Mixed fuel approach for the fabrication of TiO_2:Ce^{3+} (1–9 mol%) nanophosphors: Applications towards wLED and latent finger print detection

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ABSTRACT

TiO_2:Ce^{3+} (1–9 mol%) nanophosphors (NPs) were prepared by solution combustion method using combination of fuels. PXRD studies of pure and doped samples exhibit rutile and anatase phases respectively. SEM results indicate that the particles were found to be nearly spherical in nature. The energy band gap (E_g) of pure and doped samples was found to be in the range 3.10–3.23 eV. The active vibrational Raman modes observed at $\sim$ 141, 446 and 608 cm^{-1} were corresponds to B_{1g}, E_g and A_{1g} respectively. The mode at $\sim$ 229 cm^{-1} was due to second order effect that confirms the rutile phase of TiO_2. The CIE and CCT results of the doped TiO_2 shows that this product exhibits green colour (CIE-coordinates x = 0.3649, y = 0.4023) and was suitable for wLEDs which can be used for household applications. The optimized product was further utilized for the visualization of latent finger prints (LFPs) on various porous and non-porous surfaces. The results reveal that, all the levels (I–III) of ridge feature were clearly visualized under normal light indicating that the powder was a reliable and promising labeling agent for LFPs detection as well as wLED applications.

1. Introduction

Recently nano TiO_2 particles have received significant interest owing to its wide range of applications namely: furnishing materials [1,2], in solar cells [3,4], self-cleaning material [5,6], antireflection [7–11], LEDs, pigment in paints, antibacterial, gate insulator in the MOS, aerospace, photonics [12], sensing [13], batteries, sunscreen lotions, photo-catalyst [14], hydrogen production [15], atmospheric pollutants degradation etc. [16]. TiO_2 was chemically stable, biocompatible with excellent physical and optical electrical properties [17]. It has a polymorph of rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [18]. Further it was nontoxic with high dielectric constant ($\sim$ 67.3) and high refractive index ($\sim$ 2.6). The E_g of anatase, rutile and brookite phases were found to be 3.20 eV, 3.00 eV and 1.90 eV respectively [19].

Generally, TiO_2 nanoparticles (NPs) have been prepared by various methods namely; hydrothermal, co-precipitation, sol-gel, sono-chemical, solution combustion (SC) technique, physical vapor deposition, chemical vapor deposition, RF plasma method, pulsed laser method [20,21] etc. Among them, SC technique was found to be simple, rapid and effective for the preparation of NPs. In this method, exothermic

nature of the reduction-oxidation reaction was dominant for producing nano sized particles. Further, this technique involves different oxidizers (metal nitrates) and fuels (urea, ammonium acetate, glycine, hydrazides).

Finger prints (FPs) were found to be a vital source of evidence in Forensic science for identification and individualization of a person. The FPs ridge characteristics remain the same throughout the lifespan. Normally most of FPs visualized were latent and invisible to naked eye; as a result, an appropriate technique was essential to recognize personal identification. Till date numerous methods namely; powder dusting, ninhydrin, cyanoacrylate etc. [22] were used to recognize LFPs. Most of the techniques, the recognition was restricted to only level I and level II ridge details. The level I and II features were easily forged, by the generation and use of artificial skin imprints. However, the analyses of level III ridge details require some efficient nanopowders with uniform spherical sized particles. Hence, there was an urgent need to develop a simple and efficient route for visualizing LFPs with superior sensitivity, less background hindrance, low toxicity and stress-free detection of LFPs. From the literature, it was evident that most of the FPs detections were visualized under UV light. Conversely, UV light has many drawbacks including high background interference owing to the significant

auto-fluorescence from the substrates, photo damage to the skin and eyes of the operators, and the possibility of severe irradiation-induced damage [23,24]. Therefore, visualization of LFPs under normal light was highly essential in order to visualize level III ridge details such as sweat pores, scar, creases, warts etc.

In the present work, TiO$_2$:Ce^{3+} (1–9 mol%) NPs were prepared by SC technique using mixed fuels (such as glycine and ammonium acetate) and the product was well characterized by utilizing PXRD, FESEM, TEM, UV–visible, Raman etc. The optimized powders were utilized for display and Forensic application.
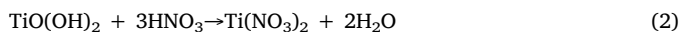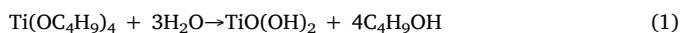
2. Experimental

2.1. Materials

In the present study, all the chemicals were used without further purification. For the preparation of pure and doped TiO$_2$ NPs; titanium (IV) butoxide (TB, Ti(OC$_4$H$_9$)$_4$ MW = 340.32 g mol^{-1}, 97%, Sigma Aldrich), nitric acid (69%, HNO$_3$), glycine (C$_2$H$_5$O$_2$N MW = 75.05 g mol^{-1}, 99.5%, Merk,) and ammonium acetate (C$_2$H$_3$O$_2$NH$_4$, MW = 77.08 g mol^{-1}, 97%, Merk), cerium(III) nitrate hexahydrate (Ce(NO$_3$)$_3$6H$_2$O, MW = 434.22 g mol^{-1}, 99.9%, Sigma Aldrich).

2.2. Preparation of TiO$_2$:Ce^{3+} (1–9 mol%)

At the beginning 10 ml of double distilled water was slowly added 10 ml of titanium butoxide and then mixed with 10 ml of 0.5 N HNO$_3$ with constant stirring at ambient temperature to get transparent solution of titanyl nitrate (TN). The chemical reactions for the formation of both meta titanic acid [MTA-(TiO(OH)$_2$)] and (TN) were given below [25].

$$Ti(OC_4H_9)_4 + 3H_2O \rightarrow TiO(OH)_2 + 4C_4H_9OH \tag{1}$$

$$TiO(OH)_2 + 3HNO_3 \rightarrow Ti(NO_3)_2 + 2H_2O \tag{2}$$

The stoichiometric compositions of the redox mixtures for combustion reaction were calculated using total oxidizing (O) and reducing (F) valencies of the components (fuels; glycine and ammonium nitrate independently) so that the equivalent ratio O:F is unity [26]. When the ratio is stoichiometrically adjusted to the oxidizer-fuel ratio (ϕ = 1), the fuel ratio is appropriate for supporting an oxidative combustion reaction throughout the volume of the reactant, promoting a rapid reaction and high temperature.

The stoichiometric quantities of TN, ammonium nitrate, glycine and cerium nitrate were again stirred over the magnetic stirrer to get the homogeneous solution. This resultant solution was kept in the preheated (~ 450 °C) muffle furnace to get the foam type powder, which was again treated in the same furnace at a temperature 700 °C for 2 h to get the Ce^{3+} doped TiO$_2$ NPs. The schematic flow chart was shown in the Fig. 1 for the synthesis of the NPs.

2.3. Characterization

The structural characterization was performed using powder X-ray diffractometer (PXRD) (model: Pananalytical X′Pert Pro MPD) in the 2θ range 10–80° with Cu-K$_\alpha$ radiation (1.54178 Å). The surface morphology was studied from FESEM (Carl Ziess Model: Neon-40), Raman studies were carried out on SEKI Technotron Corp (Model STR-300). The particle size measurement was done by TEM (Model Jeol/JEM 2100, Lamp: LaB6) PerkinElmer (Lamda-35) UV–Vis spectrometer was used to record UV visible spectra, Photoluminescence (PL) studies were carried out using Fluorolog-3 Jobin Yvon Spectroflourimeter equipped with 540 W Xenon lamp as an excitation source.

2.4. Visualization of Latent fingerprints using TiO$_2$:Ce^{3+} (1 mol%) NPs

All the LFPs were collected from a single donor of age about 35 years. The donor hands were cleaned with soap water. The hands were dried and gently rubbed on forehead and placed on the different forensic related articles. The optimized NPs were carefully stained on LFPs and excess power was removed by smooth brushing method. The normal white light was used to visualize the stained. The images were taken by digital camera (Nikon). It was positioned at a distance of about 15 cm from the stained surfaces and the following settings were fixed: 50 mm f/2.8 G ED lens Nikon D3100/AF-S under UV light.

3. Results and discussion

3.1. Structural analysis

Fig. 2 shows the PXRD profiles of pure and doped TiO$_2$ NPs. All the peaks were well matched to pure rutile phase of TiO$_2$ (standard JCPDS card no. 87-920). When the product was calcined at 700 °C for 2 h, the pure rutile phase was obtained. However, with the addition of Ce^{3+} ions, rutile phase (2θ ≈ 27°) was converted to anatase phase (2θ ≈ 25). Also, the peaks of anatase phase TiO$_2$ were matched to card no. 84-1286. Further, no impurity peaks were observed indicating that Ce^{3+} ions were successfully existed in the lattice sites rather than interstitial sites [27].

The diffraction peaks were linked with physical parameters such as crystallite size, stress, dislocation density, stacking fault (SF), texture coefficient (TC) and lattice cell parameters.

The crystallite sizes of pure and doped TiO$_2$ were estimated using the Scherrer's [28] relation and were found to be in the range 25–42 nm.

$$D = \frac{k\ \lambda}{\beta\ \cos\theta} \tag{3}$$

Where k: the shape factor (0.89 for spherical shape particles), β; full width at half maximum (FWHM) of PXRD peak.

Further, dislocation density (δ), stacking fault (SF) and texture coefficient (TC) were calculated using the following relations and were tabulated in the Table 1.

$$\delta = \frac{1}{D^2} \tag{4}$$

$$SF = \frac{2\ \pi^2}{45\ (3\tan\theta)^{1/2}} \tag{5}$$

$$TC = \frac{I_o(h_i, k_i, l_i)}{I_s(h_i, k_i, l_i)} \left[\frac{1}{N} \frac{I_o(h_i, k_i, l_i)}{I_s(h_i, k_i, l_i)} \right]^{-1} \tag{6}$$

The estimated values were shown in the Table 1, it was evident that the crystallite size and SF increases with increase of concentration of Ce^{3+} ions. The value of TC was found to be ~ 0.5 for (1 0 1) and 2 for (2 1 3) plane. The higher value of TC indicates that the crystal planes were oriented along (2 1 3) plane [29].

The cell parameters were also estimated using the relation (7). The obtained values were found to be a = b = 3.7823 Å, c = 9.4958 Å for anatase phase of TiO$_2$. These obtained values were matched with the literature a = b = 3.7822 Å, c = 9.5023 Å [30]. This was in good agreement between theoretical and experimental values.

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \tag{7}$$

Where d; the interplanar distance.

The acceptable percentage difference (D$_r$) was calculated based on ionic radii of host (Ti^{4+}, r$_h$ = 88 pm) and activator ion (Ce^{3+}, R$_d$ = 115 pm) using the relation to understand the effective replacement of Ti^{4+} ions by Ce^{3+} ions [31]: