Synthesis and characterization of Ba$^{2+}$ and Zr$^{4+}$ co-doped titania nanomaterial which in turn used as an efficient photocatalyst for the degradation of rhodamine-B in visible light

Desta Shumuye Meshesha, Ravi Chandra Matangi, Siva Rao Tirukkovalluri, Sreedhar Bojja

PII: S1026-9185(16)30027-0
DOI: 10.1016/j.sajce.2016.10.004
Reference: SAJCE 14

To appear in: South African Journal of Chemical Engineering

Received Date: 1 June 2016
Revised Date: 21 July 2016
Accepted Date: 11 October 2016

Please cite this article as: Meshesha, D.S., Chandra Matangi, R., Tirukkovalluri, S.R., Bojja, S., Synthesis and characterization of Ba$^{2+}$ and Zr$^{4+}$ co-doped titania nanomaterial which in turn used as an efficient photocatalyst for the degradation of rhodamine-B in visible light, South African Journal of Chemical Engineering (2017), doi: 10.1016/j.sajce.2016.10.004.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Ba$^{2+}$ and Zr$^{4+}$ co-doped titania nanomaterial: An efficient photocatalyst for the degradation of rhodamine-B in visible light

Desta Shumuye Meshesha$^a$, Matangi Ravi Chandra$^{a,c}$, Siva Rao Tirukkovalluri$^a$*, Sreedhar Bojja$^b$

*a. Department of Inorganic and Analytical Chemistry, Andhra University, Visakhapatnam-530003, India.
b. Department of Inorganic & Physical Chemistry Division, India Institute of Chemical Technology, Hyderabad-500007, India.
c. Advanced Analytical Laboratory, DST-PURSE Programme, Andhra University, Visakhapatnam-530003, India.

The Ba$^{2+}$ & Zr$^{4+}$ co-doped TiO$_2$ nonmaterial was synthesized by sol-gel method. The presence of Ba$^{2+}$ and Zr$^{4+}$ dopants on to the TiO$_2$ assures the enhancement of the photocatalytic activity of pure TiO$_2$ and the catalyst degrading 5 mg/L of Rhodamine-B with 120 min.
Synthesis and characterization of Ba\textsuperscript{2+} and Zr\textsuperscript{4+} co-doped titania nanomaterial which in turn used as an efficient photocatalyst for the degradation of rhodamine-B in visible light

Desta Shumuye Meshesha \textsuperscript{a}, Ravi Chandra Matangi \textsuperscript{a,c}, Siva Rao Tirukkovalluri \textsuperscript{a*}, Sreedhar Bojja \textsuperscript{b}

\textsuperscript{a} Department of Inorganic and Analytical Chemistry, Andhra University, Visakhapatnam-530003, India.
\textsuperscript{b} Department of Inorganic & Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad-500007, India.
\textsuperscript{c} Advanced Analytical Laboratory, DST-PURSE Programme, Andhra University, Visakhapatnam-530003, India.

Abstract
A Ba\textsuperscript{2+} and Zr\textsuperscript{4+} co-doped titania nano material was prepared with different weight percentages of dopants ranging from 1.00-1.5 wt% by sol-gel method. It was examined against the photocatalytic activity and was compared to undoped TiO\textsubscript{2}. The prepared samples were characterized by XRD, TEM, UV-DRS, FT-IR, XPS and SEM-EDS. The XRD data has shows that the co-doped TiO\textsubscript{2} in anatase phase without distraction of crystal patterns by the dopents. UV-DRS spectra show that the co-doped TiO\textsubscript{2} has a significant absorption shift towards the visible region than pure TiO\textsubscript{2}. The TEM and SEM confirm the co-doped TiO\textsubscript{2} in nanometer range of about 20.15 -37 nm and the particles are in spherical shape, with presence of respective elements of the catalyst. From XPS, analysis it was confirmed that the prospect of all the corresponding elements as well as the dopant Ba in 2+ and Zr in 4+ state. The photocatalytic activities of these nano catalysts were investigated with rhodamine-B (RhB) as the model pollutant and the results were found to be by comparison of dopant concentration, pH of solution, dosage of catalysts, and dye concentration. From this study, the 0.75 wt% Ba\textsuperscript{2+} & 0.25 wt% Zr\textsuperscript{4+} co-doped TiO\textsubscript{2} exhibiting
high photocatalytic activity for the degradation of RhB at pH 8, 100 mg of catalyst and 5 mgL$^{-1}$ dye concentration and finally thereby studied the mechanism of photo degradation.

**Key words:** Titania, Co-doping, Photocatalysis, Rhodamine-B, Visible light

**Corresponding author:** T. Siva Rao, Email: sivaraoau@gmail.com, sivaraotvalluri.16@gmail.com

1. Introduction

The waste water generated by textile and dyeing industry has a very bad effect on the environment, due to their large discharge volume and toxic composition (Eslamil and Eslamic, 2015). With the development of dye industry, the studies on the treatment dyestuffs waste water become increasingly important. The photocatalytic technology is known as an advanced oxidation processes (AOP), which requires low power consumption and can be easily controlled (Mijin et al., 2009). Moreover, the photocatalytic process does not produce secondary pollutants. The TiO$_2$ and ZnO powders are the two main photocatalysts, which have been studied extensively during the last few years (Bai, 2009). Based on researches done over the last decades, since TiO$_2$ nano particles have attracted great interest for the degradation of organic and inorganic pollutants and toxic compounds, in environmental purification owing to their high efficiency, low cost, and long term stability upon commercial use. However, its large band gap (3–3.2eV) the light interaction limits only to ultraviolet (UV) region. To overcome these limitations, many studies have been performed to extend the spectral response of anatase to visible light and to enhance its photo catalytic activity by doping and co-doping with metals and non-metals have been shown to be among the most effective (Zhang et al., 2013; Yu et al., 2010).
Recently, Sun woo Kim et al. (2008) reported the degradation of toluene under visible light using Zr, S co-doped TiO$_2$. Chengxin Fu et al. (2016) studied B, Zr co-doped TiO$_2$ and modulation of microstructure for degradation of methylene blue. The Zn, N-codoped TiO$_2$ nanoparticles was prepared and their photocatalytic activity was studied by Zhang et al., (2012). Considering of the above studies and importance of visible light responsive nanomaterial it is very commendable to search for new nanomaterial with appropriate crystal phase, particle size, prepared by the sol-gel method. For various combinations, the Ba and Zr codoped TiO$_2$ may draw special interest and zirconium not only increases the surface area but also thermally stabilize the TiO$_2$ which retard the combination of electrons and holes (Kim et al., 2008). On the other side Ba$^{2+}$ is more electropositive and it can facilitate to form less dense anatase phase TiO$_2$ which leads to high photocatalytic active (Venkatachalamp et al., 2007). Hence, Barium (Ba$^{2+}$) large ionic radii (1.3Å$^+$) of alkaline earth metal and Zirconium (Zr$^{4+}$) a transition metal of (0.79Å$^+$) ionic radii compared to Ti$^{4+}$ (0.68 Å$^+$), as metal ion dopants to TiO$_2$ and to inspect its photocatalytic activity by degrading a dye pollutant RhB. In the present work the comparative rate study and efficiency of pure TiO$_2$ and co-doped TiO$_2$ was performed on initial concentration of pollutant, pH of solution, and the dosage of catalyst.

2. EXPERIMENTAL DETAILS

2.1. Materials

The Chemicals were reagent grade and used without further purification and double distilled water was used for solutions preparation. Titanium tetra-n-butoxide (Ti(OBu)$_4$) and metal nitrates are obtained from E- Merck (Germany) were used as titanium, dopant sources for
preparing undoped TiO\textsubscript{2} and co-doped TiO\textsubscript{2} catalysts respectively. RhB dye was used as a model pollutant for degradation.

2.2. Preparation of Ba\textsuperscript{2+} and Zr\textsuperscript{4+} co-doped titania nanomaterials

At first, solution-I which contains 50 mL of absolute alcohol, 7.5 mL of H\textsubscript{2}O, and metal nitrates of Ba\textsuperscript{2+} and for Zr\textsuperscript{4+} are taken for the preparation of required percentages. Another solution-II was prepared using 26.25 mL of Ti(O-Bu)\textsubscript{4} dissolved in 50 mL of absolute alcohol with stirring for 10 minutes, and then 3.75 mL of HNO\textsubscript{3} was added drop wise under continuous stirring for 30 minutes. Solution-I was added to solution-II slowly from the burette with vigorous stirring at room temperature until the transparent sol was obtained, and the resulting sol was further stirred for 2 h. The gel was prepared by aging the sol for 48 h at room temperature. The derived gel was dried at 100 \textdegree C in an oven and pulverized. The catalyst powder was calcined at 450 \textdegree C in furnace for 2 hours. Undoped TiO\textsubscript{2} is also prepared with same procedure without adding the dopents.

2.3. Characterization of catalysts

The Diffuse reflectance spectra (DRS) were recorded with a Shimadzu 3600 UV-Visible NIR Spectrophotometer equipped with an integrating sphere diffuse reflectance accessory, using BaSO\textsubscript{4} as reference scatter. Powder samples were loaded into a quartz cell and spectra were recorded in the range of 200-900 nm. Crystalline structures of photocatalysts were determined by X-ray diffractometer (XRD) (Model Ultima IV, RIGAKU) using Anod Cu-WL1 (\( \lambda =1.5406 \) nm) radiation with a nickel filter. The applied current and voltage were 40 mA and 40 kV, respectively. The 2\theta scanning range was 5.000 to 90.9505 with a scan rate of 10.1600 sec\textsuperscript{-1}. The average crystallite size of anatase was determined according to the Scherrer equation using
(FWHM) data of the selected peak. X-ray photoelectron spectroscopy (XPS) was recorded with a PHI quantum ESCA microprobe system, using the AlKα line of a 250 W X-ray tube as a radiation source with the energy of 1253.6 eV, 16 mA × 12.5 kV and a working pressure lower than 1 × 10^{-8} \text{Nm}^{-2}. As an internal reference for the absolute binding energies, the C 1s peak of hydrocarbon contamination was used as reference to 284.8 eV. The fitting of XPS curves was analyzed with Multipak 6.0 A software. The morphology and size of particles was characterized using scanning electron microscope (SEM) (JSM-6610 LV) equipped with an energy dispersive X-ray (EDS) spectrophotometer and operated at 20kV. FT-IR spectra of the samples were recorded on a FT-IR spectrometer (Nicolot Avatar 360). The extent of RhB degradation was monitored using UV-vis spectrophotometer (Shimadzul 1601).

2.4. Photocatalytic activity measurements

The high pressure metal halide lamp (400W) with UV filter has been used as a visible light source (output is 436 - 546 nm) with 35000 lumen and placed 20 cm away from the photo reactor. The photoreactor setup has been given elsewhere (Wu and Chen, 2004). Cut off filter was placed in the path of light for complete removal of UV radiation and running water was circulated around the sample container to filter IR radiation and to keep the reaction mixture at room temperature.

The photocatalytic procedure was carried out with a required amount of catalyst added to fresh 10 mgL^{-1} aqueous dye solution of required concentration in 150 ml Pyrex glass vessel with continues stirring. Prior to irradiation the solution with catalyst was stirred in the dark for 30 minutes to make certain for the establishment of adsorption–desorption equilibrium of RhB dye on catalyst surface. Aliquots of the samples were withdrawn from the solution by using Millipore
syringe (0.45 µm) at every 30 min. intervals and analyzed for RhB dye concentration. The degradation percentage of dye was checked by measuring the absorbance of dye solution at 545 nm using UV–visible (Milton-Roy Spectronic 1201) Spectrophotometer. A pH meter (Digital pH meter model 111E, EI) was used for adjusting and investigation of pH variation during the process. The pH of the dye solutions was adjusted prior to irradiation by addition of 0.1N NaOH or 0.1N HCl to get required pH.

3. RESULTS AND DISCUSSION

3.1. Characterization of photocatalyst

XRD patterns of Ba$^{2+}$ and Zr$^{4+}$ co-doped TiO$_2$ nano material samples and undoped titania were prepared by sol-gel method and calcined at 450 $^\circ$C shows in Fig.1. All the samples are in anatase phase (JCPDS No.: 21-1272) with corresponding (1 0 1) plane at 2$\theta$ = 25.3$^\circ$ followed by 2$\theta$ of 37.7$^\circ$, 47.9$^\circ$, 54.1$^\circ$, 55$^\circ$ and represents the planes (004), (200), (105), (211) anatase TiO$_2$ respectively. Moreover, it was observed that, when the dopent Ba$^{2+}$ concentration increases from 0.25 to 0.5, it was not observed any respective peaks of barium oxide. After increasing the concentration of Ba$^{2+}$ as 0.75 and 1.0, it was observed additional peaks at 23.84$^\circ$, 34.1$^\circ$, 42.19$^\circ$, 46.78$^\circ$ which corresponds to the formation of BaCO$_3$ (Venkatachalam et al., 2007). Hence, there may be the formation of BaO, which is subsequently converted into BaCO$_3$ during the calcinations of 0.75 wt% of Ba$^{2+}$ & 0.25 wt% of Zr$^{4+}$ doped TiO$_2$. On the other side, there is also no detectable dopant Zr$^{4+}$ related peaks were observed. Hence, the Zr$^{4+}$ may be occupied substitutional sites of the TiO$_2$ crystal structure and it is more electro positive than TiO$_2$ which favors the formation of less dense anatase phase (Venkatachalam et al., 2007). Furthermore, as large size and more electro positive nature of Zr$^{4+}$, the lattice can exhibits a better stability than pure TiO$_2$ (Venkatachalam et al., 2007). An average crystal size of the co-doped samples was
found to be ranging from 20.15 – 37 nm and 36.03 nm for undoped sample respectively (Table 1). Which were calculated by using the Debye-Scherrer equation on the anatase (101) plane. This indicates the doping of Ba\(^{2+}\), Zr\(^{4+}\) to TiO\(_2\) can suppress the grain growth and guide to attain the smaller grain size, when compared to the undoped TiO\(_2\).

The UV-visible DRS spectrum of prepared samples was shown in Fig. 2. From the UV-visible DRS studies the characteristic band for the prepared samples was in the range of 388 to 500 nm, and the band gap energy (eV) for the selected samples had been calculated by using the formula \(E=\frac{1240}{\lambda}\) (where \(\lambda\) is wavelength) and the results are shown in Table 1. The undoped titania exhibiting the band gap of 3.17eV where as the co-doped titania showing the range of about 2.689-3.02 eV respectively. Among the different percentage co-doped titania, 0.75 wt% Ba\(^{2+}\) & 0.25 wt% of Zr\(^{4+}\) co-doped titania exhibiting the less band gap and the red shift, making it active in the visible region. By co-doping of TiO\(_2\), the band gap of the TiO\(_2\) decreases and it suppress the electron hole recombination which leads to high photocatalytic activity.

FT-IR spectra of Ba\(^{2+}\) and Zr\(^{4+}\) co-doped TiO\(_2\) in Fig. 3 shows peaks corresponding to the stretching vibrations of O-H and bending vibrations of adsorbed water molecules around 3350–3450 and 1620-1635 cm\(^{-1}\), respectively. The stretching frequency band at 512 cm\(^{-1}\) can be assigned to Ti-O-Ti band in undoped TiO\(_2\). This band shifted to 522 cm\(^{-1}\) in the co-doped sample (Pallabi and Jatindra, 2013; Andreas et al., 2009). This indicates that the presence of dopants in TiO\(_2\) lattice deforms the Ti-O-Ti network and forms the new interaction as a Ti-O-Zr and Ba leads to diminishing the octahedral coordination of Ti ions (Kapusuz et al., 2013). Moreover there is an intense broad peak close to 1400 cm\(^{-1}\) in the spectrum of BaCO\(_3\) this is carbonate vibration (Venkatachalam et al., 2007). So FT-IR studies clearly indicate the presence of BaCO\(_3\) layer in the co-doped catalysts.
The SEM images of the undoped and co-doped TiO$_2$ nano material in Fig. 4 indicates the morphological changes with an average particle size of 10 µm and 5µm respectively. This shows that the decrease in particle size imparts the increase of surface area and better photocatalytic activity of the catalyst powder. The EDX analysis shown in Fig. 5 confirms the presence of consequent elements of the co-doped TiO$_2$ catalyst with their elemental composition and the elements Ti, O corresponds to TiO$_2$ and Ba, Zr corresponds to dopants respectively.

The TEM images of undoped and co-doped TiO$_2$ shown in Fig. 6. TEM results revealed that the undoped and co-doped TiO$_2$ nano catalysts are in spherical shape and not in uniform with the crystallite size of about 36.03 and 20.63 nm respectively. Moreover, the TEM results are in good agreement with XRD results. These results strongly confirm that, due to the co-doping of Ba$^{2+}$ & Zr$^{4+}$ in TiO$_2$ lattice decrease the crystallite size of TiO$_2$ which leads to increase of surface area of the catalyst.

X-ray photoelectron spectroscopy (XPS) of Ba$^{2+}$ & Zr$^{4+}$-TiO$_2$ analysis was performed, and the high-resolution scans are shown in Fig. 7. The Fig. 7a shows the survey spectrum of co-doped titanium and it exhibits the presence of all the respective components of the catalyst. The Fig. 7e Shows two peaks of Zr 3d$^{5/2}$ and Zr 3d$^{3/2}$ are absorbed with a binding energy of 178.332 and 181.063 eV respectively; this can be attributed to Zr$^{4+}$. The Ti 2p$^{3/2}$ and Ti 2p$^{1/2}$ components of 0.75 wt% Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$ (Fig. 7f) are located at 459.227 and 464.875eV corresponding to the existence of Ti$^{4+}$ state (Zhang et al., 2013; Wang et al., 2012). In Fig. 7d shows O 1s spectrum can be resolved into two peaks at 530.266 eV and 532.593 eV and the strong peak of 530.266 eV is attributed to lattice oxygen in Ti-O bonds and small peak around 532.593 eV is attributed to weakly physical adsorbed oxygen species such as O and OH group on the surface (Zhang et al., 2013; Saquib et al., 2008). From the above XPS results a 3d
peaks at 781.171eV and 795.874eV corresponding to 3d 5/2 and 3d 3/2 respectively are assigned as Ba$^{2+}$ and does not absorbed into the TiO$_2$ being it is high atomic radii than Ti and the presence of Zirconium has certain influence on Ti$^{4+}$ pulling the electrons in Ti-O-Ti bond, a bit away from Ti atom, thus causing a little rise in Ti 2p$_{3/2}$ binding energy. Thus XPS data has confirmed that there is a substitution doping of doped metal.

4. Photocatalytic activity of catalyst - Degradation of RhB

4.1. Effect of dopant concentration on the degradation of RhB:

The high pressure mercury vapor lamp (400W, Osoram) with UV filter has been used as a visible light source (output is 436 - 546 nm) with 35000 lumen and placed 20 cm away from the photo reactor. The setup of a photoreactor has been given elsewhere (Wu and Chen, 2004). Cut off filter was placed in front of the light for the removal of UV radiation and running water was circulated around the sample container to filter IR radiation and to keep the reaction mixture at room temperature.

To obtain the optimum dopant concentrations of Ba and Zr varied from 0.25-1.0 wt% for co-doped TiO$_2$, experiments were carried by degradation of RhB under visible light irradiations. Fig. 8. Shows the codoped TiO$_2$ with different weight percentages of Ba & Zr and undoped TiO$_2$. Among all the photocatalysts, 0.75 wt% of Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$ catalyst exhibits highest photocatalytic activity and it is may be because of dopant concentration leads to increase in number of trapped charge carrier per particle (Kapusuz et al., 2011; Senthilkumar et al., 2006). On the other hand, 1.0 wt% of Ba$^{2+}$, Zr$^{4+}$-TiO$_2$ catalyst exhibiting the less crystallite size as well as more surface area when compared with remaining catalysts (Table 1). Due to the less crystallite size and more surface area, the catalyst may adsorb more number of dye molecules which leads to high photocatalytic activity.
4.2. Effect of solution pH

Solution pH is an important variable in the evaluation of aqueous phase mediated photocatalytic degradation of RhB. Fig. 9 shows the effect of pH on degradation of RhB by catalyst under visible light irradiation. When the pH of solution varying 2 to 10, the codoped TiO$_2$ exhibiting high catalytic activity and degrading completely at pH 8. Initially, degradation of RhB was less at acidic medium and increases when pH increases. Hence, RhB is a cationic dye in aqueous solution, and in an acidic pH the surface of catalyst (Ba$^{2+}$ and Zr$^{4+}$ co-doped TiO$_2$ ) and RhB dye will both attain positive charge and develop electrostatic repulsion between them and vice-versa. But in basic pH, since RhB is cationic dye which would enhance percentage of degradation and it reach maximum at pH 8. Moreover, when the pH is more than 8, the degradation of RhB decreases, it is may be due the increase of more •OH radicals and there exist a repulsion between them which leads to decrease the adsorption of dye molecules on surface of the catalyst (Tang and An, 1995; Wang et al., 2000).

4.3. Effect of catalyst dosage:

The effect of catalyst dose on degradation of RhB was given in Fig. 10. The rate of degradation was carried out by varying the catalyst amounts of 25 mg, 50 mg, 100 mg, 200 mg and 300 mg in 10 mgL$^{-1}$ of RhB. The rate of degradation increases with the increase of catalyst loading up to 100 mg; further increasing the catalyst dosage the degradation decreases (Fig. 10). This is because of catalyst powder is not effectively involved in the photocatalytic activity rather increases in the turbidity of the solution, which hinder the penetration of light transmission. Further, shielding of titania may also take place (Chen et al., 2008; Kahan et al., 2008) and the optimum catalyst dose found to 100 mg.

4.4. Effect of RhB initial concentration
The effect of initial RhB concentration have strong influence on rate of degradation, and this was studied by taking from 1 mgL$^{-1}$ to 15 mgL$^{-1}$ of RhB at a fixed dose of 100 mg of 0.75 wt % Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$ nonmaterial, at a solution pH 8. Fig. 11 shows the effect of dye concentration on rate of degradation under visible light irradiation. Photocatalytic degradation increases with the increase in the concentration of dye up to 5 mgL$^{-1}$, after increasing the dye concentration degradation decreases. This may be attributed to the fact that as the concentration of the dye increased, more dye molecules will be available for excitation and energy transfer (Sirinivasan et al., 2006; Zhang et al., 2008) which increases the percentage of degradation. But above the limit it starts to cover the surface of photocatalyst from light intensity (Kiran et al., 2010) that decreases degradation (Kusvuran et al., 2004).

5. Photocatalytic mechanism

Based on the experimental results a possible mechanism was proposed for photocatalytic reactions of 0.75 wt % Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$ nonmaterials.

i) When the visible light irradiated on the catalyst, the electrons can move from valence band to conduction band through creating the holes in valence band.

\[ \text{Ba, Zr-TiO}_2 + \text{hv} \rightarrow \text{Ba, Zr-TiO}_2 (\text{h}^+) + \text{Ba, Zr-TiO}_2 (\text{e}^-) \]

ii) The electrons can be trapped into TiO$_2$ lattice upon Ba$^{2+}$ and Zr$^{4+}$ which leads to form unstable Ba$^{+1}$ and Zr$^{3+}$. Through this process the rate of recombination can be reduced.

\[ \text{Ba, Zr-TiO}_2 (\text{e}^-) + \text{Zr}^{4+} \rightarrow \text{Ba, Zr-TiO}_2 + \text{Zr}^{3+} \]

\[ \text{Ba, Zr-TiO}_2 (\text{e}^-) + \text{Ba}^{2+} \rightarrow \text{Ba, Zr-TiO}_2 + \text{Ba}^{1+} \]

iii) The molecular oxygen present on the surface of the catalyst can be scavenged the trapped electrons, which is adsorbed on the TiO$_2$ surface, to generate superoxide
radical, and this in turn produces hydrogen peroxide (H₂O₂), hydroperoxy(HO₂ •) and hydroxyl (•OH) radicals.

\[
\text{Ba, Zr-TiO}_2 (e^-) + O_2 \rightarrow \text{Ba, Zr-TiO}_2 + O_2^{• -}
\]

\[
\text{Ba, Zr-TiO}_2 (e^-) + O_2^{• -} + H_2O \rightarrow \text{Ba, Zr-TiO}_2 + HO_2^{• -} + HO^-
\]

\[
\text{Ba, Zr-TiO}_2 (e^-) + HO_2^{• -} + H^+ \rightarrow \text{Ba, Zr-TiO}_2 + H_2O_2
\]

\[
\text{Ba, Zr-TiO}_2 (e^-) + H_2O_2 \rightarrow \text{Ba, Zr-TiO}_2 + HO^• + HO^-
\]

iv) The generated positive holes can be act as strong oxidizing agents and electrons can act as reducing agents. Thus, the RhB is attacked by hydroxyl radicals formed both by trapped electrons and holes which leads to degradation under visible light.

\[
\text{•OH(h}_{vb}) + \text{pollutant} \rightarrow \text{pollutant}^+ \rightarrow \text{Degradation product}
\]

Thus, the RhB is attacked by the hydroxyl radicals formed both by trapped electrons and hole in the VB, to generate organic radicals or other intermediates, which further undergo degradation.

6. CONCLUSIONS

The UV-DRS analysis shows that co-doping of Ba^{2+} & Zr^{4+} into TiO₂ shifts the absorbance band of TiO₂ from UV to visible region and the band gap energy is reduced for all co-doped catalysts. All the catalysts are in nano meter range, which was strongly supported by the XRD and TEM analysis. The largest reduction gap and high photo catalytic activity was observed for co-doped catalysts of 0.75 wt% of Ba^{2+} & 0.25 wt. % of Zr^{4+}. The optimum condition for the degradation of RhB by co-doped catalyst was found at catalyst weight of 100 mg, initial dye concentration 5 mgL⁻¹ and solution pH is 8 respectively.
Acknowledgments

Thankful to University of Gondar, Government of Ethiopia and DST-PURSE Programme, Advanced Analytical Laboratory, Andhra University for their support in carrying out in this research work regarding SEM-EDX, FT-IR and XRD analysis.

Reference


Bai, J. H., 2009. Synthesis and photocatalytic activity of cobalt oxide doped ZnFe\textsubscript{2}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3}-ZnO mixed oxides, Mater Lett., 63, 1485-1488.


Table 1. Shows crystallite size, Band gap and BET surface area of the prepared co-doped catalysts.

<table>
<thead>
<tr>
<th>Composition of catalyst</th>
<th>Crystallite size (nm)</th>
<th>Band gap (eV)</th>
<th>BET (m²/g) Surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% Ba²⁺,0.25 wt% Zr⁴⁺-TiO₂</td>
<td>36</td>
<td>3.02</td>
<td>65</td>
</tr>
<tr>
<td>0.25 wt% Ba²⁺,1.0 wt% Zr⁴⁺-TiO₂</td>
<td>36.9</td>
<td>2.931</td>
<td>74</td>
</tr>
<tr>
<td>0.5 wt%Ba²⁺, 0.5 wt%Zr⁴⁺-TiO₂</td>
<td>36.9</td>
<td>2.917</td>
<td>80</td>
</tr>
<tr>
<td>0.25 wt% Ba²⁺, 0.75 wt% Zr⁴⁺-TiO₂</td>
<td>36.9</td>
<td>3.009</td>
<td>70</td>
</tr>
<tr>
<td>0.75 wt% Ba²⁺, 0.25 wt% Zr⁴⁺-TiO₂</td>
<td>20.15</td>
<td>2.689</td>
<td>98</td>
</tr>
<tr>
<td>0.5 wt% Ba²⁺, 1.0 wt% Zr⁴⁺-TiO₂</td>
<td>22.5</td>
<td>2.767</td>
<td>86</td>
</tr>
<tr>
<td>1.0 wt% Ba²⁺, 0.5 wt% Zr⁴⁺-TiO₂</td>
<td>37.0</td>
<td>3.04</td>
<td>66</td>
</tr>
<tr>
<td>TiO₂</td>
<td>36.55</td>
<td>3.17</td>
<td>63</td>
</tr>
</tbody>
</table>
Figures Captions

Fig. 1. XRD pattern of the synthesized undoped and co-doped TiO$_2$ with different wt% of Ba$^{2+}$ & Zr$^{4+}$.

Fig. 2. The DRS spectra of undoped TiO$_2$, and co-doped TiO$_2$ with different wt% of Ba$^{2+}$ & Zr$^{4+}$.

Fig. 3. FT-IR spectra of (a) undoped TiO$_2$ (b) 0.75 wt% Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$.

Fig. 4. SEM images of (a) undoped TiO$_2$ (b) 0.75 wt% of Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$.

Fig. 5. EDX spectrum of 0.75 wt% of Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$.

Fig. 6. TEM images of (a) undoped TiO$_2$ (b) 0.75 wt% Ba$^{2+}$ & 0.25wt% Zr$^{4+}$ co-doped TiO$_2$.

Fig. 7. (a) XPS survey spectrum of co-doped TiO$_2$ (b) high resolution spectrum of C1s (c) Ba 3d (d) O1s (e) Zr 3d and (f) Ti 2p, respectively.

Fig. 8. Effect of dopant concentration on photocatalytic activity of co-doped titania for rate of degradation of RhB. Here, catalyst dosage 50 mg, pH=3 and [RhB] =10 mg/L.

Fig. 9. The effect of pH on the rate of degradation of rohodamin-B by Ba$^{2+}$ & Zr$^{4+}$ co-doped TiO$_2$. Here, catalyst dosage = 50 mg and [RhB] = 10 mg/L.

Fig. 10. Effect of catalyst dosage on the rate of degradation of RhB by 0.75 wt% Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$. Here, pH= 8 and RhB=10 mg/L.

Fig. 11. The effect of initial concentration of dye on the rate of degradation of RhB. Here, pH = 8, catalyst dosage =100 mg.
Fig. 1. XRD pattern of the synthesized undoped and co-doped TiO$_2$ with different wt% of Ba$^{2+}$ & Zr$^{4+}$. 
Fig. 2. The DRS spectra of undoped TiO$_2$, and co-doped TiO$_2$ with different wt% of Ba$^{2+}$ & Zr$^{4+}$. 
Fig. 3. FT-IR spectra of (a) undoped TiO$_2$ (b) 0.75 wt% Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$.

Fig. 4. SEM images of (a) undoped TiO$_2$ (b) 0.75 wt% of Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$. 
Fig. 5. EDX spectrum of 0.75 wt% of Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%)</th>
<th>Atomic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>39.51</td>
<td>65.87</td>
</tr>
<tr>
<td>Ti K</td>
<td>57.14</td>
<td>33.06</td>
</tr>
<tr>
<td>Zr L</td>
<td>1.12</td>
<td>0.28</td>
</tr>
<tr>
<td>Ba L</td>
<td>2.23</td>
<td>0.79</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 6. TEM images of (a) undoped TiO$_2$ (b) 0.75 wt% Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$. 
Fig. 7. (a) XPS survey spectrum of co-doped TiO$_2$ (b) high resolution spectrum of C1s (c) Ba 3d (d) O1s (e) Zr 3d and (f) Ti 2p, respectively.
Fig. 8. Effect of dopant concentration on photocatalytic activity of co-doped titania for rate of degradation of RhB. Here, catalyst dosage 50 mg, pH=3 and [RhB] =10 mg/L.
Fig. 9. The effect of pH on the rate of degradation of RhB by Ba$^{2+}$ & Zr$^{4+}$ co-doped TiO$_2$. Here, catalyst dosage = 50 mg and [RhB] = 10 mg/L.
Fig. 10. Effect of catalyst dosage on the rate of degradation of RhB by 0.75 wt% Ba$^{2+}$ & 0.25 wt% Zr$^{4+}$ co-doped TiO$_2$. Here, pH=8 and [RhB] =10 mg/L.
Fig. 11. The effect of initial concentration of dye on the rate of degradation of RhB. Here, pH=8, catalyst dosage =100 mg.
Highlights

- The Ba$^{2+}$ & Zr$^{4+}$ co-doped TiO$_2$ nonmaterial was synthesized by sol-gel method.
- The presence of Ba$^{2+}$ and Zr$^{4+}$ dopants on to the TiO$_2$ assures the enhancement of the photocatalytic activity of pure TiO$_2$.
- The Ba$^{2+}$ & Zr$^{4+}$ co-doped TiO$_2$ degrading 5 mg/L of Rhodamine-B with 120 min.