

Self-Cleaning Measurement of Nano-Sized Photoactive TiO₂

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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

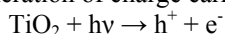
microorganisms [10]. However, the large-scale application of titanium dioxide as an efficient photocatalyst has been hampered by the notorious problem of recycling the photocatalytic powders in the aqueous purification. In this context, nano-crystalline titanium dioxide coatings on some substrates with 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

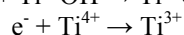
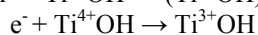
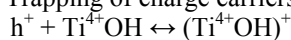
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holes. When TiO₂ catalysts are subjected to irradiation with photons of energy equal to or higher than their band gap, the generated electron-hole pairs can induce the formation of reactive oxygen species, such as hydroxyl radical and superoxide radical 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].

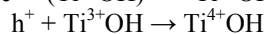
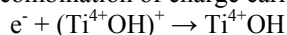
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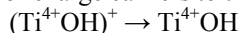
Trapping of charge carriers



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 TiO₂nanoparticles 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 TiO_2 powder samples were determined by X-ray diffraction (XRD) technique with $\text{Cu K}\alpha$ 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 TiO_2 , 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 $\text{Cu-K}\alpha$, 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 TiO_2 crystallites. The TiO_2 nanoparticles were annealed at 400°C for 2 hours. As you can see the sharp picks reveal the crystalline nanoparticles after heat treatment.

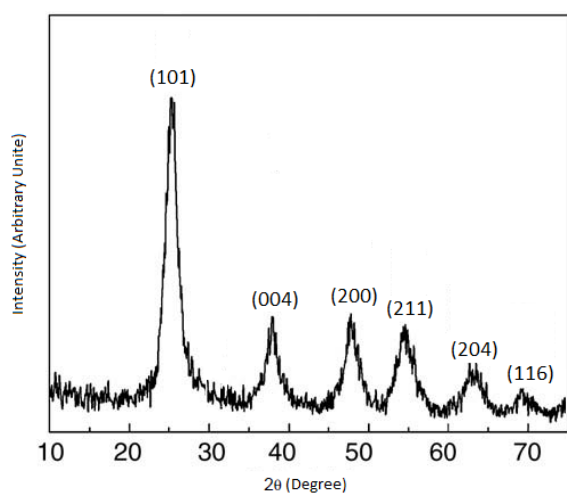


Fig. 1. X-ray diffraction ($\lambda = 1.54 \text{ \AA}$, $\text{Cu-K}\alpha$ radiation) pattern of the nanoparticles

Raman spectroscopy can be used to examine the crystal structure of TiO_2 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 TiO_2 , 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.

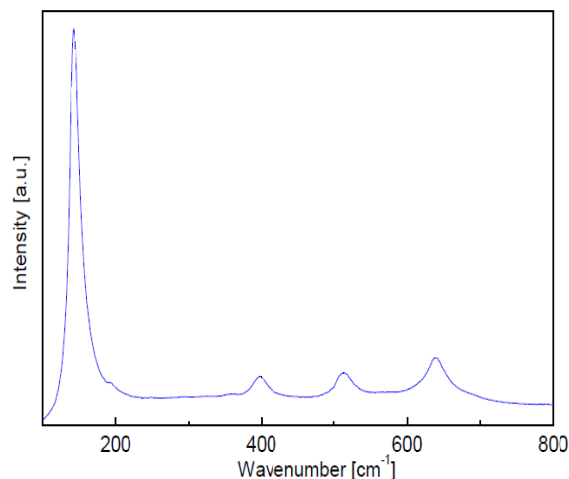


Fig 2: Raman spectrum of the as-prepared TiO_2

The UV-visible diffuse reflectance spectra of the TiO_2 samples are shown in Fig. 3. nano- TiO_2 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 TiO_2 .

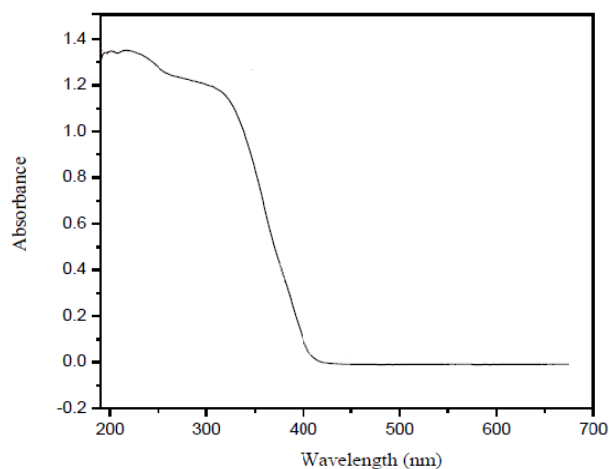


Fig. 3: UV-visible diffuse reflectance spectra of the TiO_2 powders synthesized at 400°C

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 TiO_2 nanoparticles. As you can see, the TiO_2 nanoparticles are in the size range of 20-40 nm in diameter. It has been revealed that the TiO_2 powders in rutile phase consist of both spherical and rod shapes but the particles of TiO_2 powders in anatase phase are mostly of spherical morphology.

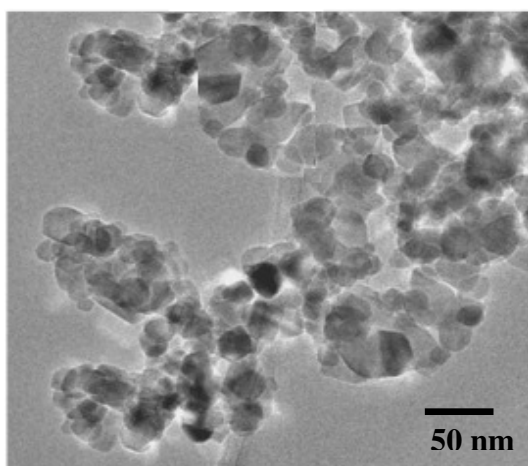


Fig. 4. TEM images of the TiO₂ nanoparticles

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

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