Original Article

Synthesis of spherical mesoporous titania modified iron-niobate nanoclusters for photocatalytic reduction of 4-nitrophenol

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Spherical mesoporous titania modified iron-niobate nanoclusters FNT1 [Fe x Nb y Ti 1−x−y O 2−x y/z (x=0.01)], with relatively small particle size 10±2 nm and S BET 145 m 2 g −1 were prepared using a sol–gel method, from the reaction of titanium and niobium tartrate with triethanol amine and ferric nitrate solution. HRTEM of FNT1 shows coexistence of porous mesostructure and high symmetric order of crystallinity in the nanoparticles. The mesopore size is in the range of 4–5 nm and the lattice fringes of 0.37 nm is observed in the mesopore walls which correspond to the d-spacing between adjacent (101) crystallographic planes of FNT1 phase. This is supported by XRD studies. In the presence of UV light, FNT1 (0.1 g/50 mL) reduces the 4-nitrophenol (4-NP) (0.0139 g L −1) to 4-aminophenol by using NaBH 4 (0.054 g L −1) in contrast to pure TiO 2 and other composites of Fe x Nb y Ti 1−x−y O 2−x y/z photocatalysts. The 4-NP is reduced to 4-aminophenol within 10 min in the presence of FNT1 and UV light, but in the absence of the catalysts, it takes approximately 82 min. The catalytic activity of FNT1 is enhanced significantly in the presence of UV light compared to the absence of UV light. We observed that the catalytic activity of the prepared catalyst also depends on crystal size, particle morphology and particle porosity, and dopant concentrations.

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1. Introduction

4-Nitrophenol (4-NP) is a very significant compound of NP group and considered as an important hazardous and toxic pollutant. Mostly they are used extensively in chemical industries for the production of different kinds of pesticides, pharmaceutical and synthetic dyes [1–6]. 4-NP can damage the central nervous system, liver, kidney and blood of animals and humans. Therefore, removal of 4-NP is essential to protect the human being. The easiest way to remove 4-NP from the environment is the reduction of 4-NP to 4-aminophenol (4-Amp).

On the other hand, the reduced product 4-aminophenol is very

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useful in a wealth of applications that include analgesic and antipyretic drugs, photographic developer, corrosion inhibitor, anticorrosion lubricant, and so on [1]. In this context, mesoporous compounds have an important role in photochemical reactions for removal of such type of pollutants. Mesoporous titanium dioxide (TiO$_2$) has continued to be highly efficient in photocatalytic applications, because of its high surface area and porous frameworks [7,8]. In the past decade, there have been few reports about mesoporous transition-metal oxides [9–11].

Generally, nanoparticles are used for the fabrication of mesoporous structure of TiO$_2$. However, nanocrystalline TiO$_2$ is a promising semiconducting material that has attracted considerable interest for their applications as electodes [12], electronics [13], capacitors [14], optics [15,16], sensors [17,18], ceramics [19], solar cells [20–22], catalysis [23,24] and photocatalysis [25–28].

Therefore, many research scientists are now-a-days involved in the research work on the photocatalytic activity of TiO$_2$ doped with different metal ions such as Ag [29], Au [30], Mn [31], Fe [32,33], Co [34], Ni [35,36], Cu [37,38], and Pd [39] etc. Recently, non-metals such as nitrogen doped La$_2$Ti$_2$O$_7$ [40,41], nitrate and nitrite doped TiO$_2$ were shown to be good photocatalysts [42]. Ismail et al. found that TiO$_2$ microspheres with porous structures have higher photocatalytic activity and they can be easily recovered for their re-use as catalysts [43]. Furthermore, photocactivity is highly dependent on surface area and crystallinity or crystal sizes, which are in turn influenced by the synthetic methods of titania synthesis [44,45].

The most recent studies show that the addition of small quantities of Nb$_2$O$_5$ into TiO$_2$ lattice significantly increases the photocatalytic activity and surface acidity of TiO$_2$ [46,47]. On the other hand, Fe(III) doped photocrystalline titania have also been widely studied in the field of photocatalysis [32,33,48–50]. The effect of simultaneous doping of Fe and Nb dopants in TiO$_2$, mesoporous structure and its photocatalytic activity has not yet been reported. Moreover, we are also interested to see how photocatalytic effect changes, when both iron and niobium are co-doped with TiO$_2$. Non-conventional synthetic procedures such as: chemical vapor deposition [51], hydrothermal [52], microemulsion [53], sol–gel [54,55], coprecipitation [56], and chemical methods [26,33,38], were already adopted to produce such compositions.

In the present work, we report the synthesis and characterization of spherical mesoporous Fe$_3$Nb$_2$Ti$_{1−x}$O$_2$$_{x}$ (x = 0.01) (FNT1) with a surface area of up to 145 m$^2$ g$^{-1}$ prepared from a titanium/niobium tartrate with triethanol amine and ferric nitrate precursor by sol–gel method. Here, the role of Fe(III) in Fe–Nb–TiO$_2$ composite is to compensate the charge imbalance caused by the replacement of Ti(IV) with Nb(V) in TiO$_2$ crystals, which result in improving charge separation among the photo-produced hole–electron pairs. However, interestingly our study show that Fe and Nb doped TiO$_2$ display good mesoporous nature and brings the photocatalytic reduction of 4-NP to 4-Amp in aqueous medium, containing NaBH$_4$ and in the presence of UV light. The mesoporous FNT1 photocatalysts has good reduction catalytic activity compared to other prepared composites of Fe$_3$Nb$_2$Ti$_{1−x}$O$_2$$_{x}$ and pure TiO$_2$. FNT1 spheres have diameters of about 8–10 nm and mesopores sizes are of about 4–5 nm. The nano-sized photocatalysts were characterized by thermal analysis, X-ray diffraction, UV–visible spectroscopy, BET surface area, UV–visible diffuse reflectance spectra, EPR spectra and transmission electron microscopy (TEM) analyses.

2. Experimental

2.1. Chemicals required

Titanium dioxide (analytical reagent), Nb$_2$O$_5$ (analytical reagent), Fe(NO$_3$)$_3$·$6$H$_2$O (analytical reagent), sodium hydroxide (analytical reagent), NH$_4$OH (25%), HF (40%), tartaric acid, ethanol, triethanolamine (TEA) and 4-nitrophenol (4-NP) were of analytical reagent grade and were procured from B.D.H., India.

2.2. Synthesis of Fe$_3$Nb$_2$Ti$_{1−x}$O$_2$$_{x}$ nanoclusters

Spherical nanoclusters of Fe$_3$Nb$_2$Ti$_{1−x}$O$_2$$_{x}$ (x = 0.01, 0.05, 0.1, 0.2) were prepared by sol–gel method. The total synthesis was carried out in two steps. In the first step, the stock solutions of ferric nitrate, titanium tartrate and niobium tartrate solutions were prepared. The solution of the titanium and niobium tartrate complexes, which are not commercially available, were prepared in the laboratory from its hydrated oxide (Nb$_2$O$_5$·$n$H$_2$O and TiO$_2$·$n$H$_2$O); the details of the preparation process are discussed elsewhere [26,33,57]. In the second step, stoichiometric amounts of titanium tartrate (100 mL; 0.2545 g L$^{-1}$), niobium tartrate (1.72 mL; 0.2167 g L$^{-1}$), ferric nitrate (0.088 g, 0.21 mmol) with triethanolamine (3 mL) and 20 mL of absolute ethanol solutions were taken in a beaker as per the predetermined chemical compositions (example shown for x = 0.01) with constant stirring for 30 min at room temperature. Then the mixture was adjusted to a pH of 9.0 with 6 M NaOH solution, and stirred for 30 min, yielding a stable light yellow homogeneous emulsion. The resulting mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated to 150 ºC for 20 h under auto generated pressure.

The reaction mixture was allowed to cool to room temperature and the precipitate was filtered, washed with distilled water five times, and dried in a vacuum oven at 100 ºC for 1 h and then heated on furnace at different calcination temperatures for removing all the oxides of carbon and water vapors. The composites with different amounts of Fe and Nb doping will be denoted as the following: Fe$_3$Nb$_2$Ti$_{1−x}$O$_2$$_{x}$, x = 0.01 as FNT1, Fe$_3$Nb$_2$Ti$_{1−x}$O$_2$$_{x}$, x = 0.05 as FNT2, Fe$_3$Nb$_2$Ti$_{1−x}$O$_2$$_{x}$, x = 0.1 as FNT3, and Fe$_3$Nb$_2$Ti$_{1−x}$O$_2$$_{x}$, x = 0.2 as FNT4. For comparison, same method was used to synthesize Fe–TiO$_2$, Nb–TiO$_2$ and pure TiO$_2$.

2.3. Characterization of nanocatalysts

Thermogravimetric (TG) and differential thermal analyses (DTA) (model: DT-40, Shimadzu, Japan) of the precursor powders were carried out in static air at a heating rate of 10 ºC/min up to 1000 ºC using alumina crucible. The crystal structure of the prepared photocatalysts was measured by X-ray diffractometer (XRD) at room temperature, using a Philips PW1710
diffractometer with Cu Ka as target material using 40 kV accelerating voltage, 30 mA emission current and 4’/min scanning speed. The XRD spectrum of Si crystal was used as a standard to calibrate the scanning angles. Absorbance of 4-nitro phenol was measured with the help of UV–Vis spectrophotometer PerkinElmer Lambda 35 (Singapore). Specific surface area and mesoporous characters of the photocatalysts were determined through Brunauer–Emmett–Teller (BET) gas sorption analysis, which was carried out with a BECKMAN COULTIER SA3100 analyzer. The fine structure of the prepared powders was analyzed by Transmission Electron Microscopy (TEM) (TM-300, Philips). The Electron Paramagnetic Resonance (EPR) spectra were recorded with BRUCKER ER083CS at room temperature (ca. 298K). The zeta potential of nanopowders was measured by Zetasizer, Nano-ZS, Malvern, UK.

2.4. Photocatalytic experiments

The photocatalytic experiments were carried out by using a 400 W ultrahigh-pressure Hg lamp (PHILIPS-HPL-N, G/74/2, MBF-400) with a maximum emission at about 364 nm as the light source. In all experiments, the reaction temperature was kept at 28 ± 0.5 °C. The photocatalytic activities of the metal oxides Fe₃NbxTi₁₋ₓO₂₋ₓ/₂ (x = 0.01–0.2) were conducted as follows:

Reaction suspensions were prepared by adding each photocatalyst nanopowder (0.1 g) into 50 mL of aqueous solution of 4-NP (0.0139 g, 0.1 mmol L⁻¹) in a 100 mL quartz beaker in dark condition for about 1 h to reach an adsorption equilibrium before photocatalysis. The photocatalytic reactions were carried out in a simple cubic system, where the beaker containing the sample was irradiated with UV light (λ > 280 nm) under constant magnetic stirring for varying durations of time. A small aliquot (1 mL) of reactant liquid was picked out at regular intervals of time for analysis. The slurry was then centrifuged at 1500 rpm for 15 min, filtered through a 0.2 μm-millipore filter to remove the suspended particles.

The recovered photocatalysts were re-used for the same experiments after proper washing with distilled water and calcining at 300 °C to check the efficiency for further applications.

2.5. 4-Nitrophenol adsorption studies of Fe₃NbxTi₁₋ₓO₂₋ₓ/₂

2.5.1. Batch adsorption studies

Adsorption studies were carried out using a standard stock solution of 4-NP (15 mg L⁻¹) prepared by dissolving appropriate amount of 4-NP in deionized water. Batch adsorption studies were executed in the 100 mL Erlenmeyer flasks by equilibrating 100 mg of Fe₃NbxTi₁₋ₓO₂₋ₓ/₂ with 50 mL of working solutions containing different initial 4-NP concentrations (0, 10, 20, 30, 100, 200, 300 mg L⁻¹). For these experiments, the flasks were capped and shaken at room temperature at 125 rpm for 20 h in a mechanical shaker in the dark condition to attain the adsorption equilibrium. Then, the supernatant was centrifuged, clear water was decanted and the concentration of 4-NP in the supernatant was determined, via UV-Vis spectrophotometer. The equilibrium adsorption capacity of Fe₃NbxTi₁₋ₓO₂₋ₓ/₂ was determined from the difference in initial and final 4-NP concentrations of the working solutions.

All the adsorption experiments were performed in triplicate for checking reproducibility.

3. Results and discussion

3.1. Thermal study of the precursors

Thermal analyses data (TG and DTA) of the precursor powder FNT2, heated at 100 °C, is given in Fig. 1, which indicates that the FNT precursor powder decomposes exothermally, with a sharp peak at 208.8 °C. This exothermic peak can be assigned to major decomposition of the metal-TEA complexes. From the graph, it is observed that the rate of mass change increases to a maximum in the temperature range 100–300 °C. The entire thermal effect was accompanied by the evolution of various gases (such as oxides of carbon and nitrogen and water vapor, etc.), which were manifested by a single-step weight loss in the TG curves shown in Fig. 1. Above 400 °C, there was no significant thermal effect as evident from the DTA curves, and the corresponding TG curves showed no weight loss, implying complete volatilization of carbon compounds.

3.2. XRD analysis software

X-Ray diffraction (XRD) was employed to further investigate the crystalline phase and particle size of the mesoporous TiO₂ modified iron-niobate sphere arrays. The XRD patterns of FNT1, FNT2, FNT3 and FNT4 (Cu-Kα radiation, λ = 1.5408 Å) (Fig. 2a) exhibit diffraction peaks at 2θ of 25.2°, 27.2°, 35.9°, 37.8°, 41.2°, 47.8°, 54.2°, 55.2°, and 62.4°, which can be readily indexed to the mixture of anatase and rutile phases of TiO₂ [58,59]. The peaks position of 25.2°, 37.8°, 47.8°, 54.2°, 55.2°, and 62.4° for anatase (JCPDS card, No. 21-1272) and 27.2°, 35.9°, 41.2°, 54.2° for rutile (Card No. 21-1276) phases of TiO₂. The XRD pattern of pure TiO₂ shows the presence of only anatase phase. The samples NT and FT have XRD patterns, which matched exactly with anatase crystal reflections in TiO₂. Fig. 2b shows the XRD patterns of FNT1 annealed at different temperatures. It indicates that at low temperature (300 °C), FNT1 has a pure anatase TiO₂ crystal structure, and there is no appearance of rutile phase. On increasing the calcination temperatures from 300 to 500 °C, the anatase phase of FNT1 remain same and peak intensity of rutile phase is increased (Fig. 2b) and finally gives rise to a mixture of anatase and rutile
phases along with grain growth. The crystalline size estimated using the Scherrer equation from the full width at half maximum (FWHM) of the (101) peak (2θ = 25.2°) is ~13.7 nm, which is in agreement with the HRTEM observation. All the composite data of crystallite sizes obtained from the diffractograms are presented in Table 1.

### 3.3. TEM analysis

TEM and HR-TEM were used to examine the mesoporous structure and crystallization of the FNT1 spheres. Fig. 3a shows a typical TEM image of these FNT1 spheres. Fig. 3b represents high magnification of FNT1 and clearly shows each particle’s shape is a unique. Fig. 3c HR-TEM of yellow and red marked of Fig. 3a particle and the inset figure indicates SAED pattern of the same sphere and the order of mesoporous structure can be observed in the same HR-TEM images. Fig. 3d shows one enlarged mesoporous spheres (from Fig. 3c), which is of yellow mark in the figure and reveals the coexistence of a porous mesostructure and high symmetric order of crystallinity in the FNT1 nanoparticles. The mesopore size is in the range of 4–5 nm (Fig. 3c), and the FNT1 nanocrystallites have average diameter of 8–10 nm. The lattice fringes of 0.37 nm (Fig. 3d) observed in the mesopore walls correspond to the d-spacing between adjacent (101) crystallographic planes of anatase FNT1 phase.

### 3.4. Specific surface area analysis

The surface area and porosity of the iron-niobate modified TiO2 microspheres are investigated using the nitrogen adsorption and desorption isotherm (Fig. 4). It can be seen from this figure that there is one hysteresis loop that appears in the isotherm. The isotherm can be classified as type IV nature curve with a type H2 hysteresis loop, indicating the presence of mesoporous materials [60]. The inset in Fig. 4 shows the pore

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe₈Nb₂</th>
<th>Abbreviation</th>
<th>Reaction composition k (×10⁻³min⁻¹)</th>
<th>Reaction rate constants</th>
<th>Time required for degradation (min)</th>
<th>S_{BET} (m²g⁻¹)</th>
<th>Crystallites size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₁₋ₓO₂₋ₓ/2</td>
<td></td>
<td></td>
<td>UV_{Pre}</td>
<td>UV_{Abs}</td>
<td>UV_{Pre}</td>
<td>UV_{Abs}</td>
<td></td>
</tr>
<tr>
<td>X = 0.01</td>
<td>FNT1</td>
<td>FNT1 + NaBH₄ + 4-NP</td>
<td>589.07</td>
<td>103.60</td>
<td>10</td>
<td>20</td>
<td>145.0</td>
</tr>
<tr>
<td>X = 0.05</td>
<td>FNT2</td>
<td>FNT2 + NaBH₄ + 4-NP</td>
<td>126.90</td>
<td>80.51</td>
<td>18</td>
<td>34</td>
<td>115.3</td>
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<tr>
<td>X = 0.1</td>
<td>FNT3</td>
<td>FNT3 + NaBH₄ + 4-NP</td>
<td>55.31</td>
<td>52.16</td>
<td>35</td>
<td>52</td>
<td>49.1</td>
</tr>
<tr>
<td>X = 0.2</td>
<td>FNT4</td>
<td>FNT4 + NaBH₄ + 4-NP</td>
<td>43.50</td>
<td>40.86</td>
<td>48</td>
<td>68</td>
<td>45.7</td>
</tr>
<tr>
<td>Nb-TiO₂</td>
<td>NT</td>
<td>NB + NaBH₄ + 4-NP</td>
<td>39.35</td>
<td>34.94</td>
<td>65</td>
<td>75</td>
<td>52.6</td>
</tr>
<tr>
<td>Fe-TiO₂</td>
<td>FT</td>
<td>FT + NaBH₄ + 4-NP</td>
<td>37.86</td>
<td>29.35</td>
<td>68</td>
<td>83</td>
<td>32.3</td>
</tr>
<tr>
<td>P25-TiO₂</td>
<td>--</td>
<td>TiO₂ + NaBH₄ + 4-NP</td>
<td>32.62</td>
<td>20.48</td>
<td>80</td>
<td>90</td>
<td>49.0</td>
</tr>
<tr>
<td>Cat_absence</td>
<td>--</td>
<td>NaBH₄ + 4-NP</td>
<td>23.94</td>
<td>16.38</td>
<td>82</td>
<td>90</td>
<td>--</td>
</tr>
</tbody>
</table>

UV_{Pre}, UV presence; UV_{Abs}, UV absence; Cat_absence, catalysts absence.

Reaction rate constants were measured after 10min reduction of 4-nitrophenol to 4-aminophenol in the presence and absence of UV light, BET surface area measured by liquid nitrogen adsorption–desorption isotherm at room temperature. Time required in different conditions for reduction of yellow color of 4-nitrophenol to colorless 4-aminophenol.
size distribution calculated by the Barrett-Joyner-Halenda (BJH) method using the desorption isotherm. The average pore diameter of the mesoporous FNT1 spheres is 4.6 nm. The BET surface area and pore volume of the mesoporous FNT1 spheres are 145 m² g⁻¹ and 0.246 cm³ g⁻¹, respectively. In addition, the mesopore size distribution is in the range of 3–7 nm, and such a narrow distribution implies substantial homogeneity of the mesopores for the TiO₂ spheres. The BJH pore size distribution results agree well with the TEM and HR-TEM characterizations. The BET surface areas (SA) of other composites of Fe₃NbxTi₁₋₂xO₂₋ₓ/3 are 115.3, 49.1 and 45.7 m² g⁻¹ for FNT2, FNT3 and FNT4 respectively. However, attempts made to prepare the solid solution using the co-precipitation method were unsuccessful.

3.5. Zeta potential measurement

The surface charges of the FNT1 material at various pHs have been investigated by measuring the electrokinetics (zeta potential) of the particles. A plot of the zeta potential against pH in Fig. 5 reveals that the isoelectric point for FNT1 is at pH 5.8 and its zeta potential value is −21 mV at pH 7 and gave high surface area. The mesoporous coating imparts a continuous positive charge over the lower pH range (below the isoelectric point) that may be due to the presence of protonated surface hydroxyl groups (Ti–OH₂⁺). Thus, the increased positive charge density on the surface of the adsorbent at lower pH increases the zeta potential value, whereas, at higher pH, the protonated surface sites decrease and the zeta potential becomes more negative.

3.6. EPR study

From the EPR spectrum of FNT1 at 295 K, which is shown in Fig. 6, a signal at a g-tensor value of 1.991 is obtained, indicating the presence of Nb(V) in TiO₂ [61]. But at a lower g-factor value a small hump or EPR signal was observed in the same
Fig. 5 – The zeta-potential of FNT1 at various pHs.

located at 464.5 eV corresponds to the Ti(2p$^3/2$). The splitting between Ti(2p$^3/2$) and Ti(2p$^1/2$) core levels is 5.6 eV, indicating a normal state of Ti$^{4+}$ in the anatase FNT1. Fig. 7c shows the photoelectron peaks at 529.8 eV corresponding to the O(1s). Fig. 7d shows the XPS spectra covering the Fe(2p) peaks. The Fe(2p) core level are split into Fe$^{3+}$ and Fe$^{2+}$ due to spin orbit coupling and appear at their normal positions at 710.8 and 724.7 eV, respectively. The XPS spectra do not show any elemental Fe peak. A hump at ~719 eV is characteristic of the presence of Fe$^{3+}$. The above results reveal that spectrum of Fe$_x$Nb$_x$Ti$_{1-x}$O$_2$ corresponds to Fe$_3$O$_4$, Nb$_2$O$_5$ and TiO$_2$.

3.7. X-ray photoelectron spectroscopy (XPS) analysis

Fig. 7 shows the XPS spectra of FNT1 in a range (binding energy 355–750 eV) covering the photoemission peaks. The photoelectron peak of Nb(3p$^3/2$) at 365.2 eV in Fig. 7a indicates +5 oxidation state of Nb. There are two peaks in the Ti(2p) binding energy region shown in Fig. 7b. The peak located at a binding energy of 458.9 eV is assigned to Ti(2p$^3/2$) and another one

spectrum, which suggested Fe(III) might be present in the composition [62]. We conclude that Fe and Nb doped in TiO$_2$ lattice are responsible for photochemical reactions, but it is not yet clear if one contributes than other. No EPR signal was detected on pure TiO$_2$.
specimens on the surface. It indicates that the metal ions exist as Fe(III), Nb(V) and Ti(IV). The surface atomic concentration of Fe$_x$Nb$_2$Ti$_{1−2x}$O$_{2−x/2}$ ($x = 0.01$) estimated from XPS is shown in Table 2. The surface concentrations for oxygen, iron, niobium and titanium atoms together with the atomic ratio for Fe/Ti (1.05), and Nb/Ti (1.04) were obtained from the results of XPS analysis.

3.8. Photocatalytic activity of Fe$_x$Nb$_2$Ti$_{1−2x}$O$_{2−x/2}$

Photocatalytic activity of Fe$_x$Nb$_2$Ti$_{1−2x}$O$_{2−x/2}$ nanoclusters is as follows: a freshly prepared aqueous solution of NaBH$_4$ (0.502 mol dm$^{-3}$) is introduced into each of the eight sets of 100 mL beaker containing 50 mL of aqueous solution of 4-nitrophenol (4-NP). Before introducing NaBH$_4$ solution into the mixture, the reaction container was kept in dark for about 1 h to reach adsorption equilibrium. In aqueous medium 4-NP dissolved slowly forming a light yellow solution. Upon addition of NaBH$_4$ dissolution was quick with the development of a deep yellow color. To the mixture, 0.1 g of each of the Fe$_x$Nb$_2$Ti$_{1−2x}$O$_{2−x/2}$ is added and then stirred continuously. In the absence of catalysts the 4-NP was reduced to 4-aminophenol (4-Amp) very slowly under UV light. Fig. 8a–d represents the reaction rate constant and reduction efficiency of 4-nitrophenol, both in the presence and absence of UV light and catalysts, respectively. Inset of Fig. 8a represents the reduction of 4-NP at small time interval (2.5 min) in the presence of FNT1. The result shows that yellow color of 4-NP disappears just after 10 min in the presence of the FNT1 and UV light. But in the absence of UV light it takes about 20 min for reduction. The other compositions FNT2 and FNT3 took much more time i.e. 18 and 35 min in the presence of UV light.

### Table 2 - The surface atom concentration for oxygen, Cr, Nb and Ti atoms of the Fe$_x$Nb$_2$Ti$_{1−2x}$O$_{2−x/2}$ ($x = 0.01$) by XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic surface concentration obtained by XPS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>Fe$<em>x$Nb$<em>2$Ti$</em>{1−2x}$O$</em>{2−x/2}$ ($x = 0.01$)</td>
<td>90.05</td>
</tr>
</tbody>
</table>

Fig. 8 - (a)–(d) represents the reaction rate constant and reduction efficiency of 4-nitrophenol, in the presence and absence of UV light and catalysts.
and their corresponding titanates (Nb–TiO₂ and Fe–TiO₂) and prepared TiO₂ takes much more time for formation of 4-Amp (shown in Table 1). With only 4-NP and NaBH₄ but without the catalyst it takes 82 and 90 min for the reduction to occur in the presence and the absence of UV light, respectively. The catalytic activity of TiO₂, and the formation of 4-Amp were not observed in presence of UV light. Therefore, FNT1 catalysts give much faster reaction kinetics (5.89 × 10⁻³ min⁻¹) than that of FNT2, FNT3, FNT4 and their corresponding Fe/Nb titanates and TiO₂ due to high porosity of the materials and small particle sizes. It has been well established that photocatalysis is a surface-based reaction, therefore a higher surface area improves the photocatalytic efficiency because of the availability of more reaction sites [63].

As a consequence, it enhanced photocatalytic activity through efficient adsorption of the reactant on the catalyst surface. FNT1 catalyst led to a significant decrease of the absorption peak at 416 nm and increase of absorbance peak at 282 nm in UV–vis spectra corresponding to 4-NP. During the reduction, the yellow color faded with the simultaneous formation of a slight shifted peak position and a new peak grows at 228 nm assigned to 4-AmP in UV–vis spectra (Fig. 9) [64,65]. The complete disappearance of the UV–vis absorption peak at 416 nm of 4-NP occurred at 10 min, which indicates to the complete reduction of 4-NP in to 4-AmP. However, the reduction of 4-NP was not accomplished well even under the condition which uses large excess of NaBH₄ in the absence of the catalyst. It is also observed that the dopant concentrations of Fe and Nb (0.5 mol%) in TiO₂ is not much more photoactive compared to FNT1. Therefore, the optimal loading of Fe and Nb in TiO₂ is 1 mol%.

**3.9 Proposed mechanism**

NaBH₄ itself reduces 4-NP to 4-AmP but in the presence of the catalyst the rate of reduction is much faster (Fig. 9). Fe, Nb and Ti exist as Fe(III), Nb(V) and Ti(IV) oxidation state (supported by XPS) in the FNT composites. Both Fe(III) and Nb(V) are active in UV light, so we cannot precisely say which ions are responsible for the generation of e⁻/h⁺ pairs. TiO₂ itself is EPR inactive but in the presence of Fe and Nb in the composites it shows good EPR signal (proved by EPR spectrum). It shows Fe and Nb to be responsible for the generation of electron/hole pair through mutual charge transfer from Fe(III) and Nb(V) with Ti(IV) ion in the presence of irradiance, with light energy (photon), which is equal to or greater than its band-gap energy, ΔEg of the photocatalyst, the excited electron in the valence band (Fe³⁺/Nb⁵⁺) is transferred to the empty conduction band (Fe²⁺/Nb⁴⁺). Hence, this Fe²⁺/Nb⁴⁺ reduces faster p-nitrophenol to 4-AmP. Furthermore, the activity of the nanostructured Fe₀.₀₁Nb₀.₀₁Ti₀.₉₈O₁.₉₉₅ catalyst is reasonably high, due to high surface area, and is largely dependent on their microstructure (mesoporous characters). In the nanoparticle phase, the surface to volume ratio increases drastically and the surface atoms include an increasing fraction of the total particulate volume having high defect structures. Thus, they are expected to show drastically improved catalytic properties.
3.10. Effect of temperature

The effect of annealing temperature of mixed oxides on the photocatalytic activity was also investigated. Fig. 10 shows the profiles of the photo-reduction of 4-NP under UV light irradiation using FNT1, calcined at 300°, 400° and 500°C. The samples calcined at 300°C showed the highest photocatalytic activity as compared to other temperatures. This may be primarily due to the anatase structure and secondly the high surface area is also responsible for the photocatalytic activity. Above 300°C the activity of catalyst decreases with rise of calcination temperatures. This phenomenon can be related to the collapsing of pores as FNT1 particles grow at higher temperatures. In other words, although a higher calcination, temperature results in greater crystallinity, which should improve photocatalytic performance; it can also lead to a drastic decrease of surface area, which results in reduced photocatalytic performance.

3.11. Stability of the Fe_{x}Nb_{x}Ti_{1−2x}O_{2−x/2} (FNT) photocatalyst

To examine the stability of the FNT photocatalyst, the photocatalytic reduction ability was investigated by repeating p-nitrophenol degradation experiments five times. After each cycle, the FNT photocatalysts were washed thoroughly with water, and a fresh solution of p-nitrophenol was added before each photocatalytic run in the reactor. Fig. 11 indicates that the photocatalytic efficiency of FNT decreased slowly with increase in the repetition of the cycles. After the fifth cycle, the efficiency of the FNT catalysts decreased about 1.5% compared to the total reduction of 4-nitrophenol. This is attributable to the loss of catalysts resulting from washing of the catalysts with water, which was not observed in the naked eye. This suggests that the FNT photocatalysts have excellent stability and reliability for photo reduction of pollutants.

Fig. 10 – The effect of calcinations temperature of FNT1 on p-nitrophenol under UV light, the catalyst concentration is C_{cat}=1 g/l, 4-NP concentration is C_{4NP}=10 mM.

Fig. 11 – Photocatalytic stability of FNT1 at same time interval and use fresh 4-NP solution for five times.

4. Conclusion

In summary, we have developed a conceptually different method to incorporate nanocluster mixtures (Fe(III) and Nb(V) species) onto TiO_{2} lattice and initially found that both the efficient photocatalytic reduction of 4-nitrophenol under UV light can be achieved in our materials. Moreover, the detailed structure for our nanoclusters was comprehensively characterized by TEM analysis, and the possible mechanism of the reduction properties could be explained. The balance between Fe(III) and Nb(V) with Ti(IV) states in Fe_{x}Nb_{x}Ti_{1−2x}O_{2−x/2} is critical to achieve efficient p-nitrophenol reduction. This is probably due to efficient generation of electron and hole under UV light through mutual charge transfer from Fe(III) and Nb(V) ion in the clusters. As a result Fe(III) transform to Fe(II) and Nb(V) convert to Nb(IV), where electron resides in the conduction band and a hole is captured forming Fe^{3+}/Nb^{4+}. Therefore, this Fe^{3+}/Nb^{4+} reduce quickly p-nitrophenol to p-aminophenol. Furthermore, mesoporous FNT1 has continued to be highly active in photocatalytic applications because it is beneficial for promoting the diffusion of reactants and products, as well as for enhancing the photocatalytic activity by facilitating access to the reactive sites on the surface of photocatalyst.

Conflict of interest

The author declares no conflicts of interest.

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