Facile Synthesis of SnO$_2$/LaFeO$_{3-x}$N$_x$ Composite: Photocatalytic Activity and Gas Sensing Performance

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Abstract: Here SnO$_2$/LaFeO$_{3-x}$N$_x$ composite was fabricated using a wet chemical method and was applied to pollutants degradation and gas sensing for the first time. The composite exhibits high performance for photocatalytic degradation of Rhodamine B (RhB) dye and selectivity sensing of various gases. On the basis of the completed experiments, the improved RhB degradation and selective gas sensing performance resulted from the extended optical absorption via N$_2$ incorporated surface states and enhanced charge separation via coupling SnO$_2$. Using the scavengers trapping experiments, the superoxide radical (O$_2$•$^-$) was investigated as the major scavenger involved in the degradation of RhB over SnO$_2$/LaFeO$_{3-x}$N$_x$ composite. In this paper, the probable reaction steps involved in the RhB dye degradation over SnO$_2$/LaFeO$_{3-x}$N$_x$ composite are proposed. This work will provide reasonable strategies to fabricate LaFeO$_3$-based proficient and stable catalysts for environmental purification. In addition, the result of the selectivity of gas performance is also presented.

Keywords: LaFeO$_3$-$x$N$_x$; RhB degradation; charge separation; gas sensing

1. Introduction

The degradation of various toxic, organic pollutants via semiconducting nanomaterials with the assistance of solar energy offers a hygienic and environmentally friendly method [1]. However, the detection and monitoring of highly toxic and flammable exhaust gases such as NO$_2$, SO$_2$, H$_2$, and CO are vital for environmental remediation [2–4]. Semiconductor photocatalysts and gas sensors are widely employed for various pollutants oxidation and gas sensing in domestic and industrial surroundings because semiconductor metal oxides are ideal photocatalysts and gas sensors [5–7]. The design of low-cost, robust, and low-power-consuming semiconductor photocatalysts and gas sensors have attracted increasing attention due to their wide range of applications [8,9]. Research has focused on finding appropriate semiconducting nanomaterials with vital surface and bulk properties for high activity, sensitivity, and selectivity [10,11]. Among various metal oxide semiconductors, perovskite-type oxides have been given tremendous attention owing to their prospective applications in advanced technologies like chemical sensors, catalysts, solid oxide fuel cells, and magnetic materials [12]. The Lanthanum Ferrite (LaFeO$_3$) perovskite ($E_g = 2.0$–$2.8$ eV) has been widely utilized in photocatalysis and gas sensing [13,14]. Yet, the performance of bare LaFeO$_3$ is not sufficient for efficient photocatalysis and gas sensing owing to the short lifetime of photo-induced charge carriers [15]. To improve its performance, doping elements and heterojunctions with other semiconductors are widely used [16,17]. SnO$_2$ is widely accepted as the best choice for gas sensing and pollutants degradation. Doping elements can greatly alter the surface states of nanomaterials, and coupling metal oxides can enhance charge separation thereby enhancing its performance for photocatalytic and gas sensing applications [18]. Thus, the unique characteristics of heterojunctions can improve the photocatalytic and gas sensing
performance by promoting the charge carrier’s separation and transfer. For example, Zhang et al. [19] reported the synthesis of novel A- or B-site substituted LaFeO$_3$/silica fiber (SF) composite photocatalysts that showed improved photocatalytic performance for degradation of Methylene blue (MB) dye under visible light irradiation. This enhanced activity was attributed to the synergistic effect caused by the doping which introduced surface states and the coupled silica fiber. Recently, Xu et al. [20] reported LaFeO$_3$/g-C$_3$N$_4$ heterojunctions that showed enhanced activities for H$_2$ evolution and MB degradation under visible light irradiation; these features were attributed to the remarkably enhanced charge carriers separation and transfer by the synergetic effect at the interface of the two components system. According to Armstrong et al. [21], LaFeO$_3$ exhibits high adsorption capacity for NOx surface conversion in comparison with the LaMnO$_3$. This difference was ascribed to the different B-site cations (Fe$^{3+}$) in LaFeO$_3$ when compared with the LaMnO$_3$ with Mn$^{3+}$ and Mn$^{4+}$ valence states. Toan et al. [22] demonstrated that LaFeO$_3$ films exhibit high sensitivity for sensing of different concentrations of CO, CH$_4$, and NO$_2$ gases in air atmosphere at various temperatures.

It is significant to explore the role of surface active species such as electron (e$^-$), hole (h$^+$), hydroxyl radical (•OH), and the superoxide radical (O$_2$•$^-$) in semiconductor photocatalysis and gas sensing. Primary oxidants (•OH) have no selectivity to organic pollutants. However, the O$_2$•$^-$ radical species generated in the conduction band of semiconductors by the interaction of electron with the adsorbed O$_2$ can oxidize a variety of organic pollutants including dioxins, pesticides, and chlorinated pollutants. The mechanisms of pollutant degradation are strongly influenced by various catalysts and the model pollutants because the designed photocatalyst and the dominant active species decide the degradation mechanism [23,24]. However, the reaction mechanisms of pollutant degradation and gas sensing over a LaFeO$_3$ semiconductor is not fully understood. Thus, it is necessary to develop a clear mechanism for pollutant degradation and gas sensing over a LaFeO$_3$ semiconductor. To date, no works related to the fabrication of SnO$_2$ coupled LaFeO$_3$–XN$_X$ catalyst for RhB dye degradation and gas sensing have been reported.

Here, we report the fabrication SnO$_2$/LaFeO$_3$–XN$_X$ composite for high performance RhB dye degradation and gas sensing. On the basis of completed experiments, results indicate that the improved photocatalytic performance of SnO$_2$/LaFeO$_3$–XN$_X$ for RhB dye degradation and gas sensing is accredited to the extended visible-light absorption via doping N$_2$ and superior charge carrier’s separation via coupling SnO$_2$. Further, it is confirmed by scavenger tapping results that O$_2$•$^-$ radical is the main oxidant species involved the degradation of RhB dye over SnO$_2$/LaFeO$_3$–XN$_X$ composite. This work will trigger the development of LaFeO$_3$-based high performance photocatalysts and gas sensors for environmental remediation and will help the scientific community to understand the surface chemistry of these processes.

**2. Experimental Section**

**2.1. Synthesis of LaFeO$_3$ Nanoparticles**

LaFeO$_3$ was fabricated via a sol–gel technique. In the given experiment, equimolar amount (i.e., 0.04 mol) of La(NO$_3$)$_3$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O was dissolved into 25 mL mixture of ethylene glycol (EG) and water (1:1). The solution was magnetically stirred at room temperature for 4 h to obtain a gel. The gel was dried in oven at 100 °C overnight. Finally, the dry powder was kept in a ceramic crucible and annealed at 600 °C (heating rate = 5 °C min$^{-1}$) in a muffle furnace for 2 h to obtain LaFeO$_3$. All reagents were purchased from Aladdin Company. (Aladdin Reagent (Shanghai) Co., Ltd., Shanghai, China).

**2.2. Synthesis of LaFeO$_{3-X}$N$_X$ Oxynitride**

To prepare LaFeO$_{3-X}$N$_X$ oxynitride, 2 g of the fabricated LaFeO$_3$ was taken in a ceramic boat and kept in a quartz reactor. Next, the quartz reactor was carefully sealed and N$_2$ gas was allowed to pass through a saturated system concentrated with aqueous ammonia solution. The N$_2$ was used as a
carrier gas for transportation of ammonia vapor into the reactor. The ammonolysis reaction was carried out at 500 °C for 6 h. When room temperature attained, the LaFeO$_{3-\chi}$N$_{\chi}$ oxynitride photocatalyst was collected.

2.3. Fabrication of SnO$_2$/LaFeO$_{3-\chi}$N$_{\chi}$ Nanocomposite

To fabricate SnO$_2$ coupled LaFeO$_{3-\chi}$N$_{\chi}$ oxynitride composite (SnO$_2$/LaFeO$_{3-\chi}$N$_{\chi}$), 1 g of LaFeO$_{3-\chi}$N$_{\chi}$ oxynitride catalyst was dispersed into a 50 mL of ethanol and water mixture (1:1). Subsequently, 5% by mass of SnO$_2$ was added to it. After continuous stirring for 6 h, the mixture was dried in an oven at 80 °C overnight. The powder was finally annealed at 450 °C (N$_2$ atmosphere) for 2 h to obtain SnO$_2$/LaFeO$_{3-\chi}$N$_{\chi}$ composite.

2.4. Characterization

The crystalline morphology of the photocatalysts was examined by an X-ray diffractometer (D8-Advance, Bruker Inc., Karlsruhe, Germany). The UV-visible, diffuse reflectance spectroscopy spectra (UV-vis DRS) were obtained with a Perkin Elmer UV/Vis spectrometer (Lambda-35, PerkinElmer Inc.). The scanning electron microscopy (SEM) micrographs and the energy dispersive spectroscopy (EDS) spectra were obtained with a scanning electron microscope (GeminiSEM-300-7112, Carl Zeiss Inc., Dresden, Germany). The elemental chemical composition was examined by the X-ray photoelectron spectrometer (AXIS-ULTRA DLD-600W, Shimadzu Inc., Kyoto, Japan). The photoluminescence (PL) and fluorescence (FL) spectra were obtained with a spectrofluoro-photometer (FP-6500, Spectroscopic Co. Ltd., Kyoto, Japan) at 325 nm excitation wavelength.

2.5. Photoelectrochemical Measurements

For photoelectrochemical (PEC) experiments, the electrode films were prepared in advance by a doctor-blade procedure using a high temperature 3 m 2380 scotch tape as the spacer. In a typical procedure, 25 mg of each photocatalyst was dispersed in 1 mL of isopropyl alcohol and kept under ultrasonic treatment for 30 min followed by magnetic stirring for 30 min. Then, 25 mg of highly ground Macrogol-6000 was added to the photocatalyst solution and the ultrasonic treatment was repeated with magnetic stirring for 30 min each. After that, acetylacetone (0.05 mL) was drop wise added to the solution and vigorously stirred for 48 h. Finally, the product was pasted on thoroughly washed, conductive, fluorine-doped, tin-oxide (FTO) glass substrates (10–15 ohm/sq, Xinyan Tech Ltd., Chengdu, China) and sintered at 450 °C (5 °C min$^{-1}$) for 30 min. The FTO glass substrates were then cut in to 1.0 cm × 3.0 cm pieces containing the film surface area of 1 cm × 1 cm.

2.6. Photoactivity Evaluation

The experiments were performed in a 100 mL volume glass beaker. A 150 W Xe-lamp (GYZ220, CEALIGHT. Inc., Beijing, China) with cut-off filter (420 nm) was used as the irradiation source. During photocatalytic process, 50 mg of the photocatalyst was taken into 40 mL of RhB-dye solution (10 mg/L) and continuously stirred for 10 min to reach the adsorption equilibrium. The solution was kept under visible-light irradiation for 2 h. After regular intervals of 30 min, an appropriate amount of RhB-dye solution was taken with a syringe and centrifuged to measure its concentration with a Perkin Elmer UV/Vis spectrometer (Lambda-35, PerkinElmer Inc.), at characteristic optical absorption of 553 nm.

2.7. Gas Sensing Evaluation

Sample preparation: A Pt interdigital electrode was coated on the alumina substrate by screen printing. After annealing at 800 °C, the Pt interdigitated electrode was firmly adhered to the alumina substrate. The photocatalyst powder was mixed with a small amount of organic binder. The binder was prepared by stirring terpineol and ethyl cellulose in a ratio of 1 g of ethyl cellulose to 10 mL of
SnO$_3$ was successfully integrated into the crystal lattice of LaFeO$_2$ was slightly changed and its particle size was enlarged. The scanning electron microscopy (SEM) micrographs of SnO$_2$ were measured to investigate the absorption behavior of the photocatalysts, as shown in Figure 1B. As seen in Figure 3C, the high resolution XPS spectra of Fe$^{2+}$ reveals the presence of Fe$^{2+}$ splitting of La$^{3+}$ levels. Notably, both of the peaks exhibit a satellite peak at a distance of 4.0 eV and the spin-orbital binding energy peaks at 833.5 and 850.4 eV, respectively, corresponds to the La$^{3+}$ Fe$^{2+}$ bonding reduced the energy band gap of LaFeO$_3$, also appeared in the composite, suggesting the successful formation of heterojunction. In addition, SnO$_2$ coupling did not affect the crystalline phase morphology of LaFeO$_3$. The UV-Visible diffuse reflectance spectra (UV-Vis DRS) were measured to investigate the absorption behavior of the photocatalysts, as shown in Figure 1B. The energy band gaps of LaFeO$_3$ and LaFeO$_3$−X$_N$ photocatalysts were estimated to be 2.0 and 1.84 eV, respectively, based on the energy band gap equation $E_g = 1240/\lambda$. Further, the SnO$_2$ coupling did not affect the energy band gap of LaFeO$_3$. The scanning electron microscopy (SEM) micrographs were obtained to examine the morphology of the photocatalysts. Figure 2A reveals that LaFeO$_3$ nanoparticles have an average crystallite size of about 100 nm and is in accordance with the XRD crystallite size. As seen in Figure 2B, after ammonolysis reaction for 6 h, the morphology of LaFeO$_3$ was slightly changed and its particle size was enlarged. The SEM micrograph of SnO$_2$/LaFeO$_3$−X$_N$ composite, as seen in Figure 2C, shows that the nano-size SnO$_2$ particles are present on the surface of LaFeO$_3$ photocatalyst. The X-ray photoelectron spectroscopy (XPS) spectra were obtained to investigate the chemical composition of the photocatalysts. The binding energies were standardized for specimen charging using C1s as the reference (peak position = 285.0 eV) [28]. The XPS survey spectra of LaFeO$_3$, LaFeO$_3$−X$_N$, and SnO$_2$/LaFeO$_3$−X$_N$ are shown in Figure 3A. From the high resolution XPS of La$^{3+}$ seen in Figure 3B, the binding energy peaks at 833.5 and 850.4 eV, respectively, corresponds to the La$^{3+}$ and La$^{3+}$/Sn$^{2+}$ energy levels. Notably, both of the peaks exhibit a satellite peak at a distance of 4.0 eV and the spin-orbital splitting of La$^{3+}$/Sn$^{2+}$ and La$^{3+}$/Sn$^{2+}$ is about 16.9 eV. This reveals that La$^{3+}$ exists in +3 oxidation state. As seen in Figure 3C, the high resolution XPS spectra of Fe$^{2+}$ reveals the presence of Fe$^{2+}$/Sn$^{2+}$ and Fe$^{2+}$/Sn$^{2+}$ energy levels at 710 and 723.5 eV, respectively. This confirms the existence of Fe$^{2+}$ in +3 oxidation state [29]. As seen in Figure 3D, the high resolution XPS spectra of O1s shows binding...
energy peaks at 529.5 and 531.5 eV, respectively, for lattice oxygen (OL, La–O, and Fe–O bonds), and hydroxyl (OH) one [30]. As seen in Figure 3E, the high resolution Ni L1s XPS spectra for LaFeO3−xNX, and SnO2/LaFeO3−xNX photocatalysts are broad and sited at binding energy of ~399 eV [31,32]. As seen in Figure 3F, the high resolution Sn3d XPS spectra display peaks at binding energies of 486.9 and 495.2 eV, respectively, that correspond to the Sn3d 5/2 and Sn3d 3/2 energy levels in pure SnO2 and SnO2/LaFeO3−xNX photocatalysts [33]. Thus, it is confirmed that N is successfully integrated into the matrix of LaFeO3 and SnO2 is coupled to it.

![Figure 1](image1.png)

**Figure 1.** XRD patterns (A) and UV-Visible diffuse reflectance spectra (B) of LaFeO3, LaFeO3−xNX, SnO2/LaFeO3−xNX, and SnO2 photocatalysts.

![Figure 2](image2.png)

**Figure 2.** Scanning electron microscopy (SEM) images (A–C) of LaFeO3, LaFeO3−xNX, and SnO2/LaFeO3−xNX photocatalysts, and Energy Dispersive X-ray (EDX) spectrum (D) of SnO2/LaFeO3−xNX photocatalyst.
Figure 3. X-ray photoelectron spectroscopy (XPS) survey spectra (A) of LaFeO$_3$, LaFeO$_{3-x}$Nx, SnO$_2$, and SnO$_2$/LaFeO$_{3-x}$Nx photocatalysts, high resolution La3d XPS spectra (B) and Fe2p XPS spectra (C) of LaFeO$_3$, LaFeO$_{3-x}$Nx, and SnO$_2$/LaFeO$_{3-x}$Nx photocatalysts, O1s XPS spectra (D) of LaFeO$_3$, LaFeO$_{3-x}$Nx, SnO$_2$, and SnO$_2$/LaFeO$_{3-x}$Nx photocatalysts, N1s XPS spectra with inset valence band XPS spectra of LaFeO$_3$ and LaFeO$_{3-x}$Nx (E) and Sn3d XPS spectra (F) of LaFeO$_{3-x}$Nx and SnO$_2$/LaFeO$_{3-x}$Nx photocatalysts.

3.2. Photo-Induced Charge Properties

To inspect the photo-induced charge properties of LaFeO$_3$, LaFeO$_{3-x}$Nx, and SnO$_2$/LaFeO$_{3-x}$Nx photocatalysts, photoluminescence (PL) spectra were measured. The PL technique is highly sensitive and is used to explore the surface active sites of semiconductor nanomaterials. From PL spectroscopy, we can obtain knowledge regarding defects in semiconductor surfaces, oxygen vacancies, trapping, immigration, and transfer of charges, [34]. As seen in Figure 4A, LaFeO$_3$ exhibits a strong PL response, which is related to the fast recombination rate of photo-generated charges. Notably, the PL intensity peak of LaFeO$_{3-x}$Nx is remarkably decreased and further decreased after coupling SnO$_2$. This demonstrates that the charge carrier’s recombination in LaFeO$_{3-x}$Nx is considerably reduced. To further investigate the enhanced charge carrier’s separation, photoelectrochemical (PEC) I-V and I-t curves were measured, as shown in Figure 4B,C. LaFeO$_3$ exhibits a low photo-current density signal. Notably, the photo-current density signal of LaFeO$_{3-x}$Nx photocatalyst is obviously improved and that of the SnO$_2$/LaFeO$_{3-x}$Nx photocatalyst is significant. The •OH radical can also provide information about the photo-induced charge carrier’s separation during semiconductor photocatalysis [35]. The strong fluorescence (FL) signal reflects a large amount of the •OH radical and high charge carrier’s separation. Thus, we have detected the •OH amount by the coumarin fluorescent method. In this method, the coumarin react with •OH radical and produce 7-hydroxy-coumarin luminescent species. As shown in Figure 4D, LaFeO$_3$ photocatalyst produced small amount of •OH radical. However, the amount of •OH radical produced over LaFeO$_{3-x}$Nx is remarkably increased and significant for the SnO$_2$/LaFeO$_{3-x}$Nx nanocomposite. This is in agreement with the PL and PEC results, signifying that charge carrier’s separation is remarkably improved.
that the EDTA-2Na and IPA scavengers while sturdily inhibited in the presence of BQ scavenger. This reveals degradation of RhB-dye over SnO$_2$ catalyst addition, the sample was illuminated under visible light for 2 h. Figure 5C shows that the stock) was added to the RhB-dye solution before adding the catalyst and stirred for 15 min. After O• trapping experiments in the presence of Isopropyl-alcohol (IPA, reaction. To confirm which radical species is involved in the reaction process, we carried out scavengers SnO$_2$ for four consecutive recycles (each lasting 3 h). As seen in Figure 5B, the photocatalyst does not show any apparent loss in the activity even after a 12-hour irradiation period. This demonstrates that the photocatalysis \[35\]. The strong fluorescence (FL) signal reflects a large amount of the •OH radical information about the photo-induced charge carrier’s separation during semiconductor.

3.3. Photocatalytic and Gas Sensing Performance

The visible-light activity of the photocatalysts was performed for the RhB-dye degradation and the results are provided in Figure 5A. Notably, LaFeO$_3$ photocatalyst degraded only 31% of RhB-dye beneath visible-light irradiation for 2 h. The degradation of RhB-dye over LaFeO$_3$-XNX photocatalyst is considerably high (i.e., 55%). Interestingly, the degradation of RhB-dye over SnO$_2$/LaFeO$_3$-XNX composite is significant (i.e., 71%), higher than reported thus far under the same experimental conditions as depicted in Table 1. Notably, the improved photocatalytic activity of LaFeO$_3$ photocatalyst for RhB-dye degradation is attributed to the extended optical absorption via doping N and to the enhanced charge carrier’s separation via coupling SnO$_2$. Thus, the designed SnO$_2$/LaFeO$_3$-XNX nanocomposite is favorable in terms of the degradation of organic dye pollutants in comparison with the LaFeO$_3$ and LaFeO$_3$-XNX photocatalysts. To check the stability of SnO$_2$/LaFeO$_3$-XNX photocatalyst for RhB-dye degradation, we carried out photocatalytic stability and recyclability tests under visible-light irradiation for four consecutive recycles (each lasting 3 h). As seen in Figure 5B, the photocatalyst does not show any apparent loss in the activity even after a 12-hour irradiation period. This demonstrates that the SnO$_2$/LaFeO$_3$-XNX photocatalyst is very stable and does not photocorrode during the photocatalytic reaction. To confirm which radical species is involved in the reaction process, we carried out scavengers trapping experiments in the presence of Isopropyl-alcohol (IPA, •OH scavenger), Benzo-quinone (BQ, O$_2^{**}$ scavenger), and EDTA-2Na (h$^+$, scavenger) \[36\]. Appropriate amounts of each scavenger (1 mM stock) was added to the RhB-dye solution before adding the catalyst and stirred for 15 min. After catalyst addition, the sample was illuminated under visible light for 2 h. Figure 5C shows that the degradation of RhB-dye over SnO$_2$/LaFeO$_3$-XNX photocatalyst is slightly suppressed in the presence of EDTA-2Na and IPA scavengers while sturdily inhibited in the presence of BQ scavenger. This reveals that the O$_2^{**}$ radical is the predominant active species involved in the degradation of RhB-dye over SnO$_2$/LaFeO$_3$-XNX photocatalyst, and the role of h$^+$ and •OH is less significant.
For the gas sensing activity, the sensing mechanism of n-type metal oxide semiconductors is normally associated with the space charge region formation on the oxide surfaces, owing to the electron capture on the adsorbed oxygen species [37,38]. Whenever a sensor detects a reactive gas, the gas reacts with the surface oxygen species to release electrons, which are then trapped by the adsorbed oxygen species. As a result, the conductivity of metal oxide increases. The mechanism for p-type metal oxide semiconductors is opposite. Thus, on the basis of the sensing mechanism, the main disadvantage of this type of sensor is its poor selectivity to various gases having the similar (reducing or oxidizing) nature [39,40]. However, the SnO2/LaFeO3−XNX material has different sensing behaviors to the homogeneous gases CO, H2, and SO2, as shown in Figure 5D. The resistance of the sensor material will increase when detecting CO and H2, but decrease when detecting SO2. SO2 commonly presents similar gas sensing behavior with CO and H2 when adsorbed on the surface of metal oxide sensing materials. However, it presented an opposite behavior here, which may contribute to the corrosive effect of SO2. The SO2 adsorbed on the surface of the sensing materials to form the adsorption species SO3 [41], which may cause a change of composition of the sensing material surface. Thus, the sensing behavior and type conductivity may transfer from p-type to n-type dominated. This indicates that the SnO2/LaFeO3−XNX material may be a promising candidate for applications in solving the poor selectivity of these types of sensors to SO2.

Figure 5. Photocatalytic activities for RhB-dye degradation (A) of LaFeO3, LaFeO3−XNX and SnO2/LaFeO3−XNX photocatalysts. Photostability and recyclability test (B) and scavengers trapping experiments for RhB dye degradation (C) of SnO2/LaFeO3−XNX photocatalyst. Gas sensing performance of SnO2/LaFeO3−XNX photocatalyst for 200 ppm of H2, CO, and SO2 gases at 400 °C (D).
with its valence and conduction bands located at 3.54 and 0.04 eV, respectively. Thus, SnO$_2$ photocatalysts are more practical. The fabricated visible-light-responsive nanocomposite can be utilized for the degradation of RhB over SnO$_2$ effectively environmental remediation. The probable stepwise reactions involved in the photocatalytic process are described in Equations (1) to (5).

$$\text{SnO}_2/\text{LaFeO}_3-\chi\text{N}_X + \text{hv} \rightarrow \text{SnO}_2 \text{(No e}^-/\text{h}^+ \text{ pairs)/LaFeO}_3-\chi\text{N}_X (e^- + h^+)} \quad (1)$$

$$\text{SnO}_2 \text{(No e}^-/\text{h}^+ \text{ pairs)/LaFeO}_3-\chi\text{N}_X (e^- + h^+) \rightarrow \text{SnO}_2 (e^-)/\text{LaFeO}_3-\chi\text{N}_X (h^+)} \quad (2)$$

$$\text{SnO}_2 (e^- + \text{O}_2) \rightarrow \text{O}_2\text{•}^- \quad (3)$$

$$\text{SnO}_2 (\text{O}_2\text{•}^- + \text{RhB}) \rightarrow \text{degradation products} \quad (4)$$

$$\text{LaFeO}_3-\chi\text{N}_X (h^+ + \text{RhB}) \rightarrow \text{degradation products} \quad (5)$$

3.4. Discussion

According to the above results, it has been demonstrated that the activity of LaFeO$_3$ photocatalyst for RhB-dye degradation can be greatly improved by doping N and then coupling SnO$_2$. This is a result of the newly formed surface states near the valence band top that effectively traps the photogenerated holes and allows the energetic electrons to transfer to the conduction band of SnO$_2$. To understand the charge transfer mechanism in the fabricated SnO$_2$/LaFeO$_3$-$\chi$N$_X$ composite, we proposed an energy level diagram, as shown in Figure 6. As confirmed by the UV-Visible DRS spectra, the energy band gap of LaFeO$_3$ photocatalyst is 2.0 eV, corresponding to the light absorption of $\lambda \leq 620$ nm according to the energy band gap equation $E_g = 1240/\lambda$ where “$E_g$” is the energy band gap (eV) and “$\lambda$” is the wavelength (nm) of absorbed photons. From the valence band XPS spectra, as seen in Figure 3E inset, the valence band level of LaFeO$_3$ photocatalyst stands at 2.2 eV. After doping N, its band gap is reduced to 1.84 eV through a shift of the valence band upward to 2.04 eV which corresponds to the light absorption of approximately $\lambda \leq 674$ nm. On the other hand, the energy band gap of SnO$_2$ is 3.5 eV with its valence and conduction bands located at 3.54 and 0.04 eV, respectively. Thus, SnO$_2$ can only be excited under UV-light ($\lambda \leq 354$ nm). It is recommended that the photogenerated electrons of LaFeO$_3$ and LaFeO$_3$-$\chi$N$_X$ could be relaxed to their conduction band bottom in a small time scale with energy loss, resulting in the poor charge carrier’s separation and low photocatalytic performance. However, when a heterojunction is formed between SnO$_2$ and LaFeO$_3$-$\chi$N$_X$ photocatalysts and the composite is excited under visible-light, the generated highly energetic electrons of LaFeO$_3$-$\chi$N$_X$ would transfer to the conduction band of SnO$_2$, leaving the excited holes in its valence band. The electrons in the conduction band of SnO$_2$ would probably react with the surface-adsorbed O$_2$ to generate superoxide radicals (O$_2$•$^-$) that will continue the oxidation of RhB-dye pollutant. On the other hand, the holes left in the valence band of LaFeO$_3$-$\chi$N$_X$ would react with the surface adsorbed water and/or OH$^-$ species to produce •OH radicals and then to evolve O$_2$. Thus, the produced active intermediates would take part in the organic pollutants degradation. In this way, the photogenerated charge carrier’s separation will significantly improve. Via this phenomenon, it is simple to make the photocatalytic activity of composite photocatalysts more practical. The fabricated visible-light-responsive nanocomposite can be utilized for effective environmental remediation. The probable stepwise reactions involved in the photocatalytic degradation of RhB over SnO$_2$/LaFeO$_3$-$\chi$N$_X$ composite are described in Equations (1) to (5).
Figure 6. Schematic of the energy band gaps, charge carrier’s transfer and separation, and the photocatalytic processes over SnO$_2$/LaFeO$_{3-x}$N$_x$ photocatalyst under visible-light irradiation.

4. Conclusions

SnO$_2$/LaFeO$_{3-x}$N$_x$ nanocomposite was fabricated via a wet chemical route that exhibited superior visible-light activity for RhB-dye degradation in comparison with the LaFeO$_{3-x}$N$_x$ and LaFeO$_3$ photocatalysts. This is attributable to the extended optical absorption and enhanced photo-induced charge carrier’s separation via N-introduced surface states and the coupled SnO$_2$. This work will trigger reasonable routes for the fabrication of highly efficient visible-light photocatalysts for effective environmental remediation. In addition, the SnO$_2$/LaFeO$_{3-x}$N$_x$ material would be a promising candidate for applications in solving the poor selectivity of this type of sensors.

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