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Green Synthesis of TiO_2 Nanoparticle Using Cinnamon Powder Extract and the Study of Optical Properties

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Abstract

The pure TiO_2 nanoparticles have been synthesized by a simplistic eco-friendly green method using extract of cinnamon powder for the first time. The cinnamic acid present in the cinnamon works as the capping agent during the reaction. TiO_2 nanoparticles were characterized by using X-ray diffraction (XRD) which conformed the anatase phase TiO_2 with average crystallite size 70.1 nm. Scanning electron microscopy (SEM) micrographs suggests that the particles exhibit spherical shapes and uniformly distributed over the surface with size range 70–150 nm. The energy dispersive X-ray spectroscopy (EDX) shows the presence of oxygen and titanium peaks which confirmed the formation of TiO_2 pure nanoparticles. From the UV–Vis spectroscopic studies the band gap comes out to be 3.2 eV which confirmed the formation of TiO_2 nanoparticles. The optical properties have also been studied by PL that indicates the formation of oxygen vacancies and self-trapped excitons in the material. The samples showed the enhanced photocatalytic property.

Keywords TiO_2 nanoparticles · Cinnamon powder · Green synthesis · Bandgap · Crystallite size

1 Introduction

Nanoparticles having a range of 1–100 nm. Nanomaterials possess different shapes and extremely small sizes that effects upon their physical, chemical and optical properties. For instance, surface area, solubility, melting point, dielectric constant etc. The decrease in the melting point of nanoparticles is a unique feature at the nano scale. Nanomaterial's being small in size show exceptional optical properties. When the particle size is reduced the band gap of nanoparticles increased. Nanoparticles emit several colors which depend on the absorption of different wavelengths and size of nanoparticles [1]. Nano titanium dioxide (TiO_2) mainly used as a semiconductor in research work on the basis of its important features such as inexpensive, strong oxidizing power, high chemical stability, high refractive index and oxygen vacancies in titanium dioxide lattice. These vacancies are essentially resulting from molecular oxygen separation and electron emission. Titanium dioxide is the best consumer of sunlight and usually, it can absorb 3% to 4% of solar energy, so that it is recognized as an efficient photo-catalyst to produce hydrogen and also fruitful to decomposed the toxic organic compounds present in water [2]. TiO_2 nanomaterials when used for commercial purposes, electron–hole recombination and small surface area are considered as main drawbacks that can be improved by bulk alteration of cation and anion doping [3].

TiO_2 consists of two forms amorphous and crystalline it mainly presents in three crystalline polymorphs like anatase rutile and brookite. Anatase and rutile having tetragonal structure and brookite is in orthorhombic structure [4]. Titanium dioxide was used as a model material because it is mostly used in experimental and theoretical studies and widely used in photocatalysis and degradation of dyes. Due to its interconnected pore network and huge surface area titanium dioxide is used in dyes solar cells [5]. TiO_2 is used in cosmetics, especially in care products and for decomposition of different microorganisms such as viruses, bacteria, cancer cells, ultraviolet light resistant oxide, toothpaste, papers, food colorants paints, plastics and inks [6]. In previous work TiO_2 has been biosynthesized by various plant extracts such as Aloe vera leaves extract [7] peel extract of Citrus reticulate [8] *Azardirachta*

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indica leaves extract [9] of *Muraya koenigii* [10] and aqueous extract of *Curcuma longa* [11]. The previous work was based on the synthesis of environmental friendly small sized nanoparticles for various applications. Cinnamon (*C. zeylanicum* bark) is a multi-faceted medicinal, nutritional and an edible plant its powder is broadly used as a spice. It is commonly used in cooking for the preparation of spicy candies, tea, hot cocoa and chocolate. In medicine It has been used to treat cough, diarrhea and digestive system problems [12]. It is higly used as antioxidant [13] and antibacterial for the preservation of food [14]. The cinnamic acid present in the cinnamon acts as the capping agent [15]. In this work TiO_2 has been synthesized by aqueous extract of Cinnamon powder (*C. zeylanicum* bark) due to its significant properties. The optical properties are studied by the UV–Vis spectroscopy and PL. The prepared specimens are employed for the photocatalytic applications. Improved photocatalytic activity is observed by the environmentally benevolent nanoparticles.

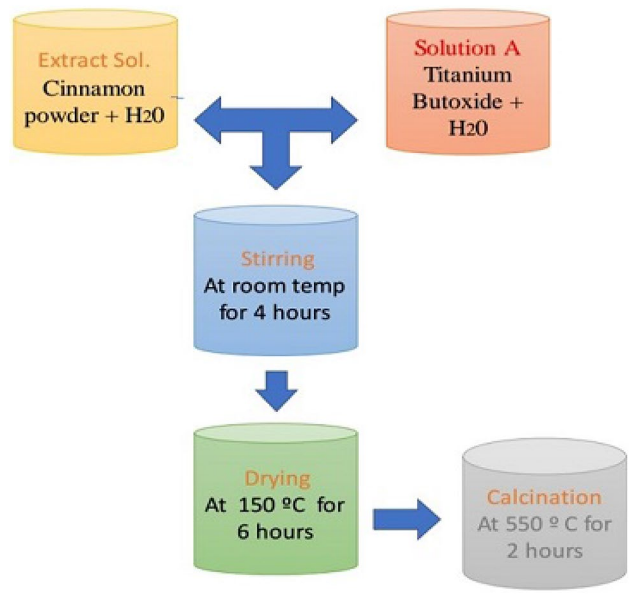
2 Materials and Methods

2.1 Experimental Details

Titanium dioxide has been prepared via green synthesis method: Aqueous extract was prepared by adding 3 g of cinnamon powder in 50 ml distilled water and boiling the solution at 100 °C for 10 min. This extract was filtered through filter paper and used for further experiments. 2 g of titanium dioxide bulk particles were added in 100 ml of distilled water to make a clear solution **A**. 20 ml of cinnamon extract was added dropwise into solution **A.** The white color of the solution turned into brown color. The solution was stirred for 4 h at room temperature and aged for 24 h. After aging it was subjected for drying till 6 h at 150 °C crystals are formed which were calcined in a furnace at 500 °C for 2 h (Fig. 1).

Fig. 1 Cinnamon powder and titanium butoxide solution

2.2 Experimental Flow Chart



3 Results and Discussion

The X-ray diffraction (XRD) pattern were analyzed by X-rays powder diffractometer by using Cu-Kα radiation source (λ = 0.15418 nm). The scanning electron microscopy (SEM) images were taken from ZESIS-V80. The energy dispersive X-rays spectroscopy (EDX) were used to studies the elemental composition of prepared material by using EDX-8000. UV–Vis spectra were taken by using scan UV–Vis–NIR spectrophotometer and Photoluminescence (PL) spectra was measured by using FLS1000 photoluminescence spectrometer. It is also tested for the efficient photocatalytic activity.

X-ray diffraction pattern of TiO_2 nanoparticles were obtained by green synthesis method is shown in Fig. 2. The

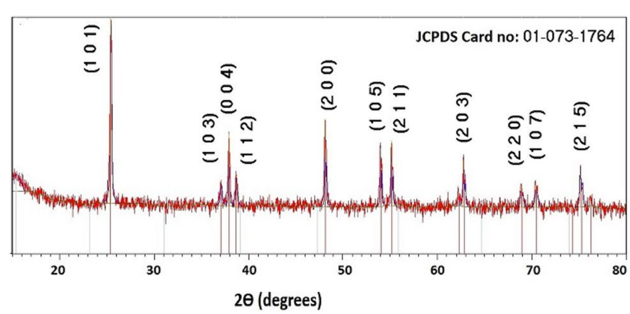


Fig. 2 XRD pattern of TiO_2 nanoparticles

sharpness of peak shows the crystalline nature of TiO_2 nanoparticles. By using Debye–Sheerer formula, we can calculate the average size of crystalline nanoparticles.

$$D = k\lambda/\beta \cos\theta \quad (1)$$

where λ is the wavelength of X-rays (λ = 1.541874 Å), D is used for the crystallite size of nanopowder, β represent full width at half-maximum (FWHM) of the representative peak and 2Θ is the Bragg diffraction angle. The XRD peaks have miller indices such as (101), (103), (004), (112), (200), (105), (211), (203), (220), (107) and (215) which also verify anatase phase structure of TiO_2 nanoparticles. The observed pattern of synthesized TiO_2 nanoparticles are in excellent agreement with reference pattern (JCPDS Card No: 01-073-1764) in the XRD literature patterns [16]. In the synthesized material only the anatase TiO_2 phase has been observed and no rutile phase can be found. This fact might be attributed by the low concentration of oxygen vacancies due to high concentration of gaseous oxygen during growth, delaying the conversion from anatase to rutile phase [17]. The average crystallite size calculated by the Eq. 1 is 70.1 nm.

The SEM images of TiO_2 material are shown in Fig. 3a which shows the formation of nanoparticles. SEM provides evidence about surface structure such as shape, structure, and size of nanomaterial. This describes the morphology of material in the nanometer scale. The TiO_2 nanoparticle size is 70–150 nm which is clearly in agreement with the XRD results. Figure 3b were taken by using image j software which shows that maximum nanoparticles are in the range of 100–120 nm. It is cleared that these particles exhibit spherical shapes and uniformly distributed over the surface from SEM images. In topical view of SEM micrographs agglomeration of nanoparticles and formation of nanoclusters has been observed. The size of nanoparticles can be changed by increasing their molar concentration.

The energy dispersive x-ray spectroscopy is used to determine the elemental composition of nanomaterial's that is a working mode of SEM and provide information about how much percentage in the materials every element occupies. EDX compositional mapping of the sample is shown in Fig. 4a. It shows the presence of oxygen, titanium peaks from the sample. The presence of Oxygen and titanium confirmed the formation of pure titanium dioxide nanoparticles. The elemental percentages in pure TiO_2 sample of green synthesis method given in Fig. 4b.

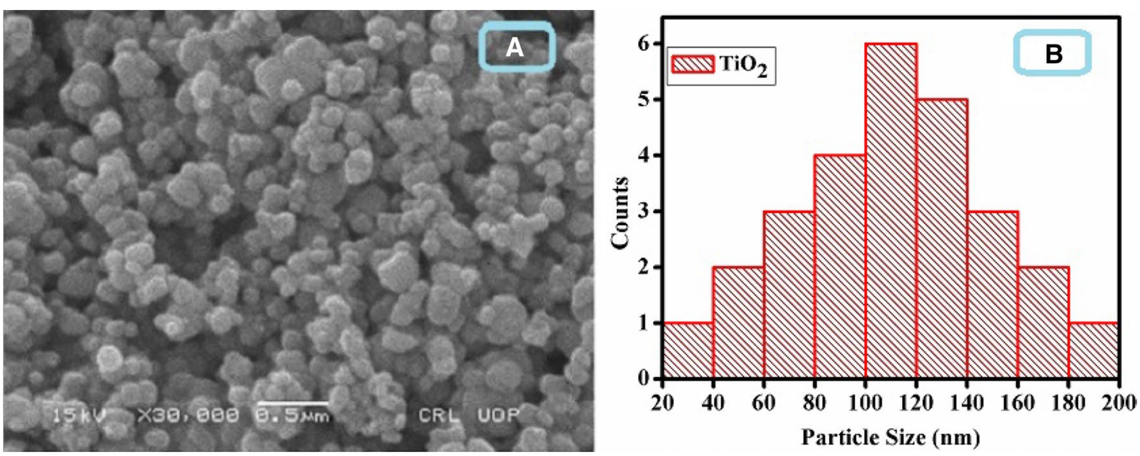
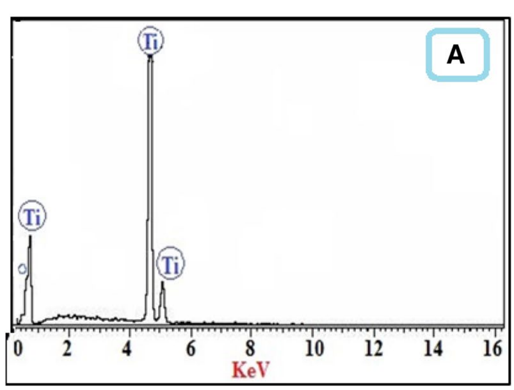


Fig. 3 **a** SEM images of TiO_2 nanoparticles **b** histogram size distribution of TiO_2 NPs

Fig. 4 **a**, **b** EDX spectra and composition of elements



B

Element	Weight (%)	Atomic (%)
Titanium	50.94	74.04
Oxygen	49.06	25.96
Sum	100.00	100.00

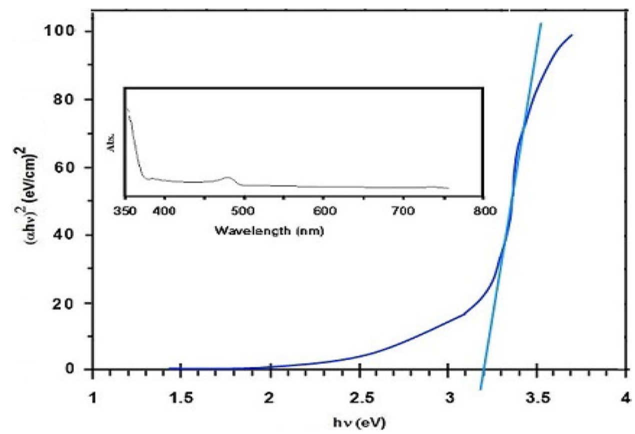


Fig. 5 Tauc Plot and UV–Vis pattern of TiO_2 nanoparticles

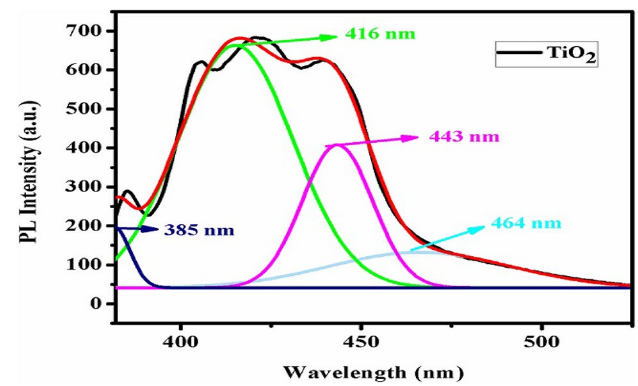


Fig. 6 Photoluminescence spectra of TiO_2 nanoparticles

The optical properties have great importance in the study of photo-catalytic materials because optical property represents the number of photons which will be absorbed during photo-catalysis. Basically, the electronic structure and optical properties of prepared samples are analyzed by UV–Vis spectroscopy. UV–Vis absorption spectra and tauc plot of prepared nanoparticles is shown in Fig. 5. The higher absorbance in the high wavelength region between 300 and 400 nm is shown in the graph. The visible regions of these nanoparticles absorption are of 385 nm. The optical energy band of a semiconductor were obtained by using the following equation:

$$\alpha = \frac{k(h\nu - Eg)n/2}{h\nu} \tag{2}$$

where k is a constant, α is the absorption coefficient, Eg is the energy band gap, and n is 1 for a direct energy band gap. The energy band gap can be estimated from tauc plot between $(\alpha h\nu)^2$ versus energy of photon (hv) [18]. The intercept of the tangent on the tauc plot give a direct band gap for n = 1. The band gap of the prepared TiO_2 nanoparticles calculated to be 3.2 eV is same as bulk TiO_2 [19].

4 Photoluminescence Spectroscopy Analysis

Photoluminescence and excitation spectra were taken at room temperature of TiO_2 nanoparticles which were synthesized by green method. PL spectrum of TiO_2 nanoparticles with excitation wavelength of 380 nm is shown in Fig. 6. TiO_2 anatase phase PL spectra are credited three types of physical origins: oxygen vacancies [20, 21], self-trapped excitons [20, 22] and surface states defects [23]. The mostly surface states are Ti^{4+} ions adjacent to oxygen vacancies [24, 25]. The defects are formed in non-equilibrium condition growth of nanoparticles which plays a significant role in the photoluminescence of TiO_2 as reported by Zeng et al. [26]. The PL spectra of TiO_2 shows a UV emission peak at 385 nm and three visible emissions peaks at 416 nm, 443 nm, and 464 nm respectively. The UV emission describe the band edge emission of the host TiO_2, which also explain the band gap of the material. The calculated band gap from UV emission peak is 3.22 eV which is approximate equal to tauc plot band gap. The two visible peaks at 416 nm and 443 nm can be ascribed the self-trapped excitons in TiO_6 octahedral [27]. The presence of oxygen vacancies in the TiO_2 nanoparticles are explain the blue emission peak at 464 nm. In addition, the TiO_2 particles at nanolevel having high area to volume ratio should favor the presence of large amount of oxygen vacancies [28].

5 Conclusion

Pure nanoparticles of titanium dioxide can be effectively prepared through an easy, low-cost and single-step green synthesis method. The structural, morphological, optical and compositional properties of Titanium dioxide nanoparticles were studied by SEM, UV–Vis spectroscopy, XRD and EDX. The results confirmed the formation of the pure spherical anatase TiO_2 nanoparticles with the average crystallite size of 70.1 nm and the overall size range of 50–100 nm. UV–Vis spectroscopy gives the 3.2 eV bandgap that means the enhancement in visible light absorption and the increment of the band gap of titanium dioxide nanoparticles as compared to the bulk material, which makes it appropriate for the use in solar cells.

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