Structural, morphological and optical characteristics of titanium–dioxide nanoparticles: a short review

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Abstract

Titanium dioxide attracted much attention due to their valuable physiochemical and biological properties. The structural, morphological, optical, catalytic and thermodynamic properties festinating the TiO_2 nanoparticles for various scientific and technological industries. Many researchers made enormous effort to fetch unique properties of titania and come up with commercial applications of TiO_2. This leads to the idea of reviewing titania so that it helps in analyzing material in a detailed manner to understand properties and their variation. This review mainly covers major properties associated with TiO_2 nanoparticles evaluated by different researchers to make titanium dioxide as a material of choice. Properties covered are crystalline nature, particle size, phases and structure of synthesized titanium dioxide by X-ray diffraction (XRD) technique. Morphological analysis has been done with the help of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fourier transforms infrared spectroscopy (FTIR) that helps in determining the types of bond and associated vibrations in a synthesized material.

Keywords: Titanium dioxide nanoparticles, X-ray diffraction (XRD), scanning electron microscopy (SEM)

Titanium dioxide is profound and highly researched material as it caters to a wide variety of applications in the fields of science and technology. Some of the applications are paint pigment, solar cells, antibacterial property, drug delivery, wastewater treatment, photochemical reaction, cosmetics and many more [1]. There are basically three crystalline phases of TiO_2 are considered namely anatase, rutile and brookite. Among three phases, anatase and rutile are thermodynamic stable phases which attracted researcher attention towards it [2]. Stability of anatase and rutile depends on many factors such as synthesis method, choice of precursor, drying temperature, atmospheric conditions and particle size. There are varieties of methods available by which TiO_2 nanoparticles can be synthesized such as sol-gel, chemical vapor deposition, precipitation, hydrolysis, hydrothermal, microwave, solvo-thermal and microemulsion. Each method alters the associated property of TiO_2 nanoparticles in a unique manner in terms of structure, morphology, particle-grain-size and band gap. The problem associated while opting thermal hydrolysis method for synthesizing TiO_2 nanoparticles was agglomeration and sol-gel method is time consuming. Although, sol-gel method is easiest and cost effective technique for synthesis TiO_2 nanoparticles [4]. TiO_2 nanoparticles have various kinds of morphologies such as rods, spheres, needles, tubes, cubes and so forth depending on synthesis method chosen. Each anatase and rutile phase have their own applications [5]. TiO_2 is a wide band gap material having band gap energy ~ 3.2 eV for anatase phase and ~ 3.0 eV for rutile phase which make it difficult for photocatalyst in visible region. It is observed that anatase phase TiO_2 nanoparticles photoactive response is more than rutile phase which probably due to free radicals formation [6]. Band gap of TiO_2 nanoparticles basically depends on structure and particle size. Hence, annealing/calcination plays an important role in characterizing properties along with textural, structural and morphological properties. Moreover, phase transformation observed in TiO_2 nanoparticles *i.e.* brookite-anatase-rutile inter transition. In general, it is observed that brookite is least stable phase, anatase is thermodynamically stable to a certain high temperature ~ 500^0C when TiO_2 nanoparticles are synthesized using $TiCl_4$ as precursor via sol-gel method and rutile phase is highly stable such that once this phase obtained it cannot go back to anatase phase under normal procedure followed for synthesizing it [6,7]. This manuscript reports the characteristics of synthesized TiO_2 nanoparticles.

N. Rathore et al. [5] picked out sol-gel method for synthesizing TiO_2 nanoparticles using titanium isopropoxide ($C_{12}H_{28}O_4Ti$) as precursor. XRD results confirm the crystalline nature of TiO_2 nanoparticles. Peaks of XRD diffractogram corresponding to (101), (250), (022) and (200) diffraction planes confirmed anatase phase along with (220), (110), (111), (210), (330), (231) and (301) diffraction planes confirmed rutile phase and single peak correspond to (121) diffraction plane confirmed presence of brookite phase when sample prepared in temperature range 300-600^0C. The estimated particle size using Scherrer formula for different samples calcinated at 300, 400, 500 and 600^0C were 6.67, 9.18, 13.1 and 26.6 nm. Morphological analysis of TiO_2 nanoparticles had done by scanning electron microscopy (SEM). According to SEM images, synthesized TiO2 nanoparticles possess spherical morphology with uniform distribution. FTIR spectra of TiO2 nanoparticles calcinated at 300 ^{o}C showed characteristic peak at 663.51 cm^{-1} and calcinated at 400, 500 and 600^0C showed characteristic peak at 764 cm^{-1}. P. Praveen et al. [6] picked out a sol-gel method for synthesizing TiO_2 nanoparticles using tetraisopropyl orthotitanate as precursor. XRD results confirm the crystalline nature of TiO2 nanoparticles. Peaks of XRD diffractogram corresponding to (101), (107), (200), (211), (004), (204) and (215) diffraction planes confirmed anatase phase at temperature 450^0C and the estimated crystallite size using Debye-Scherrer formula were ~ 15.31 nm. Morphological analysis of TiO_2 nanoparticles was done by scanning electron microscopy (SEM). According to SEM images, synthesized TiO_2 nanoparticles possess spherical shape and non- uniform distribution of TiO_2 nanoparticles with estimated particle size was 18.98 nm. FTIR spectra of TiO_2 nanoparticles at 450^0C for 4 h showed characteristic peak at 463.88 and 728.77 cm^{-1} corresponds to Ti-O and Ti-O-Ti vibrations and confirmed existence of anatase phase. The estimated band gap was found to be 3.5891 eV where direct band gap obtained was 3.5810 eV and in-direct band gap obtained was 3.5806 eV. K. Sathiyan et al. [7] picked out titanium tetrachloride ($TiCl_4$) hydrolysis methods for synthesizing TiO2 nanoparticles. XRD results confirm the crystalline nature of TiO2 nanoparticles. Peaks of XRD diffractogram corresponding to (101), (200), (105), (103) and (200) diffraction planes confirmed anatase phase and corresponding to (121) diffraction planes confirmed brookite phase of synthesized TiO_2 nanoparticles. Morphological analysis of TiO_2 nanoparticles was done by transmission electron microscopy (TEM). According to TEM images, two types of particle populations were identified i.e. long and short particles having polygonal geometry (SAED images). The estimated band gap for analysis of optical properties was 3.68 eV. S. Sugapriya et al. [8] picked out a chemical precipitation method for synthesizing TiO_2 nanoparticles using titanium isopropoxide (TIP) as precursor. XRD results confirm the crystalline nature of TiO2 nanoparticles. Peaks of XRD diffractogram corresponding to (101), (107), (200), (211), (004), (204) and (105) diffraction planes confirmed anatase phase at temperature 450^0C along with (220), (110), (111), (210), (310), (112) and (301) diffraction planes confirmed rutile phase temperature 900 ^{o}C. The estimated grain size using Scherrer formula for different samples annealed at 450^0C and 900^0C were 21-24 nm and 69-74 nm. Morphological analysis of TiO_2 nanoparticles was done by scanning electron microscopy (SEM). According to SEM images, synthesized TiO_2 nanoparticles possess uniform distribution and well connected grain and also particle size increases with increase in temperature. FTIR spectra of TiO_2 nanoparticles annealed at 450^0C showed characteristic peak at 465 and 411 cm^{-1} corresponds to Ti-O and Ti-O-Ti vibrations and TiO2 nanoparticles annealed at 900^0C showed characteristic peak at 478 and 764 cm^{-1} corresponds to rutile phase. Absorption band edge of TiO_2 nanoparticles was found to be moved towards longer wavelength as annealing temperature increases. F. B. Dejene et al. [9] picked method i.e. hydrolysis of titanium tetra isopropoxide (TTIP). XRD results confirm the crystalline nature of TiO_2 nanoparticles. Peaks of XRD diffractogram confirmed anatase phase at temperature 500^0C and rutile phase temperature 700^0C. The estimated crystallite size using Scherrer formula for different samples annealed at 500^0C and 700^0C were 10, 20 and 80 nm. Morphological analysis of TiO_2 nanoparticles had done by scanning electron microscopy (SEM). According to SEM images, synthesized TiO_2 nanoparticles possess smooth morphology having spherical shape and poor agglomeration but aggregation started appearing as rate of hydrolysis increases. Optical band gap of TiO_2 nanoparticles were to be 2.49-2.36 eV and this variation depends on hydrolysis rate. M. Imran et al. [10] picked out a sol-gel method for synthesizing TiO_2 nanoparticles using titanium tetrachloride ($TiCl_4$) as precursor. XRD results confirm the crystalline nature of TiO2 nanoparticles. Peaks of XRD diffractogram corresponding to (211), (220), (110), (221) and (210) diffraction planes confirmed the rutile phase. The estimated crystallite size using Scherrer formula for pH 3, 5, 7, 9 and 11 were found to be 20.63, 19.05, 19.05, 24.07 and 24.66 nm respectively. The estimated band gap for different pH such as 1, 3, 5, 7, 9 and 11 was found to be 3.05, 3.02, 3.01, 2.90, 2.87 and 2.95 eV respectively and had a direct band gap in the rutile phase.

Conclusion

Titanium dioxide is one of the widely used materials in nano as well as bulk scale and maintains a specific place in a variety of industries that includes food industry, medical, construction, agriculture, cosmetics and many more. The survey reports properties of prepared nanoparticles such as structural, morphological, phase and much more depend primarily on choice of precursor, synthesis method, temperature, calcination and annealing and environment. These factors affect the properties of synthesized TiO_2 nanoparticles in a variety of ways which involves particle and grain size, appearance of phase, phase transition temperature, crystallographic structure, band gap and so on. Therefore, suitable choice of precursor, synthesis method, temperature, calcination and annealing and environment give control over the properties of synthesized TiO_2 nanoparticles.

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