High Efficient and Cost Effective Titanium Doped Tin Dioxide Based Photocatalysts Synthesized via Co-precipitation Approach

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Abstract: High efficient and large surface area of titanium doped tin dioxide (SnO2) based photocatalysts with various titanium doping contents varying from 0 to 4 mol% have been successfully prepared via a facile, low cost and eco-friendly co-precipitation method. Structural, morphological, textural, microstructural and optical properties of the prepared Ti-SnO2 nanoparticles (NPs) have been investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), the Brunauer–Emmett-Teller (BET) method, Raman spectroscopy, Fourier transform infrared (FTIR), UV-Vis spectroscopy and photoluminescence (PL) spectroscopy. It was found that both undoped and Ti doped SnO2 NPs were crystallized in tetragonal structure and the crystallite sizes have been reduced from 19.9 nm to 13.1 nm for SnO2 NPs to 13.1 nm for SnO2: Ti 4%. As compared to pure SnO2, a decrease in size and a uniform distribution of spherical aggregates for 4% Ti doped SnO2 sample have been noticed. Nitrogen (N2) adsorption-desorption isotherms of all synthesized NPs indicate that each nanopowder showed a IV type- isotherm with a hysteresis loop resulted in a typical porous materials containing macropores and mesopores. The raman spectra was marked with the appearance of three well resolved peaks including one intense peak centered at 633 cm−1 and two other peaks at about 475 cm−1 and 772 cm−1 which might be ascribed to the characteristic modes of of the SnO2 rutile-type. FTIR spectra of Ti doped SnO2 NPs show a broad band situated in the region from 630 cm−1 to 625 cm−1 for all Ti-SnO2 samples which could be assigned to the stretching vibrations of Sn–O–Sn. Optical studies revealed that the absorption edge of SnO2: Ti NPs showed a redshift with rising titanium concentration. This redshift resulted in a decrease in the optical band gap from 3.31 eV for pure SnO2 to 2.87 eV for 4% Ti doped SnO2 nanoparticles respectively. Rhodamine B dye (RhB) has been adopted to study the photocatalytic degradation of all synthesized Ti–SnO2 NPs. Pure SnO2 NPs has an intrinsic large band gap and it was sensitive to UV light. Thus, pure SnO2 NPs display higher UV photocatalytic performance for decomposing the RhB. Titanium incorporation into SnO2 has widely improved its photocatalytic performance towards RhB photodegradation under UV and Visible light irradiations. Precisely, the 4% Ti–SnO2 based photocatalyst display the highest photocatalytic activity and can degrade both of 95% and 52% of RhB dye within 120 min respectively under UV and visible light irradiations. The enhanced photocatalytic activity of the 4% doped SnO2 photocatalyst was further proved with the minimum PL intensity. The homogeneous incorporation of low Ti contents into the SnO2 matrix allow to a significant reduce in the band gap leading to an efficient separation of photogenerated electron-hole pairs and consequently improves the absorption capability in the visible light.

Keywords: SnO2; Nanoparticles; co-precipitation; structural properties; morphological properties; optical properties; photocatalysis
1. Introduction

Water is one of the most crucial natural resources on the planet upon which all life depends on by covering over 75% of the earth’s surface. Its distribution is extremely uneven. Only 3% of water located on the surface is fresh. The 97% remaining amount resides in oceans. Almost 69% from this tiny 3% of the fresh water locked up in glaciers and in the icecaps of Antarctica and Greenland and most of the remainder is present as ground water which is not accessible to human use or as soil and moisture. Less than 1% of the world’s fresh water is situated in lakes, rivers and swamps and accessible for direct human use. Looked at another way, only one percent of the water on the earth’s surface is usable by human and 99% of the accessible quantity is located underground. Nowadays, the rapid industrial growth and the worldwide population explosion have resulted in a large escalation of demand for fresh water. In fact, this demand for fresh water has increased tremendously with agricultural, industrial and domestic sectors by consuming 70%, 22% and 8% of the available fresh water respectively. This increase in demand will cause a shortfall of almost 2000 ML of water by 2030. With the booming of dyeing industry and textile, the ever-increasing consumption of fresh water has caused an alarming damage to the environment and seriously threaten the sustainability of human society [1] by releasing of up to 700,000 tons of these dyes in natural water sources every year from industries such as paper making, textile dyeing, plastics, cosmetics, industrial paintings, food processing, leather goods and consumer electronic sectors during the washing cycles and finishing operations due to the inefficiency of the dyeing process [2,3]. More than 15% of these synthetic colorants are discharged into water annually [4]. Unfortunately, the surface water sources are no longer safe and serve as best sinks for the discharge of various toxic industrial dyes which can remain in the environment for an extended period of time due to its high thermal tolerance and photostability to resist biodegradation. In this context, protection of natural water resources and development of new technologies for water remediation and wastewater treatment became a major challenge and key environmental issues of the 21st century. Therefore, the removal of dyes prior to the discharge of wastewater from dye industries is of great deal. Most popular removal techniques of hazardous dyes include physicochemical and biological [5] treatment methods, such as carbon adsorption, flocculation, ozonation, and activated sludge processes, fail to completely destroy dye pollutants, slow, require expensive equipments and can lead to secondary pollution. Recently, semiconductor-based photocatalysis has been developed as an alternative to organic dyes degradation methods [6–8]. As a response, heterogenous photocatalysis has aroused tremendous worldwide attention as a promising technology in the field of green technology for water crisis thanks to its economic feasibility, simplicty, ecofriendly, high efficiency and its ability to break up long chained organic molecules into simpler fragments. Photocatalysis is a catalytic process occurring at the surface of semiconductor materials through the irradiation of photons and widely practiced for the degradation and mineralization of hazardous organic compounds to CO2 and H2O. Thus, it leads to the reduction of toxic metal ions into non-toxic states. In the photocatalytic process, illustrated in Figure 1, the light irradiation on the semiconductor, photocatalyst, causes the excitation of electrons to the conduction band when the reaction was conducted in the presence of water and oxygen. Then, the electron was picked by the oxygen giving rise to superoxide anions radicals and water was oxidized to give hydroxyl radicals in the oxidation site. After that, these radical species strongly react with the organic pollutants leading to the complete mineralization of toxic organic dyes to carbon dioxide and water. Thus, the semiconductor used as photocatalyst is of major interest and must satisfy several requirements. It should be cost effective, safe, stable and efficient. Tin dioxide satisfy all mentioned criteria along with its harmless effect to health since it is poorly absorbed by the human body when injected or inhaled and its availability on earth. Thereby, tin dioxide is widely used as an ideal photocatalyst. However, the application of SnO2 is yet restricted by the fast recombination of the electron-hole pairs. So far, in order to promote the electronic properties and enhance the photocatalytic activity of tin dioxide with upgrading its absorption towards visible region and diminishing the electron-hole
recombination rate, many attempts have been conducted to dope SnO\textsubscript{2} nanoparticles with transition metals such as iron \cite{9,10}, vanadium \cite{11,12}, cobalt \cite{13,14}, nickel \cite{13,15–17}, copper \cite{15}, silver \cite{18}, gold \cite{19} and platinum \cite{20}. Moreover, adding amounts of these dopant species may narrow the band gap of tin dioxide by generation of an impurity level, thus efficiently broaden the light absorption range. As a result, enhanced photocatalytic performance of the doped material could be achieved. In contrast, high doping content can create electron-hole recombination sites and the wide energy band gap hinders this photoactivation. Among these metals, titanium is much inexpensive and has been widely used to improve either the electrical conductivity, the ferromagnetism or the photocatalytic activity of tin dioxide nanostructure. In literature, Liu et al. 2006 \cite{21} have prepared Ti\textsuperscript{4+} doped SnO\textsubscript{2} nano-powders by the sol-gel process. Their reported results show that Ti\textsuperscript{4+} has been successfully incorporated into SnO\textsubscript{2} crystal lattice and the electrical conductivity of the doped material has significantly improved. Also, Sakthiraj et al. 2015 \cite{22} have reported the impact of titanium incorporation on the ferromagnetism of tin dioxide nanocrystals. They have found that the undoped SnO\textsubscript{2} and the 2\% Ti doped SnO\textsubscript{2} samples exhibit perfect room temperature ferromagnetism (RTFM) but 5\% and 7\% of Ti doped SnO\textsubscript{2} samples show weak ferromagnetism with diamagnetic contribution. Recently, Ran et al. 2015 \cite{23} shed the light on the enhanced photocatalytic activity of titanium doped tin dioxide lattice. They have investigated the photocatalytic performance of hollow-structured Ti-doped SnO\textsubscript{2} photocatalysts through the degradation of methylene blue (MB) under UV and visible-light illumination in a photochemical reactor. Their results revealed that hollow-structured Ti-doped SnO\textsubscript{2} spherical specimens displayed improved photocatalytic activity for decomposing MB as compared to that of a pure SnO\textsubscript{2}. The sample prepared with a doping amount of 20 mol\% displayed the highest photocatalytic activity with 92\% MB photocatalytically degraded under UV light irradiation and with 54\% MB photocatalytically decomposed under visible light irradiation within 135 min respectively. The potential poisonous of RhB dye has long been known. Rhodamine B (RhB) is a xantenic dye, shown in Figure 2, widely used as colorant in textile, food industry and as a good water tracer fluorescent \cite{24} due to its high stability. This dye is harmful, carcinogenic, toxic to human beings and animals causing irritation of the skin, eyes, respiratory tract and neurotoxicity \cite{25}. Wang et al. 2020 \cite{26} have recently elaborated the inverse opal tin dioxide via a sol gel route and tested its photocatalytic activity towards the removal of the Rhodamine B under the visible light irradiation. Their published results revealed that the inverse opal SnO\textsubscript{2} showed high photocatalytic performance for the RhB degradation which was 1.4-times greater than that of conventional SnO\textsubscript{2}. To the best of our knowledge, there has been, so far, no research dealing with the photocatalytic performance of titanium doped SnO\textsubscript{2} nanoparticles in Rhodamine B Degradation. Theryby, it has inspired as to synthesize a promising Ti doped SnO\textsubscript{2} photocatalyst via co-precipitation route thanks to its relevant advantages over other methods namely it’s a robust and dependable method, low cost and requires short period of time to prepare nanoparticles. Afterwards, we have deeply investigated the impact of Titanium doping on the structural, morphological and optical properties of tin dioxide. Finally, we have tested and analyzed its photocatalytic activity towards the RhB degradation under UV light and visible light irradiations.
2. Results
2.1. X-Ray Diffraction Analysis

In order to determine the crystal structure and phase composition of SnO$_2$ and Ti-doped SnO$_2$ at various Ti contents ranging from 1% to 4%. The prepared samples were examined by powder X-ray diffraction (XRD). In Figure 3, all the diffractograms have ten peaks located at around $27^\circ$, $33.9^\circ$, $37.9^\circ$, $39^\circ$, $51.6^\circ$, $54.6^\circ$, $57^\circ$, $61.8^\circ$, $64.7^\circ$, and $66^\circ$ which belongs to the (110), (101), (200), (111), (211), (220), (002), (310), (112) and (301) lattice planes of SnO$_2$, respectively. Both pure SnO$_2$ and Ti-doped SnO$_2$ films are of polycrystalline nature and all diffraction peaks match well with those of standard patterns for tetragonal rutile type SnO$_2$ (Joint Committee on Powder Diffraction Standards (JCPDS) no. 41-1445) with point group D$_h$ 414, space group P4$_2$/mnm and lattice constants $a = 4.74$ Å and $c = 3.19$ Å. It can be seen from the XRD patterns, both of (110) and (101) planes have the maximum intensities as compared to other peaks which designate a prominent orientation of the formed NPs. This result fits well with earlier published works concerning SnO$_2$ films doped with various atoms such as V [11,12], Cu [15], Ni [15,27], Zn [28]. No secondary derived peaks corresponding to Titanium oxide or mixed tin oxide (Sn$_2$O$_4$) phase were noted in the XRD patterns which indicates that the titanium doping didn’t affect the preferred orientation and thus maintaining good rutile-type of SnO$_2$ and good crystallinity of SnO$_2$ NPs.
Figure 3. X-ray diffraction of Ti–SnO$_2$ nanoparticles.

It also confirmed that Titanium ions are successfully substituted into SnO$_2$ lattice sites. To get more information about the structural characteristics of the prepared Ti doped SnO$_2$ NPs, we have estimated the average crystallite size $D$ and the lattice parameters $(a = b$ and $c)$ using the basic Debye-Scherer’s formula [11,29] (Equation (1)) and the Equation (2) [11] respectively

$$D = \frac{K\lambda}{\beta \cos \theta}$$

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

with $D$ is the crystalline size (nm), $k$ is a grain shape factor (0.9), $\lambda$ is the wavelength of the incident Cu-K$_\alpha$ beam ($\lambda = 1.54056$ Å), $\theta$ is Bragg’s reflection angle identified in the spectra (in radians), $\beta$ is the full width at half maximum (FWHM) having the highest XRD intensity of the (110) peak and $d$ is the inter-reticular distance and $(hkl)$ are the Miller indices. The results are summarized in Table 1. Consequently, the crystallite sizes have decreased with the addition of titanium doping contents from 19.9 nm for undoped SnO$_2$ NPs to 13.1 nm for SnO$_2$: Ti 4%. The same trend was witnessed with several research groups conducted on doping SnO$_2$ Nanoparticles with Transition metals such as Fe$^{3+}$ [30], V$^{3+}$ [11,12,31], Ni$^{2+}$ [15] Cu$^{2+}$ [15,30], Zn$^{2+}$ [28,30], Zr$^{4+}$ [32] Ti$^{4+}$ [22]. This behavior could be attributed not only to the difference in ionic radius of host and dopant ions but also to the enhancement in the density of nucleation centers in the doped samples, which results in the formation of smaller crystallites. This size decrement of nanocrystals increase the active surface of the nanoparticles and material efficiency. Furthermore, the lattice parameters $(a$ and $c$) have slightly increased after Ti doping which could be related to the substitution of Sn$^{4+}$ ions (ionic radius = 0.69 Å) by the smaller Ti$^{4+}$ ions (ionic radius = 0.56 Å).
Table 1. Crystallographic data including lattice parameters (a, c) and the average crystallite size of Ti–SnO$_2$ nanopowders.

| Sample         | (hkl)    | d-Spacing (Å) | a = b (Å) | c (Å) | Average Crystallite Size from XRD (nm) |
|----------------|----------|---------------|-----------|-------|---------------------------------------|
| Pure SnO$_2$   | (110)    | 3.346         | 2.641     | 1.764 | 19.9                                  |
|                | (101)    | 3.347         | 2.657     | 1.762 | 14.5                                  |
|                | (211)    | 3.361         | 2.651     | 1.765 | 14                                    |
| SnO$_2$: Ti 1% | (110)    | 3.344         | 2.645     | 1.762 | 14.5                                  |
|                | (101)    | 3.361         | 2.651     | 1.765 | 14                                    |
|                | (211)    | 3.357         | 2.646     | 1.766 | 13.1                                  |

2.2. Morphological Properties

Surface morphology of Nanoparticles is a very crucial tool to investigate its microstructure. The scanning electron micrographs of pure SnO$_2$ and SnO$_2$: Ti 4% nanoparticles are shown in Figure 4. As shown in Figure 4a, undoped SnO$_2$ surface morphology has covered with spherical shapes and marked with the presence of inhomogeneity of large isolated aggregates. Whereas, we have noticed a decrease in size and a uniform distribution of spherical aggregates for 4% Ti doped SnO$_2$ sample showed in Figure 4b. Obviously, Titanium incorporation into SnO$_2$ NPs resulted in more uniform particles, more homogeneous surface and better dispersity. This result is in well agreement with the XRD results. A similar trend was also reached with Divya et al. [15]. The chemical composition and element distribution of the synthesized Ti doped SnO$_2$ samples was examined by EDX analysis and represented in Figures 4c and 5d. EDX spectra confirms the presence of Tin (Sn) and Oxygen (O) in the sample revealing the formation of pure SnO$_2$ nanoparticles. Small portions of chloride (Cl), sodium (Na) and carbon (C) have been observed comes from precursors. The weight percentage and atomicity of Sn and O were found to be 70.23, 28.29 and 24.15, 72.15 for undoped SnO$_2$ and 4% Ti doped SnO$_2$ sample respectively. It is clearly seen in Figure 4d that for Ti doped SnO$_2$ sample, only the peaks corresponding to Sn, O and Ti has been shown. The elemental weight percentage of Sn, O and Ti present in the 4% Ti doped sample are 70.04%, 24.44% 3.9%. The atomicity of these mentioned three elements are 25.44%, 65.86% and 3.65% respectively.
Figure 4. Cont.
Figure 4. FESEM images of the as-prepared samples: (a) Pure SnO₂, (b) SnO₂: Ti 4%. EDAX spectra of: (c) pure SnO₂ NPs, (d) SnO₂: Ti 4%.

Figure 5. Nitrogen adsorption-desorption isotherms of Ti-SnO₂ NPs (a), Pore size distribution of Ti-SnO₂ NPs (b).
2.3. Textural Properties

There is a scientific consensus that the surface area of the photocatalyst has a considerable effect on the degradation of pollutants. Thus, as much this surface area was higher as much its ability to absorb the dye pollutants from the solution was higher. The textural properties of the prepared samples including its microstructure and surface area of the synthesized samples of SnO$_2$:Ti were investigated by the Brunauer-Emmett-Teller (BET) method at 77 K. Nitrogen (N$_2$) adsorption-desorption isotherms are shown in Figure 5a. As depicted in the isotherms, each nanopowder exhibited a type-IV isotherm according to the Brunauer-Deming-Teller classification with a typical type II curve with a hysteresis loop resulted in a typical porous materials containing macropores and mesopores. This type-II hysteresis loop indicating the presence of ink-bottle-like mesopores with narrow necks and wide bodies typical of an aggregated nanoparticles network. As illustrated in the Table 2, the BET surface area has increased with an appropriate increase in titanium doping amount. The obtained values of surface area are 16.12 m$^2$/g, 19.03 m$^2$/g, 23 m$^2$/g and 55.3 m$^2$/g for pure SnO$_2$; SnO$_2$: Ti 1%; SnO$_2$: Ti 2% and SnO$_2$: Ti 4% samples, respectively. Ran et al. [23] has developed a facile infiltration route for synthesizing hollow-structured SnO$_2$ with an adjustable Ti doping content using SiO$_2$ microspheres as hard templates via an improved Stober method. They found that the surface area has increased from 26.2 m$^2$/g for the pure SnO$_2$ sample to 35.6 m$^2$/g for 20% Ti-doped SnO$_2$ sample respectively. Consequently, the large specific surface area of Ti doped SnO$_2$ NPs can facilitate the electron transfer and provide a sufficient amount of interface for photocatalysis reactions, which leads to an enhanced photocatalytic activity [33]. All measured values of pore volume and pore size were shown in Figure 5b illustrated in Table 2. Titanium doping has resulted in an increase in both of pore volume and average pore size. The highest values were evaluated to be 0.3241 (cm$^3$/g) for pore volume 2.5 nm for average pore size obtained with a proper titanium amount fixed at 4%. Titanium incorporation has led to an increase in BET surface area, pore volume and pore size. As a result, an improvement in the photocatalytic activity could be expected for Ti-SnO$_2$ nanopowders due to their higher surface area as compared to the undoped one.

Table 2. Nitrogen sorption, porosimetry data and band gap energies of Ti-SnO$_2$ NPs.

| Samples       | Specific Surface Area (m$^2$/g) | Pore Volume (cm$^3$/g) | Average Pore Size (nm) | Band Gap [eV] |
|---------------|---------------------------------|------------------------|------------------------|---------------|
| pure SnO$_2$  | 16.12                           | 0.1274                 | 2.06                   | 3.31          |
| SnO$_2$:Ti 1% | 19.03                           | 0.1428                 | 2.09                   | 3.16          |
| SnO$_2$:Ti 2% | 23                              | 0.2161                 | 2.15                   | 3.01          |
| SnO$_2$:Ti 4% | 55.3                            | 0.3241                 | 2.5                    | 2.87          |

2.4. Raman Analysis

To further study the crystallinity and the effect of Ti incorporation into SnO$_2$ tetragonal structure, raman spectra of Ti-SnO$_2$ NPs were performed in Figure 6. The raman spectra was marked with the presence of three distinguished peaks including one intense peak centred at 633 cm$^{-1}$ and two other peaks at about 475 cm$^{-1}$ and 772 cm$^{-1}$. These three well resolved peaks might be ascribed to the characteristic modes of rutile-type SnO$_2$ lattice [34]. Thus, the intense peak could be attributed to A$_{1g}$ mode resulted from symmetric Sn–O stretching. The other two peaks located at 475 cm$^{-1}$ and 772 cm$^{-1}$ are assigned to the Eg translational mode originated from the vibration of oxygen in the oxygen plane [35] and B$_{2g}$ mode which could be attributed to the expansion and contraction of the vibrating mode of Sn–O bonds (asymmetric Sn–O stretching) respectively. Titanium incorporation into SnO$_2$ crystal lattice doesn’t lead to get appeared another peaks but the well resolved three peaks get small shifting in frequency, widening and intensity get decreased in the Ti–SnO$_2$ sample. This trend might be ascribed to the disorder induced defects or oxygen vacancies and crystal lattice distortion [35]. These results are consistent with those reported in [12,36,37].
2.5. FTIR Analysis

In order to investigate the functional groups of elaborated nanoparticles, the chemical structures of Ti doped SnO$_2$ were characterized through FTIR spectroscopy. Figure 7 displays the FTIR spectra of pure SnO$_2$ and Ti doped SnO$_2$ NPs. The spectra show a broad band in the region of 630 cm$^{-1}$–625 cm$^{-1}$ for all Ti–SnO$_2$ samples which could be assigned to the stretching vibrations of Sn–O–Sn [38,39]. A small shift was detected toward lower wavenumbers position of O–Sn–O peak from 632.5 cm$^{-1}$ in pure tin oxide to 618 cm$^{-1}$ for the sample prepared with 4% Ti doping content. Sujatha et al. has reported the same trend and they attributed this shift to lower wavenumbers in Zn doped SnO$_2$ nanoparticles to the decrease of nanoparticles size [40].
oxide and SnO$_2$: Ti NPs at different Titanium doping levels in the wavelength range of 200 nm–1000 nm. A sharp absorption edge occurred at around 400 nm was clearly noticed which could be ascribed to the intrinsic band gap absorption of SnO$_2$ [11]. Titanium ions incorporation into SnO$_2$ nanoparticles extends the absorption edge to the visible region. Therefore, the edges of the absorption bands show a redshift when the Titanium doping level rises from 0 to 4%. This behavior is mainly attributed to the narrower band gap caused by the evolution of the electronic transition between the two components and results in an increase in photon harvesting and photo-responsive.

![Figure 8. UV-vis spectra of Ti-SnO$_2$ NPs (a). Plots of $(\alpha h\nu)^2$ versus $h\nu$ of Ti-SnO$_2$ NPs (b).](image)

The band gap energies of Ti-SnO$_2$ NPs were determined using Tauc-Lorentz approach through the expression (Equation (3)) [41]:

$$\alpha h\nu = A(h\nu - E_g)^n$$  \hspace{1cm} (3)
where $\alpha$ is a linear absorption coefficient of the sample, $hv$ is the incident photon energy ($h$ is Planck’s constant and $\nu$ is the light frequency), and $A$ is a constant. $E_g$ is an optical band gap and $n$ is the parameter according to the nature of the semiconductor. $n$ is a constant which determines the type of optical transition, for direct transition $n = 1/2$. SnO$_2$ possesses direct transition so the exponent $n$ was chosen to be 1/2.

A plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) and the intercept of tangent to the X-axis gives the band gap. Tauc plots of Titanium doped SnO$_2$ NPs are shown in Figure 8b. The estimated band gap values of all synthesized samples are listed in Table 2. The band gap energies were narrowed from 3.31 eV for pure SnO$_2$ to 2.87 eV for 4% Ti–SnO$_2$ NPs respectively. Titanium incorporation into SnO$_2$ NPs has led to reduced band gap energy. It would be expected that the sample with lower band gap should show higher photo catalytic activity than other samples. A similar trend was previously reported by Sakthiraj et al. [22]. They ascribed the decrement in energy band gap after titanium incorporation into sol-gel prepared SnO$_2$ NPs to the basis sp-d exchange interaction between the band electrons and the localized d electrons of Ti$^{4+}$ ions replacing Sn$^{4+}$ ions in SnO$_2$ semiconducting host lattice. Thus, due to the increase of Ti$^{4+}$ ions donor energy levels in the SnO$_2$ band gaps would be shortened. Ran et al. [23] has found the same trend of narrowed band gap after adjustable Ti addition into Stober route synthesized hollow-structured SnO$_2$. Therefore, they have concluded that Ti incorporation has resulted in a transition in responsiveness of light from UV to visible light in Ti-doped SnO$_2$ samples. Other reported works studying the effect of other dopants into optical properties of SnO$_2$ Lattice and they have found the same behaviour of band gap redshift such as Ben Soltan et al. [42]. They ascribed the band gap decrement after Zn incorporation into polyol elaborated SnO$_2$ NPs to the melting of an impurity band into the conduction band, thus yielding to reducing the width of the band and to the presence of Zn$^{2+}$ in the Sn$^{4+}$ cation sites in the host matrix. Also, the same trend was noticed with Letifi et al. [11] when they doping tin oxide with vanadium. Wherein, the band gap reduction (red-shift) was rationalized on the basis of s–d and p–d exchange interactions between the band electrons of tin dioxide and the localized d electrons of the transition metal ions substituting Sn$^{4+}$ ions.

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2.7. Photocatalytic Activity of Nanostructured Ti–SnO$_2$ Photocatalysts

Rhodamine B is one of the well known basic dye of the xanthenes class. It has been considered as a virulent organic pollutant widely used in the textile industry and pharmaceutical industries which seriously threaten the environment. Thus, in this work, we have chosen RbB as a target organic pollutant to appraise the photocatalytic efficiency of the prepared Ti–SnO$_2$ NPs under UV and visible light irradiation and tackling to environmental issue. The photocatalytic activities of as prepared Ti–SnO$_2$ photocatalysts were conducted by photodegradation of Rhodamine B RhB dye under UV and visible-light irradiation respectively.

$C/C_0$ was used to describe the degradation efficiency of pure SnO$_2$ and Ti-doped SnO$_2$ nanostructures with $C$ and $C_0$ are RhB concentrations at Time $t$ and 0 respectively.

The changes in concentration of RhB as a function of time in the presence of Ti–SnO$_2$ photocatalysts under UV and visible-light irradiation are displayed in Figure 9. It is evident
that all titanium doped SnO\textsubscript{2} based photocatalysts showed enhanced photocatalytic activity toward the degradation of RhB as compared to pure SnO\textsubscript{2} ones. The degradation of RhB increase with further increase in Titanium doping content from 1% to 4%. Precisely, the 4% Ti–SnO\textsubscript{2} based photocatalyst has the highest photocatalytic activity and can degrade 95% RhB within a degradation time of 120 min under UV irradiation as seen in Figure 9a. This proper content of Titanium doping content 4% yielded also to the highest photocatalytic performance of 52% within a degradation time of 120 min under visible-light irradiation as depicted in Figure 9b. The increase in the RhB photocatalytic decomposition by further increase of titanium doping content from 0 to 4% may be ascribed, at one hand, to the shortening of the band gap leading to more light absorption. It is pertinent to mention here that the band gap shortening was due to the formation of new trapping sites which affects the lifetime of charge by splitting the arrival time of photogenerated electron and hole to reach the surface of photocatalyst and thus electron hole recombination is reducing leading to fast degradation of pollutant dye. At another hand, the interaction between RhB and synthesized Ti doped tin oxide photocatalyst was excellent. Thereby, good adsorption of RhB takes place on the photocatalyst surface. This selective adsorption of dye on the surface of 4% Ti doped SnO\textsubscript{2} would be promised as a green method for water remediation.

Figure 9. Plots of (C/C\textsubscript{0}) versus irradiation time (t) for pure and Ti doped SnO\textsubscript{2} nanoparticles under (a) UV light and (b) visible light.
The degradation of dyes can be attributed to a pseudo-first-order reaction with a simplified Langmuir-Hinshelwood model represented in the following equation (Equation (4))

\[ k \times t = \ln \frac{C}{C_0} \]  

where \( C \) and \( C_0 \) are the amounts of dye degradation (mg.L\(^{-1}\)) at equilibrium and at time \( t \) (min) respectively. \( k \) is the rate constant of first order reaction (min\(^{-1}\)). The measured values of first order kinetics \( k \) were shown in Figure 10 and summarized in Table 3.

![Figure 10](image_url)

**Figure 10.** Plots of \( \ln (C/C_0) \) as a function of the irradiation time for Ti–SnO\(_2\) based photocatalysts (a) under UV irradiation and (b) under visible irradiation.
Table 3. Apparent constant rates (K_{app}) for the degradation of RhB for Ti–SnO$_2$ NPs under UV and Visible light irradiations.

| Sample           | $K_{app}$ (min$^{-1}$)$_{d1}$ | $K_{app}$ (min$^{-1}$)$_{d2}$ |
|------------------|------------------------------|------------------------------|
| Pure SnO$_2$     | 0.011                        | 0.0002                       |
| SnO$_2$: Ti 1%   | 0.022                        | 0.004                        |
| SnO$_2$: Ti 2%   | 0.031                        | 0.005                        |
| SnO$_2$: Ti 4%   | 0.04                         | 0.0057                       |

$K_{app}$ (min$^{-1}$)$_{d1}$: value of apparent constant rate $K_{app}$ under UV light. $K_{app}$ (min$^{-1}$)$_{d2}$: value of apparent constant rate $K_{app}$ under Visible light.

These measured kinetic rate constants of Ti–SnO$_2$ based photocatalysts prepared with various Ti Doping content respect the following order: 4% Ti–SnO$_2$ (0.04 min$^{-1}$) > 2% Ti–SnO$_2$ (0.031 min$^{-1}$) > 1% Ti–SnO$_2$ (0.022 min$^{-1}$) > SnO$_2$ (0.011 min$^{-1}$). It is evident that the 4% Ti–SnO$_2$ photocatalyst displays the highest rate constant around 0.04 min$^{-1}$ recorded under UV irradiation. The same trend for the kinetic rate constants was also noticed under visible light for Ti doped SnO$_2$ based photocatalysts and obey to the following order: 4% Ti–SnO$_2$ (0.0057 min$^{-1}$) > 2% Ti–SnO$_2$ (0.0055 min$^{-1}$) > 1% Ti–SnO$_2$ (0.004 min$^{-1}$) > SnO$_2$ (0.0002 min$^{-1}$). The 4% doped tin oxide photocatalyst was the high efficient photocatalyst by showing the highest photocatalytic activity and highest kinetic rate constants under UV and visible light irradiations. Thereby, the homogeneous Titanium doping into SnO$_2$ matrix hinders the recombination of electron-hole pairs and extends the absorption edge into the visible light region. The enhanced photocatalytic activity of Ti-doped SnO$_2$ photocatalysts could be arised from the small size of Ti–SnO$_2$ NPs, large surface area along with the high rate of e-hole separation.

Under light irradiation exposure, the electrons were excited from the valence band to the conduction band yielding to electron-hole pairs. These photogenerated charge carriers migrate to the surface and react with adsorbed molecules of RhB. However, during the migration process, many electrons and holes may recombine leading to decreased photocatalytic efficiency. That is the case of pure SnO$_2$. Since, its band gap energy was estimated to be 3.31 eV so its optical response was limited in the UV light range. As a result, its application in photocatalysis was only restricted to the UV region. Ti doping has improved the photoreactivity of SnO$_2$ by providing electron traps and thus reducing the electron-hole recombination rate. In our work, the titanium incorporation into the SnO$_2$ matrix enhance the photocatalytic efficiency of SnO$_2$. This improvement was due thanks to the extended absorption edge from the UV region to the visible light region and resulted in narrowed band gap of Ti–SnO$_2$ samples. This band gap shortening effiently decrease the recombination rate of photogenerated e-h pairs and allowing more photons to be absorbed. Titanium doping generates allowed energy levels in the band gap of SnO$_2$ creating photoactive transitions due to excitation of an electron from these energy states to the SnO$_2$ conduction band. The photocatalysis mechanism of Ti–SnO$_2$ based photocatalysts under visible light was shown in Figure 11.
In this process, photogenerated electrons can be capped by dissolved oxygen molecules (O$_2$) on or near the surface’s photocatalyst yielding to a superoxide radical anion (O$_2^-$) and hydrogen peroxide (H$_2$O$_2$). The formed O$_2^-$ might either directly oxidize RhB or yield hydroxyl radicals (·OH) by reacting with hydrogen ions (H$^+$) and photogenerated electrons (e$_{CB}^-$). Photoinduced holes (h$_{VB}^+$) in the valence band can be trapped by OH$^-$ or H$_2$O species adsorbed on the surface of the catalyst to further generate reactive ·OH species, which is an extremely strong oxidizing agent for the partial or complete decomposition of RhB molecules. With a lower Ti dopant concentration (<4%), Ti doping was helpful for trapping photogenerated electrons so as to limit charge recombination, which is one of the main factors determining the photocatalytic activity of SnO$_2$. Therefore, electron-hole pairs are efficiently prevented from recombination by the large electric field. It results in the generation of more e$^-$ and h$^+$ pairs characterized with high life time thereby enhancing the photocatalytic activity of Ti-SnO$_2$ catalysts for decomposing RhB pollutants under.

We proceed to PL emission spectra of Ti-doped SnO$_2$ NPs to illustrate the recombination rate of photoexcited electrons and holes, as depicted in Figure 12. It is obvious that all Ti-doped SnO$_2$ NPs reveal lower PL emission intensity than that of pure SnO$_2$ sample, indicating the enhanced rate of electron-hole pairs separation. Consequently, the recombination of photoexcited electrons and holes in Ti-doped SnO$_2$ based photocatalysts is efficiently hindered. Therefore, the efficient separation of electron-hole pairs was highly recommended for improvement of the photocatalytic activity of Ti-doped SnO$_2$ photocatalysts.
In order to confirm the efficiency of SnO$_2$: Ti photocatalysts in the treatment of dangerous pollutants, the mineralization of RhB organic molecules was evaluated from the total organic carbon (TOC). The results of the total organic carbon (TOC) study were presented in Figure 13. Under UV irradiation, the mineralization rates reach 60% for pure SnO$_2$, 80% for SnO$_2$: Ti 1%, 95.4% for SnO$_2$: Ti 2% and 97% for SnO$_2$: Ti 4% respectively after 120 min of treatment as depicted in Figure 13a. These results show the role of titanium doping in the improvement of the RhB mineralization. Under Visible irradiation, we have also noticed an improvement in the RhB mineralization rate with increasing the titanium amount but the mineralization values have only reached 10%, 18%, 25% and 38% for pure SnO$_2$, SnO$_2$: Ti 1%, SnO$_2$: 2% and SnO$_2$: Ti 4% respectively after 120 min, as shown in Figure 13b. It could be concluded that the mineralization of RhB under visible irradiation was slower and requires more time than that tested under UV light irradiation.
Figure 13. Bar diagram for the degradation rate of rhodamine B dye (TOC) in the presence of SnO2: Ti photocatalysts (a) Under UV irradiation and (b) under visible exposure.

3. Experimental Details

All reagents were analytical grade and used without any further purification.

3.1. Preparation of Pure and Ti Doped SnO2 Nanoparticles

Ti doped SnO2 nanoparticles (Ti: 0–4 mol%) have been prepared via the chemical co-precipitation approach. In this procedure, 0.1 M of tin chloride dihydrate (SnCl2 2H2O, 99.99%) was dissolved in a fixed volume of ultra-pure water followed by stirring for 1 h. Then, various amounts of Titanium Isopropoxide corresponding to 0, 1, 2, and 4 (mol%) have been added under vigorous stirring for 1 h. The pH of the above solution was adjusted
by adding drop wise from ammonia aqueous solution until its pH reached a value of 9. Afterwards, the as prepared solution was heated at 80 °C for 4 h. After cooling at room temperature, centrifugation was used to separate the obtained precipitates. The latter was washed with ethanol (C₂H₅OH) and ultra-pure water so many times in order to remove the residual impurities. Next, the resulting products were dried for 12 h at 80 °C. In order to get crystallized products, the obtained powders have been grounded using a mortar and finally get calcined for 4 h at 600 °C. The Flow process chart for the synthesis of SnO₂: Ti NPs was illustrated in Figure 14.

![Flow process chart for the synthesis of Ti-SnO2 NPs.](image)

**Figure 14.** Flow process chart for the synthesis of Ti-SnO2 NPs.

### 3.2. Samples Characterization

The X-Ray Diffraction (XRD) analysis of the samples was evaluated at room temperature using the Shimadzu Lab XRD-6000 (Shimadzu, Kyoto, Japan) with Cu Kα radiation of 1.54 Å and a secondary monochromator. The XRD tube was operated at a voltage of 30 kV and a current of 30 mA in the 2θ range from 20° to 80°. The surface morphology of all samples was studied using the scanning electron microscopy (SEM, JEOL JSM-6700, JEOL Ltd., Tokyo, Japan) operating at 15 KV and equipped with an energy-dispersive X-ray instrument (EDX) for the elemental analysis. The surface area and porosity analysis of the sample were obtained by nitrogen adsorption-desorption at 196 °C on an ASAP 2000 apparatus (Micromeritics). The specific surface area was evaluated by the Brunauer-Emmett-Teller (BET) model, while the pore size distributions were evaluated by the Barrett-Joyner-Halenda (BJH) model applied to the adsorption branch of the isotherms. Raman spectra were recorded using a Horiba LabRam HR Evolution (Horiba Ltd., Irvine, CA, USA). The Fourier-transform infrared (FT-IR) spectra of pure and Ti doped SnO₂ were measured at room temperature using the Bruker FT-IR IFS 66 spectrophotometer (Bruker, Billerica, MA, USA) over the range of 400–4000 cm⁻¹. The photo-luminescence (PL) measurements were determined by Perkin Elmer-LS45 spectrofluorimeter (PerkinElmer, Waltham, MA, USA) with an excitation wavelength of 300 nm. Diffuse reflectance UV visible spectra were performed using a Schimadzu UV-3101 PC spectrophotometer (Shimadzu, Kyoto, Japan) in the wavelength range of 200–800 nm. The absorption spectra were monitored with Perkin Elmer Lambda UV/Vis 950 spectrophotometer (PerkinElmer, Waltham, MA, USA) using a quartz cuvette, with an optical path length of 1 cm, in the range of 400 nm and 800 nm during the photodegradation process.
3.3. Photocatalytic Performance

The photocatalytic degradation of RhB aqueous solution was performed in the presence of Ti-SnO$_2$ based photocatalysts. Typically, 50 mg of the prepared sample was dipped in 10 mgL$^{-1}$ of RhB. The mixture was illuminated with a 125 W high pressure mercury lamp (Philips, HPL-N 125 W/542 E27, Philips, Amsterdam, The Netherlands), emitting UV light ($\lambda = 365$ nm) and 350 W Xe lamp emitting visible light ($\lambda \geq 400$ nm) for 2 h with cutting off the UV light via the L39 UV optical filter and collected at regular time intervals during irradiation to get the measurements of the photocatalytic degradation. The concentration of RhB was estimated by recording its absorbance at a wavelength of 554 nm using a UV-Vis spectrophotometer (Perkin Elmer Lambda UV/Vis 950) for the determination of the photodegradation efficiency. Before applying the irradiation, the suspension was magnetically stirred for 30 min in the dark to ensure that an adsorption-desorption equilibrium between the photocatalyst powders and the aqueous dye solution was reached. During the experiment, 5 mL of sample suspension was picked from the cell at certain time intervals and the photocatalyst powder was separated with filtration. The residual RhB concentration was analyzed with UV-Vis spectrophotometer (Perkin Elmer Lambda UV/Vis 950) at 554 nm. The $C/C_0$ is used to illustrate the degradation rate of RhB, where $C$ is the RhB concentration at each experimental interval, and $C_0$ is the initial concentration after reaching the adsorption/desorption equilibrium.

4. Conclusions

Pure and Ti–SnO$_2$ photocatalysts with adjustable band gap structure, high surface area and visible light photocatalytic activity have been successfully synthesized via a simple, low cost co-precipitation method. In view of structure, we have distinguished that the crystal structure of tin dioxide has been conserved and no other peaks referring to titanium oxide have found which revealing that Titanium were well incorporated into tin oxide lattice. Furthermore, the size of nanoparticles was decreased with rising the Titanium content while the BET surface area, pore volume and pore size have increased which had effectively induced a transition in its sensitivity to light from the UV region to the visible region and greatly inhibits the recombination of electron–hole pairs in SnO$_2$ and plays an essential role in improving the photocatalytic activity of Ti-doped SnO$_2$ NPs. An optimal doping concentration of Ti about 4% was sufficient to photocatalytically decompose 95% of RhB dye under UV light and 52% RhB under visible light within 120 min respectively. The large specific surface area of this proper content of titanium fixed at 4% can urge electron transfer and provide a sufficient amount of interface for photocatalysis reactions, which results in enhanced photocatalytic activity. The 4% Ti SnO$_2$ nanoparticles exhibit excellent degradation efficiency under UV light and visible light due to the large surface area, excellent absorption of light, and the ability to create electron-hole pairs with a long lifetime. Thereby, Ti doped SnO$_2$ nanoparticles including distinct morphologies have appeared as best candidates for water remediation.

Author Contributions: The wide majority of the work has been carried out by H.L. (Unité de Recherche Electrochimie, Matériaux et Environnement (UREME), Université de Gabès, Faculté des sciences de Gabès, Tunis, Tunisia) under the direction of S.A., Faculty of sciences of Gabès, co-supervised by both of Y.L. Laboratory of Nanomaterials and Systems for Renewable Energies (LaNSER) and D.D. in Laboratory of nanomaterials and systems for renewable energies who played essential roles of counselling during the research works and the redaction phase respectively S.A., W.D. and R.C. have essential roles in the results discussion. All authors have read and agreed to the published version of the manuscript.

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