Photocatalytic oxidation of benzene to phenol and dye over N and S doped ferromagnetic nanosize TiO₂

Madhavi Shete (✉ smadhavi91@gmail.com)
Goa University

Julio Fernandes
Goa University

Research Article

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Abstract

In the present investigation we report presence of N, S and Ti$^{3+}$ in the TiO$_2$ samples and surface exhibits acidic characteristics. Synthesized TiO$_2$ samples were also found to be ferromagnetic in nature at room temperature and shows high photocatalytic activity in comparison to commercially available TiO$_2$ (DP-25). Nanosize TiO$_2$ with high surface area was obtained by simple sol – gel method of synthesis and during the synthesis hydrazine sulphate was used as fuel. Synthesized TiO$_2$ was found to be with N and S doping and also surface defects were present due to cationic and anionic vacancies. The presence of defects were confirmed from the Raman, IR, SEM-EDAX, PL analysis. Presence of Ti$^{3+}$ in the TiO$_2$ samples was confirmed from the ESR and XPS Spectra. XPS also showed presence of nitrogen and sulphur doping in the TiO$_2$ samples. Synthesized TiO$_2$ possesses acidic surface and surface acidity was measured from the pyridine adsorption and NH$_3$-TPD studies. Ferromagnetic behavior of the synthesized samples was confirmed from the VSM measurements. Synthesized samples were further studied for their photocatalytic activity towards methylene blue dye and 4-nitrophenol degradation and for photo-oxidation benzene to phenol conversion.

1. Introduction

In order to act as good photocatalyst semiconductor should possess high band gap property. TiO$_2$ is one of the metal oxide semiconductor with high band gap and acts as good photocatalyst. TiO$_2$ is well known as semiconductor photocatalysts due to its high band gap which is an important property for semiconductor to act as photocatalyst. TiO$_2$ mainly exists in three phases anatase, rutile and brookite. The most commonly studied phases of TiO$_2$ in photocatalysis are anatase and rutile phase. Since Anatase has high band gap (Eg = 3.2 eV) and in anatase TiO$_2$ has less possibility for the electron – hole (e$^-$$-$$h^+$) recombination thus mostly preferred as photocatalyst while rutile (Eg = 3.0 eV) phase is most stable phase. Photocatalytic properties are dependent on the physicochemical variables such as particle size, pore volume, surface area, crystallinity. Other then surface area and crystallanity, activity of TiO$_2$ also dependent on the morphology, therefore soft template synthesis of mesoporous anatase TiO$_2$ nanosphere were synthesized and found to be having enhanced photocatalytic activity [X. Li et al. 1943]. TiO$_2$ with acidic surface is found to be more photocatalytically active material. Suphation and desulphated TiO$_2$ are found to be with high acidic surface character then the other synthesized TiO$_2$ [J.Papp et al. 1994]. Sulphation in TiO$_2$ leads to increase in the acidity and also gives TiO$_2$ with high surface area with anatase phase [X.H. Lin et al. 2015]. The presence of surface oxygen deficiencies can act as capture centers for the photoexcited electrons and holes, while the surface hydroxyl group acts as centers for the photocatalytic reaction. Oxygen defects are located in the vicinities of rutile -anatase border. In terms of energy, these oxygen vacancy states in the anatase were determined to be located 2.02 - 2.5 eV above valence band and band gap corresponds to wavelength 506 – 614 nm. Besides other properties hydrophilicity in TiO$_2$ also enhances the rate of photocatalysis [L.B.Xiong et al. 2012]. Presence of pollutants such as organic dyes and phenols in the waste waters have became one of the crucial
problems and to overcome with this photo-oxidation is most convenient process. Photo-oxidation process by using semiconductors as photocatalyst are well known and TiO$_2$ as photocatalyst is more preferred mainly due to its favourable properties like non-toxicity, chemical inertness, stability over a wide pH range.

Photocatalytic activity usually depends on the surface properties such as surface area, surface acidity and presence of other impurities and defects [G. Colon et al. 2006; C. Xie et al. 2014; A.R gandhe et al. 2005; A.R. Gandhe et al. 2005]. One of the potential solutions for improving efficiency of TiO$_2$ is to shift its absorption from UV region into the visible light region, allowing for more photons to be adsorbed and utilized in decomposing the pollutants. TiO$_2$ with Ti$^{4+}$ oxidation state usually shows least activity in the visible light. In order to overcome this imitation its necessary to have reduced TiO$_2$ containing Ti$^{3+}$ to be an visible light active photocatalyst. Apart from Ti$^{3+}$, TiO$_2$ with nitrogen and sulphur doping also shows visible light activity by altering their band gap and energy levels [S.T. Hussain et al. 2009]. Presence of oxygen vacancies and Ti$^{3+}$ introduces ferromagnetism in the TiO$_2$. It is interesting to know that Ti$^{3+}$ ions with one 3d electron are usually generated in slightly reduced TiO$_2$. In such case oxygen is removed and the excess electrons are unpaired and can occupy nearby localized Ti 3d orbit and therefore convert Ti$^{4+}$ ions to Ti$^{3+}$ ions [D. Kim et al. 2009]. Presence of oxygen vacancies on the surface of TiO$_2$ play important role in the adsorption of the O$_2$ producing superoxide species, O$_2^-$. Adsorbed O$_2^-$ will later react with photogenerated hole resulting in the desorption of O$_2$ (g) and forming oxidizing agent in the photocatalytic process [T. Thomson et al. 2015]. It is well known that ferromagnetism exist in the TiO$_2$ thin films [S. Wang et al.2015]. Such ferromagnetism exist in the nanorod and films due to high surface area which possess abundant of surface defects.

Our present attempt is to synthesize N and S doped nanposize TiO$_2$ with high surface area to investigate room temperature ferromagnetism and its activity towards photocatalysis.

We herein report synthesis of ferromagnetic N and S doped TiO$_2$ and effect of surface defect and acidity of catalyst on photocatalytic activity. In the present study we have used hydrazine sulphate as fuel during the synthesis and the following synthesis is carried out by simple sol-gel method. In comparison to the hydrazine sulphate another TiO$_2$ was also synthesized by using ammonium sulphate as fuel. We investigate the surface, optical and magnetic properties of the synthesized TiO$_2$ in order to study particle size, surface area, band gap and origin of ferromagnetism in the samples.

The samples with small particle size, high surface area and presence of Ti$^{3+}$ could have lead to enhanced ferromagnetism at room temperature. Use of hydrazine sulphate during the synthesis has led to the incorporation of nitrogen and sulphur into the lattice thus showing high photocatalytic activity in the sunlight. In the present investigation it will be studied that synthesized TiO$_2$ exhibits highly reactive surface with nitrogen, sulphur and Ti$^{3+}$ species. Surface is also acidic and ferromagnetic behavior at room temperature and such reactive samples are further studied for their photocatalytic activity by selecting two pollutants methylene blue and 4-nitrophenol. The production of phenol is an important
industrial process due to its high demand in manufacturing of very important polymers, including polyamides, polycarbonates and phenolic resins. Phenol was obtained primarily from coal tar in small amounts [F. Iioffmann 1900]. Hock process was later developed to obtain phenol from cumene through intermediate formation of hydroperoxide and giving acetone as a co-product [N. Herron et al. 1987]. Direct oxidation of benzene was also carried out by using N₂O on a zeolite catalyst; but use of nitrous oxide involves formation of adipic acid and also requires purification step to remove various nitrous oxides and oxygen [E.J.M. Hensen et al. 2005]. Although there are also other processes to obtain phenol these still involve difficulties either in number of steps in the process or in purification of the product. Therefore there is a need for developing a suitable green method for the synthesis of phenol.

A photocatalytic process constitutes a greener approach to obtain industrially important compounds such as phenol, in presence of an environmentally safe oxidant such as H₂O₂. Recently photocatalytic phenol production was carried out by direct oxidation of benzene using Au-Pd metal nanoparticles supported on TiO₂ [R. Su et al. 2014]. Ambient oxidation of benzene to phenol was carried out on V-doped TiO₂ under UV irradiation. Higher catalytic activity was observed on a gold supported catalyst. The enhanced activity was attributed to the presence of Schottky junction, mesoporosity and charge carriers. A highest % conversion of benzene to phenol was 18% [P. Devraji et al. 2014]. For the comparative study between the synthesised TiO₂ and DP-25 photooxidation of benzene to phenol was carried out. Further properties of the synthesized samples and reactivity compared with reference to commercial DP-25 sample.

2. Chemical Synthesis

TiO₂ was synthesized by using Titanium isopropoxide as the Ti precursor and Hydrazine sulphate. Hydrazine sulphate was dissolved separately in minimum quantity of distilled water and to that titanium isopropoxide was added at 0 °C such that final molar composition of Titanium isopropoxide to hydrazine sulphate is 1:2 and 1:3 was stirred for 2 h. The resulting solution was dried at 70 °C thus forming white color precursor. Thermal analysis of the dried precursor was carried out and further precursor was calcined at 600 °C for 3 h to give final TiO₂ samples as T1 and T. Similarly another TiO₂ was synthesized by using Titanium isopropoxide and ammonium sulphate and its code is T2.

2.1 Catalyst characterization

Phase identification was carried out from X-ray powder diffraction the patterns (XRD) recorded on a Rigaku Ultima IV diffractometer, using Ni filtered Cu Ka radiation (λ=1.5406 Å). The crystallite sizes were determined using the Scherrer formula t = 0.9λ / b×cosθ, where λ is the wavelength characteristic of the Cu Ka radiation, b is the full width at half maximum (in radians) and θ is the angle at which the 100 intensity peak appears.

Nitrogen adsorption isotherms were obtained by using Quantacrome Autosorb iQ and Asiqwin gas sorption system to find the surface area and their respective pore size distributions was obtained by BJH
pore size distribution analysis. Morphology and elemental study was carried by the SEM – EDAX analysis. Thermal studies were carried out on NETZSCH STA 409PC by using Al₂O₃ crucible at the heating rate of 10°C /min in oxygen atmosphere. TEM analyses were carried out to find the particle size of the synthesized catalyst on Phillips CM 200 operating voltages: 20 – 200 kV resolution: 2.4 Å. IR absorption spectra were recorded in 4000 - 400 cm⁻¹ range on Shimadzu IR Prestige-21 by diluting a few milligrams of sample in KBr. PL measurements were performed using a Horiba Jobin Yvon Fluorolog 3 spectrophotometer equipped with a 450 W xenon lamp with a tunable excitation wavelength. Raman scatterings were recorded on Horiba JY Lab Raman HR 800 Micro Raman Spectrometer and excitation wavelength is 632.8 nm. Band gap determination is carried out by using UV-VIS spectrophotometer (Shimadzu UV-2450).

ESR measurements were carried out on JEOL, Japan JES-FA200 ESR spectrometer. XPS spectra recorded for the representative sample on microtech multiple ESCA 3000 spectrometer.

The magnetic properties were measured on Quantachrome Versa Lab vibrating sample magnetometer (VSM) at 300 K.

TPD Analysis was carried out to measure the acidity of the samples using ammonia as a probe on a Chemisorb 2720, Micromeritics instrument. Typically, in a quartz tube, 100 mg of the sample (-100 mesh) was held between small lumps of inert quartz wool. The sample tube was connected to the device and heated to 120 °C, 12 h, to remove adsorbed water and other volatile impurities. After cooling to 25 °C, dry ammonia gas (20 % NH₃, He (UHP); 20 mL/min) was then passed at for 15 minutes. The physically adsorbed ammonia was flushed out by He (UHP) carrier gas at 25 °C. The sample was heated from 25 °C to 600 °C at a heating rate of 5 °C/ min and the desorbed ammonia was measured using a thermal conductivity (TCD) detector.

2.2 Photocatalytic activity

(i) Photodegradation of methylene blue dye

The photocatalytic activity was evaluated using methylene blue degradation as a test reaction. The experiment was carried out simultaneously for both catalysts in sunlight for 120 min, between 10.00 am and 12.00 noon. In a typical run, 100 ml of aqueous dye solution (12 ppm, pH 7.5) and 0.4 g of the catalyst were taken in a 250 ml beaker and was exposed to sunlight for the duration of the experiment. The pH was adjusted with 0.1 M NaOH solution. The solutions thus exposed to sunlight were stirred intermittently. After every 15 min 0.5 ml aliquots were pipetted out, centrifuged and the absorbance of the clear supernatants was determined at 660 nm wavelength against appropriate blanks

(ii) Photodegradation of 4-Nitrophenol

Photocatalytic degradation of 4-Nitrophenol (4-Np) was carried out for all catalyst (0.01 g) in 50 mL of 0.1 mmol/L 4-Np in presence of 5 mL of 0.1M H₂O₂ (pH = 5). The solutions were exposed to sunlight. The
solutions thus exposed to sunlight were stirred intermittently. After every 20 min 2 mL of reaction mixture was centrifuged and analyzed by UV-Vis spectroscopy against appropriate blank.

### (iii) Photooxidation of benzene to phenol

Photocatalytic oxidation reaction were conducted in a quartz RB flask for different periods of time with a 400 W mercury lamp (l=200 - 400 nm) using a flow-type double-jacketed quartz reactor. In a typical experiment, 30 mg of catalyst was added to reactant mixture of 2 mL of CH\textsubscript{3}CN, 1 mL of benzene, and 2 mL of 25 % H\textsubscript{2}O\textsubscript{2}. The temperature of the double jacketed reactor and quartz RB was maintained at 25 °C by allowing water circulation. Before any irradiation, the reaction mixture was stirred for 30 min in the dark and irradiation was conducted for time between 5 to 18 h. After irradiation, organic and aqueous layers were separated with separating funnel. Oxidized products of benzene were analyzed with an Agilent 6890 gas chromatograph (GC) equipped with a flame ionization detector (FID) and a HP-5.5% phenyl methyl siloxane capillary column. The presence of phenol was confirmed by analyzing both organic and aqueous layers.

### 3. Results And Discussion

#### 3.1 Structure, surface and morphology study

Several methods for preparation of TiO\textsubscript{2} are reported most of them belongs to the wet chemical methods. Among others wet chemical method hydrothermal and sol-gel method can be selected as best method. Sol-gel method is simple economical and most frequently used method that give TiO\textsubscript{2} with interesting properties such as different morphologies, small particle size and high surface area [A. Sharma et al. 2014]. In the present investigation synthesis of TiO\textsubscript{2} catalyst was carried out by using hydrazine sulphate as fuel during the synthesis. Figure 1. Shows XRD pattern of synthesized samples T, T1 and T2. All the samples were calcined at 600 °C as seen from the TG curve in Fig. 2 complete desulphation and samples attains stability at temperature 600 °C. All the samples showed diffraction peaks associated with the tetragonal anatase phase of TiO\textsubscript{2} (JCPDS – 782486). As seen from the Fig. 1 change in the ratio of titanium isopropoxide to the hydrazine sulphate have slightly affected the crystallization of the titania. In case of sample T and T1 peak broadening is observed then the T2 sample. The observed decrease in the peak intensity in T and T1 then the T2 signifies the amorphous nature of the samples. peak broadening indicates that particle were in the nanosize. For the nanosize powders XRD peak broadening is observed due to insufficient diffraction planes cancels the intensity outside the peak centers.

Table 1 Synthesis and properties of TiO\textsubscript{2} samples.
It is well known that particle sizes play an important role and are affected when the fuel is used during the synthesis. Figure 3 shows TEM images of the synthesized samples. All the synthesized samples show samples with particle size in the nanometer range and are spherical in shape. Calculated particle sizes of the synthesized samples are given in Table 1.

TiO₂ samples were investigated by N₂ adsorption – desorption isotherms. Figure 4a) and b) shows the obtained results analyzed by BET method for the surface area and BJH pore size distribution. The relative isotherms of the samples were of type IV, which is characteristics of mesoporous materials. The respective surface area values are given in Table 1. Samples are seen to be with high surface area and pore radius, which ensure enhanced reaction rates due to high level of interaction of the reactant with the active sites.

The surface morphology of the samples is studied by scanning electron microscopy and micrograph are given in the Fig. 5. The samples appeared as agglomeration of the smaller particles. The surface of the particles is rough and large number of the pores found to be seen. The elemental data of the respective samples are given in the Table 1. The presence of sulphur element peak was observed other than Ti and O. It is seen that as the surface area increases, there is decrease in the O/Ti ratio. The decrease in the O/Ti ratio indicates that there is large number of surface defects present in the samples. This defects could be either cationic or anionic vacancies.

### 3.2 Spectroscopic study

Figure 6 shows Raman spectra of the synthesized TiO₂. As seen in the figure Raman spectra shows six bands at Eg (1) → 142.8 cm⁻¹, Eg (2) → 197.6 cm⁻¹, B1g → 396.15 cm⁻¹, A1g + B1g → 514.8 cm⁻¹, Eg (3) → 639.7 cm⁻¹. The absence of the weak band around 140 cm⁻¹ demonstrate that no rutile phase was present in the synthesized samples. There was also no band seen in range of around 1000 cm⁻¹ which corresponds to the presence of the sulphate groups. Figure 6 inset depicts that Eg (1) signal is broad in T and T1 then the T2 and becomes intense. Raman signal of TiO₂ is very sensitive to the vibrational mode of O²⁻ ions in the Ti-O bond [19–20]. The strength of the Raman signal depends upon the polazibility of O²⁻ surrounding Ti⁴⁺ ion in basic TiO₆ unit. Presence of oxygen vacancies will affect the vibration of Ti-O.
bond and thus effect the intensity, position and width of the Raman bands. It is seen from the Raman intensity of T2 is very low and inset shows normalized spectra of the samples. From the normalized spectra it is seen that Eg (1) band of T and T1 are highly intense, broad and are slightly blue shifted then the T2 sample. This shift in the position and peak broadening signify presence of oxygen vacancies in the TiO$_2$ octahedra.

Figure 7 shows IR spectra of the synthesized samples. Figure 7 shows peak in the samples at around 3300–3500 cm$^{-1}$ due to stretching vibrations of O-H and bending vibrations of adsorbed water molecules. All the samples present spectra with strong band located at around 700 cm$^{-1}$ attributed to Ti-O stretching and Ti-O-Ti bridging stretching modes. The peak at around 1640 cm$^{-1}$ corresponds to bending vibrations of the O-H and N-H. The bands are seen in the range of 1000 to 1400 cm$^{-1}$ in the T, T1, T2 and are absent in the DP-25. The presence of this bands could be due to S-O bond. This confirms our argument that the N and S doped TiO$_2$ is formed. Figure 6 inset give high resolution of the bands in the range from 400 to 700 cm$^{-1}$. The original vibration band in TiO$_2$ at 476 cm$^{-1}$ is blue shifted to 482 cm$^{-1}$ and vibrational modes at 574 cm$^{-1}$ and 708 cm$^{-1}$ are red shifted to 563 cm$^{-1}$ and 689 cm$^{-1}$.

Presences of sulphur in the synthesized catalyst were confirmed from SEM-EDAX analysis and the respective quantities of Ti, O and S are given in the Table 1. As seen from the Table 1 decrease in the O/Ti ratio indicates deficiency in oxygen i.e more oxygen vacancies in T2. The oxygen vacancies are generally created by the elimination of sulphate and OH functional groups elimination during the synthesis. ESR is an powerful tool in detecting the spin polarized change state of defective TiO$_2$ nanostructure. ESR analysis was carried out to detect Ti$^{3+}$. Figure 8. gives ESR spectra of the synthesized TiO$_2$ samples. Presence of ESR signal at 2.003 is due to O$^-$ whereas, signal at 1.980 is due to presence of Ti$^{3+}$ [B. Santara et al 2013] presence of peak at 2.003 in T, T1 and T2 is due to Ti$^{4+}$ - O$_2^-$ peroxide species which is result of chemisorbed bonding of O$_2$ with Ti$^{3+}$ centers [S. Chang et al 2009] In order to investigate chemical state of the possible dopants into the TiO$_2$ lattice, XPS measurements are carried out and the binding energies of the Ti2p, O1s, N1s, and S2p are studied. The results obtained with peak positions are shown in the Fig. 9. According to the literature standards binding energy of Ti2p$_{3/2}$ in TiO$_2$, that for Ti$^{3+}$ is located at 457.7 eV and for Ti$^{4+}$ is located at 459.5 eV. All the peak positions with respect to their binding energies are shifted towards higher values. This could be due to presence of defects in the lattice. The high resolution spectra shows two peak at 458 eV and 464 eV and this two peaks are due to presence of Ti$^{3+}$ and Ti$^{4+}$ in the samples. The binding energies for the Ti2p$_{3/2}$ and Ti2p$_{1/2}$ are appeared at 464 eV and 469 eV respectively. This result shows that Ti$^{4+}$ ions near oxygen vacancies occupy an electron from the oxygen vacancy cavity Vo and transforms to Ti$^{3+}$ ions yielding an F$^+$ center. An increase intensity of Ti$^{3+}$ strongly indicates presence of high concentration of oxygen vacancies which are created during the synthesis process as compared to DP-25. Also shift in the peak position towards higher binding energy in T, T1a and T2 was observed as compared to DP-25 could be due to nitrogen and sulphur doping. Figure 9d) shows O1s spectra for the samples T, T1, T2 and DP-25. The O1s peak for the samples
appeared at around 528 eV. Existence of O1s spectra asymmetric curve at high binding energy indicates that several oxygen species are present in the near surface region [21–22]. Figure 9c) shows peak at 397 eV which is due to existence of nitrogen doping into the TiO$_2$ lattice. Figure 9b) shows peak at 168–169 eV corresponding to the sulphur binding energies. Therefore from the figure it is clear that sulphur was doped into the lattice. Presence of Ti$^{3+}$, N, S was therefore confirmed from the XPS studies.

Figure 10 shows UV-Vis spectra of the synthesized samples. All the samples shows absorbance at 350–400 nm with shift towards visible region. The red shift in the samples could be due to either presence of Ti$^{3+}$ in the octahedral lattice of TiO$_2$ and is confirmed from the ESR and XPS studies. From the XPS studies it was also confirmed that there is presence of nitrogen and sulphur in the T, T1 and T2 samples and is absent in the DP-25. Whereas Ti$^{3+}$ is present in all the samples including DP-25. Therefore red shift of DP-25 is due to presence of Ti$^{3+}$ and red shift in T, T1 and T2 then the DP-25 is due to presence of nitrogen and sulphur doping taking place into the lattice [G. Yang et al 2010; T. Ohno et al. 2004; S. Pany et al. 2014; N. Serpone et al. 1995]. Photoluminescence is a result of surface phenomenon and a change in the surface environment would have a significant effect on the photoluminescence scan process. Large surface area and strong presence of defect, effect of defect related PL emission to be strong. Figure 11 shows PL spectra for the synthesized samples. All the samples shows emission peak at 370–390 nm corresponding to the phonon assisted indirect L → M transition from the conduction band edge to the valence band in the Brillouin zone [X. Xin et al 2016]. The emission peak originating in the wavelength range between 400–800 nm are usually associated with self trapped excitons, oxygen vacancies and surface defects. Visible luminescence band originate in the TiO$_2$ mainly due to the oxygen vacancies with Ti$^{3+}$.

Presence of oxygen vacancies are confirmed from the earlier characterized techniques. The presence of oxygen vacancies are mainly considered as F centers. Most of the surface and grain boundary oxygen vacancies act as non-radiative centers and therefore PL spectra is seen to be less intense. The intensity of bands were high in case of T then those of other samples and this could be due to large number of N and S doping in the T than other samples. Presence of oxygen defects result to occupy position below conduction band at level of 0.7 to 1.0 eV, which further result electrons to take longer time to recombine with the holes resulting the PL spectra with less emission intensity. Whereas nitrogen and sulphur doping will occupy level just above the valence band and will inhibit the facile recombination of the electron and hole. Therefore from the above spectra it can be seen that high intensity peak are due to presence of nitrogen and sulphur doping whereas reduction in the peak emission intensity takes place due to oxygen vacancies. Thus PL analysis evidence that there is presence of oxygen vacancies and nitrogen and sulphur doping in the synthesized samples.

### 3.3 Surface acidity

Raman analysis predicts the presence of defects in the samples and IR, SEM-EDAX, ESR analysis gives evidence for presence of oxygen vacancies due to shifts in bond vibration modes and elimination of sulphate and decrease in O/Ti causing defect in the samples. In order to study type of acid strength
pyridine adsorption was carried out on the synthesized samples. After pyridine adsorption samples showed bands at 1600 cm\(^{-1}\) and 1402 cm\(^{-1}\) and are associated with is Lewis acid site as shown in the Fig. 12b) [L. K. Noda et al 2003]. There were no bands seen due to presence of Bronsted acid sites. This could be due to lack of OH groups. pyridine adsorbed IR spectra shows presence of Lewis acidity in the all synthesized samples. In order to know the amount of acid sites NH\(_3\) – TPD analysis was carried out. The results of the NH\(_3\)-TPD are given in the Fig. 12a). Table 2 gives amount of acidic sites on the synthesized TiO\(_2\) samples T and T1 show high acid values as compared to T2. ESR and XPS spectroscopy confirmed the presence of Ti\(^{3+}\) and nitrogen and sulphur doping in the samples in comparison to the DP-25. Lewis acidity originated due to presence of Ti\(^{4+}\) and Ti\(^{3+}\) in the samples. T2 shows only medium strength acid site due to presence of less quantity of Lewis acid sites whereas in case of T1 and T there is presence of both weak and medium type acidity and are found to be highly acidic due to more Lewis acid sites. It is also stated by L. Xiong et al that TiO\(_2\) surface with Ti\(^{3+}\) will give low acidic value in TPD profile than the Ti\(^{4+}\), due to strong binding of Ti\(^{3+}\) site. Therefore from the 10 a) one can conclude that the T2 with low acidic value is due to presence of more number of Ti\(^{3+}\) and high oxygen vacancies.

Table 2 : NH\(_3\)-TPD data of synthesised samples

<table>
<thead>
<tr>
<th>Catalyst code</th>
<th>Strength of acid sites ((\mu)mol(g^{-1}))</th>
<th>Total acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak (100 °C -250 °C) Medium (250°C-350°C)</td>
<td>Strong (350°C-450°C)</td>
</tr>
<tr>
<td>T</td>
<td>36</td>
<td>36 18</td>
</tr>
<tr>
<td>T1</td>
<td>36</td>
<td>30 0</td>
</tr>
<tr>
<td>T2</td>
<td>6</td>
<td>12 18</td>
</tr>
</tbody>
</table>

3.4 Magnetic measurement

Magnetic measurements of the synthesized samples were carried out using VSM. Figure 13. gives hysteresis loop profiles of the synthesized samples and also compared with Degussa (DP-25). Ferromagnetic property in the metal oxide depends on the shape, size and porosity of the catalyst. [21] Sample T2 shows highest magnetism upto 0.07emu/g given in Table 3 and this high magnetism in T2 could be due to high particle size, porosity and presence of oxygen vacancies. Catalyst with high porosity is obtained when there is sudden increase in calcinations temperature or at high temperature and this takes place due to elimination of organic matter or water molecules. When such process accurs it
developes porosity and defects or vacancies. T2 is highly porous with high surface area of 55.99 m²/g and oxygen vacancies as seen from the IR, Raman, UV and EDAX analysis. Presence of oxygen vacancies is the reason for high magnetic moment in T2 and T1, T shows lower magnetic moment compared to T2 but in case of DP-25 magnetism is high compared to T1. This could be due to existence of mixed phases in commercial DP-25 catalyst. The respective magnetic values are given in Table 3. Presence of vacancies changes the band structure by occupying localized Ti 3d orbit and thus reduces Ti⁴⁺ to Ti³⁺ ions and F⁺ centre formed. s - d exchange interaction between F⁺ centre and Ti³⁺ favors the existence of ferromagnetism in TiO₂ [B Santara et al. 2013]. In the present study it is seen that the ferromagnetism exist because of oxygen vacancies, high surface area and porosity of the catalyst. Existence of ferromagnetism is due to both due to oxygen vacancy and porosity which further improves the visible light activity of the catalyst and such catalyst could be well suitable for photocatalysis and spintronics.

Table 3 Magnetic properties of the samples

<table>
<thead>
<tr>
<th>Catalyst Code</th>
<th>Magnetic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ms</td>
</tr>
<tr>
<td>T</td>
<td>0.067</td>
</tr>
<tr>
<td>T1</td>
<td>0.043</td>
</tr>
<tr>
<td>T2</td>
<td>0.071</td>
</tr>
<tr>
<td>DP-25</td>
<td>0.053</td>
</tr>
</tbody>
</table>


From the results of various characterization techniques and NH₃-TPD profiles it is seen that T2 catalyst possesses more number of oxygen defects of oxygen vacancies, whereas catalyst T1 and T possesses more surface acidity. Photocatalytic activity of all the synthesized catalyst were evaluated for the photodegradation of methylene blue dye and 4-Nitrophenol as pollutants.

Compared to commercial TiO₂ i.e DP-25 the synthesized catalyst T2, T1 and T showed higher and much competitive photocatalytic activity. The higher activity shown by catalyst T2 could be due to presence of surface oxygen defects and high surface area. Similarly high activity in T and T1 catalyst could be due to its small particle size and acidic nature. In metal oxide presence of oxygen vacancies will act as electron trapping site which further inhibits the electron – hole recombination. Oxygen vacancies in metal oxides will occupy the level below conduction band and thus trap the electron which leads to inhibition of electron hole pair recombination process.
In case of catalyst with higher surface area process of adsorption onto the surface of the catalyst is more facile. More the adsorption high will be the activity of photocatalytic result. In case of catalyst T1 and T presence of Lewis acidity will help in O\textsubscript{2} adsorption process wherein further helps trap electron in photocatalytic process.

Lewis acidity in the samples helps in the chemisorptions of water to generate reactive hydroxyl radicals which further enhance the rate of photocatalysis. Whereas, adsorption of oxygen is more predominant on the oxygen deficient surface thus facilitating interfacial charge transfer [J. Papp et al 1994]. The high activity of T, T1 and T2 then the DP-25 could be also due to nitrogen and sulphur doping as evident from XPS studies.

All the three catalyst were N and S doped and shows high photocatalytic activity then DP-25 therefore one of the catalyst T with 1:3 molar ratio of titanium isopropoxide and hydrazine sulphate and with small particle size was further studied for photooxidation of benzene to phenol reaction. Results of the photooxidation of benzene to phenol is summarized in Table 4. Photocatalytic activity was measured at different time intervals under UV irradiation. The results shows that after irradiation of 20h. T showed 11.8 % of the benzene conversion with 86 % selectivity. The level of benzene conversion increases as the irradiation time increases from 5 to 20 h, respectively, decrease in the phenol selectivity was also observed from 100 % to 86 %. The decrease in the phenol selectivity is mainly due to further oxidation of phenol to other side products, such as hydroquinone. Many control experiments were also conducted, such as benzene oxidation without catalyst. In dark or without irradiation, there is no much reaction. Irradiation for 20h without catalyst induces photochemical oxidation of benzene. Large amount of side products were observed in case of without catalyst, indicating presence of free radicals which enhances the free radical mechanism due to photochemical conversion and homogeneous cleavage of hydrogen peroxide decomposition. The high benzene conversion was observed in case of UV irradiation then the visible light thus facilitating the necessary of the energetic holes on the titania surface. Without hydrogen peroxide there was no conversion of benzene was observed therefore highlighting the role of dissolved oxygen thus pathway of green chemistry.

Comparative study between DP-25 and synthesised catalyst T shows that T gives high % conversion of benzene then the DP-25. As from the XPS data DP-25 being N doped and T is N and S doped thus indicating that addition sulphur doping enhances the % conversion of the benzene this could be due to different energy levels of the N and S in the TiO\textsubscript{2}. 
### Table 4
Photocatalytic benzene to phenol oxidation measured under different conditions

<table>
<thead>
<tr>
<th>Catalyst and irradiation conditions</th>
<th>t (h)</th>
<th>Benzene Conversion (%)</th>
<th>Phenol Yield (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without catalyst</td>
<td>5</td>
<td>0.25</td>
<td>0.25</td>
<td>100</td>
</tr>
<tr>
<td>DP-25 (UV)</td>
<td>5</td>
<td>0.83</td>
<td>0.78</td>
<td>94.19</td>
</tr>
<tr>
<td>T (UV)</td>
<td>5</td>
<td>1.13</td>
<td>1.13</td>
<td>100</td>
</tr>
<tr>
<td>T (Visible)</td>
<td>5</td>
<td>0.3</td>
<td>0.3</td>
<td>100</td>
</tr>
<tr>
<td>T (UV)</td>
<td>15</td>
<td>9.1</td>
<td>9.1</td>
<td>100</td>
</tr>
<tr>
<td>T (UV)</td>
<td>20</td>
<td>11.8</td>
<td>10.2</td>
<td>86</td>
</tr>
<tr>
<td>T (no light)</td>
<td>20</td>
<td>2.0</td>
<td>2.0</td>
<td>100</td>
</tr>
<tr>
<td>Without catalyst</td>
<td>20</td>
<td>1.2</td>
<td>0.6</td>
<td>50</td>
</tr>
</tbody>
</table>

### 5. Conclusions

Synthesis of TiO$_2$ was carried out using hydrazine sulphate as fuel. Synthesized TiO$_2$ were found to be with smaller particle size and high surface area confirmed form the TEM and BET analysis. SEM-EDAX elemental analysis, Raman and PL spectra showed the presence of oxygen vacancies in the TiO$_2$ samples. From the ESR and XPS studies it was seen that there is presence of Ti$^{3+}$. XPS also showed that there is nitrogen and sulphur doping has occurred in the synthesized TiO$_2$ samples. Acidic nature of the synthesized TiO$_2$ was confirmed from the NH$_3$-TPD profiles. Our results provide convincing evidence for the occurrence of room temperature ferromagnetism in the TiO$_2$ samples. Synthesized TiO$_2$ catalyst shows high photo degradation activity for methylene blue dye then the DP-25 catalyst. T synthesised catalyst showed high activity for the photocatalytic oxidation of benzene to phenol then the DP-25.

### Declarations

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#### Author information

**Ethical approval**

Not applicable
Contributions

Madhavi shete : design of the research, sampling, data analysis, writing original draft; Julio Fernandes: field work coordination, data collection and support;

Consent to participate
All authors consent to participate in this research.

Consent for publication
All authors consent to publish this research in ESPR if accepted.

Competing interests
The authors declare no competing interests.

References

F. Iioffmann 1900 U.S. Pat 644,077


S. T. Hussain, K. Khan, R. Hussain, 2009 *Journal of Natural Gas Chemistry*, **18**


X. Xin, T. Xu, C. Wang 2016 *Scientific reports 6*, article number: 23684


X. Li, M. Zou, Y. Wang 2017 *Molecules 22 (11)* 1943.


**Figures**

**Figure 1**

XRD pattern of the synthesized samples

**Figure 2**

TG curves of the synthesized precursors.
Figure 3

TEM images of the synthesized T, T1 and T2 samples.
Figure 4

a) $N_2$ adsorption-desorption isotherm. b) Pore size distributions of synthesized samples.

Figure 5

SEM-EDAX images of the synthesized samples.

Figure 6

Raman spectra of synthesized samples.

Figure 7

FTIR spectra of synthesized samples

Figure 8

ESR spectra of synthesized TiO$_2$ samples
Figure 9

High resolution XPS of T, T1, T2 and DP-25 samples a) Ti2p b) S2p c) N1s d) O1s.

Figure 10

UV-Vis spectra of the synthesized samples

Figure 11

Photoluminscence spectra of the samples.

Figure 12

a) NH$_3$ – TPD profile for synthesized samples and b) IR of pyridine adsorbed on samples.

Figure 13

VSM analysis of T, T1, T2 and DP-25.

Figure 14

Photodegradation of methylene blue dye and of 4-Nitrophenol.