TiO<sub>2</sub> crystal structure has been studied widely as it produced alike band gap tapering effect as observed in case of other non-metals doping [8,9], due to increased width of the valence band (VB) by mixing 3p states of the sulfur with the VB to narrowing the bandgap. Recently, it has been recognized that sulfur sources and preparation routes promote the ionic form of the S-doping. Ohno and other groups [18,19] reported that use of thiourea or sulfate as sulfur sources could incorporate sulfur atoms as cations by substitution of Ti ions in the S-doped TiO2 nanopowders. It was found that the cationic substitution of Ti<sup>4+</sup> by S<sup>6+</sup> was more favorable chemically due to their different ionic radius, and this substitution induced new states into the CB of TiO<sub>2</sub> from the S3s states just exceeding the valence states of O2p [18]. Whereas, Umebayashi et al. [20] have reported that use of TiS<sub>2</sub> as the sulfur source was more favorable for anionic doping of sulfur by replacing oxygen atoms of TiO<sub>2</sub> crystal lattice. In the following years, it was pledged that use of TiS<sub>2</sub> or CS<sub>2</sub> as sulfur sources also promote the anionic doping of sulfur atoms into TiO<sub>2</sub> crystal lattice [21]. They suggested that excess of sulfur oxidation occurred in the case of TiS<sub>2</sub> or CS<sub>2</sub> precursors and remaining sulfur naturally exists as S<sup>2-</sup> that favors the replacement of oxygen atoms in the O-Ti-O framework. More interestingly, some of the reports later suggest that use of thiourea as sulfur precursors could promote the formation of ionic form in the TiO<sub>2</sub> crystal lattice [22]. Many other studies have probe the photocatalytic activity of doped titania by using dyes as chemical inquiries to follow either easily oxidative or reductive degradation pathways as compared to other common pertinent pollutants. An

adverse peculiarity of dyes is that it also absorbs light in the visible region.

Perhaps, the most scorching research topic continues to be on S-doped TiO<sub>2</sub> photocatalysis. Generally, it is mentioned that nonmetal doping into TiO<sub>2</sub> is regarded as difficult and hectic route especially for large atomic radius S atom [30]. For this purpose, common routes adopted for the successful synthesis of anionic Sdoped TiO<sub>2</sub> materials include the oxidation of TiS substrate [31] and/or high-temperature heating of the titania film under the flow H<sub>2</sub>S gas [32]. Later on, both of these approaches have encountered serious limitation to control the concentration of doping elements into TiO<sub>2</sub> crystal lattice [30]. Afterward, different forms of Sol-gel method have been adopted for the synthesis of S-doped TiO<sub>2</sub> materials with controlled doping concentration, but Sol-gel method lacks serious drawback due to the use of expensive starting materials and worthless of reproducibility [33,25,31]. Nevertheless, to the best of our knowledge, no report has been cited yet for the synthesis of visible-light-activated S-doped TiO<sub>2</sub> nanorods by surfactant-free, low temperature and facile OPM route, which is expected to be both practically and scientifically important as compared to previously reported methods [21,23-25]. Herein, we have developed a simple OPM route for the synthesis of S-doped TiO<sub>2</sub> nanorods followed by crystallization through hydrothermal treatment. In this work, carbon disulfide and thiourea (S donating chelating ligands) were used as sulfur sources and were added into the stabilized Ti-peroxo complex solution to form a Ti-monometallic complex for the incorporation sulfur into TiO<sub>2</sub> crystal lattice and crystallized through hydrothermal treatment to prepare S-doped TiO<sub>2</sub> nanorods. The cited route proofed to be more feasible for the incorporation of S into TiO<sub>2</sub> crystal lattice due to the negative enthalpy of formation for the chelating agents to form a stable Ti-monometallic complex. The chelating ligands attained the stable geometry for the most accessible substitution among departing/incorporating atoms into TiO<sub>2</sub> crystal lattice to occur i.e. Ti<sup>4+</sup> substitution by S<sup>6+</sup> to form cationic doped samples and O<sup>2-</sup> substitution by S<sup>2-</sup> to form anionic doped samples. To evaluate the mechanism of photocatalytic activity of the nanorods under visible-light irradiation, either colored (MO) or colorless (phenol) dyes were used as model pollutants.

### 2. Experiment

#### 2.1. Sample preparation

All chemicals used in the synthesis of S-doped TiO<sub>2</sub> photocatalysts were of analytical grade and were used without any further purification. The undoped TiO<sub>2</sub> and cationic S-doped TiO<sub>2</sub> photocatalysts were prepared via OPM route as described in detail by our group [26,27] and were crystallized through the decomposition of Ti-peroxo complex via hydrothermal treatment. For the preparation of anionic S-doped TiO<sub>2</sub> photocatalysts, the cited method is modified with the introduction of carbon disulfide as S chelating ligands into the stable Ti-peroxo complex solution i.e. carbon disulfide is reported as an anionic S-doping source into TiO<sub>2</sub> crystal lattice [20,21]. Briefly described, the synthesis process starts with the dissolution of the specific amount (250 mg) of metallic Ti (99.7%, Aldrich) into a mixture of 80 mL(3:1 ratio) H<sub>2</sub>O<sub>2</sub>-NH<sub>3</sub> (both 29.0%, Synth) solution. The mixture solution was placed on ice-bath until the complete dissolution of metallic Ti and this results in the appearance of yellow transparent solution due to the formation of stable peroxytitanate ion [Ti(OH)<sub>3</sub>O<sub>2</sub>]<sup>-</sup> [28]. Different amount of thiourea and carbon disulfide was added to different batches of the peroxytitanate ion precursor solution with different starting Ti:S molar ratios of 1:0.01, 1:0.02 and 1:0.03. The basin precursor solutions were marked as CTO and ATO correspond to cationic and anionic S-doped TiO<sub>2</sub> samples. General scheme for the prepa-



Fig. 1. Proposed mechanism for the incorporation of S-doping into the TiO<sub>2</sub> crystal lattice.

ration and incorporation of S into the TiO<sub>2</sub> to form S-doped TiO<sub>2</sub> photocatalysts is presented in Fig. 1. A similar procedure was followed to prepare the pristine TiO<sub>2</sub> sample without the addition of any S-doping source and was marked by TO sample. To remove the excess of solvents, the precursor solution was heated to the boiling point and then placed on ice-water cooling bath for quick cooling to obtain the precipitate, which was vigorously stirred for overnight to vaporize any excess of solvents ( $NH_3$  and  $H_2O_2$ ). In the next step, a relevant amount (200 mg) of freeze-dried precipitate was suspended in the water for annealing in a temperature control hydrothermal cell. The synthesis conditions for all the samples were set for 4 h heating at 200 °C. After the treatment, a crystalline material was obtained by centrifugation of rapidly quenched samples in an ice bath. Finally, the samples were washed with doubly deionized water for several times until to neutral pH and then with isopropanol, and were dried for 8 h at 60 °C.

## 2.2. Characterization of material

X-ray powder diffraction (XRPD) was used for semi-quantitative phase analysis of the crystalline phases in the samples by using Rigaku D-Max 2500 diffractometer having Cu anode ( $\lambda_{Cu-K\alpha} = 1.5456$  Å). The range of 10° and 75° was investigated as the width of scanning routine to define peak position at 1 min at 2 $\theta$  between an angular pass of 0.02° and having an exposure time of 1 s. Scherer s equation and Lorentzian approximation were used to calculate the length of crystallographic coherence and full width at half maximum (FWHM) from (101) of monocrystalline Silicon wafer reflection [29]. PANalytical X'Pert Pro (NL)  $\theta/\theta$  diffractometer was used to collect data having 0.5° divergence and antiscattering slits, and a 15 mm copper mask with 0.04 rad Soller slits for the pathway of the incident beam. Diffracted arm consisted of fast

RTMS detector (PIXcel 1D, PANalytical). Field emission gun scanning electron microscope (FEG-SEM) used for characterization of surface morphology of samples as STEM FESEM, Zeiss Supra 35, at 4.0 kV. Brunauer–Emmett–Teller (BET) method was used to estimate specific surface area (SA) of the sample using Micromeritics ASAP 2000 adsorption analyzer operated at 77 K from physical adsorption of nitrogen. Raman spectra was obtained at room temperature from FT-Raman Bruker RFS100/S spectrometer operated between 100–1000 cm<sup>-1</sup> frequency range to the yttrium aluminum garnet laser (1064 nm line to 450 nm) at scans rate of 200. Cary 5 G spectrophotometer was used to measure the diffuse reflectance spectra of samples and Fourier transforms infrared spectra (FTIR) was obtained from PerkinElmer Spectrum 1000.

Osram radiation source was used to test the photocatalytic activity of samples for MO dye (Aldrich, 10.0 mg L<sup>-1</sup>) and phenol (sigma Aldrich,  $10.0 \text{ mg L}^{-1}$ ) photodegradation under visible-light irradiation, having a model of ModelL18/10 daylight with the intensity of 18W and at the 440 nm maximum intensity. For this purpose, 10 mg of photocatalyst was dispersed in 20.0 mL of the aqueous dye solution. Shimadzu-UV-1601 PC spectrophotometer was used for absorbance spectra of samples to monitor the degradation of dyes for different light exposure periods. Effect of dye adsorption on the catalytic activity of photocatalyst was tested before the photocatalytic test by soaking all samples in the aqueous dye solution for overnight. Different radical scavengers were added to the reaction system to monitor the role of active species in the photocatalytic degradation of MO including AgNO<sub>3</sub> (electrons scavenger), t-BuOH (•OH scavenger), Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (holes scavenger), and benzoquinone (•O<sub>2</sub> scavenger), respectively. An Auto Lab PGSt (Methrom, Autolab) was used for photocurrent measurements of S-doped TiO<sub>2</sub> photocatalyst using the three-electrode configuration from 302 N potentiostat-galvanostat system. The modified



**Fig. 2.** (a) Rate of MO photocatalytic degradation over pristine and S-doped TiO<sub>2</sub> photocatalysts, (b) phenol photocatalytic degradation kinetics over pristine and S-doped TiO<sub>2</sub> photocatalysts. Effect of scavenger's addition on the photocatalytic degradation of MO over (c) 2CTO and (d) 2ATO samples.

electrode was dipped into  $1 \text{ mol } L^{-1} \text{ Na}_2 \text{SO}_4$  (pH = 13.6) electrolyte and the system consist of working electrode consists of nanorods (active surface area of  $0.5 \text{ cm}^2$ ) covered by titanium foil, a reference electrode (Ag/AgCl/0.1 M KCl) and a counter electrode of Pt net. The electrochemical workstation (CHI750B) was used for linear sweep voltammograms was in simulated illumination source and the reversible hydrogen electrode (RHE) was used to monitor the potential of the photoelectrode.

## 3. Result and discussion

The undoped and S-doped TiO<sub>2</sub> photocatalysts were prepared by OPM route and crystallized through hydrothermal method. Prior to photocatalytic studies, the as-prepared samples were characterized by XPS, SEM/TEM, XRD, and DRS analysis to have better comparison and understanding of their expected visible-lightdriven photocatalytic activity for the degradation of the organic pollutants aqueous solution. It was noted that the color of the as-prepared samples changes with different S-doping level from gray-white (for pristine TiO<sub>2</sub>) to yellowish appearance for high sulfur concentration samples. Herein, we have reported a facile, low-temperature, surfactant-free and template-free OPM route assisted by hydrothermal treatment for the synthesis of anionic and cationic S-doped TiO<sub>2</sub> photocatalysts. More interestingly, the cited route is more compatible with an industrial process for the incorporation of the sulfur source and superior to the sol-gel synthesis which required post annealing process.

The photocatalytic activities of the as-prepared pristine and S-doped  $TiO_2$  photocatalysts were assessed for the degradation of organic pollutants (MO and phenol) aqueous solution under

visible light irradiation ( $\geq$ 420 nm). Prior to the photocatalytic experiment, a separate experiment has been performed to observe the adsorption-desorption equilibrium between the photocatalysts and MO molecules in dark condition as shown in Fig. 1S. The change in absorbance of MO aqueous solution over the as-prepared samples under the visible-light irradiation is shown in Fig. 2S. The photocatalytic efficiency was higher for the ambient amount of sulfur dopants samples (2CTO and 2ATO) than the other samples and showed the photocatalytic efficiency of 89.32% and 85.43% for 2ATO and 2CTO samples, respectively. The synergistic effect of S-doping levels into TiO<sub>2</sub> crystal lattice is proved beneficial for enhancing the photocatalytic activity. For the higher concentration of sulfur dopant samples, the photocatalytic efficiency is lower. This is expected due to increased concentration of dopant elements into the TiO<sub>2</sub> crystal lattice started to act as recombination center and increased the recombination rate of photogenerated electron-hole pair as observed for higher S-doping concentration samples (3CTO and 3ATO). Thus, the photocatalytic activity has been increased for S-doped TiO<sub>2</sub> photocatalysts to an ambient dopant concentration and rests unaffected at upper proportion. Therefore, it was critical to control the S-doping level into TiO<sub>2</sub> crystal lattice to obtain optimal photocatalytic efficiency. The MO photodegradation efficiency rate over as-prepared photocatalysts for the different interval of visible-light irradiation is shown in Fig. 2(a). The concentration of blank MO aqueous solution deteriorated dimly after 240 min under visible-light irradiation without adding any photocatalyst into the MO aqueous solution. This indicates that no photolysis of MO aqueous solution occurred under visible-light irradiation. In the case of TO sample, a dark adsorption is obtained from the photodegradation plot, which indicates that TiO<sub>2</sub> is not



Fig. 3. Proposed pathway for the photodegradation of MO.

active in the visible-light region. Whereas, higher visible-lightdriven photocatalytic efficiency was noted in the case of S-doped  $TiO_2$  photocatalysts with optimum S doping level after 240 min of visible-light irradiation. The photocatalytic activity of S-doped  $TiO_2$  photocatalysts remains unchanged after 240 min of visiblelight irradiation, which is expected due to the successful/brilliant partition of photogenerated charge carriers.

Phenol, a typical organic pollutant found in industrial effluent waste water and having no absorbance in visible-light region, was tested for photocatalytic activity experiment to avoid the chance of photosensitization of MO aqueous solution under visible-light irradiation. The change in absorbance of phenol aqueous solution under visible-light irradiation over S-doped TiO<sub>2</sub> samples is shown in Fig. 3S. The rate of phenol photodegradation over as-prepared samples under visible-light irradiation is shown in Fig. 2(b). It was observed that phenol follows similar photodegradation pathway as

was observed for MO photodegradation under visible light irradiation. This indicates the photocatalytic capability of anionic and cationic S-doped  $TiO_2$  photocatalysts for colorless organic compounds. Thus, indirect dye photosensitization process was not occurred on the surface of photocatalysts under visible-light irradiation. Therefore, photoinduced charge carriers separation could be the effective photodegradation mechanism due to band gap excitation in anionic and cationic S-doped  $TiO_2$  photocatalysts. The high TOC (total organic compound) removal rate (50%) indicates that the mineralization of phenol occurred over the surface of S-doped  $TiO_2$ photocatalysts.

A number of scavengers were added into the MO aqueous solution to detect the role of main active species in the photodegradation process over highly active cationic and anionic S-doped  $TiO_2$  photocatalysts (2CTO and 2ATO). The main active species which are involved in the mineralization of organic molecules includes; the



Fig. 4. The ratios of residue concentration based on the TOC and absorbance of (a) MO and (b) phenol solution mineralization over as-prepared samples under visible-light irradiation.



Fig. 5. Comparison of five consecutive recycling runs for the degradation efficiency of MO over (a) 2ATO and (b) 2CTO samples under visible-light irradiation.



Fig. 6. Schematic representation of mechanism involved in the photocatalytic degradation of MO.

hydroxyl radical (•OH), holes (h<sup>+</sup>), electrons (e<sup>-</sup>), and superoxide radical (•O<sub>2</sub><sup>-</sup>). Therefore, different scavengers were added separately on the photodegradation experiment of MO aqueous solution under visible-light irradiation for 120 min. They were added to eliminate the specific reactive species and to have clear authentication of the photocatalytic mechanism. For this purpose, sodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), silver nitrate (AgNO<sub>3</sub>), *tert*-butyl alcohol (t-BuOH) and benzoquinone (BQ) were added as scavengers into the individual MO aqueous solution for h<sup>+</sup>, e<sup>-</sup>, •OH, and •O<sub>2</sub><sup>-</sup>, respectively [34–37]. In particular, the addition of scavenger suppressed the photocatalytic degradation reaction of MO aqueous solution. The extent of decrease in photodegradation rate by individual scavenger helps to locate the role of corresponding active species taking part in the photo-oxidation mechanism.

Fig. 2(c) shows the substitution of •OH radical on 2CTO surface by the addition of t-BuOH (5 mmol  $L^{-1}$ ) into the MO aqueous solution. This indicates that •OH radicals taking an active part in the photo-oxidation reaction mechanism over CTO sample. Similarly, an addition of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (0.5 mmol  $L^{-1}$ ) significantly reduced the photodegradation efficiency of MO aqueous solution under visible light irradiation. This indicates that photogenerated hole (h<sup>+</sup>) has also participated in the photo-oxidation mechanism of MO aqueous solution. Furthermore, photodegradation efficiency did not vary noticeably with the addition of AgNO<sub>3</sub> (1 mmol  $L^{-1}$ ) and BQ (1 mmol  $L^{-1}$ ) for the similar interval of time (120 min).



Fig. 7. Photocurrent responses of the undoped and S-doped TiO<sub>2</sub> (2ATO and 2CTO) photocatalyst in 1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> (pH = 13.6) solution under visible-light irradiation.

Thus, the photogenerated electrons (e<sup>-</sup> located in the CB) and  $\bullet$ O<sub>2</sub><sup>-</sup> played the minor role in the photodegradation of MO aqueous solution over CTO sample. Interestingly, e<sup>-</sup> scavenging could limit its recombination rate during the photogeneration of e<sup>-</sup>-h<sup>+</sup> pairs and, therefore, a slight increase in the photodegradation rate was observed.

Fig. 2(d) shows the photodegradation plot of MO aqueous solution over 2ATO sample. It was observed that addition of t-BuOH  $(5 \text{ mmol } L^{-1})$  did not make a significant change to the photodegradation reaction. This indicates that less amount of hydroxyl ions are present on the surface of ATO samples. Whereas, an addition of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (0.5 mmol L<sup>-1</sup>) into MO aqueous solution reduced the photodegradation efficiency markedly from 89% to 55%. This suggests that photoinduced h<sup>+</sup> has played an important role for the visible-light photodegradation reaction of MO aqueous solution over ATO samples. In particular, the addition of h<sup>+</sup> scavenger promotes the photoinduced e<sup>-</sup> to play an active role for the photodegradation of MO aqueous solution. More interestingly, photodegradation efficiency of MO aqueous solution followed different mechanism over ATO and CTO photocatalysts. The addition of e<sup>-</sup> and •O<sub>2</sub><sup>-</sup> scavengers have hindered the rate of recombination for photoinduced e<sup>-</sup>-h<sup>+</sup> pairs.

One the basis of these findings, it could be inferred that photooxidation reaction of MO aqueous solution followed different pathway over the anionic and cationic S-doped TiO<sub>2</sub> photocatalysts. GC–LC analysis was performed on the different batches of MO aqueous solution taken during the course of photodegradation experiment for the different interval of visible-light irradiation as shown in Fig. 4S. A schematically representation for the most probable pathway for photodegradation of MO molecule over anionic and cationic S-doped TiO<sub>2</sub> photocatalysts under visible light irradiation is shown in Fig. 3.

To reconfirm the production of  $\bullet O_2^-$  under visible-light irradiation over S-doped TiO<sub>2</sub> photocatalysts, the photodegradation experiment of MO aqueous solution was performed under aerobic and anaerobic conditions. For this purpose, MO aqueous solution was sparked with air and/or nitrogen gas before illumination to the visible-light irradiation. For CTO samples, the photodegradation efficiency of MO aqueous solution was marginally changed after 120 min of visible-light irradiation in the aerobic and anaerobic condition. Whereas, in the case of ATO samples, the photodegradation efficiency of MO aqueous solution was largely affected due to the generation of  ${}^{\bullet}O_2^{-}$  radicals under visible-light irradiation. Thus, it was concluded that for CTO samples,  ${}^{\bullet}O_2{}^{-}$  did not take part in the photodegradation of MO aqueous solution, and •O<sub>2</sub><sup>-</sup> radicals did not exist in the photodegradation reaction of MO aqueous solution over cationic S-doped TiO<sub>2</sub> photocatalysts. However, in the case of anionic S-doped TiO<sub>2</sub> photocatalysts, the photodegradation efficiency of MO aqueous solution is dependent on the concentration of  ${}^{\bullet}O_2^{-}$  radicals. Thus, photocatalytic degradation of MO aqueous solution followed different pathway over anionic and cationic Sdoped TiO<sub>2</sub> photocatalysts.

The photodegradation of organic compounds (MO and phenol) was evaluated by total organic carbon (TOC) mineralization index during the photocatalysis experiment over anionic and cationic S-doped TiO<sub>2</sub> photocatalysts. Fig. 4(a) and (b) shows the ratio of residue concentration (TOC) of MO and phenol in solution as a function of visible-light irradiation time [38]. It was found that as-prepared S-doped TiO<sub>2</sub> photocatalysts showed substantial mineralization ability for organic compounds (MO and phenol) under visible-light irradiation. After 2 h of visible-light irradiation, the TOC removal rate of MO dye and phenol was reached to 48% and 44%, respectively. Thus, the photodegradation efficiency of S-doped TiO<sub>2</sub> photocatalysts is good enough to degrade not only the bleaching (chromophore groups) but also to mineralize the aromatic rings

in MO molecule to small fragments (CO<sub>2</sub> and H<sub>2</sub>O) and to evade secondary pollution for industrial applications.

The stability of the S-doped TiO<sub>2</sub> photocatalysts was studied by performing repeated photodegradation experiments of MO aqueous solution under the same conditions. Fig. 5(a) and (b) show the photocatalytic activity of 2ATO and 2CTO samples for degradation of MO(10 mg/L) after five consecutive cycles with the minor change in the photodegradation efficiency. It is noteworthy that photocorrosion did not occur and as-prepared photocatalysts are stable to show enhanced photocatalytic activity. Thus, the recycling ability of S-doped TiO<sub>2</sub> photocatalysts has shown an improved constancy for higher photocatalytic activity. Fig. 6 shows the schematic representation of mechanism involved in the photocatalytic degradation of organic compounds on the surface of S-doped TiO<sub>2</sub> photocatalysts. The substitution of Ti<sup>4+</sup> by S<sup>6+</sup> in CTO samples, where thiourea was used as a source of sulfur doping, would be a kind of transitionmetal ion doping into the  $TiO_2$  crystal lattice [39]. This results in the creation of an intra-band-gap state between VB and near to the CB edges that encourage the visible-light absorption. As a result, this substitution of Ti<sup>4+</sup> ions by S<sup>6+</sup> ions has created a charge disparity in the bulk TiO<sub>2</sub> crystal structure. The resulted charge disparity attracts a number of anions (e.g. hydroxyl ions) from the organic pollutant aqueous solution towards the surface of the photocatalyst and assisted in the neutralization of the additional positive charge [40]. Whereas, the visible-light absorption in the CTO sample is expected due to the creation of confined sulfur mid-gap levels from the replacement of Ti<sup>4+</sup> by S<sup>6+</sup> into the TiO<sub>2</sub> crystal lattice below the Ti 3d CB and likely narrow the band-gap level as compared to pristine TiO<sub>2</sub>. Another interesting factor is the generation of photoinduced h<sup>+</sup> and it played an important role to generate •OH radical from the oxidation of hydroxyl ions in the solution. The similar kind of finding was observed in the h<sup>+</sup> scavenger experiment. As we know that hydroxyl radicals are the most active species to perform the photo-oxidation reaction. The creation of charge imbalance into the structure of bulk TiO<sub>2</sub> crystal lattice enabled the adsorption of more hydroxyl ion on the surface of the photocatalyst and has facilitated them to capture photoinduced h<sup>+</sup> to form hydroxyl radicals. The newly generated •OH radical played a major part in the mineralization of organic pollutants. In the sideway, partial e<sup>-</sup> transferred from less electronegative sulfur atoms to more electronegative oxygen atoms through Ti-O-S bonds. As a result, electron deficient sulfur atoms hold on photoinduced e<sup>-</sup> for more time to reduce the recombination rate and facilitated h<sup>+</sup> to spend more time on the surface of the photocatalyst to generate more •OH radical, and resulted in enhanced quantum efficiency. Therefore, the higher photocatalytic efficiency of the CTO samples could be explained due to an involvement of above possible parameters. These are main parameters to sum-up the enhanced photocatalytic activity of cationic S-doped TiO<sub>2</sub> photocatalysts such as; (1) quick rate of separation for photoinduced charge carriers, (2) enhanced absorbance in the visible-light region due to partial substitution of Ti<sup>4+</sup> by S<sup>6+</sup> and surface adsorbed hydroxide ions capture the excited holes to form •OH radicals, (3) partial transfer of electrons from S to O atoms due to formation of Ti-O-S bonds, (4) and inhibition of photoinduced e<sup>-</sup>-h<sup>+</sup> pairs recombination rate due to capture of e<sup>-</sup> by electron deficient S atoms.

For anionic S-doped TiO<sub>2</sub> photocatalysts, we employed CS<sub>2</sub> as the sulfur originators. Higher photodegradation efficiency and narrow band gap were observed in the case of ATO samples from the photocatalytic experiments of organic pollutants (MO and phenol) and DRS spectra as compared to the pristine and CTO samples. It is expected that anionic S-doping into the bulk of TiO<sub>2</sub> lattice structure has generated more oxygen defects/vacancies and it has shifted the absorption edge in the visible-light region [41,42]. This also inhibits the recombination rate of photoinduced  $e^--h^+$  pair's by capturing the photoinduced  $e^-$ . Thus, enhanced the quantum



Fig. 8. (a) to (c) SEM images of undoped TiO<sub>2</sub> (d) EDX of S-doped TiO<sub>2</sub> sample, (e) to (g) HR-TEM analysis of S-doped TiO<sub>2</sub> sample, and (h) FFT of S-doped TiO<sub>2</sub> sample.

efficiency. As discussed above for anionic S-doped samples, the transfer of photoinduced e<sup>-</sup> at the surface of the photocatalyst prompts the degradation of MO aqueous solution by producing hydroxyl and superoxide radicals via reacting with adsorbed O<sub>2</sub> and H<sub>2</sub>O. Another important factor is the formation of Ti–O–S and O-Ti-S bonds in the TiO<sub>2</sub> crystal structure. These bonds tempt fresh impurity levels among the VB and CB bands that result in the promotion of more photoinduced h<sup>+</sup> to produce active radicals (hydroxyl and peroxide) due to the transfer of more photoinduced e<sup>-</sup> to the CB under visible-light irradiation. Additional characteristics for enhanced photocatalytic activity of anionic S-doped TiO<sub>2</sub> photocatalysts include; (1) presence of (101) facets entertained the photoinduced electron as reservoir to slow down the recombination rate of photoinduced electron-hole pairs and to produce •O<sub>2</sub>by reduction of surface adsorbed  $O_2$  atoms, (2) anisotropic shape of nanorods having larger surface area facilitate the fast transport of photoinduced charge carriers to pass through different longitudinal directions for successive photocatalytic oxidation reactions, (3) creation of oxygen vacancies causes red shift for optical energy

gap, (4) and formation of stabilized anatase structure by anionic S-doping enhanced the photocatalytic activity.

Furthermore, the cylindrical-shaped nanorods structures have many porous channels on the surface which endorse their photocatalytic activity. The responses of transient photocurrent of S-doped TiO<sub>2</sub> modified electrode confirmed this phenomenon when irradiated with visible-light (Fig. 7). The S-doped TiO<sub>2</sub> modified electrodes showed enhanced photocurrent response as compared to undoped TiO<sub>2</sub> electrode under visible-light irradiation. The enhanced photocurrent response is generated due to more efficient separation of photoinduced charge carriers and fast transfer pathway through the nanorods structure. As a result, 1-D S-doped TiO<sub>2</sub> under visible-light irradiation.

Fig. 5S shows the XRD diffraction patterns for anatase  $TiO_2$  and S-doped  $TiO_2$  photocatalysts. The presence of well-defined and broad diffraction peak at (101) crystal plane revealed that diffraction planes are alignment along the favored (101) direction for anatase pristine sample. No badge of diffraction peaks was noted



Fig. 9. XPS survey spectra of undoped and S-doped TiO<sub>2</sub> nanorods, (b), (c) and (d) XPS spectra for Ti3p, O1s and S2p region, respectively.

which corresponds to the presence of rutile phase in the XRD diffraction patterns of as-prepared samples. It was evident that sulfur doping could inhibit the growth of rutile phase. The Debye-Scherrer equation was used to calculate the average crystallite size of the pristine and S-doped samples and is given in Table 1. It was found that S-doping strongly influenced the anatase degree of crystallization in the photocatalysts. For higher concentration of S-doping levels, the crystallinity of samples slightly decrease and is an indication of successful S-doping into TiO<sub>2</sub> crystal lattice as reported for other non-metal doping e.g. for nitrogen doping [43,44]. Meanwhile, systems with higher crystallinity are established to ensure superior photocatalytic activity as compared to ailing crystalline systems and thus, the higher concentration of doping element could halt the photocatalytic activity [45]. The lattice parameters for the pristine sample having tetragonal crystal system were slightly varied after S-doping samples and were ascribed due to an assimilation of the larger sulfur atoms into the crystal lattice of TiO<sub>2</sub>.

Fig. 8(a–c) shows the FE-SEM images of the undoped  $TiO_2$  sample that consist of slanting or vertically allied uniformly grown nanorod arrays. The pristine nanorods have the uniform rectangular cross section and diameter in the range of 20–30 nm with the distinctive length of nanorods are about 50–70 nm. From the FE-SEM images, no clear noticeable change in the morphology of nanorods was observed for the pristine and S-doped TiO<sub>2</sub> samples.

More FE-SEM images of anionic and cationic S-doped TiO<sub>2</sub> samples are shown in supporting information Fig. 6S.

It was observed that the S-doped TiO2 nanorods consist of hierarchical core-shell structure and are compactly aligned having an anatase phase. From the EDX mapping of S-doped TiO<sub>2</sub> samples (see Fig. 7S), it was observed that sulfur atoms are equivalently disseminated in the TiO<sub>2</sub> crystal lattice structure. EDX analysis was performed to analyze the S-doping concentration in the asprepared samples as shown in Fig. 8(d). It was found that sulfur atoms are almost uniformly distributed along the axial and radial direction of nanorods. A sharp peak at about 2.45 keV was observed for the sulfur element in the S-doped TiO<sub>2</sub> samples and was ascribed due to the presence of small amount of S dopant element. This peak is absent in the EDX spectrum of pristine sample. More interestingly, the edges and surfaces of S-doped TiO<sub>2</sub> nanorods started to develop out of flatness for higher sulfur content (3ATO and 3CTO). It is expected due to the decrease of overall crystallinity to a certain level. TEM and HR-TEM analysis were used for structural characterization of pristine and S-doped TiO<sub>2</sub> samples. The TEM and HR-TEM images of S-doped  $\mathrm{TiO}_2$  photocatalysts confirm the presence of the anatase phase with hierarchical core-shell nanostructure. The calculated values for average diameter and length of nanorods are consistent with the FE-SEM results. Fig. 8(g) shows the HR-TEM image of the pristine sample which comprises of the single-crystalline anatase structure with well-defined/resolved inter-planer spacing and having lattice fringes of about 0.352 nm.

The dominant facets, expected from the symmetry of crystallographic anatase  $TiO_2$  structure was corresponding to the (101) planes and, which is considered as the most stable anatase  $TiO_2$ facets plane for thermodynamically [46]. Furthermore, the HR-TEM image demonstrates the high crystalline nature of the as-prepared samples.

Recently, it was found that the reductive (101) facets of anatase nanocrystals facilitate the reduction of  $O_2$  to  $O_2^{\bullet-}$  by providing a highly reactive surface and were likely acting as a reservoir for photogenerated electrons [47,48]. Likewise, the sole structure features of octahedral anatase crystals having (101) facets assist the oxidative reduction/disintegration of pollutant molecule and enabled the higher photocatalytic activity [49]. Therefore, we could expect that S-doped TiO<sub>2</sub> photocatalysts with preferential reductive (101) facets displayed important role to improve the photocatalytic efficiency by lowering the rate of recombination for photogenerated electron-hole pairs. Conversely, it was noted that particles having anisotropically shaped including nanorods [50], nanobelts [51], and nanotubes [52] have a lower rate of electron-hole pairs recombination due to their structural characteristic of providing a quick pathway for transport of charge carriers alongside the longitudinal track. Thus, this results in enhanced mobility for charge carriers. We can infer from these findings that S-doped TiO<sub>2</sub> nanorods with anisotropically long shape are efficient materials for relatively ambient separation of photogenerated electron-hole pairs and for subsequent supply of charge carriers towards reactive sites to carry out photocatalytic reactions.

High-resolution XPS analysis was used to quantify the existence of sulfur atoms in the  $TiO_2$  crystal lattice. Fig. 9(a) shows wide-scan survey spectra for the pristine and S-doped  $TiO_2$  photocatalysts, which consist of Ti, O, and S elements corresponding to Ti2p, O1s, and S2p peaks, respectively. The presence of carbon peak is ascribed due to XPS instrument as adventitious hydrocarbon and no peak corresponding to nitrogen atoms was observed in the XPS spectrum. It was observed from the XPS spectra in the S2p region that sulfur atoms are presents for the ATO and CTO samples. Whereas, for the pristine sample, there is no speak for S atom presents in the S2p region. This finding suggests that sulfur atoms have been effectively introduced into the crystal lattice of TiO<sub>2</sub> photocatalyst.

It can be seen in the XPS spectra of Ti 2p for pristine and S-doped photocatalysts that comprise of two peaks for Ti 2p<sub>3/2</sub> (458.3) and Ti  $2p_{1/2}$  (464.1 eV) as shown in Fig. 9(b). It was found that the binding energy of Ti 2p slightly shifted negatively after S-doping as compared to pristine TiO<sub>2</sub> photocatalyst and which is possibly due to the rise of interaction between coordinated SO<sub>4</sub><sup>2–</sup> anions to titanium atoms. This interaction drags more electrons towards Ti atoms. As is mentioned above, that this interaction is more favorable due to the formation of O-Ti-S and Ti-O-S bonds by anionic and cationic Sdoping into TiO<sub>2</sub> lattice and enable the most electronegative atoms (Ti and O) to drag electrons from the sulfur atoms that cause a charge disparity. This results in shifting of binding energy negatively due to the formation of new band energy structure [53,54]. Fig. 9(c) shows the O1s XPS spectrum that consists of two peak fittings. The main peak ascribed to lattice oxygen appeared at about 529.6 eV of lower binding energy and peak at higher binding energy (530.8 eV) is attributed to the oxygen atoms of sulfate groups and surface adsorbed hydroxyl groups [54].

Fig. 9(d) shows the XPS spectra for the 2CTO and 2ATO samples. For 2CTO sample, thiourea was used as precursor for S-doping, and it showed two strong broadened peak probably due to spin–orbit coupling [55], of the split sublevels of 2p3/2 and 2p1/2 states, at 168.3 and 169.5 eV with a separation of 1.4 eV corresponding to presence/incorporation of S<sup>6+</sup> into TiO<sub>2</sub> lattice by partial substitution of Ti<sup>4+</sup> to form Ti–O–S bonds [40]. In order to eliminate the chance of presence/indication of physisorbed sulfur species from the experimental process on the surface of the photocatalyst, the

S-doped TiO<sub>2</sub> samples were washed vigorously with double deionized water prior to the XPS analysis. The XPS findings suggest that none of the physisorbed sulfur species such as SO<sub>4</sub><sup>2-</sup> are present on the surface of photocatalysts and  $SO_4^{2-}$  are chemically coordinated at the surface of S-doped  $TiO_2$  nanorods. The probable coordination binding between TiO<sub>2</sub> lattice and SO<sub>4</sub><sup>2–</sup>, which could play a vital role as an efficient electron trapper (see Fig. 1). It was reported that thiourea is mainly responsible for cationic S-doping due to the substitution of  $Ti^{4+}$  by  $S^{6+}$ , and is in accordance with our results as shown in Fig. 9(d) [40,19,24]. The insertion of S atoms as cations into TiO<sub>2</sub> crystal lattice generates a charge disparity that results in to bring the additional positive charge on the surface of the photocatalyst which is nullified by the free hydroxide ions [40]. As a result, photoinduced holes on the surface of photocatalysts are captured by adsorbed hydroxide ions to form hydroxyl radical, an important active species to bring photocatalytic reaction for the degradation of pollutant molecules. More interestingly, the relatively larger atomic radius of Ti<sup>4+</sup> (0.64 Å) as compared to S<sup>6+</sup> (0.29 Å) might cause a decrease in the crystal size due to the replacement of Ti<sup>4+</sup> by S<sup>6+</sup> in S-doped TiO<sub>2</sub> samples (CTO). By comparison of the XPS finding to the XRD result, we have observed that the lattice parameters for CTO samples were smaller than the pristine sample.

The XPS spectrum of 2ATO sample in the S 2p region corresponds to the binding energy at about 162.7 eV for sulfur atoms and has been assigned to the replacement of O<sup>2-</sup> by S<sup>2-</sup> to form Ti-S bonds [20,23,31]. This peak is regarded to the presence of  $S^{2-}$  at lower valence state for sulfur atoms in the ATO samples. It was found that use of either CS<sub>2</sub> or TiS<sub>2</sub> precursors for S-doping are mainly responsible for anionic form in the S-doped TiO<sub>2</sub> samples [21,56]. Therefore, the presence of sharp XPS peak at about 162.7 eV in the S 2p region for 2ATO sample is accredited to the S<sup>2-</sup> species due to the exchange of O<sup>2-</sup> by S<sup>2-</sup> during the curse of S-doping into the crystal lattice of TiO<sub>2</sub>. Umebayashi et al. [23] and Hebenstreit et al. [57] reported that a binding energy of 162 eV could be assigned to the substitutional sulfur for oxygen either anatase and/or rutile phase S-doped TiO<sub>2</sub>. Thus, sulfur atoms from the CS<sub>2</sub> precursor replaced oxygen atoms to form Ti-S bond. As expected, the anionic S-doping into the TiO<sub>2</sub> crystal lattice would result in changing the unit cell parameters of pristine TiO<sub>2</sub> due to a difference in the ionic radius of  $S^{2-}$  (1.7 Å) and  $O^{2-}$  (1.22 Å). As a result, the unit cell parameters of 2ATO sample after successful substitution of O<sup>2-</sup> by S<sup>2-</sup> were slightly increased than the pristine and CTO samples, probably due to the incorporation of  $S^{2-}$  with larger ionic radius into the crystal lattice of TiO<sub>2</sub>, which is in accordance with the XPS results.

Fig. 8S shows the FT-IR spectra of pristine and S-doped TiO<sub>2</sub> samples. It was attributed that the stretching vibration of Ti-O-Ti bonds are mainly responsible for the generation of an intense broadband at around 900–700 cm<sup>-1</sup>. Moreover, the characteristic peaks at around 1080 and 1423 cm<sup>-1</sup> for S-doped TiO<sub>2</sub> samples are ascribed due to coordinated sulfate groups [58]. The presence of SO stretching vibration is attributed at about 1365 cm<sup>-1</sup> [59] in the S-doped TiO<sub>2</sub> samples. As discussed in the XPS analysis that these peaks further support the presence of chemically coordinated sulfate groups in the S-doped TiO<sub>2</sub> samples. It is noted that distinct band was observed for Ti-O-S bonds at 1043 cm<sup>-1</sup> for CTO sample [60]. Furthermore, the presence of Ti–S stretching vibration is confirmed from absorbance band at 1135 cm<sup>-1</sup> in the ATO sample [59]. These findings further confirmed the successful substitution of O<sup>2-</sup> by S<sup>2-</sup> in anionic S-doping and substitution of Ti<sup>4+</sup> by S<sup>6+</sup> in the cationic S-doping TiO<sub>2</sub> samples. Whereas, in the case of the pristine sample, no such bands corresponding to either Ti-S or S-O/S=O was observed, which indicate that opted OPM route is superior to number of early reported methods for the synthesis of S-doped TiO<sub>2</sub> and it limits the use of expensive organic compounds to prevent the involvement/doping of impurities from synthesis

1	2	

Table 1
Structural parameters and photocatalytic performance of TO. ATO and CTO samples.

Sample	Ti:S molar ratio	Crystallite size (nm)	Lattice constants of cell unit (Å)		SA (m²/g)	V <sub>p</sub> (cm <sup>3</sup> /g)	Band gap (eV)	IEP	Photodegradation efficiency (%)
			(a)	(c)					
ТО	1:0.0	19	3.7852	9.4558	71	0.41	3.09	4.30	5
1ATO	1:0.01	20	3.7859	9.4837	77	0.43	2.91	4.40	81.38
2ATO	1:0.02	22	3.7865	9.5182	90	0.44	2.86	4.70	89.32
3ATO	1:0.03	23	3.7916	9.5203	79	0.48	2.82	5.10	83.57
1CTO	1:0.01	17	3.7803	9.4505	80	0.42	2.94	4.33	82.19
2CTO	1:0.02	16	3.7758	9.4489	88	0.43	2.88	4.35	85.43
3CTO	1:0.03	14	3.7737	9.4453	81	0.45	2.85	4.39	81.21

steps. The reproducibility of the as-prepared material through OPM route with the same phase composition make this another advantage over other previously reported methods. More interestingly, intense broad peak at around 1640 cm<sup>-1</sup> was observed corresponding to OH bending vibrations in the CTO sample, and the broad band is more intense as compared to pristine and ATO samples. Thus, we can conclude that cationic S-doping favored the presence of more hydroxyl groups on the surface of the photocatalyst as compared to anionic S-doping and this could enhance the photocatalytic activity of cationic S-doped TiO<sub>2</sub> photocatalysts.

Fig. 10 shows the UV-vis diffuse reflectance spectra of 1-D undoped and S-doped TiO<sub>2</sub> nanorods to investigate the optical absorptions. The sulfided surface shows stronger solar light absorbance in visible-light region for the S-doped TiO<sub>2</sub> photocatalysts as compared to pristine sample. Compared to the pristine sample, all S-doped TiO<sub>2</sub> samples show significantly improved absorptions in the visible region while highest absorption edge was observed near 400 nm for higher sulfur level samples and is ascribed due to S-doping effect. This absorption enrichment is greatly reliant on the S-doping levels and reaches to the sulfidation saturation for higher sulfur concentrated samples and prolongs the light absorption from UV into the visible region and broadens the solar spectrum absorption due to the successful incorporation of S dopants. From the comparison of absorption spectra for pristine and S-doped TiO<sub>2</sub> nanorods, it was demonstrated that creation of oxygen deficiencies could enhance the wide-spectrum absorption due to the high electron concentration in the surface layer. Inset of Fig. 10 shows the plot of Kubelka-Munk function versus energy of light for the pristine and S-doped samples. For the pristine TiO<sub>2</sub>



**Fig. 10.** DRS absorbance spectra of pristine and S-doped  $TiO_2$  samples, Inset shows the band-graph plot of all samples.

sample having a large value of band gap (3.09 eV), no appropriate light absorbance was observed in the visible region. Whereas, the S-doped TiO<sub>2</sub> nanorods (ATO and CTO) showed enhanced light absorbance in the visible region due to the decrease in band gap energy by S-doping to 2.82 eV (ATO) and 2.85 eV (CTO). It is expected that this alternation/reduction in band gap energy is due to the incorporation of the sulfur atoms into the bulk of  $TiO_2$  and, as a result, the electronic and crystal structure of the doped material altered which result in strong absorption edge into the visible light region. A broad absorption background was observed for both doped samples (ATO and CTO) as compared to the pristine sample in the visible region and is ascribed due to the creation of new bonds (Ti-O-S or O-Ti-S) into TiO<sub>2</sub> crystal structure, as discussed in the XPS results and discussion session. This could facilitate the partial flow of electron from low electronegative atom (S) towards higher electronegative atoms (Ti and O). Furthermore, this could result in the creation of a new low-valence state [61] between the valence and conduction band of TiO<sub>2</sub> and enhanced the light absorption in the visible region greater than 500 nm.

The photocatalytic ability of nanoparticle for the degradation of organic compounds depends on the particle size distribution in solution and aggregation in solution caused the derivation of measured particle size from the actual powder form. Therefore, the zeta potential measurements were calculated for undoped and Sdoped TiO<sub>2</sub> photocatalysts as shown in Fig. 9S. Table 1 shows the measured value of the isoelectric point (IEP) for undoped and Sdoped TiO<sub>2</sub> photocatalysts. As expected, undoped TiO<sub>2</sub> sample has the lower zeta potential as compared to S-doped TiO<sub>2</sub> samples. For anionic S-doped TiO<sub>2</sub> samples, the increase in the IEP value was more prominent with the increase of S-doping level and shifted towards negative pH (<6.8). Whereas, for cationic S-doped TiO<sub>2</sub> the increase of IEP value is not so convenience for negative pH [62]. As a result, the surface of S-doped TiO<sub>2</sub> photocatalysts is engaged by the more net charge as compared to undoped TiO<sub>2</sub> and make it more feasible for organic compound to approach on the surface of photocatalysts. Therefore, an increase in the S-doping concentration resulted in the increase concentration of approaching organic compounds on the surface of photocatalyst due to increasing the number of net charge on the surface of the photocatalyst. One can predict from these findings that one factor for the enhanced photocatalytic degradation efficiency of S-doped TiO<sub>2</sub> nanorods in solution is due to increasing net charge on the surface as compared to undoped TiO<sub>2</sub>. The surface adsorbed hydroxyl groups increase the wettability and contact angles of S-doped samples due to the photocatalytic oxidation reaction of organic compounds on the surface. Conversely, the pH of solution played an important part for the enhanced photocatalytic performance of S-doped TiO<sub>2</sub> in an aqueous medium. Higher zeta potential suggest increased the number of surfaces adsorbed organic compound for S-doped TiO<sub>2</sub> photocatalysts to perform photodegradation reactions [63]. More interestingly, after an ambient concentration of S-doping level, the photocatalytic efficiency started to decrease due to higher surface wettability and higher surface net charge [64].



Fig. 11. N<sub>2</sub> absorption-desorption plot of pristine and S-doped TiO<sub>2</sub> samples, inset shows the pore volume distribution graph of TiO<sub>2</sub>.

The incorporation of S atoms into the TiO<sub>2</sub> crystal structure was further confirmed with the help of Raman spectroscopy. Fig. 10S shows the Raman spectra for pristine and S-doped TiO<sub>2</sub> samples. The Raman spectra was executed in the range of 100–800 cm<sup>-1</sup> and corresponds to the existence of pure anatase phase. These findings are consistent with XRD results for all samples and further confirmed the absence of any other phase impurity. The six Raman active modes  $[3E_g + 2B_{1g} + A_{1g}]$  are assigned to the anatase phase at frequencies  $143 \text{ cm}^{-1}$ ,  $197 \text{ cm}^{-1}$ ,  $397 \text{ cm}^{-1}$ ,  $514 \text{ cm}^{-1}$ , and  $638 \text{ cm}^{-1}$  [65]. It was found that the main anatase Raman active band sharpened with the increase of S-doping concentration at about  $143 \text{ cm}^{-1}$  ( $E_g$  mode) and attributed to a considerable blue shift in the Raman band. The characteristic shift and broadening of Raman peaks are attributed due to change in the original symmetry/structure of TiO<sub>2</sub> crystal lattice caused by S-doping.

The Raman peak intensities increased with sulfur concentration and is expected due to Raman resonance effect of TiO<sub>2</sub> due to change in electronic environment [66]. Fig. 11 shows the nitrogen adsorption–desorption isotherm measurements for pristine and S-doped TiO<sub>2</sub> photocatalysts to characterize the specific surface areas. It is well-known that high surface area enhanced the photocatalytic activity due to increased number of active sites per unit mass for photocatalysts (ATO and CTO) was much larger than the pristine sample. Furthermore, the small diameter of TiO<sub>2</sub> photocatalyst reduce the detrimental size effects by tumbling the distance between electron–hole pair which limits the recombination rate of the free hole at the surface with a trapped electron.

Thus, the proposed pathway for S-doping into the TiO<sub>2</sub> crystal lattice and arrangements of impurity dopant atoms (S) into the TiO<sub>2</sub> crystal lattice (see Fig. 1) are confirmed by the XRD, XPS, EDX and FT-IR findings. In fact, S-doping precursors (thiourea and CS<sub>2</sub>) played an important role in the creation of valence states of sulfur and correspondingly helped in the incorporation of S atoms into the TiO<sub>2</sub> structure to form cationic and anionic S-doped TiO<sub>2</sub> nanorods. The negative enthalpy or formation for the chelating ligand (CS<sub>2</sub>) enabled to replace oxygen atoms in the TiO<sub>2</sub> crystal lattice. In detail, the formation of Ti-O-S bonds due to substitution of S<sup>6+</sup> for Ti<sup>4+</sup> cation generated charge imbalance between the neighboring atoms

(S and O), and surface adsorbed negatively charged hydroxide neutralized the positive charge at the surface of the photocatalyst. Some chemisorbed sulfate groups ( $SO_4^{2-}$ ) were also present on the photocatalyst surface. In the case of anionic S-doped TiO<sub>2</sub> photocatalyst, sulfur atoms substitute the oxygen atoms in the O–Ti–O network to form O–Ti–S bonds and sulfur atoms exist in the S<sup>2–</sup> valence state in the crystal lattice of TiO<sub>2</sub>.

## 4. Conclusion

A facile, surfactant-free chemical route has been developed to synthesize anionic and cationic S-doped TiO<sub>2</sub> photocatalysts via OPM assisted hydrothermal treatment. The as-prepared Sdoped TiO<sub>2</sub> photocatalysts demonstrated worthy visible-light photocatalytic activity and mineralization performance for organic compounds (MO and phenol) as compared to pristine sample. It was found that S<sup>6+</sup> substituted for Ti<sup>4+</sup> in cationic S-doped sample reduced the crystalline grain size due to a smaller ionic radius of S<sup>6+</sup> as compared to Ti<sup>4+</sup>. Whereas, S<sup>2-</sup> substitution for O<sup>2-</sup> increased the crystalline grain size in anionic S-doped TiO<sub>2</sub> samples and reduced the BE shifting of parent atoms (Ti and O) peaks due to higher electronegativity difference, which consequently enhanced the absorbance in the visible-light region. The surface adsorbed  $\mathrm{SO_4^{2-}}$  groups were observed for both samples and intimated due to either chemisorptions or surface oxidation of sulfur atoms. The anionic S-doped TiO<sub>2</sub> photocatalysts showed higher photocatalytic activity due to reduced crystallite size and scavengers test revealed that holes and electrons played the nearly equal role for its higher photocatalytic activity. Whereas, in the case of cationic S-doped TiO<sub>2</sub> photocatalysts the creation of new impurity levels could be mainly responsible for enhanced higher photocatalytic efficiency due to oxidation of surface chemisorbed hydroxyl ions by photoinduced holes. Therefore, it was revealed that doping levels and degree of surface chemisorbed hydroxylation are largely accountable for the enhanced photocatalytic activity of S-doped TiO<sub>2</sub> photocatalysts. Thus, the present report may offer a significant suggestion for the construction of visible-light photocatalysts through doping and morphology designing.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.05. 003.

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