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Synthesis and Characterization of TiO_2 Nanocrystalline Particles via Chemical Co-Precipitation Method for Industrial Applications

K. Jhansirani[a], R. S. Dubey and *Y. B. R. D. Rajesh[b]

[a]Advanced Research Laboratory for Nanomaterials and Devices,

Department of Nanotechnology, Swarnandhra College of Engineering and Technology, Seetharampuram, Narsapur-534280 (A.P.), India

[b]Department of Chemistry, School of Chemical & Biotechnology,

SASTRA University, Tirumalaisamudram, Thanjavur-613401 (T. N.) , India

ABSTRACT
Nanocrystalline materials have received great attention of scientific community due to its industrial applications. Due to its large band gap TiO_2, it is demanded for its broad applications in water & air pollution treatments, sensors, solar cells, etc. In this paper, synthesis and characterization of TiO_2 nanoparticles have been reported by using chemical co-precipitation method. The anatase phase of prepared nanoparticles has been confirmed by XRD measurement. FTIR analysis showed peak at 1635 cm^{-1} corresponding to the stretching of titanium carboxilate and Ti-O stretching bands between 800 and 500 cm^{-1}. Using TEM, the prepared anatase TiO_2 nanoparticles were found to be polycrystalline in nature with the average diameter ~20-30 nm.

Keywords: TiO_2 Nanoparticles, Polycrystalline Nature, Anatase Phase, Chemical Co-precipitation Method.

INTRODUCTION

Titanium dioxide (TiO_2) semiconductor material has a large band gap of 3.2 eV and a promising candidate for its numerous applications such as in water and air pollution treatments, humidity sensors, gas sensors and membranes, solar cells and laser diodes for its high refractive index and stability [1-6]. TiO_2 is widely used as white pigment in paint and cosmetic products, photonic crystals, coating for bone implants and corrosion protecting coatings [7-9]. Another interesting application of TiO_2 is its use for destruction of inorganic and organic pollutants present in the water [10]. TiO_2 exists in three polymorphic phases such as rutile, anatase and brookite. Structure wise both anatase and rutile have tetragonal crystal structures with different space groups. However, the anatase crystal structures of TiO_2 possesses high photocatalytic activity hence has promising application to photocatalysis [11]. The photocatalyst materials are activated with the exposure of sunlight and produce electron hole pairs with their different life times. These two carriers participate in the reduction and oxidation at the catalyst surface. However, the efficiency of catalyst is limited due to the recombination of negatively and positively charged carriers which yields either photon or phonon. These effects can occur by volumetric and surface recombination. Nanoparticles in the range of ~20-30nm is well suited to photocatalysis as it balances these effects in addition it has large surface/volume ratio helps the timely utilization of photogenerated carriers in interfacial processes.

There are variety of techniques are available for the production of TiO_2 nanoparticles such as sol-gel, chemical, co-precipitation, sulfate process, chloride process, impregnation, sol-gel, hydrothermal, direct oxidation of $TiCl_4$, metal organic chemical vapor deposition method etc.[12-21]. Among these, chemical co-precipitation method is easy and low cost and method for the preparation of TiO_2 nanoparticles.

Recently, photonic crystal based photovoltaics has created the interest of researchers because of increased efficiency by means of trapping of photons. In DSSCs, the improved spectral response of photosensitizers has not reached to its satisfaction as it has low quantum yield. By increasing the film thickness beyond 10-12 micron there is a decrease in the photocurrent due to an increase in the electron transport length and the recombination rate. To overcome these problems in photovoltaics, a light trapping mechanism is needed which can increase the path length of light by enhancing light scattering in the TiO_2 films. In this view, small size of TiO_2 nanoparticles of size 10-30 nm is employed to ensure a high surface area and has been attempted to increase the light harvesting by enhancing the scattering of light [22]. The mesoporous TiO_2 nanoparticles yields better light harvesting in photoelectrochemical and dye-sensitized solar cells due to its high chemical stability and lifetime of photogenerated charge carriers [23].

In this paper, the synthesis of pure anatase TiO_2 nanoparticles with high crystallinity and large surface area is presented by using chemical co-precipitation method. In Section 2, the details of synthesis of TiO_2 nanoparticles have been presented. The structural and optical properties of synthesized particles are discussed in Section 3. Finally, Section 4 concludes the paper.

MATERIALS AND METHODS

The chemical co-precipitation method was employed for the preparation of TiO_2 nanoparticles. All the reagents used were of analytical grade without any further purification. Titanium tetrachloride (99.9%, Aldrich), ammonium hydroxide (25%, S.D. Fine), PEG-600 (S.D. Fine) and Isopropanol (LOBA) have been used in this work. With vigorous stirring, pure $TiCl_4$ (2.2 mL) was added drop wise to a mixture of ammonium hydroxide (1.5 mL), PEG-600 (0.5 mL) and isopropanol (3 mL) and continued stirring for 10 min. The reaction was highly exothermic. A large amount of HCl gas was exhausted during the mixing process. A precipitate was formed and later was dissolved to get a transparent solution. Then an aqueous solution of NaOH (2 M) was added drop wise until the solution's pH was reached up to 8.5. Precipitates were formed and further it was washed several times with hot water to remove chlorine impurities followed by acetone wash and filtered. The residue was dried in furnace at 100 ^{0}C for 1hr and calcinated at 550 ^{0}C for 3hrs. Finally, the samples were grinded to form a fine powder.

The produced nanoparticles were characterized for the structural and optical properties. The XRD pattern of TiO_2 was obtained using X-ray diffractometer (Schimadzu Model: XRD 6000) with CuKα radiation in the range of 20-80^o (λ=0.154nm). The surface morphology of particles was measured by Transmission Electron Microscope (TEM: JEOL-2010) with an accelerating voltage of 100kV. The infrared spectra were recorded using Fourier-Transformed Infrared Spectrophotometer (FT/IR-610, JASCO) in transmission mode in the wave number region between 4000 and 400 cm^{-1}. UV-VIS absorption spectra TiO_2 was recorded using a spectrophotometer (Varian Cary 5E) at room temperature in the range of 200-800 nm. In order to observe the morphology and acquisition, EDX analysis is done by using scanning electron microscopy (SEM: JEOL JSM-5800 LV/EDS).

RESULTS AND DISCUSSION

Usually, TiO_2 has anatase, rutile and brookite phases where rutile is more thermodynamically stable. When TiO_2 particles are calcinated at higher temperature, crystal structure transformations may occur such as amorphous-anatase and anatase-rutile transitions depending upon the preparation method, the nature of the precursor and calcination conditions. Generally, the complete transformations of amorphous to anatase has been found to be at temperature 350 ^{0}C and 450 ^{0}C whereas the anatase-rutile transformation has been reported to occur in different temperature ranges from 600 ^{0}C to 1100 ^{0}C [24]. Mesoporous nanoparticles were produced by chemical co-precipitation method and XRD measurement was done.

Figure 1 shows the XRD pattern of prepared TiO_2 nanoparticles which confirms an anatase Phase. Pattern shows the intense peaks at 2θ values corresponding to (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of tetragonal anatase phase.

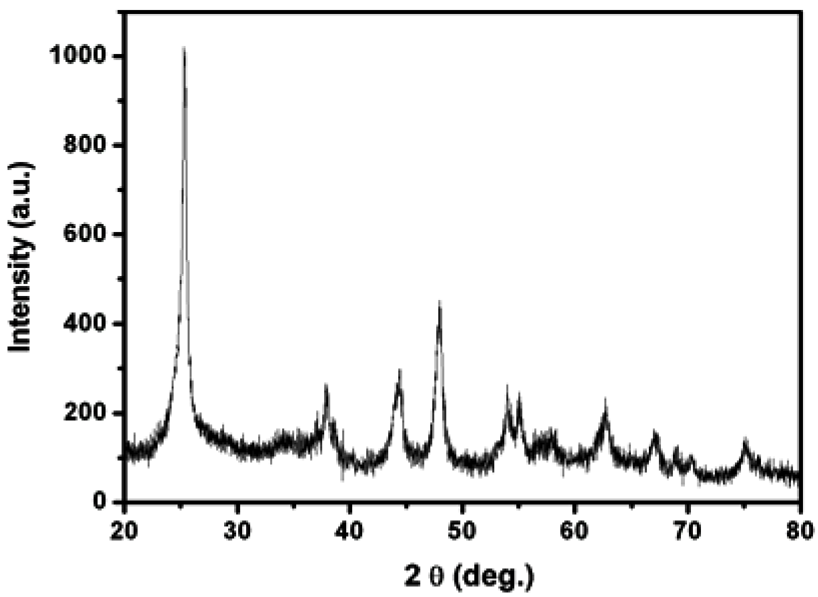

Figure 1. XRD pattern of TiO_2 nanoparticles.

The obtained XRD pattern has got good matching with standard JCPDS data (Card No.711166). Average size of the particles was found to be ~ 23 nm calculated using Debye Scherer equation [D= 0.9 λ/(β Cosθ)], where λ is the wavelength of X-ray beam ($Cu_{k\alpha}$=1.5406A), β is the fullwidth at half maximum of the (hkl) diffraction peak and θ is the Bragg angle.

Figure 2 shows the FTIR spectra of as prepared TiO_2 nanoparticles measured in transmission mode from the range 4000 to 400 cm^{-1}. A broad peak can be seen between 3800 to 3000 cm^{-1} which has been attributed to the stretching hydroxyl (O-H) and represents the water as moisture.

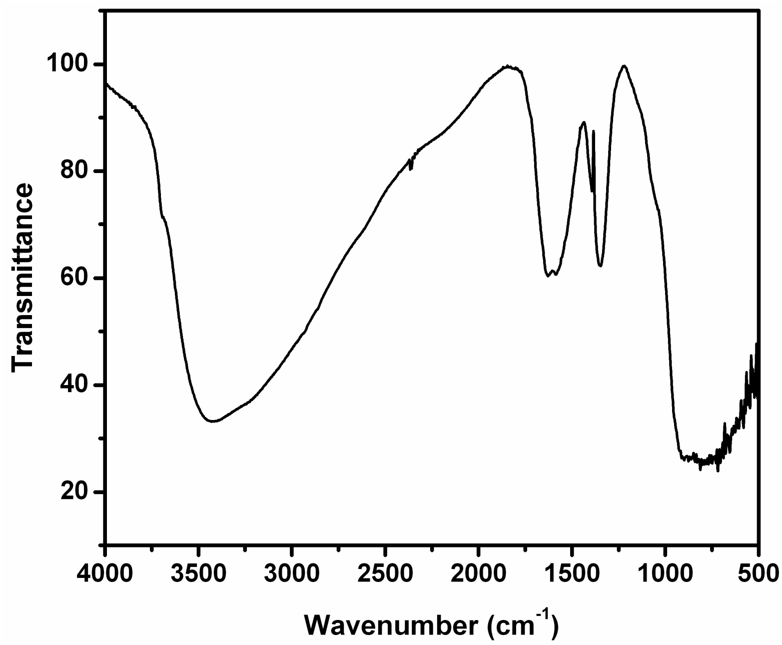

Figure 2. FTIR spectra of as prepared TiO_2 nanoparticles.

The other peaks at 1635 cm^{-1} were indicated the stretching of titanium carboxilate which formed due to used $TiCl_4$, ethanol and PEG as precursors [25]. The peak between 800 and 500 cm^{-1} was assigned to the Ti-O stretching bands.

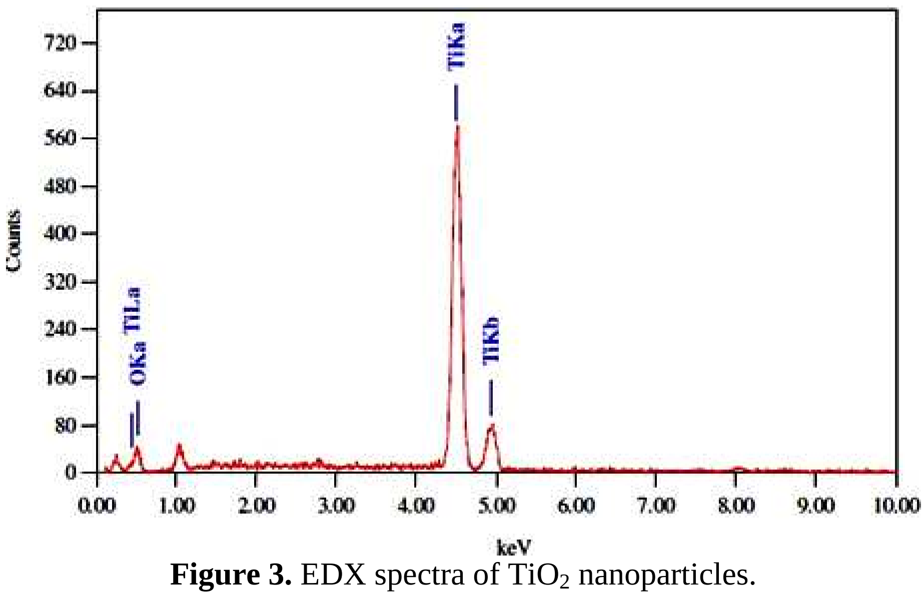

Figure 3. EDX spectra of TiO_2 nanoparticles.

Compositional analysis of prepared particles was done by EDX and shown in **figure 3**. From this figure, it is observed that for anatase TiO_2, the required composition of Ti and oxygen was achieved without the presence of any impurity and atomic % of Ti and O_2 was that of TiO_2 as shown in figure.

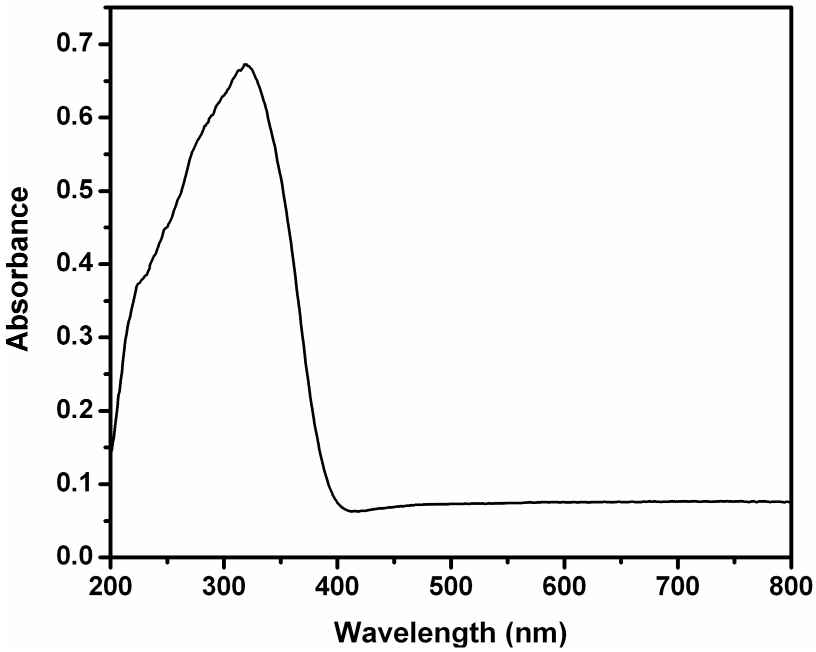

Figure 4. UV-VIS absorbance spectra of TiO_2 nanoparticles.

The optical absorbance spectra of TiO_2 nanoparticles measured at room-temperature is shown in **figure 4**. The absorption spectra showed a strong absorption below 400 nm.

TEM measurement of nanoparticles is done to observe the particle size and surface morphology. **Figure 5** shows high resolution (HR)-TEM images along with selected area electron diffraction (SAED) pattern of the nanoparticles. TEM image at low and high magnifications is depicted in **Figure 5(a)** and **(b)** and observed particle diameter in the range of ~20-30 nm which is in good agreement with XRD measuremnet. In HR-TEM image of **Figure 5(c)**, nanoparticles showed two different crystal lattices in the matrix. **Figure 5(d)** shows the SAED pattern which is composed of some bright points and rings which support the polycrystalline nature of as-prepared particles. The TEM images illustrate that the crystallites are more in angular shape and little elongated.

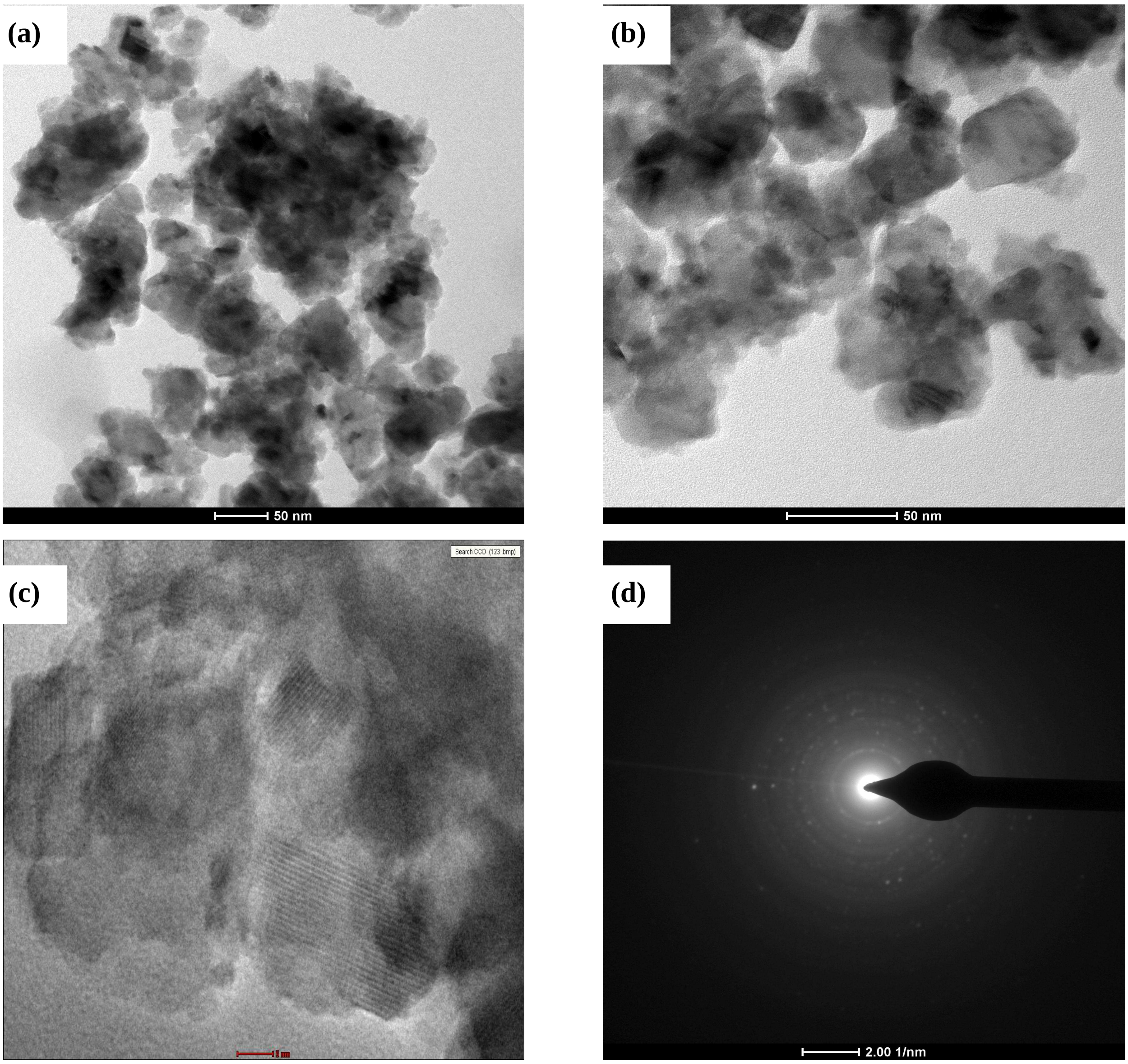

Figure 5. HR-TEM images and diffraction pattern of TiO_2 nanoparticles calcinated at 550 ^{0}C.

CONCLUSION

By employing chemical co-precipitation method, nanocrystalline TiO_2 particles have been synthesized and characterized. For the synthesis of anatase nanoparticles, $TiCl_4$ was used as the primary precursor with PEG as a surfactant and NaOH. In XRD spectra, intense peaks at 2θ values corresponding to (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of tetragonal anatase phase has been observed. In FTIR analysis, peaks at 1635 cm^{-1} has been corresponding to the stretching of titanium carboxilate while peak between 800 and 500 cm^{-1} was assigned to the Ti-O stretching bands. EDX of prepared anatase TiO_2 has confirmed the required composition of titanium and oxygen without any contaminants. By TEM measurement, the polycrystalline nature of the as-prepared particles is confirmed and the average diameter of TiO_2 nanoparticles was observed to be ~20-30 nm which is in good agreement with the XRD result. The prepared mesoporous particles are suitable for dye sensitized solar cells which can increase the harvesting of light in an efficient way. Finally, the chemical co-precipitation method is easy and inexpensive for the production of TiO_2 nanoparticles for industrial applications.

REFERENCES

[1]. Dong Suk Kim, Seung-Yeop Kwak, The hydrothermal synthesis of mesoporous TiO_2 with high crystallinity, thermal stability, large surface area, and enhanced photocatalytic activity, Applied Catalysis A: General 323, pp. 110–118 (**2007**).
[2]. Pi-Guey Su and Yi-Po Chang, Low-humidity sensor based on a quartz-crystal microbalance coated with polypyrrole/Ag/ TiO_2 nanoparticles composite thin films, Sensors and Actuators B 129, pp.915–920 (**2008**).
[3].G. Sarala Devi, Takeo Hyodo, Yasuhiro Shimizu and Makoto Egashira, Synthesis of mesoporous TiO_2-based powders and their gas-sensing properties, Sensors and Actuators, B 87, page 122–129 (**2002**).
[4]. Arcadio Sotto, Arman Boromand, Stefan Balta, Siavash Darvishmanash, Jeonghwan Kim and Bart Van der Bruggen Nanofiltration membranes enhanced with TiO_2 nanoparticles: a comprehensive study, Desalination and Water Treatment, Volume 34, Issue 1-3, pp. 179-183 (**2011**).
[5]. Xukai Xin, Margaret Scheiner, Meidan Ye and Zhiqun Lin, Surface-Treated TiO_2 Nanoparticles for Dye-Sensitized Solar Cells with Remarkably Enhanced Performance, Langmuir, Vol. 27, No.23, pp.14594–14598 (**2011**).
[6]. Jong Kyu Kim, Martin F. Schubert, E. Fred Schubert and Richard W. Siege, High-refractive-index TiO_2 nanoparticle-loaded encapsulants for light-emitting diodes Frank W. Mont, J. Appl.Phys., Vol. 103, pp.083120-1-6 (**2008**).
[7]. C. Xiaobo, S. S. Mao, "Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications" Chem. Rev. Vol. 107, No. 7, pp.2891-2959 (**2007**).
[8]. G. Wijnhoven, W. L. Vos, "Preparation of Photonic Crystals Made of Air Spheres in Titania" Science, Vol. 281, No. 5378, pp.802-804 (**1998**).
[9]. U. Diebold, The surface science of titanium dioxide, Surf. Sci. Rep. Vol. 48, No. 5-8, pp. 53-229 (**2003**).
[10]. Kazuhito Hashimoto, Hiroshi Irie and Akira Fujishima, TiO_2 Photocatalysis: A Historical Overview and Future Prospects, Jpn. J. Appl. Phys,. Vol. 44, pp. 8269-8285 (**2005**).
[11]. Eun-Young Kim, Dong Suk Kim and Byung-Tae Ahn, Synthesis of Mesoporous TiO2 and its Application to Photocatalytic Activation of Methylene Blue and E. col, Bull. Korean Chem. Soc, Vol. 30, No. , pp.193-196. (**2009**).
[12]. M. Howe-Grant (Ed), Kirk-Othmer Encyclopedia of Chemical Technology, Vol.24, John Wiley & Sons, Inc, p.225, **1997**.
[13]. M. I. Litter, J. A. Navio, "Comparison of the photocatalytic efficiency of TiO_2, iron oxides and mixed Ti(IV)/Fe(III) oxides: photodegradation of oligocarboxylic acids". J. Photochem. Photobiol. A. Chem., Vol. 84, No. 2, pp.183-193, (**1994**).
[14]. C. C. Wang, Z. Zhang, J. Y. Ying, "Photocatalytic decomposition of halogenated organics over nanocrystalline titania" NanoStructured Mater., Vol. 9, No. 1-8, pp.583-586 (**1997**).
[15]. Burns, W. Li, C. Baker, S. I. Shah, "Sol-gel synthesis and characterization of neodymium-ion doped nanostructured titania thin films". Mater. Res. Soc. Symp. Proc., Vol. 703, V5.2 (**2001**).
[16]. Y.Wang, H.Cheng, Y. Hao, J. Ma. W. Li. S. Cai, "Preparation, characterization and photoelectrochemical behaviors of Fe(III)-doped TiO_2 nanoparticles". J. Mater. Sci., Vol. 34, No. 15, pp.3721-3729 (**1999**).

[17]. H. Cheng. J. Ma, Z. Zhao, L. Qi, "Hydrothermal Preparation of Uniform Nanosize Rutile and Anatase Particles". Chem. Mater., Vol. 7, No. 4, pp.663-671 (**1995**).

[18]. Y. Wang, Y. Hao, H. Cheng, J. Ma, B. Xu, W. Li, S. Cai, "The photoelectrochemistry of transition metal-ion-doped TiO_2 nanocrystalline electrodes and higher solar cell conversion efficiency based on Zn^{2+}-doped TiO_2 electrode". J. Mater. Sci., Vol. 34, No. 12, pp.2773-2779 (**1999**).

[19]. M. K. Akhtar, Y. Xiong, S. E. Pratsinis, "Vapor Synthesis of Titania Powder by Titanium Tetrachloride Oxidation" AIChE J, Vol. 37, No.10, pp.1561-1570 (**1991**).

[20]. Z. Ding, X. Hu.G. Q. Lu, P. L. Yue, P. F. Greenfield, "Novel Silica Gel Supported TiO_2 Photocatalyst Synthesized by CVD Method" Langmuir Vol. 16, No. 15, pp.6216-6222 (**2000**).

[21]. Pramod H. Borse, Laxman S. Kankate, F. Dassenoy, W. Vogel, J. Urban and Sulabha K. Kulkarni, Synthesis and Investigation of Rutile Phase Nanoparticles of TiO2, J Mater. Sci.: Materials in Electronics, Vol. 13, pp.553-559 (**2002**).

[22]. Usami, A. Sol. Energy Mater. Sol. Cells 2000, 64, 73. Akira Usami, Theoretical simulations of optical confinement in dye-sensitized nanocrystalline solar cells, Sol. Energy Mater. Sol. Cells, Vol. 64, No. 1, pp.73-83 (**2002**).

[23]. K.P.S. Parmar, Easwaramoorthi Ramasamy, Jin Woo Lee and Jae Sung Lee A simple method for producing mesoporous anatase TiO2 nanocrystals with elevated photovoltaic performance, Scripta Materialia, Vol. 62, pp.223–226 (**2010**).

[24]. J. Ovenston, K. Yanagisawa, "Effect of Hydrothermal Treatment of Amorphous Titania on the Phase Change from Anatase to Rutile during Calcination" Chem. Mater., Vol. 11, No. 10, pp.2770-2774 (**1999**).

[25]. J. García-Serrano, E. Gómez-Hernández, M. Ocampo-Fernández, U. Pal, "Effect of Ag doping on the crystallization and phase transition of TiO_2 nanoparticles" Curr. Appl Phys., Vol. 9, No. 5, pp.1097-1105 (**2009**).