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# New synthetic approach, mesoporous properties and photocatalytic activity of titania adapted chromium-niobate nanocatalysts

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# ABSTRACT

Mesoporous titania adapted chromium-niobate nanocatalysts  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$  (x = 0.01-0.2) were synthesized by a new synthetic approach, using *N*,*N*,*N'*,*N'*-tetrakis(2-hydroxyethyl)ethylenediamine (edteH<sub>4</sub>) precursors and their photocatalytic activities were investigated. TiO<sub>2</sub> nanomaterials have continued to be highly active in photocatalytic applications because these are useful to break down the organic molecules in water for endorsing the diffusion of reactants and products.  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$  (x = 0.01)(CNT1) nanoparticles with the smaller particle sizes  $12\pm1$  nm and have mesoporous characteristics (S<sub>BET</sub> = 162 m<sup>2</sup> g<sup>-1</sup>). The energy band gap of CNT1 was found 1.85 eV obtained from optical emission spectrum. The XRD peaks revealed a mixture of anatase and rutile phases in the synthesized powders. EPR spectroscopy showed the characteristic features of Nb<sup>5+</sup> ions, whose existence was confirmed by XPS. The CNT1 powders display good (2.5 times greater) photocatalytic activity for degradation of Rhodamine B (RhB) as opposed to pure anatase TiO<sub>2</sub> and other compositions of  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$ . Copyright © 2013 VBRI Press.

Keywords: Sol-gel synthesis; mesoporous; titanium dioxide; optical properties; nano-photocatalysts.



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# Introduction

Titanium dioxide  $(TiO_2)$  is a good semiconducting material with pretty industrial applications in different areas such as: cosmetics, paint pigments [1], preparation of different types of titanium based electrodes [2], electronics [3], capacitors [4], optics [5], sensors [6-7], ceramics [8], solar cells [9-10], catalysis, and photocatalysis [11-12]. In the past decade, very few reports are available with mesoporous TiO<sub>2</sub> acting as photocatalyst. Mesoporous TiO<sub>2</sub> are highly effective catalyst because of their large surface area and porous framework [13]. However, for specific advanced applications in photo-catalysis, specifically in the degradation of organic pollutants, the optical and electrical properties of TiO<sub>2</sub> have been extensively studied by several researchers [14-19]. The possibility of carrying out

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selective photooxidations in nonaqueous media is interesting in the context of Green Chemistry [20-21]. However, it has wide band-gap energy (3.0 eV for rutile and 3.2 eV for anatase), which means that UV light (wavelength < 387 nm) can excite anatase TiO<sub>2</sub> to generate  $e^{-cb}/h^{+vb}$  pairs which cause the photocatalytic reactions. Moreover, TiO<sub>2</sub> presents a relatively high electron-hole recombination rate which is detrimental of its photo catalytic activity. In this situation, doping with metals or metal oxides produces a double effect without changing the crystallographic structure. Firstly, this reduces the band gap energy, which shifts the absorption band to the visible region. Secondly, metals could provoke a decrease in electron-hole recombination rate, acting as electron traps. Therefore, lots of researches have been done on the photo catalytic activity of TiO<sub>2</sub> doped with different metal ion such as Ag [22], Au[23], Mn [24], Fe [25-26], Co [27], Ni [28], Cu [29-30], Pd [31] and recently nitrogen and nitrate doped TiO<sub>2</sub> [32-33]. Previously, Zhang et al. and recently Adel A. Ismail et al. were found that TiO<sub>2</sub> microspheres with porous structures have higher photocatalytic activity and are easily recovered for re-use [13, 34]. Recently, Han el. al. was study the photocatalytic degradation of 2,4 dichlorophenol with SiO<sub>2</sub>-TiO<sub>2</sub> nanomaterials [35] and Tiwari et. al. synthesized the different type of nanomaterials compounds [36]. So, the innovation of a novel pathway for synthesis of TiO<sub>2</sub> nano materials is challenge to every scientist. Furthermore, photo catalytic activity is highly dependent on surface area and crystallinity or crystal sizes, which are influenced by the synthetic methods of titania [37-38].

Recently it was observed that the photocatalytic activity and surface acidity of TiO2 significantly increases with the addition of small quantity of  $Nb^{5+}$  to  $TiO_2$  [39-40]. Simultaneously, the effect of chromium doping on titania have been widely studied by a number of researcher [41-**43**]. These photocatalysts are used in various systems, such as the photoreduction of dinitrogen to NH<sub>3</sub> and the photodegradation of phenol in the gas-solid and liquidsolid regimes respectively. The effect of simultaneous doping with Cr and Nb in the TiO<sub>2</sub> anatase mesoporous structure and its resulting photocatalytic activity has not yet been reported. However, interesting studies show that Cr and Nb doped anatase TiO<sub>2</sub> display good mesoporous and photoactivity in the degradation of Rhodamine B in aqueous solution under UV irradiation. The role of Cr(III) in Cr-Nb-TiO<sub>2</sub> composite is to compensate for the charge imbalance caused by the replacement of Ti(IV) with Nb(V) in TiO<sub>2</sub> crystals, which results in improved the charge separation among the photo-produced hole-electron pairs by means of a permanent electric field. It is very important to synthesis a catalyst like TiO<sub>2</sub> with high surface area and small particle size. Non-conventional synthetic procedures such as: chemical vapour deposition [44], hydrothermal [45], microemulsion [46], sol-gel [47-49], coprecipitation [50], and chemical methods [51], were adopted to produce such compositions. The conventional method i.e. solid state [24] method was also used to produce such  $TiO_2$ compositions.

In this study, we have first time synthesis of a new titania adapted chromium-niobate in various compositions

of  $Cr_xNb_xTi_{1-2}xO_{2-x/2}$  (x = 0.01, 0.05, 0.1, 0.2) nanophotocatalysts with mesoporous characteristics using N, N, N', N'-tetrakis(2-hydroxyethyl)ethylenediamine in a modified sol-gel method. Unfortunately, the non-aqueous based solution methods (i.e. the alkoxide based solution methods using organic solvents) [51] experience hindrance in the synthesis of compositions that contain Nb<sup>5+</sup>/Ti<sup>4+</sup> ions because of the cost, and moisture sensitivity of the starting materials (such as niobium ethoxide and other alkoxides). On the other hand, the alternative aqueous based chemical processes get complicated due to scarcity of water-soluble salts of niobium/titanium and easy hydrolysis of the available ones (such as NbCl<sub>5</sub> or TiCl<sub>4</sub>). Therefore, our main challenge is to dissolve TiO2/Nb2O5 into their solution form. TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> were slowly dissolved in an equivalent amount of hydrofluoric acid and water mixture with vigorous stirring in a hot water bath. The mesoporous properties and photocatalytic activities of the synthesized powders were tested in the presence of Rhodamine B (RhB) and UV light. The  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$  (x = 0.01)(CNT1) was found to show good photocatalytic activity compared to that of pure TiO<sub>2</sub>. Because it has high surface area ( $S_{BET} = 162 \text{ m}^2 \text{ g}^{-1}$ ), small particle sizes (12±1 nm) and lower band gap energy (1.85 eV) compared to TiO<sub>2</sub>. The remaining Cr<sub>x</sub>Nb<sub>x</sub>Ti<sub>1-2x</sub>O<sub>2-x/2</sub> compositions, where x = 0.05-0.2, and TiO<sub>2</sub> doped with Nb and Cr separately (in these cases x = 0.01) were observed by studying photo degradation of RhB under UV light irradiation.

# Experimental

#### Chemicals

Titanium dioxide (analytical reagent), Nb<sub>2</sub>O<sub>5</sub> (analytical reagent),  $(NH_4)_2Cr_2O_7$  (analytical reagent), NaOH (analytical reagent), NH<sub>4</sub>OH (25%), HF (40%), *N*,*N*,*N'*,*N'*-tetrakis(2 hydroxyethyl) ethylenediamine (edteH<sub>4</sub>)(Sigma Aldrich), Methanol, tartaric acid, and Rhodamine B were of analytical reagent grade and were procured from B.D.H., India.

# Synthesis of $Cr_xNb_xTi_{1-2x}O_{2-x/2}$ nanophotocatalyst

Nano-sized metal oxide photocatalysts of Cr<sub>x</sub>Nb<sub>x</sub>Ti<sub>1-2x</sub>O<sub>2-x/2</sub> (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 ammonium dichromate, titanium tartarate and niobium tartarate solutions were prepared. The synthesis of titanium/niobium tartarate solutions were reported in elsewhere [12, 24]. In the second step, stoichiometric amounts of titanium and niobium tartarate with complexing agent N,N,N',N'tetrakis(2-hydroxyethyl) ethylenediamine (edteH<sub>4</sub>) (molar ratio of metal ion:  $edteH_4 = 1:2$ ) solutions were taken in a beaker as per the predetermined chemical compositions. After, stoichiometric amounts of ammonium dichromate solutions and 20 mL of absolute methanol were added to the mother solutions and constant stirring for 30 min at room temperature. Then the mixture was adjusted to a pH of 9.0 with 6M NaOH solution, and stirred for another 30 min, yielding a stable light yellow homogeneous emulsion.

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The resulting mixture was transferred into a 100 mL teflon-lined stainless steel autoclave and heated to 150 °C for 22 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 °C for 1 h then heated on furnace in different calcination. The compositions with different amount of Cr and Nb doping will be denoted as the following:  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$ , x=0.01 as CNT1,  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$ , x=0.05 as CNT2,  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$ , x=0.2 as CNT4. For comparison, same method was used to synthesize Cr-TiO<sub>2</sub>, Nb-TiO<sub>2</sub> and TiO<sub>2</sub>.

# Physical measurements 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 °C/min up to 1000 °C using as alumina crucible. The crystal phase composition of the prepared photocatalysts X-ray diffraction (XRD) measurement was carried out at room temperature by 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. All binding energy values were determined by calibration and fixing the C(1s) line to 285 eV. The pure powdered BaSO<sub>4</sub> was used as a reference sample. To determine the specific surface area and mesoporous characters of the photocatalysts, Brunauer-Emmett-Teller (BET) gas sorption analysis was carried out by using a BECKMAN COULTER SA3100 analyzer. The fine structure of the prepared powders was analyzed by transmission electron microscopy (TEM) (TM-300, Philips). The electron spin resonance (ESR) spectra were recorded by using a BRUCKER ER083CS at room temperature (ca. 298 K). The zeta potential of nanopowders was measured by Zetasizer, Nano-ZS, Malvern, UK. X-ray photoelectron spectroscopy (XPS) measurements were carried out in an Axis-Ultra X-ray photoelectron spectrophotometer in vacuum  $(1 \times 10^{-5} \text{ Pa}).$ 

# Photocatalytic experiments

The photocatalytic activities of the above metal oxides  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$  (x = 0.01-0.2) were studied in the following path. 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  $28 \pm 0.5$ °C. Reaction suspensions were prepared by adding each photocatalyst nanopowder (0.1 g) into 50 mL of 10 mM RhB solution in a 100 mL beaker. The photocatalytic reactions were carried out in a simple cubic system, where the beaker containing the sample was irradiated with UV light ( $\lambda > 280$  nm) under constant magnetic stirring for various durations of time. A small aliquot (1 mL) of reactant liquid was picked out at regular interval of time for analysis. The slurry was then centrifuged at 1500 rpm

for 15 min, filtered through a 0.2  $\mu$ m-millipore filter to remove the suspended catalyst particles, and then the concentration of dye was measured by absorption spectrometry using a UV-VIS spectrophotometer (PerkinElmer, LAMBDA35) at its maximum absorption wavelength (at 554 nm). After proper washing with distilled water and calcining at 500 °C the photocatalysts were reused for the same experiments to check the efficiency for further applications.

# Rhodamine B adsorption studies of Cr<sub>x</sub>Nb<sub>x</sub>Ti<sub>1-2x</sub>O<sub>2-x/2</sub>

For the adsorption studies, a standard stock solution of RhB (5 mg/L) was prepared by dissolving the appropriate amount of RhB in deionized water. Batch adsorption studies were executed in the 100 mL Erlenmeyer flasks by equilibrating 100 mg of Cr<sub>x</sub>Nb<sub>x</sub>Ti<sub>1</sub>-<sub>2x</sub>O<sub>2-x/2</sub> with 50 mL of working solutions containing different initial RhB concentrations (0, 10, 20, 30, 100, 200, 300 mg/L). 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. After that, the supernatant was centrifuged and decanted and the concentration of the RhB in the supernatant was determined spectrophotometrically PerkinElmer, using the LAMBDA35. The equilibrium adsorption capacity of  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$  was determined from the difference in initial and final RhB concentrations of the working solutions. All the adsorption experiments were performed in triplicate in order to check the reproducibility. After the RhB adsorption study using our developed adsorbent, the Cr<sub>x</sub>Nb<sub>x</sub>Ti<sub>1-2x</sub>O<sub>2-x/2</sub> FTIR spectrum was recorded, which showed no distinguishable band is appeared.



Fig. 1. DTA-TG and DTG of CNT2 precursor.

# **Results and discussion**

# Thermal study

Thermal analysis data (TG and DTA) of the precursor powder CNT2, heated at 200 °C, is given in **Fig. 1** which indicates that the CNT precursor powder decomposes exothermally, with a sharp peak at 348.8 °C. This exothermic peak can be assigned to major decomposition of metal-TEA complexes. From the graph, it can be observed that the rate of mass change increased to a maximum in the temperature range from 300-400 °C. The entire thermal effect was accompanied by the evolution of various gases (such as oxides of carbon, nitrogen and Table 1. Resultant properties of CNT1, CNT2, CNT3, CNT4, NT, CT and Pure  $TiO_2$  clusters

SampleActorymReaction $S_{BET}$ (m/g)CrystantesDatagapRindTime $(Cr_xNb_xTi_1.Ratesize (nm)Energy (eV)decolorizatirequired_{2x}O_{2-x/2})Constanton,t_{1/2}degradak(\times 10^{-3} \text{ min}^-)(min)of1)(min)(min)$	l for tion RhB
x = 0.01 CNT1 27.31 162.24 13.70 1.85 25.37 180	
x = 0.05 CNT2 23.07 125.32 13.98 1.85 30.03 210	
x = 0.1 CNT3 17.08 59.11 14.08 1.85 40.57 330	
x = 0.5 CNT4 9.48 45.73 14.17 - 71.30 720	
Nb-TiO <sub>2</sub> NT 18.74 52.69 12.14 2.2 36.97 270	
Cr-TiO <sub>2</sub> CT 6.37 32.33 12.39 - 108.79 -	
TiO2         -         11.68         49         12.42         3.2         59.33         540	

Reaction rate constants were measured after 50% decolorization of RhB solution, BET surface area measured by liquid nitrogen adsorption-desorption isotherm at room temperature.

water vapor, etc.), which were manifested by a single-step weight loss in the TG curves shown in **Fig. 1**. Above 550 °C, there was no significant thermal effect observed in DTA curves and the corresponding TG curves showed no weight loss, implying the complete volatilization of carbon compounds.



Fig. 2. (a) XRD patterns of  $TiO_2$ , Nb- $TiO_2$  (NT), Cr- $TiO_2$  (CT), CNT1, CNT2, CNT3 and CNT4 pure photocatalyst heat treated at 500 °C for 30 min. (b) XRD of CNT1 at different temperatures.

#### XRD analysis

The XRD patterns of CNT1, CNT2, CNT3, CNT4, chromium doped TiO<sub>2</sub> (CT), niobium doped TiO<sub>2</sub> (NT) and pure TiO<sub>2</sub>, calcined at 500 °C for 30 min, are presented in Fig. 2a and 2b. The XRD analysis of pure  $TiO_2$  shows the presence of only the anatase phase. The samples NT and CT have XRD patterns matched exactly with anatase crystal reflections in TiO<sub>2</sub>. However, the XRD pattern of CNT1, CNT2, CNT3 and CNT4 produced a mixture of anatase and rutile phases of TiO<sub>2</sub>. Fig. 2b shows the XRD of CNT1 annealed at different temperatures. It indicates that at low temperature (500 °C), CNT1 has a pure anatase TiO<sub>2</sub> crystal structure. On increasing the calcination temperature, the anatase phase in CNT1 is converted to a mixture of anatase and rutile phases along with grain growth. The average crystal size for CNT1 is ~13.7 nm. This size is probably due to the higher reactivity of crystallites grown below 13.7 nm. The sizes of crystallites separated from various compositions at their phase separation temperatures have been evaluated using the Scherrer equation. The data of crystallite sizes obtained from the diffractograms are presented in Table 1.



Fig. 3. FTIR spectra of  $TiO_2$  and CNT1 at 500 <sup> $\circ$ </sup>C for 30 min.

## FTIR of CNT1

The FTIR spectra of TiO<sub>2</sub> and CNT1 as shown in **Fig. 3**, display a strong absorption at 674 cm<sup>-1</sup>, which indicates the presence of titanium oxide and the bands at 3434 cm<sup>-1</sup> and 1637cm<sup>-1</sup> are due to the presence of –OH and H-O-H groups. Additional bands appearing at 567 cm<sup>-1</sup> and 825 cm<sup>-1</sup> in CNT1 are characteristic for Cr-O and Nb-O respectively. Therefore, we conclude that the Cr and Nb both ions are present in the TiO<sub>2</sub> lattice or CNT1 clusters.



**Fig. 4.** (a) TEM images of CNT1 (inset: Particle size distribution histogram), (b) SEAD pattern of CNT1, (c) Mesoporous structures of CNT1 observed from HRTEM and (d) SEM images of CNT1.

#### TEM analysis

The finer details of the particles and their morphologies have been investigated by TEM (Model Philips TM-30, Philips Research Laboratories). The bright-field (BF) electron micrograph of the CNT1 powder produced at 500 °C reflects a narrow distribution of particles, with an average particle diameter of 12±1 nm which is shown in Fig. 4. The particle sizes were obtained from multiple TEM images Fig. 4a (particle size distribution histogram inset in 4a), Fig. 4b represents the SAED pattern of CNT1, Fig. 4c indicates the mesoporous structures of CNT1 observed from HRTEM and Fig. 4d represents the scanning electron microscopy (SEM) of CNT1. The average grain sizes of CNT1 are ~15nm measured from SEM. Therefore, Fig. 4 concludes that the synthesized materials are in nanometer range and developed mesoporous characters. Compared TEM and SEM figures observed that the particle sizes and grain sizes are almost same.

#### BET surface area and zeta potential measurement

During annealing, the decomposition of CNT powders obtained from  $edteH_4$  in methanol and its complexes precursor solutions and finally gets mesoporous clusters of CNT. The N<sub>2</sub> adsorption-desorption isotherms (**Fig. 5**) of CNT1 nanopowders indicates the type IV nature of the



Fig. 5. An  $N_2$  adsorption-desorption isotherm and (inset) a pore size distribution curve of CNT1



Fig. 6. The zeta-potential of CNT1 at various pHs

data, corresponding pore size distribution The calculated by the BJH method from the adsorption branch of the N<sub>2</sub> isotherm, shows a narrow pore size distribution (Fig. 5, inset) with a peak pore diameter of 4.9 nm. The BET surface areas (SA) of other compositions of  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$  are shown in **Table 1**. Attempts to make the solid solution using the co-precipitation method were unsuccessful. The surface charges of the CNT1 material at various pHs have been investigated by measuring the electro kinetics (zeta potential) of the CNT1. A plot of the zeta potential against pH in Fig. 6 reveals that the isoelectric points for CNT1 are at pH 5.85 and its zeta potential values are -24mV 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– $OH_2^+$ ). 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.



**Fig. 7.** EPR of  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$  (x = 0.01)(CNT1).

#### EPR study

From the electronic paramagnetic resonance spectrum (EPR) of CNT1 at 295 K, as shown in **Fig. 7**, a signal at a g-tensor value of 1.9565 is obtained, indicating the presence of Nb(V) in TiO<sub>2</sub> [**52**]. But at a lower g-factor value no EPR signal was observed, which proved that the EPR signal of Cr(III) is absent in the composition [**53**]. The role of Cr(III) ions helps to compensate the charge of the metal (Nb, Ti) ions on the compositions. So, we can conclude that the Nb doped in TiO<sub>2</sub> lattice is responsible for photochemical reactions. Lastly, due to the absence of any hyperfine lines in ESR spectra, it could be suggested that  $Cr^{3+}/Nb^{5+}$  cations are well separated. No EPR signal was detected on pure TiO<sub>2</sub>.

#### XPS analysis

Fig. 8 shows the XPS spectra of CNT1 in a range (binding energy 355-595 eV) covering the photoemission peaks. Fig. 8a shows the photoelectron peaks at 577.1 eV and 586.8 eV correspond to the binding energy of  $Cr(2p_{3/2})$ and  $Cr(2p_{1/2})$  of  $Cr^{3+}$ , which is consistent with the values reported by Koppelman et al. [54]. The splitting between  $Cr(2p_{3/2})$  and  $Cr(2p_{1/2})$  core levels is 3.5 eV indicating a normal state of  $Cr^{3+}$  in the  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$  (x = 0.01). This was proved by the time of synthesis of our studied materials. During the synthesis Cr(VI) was converted to Cr(III) by using dilute nitric acid and ethanol and as a result, the color of the solutions changed from yellow to green [55-56]. The photoelectron peak of Nb(3p3/2) is at 365.2 eV was as in Fig. 8b. There are two peaks in the Ti(2p) binding energy region was shown in Fig. 8c. The peak located at a binding energy of 464.5 eV is assigned to the Ti(2p1/2) and another one located at 458.9 eV, corresponds to the Ti(2p3/2). The splitting between

Ti(2p1/2) and Ti(2p<sup>3/2</sup>) core levels is 5.6 eV, indicating a normal state of Ti<sup>4+</sup> in the  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$  (x = 0.01). **Fig. 8d** shows the photoelectron peak at 529.8 eV corresponds to the O(1s).

The above results reveal that the spectrum of  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$  corresponds to  $Cr_2O_3$ ,  $Nb_2O_5$  and  $TiO_2$  specimens on the surface. It indicates that the metal ions exist as Cr(III), Nb(V) and Ti(IV) oxidation states. The surface atomic concentration of  $Cr_xNb_xTi_{1-2x}O_{2-x/2}$  (x = 0.01) estimated from XPS is shown in supporting Information 1. The surface atom concentrations for oxygen, chromium, niobium and titanium atoms and the atomic ratio for Cr/Ti (1.05), and Nb/Ti (1.04) were obtained from the results of XPS analysis.



Fig. 8. XPS spectra of CNT1 [(a) Cr2p3/2 and Cr2p1/2, (b) Nb3p3/2, (c) Ti2p3/2 and Ti2p1/2 and (d) O1s].

#### Optical transmittance spectra of CNT1

The optical transmittance spectra of CNT1 and NT have been shown in Fig. 9. Fig. 9 shows typical absorption spectra of CNT1 and NT pallets by plotting  $(\alpha thv)^2$  vs. hv, where hv is the photon energy and t is thickness of the pallet(s). In addition, it was calculated using the relation,  $\alpha t = \ln(T)$  in which T is the transmittance of the pallet. Using the intersection of the linear fit and the abscissa, band-gap of the CNT1 and NT were calculated about 1.85 and 2.1 eV, corresponding absorption edges at 670 nm and 590 nm, respectively. The band gap energy of pure  $TiO_2$  is 3.2 eV [24]. Although the band gap energy of CNT1 is the same when compared to other CNT compositions, its surface area is high (~162 m<sup>2</sup>g<sup>-1</sup>). A result it shows the highest photocatalytic activity when compared to other compositions and TiO<sub>2</sub>. Photocatalytic activity depends on two factors, band gap energy and surface area. Both results are favor for CNT1. CNT1 has lower band gap energy (1.85eV) and high surface area; therefore, the ejection of an electron (under UV/VIS light irradiation) from the valence band is easy and can be transmitted to the conduction band, leading to faster photochemical reactions.

#### Photocatalytic study

In order to obtain some information on the potential application of our material in photocatalysis, UV-Vis

spectra were done. The changes in concentration of RhB as a function of UV-light exposure time in the presence of the prepared photocatalysts are shown in Fig. 10. The photocatalytic activity of CNT1 (27.31×10<sup>-3</sup> min<sup>-1</sup>) is 2.5 times higher than that of pure  $TiO_2$  (11.68×10<sup>-3</sup> min<sup>-1</sup>) and other compositions of Cr<sub>x</sub>Nb<sub>x</sub>Ti<sub>1-2x</sub>O<sub>2-x/2</sub> under UV light. Time required for the degradation of RhB by using CNT1 is 3 h. The degradation rate constant (k) for RhB using CNT1, CNT2, CNT3, CNT4, NT, CT, and TiO<sub>2</sub> photocatalysts have been presented as the time required for 50% decolourization of dyes solutions in **Table 1**. Increase of the different dopant (Cr and Nb) concentrations in TiO<sub>2</sub> solid solution, decreased the rate of photodegradation due to the decrease of specific surface area for the different doped catalysts. The photocatalytic activity was also observed in presence of visible light but the catalytic activity was not so significant like UV light. The photocatalytic oxidation of RhB in the presence of CNT1 also depended on its annealing temperatures (see supporting information 2). The samples calcined at 500 °C showed the highest photocatalytic activity as compared to samples calcined at other temperatures (600 °C and 700 <sup>o</sup>C). This is due to the anatase structure being the primary factor, and the second factor is the high surface area responsible for the photocatalytic activity. Above 500 °C, the activity of catalyst decreases with rise of calcination temperatures, due to an increase in particle size and a decrease of defect-structure on the surface of solid catalyst.



Fig. 9. Optical transmittance spectrums of CNT1 and NT.

#### Stability of CNT clusters

To examine the stability of the CNT photocatalyst, the photocatalytic degradation properties of the photocatalyst was investigated by repeating RhB photocatalytic degradation experiments five times. After each cycle, the CNT photocatalysts were washed thoroughly with water, and a fresh solution of RhB was added before each photocatalytic run in the reactor. **Fig. 11** indicates that the photocatalytic degradation of CNT decreased slowly with increase the repetition of the cycles. After fifth cycle the efficiency of CNT catalysts decreased about 1.5% compared to the total degradation of RhB. This is due to

the loss of catalysts during the water washing of catalysts, which was not observed in the naked eye. Thus suggests that CNT photocatalysts have excellent stability and reliability for photodegradation of pollutants.



Fig. 10. The changes in concentrations of RB solution at 554 nm in the presence of CNT1, CNT2, CNT3, CNT4, NT, CT,  $TiO_2$  and Hg- lamp.



Fig. 11. Photocatalytic stability of CNT1 at same time gap interval and use fresh RhB solution for five times.

#### Rhodamine B adsorption studies using CNT1

Adsorption isotherm: The RhB adsorption on the CNT1 plotted against different initial RhB equilibrium concentrations is presented in Fig. 12. It is evident from the plot that the RhB adsorption capacity increases with the increase in RhB equilibrium concentrations from 0 to 130 mg/L and then a saturation behavior is observed for high equilibrium concentrations (from 130 to 300 mg/L). The initial increase in the RhB adsorption takes place due to the accelerated diffusion of RhB ions from the bulk solution to the surface of the adsorbent molecule. This diffusion occurs due to the increase in the driving force of the concentration gradient [57]. To fit the equilibrium data, the Langmuir isotherm model, defined by the following equation has been used.

$$C_{e}/q_{e} = (1/Q^{o}b) + (C_{e}/Q^{o})$$
(1)

where,  $C_e \text{ (mg } \text{L}^{-1})$  is the equilibrium concentration of RhB ion,  $q_e \text{ (mg } \text{g}^{-1})$  is the amount of RhB adsorbed at equilibrium,  $Q^{\circ} \text{ (mg } \text{g}^{-1})$  is the monolayer capacity of the adsorbent and  $b \text{ (L } \text{mg}^{-1})$  is the adsorption constant. The plot of  $C_e/q_e$  against  $C_e$  (**Fig. 12**, inset) gives a straight line with slope  $1/Q^{\circ}$  and intercept  $1/Q^{\circ}b$ . The correlation coefficient ( $R^2$ ) obtained from the Langmuir equation is 0.9894. The plot indicates that the Langmuir model has been well fitted with the experimental data . The values of  $Q^{\circ}$  and b are found to be 30.1 mg g<sup>-1</sup> and 0.054 L mg<sup>-1</sup>, respectively. Thus, the high adsorption capacity, as obtained from the experiment of the compound at equilibrium concentration indicates the possibility that the material can be used in treating waste effluents.



Fig. 12. The RhB adsorption isotherm of CNT1 and (inset)  $C_e/q_e$  versus  $C_e$  plot.



Fig. 13. Discoloration of 10 mM RhB by using CNT1 nanocatalyst at an initial solution pH 7.02: (a) only RhB solution and UV light; (b) RhB solution + UV light + 10 mM H<sub>2</sub>O<sub>2</sub>; (c) Nanocatalyst + RhB solution + Dark Condition; (d) Nanocatalyst + RhB solution + Dark Condition; (d) Nanocatalyst + RhB solution + UV light + 10 mM H<sub>2</sub>O<sub>2</sub>; (e) Nanoatalyst + RhB solution + UV light + 10 mM H<sub>2</sub>O<sub>2</sub>, Catalyst concentration is  $C_{catalysts} = 1$  g/l and RhB concentration is  $C_{RB} = 10$  mM.

#### *Effect of* $H_2O_2$ *in presence of catalyst*

The photocatalytic activity of the CNT1 nanocatalyst was also evaluated for discoloration and mineralization of 10 mM RhB in presence of 10 mM H<sub>2</sub>O<sub>2</sub>, 1.0 g/l CNT1, and UV light at an initial solution pH of 7.02. Fig. 13 shows the discoloration kinetics of 10 mM RhB under different conditions. Control experiments were carried out on RhB solution in absence of any catalyst as well as  $H_2O_2$  (curve a) under UV irradiation resulting in insignificant color degradation. This shows that RhB itself can resist UV light. Similar tests were carried out with 10 mM H<sub>2</sub>O<sub>2</sub> under UV light in absence of any TiO<sub>2</sub> catalyst (curve b), where significant discoloration of 10 mM RhB was observed. The concentration of RhB decreased quite quickly in the first 30 min and then attained an asymptotic value. After 200 min, the discoloration of RhB solution was achieved. This is due to the oxidation of RhB by the OH radicals generated by photolytic peroxidation (UV and  $H_2O_2$ ) as shown in the following equations:

$$H_2O_2 \xrightarrow{\text{UV light}} 2 \text{`OH}$$
 (2)

 $OH + Rhodamine B \rightarrow Reactions Intermediates \rightarrow H_2O + CO_2 + Inorganic ions$  (3)

The third experiment was carried out without UV light and  $H_2O_2$ , but in the presence of 1.0 g CNT1 in the dark (curve c). The decreases in concentration of RhB in the first 30 min are due to the adsorption of RhB on the surface of CNT1 nanocatalysts and then further slight decrease of RhB due to decomposition process.

Fourthly, without UV light, and with 10 mM H<sub>2</sub>O<sub>2</sub> and 1.0 g CNT1/l in the dark (curve d), the concentration of RhB decreased in the first 30 min, followed by a slow continuous decrease. The decrease in RhB in the first 30 min is again caused by the adsorption of RhB on the surface of CNT1 nanocatalysts. The subsequent decrease after 30 min resulted from oxidation of RhB by OH radicals coming from the "dark" Fenton reaction. It can be seen that the dark Fenton reaction does not give rise to fast degradation of RhB. Finally, with 1.0 g CNT1/l nanocatalysts, 10 mM H<sub>2</sub>O<sub>2</sub>, and UV lamp (curve e), the discoloration is very fast. After 100 min of reaction, 100% discoloration of 10 mM RhB was achieved. The leaching of Cr/Nb ions from the Cr<sub>x</sub>Nb<sub>x</sub>Ti<sub>1-2x</sub>O<sub>2-x/2</sub> at this initial solution with pH of 7.02 is negligible. With sufficiently high activity and negligible loss of Cr/Nb ions from the Cr<sub>x</sub>Nb<sub>x</sub>Ti<sub>1-2x</sub>O<sub>2-x/2</sub> nanocatalysts, a practical treatment application is feasible.

#### Conclusion

In summary, we have succeeded in developing a conceptually different method to acquire nanocluster mixtures ( $Cr^{III}$  and  $Nb^{V}$  species) onto  $TiO_2$  lattice and initially found that the CNT1 cluster is more photoactive than pure  $TiO_2$  and other metal clusters of  $TiO_2$  due to

high surface area (~162 m<sup>2</sup>g<sup>-1</sup>), lower band-gap (1.85 m<sup>2</sup>g<sup>-1</sup>) <sup>1</sup>) and photo chemical generation of dye cation under UV light can be achieved in our materials. Furthermore, the detailed structure for our nanoclusters was comprehensively characterized by synchrotron analysis, and the possible mechanism of the degradation of RhB could be elucidated. It is well established that the conduction band electrons (e<sup>-</sup>) and valence band holes (h<sup>+</sup>) are generated when aqueous TiO<sub>2</sub> suspension is irradiated with light energy greater than its band-gap energy (Eg, 3.2 eV) [58-60]. Recently, Han el. al. was study the photocatalytic degradation of 2,4 dichlorophenol with SiO<sub>2</sub>-TiO<sub>2</sub> nanomaterials. When the RhB dye is irradiated with UV light, the dye is discolored within the time of reaction through the mutual contact between the dye and catalyst. The discoloration of the dye occurs because the dye is sensitized and the dye cation is formed. The dye cation is unstable and decomposes injecting an electron on the conduction band of TiO<sub>2</sub>. This band-gap-electron starts the production of highly oxidative radical species through the formation of super oxide radical anion  $O_2^{-}$  on the surface of the catalyst as long as the dye is present. In later steps of the reaction when long-lived colorless intermediates are present, the TiO<sub>2</sub> absorbs the light and produces the conduction-band electron and valence-bandholes. Electron goes to conduction band and hole is captured by Nb<sup>5+</sup>, which has been noticed by EPR spectrum and helps to degrade the dye molecule faster.

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