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SYNTHESIS AND OPTICAL PROPERTY CHARACTERIZATION OF METAL ION AND HETERO ATOM DOPED TiO_2 NANOCOMPOSITE FABRICATION FOR PHOTO CATALYSIS

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The transition metal ions and heteroatoms such as iron cobalt and nickel modified titania were synthesized by *insitu* precipitation and hydrothermal technique. Prepared materials are further treated by thermal analysis towards crystalline phase formation. The particle size of prepared titania calculated from intense d-space values of prepared materials and it is found to be 22-23 nm. Raman spectra and the DR UV-Visible spectra of metal ion and nitrogen doped titania extends to the visible region (450-650 nm). Methylene blue (MB) dye degradation was performed to evaluate the photosensitivity property of the as prepared materials under sun light irradiation. Metal ion modified titania (0.01Fe- TiO_2, 0.01Co-TiO_2 and 0.01Ni-TiO_2) materials are showing complete degradation of MB. For the comparison purpose, the powder nanotitania samples are prepared and also coated on ITO (indium tin oxide) plates by electrodeposition method. XRD and DRS properties of coated titania were tested for electrode application.

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1. Introduction

In the past decades the research study related with TiO_2 focused on catalytic reaction under, under UV light irradiation [1-3]. Doping of foreign metal ion intoTiO_2 is an important composite with a huge application in of photo-catalysis and it possibly shows high efficiency in the removal of hazardous materials from water and waste water [4-6]. The major disadvantages of undoped or pure TiO_2 is sluggish activity in visible region due to its large bandgap values. It is necessary to fabricate photo sensitive materials that can produce high activity under visible light irradiation. The modification on TiO_2 or doping the organic dye molecules like adopting sensitizer can be applied to reduce the band gap of TiO_2. The maximum utilization of direct solar energy on sensitized photocatalytic reaction is highly interesting developing area of research. Recently, many research work reported the doping of foreign metal ion on Titania has the ability to simultaneously increase the photocatalytic efficiency of TiO_2 under visible light irradiation [7]. In addition, with this, the electron-hole recombination will be suppressed by the mixed valence ions or transition metal ion doping by deposition method [8, 9]. Thus incorporation or doping in Titania is a promising route to extend the optical absorption to the visible light spectra region [10]. It was observed that cationic doping in TiO_2 leads to decrease in band gap values and enhances the photo sensitive property of catalyst under sunlight irradiation [11]. Hetero atom doping on TiO_2 is explained by the generation of new energy level in the band gap of titania via nano particles dispersion in the lattice structure of TiO_2 [12,13]. In the past few decades many synthetic preparation strategies have been developed to produce different structures of doped and undoped porous TiO_2 and the hydrothermal process is more effective for create high purity, narrow particle size distribution, high crystallinity and interesting structural morphology formation [14].

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Therefore, In the present study, titania doped with different transition metal ion and nitrogen doped titania were synthesized by insitu hydrothermal technique via precipitation method. The surface and catalytic properties were characterized by various instrumental techniques.

2. Experimental

2.1. Preparation of materials

All materials are Analytical grade compounds and are used without further purification. Titanium (IV) butoxide is chosen as the titania precursor in the present work. Other chemicals such as Fe $(NO_3)_3.9H_2O$, Co $(NO_3)_2.6H_2O$ and Ni $(NO_3)_2.6H_2O$ and ammonia. TBO is first treated hydrolysis process and mainted the pH to basic with adding NH_3 solution in the ratio TBO: NH_3: dH_2O (1:0.1:100). The as prepared mixture was pour into the Teflon coated autoclave follows placed in an oven at 393 K for 24 h. After one day the white precipitate obtained was centrifuged, dried at 343 K to get parent titania. The same procedure was followed for the preparation of insitu doping of 0.01 mol% of iron, cobalt and nickel ions addition to the precursor, Co and Ni addition on initial titania precursor. Nitrogen doped TiO_2 prepared in the similar fashion as mentioned above with the addition of NH_3 solution by maintain following ratio xN:T, x=0.25,0.5 and 1.0 molar ratio. Photocatalytic methylene blue Degradation was carried out in an immersion type photo-reactor at visible light irradiation. Heteroatom substitution in TiO_2 film based photo anodes is produced by electro-deposition technique using Indium tin oxide (ITO) plates are substrates. In the present study, 3 mg of Iodine and 15 mg of N-TiO_2 powder were dispersed in 15 ml acetone followed by ultrasonic ate in water bath for 15 minutes to obtain ordered dispersion of doped nano titania film formation on ITO plates.

2.2. Materials characterization

The crystal structure and crystalline phase of prepared material was characterized by XRD; AXS Bruker D5005 X-ray diffractometer (Copper Kα radiation). Scherer equation is utilized to determine the crystallite size of prepared materials. The Raman spectra is utilized to study the surface band structure of the materials. The band gap energy values of metal ion modified of TiO_2 were calculated using the absorbance data obtained from diffuse reflectance ultraviolet visible spectrometer (JASCO UV-Visible spectrophotometer V550 ISV469) analysis. The data of DRS UV is further analyzed by plotting Tauc's relation $\{(\alpha\eta\nu) = \chi (\eta\nu - E_\gamma)^\nu$.

2.3. Photosensitive studies

The immersion type photo reactor (Heber Scientific) is utilized to study the photocatalytic activity of the transition metal ion doped titania and nitrogen doped titania in the presence of aqueous methylene blue. In a typical procedure, the as prepared catalyst was measured appropriate quantity in fixed amount of aqueous dye solution to form a slurry suspension followed by pour into the reactor to reaction carry out by stirring for about 30 minutes to attain the adsorption equilibrium [16]. After half an hour of reaction of stirring, the dye solution was irradiated with visible lamp (300W Tungsten halogen lamp, 50 Hz, 230 V). The reaction solution was withdrawn at particular intervals and concentration of dye solution determined at fixed wavelength of 665 nm using ultraviolet visible spectrophotometer

3. Results and discussion

The powder XRD patterns of nitrogen doped TiO_2 and transition metal ion doped titania are shown in Fig. 1 and 1 a (Fe-, Co- and Ni-TiO_2). The intense peak of transition metal ion incorporated titania indexed as follows (101), (004), (200), (211) and (204) with respective *d*-space values and it shows the well crystalline anatase phase in the case of Nickel ion doped titania. No additional peaks corresponding to the dopants were observed and it means successful insitu incorporation in titania lattice or may be due to super imposition of major components of titania diminishes the metal ion doped oxide phases in XRD [14]. The crystallite size is calculated based on d-space values of major intense peaks using Scherer equation and is obtained in the range of 20-23 nm. Fig 1a shows the different mole ratio of nitrogen doping in the matrix of titania. All samples are showing anatase phase as major crystalline phase formation for the prepared sample. Increase the amount of nitrogen doping is not altered the crystalline phase of titania formation.

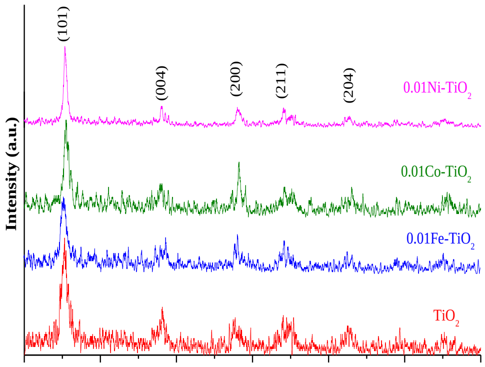


Fig. 1. Powder X-ray diffraction pattern of TiO_2 *and 0.01(Fe, Co, Ni)-*TiO_2*.*

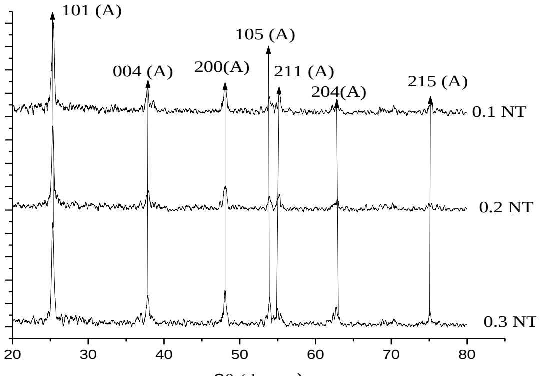


Fig. 1 a. Powder X-ray diffraction pattern of different moles of Nitrogen doped titania.

Table 1. BET surface area analysis results.

No.	**Material**	**Bandgap (eV)**	**SBET (m^2 g^{-1})**	**Average particle size (nm)**
1.	TiO_2	2.9	125.3	12.6
2.	0.01Fe-TiO_2	2.7	83.5	18.9
3.	0.01Co-TiO_2	2.6	83.5	18.9
4.	0.01Ni-TiO_2	2.7	65.4	24.1

The BET surface area values, band gap values and average particle size were measured by various surface analysis and diffraction technique and the same is shown in Table 1. The improved specific surface area value is obtained for our method synthesized pristine Titania. After doping of foreign metal ion decrease the surface area values slightly and nickel doping causing the more decrease in surface are due to more replacement of titanium species in the matrix of titania with Ni

(II) ions. The decrease in BET surface area upon doping corresponds to an increase in particle size may due to agglomeration as evidenced by the obtained average particle size.

The TG-DSC pattern of as prepared nanoparticle of TiO_2 is shown in Fig. 2. Thermal pattern of the parent titania prepared by hydrothermal method shown the first weight loss around 200 °C which is due to the loss of moisture, hydroxide into transformation into oxide phase.

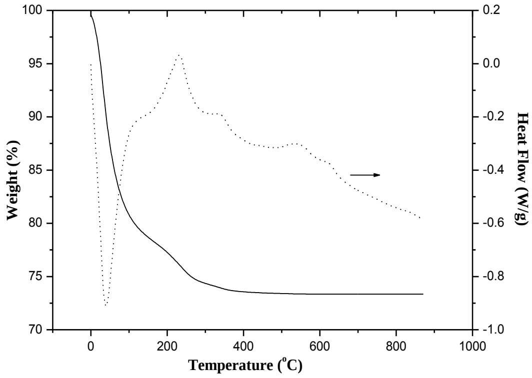


Fig. 2. TG-DSC of TiO_2.

The Differential scanning calorimetric curve shows endothermic peak at 373 K due to decomposition of water molecules bound on the surface. A minor exotherm peak at 673 K indicates the crystallization of amorphous titania. The as prepared solid sample is transformed into crystalline titania phase formation after 773 K (Weight changes after 500 °C) was quite small, which is clear evidence of formation of anatase phase titania [17].

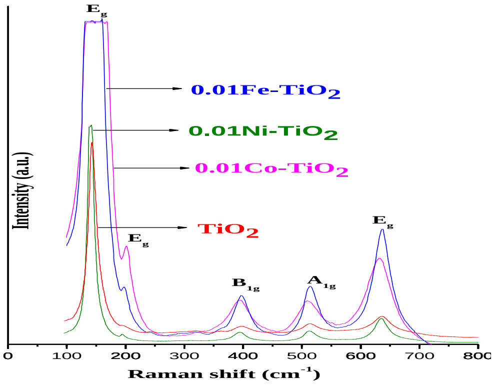


Fig. 3. Raman spectra of TiO_2 and 0.01 (Fe, Co, Ni)-TiO_2.

As prepared metal ion modified titania shows the characteristics Raman active modes for the anatase phase titania prepared by our method. The assigned Eg and B1g modes coincides with the XRD results of the metal ion modified titania [18]. All synthesized titania samples are displaying four modes of vibration, with an additional very weak shoulder at 195 cm^{-1}. Based on factor group analysis, six modes (A_{1g}+ $2B_{1g}$+ $3E_g$) of anatase TiO_2 are Raman active. The predicted Raman active modes for the tetragonal anatase phase observed are two B_{1g} modes at 399 and 519 (cm^{-1}); three E_g modes centered at 145, 197 and 639 (cm^{-1}) and one A_{1g} mode at 513 (cm^{-1}). Hence the Raman spectra is further confirming the only anatase phase obtained by our method synthesized titania nanopowder instead of partial rutile phase formation in the hydrothermal method synthesized metal ion doped titania and nitrogen doped titania samples.

The DR (diffuse reflectance) UV-Visible spectroscopic analysis of undoped titania and metal ion doped TiO_2 are shown in Fig. 4 and Fig. 5. The band gap values are calculated by Tauc's plot method and calculated values are presented in Table 1.

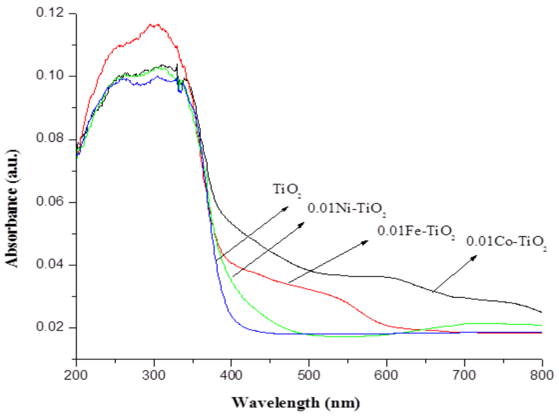
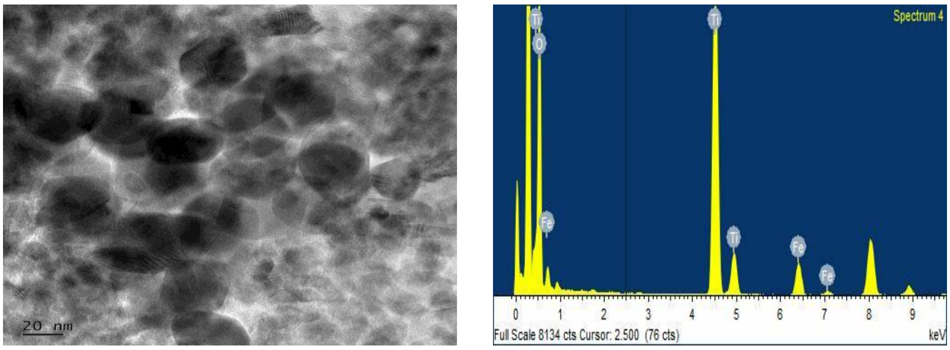


Fig. 4. Diffuse reflectance spectra of Metal ion modified titania.

The band gap values from the Table I is clearly evident that the metal ion doped titania samples could enhances the visible light absorption for photo catalytic reactions. The reported research report has also confirmed that the shifting in band gap energy levels could shifts the absorption edge from UV region to visible sunlight irradiation for solar light driven catalytic process [19].

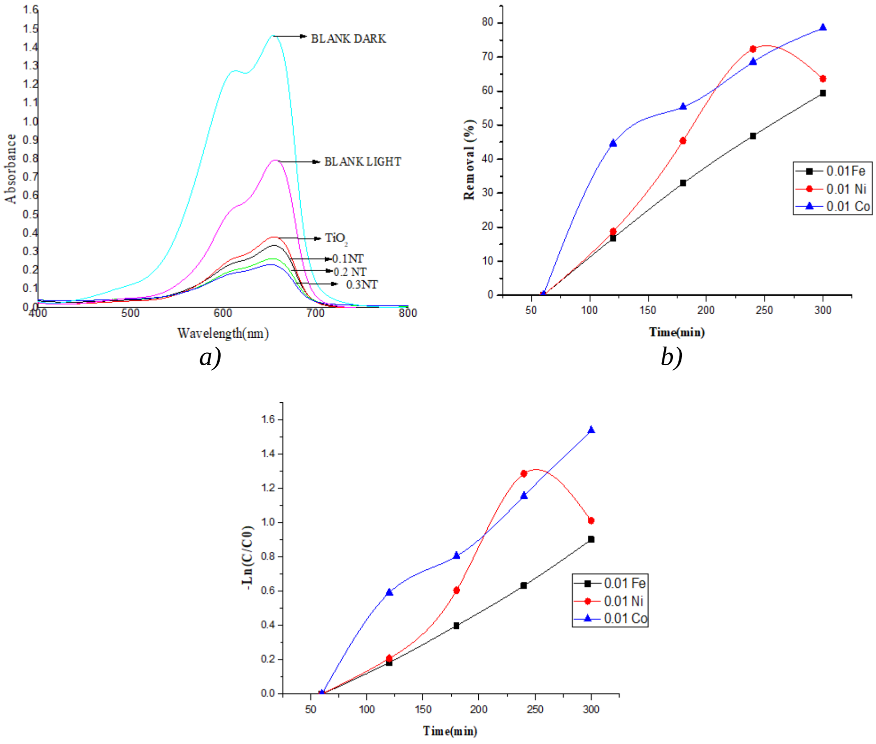
The TE (transmission electron) micrographs of 0.01Fe-TiO_2 is shown in Fig. 6. The average particle size of iron doped titania is calculated as 20 nm, which is shown in the micrograph. The particle size obtained from TEM analysis coincides with the shearer equation route calculated particle size of XRD data. From Energy Dispersive X-ray analysis (EDAX), it is clear that the material shows the presence of both Ti, Iron(II) and major oxygen and thus confirms the formation of pure majority phase of TiO_2.



a) *b)*

Fig. 6. (a) HR-TEM images of 0.01Fe-TiO_2
(b) Eelemental composition of the Fe-TiO_2

Visible light photosensitive catalytic activity: the pollutant dye absorption analysis in absence of titania catalysis no color change or methylene blue degradation was carry out. However, in the absence of light with as prepared photoactive pristine titania material shows slight degradation for methylene blue discoloration reaction. Methylene blue is used as model compound for the all photo sensitive catalytic reaction study in presence and absence of sunlight and photo light irradiation at visible region and already some reports are reported using visible light driven catalysis on methylene blue degradation [20].

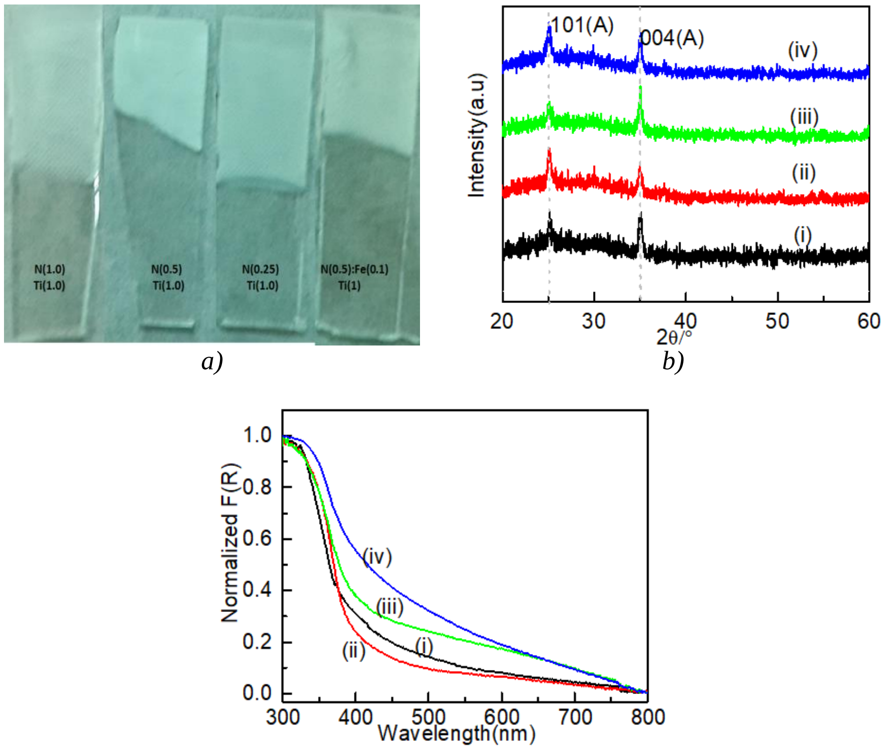


a) *b)*

c)

Fig. 7. (a) Dey degradation phenomenon against various metal ion modified titania and (b&c) kintecits of removal (%) of titania and doped titanta and its respective ln(C/Co) kinetics.

Fig 7 shows the MB degradation pristine and other metal ion modified titania against MB removal experiment. Nitrogen doped and iron modified titania shows equal activity. Cobalt ion modified titania shows higher removal percentage for MB degradation up to 70%. The next active photo active material is nickel modified titania catalyst shows higher degradation activity. The kinetics of the MB degradation on titania and doped titania is shown Fig 7c and it shows cobalt doped titania shows slow and steady increase in degradation of methylene blue with respect to reaction time. In the present method prepared cobalt and nickel doped nano titania photo catalysts shows higher conversion and reactivity for MB degradation compared other reported metal ion modified titania photo catalysts. [21-25]. It also shown that weight of catalyst is plying important role in increasing reaction rate and also increases and as the dye concentration increased degradation also increased.



a)

b)

c)

Fig. 8. (a) Schematic image of different amount of Nitrogen mixed titana precursor deposited on ITO substrate (b)Normalized XRD patterns and (c) UV-Vis diffuse reflectance spectra (DRS) different N Content of titania modification (i) NT1, (ii) NT2 (iii) NT3, and (iv) NT1/FeN.

The as prepared precursor solution of different mole percent of nitrogen doped titania precursors are directly electrodeposited on Indium tin oxide plate and studied their surface characterization and optical property variation and it presented in Fig. 8 (a-c). Fig. 8 b and c shows the XRD and bandgap property of the prepared nitrogen incorporated titania samples. The pure anatase formation confirmed by XRD and the band gap values are optimized based on mole percentage of nitrogen addition in titania. Nitrogen (0.5) addition on titania (Fig. 8 c (iii)) shown the altered band gap values equal to iron and nitrogen modified titania (Fig. 8 c(iv)) samples. Hence, the shifted band gap values could play electron hole transport mechanism in visible light sensing activity for catalytic reactions.

4. Conclusions

The transition metal ion and nitrogen modified titania Nano powder are synthesized by photo deposition process. The as prepared photo catalysts (0.1Fe,-TiO2, 0.01Co-TiO2 and 0.01Ni-TiO_2) are characterized in detail by various physico-chemical techniques. XRD and Raman spectra confirms the purity of anatase titania formations. The absorption spectra extend to the red shift (visible) region with band gap values of 2.7, 2.6 and 2.7, respectively for the prepared doped titania. The enhanced activity with a photocurrent of 0.25 mA/cm^2 at 1 V vs RHE was obtained for the nitrogen doped titania prepared by photo deposition method with mole ratio of (0. 5N:1Ti). The improved degradation activity was achieved for as prepared photo sensitive materials under visible light condition towards efficient waste water treatment applications.

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References

[1] J. Nowotny, T. Bak, M. K. Nowotny, L. R. Sheppard, Int. J. Hydrogen Energy **32**, 2609 (2007).
[2] A. Kudo, Int. J. Hydrogen Energy **31**, 2197 (2006).
[3] L. J. Minggu, W. R. Wan Daud, M. B. Kassim, Int. J. Hydrogen Energy **35**, 5233 (2010).
[4] H. Kato, K. Asakura, A. Kudo, J. Am. Chem. Soc. **125**, 3082 (2003).
[5] W. L. Suchanek, R. E. Riman, Adv. Sci. Tech. **45**, 184 (2006).
[6] Jakkidi Krishna Reddy, Kannekanti Lalitha, Pullagurla Venkata Laxma Reddy, Gullapalli Sadananda, Machiraju Subrahmanyam, Valluri Durga Kumari, Cat. Lett. **144**, 340 (2014).
[7] Shou-Hein Liu, Han-Ren Syu, J. Appl. Energy **100**, 148 (2012).
[8] Tao Sun, Jun Fan, Enzhou Liu, Yan Wang, Hongzhe Dai, Yuhao Yang, Wenqian Hou, Xiaoyun Hu, Zhenyi Jiang, J. Power Tech. **228**, 210 (2012).
[9] Yaqin Wang, Ruirui Zhang, Jianbao Li, Linangliang Li, Shiwei Lin, J. Nanoscale Research Letters. **9**, 46 (2014).
[10] B. Naik, S. Martha, K. M. Parida, Inter. Hydrogen Energy **36**, 2794 (2011).
[11] T. R. Cook, D. K. Dogutan, S. Y. Recee, Y. Surendranath, T. S. Teets, D. G. Nocera, Chem. Rev. **110**, 6474 (2010).
[12] Adriana Zaleska, J. Recent patents on Engng. **2**, 157 (2008).
[13] Akihiko Kudo, J. Pure Appl. Chem. **79**, 1917 (2007).
[14] Mohd Hasmizam Razali, M. N. Ahmad-Fauzi, Abdul Rahman Mohamed, Srimala Sreekantan, Int. J. of Mater. Mech. Manuf. **1**(4), 2013.
[15] Yulia Galagan, Sheng-Hao Hsu, Wei-Fang Su, J. Sensors and Actuators B **144**, 49 (2010).
[16] Bin Zhao, Yu-Wen Chen, J. Phy Chem. of solids **72**, 1312 (2011).
[17] W. Y. Teoh, E. E. Wolf, P. V. Kamat, J. Phys. Chem. B **105**, 7479 (2001).
[18] T. Ohsaka. F. Izumi, Y. Fujiki, J. Raman Spectroscopy **7**, 321 (1978).
[19] A. L. Castro, M. R. Carvalho, M. D. Ferreira, L. P. Jumas, J. Solid State Chem. **182**, 1838 (2009).
[20] Farook Adam, Lingeswarran Muniandy, Radhika Thankappan, J. Colloid Inter. Sci. **406**, 209 (2013).
[21] Farook Adam, Jimmy Nelson Appaturi, Zakia Khanam, Radhika Thankappan, Mohd. Asri Mohd Nawi. J. Appl. Surf. Sci. **264**, 718 (2013).
[22] Tan Chuan Hong, T. Radhika, R. Jothi Ramalingam, Farook Adam, Metal-organic and Nano-metal chemistry **46**, 741 (2016).
[23] L. J. Alemany, M. A. Banares, E. Pardo, F. Martin-Jimenez, J. Elsevier Sci. **44**, 271 (2000).
[24] Youkui Zhang, Wenkun Zhu, Xudong Cui, Weitang Yao, Tao Duan, Cryst. Eng. Comm. **17**, 8368 (2015).
[25] K. R. Anju, T. Radhika, R. Jothi Ramalingam, Hamad Al-lohedan, Optik **165**, 408 (2018).