INTRODUCTION

In current years, semiconductor mediated photocatalytic treatment of organic pollutants has established much attention. After the finding of photoelectrochemical splitting of water on titanium dioxide TiO$_2$ electrodes [1], semiconductor-based photocatalysis has received a lot of attention [2,3]. Many other significant uses have also been studied, particularly in the medical and biological fields, where TiO$_2$-based nanomaterials have been explored for in cancer therapy [5], vivo imaging [4], protein separation purification, and as bactericides [6]. These applications exploit TiO$_2$ across a broad range of sizes from hundreds of nanometers to several micrometers. Even though these applications account for the greater part of global TiO$_2$ consumption, its consumption in nanoscale research has mainly focused on it’s in the vicinity of semiconductor photocatalytic properties. TiO$_2$ has showed to be an excellent catalyst in the photocatalytic degradation of organic pollutants since it is effective, photostable, non-toxic and easily available [7]. TiO$_2$ n-type semiconductor consists of three polymorphs (rutile, anatase, and brookite), and is a large amount widely applied heterogeneous photocatalyst for environmental pollutant treatment due to its oxidation capacity, thermal and chemical stability, and low cost [8, 9]. Two major factors govern the photocatalytic activity of TiO$_2$: lowering of band gap energy in visible region & prevention of electron hole recombination rate. One of the methods to get better photocatalytic activity of TiO$_2$ is to add non-metal or metal impurity in the TiO$_2$ lattice or to couple with lower band gap semiconductor [10, 11].

Most of these explorations have been carried out under ultraviolet (UV) light, because TiO$_2$ photocatalyst explains relatively high activity and chemical stability under UV light, which exceed the band-gap energy of 3.0 or 3.2 eV in the rutile crystalline phase, respectively. Thus TiO$_2$ cannot be making active in visible light or sunlight. Doping is one of the distinctive approaches to extend the spectral reply of a wide band gap semiconductor to visible light, where several metal ions can be used as a dopant [12]. Still, photocatalytic activity of most of these catalysts decreases even in the UV region, since the doped materials endure from a thermal instability or an increase in the carrier-recombination centers [13].

A variety of approaches have been made in the bid to delay recombination of the photogenerated electron-hole pairs in nano-TiO$_2$. Nonmetal doping has been thoroughly investigated since the electronic states of nonmetals are above the valence band edge of TiO$_2$ compared with pure TiO$_2$. Consequently, different nonmetal dopants including nitrogen (N), carbon (C), and sulfur (S) have been tested for their capability to improve the morphology and photocatalytic performance of TiO$_2$ [14, 15].

SYNTHESIS AND CHARACTERIZATION OF SULFUR DOPED TiO$_2$ NANO PARTICLES FOR THE IMPROVED PHOTOCATALYTIC DEGRADATION OF RHODAMINE B BY SOL-GEL ROUTE

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15]. The presence of nonmetal anions increases the percentage of the rutile phase in TiO₂, restrains the growth of crystallite size of TiO₂, and increases the specific surface area of TiO₂ [16]. In this direction, sulfur doping is described to be beneficial for rising highly efficient titania that is responsive below wide spectral range. The substitution of sulfur in either cationic or anionic sites depends on the experimental conditions as well as on the choice of precursor. The sulfur replaces Ti⁴⁺ ions in TiO₂ lattice in both anatase and rutile phases; additional it reduces the band gap absorption energy [17].

In the present study, the most convenient ways of synthesizing various nanomaterials are preferable due to low cost, ease fabrication and low temperature. This method has various advantages over other methods, such as co-precipitation or allowing impregnation, which can be achieved by introducing dopant, molecular scale mixing, high purity of the precursors and homogeneity of sol-gel products with high purity physical, morphological and chemical properties of nanomaterial. Consequently, that was the reason why sol gel synthesis method is chosen as the method of titanium dioxide nanomaterials.

Rhodamine B is a dye that belong to a class of compounds called xanthenes, with a Mol. Wt.479.02 gmol⁻¹ and a formula C₂₃H₁₈N₂O₂Cl. It is expansively used as model compound since it shows a strong absorption band in the visible region of the electromagnetic spectrum (555 nm) [18]. Now this dye has been forbidden for the use as food color because it is suspected that RhB could be a carcinogenic substance [19, 20], inducing mutagenesis and teratogenesis in rats [21]. Their stability, resistance to biological & chemical degradation, presence in textile industry effluents, and it was suspected that this dye could be a possible carcinogenic substance, implies that Rhodamine B is an excellent model compound for this type of study.

**Experimental**

**Materials**

All chemicals were in analytical grade and were used as received without any additional purification. Titanium (IV) isopropoxide, (C₂H₅O)₃Ti, purity 97% Aldrich) was used as starting precursor for synthesizing crystalline TiO₂ particles, sodium sulfate Na₂SO₄.5H₂O as a dopant precursor, and nitric acid obtained from Hi-media. Deionized water was employed throughout the experiments.

**Synthesis**

5 ml Titanium tetra isopropoxide (TTIP) was dissolved with 20 ml of isopropanol. This solution was added dropwise to the distilled water maintained at appropriate PH (3-4) using conc. HNO₃. This solution was stirred for 30 mins. To required amount of Na₂SO₄ as a dopant precursor (0.2 to 0.6 M) was dissolved in water. This dopant solution was then added to the above mixture solution and stirred vigorously for 8 hrs. This solution was then aged at room temperature for several hrs; the solids were transformed into gels, and washed with ethanol. The catalyst was dried at 80 °C in the oven. Finally, the dried samples calcined at 500 °C for 5 hrs, which resulted in S-TiO₂ nano particles. For comparison, pure TiO₂ was also prepared in the absence of Na₂SO₄ under similar approach.

**Characterization**

The X-ray diffraction patterns of the samples were recorded on an XPERT-PRO X-ray diffractometer with Cu-Kα radiation of wavelength 1.5406 Å in 20 range from 20° to 70°. UV-visible spectrophotometer was using Shimadzu UV-1650. Fourier transform infrared (FT-IR) spectroscopy measurement was recorded with AVATAR 330 FT-IR spectrometer in the range of 4000-500 cm⁻¹. SEM image was taken using JEOL, Model JSM 6390.

**RESULTS AND DISCUSSION**

**X-ray diffraction studies**

Fig.1 shows the X-ray diffraction (XRD) patterns of pure TiO₂ and S doped TiO₂. The diffractograms for TiO₂ are essentially equivalent, exhibiting peaks at 25.23, 38.9, 48.3, 55.28 and 62.88° that are consistent with the (1 0 1), (112), (2 0 0), (2 1 1) and (2 0 4) planes associated with tetragonal anatase (JCPDS No. 21-1272). There are four typical peaks with 20 values of 27.38, 35.98, 41.18 and 54.18°, corresponding to the (1 1 0), (1 0 1), (1 1 1) and (2 1 1) crystal planes of the rutile phase (JCPDS No. 21-1276) [22], respectively. Compared with pure TiO₂, the (0.4M &0.6M) S-TiO₂ mainly shows the reflections corresponding to the rutile phase, and a trace amount of anatase phase. However, on further increasing the amount of the incorporation of S, the anatase phase gradually increases. It means that the ratio of anatase to rutile in the S-doped TiO₂ photocatalysts is strongly affected by the S dopant amount. In this study, some S peaks were observed. The peaks resulted from the reflection at 28.9, 33.48, 59.95° that was found for 0.4M & 0.6M sulfur doping, and it accords well with that in JCPDS 78-1889. The data obtained from the Scherer equation show increase in crystallite size (13 to 28 nm) with increase in sulfur content.

![Fig 1 XRD Pattern of (a) Pure TiO₂ (b) (0.2M) S-TiO₂ (c) (0.4M) S-TiO₂ (d) (0.6M) S-TiO₂ A- Anatase R- Rutile *- Sulfur](image-url)
samples correspond to their phase compositions and TiO\(_2\) caves, which mainly resulted from the agglomeration of nano particles. There were many irregular shape nanoparticles with various shapes and sizes. The particle size increases with increase in doping concentration.

**Functional group Analysis (FT-IR)**

FT-IR spectra of S-doped TiO\(_2\) nanoparticles are shown in Fig.2. The peaks correspond to stretching vibrations of the O-H and bending vibrations of the adsorbed water molecules about 3350-3450 and 1620-1635 cm\(^{-1}\). These results strongly confirm the presence of hydroxyl ions in the structure of the samples [23]. The strong band in the range of 490-750 cm\(^{-1}\) is attributed to stretching vibrations of Ti-O-Ti bond [24, 25]. The peak observed in the range of 2356-2364 cm\(^{-1}\) was due to amine (NH) group stretching frequency [26]. The band at 2860 cm\(^{-1}\) was due to the C-H bonds of the organic compounds [27].

**Surface Morphological Analysis**

**Scanning Electron Microscopy (SEM/EDS)**

The morphology of the synthesized S-doped TiO\(_2\) nanoparticles measured by SEM is given in Fig.3. It can be seen that there were many irregular shape nanoparticles with various shapes and sizes, which mainly resulted from the agglomeration of nano TiO\(_2\). The images also show that the morphologies of TiO\(_2\) samples correspond to their phase compositions and preparation conditions. The elemental composition of the obtained powder was determined using energy dispersive X-ray spectroscopic (EDS) analysis.

**Optical Analysis**

**UV-Visible absorption spectrum**

The optical properties and the energy band gap of pure and S-doped TiO\(_2\) nanostructures were studied by UV-Visible absorption spectroscopy. The UV-Vis absorption spectra of the undoped and doped TiO\(_2\) samples are shown in Fig.4. The corresponding absorption edge of pure TiO\(_2\) and S-doped TiO\(_2\) were 370 and 360, 365, 415 nm, respectively. Compared with the pure TiO\(_2\), the doping samples showed a stronger absorption in the UV range and a slight shift to visible light range. While the absorption curve of the S-TiO\(_2\) displayed a significant red shift compared with the undoped TiO\(_2\) samples. According to the UV-Vis absorption spectra, the S-TiO\(_2\) may have an excellent photocatalytic effect under the UV light region.

The band gap was calculated by using the plot of \(\alpha h\nu\) vs. \(h\nu\) which is shown in Fig. 5. By assuming that TiO\(_2\) has a direct type of transition

\[ \alpha h\nu = A(h\nu - E_g)^{\frac{1}{n}} \]

where \(\alpha\), \(h\nu\), A, \(E_g\) and \(n\) are the absorption coefficient, photon energy, proportionality constant, band gap and a constant respectively, where \(n\) decides the type of transition. The result shows that pure TiO\(_2\) has a large band gap (3.4 eV) and S-doped TiO\(_2\) has band gap energy which decreases with increase in concentration 3.33 eV, 3.25 eV, 2.93 eV, respectively, by extrapolation of the linear portion of the absorption coefficient \(\alpha\) to zero. The band gap energy decreases with the doping of sulfur ions, which allow the delay in recombination rate and enhance the photocatalytic activity.
In Table 2 shows the optical band gap energy decreases with increase in particle size, which can be attributed to the quantum size effect, improvement in morphological and crystallinity of the samples. which is confirmed by the detailed XRD analysis and the derived structural parameters. From SEM images there were many irregular shape nanoparticles with various caves, which mainly resulted from the agglomeration of nanocrystalline TiO₂. The EDS result showed the elemental mapping was performed by EDS analysis consisting of Ti, O, S. The presence of functional groups and the chemical bonding with S are confirmed by FTIR spectra. The PL spectrum of the TiO₂ shows a dominant emission band centered at 453 nm (2.74 eV), which is consistent with absorption measurement. This blue range emission peak is attributed to the near-band-edge emission. The low PL intensity of S-TiO₂ is ascribed to reduced recombination, which contributes to the photocatalytic activity.

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