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Photoactivity of tungsten and niobium composite of titania under UV irradiation

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Abstract: TiO_2 has been shown to be excellent photoactive material in the presence of UV light. In order to make TiO_2 a more efficient photocatalyst several attempts are being made. The present work attempts to address the issue through WO_3-TiO_2 (TW sample) and Nb_2O_5-TiO_2 (TN sample) composites. Both the composite were synthesized through sol-gel process. The composites were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and UV–Visible spectrophotometer. The composites lower band gap value than DP25. This effect also seems to be reflected in photo-degradation experiment. Photo-degradation of methylene blue (MB) dye, in the presence of Nb_2O_5-TiO_2, WO_3–TiO_2 composite and DP25 under UV irradiation was studied. WO_3–TiO_2 composites have superior photoactivity than Degussa P25 (DP25) while Nb_2O_5-TiO_2 composite seems to have deteriorating effect on photoactivity of TiO_2.

Keywords: Metal oxide, Photocatalyst, WO_3-TiO_2 composite, Nb_2O_5-TiO_2 composite, Methylene Blue, Photodegradation.

1. Introduction: Ecologically bening characteristic, physical and chemical stability and favorable optical and electronic properties makes titanium dioxide (TiO_2) as suitable choice for photoactive application [1]. Efficient utilization of photons for charge carrier generation, availability of trap sites and their swift availability at catalyst surface makes an efficient photocatalyst **[2]**. Large band gap, low surface area and charge carier recombination limits the photoactivity of pristine TiO_2 **[2]**. Several approaches such as metal oxide composites, doping with other metal/non-metal has been adopted to make an efficient photocatalyst **[3]**. Coupling TiO_2 with WO_3 may affect its surface and bulk properties and thus affects the photo-activity **[4 - 8]**. Migration of tungsten (W) ions towards the titania surface may modify isoelectric point to lower values **[8]**. Isomorphic substitution of titania by tungsten within lattice affects its bulk properties **[7, 8]**. Presence of W (VI) improves the photo-degradation ability of titania by two mechanisms: (a) reduced recombination of charge carriers and (b) narrowing the effective bandgap **[9 - 11]**. Niobium is not widely known as a photocatalyst despite increasing interest in the application of niobium. Nb_2O_5 coupled TiO_2 has been in focus recenty for its promising applications in transparent conductive films, dye-sensitized solar cells, sensors **[12 - 14]**. Some significant findings on the photocatalytic activities of TiO_2 include the use of TiO_2 nanotubes, low temperature synthesis, semicrytstalline fame work of mesoporous titania and anatase to rutile phase conversion **[15 - 20].**

In this study, tungsten and niobium composite of titania are synthesized using sol-gel method and evaluated as a photo-catalyst for the degradation of MB dye. In the present work, WO_3 seems to have positive impact on photoactivity whereas Nb_2O_5 has negatively affected the photoactivity of TiO_2.

2. Experimental:

2.1. Material Synthesis: The samples were synthesized using analytical grade titanium iso-propoxide [$Ti(OCH(CH_3)_2)_4$], sodium tungstate dihydrate ($Na_2O_4W.2H_2O$) and niobium pentaoxide (Nb_2O_5) purchased from Sigma-Aldrich. The isopropyl alcohol [$(CH_3)_2CHOH$] was purchased from Merck, India.

In typical sol-gel method, titanium isopropoxide and isopropyl alcohol was mixed in 1:10 ratio (v/v). The HNO_3 was added to this sol to make pH~ 4. Aqueous solution of $Na_2O_4W.2H_2O$ (molar ratio of $Na_2O_4W.2H_2O$ and $Ti(OCH(CH_3)_2)_4$ was 1:100 was prepared in 10 ml double distilled water. The aqueous $Na_2O_4W.2H_2O$ was added drop-wise to titanium sol. This sol was finally left for aging for 12 h which resulted in gel-like condition before heating it at 80 ˚C for 12 h. The resultant powder was then calcined at 650 ˚C for 1 h at a ramping rate of 5 ˚C/min.

Nb_2O_5-TiO_2 composite (TN sample) were synthesized similarly by adding ultrasonically dispersed Nb_2O_5 in isopropanol. This sol was left to age for 12 h to form the gel and finally heat treated at 80 ˚C for 12 h to make powder. The resultant powder (TN) was calcined at 300 ˚C.

2.2. Characterization: The phase and crystal structure of photocatalyst were identified by X-ray diffraction (Proto AXRD Benchtop diffractometer, Canada) using Cu anode target, tube voltage 30 kV, tube current 20 mA and scanning range 10˚ – 80˚. The surface morphology of composites were characterized by scanning electron microscope (SEM; JEOL, Model: JSM-6390LV) equipped with Energy dispersive X-ray (EDX) Spectrometer (Oxford INCA, Model: DCL-7673). The UV–Vis absorption spectra were obtained by UV–Visible spectrophotometer (UV 3600 Plus, Shimadzu, Japan). The trap states were characterized using photoluminescence (PL) spectra using the photoluminescence spectrometer (Fluromax-4, Horiba Scientific, USA).

2.3. Photocatalytic test: Photocatalytic activity of TN, TW and Degussa P25 (Reference) were compared by degradation of MB under UV-light source (Philips TUV 15W/G15T8) maintaining a temperature of 35 ˚C in the reactor. Same environmental conditions were maintained during the tests on both the samples and the reference (DP25). The aqueous methylene blue solution was left in dark for one hour after adding catalyst. The samples were then exposed to the UV radiation flux and sampling was done at regular interval (4 min for DP 25, TW and 10 min for TN).

3. Results and discussion:

Figure (1) shows the XRD pattern of the samples DP25 and WO_3-TiO_2 composite as available in literature **[15, 16]**. Because of similar size of Ti^{4+} (0.68 Å) and W^{n+} (0.41-0.70 Å), W^{n+} may replace Ti^{4+} in lattice and thus no observable peak in XRD pattern **[15]**. The W^{n+} incorporated into Ti^{4+} hinders the formation of rutile phase even at higher temperature. All peaks of the TN samples consist primarily of anatase phases of TiO_2 without any detectable niobium oxide peak. Slight angle shift in the diffractive peak of anatse phase of TiO_2 indicates that Nb^{5+} has been successfully doped in TiO_2 crystal structure **[12]**.

Table (1): Estimated band gap and the crystallite sizes for different photocatalysts.

Catalyst	Crystallite size (nm)	Band gap (eV)	Rate Constant, k_{app} (hour^{-1})
TW	17.82	3.02	4.000
TN	15.9	3.08	0.009
DP 25	21.09	3.22	3.700

The powder morphology and microstructures of the sample were analysed using the SEM micrograph of the prepared catalytic materials [Figure (2a and (b)]. The particle size of the developed material in the micrograph shows a homogeneous distribution of the crystalline material although not fully resolved. The EDX spectrum [Figure (2c and d)] shows the presence of titanium, oxygen and tungsten.

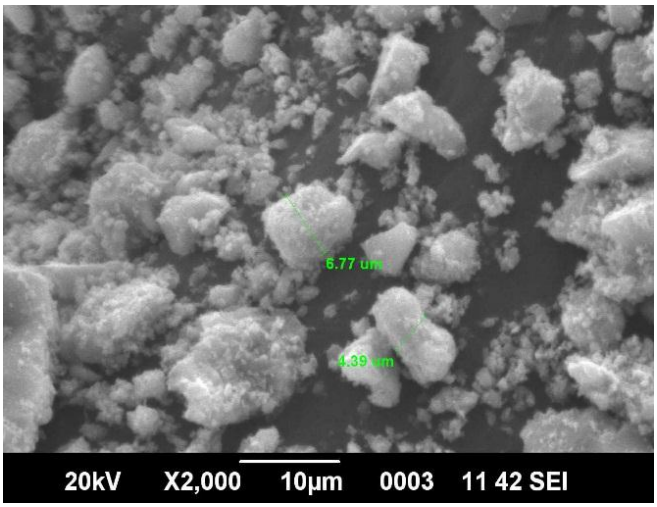

Figure (2a): SEM image of TW.

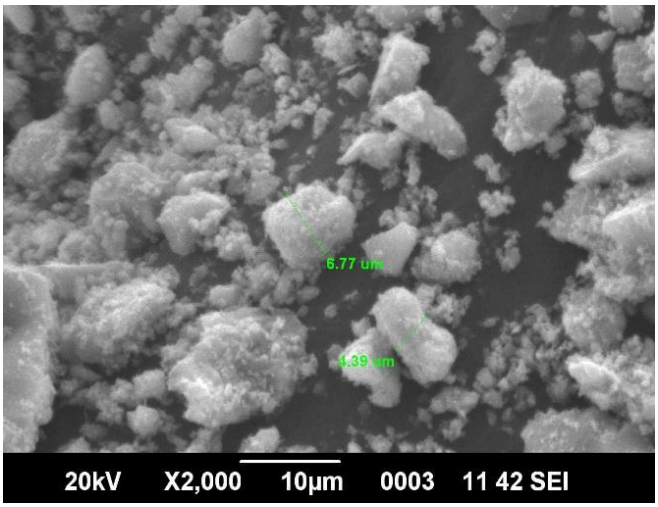

Figure (2b): SEM image of TN.

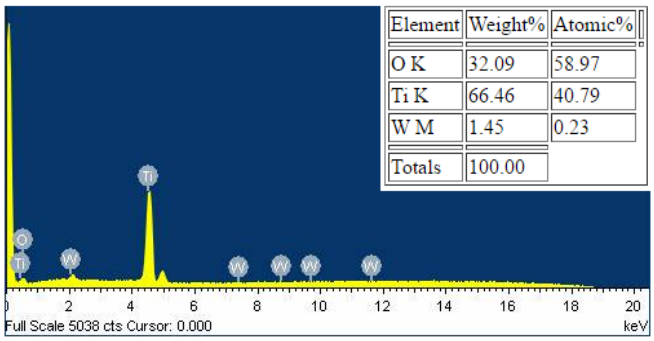

Figure (2c): EDX spectrum of TW samples.

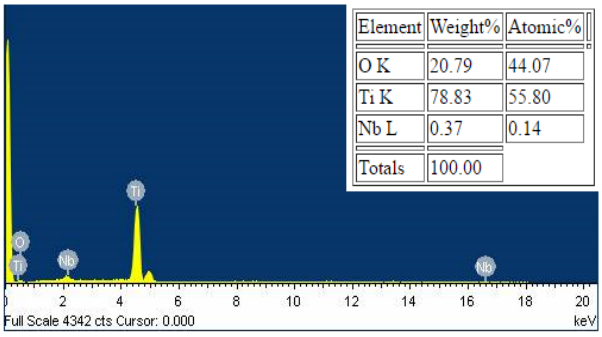

Figure (2d): EDX spectrum of TN samples.

The reflectance spectra was obtained using the UV–Vis spectroscopy. As shown in Figure (3a), the inflection at about 400 nm in diffuse reflectance spectra indicates that there are no visible light absorption for Nb_2O_5-TiO_2, WO_3-TiO_2 and DP 25 **[16]**. It suggests that the photocatalytic activity of Nb_2O_5-TiO_2, WO_3-TiO_2 and DP 25 is mainly under UV light irradiation. The band gap energy of Nb_2O_5-TiO_2, WO_3-TiO_2 and DP 25 can be calculated by Kubelka–Munk equation:

$$\alpha = F(R) = \frac{(1-R)^2}{(2R)} \quad (1)$$

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (2)$$

where α is the absorption coefficient, R is reflectance, hν is the incident photon energy; A is a constant, and n depends on the type of transition: n = 1/2 and 2 for direct and indirect transition, respectively. Since TiO_2 has an indirect band gap transition, n equals to 2 in this equation **[16]**. The band gap of Nb_2O_5-TiO_2, WO_3-TiO_2 composite and DP 25 is 3.08, 3.02 and 3.22 eV respectively.

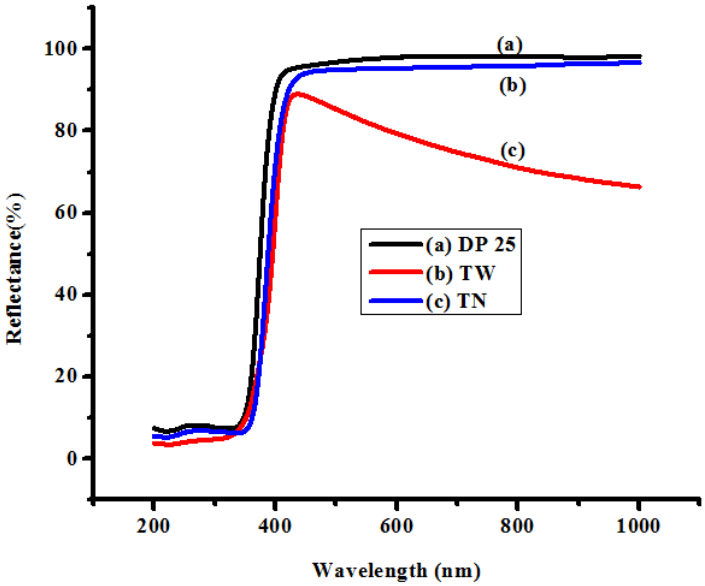

Figure (3a): UV–Vis diffuse reflectance spectra of DP 25, TW and TN samples.

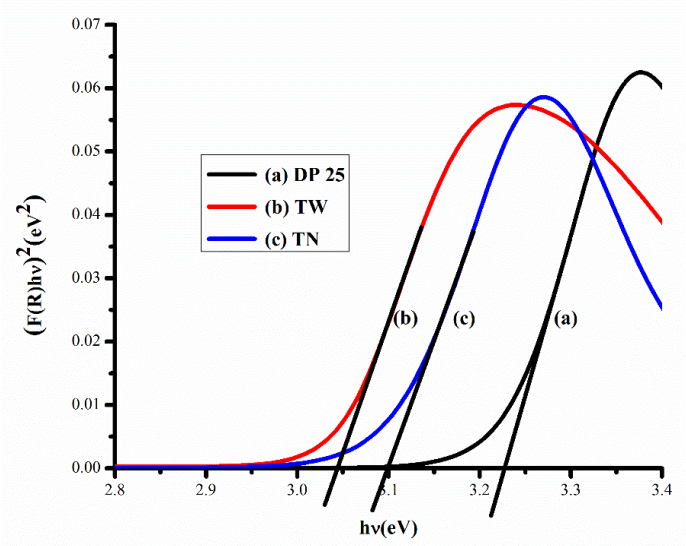

Figure (3b): Kubelka–Munk transformed reflectance spectra for DP 25, TW and TN samples.

Photoluminescence (PL) spectra analysis is a powerful tool to understand the fate of electron–hole pairs in semiconductor **[17]**. Photoluminescence (PL) spectra may help to understand role surface oxygen vacancies and defects, charge carriers trapping/immigration/transfer. DP 25 and composites exhibit the PL peaks with excitation at 325 nm. The increase of PL intensity corresponds to fast recombination of electron–hole pairs, indicating decrease of photocatalytic activity of the composites. The TN samples seems to have higher recombination than TW and DP 25 samples.

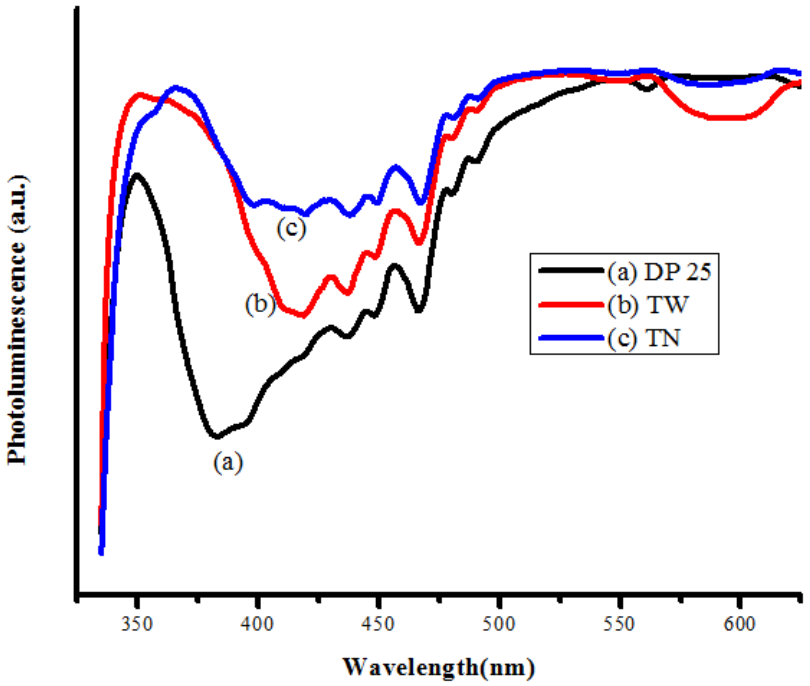

Figure (4): Photoluminescence spectrum of DP 25, TW and TN samples.

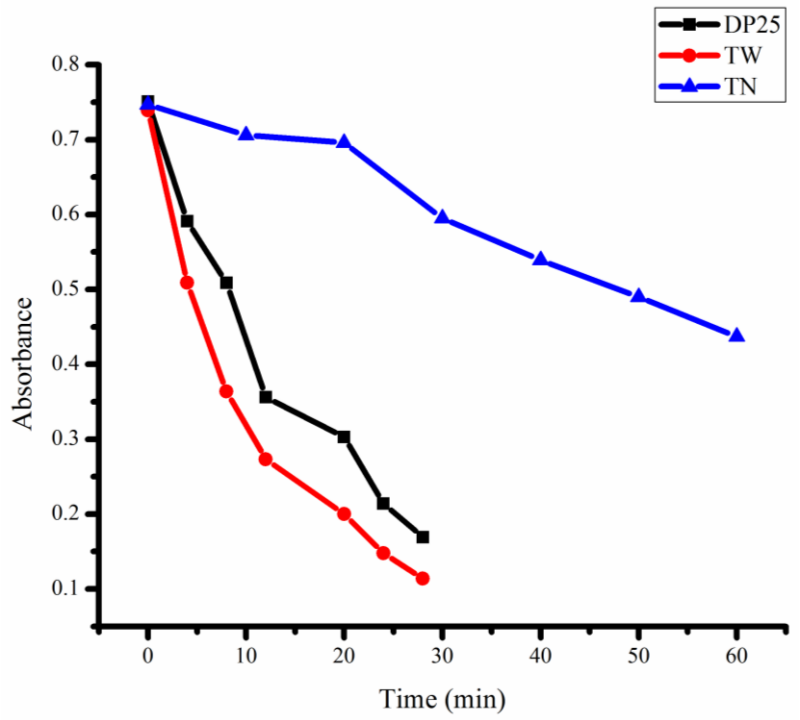

Figure (5): Degradation of methylene blue (MB) dye with time.

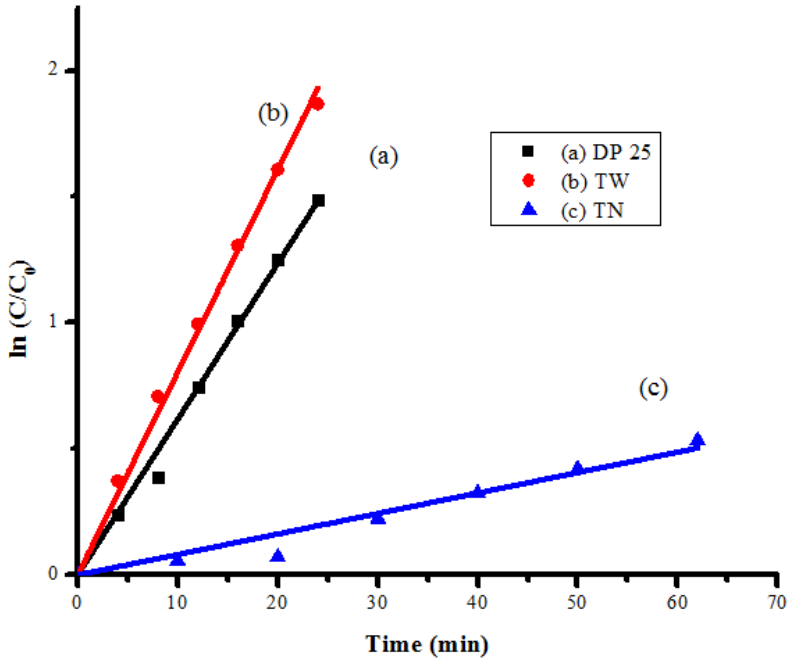

Figure (5): $\ln C/C_o$ vs. time plot to determination of rate of degradation under UV-light for DP 25, TW and TN samples.

Photocatalytic studies: No significant degradation in the initial concentration of MB by the catalysts is observed under dark condition. Afterward, UV lights is illuminated for the catalytic degradation. Figure. (5) shows the photo-degradation profiles of MB under UV light using DP 25, TW and TN samples and are found to be well fitted with the first order kinetics. The rate of degradation of MB was calculated using the plot of ln(C/Co) versus time graph (Figure 6). The Langmuir– Hinshelwod kinetic expression is well established photo-oxidation kinetics model of dyes **[1, 2, 15, 18]**.

$$\ln\frac{C_0}{C} = k_{app}t \qquad (3)$$

where C is the concentration of solute remaining in the solution at irradiation time of t and C_0 is the initial concentration at t = 0. k_{app} denotes the degradation rate constant which enable to determine the photocatalytic activity.. The rate constant of all the catalysts are shown in Table (1). Under UV light illumination the Nb_2O_5 seems to have negative impact on photocatalytic property of TiO_2. The negative impact of Nb_2O_5 is also reflected by PL data (Figure. 4). The rate constant of WO_3-TiO_2 are found to be slightly higher compared to commercially available Degussa P25 in degradation of the MB. However the PL results are in not agreement with photocatalytic activity of TW sample and may need further analysis.

4. Conclusions: The reason of enhancement in photo-activity of titania-tungsten composite could be due to three factors: (i) more adsorption of organic molecules, to be degraded, due to charged crystallite surface and (ii) increased surface area due to small crystallite size. The small crystallite size and more adsorption of MB molecule seems to facilitate the slightly higher photoactivity of WO_3-TiO_2 composite. However the PL data suggest more recombination in WO_3-TiO_2 composites than DP25. It needs detailed investigation. The titania-niobium composite is showing low photoactivity as compared to DP 25 and titania-tungsten composite. The significant decrease in band gap of the WO_3-TiO_2 Composite indicates that WO_3-TiO_2 composite could be useful for visible light harvesting also.

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Conflict of interest statement: On behalf of all authors, the corresponding author states that there is no conflict of interest.

References:

[1] A. Ramchiary, S. K. Samdarshi, Ag deposited mixed phase titania visible light photocatalyst – Superiority of Ag-titania and mixed phase titania co-junction, Appl. Surf. Sci. 305 (2014) 33-39.
[2] A. Ramchiary, S. K. Samdarshi, High visible light activity of hydrogenated structure-engineered mixed phase titania photocatalyst Chem. Phys Lett. 597 (2014) 63 - 68.
[3] Girish Kumar S, Koteswara Rao KSR, Comparison of modification strategies towards enhanced charge carrier separation and photocatalytic degradation activity of metal oxide semiconductors (TiO_2, WO_3 and ZnO), Appl. Surf. Sci. 391 (2017) 124 - 148.
[4] L. J. Alemany et al. WO_3/TiO_2 catalysts: Morphological and structural properties, React. Kinet. Catal. Lett. 60 (1997) 41.
[5] M. B. Tahir et. al., Nanostructured-based WO_3 photocatalysts: recent development, activity enhancement, perspectives and applications for wastewater treatment, Int. J. Environ. Sci. Technol. 14 (2017) 2519 - 2542.
[6] G. Žerjav et. al., Electron trasapping energy states of TiO_2-WO_3 composites and their influence on photocatalytic degradation of bisphenol A, Applied Catalysis B: Environmental 209 (2017) 273 - 284.
[7] N. Couselo et al., Tungsten-Doped TiO_2 vs Pure TiO_2 Photocatalysts: Effects on Photobleaching Kinetics and Mechanism, J. Phys. Chem. C 112 (2008) 1094 - 1100.
[8] S. Hager, R. Bauer, G. Kudielka, Photocatalytic oxidation of gaseous chlorinated organics over titanium dioxide, Chemosphere 41 (2000) 1219 - 1225.
[9] A. Fuerte et al., Nanosize Ti–W Mixed Oxides: Effect of Doping Level in the Photocatalytic Degradation of Toluene Using Sunlight-Type Excitation, J. Catal. 212 (2002) 1 - 9.
[10] T. Tatsuma et al., TiO_2-WO_3 Photoelectrochemical Anticorrosion System with an Energy Storage Ability, Chem. Mater. 13 (2001) 2838 - 2842.
[11] Y. T. Kwon et al., Photocatalytic behavior of WO_3-loaded TiO_2 in an oxidation reaction, J. Catal. 191/1 (2000) 192-199.
[12] Y. Kou et al., Solar photocatalytic activities of porous Nb-doped TiO_2 microspheres by coupling with tungsten oxide, Material Research Bulletin 63 (2015) 105-111.
[13] A. V. Emeline et al., Photoelectrochemical Behavior of Nb-Doped TiO_2 Electrodes, J. Phys. Chem. B, 109 (2005) 24441 - 24444.
[14] Y. Furubayashi et al., A transparent metal: Nb-doped anatase TiO_2, Appl. Phys. Lett. 86 (2005) 252101.
[15] K. Zimny, T. Roques-Carmes, C. Carteret, M. J. Stébé and J. L. Blin, Mesoporous Titania and Semicrystalline Framework. J. Phys. Chem. C 116/11 (2012) 6585–6594
[16] A. Fujishima, X. Zhang, et al., A TiO_2 photocatalysis and related surface phenomenon, Surf. Sci. Rep. 63 (2008) 515 – 582.
[17] O. D. Scanlon et al, Band gap alignment of Rutile and Anatase phase of TiO_2, Nature Materials 12 (2013) 798 - 401.
[18] T. Luttrell, S. Halpegamge, J. Tao, A.Kammer, et al. Anatase to Rutile transformation in TiO_2 film Sci. Rep. 4 (2014) 4043.

[19] P. Chaudhuri, V. Chaudhuri, S. Mishra, Low temperature synthesis of mixed phase Titania with high yield. Mat. Res. 19/2 (2016).
[20] C. Massand, S. Pairis et al. Titania nanotube layer doped with suspension of gold nanoparticles Adv. in Nanoparticle 06/03 (2017) 114 - 127.
[21] Y. Zou et al. Photodegradation of methylene blue in the visible spectrum: An efficient W^{6+} ion doped anatase titania photocatalyst via a solvothermal method, Vacuum 126 (2016) 63-69.
[22] H. Sun et al., Modification of TiO_2 nanotubes by WO_3 species for improving their photocatalytic activity, Appl. Surf. Sci. 343 (2015) 181–187.
[23] R. Verma and S. K. Samdarshi, Correlating oxygen vacancies and phase ratio/interface with efficient photocatalytic activity in mixed phase TiO_2, J. Alloys Comp. 629 (2015) 105 – 112.
[24] J. Yang et al., Mechanism of TiO_2-Assisted Photocatalytic Degradation of Dyes under Visible Irradiation: Photoelectrocatalytic Study by TiO_2-Film Electrodes, J. Phys. Chem. B 109 (2005) 21900-21907.

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