Enhanced solar light photodegradation of brilliant black bis-azo dye in aqueous solution by F, Sm$^{3+}$ codoped TiO$_2$

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Abstract. This research focuses on improving the photocatalytic efficiency of TiO$_2$ during the photo-mineralisation of brilliant black (BN) bis-azo dye pollutant in aqueous solution. This was achieved by improving the visible light activity of TiO$_2$ photocatalyst semiconductor through co-doping of fluorine (F) and trivalent samarium ions (Sm$^{3+}$) into a TiO$_2$ matrix using a modified sol-gel synthesis method. Structural, morphological, and textural properties were evaluated using ultra-violet/visible spectroscopy (UV-visible), Raman spectroscopy, scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM/EDX) and X-ray diffraction spectroscopy (XRD). Photocatalytic and degradation efficiencies were assessed by decolourisation of BN dye in aqueous solution. Complete degradation of BN was attained after an irradiation time of 3 h using F, Sm$^{3+}$-TiO$_2$ (0.6% Sm$^{3+}$) compared to 73.4% achieved using pristine TiO$_2$. Pseudo first order kinetics rate constants ($K_a$) were $2.73 \times 10^{-2}$ and $6.6 \times 10^{-3}$ min$^{-1}$ for Sm$^{3+}$-TiO$_2$ (0.6% Sm$^{3+}$) and pristine TiO$_2$, respectively, which translates to a remarkably high enhancement factor of 4. The results obtained established that doping of TiO$_2$ by F and Sm$^{3+}$ enhances the photocatalytic performance of TiO$_2$ during solar light radiation which enables the utilisation of freely available and clean solar energy.

1. Introduction

Widespread applications of brilliant black (BN) bis-azo dye in food dyeing, auto-mobile painting and textile dyeing industry implies that BN dye has got a higher likelihood of polluting water sources. The presence of the diazo group in BN prompts intolerance to people with allergies to salicylates. Additionally, it is a histamine liberator with a tendency to amplify the symptoms of asthma, its combination with benzoates has got adversarial effects in children leading to hyperactivity and there is sufficient grounds for suspicion that bacterial presence in intestines can decompose them into much more dangerous metabolites.

Semiconductor photocatalysis is an advanced oxidation process (AOP) for complete mineralisation of organic pollutants with more advantages compared to other conventional water treatment
methods. TiO$_2$ which is the commonly used photocatalyst due to its relative affordability, nontoxicity and photo-chemical stability, has got its downsides. These drawbacks includes inactivity in the visible and near infra-red (NIR) region of the solar spectrum and low quantum efficiency resulting from higher carrier charge recombination. TiO$_2$ multi-doping combination of nonmetals and metals has provided solutions to deal with TiO$_2$ drawbacks and has been found to consequentially improve the rate of photocatalysed reaction. Fluorine doped TiO$_2$ matrix improves both ultra violet and visible light driven photocatalysis of organic pollutants.

There have been contradictory explanations as to what brings about the photocatalytic enhancement of F-TiO$_2$ degradation of organic pollutants. This has resulted in the proposition of different models of F-doping effects. Firstly, substitutional doping with F$^-$ either doubly or singly occupying vacant O$^{2-}$ in the TiO$_2$ matrix as proved by photoluminescence (PL) spectra in work done by Czoska et al [1]. The PL spectra shows that there are two major different types of O$^{2-}$ vacancies namely F and F$^*$ in F doped TiO$_2$ which results in two different intraband gap states impurity energy levels below the CB at 0.53 and 0.84 eV respectively as shown in figure below [2].

![Figure 1: Schematic diagram of two O$^{2-}$ vacancies in F- doped TiO$_2$](image)

These impurity energy levels results in reduced band gap, an oxygen vacancy induced red shift extending the absorption into the visible region [2] - [3]. Secondly, the presence of singly charged F$^{1-}$ dopant in the doubly charged O$^{2-}$ vacant creates a charge imbalance that is compensated by the formation of Ti$^{3+}$ which could be responsible for the UV activity of F-doped TiO$_2$. The generated Ti$^{3+}$ reduced centers also results in improved quantum efficiency by acting as electron capture centers for reduced carrier-charge recombination [4]. Thirdly, surface doping by formation of coordinate compounds of Ti$^{4+}$ central metal ion bound by F$^-$ ligands on TiO$_2$ surface displacing OH$^-$ changing the surface mechanism. This process favours the formation of OH$^-$ radicals which in turn increase the kinetic degradation of free radical attacks of organic pollutants [1]. F-doping of TiO$_2$ alters the surface morphology by enhanced exposition of the {001} facets which are highly photocatalytic active in the UV electromagnetic spectrum [5].
F and metal ion codoped TiO\(_2\) as reported by Lin et al results in improved photocatalytic activity due to the combined effects of F and metal ion on the properties of TiO\(_2\). They found out that the synergistic effects of co-doping F and Ag resulted in extended absorption in the visible region, which could be interpreted as band gap reduction although they did not report calculated band gaps [4]. The presence of Ag also acted as an electron capture center for reduced carrier-charge recombination resulting in improved quantum efficiency.

In metal doping there are mainly four various types of metal dopants that are used namely alkaline [6], transition [7], rare earth [3] and noble [4] metals. Metal dopants function as electron sinks, promotes interfacial charge transfer mechanisms and inhibits recombination of photo-generated carrier charges. The Fermi level for these various metals are lower than the conduction band of TiO\(_2\) therefore photoexcited electrons can be transferred from the CB to the surface of the metal dopant. This on its own is a way of preventing charge carrier recombination [7].

This research focuses on the use of rare earth (RE) metal dopant, Sm\(^{3+}\) as a metal dopant in the TiO\(_2\) matrix. The use of RE has generated a lot of research interests due to the unique nature and properties of their 4f electronic orbitals. Due to the higher energy levels possessed by 4f orbitals they can easily duplicate different electronic configurations which are of interesting fluorescence and phosphorescence properties emanating from intra 4f-4f electronic transitions which alters the optical properties of TiO\(_2\) in various ways [8]. This includes among others effective band gap reduction [9], increased absorption intensities in the visible and near infrared (NIR) [9] and conversion phosphors, upper conversion phosphors (UCPs) and lower conversion phosphors (LCPs) [8]. However, the 4f orbitals brings in an added advantage of improved adsorption due to the formation of complex compounds through dative bonding between vacant 4f sub-orbitals and Lewis acids such as functional groups of organic pollutants [10] - [6]. This study also specifically examines the synergistic effects of F and Sm\(^{3+}\) codoped TiO\(_2\) for photocatalytic degradation of Brilliant Black (BN) bis-azo dye.

2. Methods and Procedures

2.1 Materials
Titanium isopropoxide (TTIP) 97%, 2-propanol anhydrous 99.5%, formic acid 90%, samarium nitrate hexahydrate (Sm(NO\(_3\))\(_3\).6H\(_2\)O) 99.9%, ammonium fluoride (NH\(_4\)F) 98%, brilliant black 40% and concentrated HCl 32%. All reagents were supplied by Sigma Aldrich (Germany) and were analytical reagent grades which were used without further treatment. In all cases where water was used deionised water (DI) purified in the laboratory using the Milli Quant water purification system was used.
2.2 Synthesis

2.2.1 Synthesis of fluorine, Sm$^{3+}$ codoped TiO$_2$ (0.6% Sm$^{3+}$)

F, Sm$^{3+}$ co-doped TiO$_2$ was prepared by a simple sol-gel method. TTIP (10 mL) was dissolved in 2-propanol (50 mL) and vigorously stirred for 10 min to make solution A. A mass of 46.4 mg of samarium nitrate hexahydrate used as Sm$^{3+}$ precursor was weighed and dissolved in a mixture of 2-propanol (10 mL) and DI water (5 mL) (in a ratio of 1:2) by continuously stirring for 30 min to make up solution B. The mass weighed gave a 0.6% Sm$^{3+}$ dopant loading w.r.t TiO$_2$. NH$_4$F (510.2 mg), F precursor was weighed to give 10% dopant loading of F dopant. NH$_4$F was dissolved in a mixture of 2-propanol (40 mL), formic acid (10 mL), DI water (3 mL) and HCl (3 mL) and continuously stirred for 30 min to make up solution C. Solution C was added dropwise to solution A while simultaneously stirring the resultant solution. This was followed by the addition of solution B to the mixture of solutions A and C and vigorously stirred for 1 h. The resultant solution was aged for a period of 24 h and the resultant gel was oven dried over night at 80ºC. The drying oven model DHG 9053A operating at 220 V, 50 Hz and 800 W was used. The pulverized sample was subsequently calcined at 450ºC in a muffle furnace in open air. Muffle furnace model SNOL 8, 2/1100-1 operating between 220-230 V at ~50 Hz and 1.8 KW was used for calcination.

2.2.2 Synthesis of Sm$^{3+}$ doped TiO$_2$

Sm$^{3+}$ doped TiO$_2$ was prepared by the same method as explained above but with solution C containing formic acid (10 mL) only. Solution B comprising of various appropriate amounts of samarium nitrate hexahydrate ranging from 0.2 to 1% dopant loading of each Sm$^{3+}$ while the composition of solution A did not change.

2.2.3 Synthesis of pristine TiO$_2$

Pristine TiO$_2$ was synthesised using the same sol gel method mentioned in Section 2.2.1. However, in this case TTIP was dissolved in 2-propanol solvent and added dropwise to formic acid (10 mL).

2.3 Characterisation

Optical properties were measured using the PerkinElmer Lambda 1050 UV-visible-NIR. The 150 mm sphere reflectance method was used to scan the samples. D2 and Tungsten lamps were used and the operating parameters slit width of 4 mm and a photomultiplier response of 0.2 seconds. Powdered samples were scanned from 200 – 800 nm range with a data interval of 2 nm. Raman spectra were collected from a Raman II FT-Raman module spectrometer coupled to a VERTEX 70 FT-IR spectrophotometer, Germany. Resolution of 4 mc$^{-1}$, sample scan: 64, laser source setting, and scanning range stokes shift 20-700 cm$^{-1}$.

Crystallinity properties were measured using XRD type Rigaku Smartlab, Japan X-ray diffractometer and the operating parameters were 45 kV and 200 mA. The analysis range was 20 - 80º (2θ), Cu-Ka radiation wavelength ($\lambda = 1.54$ Å) and powdered samples were analysed. Data analysis was carried out using Smartlab Rigaku instrument control software PDXL. Crystallite
particle size (D) and lattice strain (ƞ) were calculated using the Scherrer equation, full width half maximum (FWHM) of 101 anatase phase peak.

Surface morphology and elemental composition analysis of the synthesised photocatalyst were performed using the scanning electron microscopy (SEM) with an attachment of energy dispersive X-ray spectrometer called JOEL IT 300 & Oxford SEM Integrated System.

**Evaluation of photocatalytic activity**
The photocatalytic activity of Sm$^{3+}$ doped TiO$_2$ (0 – 1%), F doped TiO$_2$ and F, Sm$^{3+}$ codoped TiO$_2$ was evaluated by measuring the photocatalytic degradation of brilliant black (BN) bis-azo dye under solar light irradiation. For every sample 0.1 g of photocatalyst in 100 mL of 50 ppm BN bisazo dye was mixed and stirred in darkness for 1 h to attain absorption equilibria before solar light irradiation. Solar simulator (HAL – 320) supplied by ASAHI SPECTRAL, Japan was used to generate the required spectral irradiance for photocatalysis. The 300 W compact Xenon lamp was the light source, and a light intensity of 60 was used. Solar simulator radiation spectrum output wavelength range was set from 350 – 1100 nm and an air mass filter 1.5 G filter was used to filter the unwanted wavelength. Illuminance distance, which is distance from collimator lens to sample surface was approximately 370 mm creating an effective radiated area of 50 mm$^2$ and an irradiance of 100 mWcm$^{-2}$ (1 SUN). The simulator was warmed up 30 min prior to application and was used as solar light source for irradiation. Sampling frequency was after every 30 min interval which also included initial sample after attaining absorption equilibria, before solar light irradiation. Samples of 4 mL aliquots were drawn using a 10 mL syringe were filtered through the GH Polypro membrane (GHP) syringe disc filter fitted at the discharge of the syringe. Filtered samples were analysed for absorbance using the UV-visible spectrophotometer at wavelength 574.9 nm. Calibration range of 10 to 50 ppm standards was performed which gave $R^2$ of 0.9999997 and regression line:

$$y = 0.044994x - 0.003554$$

Equation 1

where y is absorbance and x is the BN concentration in ppm.

This equation was used to determine the BN concentration for every sample and the BN concentrations at different sampling times were used to calculate the percentage degradation of BN using the following formula:

$$\% \text{ Degradation of BN} = \frac{(C_o - C_t)}{C_o} \times 100$$

Equation 2

where $C_o$ and $C_t$ are initial concentration and concentration at time t respectively.

The degradation progress was monitored using total organic carbon (TOC) torch analysis wastewater method. Total organic carbon (TOC) analysis which basically measures the amount of organic carbon in the samples was done in a Teledyne Tekmar TOC torch (USA). Standard
solutions of 1 ppm, 5 ppm, 10 ppm, 20 ppm and 30 ppm carbon were prepared using potassium hydrogen phthalate (KHP) and DI water. Calibration standards were measured prior to sample analysis for instrument calibration.

3. Results and Discussion
UV-visible reflectance spectra showed the optical activity of various synthesised samples of pristine TiO$_2$ and various doped samples. For pristine and Sm$^{3+}$ doped TiO$_2$ there was a slight shift in the band gap, as Sm$^{3+}$ dopant loading increased the band gap was progressively narrowed but Sm$^{3+}$ doped TiO$_2$ showed varying and increased absorption intensity spanning from 400 to 800 nm. This increased absorption intensity extends to the NIR region of the electromagnetic spectrum. This phenomenon also persists in the UV region as shown in Figure 2. Fluorine doped TiO$_2$ and F, Sm$^{3+}$ codoped TiO$_2$ showed significant shifts of the band gap. Converting diffuse reflectance data to Kubelka-Munk function using the following equation below:

$$F(R) = \frac{(1 - R)^2}{2R}$$

**Equation 3**

![Figure 2](image)

**Figure 2:** Diffuse reflectance UV-visible spectra for doped TiO$_2$ (a) different Sm$^{3+}$ concentrations and (b) F-doped TiO$_2$ and F, Sm$^{3+}$ codoped TiO$_2$ (0.6% Sm$^{3+}$)

The Kubelka-Munk function, F(R) is an absorption coefficient showing the magnitude of absorption for a sample. F(R) is plotted against wavelength to show different absorption behaviour of different photocatalysts as shown in Figure 3 which confirms reflectance data shown by UV-visible spectra. Further treatment of the reflectance data to Tauc plots gave a good estimate for indirect band gap energies for pristine TiO$_2$ and Sm$^{3+}$ doped TiO$_2$ showing the indirect band gaps
in Tables 1 and 2 below. Tauc plots below (Figure 4) plots point of \( [F(R) \times h\nu]^{1/n} \) against \( h\nu \) where \( h\nu \) is photon energy and \( n \) is the numerical value corresponding to type of transition. The values of \( n \) can be \( \frac{1}{2}, 2, 3/2, 3 \) corresponding to allowed direct, allowed indirect, forbidden direct or forbidden indirect transition. In the case of TiO\(_2\) \( n=2 \) to estimate the indirect band gap.

This is largely attributed to phosphorescence and fluorescence optical properties of lanthanides trivalent ions. The unique electronic configuration of Sm\(^{3+}\) consisting of partially filled 4f electronic orbitals responsible for distinctive optical transitions behaviour of lanthanides. The increased absorption intensity in UV, visible to NIR by the Sm\(^{3+}\) doped TiO\(_2\) is due to weak, narrow sharp optical absorption by Sm\(^{3+}\). This narrow sharp optical absorption is attributed to intra 4f-4f electronic transitions in Sm\(^{3+}\) [11].

![Figure 3](image1)

**Figure 3:** Kubelka-Munk function plots for doped TiO\(_2\) (a) different Sm\(^{3+}\) concentrations and (b) F-doped TiO\(_2\) and F, Sm\(^{3+}\) codoped TiO\(_2\) (0.6% Sm\(^{3+}\))

While pristine and Sm\(^{3+}\) doped TiO\(_2\) showed a slight band gap narrowing, the doping of TiO\(_2\) with nonmetal dopants F has shown significant band gap narrowing as shown in Figure 4 below. Doping TiO\(_2\) with F and Sm\(^{3+}\) narrowed the band gap of TiO\(_2\) and consequently increased the wavelength absorption edge of doped TiO\(_2\) into the visible region of the electromagnetic spectrum as shown in Table 1 and 2 below. This is because the introduction of F and Sm\(^{3+}\) introduced impurities which in turn introduced intra-band gap energy states in between the TiO\(_2\) VB and CB. F\(^-\) anionic radius is much less than that of the O\(^2-\) (1.33 Å < 1.4 Å) [4], so there is a high probability that F\(^-\) occupies a substitutional doping site replacing O\(^2-\) resulting in a 2p energy sub-state above the VB, while Sm\(^{3+}\) is much larger than O\(^2-\) (0.96 Å >> 0.68 Å) [12], and is more likely to occupy the interstitial doping site or substitute Ti\(^{4+}\) resulting in a 3p energy sub-states slightly below the CB [13]. Below Figure 10 shows the possible band gap modification of TiO\(_2\) by doping with F, Sm\(^{3+}\) codoped TiO\(_2\).
As illustrated below in Table 1 and 2 below, the estimated band gap energies and calculated wavelength for pristine and the different doped TiO$_2$ samples are shown. The calculated wavelength were derived from the Planck-Einstein relationship giving the Planck’s equation below [14]:

$$E_g = hv = \frac{hc}{\lambda} = \frac{1240}{\lambda}$$  \hspace{1cm} \text{Equation 4}$$

Where h is Planck’s constant, v is frequency, c is speed of light and $\lambda$ is wavelength.

Table 1: Indirect band gap energy estimates and calculated absorption wavelength for different Sm$^{3+}$ dopant concentrations

| Sample                  | Indirect band gap (eV) | Estimated $\lambda$ (nm) |
|-------------------------|------------------------|--------------------------|
| Pure TiO$_2$            | 3.15                   | 393.7                    |
| Sm$^{3+}$-TiO$_2$ (0.2% Sm$^{3+}$) | 3.14                   | 394.9                    |
| Sm$^{3+}$-TiO$_2$ (0.4% Sm$^{3+}$) | 3.07                   | 403.9                    |
| Sm$^{3+}$-TiO$_2$ (0.6% Sm$^{3+}$) | 3.00                   | 413.3                    |
| Sm$^{3+}$-TiO$_2$ (0.8% Sm$^{3+}$) | 2.97                   | 417.5                    |
| Sm$^{3+}$-TiO$_2$ (1% Sm$^{3+}$) | 2.95                   | 420.3                    |
Table 2: Indirect band gap energies and calculated absorption wavelength for F-doped TiO$_2$ and F and Sm$^{3+}$ codoped of TiO$_2$ on band gap and estimated wavelength

| Sample                     | Indirect band gap (eV) | Estimated λ (nm) |
|----------------------------|------------------------|------------------|
| F-TiO$_2$                  | 2.95                   | 420.3            |
| F, Sm$^{3+}$-TiO$_2$ (0.6% Sm$^{3+}$) | 2.00                   | 620.0            |

Figure 5 below shows Raman spectra of pure TiO$_2$ and Sm$^{3+}$ doped TiO$_2$ with well-defined high intensity sharp $E_g$ peaks at 146 cm$^{-1}$ and 646 cm$^{-1}$, these peaks confirms the presence of crystalline lattices of TiO$_2$. Peaks $B_{1g}$ (397 cm$^{-1}$) and $A_{1g}+B_{1g}$ (516 cm$^{-1}$) are also well defined but with low Raman intensity and broader peaks and an offshoot $E_g$ peak at 197 cm$^{-1}$ is observed [15]. All these peaks confirms the presence of a predominantly anatase TiO$_2$ phase and these findings are consistent with the XRD spectra data. The presence of the various Sm$^{3+}$ dopants in TiO$_2$ can be explained by the shifting of peak wavenumber coordinate points along the x-axis [16].

Widespread literature survey reported the main $E_g$ peak to be at 146 cm$^{-1}$ for pure TiO$_2$ this is exactly what is experimentally obtained in this research while its corresponding Sm$^{3+}$ doped TiO$_2$ sample had this same peak translated to 149 cm$^{-1}$, this major shift may represent the presence of Sm$^{3+}$ dopants. Raman active properties of Sm$^{3+}$-TiO$_2$ compounds are mainly due to O-Sm-O bending appearing in the region of 304 cm$^{-1}$ and 308 cm$^{-1}$ ($E_g$ and $F_{2g}$ modes) and Sm-O stretching appearing in the region of 515 cm$^{-1}$ and 519 cm$^{-1}$ ($A_{1g}$ mode). These various Raman active modes peaks of Sm$^{3+}$-TiO$_2$ compounds are not visible due to low intensity and overlapping of major TiO$_2$ peaks appearing in the same region. Low intensity is due to low Sm$^{3+}$ dopant concentration [16].

Figure 5: Raman spectra of (A) TiO$_2$ doped with different Sm$^{3+}$ concentrations and (B) pure TiO$_2$, F-TiO$_2$ and F, Sm$^{3+}$ codoped TiO$_2$ (0.6% Sm$^{3+}$)
The effect of Sm$^{3+}$ concentration is shown in figure (A), intensity of all the anatase peaks was significantly reduced as the Sm$^{3+}$ dopant concentration levels are increased. This confirms reduced crystallinity as the amount of dopant is also increased and this finding is corroborated by XRD crystallite particle size results.

Both pristine and different concentrations Sm$^{3+}$ doped TiO$_2$ were calcined at 450°C. At 450°C calcination temperature, sharp well defined, intense peaks of anatase polycrystalline structure at different 2Ɵ angle positions were observed with the major peak being at 25.3º position. The observations were made for both pristine and Sm$^{3+}$ doped TiO$_2$. These peaks showed a higher degree of crystallinity. Other anatase diffraction peaks existing at 2Ɵ position 25.3º, 37.6º, 48.2º, 53.9º, 54.8º, 62.7º and 75.2º shown in figure 6 below. These diffraction peaks corresponding to (101), (004), (200), (105), (211), (204) and (215) crystallographic planes respectively [13]. Three low intensity peaks of rutile TiO$_2$ are seen at 27.5º, 41.3º and 56.7º corresponding to crystallographic plane (110), (111) and (220) [17]. The rutile peaks disappeared as the concentration of Sm$^{3+}$ dopant was increased. This implies that Sm$^{3+}$ doping inhibited phase transformation from anatase to rutile. Anatase remained the dominant phase after doping as shown by the XRD peaks. Crystallite particle size (D) and lattice strain (ƞ) were calculated using the formula below:

\[ D = \frac{k\lambda}{\beta\cos\theta} \]

where K is a constant 0.94, λ is the characteristic X-ray wavelength of Cu 1.54 Å, β is full width half maximum (FWHM) for plane 101 and θ is the Bragg angle in radians. Lattice strain (ƞ) is obtained from online XRD calculator. Introduction of dopant Sm$^{3+}$ broadened the width measured at FWHM with respect to plane 101 confirming reduced particle size. This may be attributed to internal lattice strain induced into the TiO$_2$ matrix by trivalent samarium [16]. Table 4 below shows the crystallite particle size and lattice strain for the different samples. The higher lattice strain experienced by Sm$^{3+}$ doped TiO$_2$ might be due to the large difference in cationic radii of the dopant ( Sm$^{3+}$: 0.96 Å ) [18] and that of host matrix cation (Ti$^{4+}$=0.68 Å) [16]. This is because when substitutional doping is experienced, the Sm$^{3+}$ substituting the Ti$^{4+}$ causes both strain and stress to bond length and bond angles (lattice straining). The general trend reveals that there is a decrease in crystallite particle size of TiO$_2$ with increasing Sm$^{3+}$ concentration.

| Sample                  | Crystallite particle size (D)/ nm | Lattice strain (ƞ) |
|-------------------------|----------------------------------|--------------------|
| Pure TiO$_2$            | 15.14                            | 0.0119             |
| Sm$^{3+}$-TiO$_2$ (0.2% Sm$^{3+}$) | 14.9                            | 0.0111             |
| Sm$^{3+}$-TiO$_2$ (0.4% Sm$^{3+}$) | 14.4                            | 0.0115             |
| Sm$^{3+}$-TiO$_2$ (0.6% Sm$^{3+}$) | 14.18                           | 0.0117             |
| Sm$^{3+}$-TiO$_2$ (0.8% Sm$^{3+}$) | 13.29                           | 0.0124             |
| Sm$^{3+}$-TiO$_2$ (1% Sm$^{3+}$)    | 12.84                            | 0.0140             |
Figure 6: XRD spectra of (A) TiO$_2$ doped with different Sm$^{3+}$ concentrations and (B) pure TiO$_2$, F-TiO$_2$ and F, Sm$^{3+}$ codoped TiO$_2$ (0.6% Sm$^{3+}$)

SEM micrographs digital pictorial images of surface morphology and surface elemental composition of F, Sm$^{3+}$ codoped TiO$_2$ shown in Figure 7 below (a) which is high magnification at x2000 and (b) at lower magnification at x450. At lower magnification the digital photo shows an aerial view of small spherical particles with an off whitish colour confirming TiO$_2$ as the major component of the sample and this is corroborated by the EDX spectra. On zooming in closely the picture revealed further detailed information as shown in picture (a), showing homogeneously dispersed regular spherical and near spherical particles. Figure 7(b) show neither agglomeration nor aggregation of titanium dioxide particles. Figure (c) is EDX spectra showing Ti and O as the major components of the sample. Minute quantities of F and Sm confirms their presents as co-dopants. Sm and Ti have three or more peaks each appearing at different binding energies confirming that both Sm and Ti exists in different oxidation states in the catalyst. However, Si peak shows the presence of minute Si as a contaminant probably from borosilicate glassware used during synthesis. The higher counts per second of the carbon peak is due to the carbon tape which was used as a sample holder.
3.1 Dye degradation

Figure 8 shows the ratio of concentration of the dye present at time (t) to initial dye concentration of BN bis-azo dye as a function of irradiation time. A 100% degradation of BN was realized after 3h irradiation for the F/Sm$^{3+}$-TiO$_2$ (0.6% Sm$^{3+}$) sample. The plots shows different rates of degradation for various TiO$_2$ samples. Pristine TiO$_2$ has the least photocatalytic activity, however, the percentage degradation of BN dye by pristine TiO$_2$ under solar light irradiation is significantly higher (73.8%) which might be due to either dye sensitisation or BN bis-azo dye being easier to photodegrade. F- doped TiO$_2$ marginally increased the photocatalytic degradation of BN to 78.4%.

After 180 min of solar light illumination, different Sm$^{3+}$ doped TiO$_2$ samples showed remarkable enhancement of degradation relative to pristine TiO$_2$ which may be attributed to the improved quantum efficiency with Sm effectively acting as an electron capturing centres for photoinduced electrons. This avoided recombination with positive holes and improved the photocatalytic activity. Schottky barriers formed at the semiconductor-Sm$^{3+}$ interface also acted as electron sinks reducing recombination rate. Increasing Sm$^{3+}$ concentration up to 0.6%, resulted in increased photocatalytic efficiency of TiO$_2$ but a further increase in Sm$^{3+}$ concentration resulted in diminishing activity. The diminishing activity at higher concentrations of Sm$^{3+}$ is due to Sm$^{3+}$ acting as recombination centers further facilitating recombination by short circuiting the electrical circuit which is detrimental to photocatalytic improvement. Increased Sm$^{3+}$ concentration on the TiO$_2$ surface leads to shading of
photo-sensitive reaction sites of TiO$_2$ by the metal cations. Optimum metal dopant loading for different Sm$^{3+}$ was found to be 0.6%.

The photocatalytic activity of BN bis-azo dye can also be described by the Langmuir-Hinshelwood model, where the photocatalytic activity of the catalysts can be quantitatively evaluated by Equation 6 [19].

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$  \hspace{1cm} \text{Equation 6}

where $k$ is the apparent reaction rate constant and $C_0$ and $C_t$ represent the concentrations at the initial time and time $t$, respectively.

The kinetics of BN degradation is presented in Figure 9 and Table 4. Plotting the logarithm of the normalized dye concentration against irradiation time for 180 min gave a good approximation of the rate constants. Nearly perfect linear relationships with high value of $R^2$ were observed, indicating that all reactions followed pseudo first order kinetics. The kinetics data shows that F, Sm$^{3+}$ codoped TiO$_2$ (0.6% Sm$^{3+}$) has the fastest rate of reaction compared to all the other photocatalysts. This is supported by the trends observed in photodegradation rate and percentage TOC removal.

Comparing the photocatalytic activity of the synthesised F, Sm$^{3+}$ codoped TiO$_2$ with data in literature showed that F, Sm$^{3+}$ codoped TiO$_2$ performed relatively well. Sun and co-workers reported a $k$ value of $1.6 \times 10^{-3}$ min$^{-1}$ for N-doped TiO$_2$ prepared at a pH of 5.5 [20]. While, Kuvarega et al. synthesised N/Pd doped TiO$_2$ (0.0% Pd), N/Pd-codoped TiO$_2$ (0.6% Pd) which showed a $k_a$ value of $2.35 \times 10^{-3}$ min$^{-1}$ with highest initial rate ($1.86 \times 10^{-2}$ min$^{-1}$) for the degradation of Eosin yellow [13]. The values reported by the two authors showed much lower catalytic activity compared to findings of the present work. F-doped TiO$_2$ and F, Sm$^{3+}$ codoped TiO$_2$ (0.6% Sm$^{3+}$) showed $K_a$ values of $8.6 \times 10^{-3}$ and $2.73 \times 10^{-2}$ min$^{-1}$ respectively which were higher than those reported by the two authors.
Figure 8: BN bis-azo dye degradation efficiency of various photocatalysts
Figure 9: Pseudo first order kinetics for degradation of BN bis-azo dyes for 180 min

Table 4 shows the rate constants for different TiO$_2$ samples after 3 h of irradiation with solar light. F, Sm$^{3+}$ codoped TiO$_2$ (0.6% Sm$^{3+}$) showed the highest degradation rate and the highest K$_a$ value due to the synergistic effects.

Table 4: Degradation rates and pseudo first order rate constants after 3 h solar irradiation

| Sample                      | Degradation after (%) | Rate constant (K$_a$/min)$^{-1}$ |
|-----------------------------|-----------------------|----------------------------------|
| Pure TiO$_2$                | 73.8                  | 6.6×10$^{-3}$                    |
| F-TiO$_2$                   | 78.4                  | 8.6×10$^{-3}$                    |
| Sm$^{3+}$-TiO$_2$ (0.2%)    | 93.8                  | 1.5×10$^{-2}$                    |
| Sm$^{3+}$-TiO$_2$ (0.4%)    | 96.6                  | 1.86×10$^{-2}$                   |
| Sm$^{3+}$-TiO$_2$ (0.6%)    | 98.4                  | 2.24×10$^{-2}$                   |
| Sm$^{3+}$-TiO$_2$ (0.8%)    | 98.2                  | 2.19×10$^{-2}$                   |
| Sm$^{3+}$-TiO$_2$ (1%)      | 98                    | 1.88×10$^{-2}$                   |
| F-Sm$^{3+}$-TiO$_2$ (0.6%)  | 100                   | 2.73×10$^{-2}$                   |

Figure 10 shows the proposed mechanism for the synergistic effects of F and Sm$^{3+}$ on TiO$_2$. Fluorine and Samarium have synergistic effects responsible for improving the photocatalytic activity of TiO$_2$ under visible light irradiation. Under visible light irradiation, substitutional F dopant creates two intra band gap states below to the conduction band edges leading to a narrower band gap than pristine TiO$_2$. The schematic diagram presented in Figure 10 shows the proposed possible mechanism for the synergistic effects of fluorine and samarium on the codoped photocatalysts.

Under light irradiation, electrons (e$^-$) are photo-excited from the valence band (VB) to the conduction band (CB), creating positive holes (h$^+$) in the VB. The introduction of a substitutional or interstitial fluorine in the TiO$_2$ results in the formation of intra band gap states close to the valence band. This enhances the visible light activity of the nanoparticles as electrons can be excited from the fluorine 2p orbitals to the conduction band. In pristine TiO$_2$, the generated carrier charges recombines and only a smaller fraction of the electrons and holes participate in the photocatalytic
reaction, resulting in low photocatalytic activity. In the presence of Sm, the photogenerated electrons are trapped, leading to electron-hole separation. The holes scavenge surface adsorbed water or hydroxyl molecules generating highly reactive hydroxyl radical species. The electrons, on the other hand, scavenged the oxygen molecules to form very reactive superoxide radicals. Both radicals are highly reactive towards the degradation of the azo dye compounds and other organic compounds such as BN dye.

Figure 10: Proposed synergistic effects of F and Sm$^{3+}$ doping on TiO$_2$

Figure 11 (a) and (b) shows colour disappearance and the disappearance of the absorption peak at 574.9 nm absorption wavelength. This is evidence that the chromophore responsible for absorption of visible light that is characteristic colour of the dye was being split into smaller and simpler molecules.
Figure 11: Degradation profile for BN dye using F, Sm$^{3+}$ codoped TiO$_2$ (0.6% Sm$^{3+}$) (a) UV-visible absorption spectra and (b) digital photograph showing decolourisation of BN dye.

Monitoring dye degradation profile is important to establish the degree of mineralisation and products of photodegradation. This is because some intermediate products like nitrated poly aromatic compounds are toxic, mutagenic, teratogenic and carcinogenic therefore not desirable [21]. Complete mineralisation of dye molecules to simpler and non-toxic compounds like CO$_2$, H$_2$O and inorganic ions is ideally desirable [14]. TOC analysis was used to monitor the organic carbon bound in the BN molecule as an indicator to complete mineralisation of BN dye. Figure 12 and Table 5 below show initial TOC concentration of 15 ppm and removal of 82% corresponding to 2.7 ppm concentration of TOC after 3 h irradiation time. This was significantly a higher fraction of TOC removal but the TOC concentration at 2.7 ppm was well above the maximum permissible limit which is 0.05 ppm. A further increase in degradation time to 4 h achieved complete TOC removal which means that BN dye was completely mineralised to simpler less toxic molecules and ions. The initial total organic concentration was 15 ppm and the final concentration after 4 h was 0 ppm.
Table 5: TOC removal during 4 h irradiation time

| Irradiation time (h) | TOC (ppm) | % TOC removal |
|----------------------|-----------|---------------|
| 0                    | 15.0      | -             |
| 1                    | 5.6       | 62.4          |
| 2                    | 4.2       | 71.7          |
| 3                    | 2.7       | 82            |
| 4                    | 0         | 100           |

Figure 12: The extent of TOC removal after 4 h

4. CONCLUSION

F, Sm$^{3+}$ co-doped TiO$_2$ was successfully synthesised by the sol-gel method and was open air calcined at 450 °C. F, Sm$^{3+}$ co-doped TiO$_2$ showed crystalline particles of predominantly anatase phase which were solar responsive. F and Sm$^{3+}$ codoping significantly reduced TiO$_2$ band gap and improved the quantum efficiency of the photocatalyst. This significantly improved the photocatalytic effect of F, Sm$^{3+}$ co-doped TiO$_2$, relative to that of pristine TiO$_2$ by an enhancement factor of 4. The different photocatalytic reactions followed pseudo first order kinetics with higher $R^2$. A higher reaction rate resulted in complete degradation of BN dye after 3 h of solar irradiation. TOC confirmed complete dye mineralisation after irradiation of 4 h, an indication that there was low probability of producing toxic metabolites. This is a successful, effective and innovative wastewater treatment method for the remediation of BN in aqueous water.
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