

Self-Cleaning Measurement of Nano-Sized Photoactive TiO₂

Majid Farahmandjou

Faculty of Computer and Information Technology Engineering, Qazvin Branch, Islamic Azad University, Qazvin, Iran

Received 21 December 2011; accepted 20 January 2013

Abstract

Titanium dioxide (TiO₂) nanoparticles have been frequently employed in the environmental treatment and purification purposes as a cheap and highly efficient photocatalyst. A photocatalyst can facilitate the breakdown and removal of a variety of environmental pollutants at room temperature. TiO₂ photocatalyst is the best candidate because of its strong oxidized ability, non-toxicity and long thermal photostability. The TiO₂ is also important and need deep studies because it can be used as self-cleaning and anti-fogging glass in future. In this paper, TiO₂ nanoparticles were synthesized by liquid phase method. The samples were characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses after heat treatments. The XRD results show the sharp peaks after annealing process. The TEM results reveal that the size of nanoparticles is in the range of 20-40 nm in diameter. Raman scattering pattern of the TiO₂ nanoparticles confirm the TEM analysis and indicate the anatase phase.

Keywords: Photoactive, self-cleaning, Nano TiO₂ particles, Super-hydrophobic

1. Introduction

The potential benefits of photocatalysis have been reported in a large number of studies published in recent decades. Photo-catalysis has been applied in water treatment and air pollution control. Super-hydrophobic self-cleaning, called Lotus effect, utilizes right combination of surface chemistry and roughness to force water droplets to form high contact angle on a surface, easily roll off a surface and pick up dirt particles. A photocatalyst can facilitate the breakdown and removal of a variety of environmental pollutants at room temperature by oxidation, using either sunlight or artificial light as an energy source. Nano-TiO₂ photocatalysis has drawn much attention recently due to its promising application in chemical conversion and storage of solar energy for solar cells, hydrogen production, refractory pollutants elimination and self-cleaning surface [1–4]. Titanium dioxide, as a cheap, nontoxic, and highly efficient photocatalyst, has been frequently employed in the environmental treatment, purification purposes and computer sciences. [4–9].

The pairs of free electrons and holes are formed in the conduction and valence band region of TiO₂ under the UV irradiation, which react with oxygen and adsorbed hydroxyl group [4]. These highly reactive oxygen species possess strong oxidation potential to decompose a variety of calcitrant organic pollutants and kill pathogenic

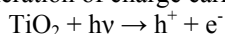
microorganisms [10]. However, the large-scale application of titanium dioxide as an efficient photocatalyst has been hampered by the notorious problem of recycling the photocatalytic powders in the aqueous purification. In this context, nano-crystalline titanium dioxide coatings on some substrates with large surface areas have received much attention in recent years. Through various coating techniques, the optical coating of TiO₂ films were successfully achieved on different substrates, such as glass [11–15], silica [13], stainless steels [16–19]

In the photo-oxidative removal of potentially toxic organic or inorganic compounds present in the environment, primary attention has been devoted to the role of titanium dioxide (TiO₂) over compounds such as ZnO, CdS. This attention is due to its high photocatalytic activity, biological and chemical inertness and stability, resistance to photo-corrosion, low cost, nontoxicity, and favourable band-gap energy [20]. The photo-catalytic activity of titania is strongly affected by physicochemical features of the particles, with respect to both structural and morphological characteristics. From a structural point of view, TiO₂ can crystallize in three different polymorphic forms: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). The anatase polymorph is generally reported to show the highest photo-activity compared to either brookite or rutile polymorphs because of the low recombination rate of its photo-generated electrons and

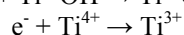
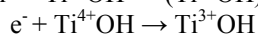
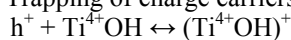
* Corresponding author. Email: Farahmandjou@iauvaramin.ac.ir

holes. When TiO₂ catalysts are subjected to irradiation with photons of energy equal to or higher than their band gap, the generated electron-hole pairs can induce the formation of reactive oxygen species, such as hydroxyl radical and superoxide radical that are directly involved in the oxidation processes leading to the degradation of both contaminants and microorganisms [21–25]. Evidence for the low toxicity of TiO₂ nanoparticles comes from cosmetics industry, with the 20-year long history of human use in sun screen preparations. There are a lot of studies which prove that micro- or nano-sized TiO₂ particles are not (photo) mutagenic or (photo) genotoxic to humans. Above all, there is no difference between micro and nano TiO₂ in distribution and elimination from the body [26].

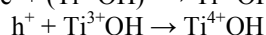
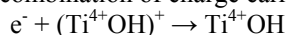
Generation of charge carriers:



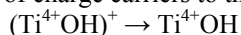
Trapping of charge carriers



Recombination of charge carriers



Transfer of charge carriers to the surface



Scheme 1. Mechanism of photocatalysis by TiO₂

Moreover, other properties of self-cleaning could be modified with the use of TiO₂ nanoparticles, such as: hydrophobicity/hydrophilicity, UV protection, antibacterial properties and anti-wrinkle resistance.

Photocatalysis represents a photo-induced chemical reaction accelerated in the presence of the catalyst. This implies that both light and a catalyst are necessary for a chemical reaction to occur. TiO₂ is a semiconductor and its molecular orbitals can be approximated with bands, out of which the valence band and the conductive band, separated by the energy gap, are the most important. The mechanism of TiO₂ photocatalysis involves few stages (Scheme 1).

When TiO₂ particles absorb light, electrons are excited to the conduction band, and positively charged holes remain in the valence band. Generated charge carriers can recombine nonradiatively or radiatively, or migrate to the surface of the photocatalyst, and get trapped at certain places of the crystal lattice, subsequently reacting with e-donor or e-acceptor molecular species adsorbed at the photocatalyst surface. The competition between these two processes determines the overall efficiency of the photocatalyst. The electrons and the holes generated in TiO₂ nanoparticles are localized in different defect sites of the material.

The mechanism of oxidation and reduction of molecular species involves the generation of superoxide anions and hydroxyl radicals. The conduction band e- reacts with adsorbed oxygen leading to the formation of superoxide anions. The holes in the valence band react with water and generate hydroxyl radicals, or react directly with adsorbed organic molecules. Also, hydroxyl radicals can oxidize

wide a variety of organic molecules. This process in large excess of photocatalyst finally leads to the complete mineralization of organic molecules yielding CO₂ and H₂O molecules. There are a number of papers describing the decomposition routes of chemical warfare agents and their simulants. Artificial superhydrophobic surfaces can be produced in many ways, including template synthesis, phase separation, crystallization control, etching, sol-gel processing, layer by layer deposition, and electrospinning [27].

In this article, TiO₂ nanoparticles are successfully synthesized by liquid phase method under given conditions with Titanium (IV) oxide sulfate (TiOSO₄), sulfuric acid (H₂SO₄) and urea. The characterization of the samples is studied by TEM and XRD analyses after calcination.

2. Materials and Methods

The synthesis of TiO₂ nanoparticles was carried out by chemical method. The liquid phase process of the nanoparticles is as follow: TiOSO₄ as the source for the oxidizing elements, H₂SO₄ and urea were used as fuels (reducing agents). The reaction was started with the stoichiometric mixture of fuel and the oxysulfate. Next, the mixture was placed on a preheated hot plate, with the objective of ensuring homogeneous mixing and starting dehydration of the aqueous mixture. The reaction was transferred to a preheated furnace and calcinated, where the reaction was accompanied by release of a large amount of gases.

The automotive glasses were used as the substrates. The specimens in the form of slides with dimension of 100mm×20mm×2mm were used as the substrate to support the TiO₂ films. Before the deposition, glass substrates were ultrasonically cleaned using acetone and ethanol respectively. Finally they were thoroughly washed with water and dried. TiO₂ thin film was deposited on substrate at room temperature. Substrates were immersed in the TiO₂ sol prepared for 30 minutes and dried at room temperature followed by the drying at 120 °C for 1 hour in an oven. In order to obtain nano-TiO₂ powder, the TiO₂ sol prepared was oven dried at 110 °C and calcined at 400 °C for 1 hour.

The morphology and structure of the prepared nanoparticles were characterized by TEM and XRD. The specification of the size and shape of the nanoparticles were examined by TEM analysis using a Philips EM 208. To determine the nanoparticles' structure, the XRD was performed using a Seifert with Cu-Kα radiation (wavelength=1.54 Å). The Raman spectrum of the as-prepared TiO₂ nanoparticles were collected by using a Thermo Nicolet Almega dispersive micro-Raman scattering spectrometer operating by a 532 nm laser line as the second harmonic of a Nd:YLF laser.

3. Results and Discussion

As a new material, nano-sized TiO₂ is a great interest of many scientists in the recent years. Its small size and large specific surface area allow for certain unique unusual physio-chemical properties. Nano- TiO₂ has the tightly

controlled particle size that increases both the refractive index and light scattering properties as a result of the uniform particle size distribution and additional surface area. The crystallinity of the synthesized TiO₂ powder samples were determined by X-ray diffraction (XRD) technique with Cu K α radiation. The average particle size was estimated by applying the Scherrer equation to the apparent full-width-at-half maximum intensity (FWHM) of the (101) peak of anatase TiO₂, as follows by equation:

$$d = (k\lambda) / (\beta \cos \theta)$$

where d denotes the average crystallite size, $k = 0.9$, $\lambda = 0.15405$ nm is the X-ray wavelength of Cu- K α , β is the full-width of the peak measured at the half-maximum intensity (FWHM) and θ is the Bragg angle of the peak. X-ray diffraction (XRD) measurements were carried out as shown in Fig. 1. The pattern of the sample showed the presence of peaks ($2\theta = 25.32^\circ, 37.96^\circ, 47.78^\circ, \text{ and } 54.38^\circ$), which is regarded as an anatase phase TiO₂ crystallites. The TiO₂ nanoparticles were annealed at 400°C for 2 hours. As you can see the sharp picks reveal the crystalline nanoparticles after heat treatment.

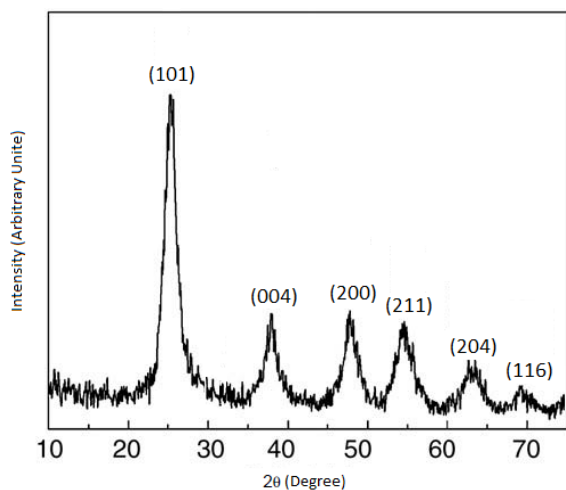


Fig. 1. X-ray diffraction ($\lambda = 1.54 \text{ \AA}$, Cu-K α radiation) pattern of the nanoparticles

Raman spectroscopy can be used to examine the crystal structure of TiO₂ samples as a more sensitive technique compared to X-ray diffraction method for the identification of anatase and rutile crystals in a variety of natural and synthetic materials over a wide range of concentrations. Fig. 2 shows the Raman scattering pattern of the as-prepared TiO₂, with standard peaks (144, 197, 399, 513 and 639 cm⁻¹). As you can see, there are five peaks which indicate the anatase phase.

The anatase phase is not stable and tends to be stable at annealed states.

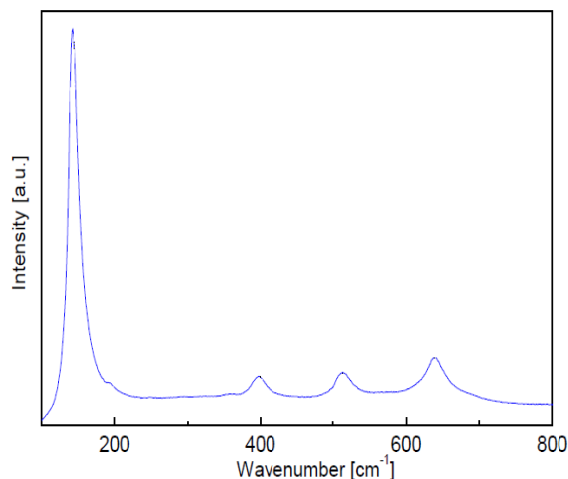


Fig 2: Raman spectrum of the as-prepared TiO₂

The UV-visible diffuse reflectance spectra of the TiO₂ samples are shown in Fig. 3. nano-TiO₂ synthesized at 400 °C gave the maximum absorption band at 240 nm wavelength. The absorption quickly decreased above 355 nm due to the non-absorption of light caused by the excitation of electrons from the conduction band to the valence band of TiO₂.

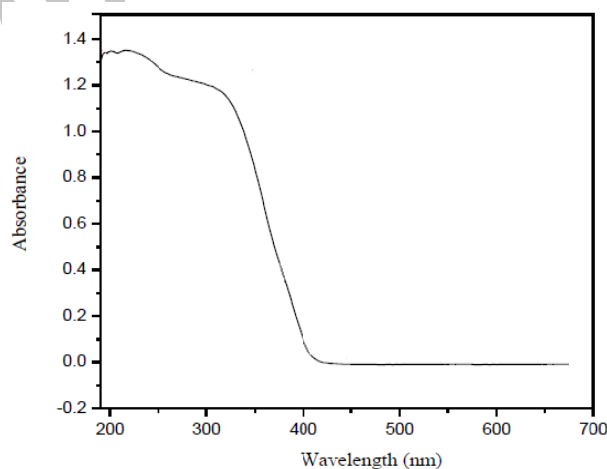


Fig. 3: UV-visible diffuse reflectance spectra of the TiO₂ powders synthesized at 400 °C

To investigate the size of nanoparticles, the dispersion of the nanoparticles was sonicated at 25 °C for 3 hours and the morphology of the dispersed samples was observed by TEM. Fig. 4 shows the TEM image of the TiO₂ nanoparticles. As you can see, the TiO₂ nanoparticles are in the size range of 20-40 nm in diameter. It has been revealed that the TiO₂ powders in rutile phase consist of both spherical and rod shapes but the particles of TiO₂ powders in anatase phase are mostly of spherical morphology.

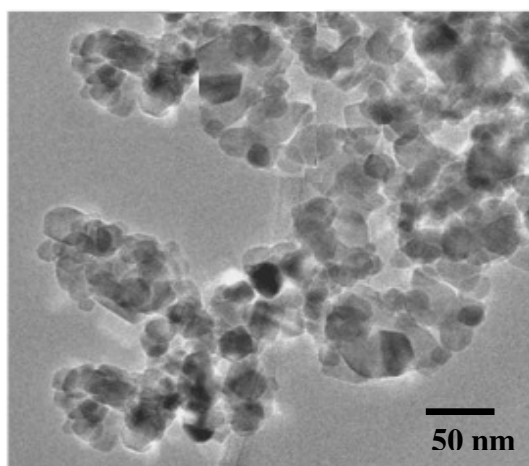


Fig. 4. TEM images of the TiO₂ nanoparticles

4. Conclusion

In conclusion, the self-cleaning TiO₂ superhydrophobic layers were successfully fabricated on glass. The XRD pattern of annealed TiO₂ nanoparticles showed the sharp peaks that reveals the crystalline nanoparticles. TEM image of the TiO₂ indicated the uniform nanoparticles. The peaks appeared in Raman scattering is ascribed to the anatase phase TiO₂.

Acknowledgments

The authors are thankful for the financial support of the research plan at Islamic Azad University, Qazvin branch.

References

- [1] M. Gratzel, Photoelectrochemical cells, *Nature*, Vol. 414, pp. 338-344, 2007.
- [2] E. Allain, S. Besson, C. Durand, M. Moreau, T. Gacoin and J.P. Boilot, Transparent Mesoporous Nanocomposite Films for Self-Cleaning Applications, *Advanced Functional Materials*, Vol. 17, pp. 549-554, 2007.
- [3] M.C. Long, W.M. Cai, J. Cai, B.X. Zhou, X.Y. Chai and Y.H. Wu, Efficient Photocatalytic Degradation of Phenol over Co₃O₄/BiVO₄ Composite under Visible Light Irradiation, *Journal of Physics Chemistry B*, Vol. 110, pp. 20211-20216, 2006.
- [4] M.R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, Synthesis of Raspberry-Like SiO₂-TiO₂ Nanoparticles toward Antireflective and Self-Cleaning Coatings, *Chemical Review*, Vol. 95, pp. 69-74, 1995.
- [5] X. Li and J. He, Synthesis of Raspberry-Like SiO₂-TiO₂ Nanoparticles toward Antireflective and Self-Cleaning Coatings, *Applied Mater Interfaces*, Vol. 5, 5282-5290, 2013.
- [6] M.C. Long, W.M. Cai, Z.P. Wang and G.Z. Liu, Correlation of electronic structures and crystal structures with photocatalytic properties of undoped, N-doped and I-doped TiO₂, *Chemical Physics Letter*, Vol. 420, pp. 71-76, 2006.
- [7] S. Yin, B. Liu, P.L. Zhang, T. Morikawa, K. Yamanaka and T. Sato, Photocatalytic Oxidation of NO_x under Visible LED Light Irradiation over Nitrogen-Doped Titania Particles with Iron or Platinum Loading, *Journal of Physics Chemistry C*, Vol. 112, pp. 12425-12431, 2008.
- [8] H. Taoda, Development of TiO₂ photocatalysts suitable for practical use and their applications in environmental cleanup, *Research Chemical Intermediate*, Vol. 34, pp. 417-426, 2008.
- [9] S. Yuan, Q. R. Sheng, J. L. Zhang, H. Yamashita and D.N. He, Synthesis of Thermally Stable Mesoporous TiO₂ and Investigation of Its Photocatalytic Activity, *Microporous and Mesoporous Materials*, Vol. 110, pp. 501-507, 2008.
- [10] W. Choi, Pure and modified TiO₂ photocatalysts and their environmental applications, *Catalysis Surveys from Asia*, Vol. 10, pp. 16-28, 2006.
- [11] C. Euvananont, C. Junin, K. Inpor, P. Limthongkul and C. Thanachayanont, TiO₂ optical coating layers for self-cleaning applications, *Ceramics International*, Vol. 34, pp. 1067-1071, 2008.
- [12] M. Saif, S.A. El-Molla, S.M. Aboul-Fotouh, H. Hafez, M.M. Ibrahim, M.S. Abdel-Mottaleb and L.F. Ismail, Synthesis of highly active thin film based on TiO₂ nanomaterial for self-cleaning application, *Spectrochim Acta A Molecular and Bimolecular Spectroscopy*, Vol. 112, pp. 46-51, 2013.
- [13] K.K. Saini, S.D. Sharma Chanderkant, M. Kar, D. Singh and C.P. Sharma, Structural and optical properties of TiO₂ thin films derived by sol-gel dip coating process, *Journal of Non-Crystal Solids*, Vol. 353, pp. 2469-2473, 2007.
- [14] H.G. Yang and H.C. Zeng, Control of Nucleation in Solution Growth of Anatase TiO₂ on Glass Substrate,

- Journal of Physics Chemistry B, Vol. 107, pp. 12244-12255, 2003.
- [15] N.P. Mellott, C. Durucan, C.G. Pantano and M. Guglielmi, Commercial and laboratory prepared titanium dioxide thin films for self-cleaning glasses: Photocatalytic performance and chemical durability, *Thin Solid Films*, Vol. 502, pp. 112-120, 2006.
- [16] R. Tomaszek, L. Pawlowski, L. Gengembre, J. Laureyns, Z. Znamirovski and J. Zdanowski, Microstructural characterization of plasma sprayed TiO₂ functional coating with gradient of crystal grain size, *Surface and Coating Technology*, Vol. 201, pp. 45-56, 2006.
- [17] D.S.R. Krishna and Y. Sun, Thermally oxidised rutile-TiO₂ coating on stainless steel for tribological properties and corrosion resistance enhancement, *Applied Surface Sciences*, Vol. 252, pp. 1107-1116, 2005.
- [18] Y. Chen and D.D. Dionysiou, A comparative study on physicochemical properties and photocatalytic behavior of macroporous TiO₂-P25 composite films and macroporous TiO₂ films coated on stainless steel substrate, *Applied Catalysis A: General*, Vol. 317, pp. 129-137, 2007.
- [19] E. Pakdel and W.A. Daoud, Self-cleaning cotton functionalized with TiO₂/SiO₂: focus on the role of silica, *Journal of Colloid Interface Sciences*, Vol. 401, pp. 1-7, 2013.
- [20] M. Ma and R.M. Hill, A Review of Recent Results on Superhydrophobic Materials Based on Micro- and Nanofibers, *Journal of Adhesion Science and Technology*, Vol. 22, pp. 1799-1817, 2008.
- [21] C.H. Xue, S.T. Jia, J. Zhang and J.Z. Ma, Large-area fabrication of superhydrophobic surfaces for practical applications: an overview, *Science and Technology of Advanced Materials*, Vol. 11, pp. 033002-033017, 2010.
- [22] M. Stamate and G. Lazar, Application of titanium dioxide photocatalysis to create self-cleaning materials, *Modelling and Optimization in the Machines Building Field*, Vol. 3, pp. 280-285, 2007.
- [23] H.J. Lee and S. Michielsen, Lotus effect: Superhydrophobicity, *Journal of the Textile Institute*, Vol. 97, pp. 455-462, 2006.
- [24] V. Rossbach, P. Patanathabutr and Wichitwechkarn, Copying and manipulating nature: Innovation for textile materials, *Fibers and Polymers*, Vol. 4, pp. 8-14, 2003.
- [25] X.J. Feng and L. Jiang, Design and creation of superwetting/antiwetting surfaces, *Advance Materials*, Vol. 18, pp. 3063-3078, 2006.
- [26] K. Schilling, B. Bradford, C. Castelli, E. Dofour, J.F. Nash, W. Pape, S. Schiulle, I. Tooley, J.V. Denbosch, F. Schelauf, Human safety review of nan titanium dioxide and zink oxide, *Photochemistry and Photobiological Sciences*, Vol. 9, pp. 495-509, 2010.
- [27] G. Gogniat, M. Thyssen, M. Denis, C. Pulgarin and S. Dukan, The bactericidal effect of TiO₂ photocatalysis involves adsorption onto catalyst and the loss of membrane integrity, *FEMS Microbiology Letters*, Vol. 258, pp. 18-24, 2006.