Fabrication and photocatalytic characterization of SnO$_2$ and SnO$_2$/TiO$_2$ nanostructure films

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Abstract. Pure spherical-like SnO$_2$ and agglomerated spherical SnO$_2$/TiO$_2$ nanostructures (NS) films were effectively synthesized via hydrothermal route and modest combination of pulse laser ablation besides hydrothermal (PLAL-H) methods, respectively. The as-prepared samples were deposited on glass substrates at growth temperature 100 °C and characterized by FESEM, X-ray diffraction, and UV-Vis absorption and Photoluminescence (PL) measurements. Both samples exhibit a pure tetragonal rutile and anatase polycrystalline structure. The PL spectrum of pure SnO$_2$ NSs reveals five emission peaks in UV and visible regions. In contrast, a red shift in UV emission peak was clearly observed in SnO$_2$/TiO$_2$ nanocomposite spectrum and disappeared all visible emission peaks. Moreover, the samples as photocatalysts films were examined under sunlight irradiation driven photodegradation of methylene blue (MB) dye. The findings exposed that the photodegradation efficiency toward MB dye at maximum irradiation time 150 min was mostly similar around 21.5 % of both as-growth films.

1. Introduction
At present, environmental remediation owing to pollutants from organic dyes caused by various enormous industries processes such as leather, textiles, cosmetic and domestic wastes have become a hurtful serious topic to human health. Research area comprised photocatalysts of semiconductor nano/micro-materials has received great attention for environmental remediation. Recently, different photodegradation efficiency toward organic dyes (MB, MO, AZO etc.) via semiconductor nano/micro-materials (ZnO, TiO$_2$, CdS, ZnS, SnO$_2$, etc.) have diverse physical structure [1-4]. Rajkumer et al., [5] reported that titania (TiO$_2$) compounds consider as the promising photocatalyst because of its high photocatalytic efficiency, low cost, non-toxicity, and physicochemical stability. Furthermore, tin oxide (SnO$_2$) is a significant material of the n-type semiconductor, which is widely used in many fields such as optical devices and gas sensing. It was also suggested as a substitute for the conventional TiO$_2$ catalysts for improved degradation of organic dyes.

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under visible light [6, 7]. Recently, several studies conducted in this field, the satisfactory photocatalytic activity-dependent SiO$_2$/TiO$_2$ nanocomposite for organic dyes under natural light is not fully achieved [8]. Degradation of industrial toxic organic dyes under sunlight is an extremely challenging aspect; further research is therefore needed in order to accomplish optimum environment remediation of the surroundings. Consequently, many groups reported that the photocatalytic activity of semiconductor materials under visible light might be improved by assuming an effective strategy. It includes band-gap manipulation via doping or sensitizing processes through metals or produce mixed structure [5].

In this current view, we produced a pure SnO$_2$ and SnO$_2$/TiO$_2$ nanostructure-based films by combination of pulse laser ablation and hydrothermal PLAL-H techniques. Where, comparative study of pure SnO$_2$ and SnO$_2$/TiO$_2$ nanostructure films was explored and synthesized for first time via (PLAL-H) method at low growth temperature 100 °C. Conversely, various synthesis routes for pure and doped 1-D, 2-D and 3-D nano/micromaterials includes sol-gel route, electric-field assisted growth method, chemical vapor deposition (CVD) method, hydrothermal approach, pulse laser ablation in gas/liquid environment route, etc. are extensively done [5, 9-12]. Moreover, a comparative study of as-prepared films-driven photodegradation of methylene blue (MB) dye under natural sunlight is presented. The present synthesis approach to produce pure SnO$_2$ and SnO$_2$/TiO$_2$ nanocomposites films is a cost-effective way to manufacture organic pollutant remediation.

2. **Experimental**

2.1. **Samples Fabrication**

The experimental section included two synthesis approaches. First, a direct hydrothermal method was applied for growth pure SnO$_2$ nanostructure film. In brief, SnCl$_2$.2H$_2$O 0.1 M and hexamethylenetetramine (HMT) with purity 99% and concentration 0.05 M were mixed and dissolved in deionized water (DW) 80 mL. The as-prepared mixture was stirred for 10 min to improving the reactivity of the precursor solution. A desired amount of NaOH was gently added to regulate the pH value at 13 of precursor solution. Subsequently, the as-prepared mixture was transferred into an autoclave 100 ml contains clean glass substrates fixed at the bottom of autoclave. This autoclave was placed inside an oven at treatment temperature of 100 °C for 4 hrs, followed by cooling down the reactor to room temperature (RT). Finally, pure monodispersed spherical-like SnO$_2$ nanostructure deposited on a glass substrate was obtained.

The second growth approach included the deposition of SiO$_2$/TiO$_2$ nanocomposite film on a glass substrate using the modest combination of pulse laser ablation and hydrothermal (PLAL-H) techniques. TiO$_2$ colloidal solution was produced by pulsed-laser ablation (PLAL) technique, which was then used as nutrients for further hydrothermal interaction. An analytical grade metallic Ti square plate with surface area 9 cm$^2$ and purity 99.99% was used as target material. This target was cleaned in an ultrasonic ethanol bath for 25 min and rinsing with DW to remove the contaminants. Afterward, the Ti target was fixed at the bottom of a vessel filled with 40 mL of distilled water. The ablated process was achieved using a Nd:YAG pulsed-laser source with second harmonics wavelength 532 nm, pulse duration of 10 ns, repetition rate of 10 Hz, laser energy of 200 mJ/pulse and 2000 pulses. To avoid the hindrance to the pulse irradiation path, the as-synthesized colloidal was constantly stirred through ablation procedure to reduce the accumulation of nanoparticles. The colloidal obtained via PLAL method was subsequently mixed with the aforementioned precursor solution for preparing SnO$_2$ composite at 1: 3 ratios before the mixture with pH value 13 was exposed to hydrothermal treatment at 100 °C for 4 hrs. The agglomerated spherical-like SnO$_2$/TiO$_2$ nanocomposite film was successfully deposited on the glass substrate via PLAL-H technique. All as-growth samples were obtained in this work were cleaned many times by ethanol and DW, and then dried at 60 °C.
2.2. Sample Characterization

The topography and the structural characteristics of as-prepared SnO$_2$ and SnO$_2$/TiO$_2$ nanostructures-based films were examined by FESEM (Hitachi-S 4160) and XRD (Rigaku D/max- 2500, Cu Ka radiation, $\lambda = 0.1540$ nm) measurements. The UV-Vis absorption spectra in the wavelength range of 300-900 nm were recorded using a Lasany LI-2800, double beam spectrometer. The photoluminescence (PL) emission spectra were captured using fluorescence (RF-5301PC, Shimadzu) spectrofluorophotometer equipped by a Xenon-lamp as excitation source wavelength of 325 nm. All the measurements are done at RT.

3. Photocatalytic activity of pure SnO$_2$ and SnO$_2$/TiO$_2$ nanocomposites films

The photocatalytic performance of the as-grown films was examined by irradiating them under natural sunlight using the following approach. Pure SnO$_2$ and SnO$_2$/TiO$_2$ nanocomposites based films with square surface area around 1.4 cm$^2$ as catalyst was placed at bottom of speaker with precursor of methylene blue day (50 mL of 30 ppm MB) and the contents stirred in darkness for 30 min for supporting adsorption/desorption equilibrium process. Photodegradation experiment was carried out and done under natural sunlight in the July month between 11 am and 1.30 pm. At constant time intervals 30 min, systematically drawn 5 mL of MB solution and measurable determination of MB dye was estimated via examined the absorption intensity of UV-Visible spectra of samples under UV-Vis spectrophotometer. The photocatalytic efficiency of as-synthesized films is assessed depending on Eq. (1) [5]:

$$\eta = \frac{C_o - C}{C_o} \times 100\%$$

where $\eta$ is the estimated photodegradation efficiency, $C_o$ is the initial concentration of the MB dye and $C$ is the concentration of solution of the MB dye after photodegradation process.

4. Results and Discussion

The topography of the as-synthesized SnO$_2$ and SnO$_2$/TiO$_2$ films are considered using FESEM images. FESEM (Figures 1(a-d)) images show the discriminate formation of pure monodispersed spherical-like SnO$_2$ nanostructure (NS) and agglomerate spherical-like SnO$_2$/TiO$_2$ nanocomposite films. Figures 1(a-b) illustrate the morphology of SnO$_2$ sample, a square-base possess multi-pods-like SnO$_2$ structures. Finally, the SnO$_2$ structures were developed to form the final uniform monodispersed spherical-like SnO$_2$ NSs based film by hydrothermal method at low growth temperature 100 °C. The FESEM image inset in Figure 1(b) presents a high-resolution image of a single SnO$_2$ nanosphere shape.

Furthermore, FESEM images in Figures 1(c-d) display the micrographs of dense SnO$_2$/TiO$_2$ nanocomposite based film. Clearly, the morphology of as-growth sample has completely changed toward agglomerate shape depending mostly on the spherical nanoparticles. Theses FESEM images confirm that the apply mix process of precursor solutions dependent PLAL-H growth technique at 100 °C were successfully approched for the synthesis of SnO$_2$/TiO$_2$ nanocomposite film with specific architecture.
Figure 1. (a-b) shows FESEM images of pure monodispersed spherical-like SnO$_2$ nanostructure (NS) film grown by hydrothermal method, and (c-d) FESEM images of the agglomerate spherical-like SnO$_2$/TiO$_2$ nanocomposite film grown via PLAL-H technique at 100 °C for 4 hrs.

The X-ray diffraction (XRD) measurements of as-prepared SnO$_2$ and SnO$_2$/TiO$_2$ nanocomposite films are shown in the Figure 2 (a,b). Figure (2-a) shows XRD pattern of pure SnO$_2$ film prepared by direct hydrothermal method at 100 °C for 4 hrs. It is evident that the XRD pattern shown several diffraction peaks, where the crystal structure exhibits two phases comprise SnO$_2$ film possesses tetragonal rutile phase (JCPDS file No. 98-005-8477), and tetragonal cell of metallic Sn (JCPDS file No. 01-086-2264). These results indicate that the Sn structure is not totally oxidized at a low-oxidation temperature 100 °C dependent hydrothermal method. This can be attributed to the Sn has very slow oxidation kinetics at low growth temperatures for extended periods of time [13-16].

Furthermore, the XRD pattern in Figure 2(b) displays diverse diffraction peaks of the SnO$_2$/TiO$_2$ film grown by PLAL-H technique at 100 °C for 4 hrs. This XRD pattern demonstrates that the formation of the crystalline structure of SnO$_2$ with tetragonal rutile phase (JCPDS file No. 98-005-8477), Sn tetragonal cell (JCPDS file No. 01-086-2264) as well as very weak XRD peaks corresponding to rutile phase of TiO$_2$ composite (JCPDS file No. 77-0441) [13-15, 17]. Both XRD measurements reveal the distinct crystalline peaks found in both patterns mean that both the produced samples crystallize well, and no further impurities peaks appear, as confirmed in Figures 2 (a, b).
Figure 2. (a) XRD pattern for pure SnO\textsubscript{2} film grown by hydrothermal method and (b) XRD pattern of SnO\textsubscript{2}/TiO\textsubscript{2} nanocomposites film developed via PLAL-H route; Both samples treatment at growth temperature 100 °C for 4 hrs.

To study the optical properties, the photoluminescence (PL) emission spectra of pure SnO\textsubscript{2} and SnO\textsubscript{2}/TiO\textsubscript{2} nanocomposite films are examined at an excitation wavelength of 325 nm as presented in Figures 3 (a,b). Figure 3(a) illustrates the PL spectrum of pure SnO\textsubscript{2} sample, the main PL emission peak is found at around 362 nm in UV region. Moreover, the PL spectrum reveals four distinct emission peaks at 452, 469, 484 and 493 nm in visible (Vis) region. Emissions of bluish-green are ascribed to deep-level defects in the SnO\textsubscript{2} structure, such as oxygen vacancies and single ionization and dual ionization interstitial (Sn) vacancies [18]. In contrast, Figure 3(b) shows the PL spectrum of SnO\textsubscript{2}/TiO\textsubscript{2} nanocomposite film with a single broad emission peak seen in UV region at 371 nm corresponding to the band-to-band transition due to excitation of the valence band electrons to the conduction band [18]. As revealed from the emission spectrum in Figure 3-b, no discrete PL emission peak is detected in the visible region of the SnO\textsubscript{2}/TiO\textsubscript{2} film grown by PLAL-H technique. These results confirm the nanocrystalline character of the as-grown films.

Figure 3. (a) Room-temperature PL spectrum of pure SnO\textsubscript{2} film synthesis by hydrothermal method at 100 °C for 4 hrs, and (b) PL emission spectrum of SnO\textsubscript{2}/TiO\textsubscript{2} nanocomposite films prepared by PLAL-H technique at 100 °C for 4 hrs; under excitation wavelength at 325 nm.
The photoactivity of both samples is evaluated from Figures 4(a,b), which shows that the photodegradation plots of pure SnO$_2$ and SnO$_2$/TiO$_2$ nanostructures based films under solar illumination for various time intervals from 0-150 min. These Figures 4 (a, b) confirm that the as-prepared films are active under natural sunlight irradiation. In both cases, the films under larger time intervals exhibited higher photodegradation efficiency, it is mostly comparable around 21.5 % at irradiation time of 150 min. Irrespective of nanomaterial type and the morphology of each films, these results could be attributed to the special character of each sample, which strongly depends on the surface area, XRD and PL properties of films as explored in this study, which consistent with previous literature [6, 19, 20]. However, this study proves the successful synthesis of SnO$_2$/TiO$_2$ nanocomposite-based film by green-chemistry PLAL-H technique at low growth temperature 100 $^\circ$C, first time to our knowledge. Besides, both pure SnO$_2$ and SnO$_2$/TiO$_2$ films are exhibited actively photocatalytic performance toward MB dye under solar irradiation.

![Figure 4](image.png)

**Figure 4.** UV-Vis absorption spectra show the time-based development of photo-degradation of MB dye under solar illumination; (a) for pure SnO$_2$ film prepared by hydrothermal method at 100 $^\circ$C for 4 hrs, and (b) for SnO$_2$/TiO$_2$ nanocomposite film grown by PLAL-H technique at 100 $^\circ$C for 4 hrs.

### 5. Conclusions

The preparation of pure SnO$_2$ and SnO$_2$/TiO$_2$ nanocomposite films was successfully achieved using two different growth approaches. It involves hydrothermal way and green-chemistry technique dependent combination of pulsed-laser ablation and hydrothermal (PLAL-H) methods at growth temperature 100 $^\circ$C, respectively. Both samples were characterized using FESEM, XRD, PL and UV-Vis spectrometers. From inspections of FESEM images development of uniform monodispersed spherical-like SnO$_2$ NS film, as well as non-uniform agglomerated spherical-like SnO$_2$/TiO$_2$ nanocomposite-based film was realized. XRD patterns of both samples confirm the formation of rutile polycrystalline structures. The PL measurements have been executed to study the optical emission characteristics of as-grown films. The pure SnO$_2$ NS film exhibited five emission peaks in both UV and Visible regions. Whereas, the SnO$_2$/TiO$_2$ nanocomposite film shows a broad single UV emission peak with disappeared any distinguished emission peak in the visible region. Furthermore, depending upon using pure SiO$_2$ NS and SiO$_2$/TiO$_2$ nanocomposite films assessed the photodegradation efficiency of MB dye under solar irradiation was examined. Both films were exhibited similar decolonization efficiency around 21.5% at maximum illumination time 150 min. These findings reveal that the absorption intensity was gradually reduced with the increase of illumination time periods. It
was concluded that every film possesses distinct character related to defects density and their type, and surface area of nanostructure regardless of nanomaterial type, which can play a vital role in the enhancement of the photocatalytic efficiency toward toxic organic dyes.

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