Boron-Doped TiO$_2$-CNT Nanocomposites with Improved Photocatalytic Efficiency toward Photodegradation of Toluene Gas and Photo-Inactivation of Escherichia coli

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Abstract: An in-situ sol-gel method was used for the synthesis of boron-doped TiO$_2$-CNT nanocomposites with varied boron concentrations from 1 to 4 mol%. The synthesized nanocomposites were characterized by various techniques, namely XRD, UV-DRS, TEM, PL, and XPS; all results show that 3 mol% B-TiO$_2$-CNT nanocomposites have superior properties to pure TiO$_2$, 3B-TiO$_2$ nanoparticles, and other nanocomposites. TEM images clearly show the B-TiO$_2$ nanoparticles decorated on the CNT surface. Photo-luminescence studies confirm that boron doping of up to 3 mol% in TiO$_2$-CNT nanocomposites reduces the electron-hole pair recombination rate. The photocatalytic performance of the B-TiO$_2$-CNT nanocomposites was tested against the photodegradation of toluene gas and the photocatalytic inactivation of E. coli in the presence of UV and visible light respectively. B-TiO$_2$-CNT (3 mol%) nanocomposites show the highest photocatalytic activity.

Keywords: B-TiO$_2$-CNT nanocomposites; photocatalysis; UV and visible light; organic pollutants

1. Introduction

The nonstop rise in environmental pollution is responsible for several critical and detrimental global problems. For example, the release of large amounts of toxic dyes into wastewater, as well as the release of toxic environmental gases such as volatile organic compounds (VOCs), are destroying our ecosystem. Another worldwide problem arises from continuous and serious health issues due to infections from microorganisms. Moreover, indoor air quality is increasingly deteriorating because various industries are releasing unpurified VOCs into the environment [1]. It is well known that VOCs are highly toxic and hazardous to human health. This category of compounds includes toluene, xylene, ethylbenzene, and benzene, of which toluene is the most generally known [2,3]. The inhalation of toluene can harm the central nervous system, causing loss of hearing and color vision, as well as the loss of cognitive abilities and muscle memory [4,5]. Therefore, it is necessary to develop effective technology to degrade and eliminate VOCs from the environment. In the literature, the photocatalytic degradation of VOCs has recently attracted considerable attention, as it is considered to be one of the most potent methods for environmental purification [6,7].
Infectious diseases that are caused by pathogenic microorganisms may result in lifelong damage if detection and medical treatment are not managed in a timely fashion [8], and even death of a patient can occur [9]. Pathogenic bacteria, including *Staphylococcus aureus*, *Salmonella enterica*, *Streptococcus pyogenes*, *Streptococcus pneumonia* and *Escherichia coli*, cause serious diseases [10–14] and enjoy an environmentally stable and high production rate. To control these types of infections, many strategies are available, such as heat treatment, UV light irradiation, chemical agents, and a few biological agents, but these strategies are expensive and produce toxic byproducts in the environment.

Photocatalytic inactivation of bacteria has attracted great attention [15]. In particular, TiO$_2$ nanoparticles (NPs) are attractive photocatalysts due to features such as corrosion resistance, low cost, structure, thermal stability, and environmental friendliness [16,17]. The large surface area of TiO$_2$ NPs lends them to applications in various fields, such as degradation of various contaminants [16,18] and oxidative reactions [19,20]. Recently, TiO$_2$ NPs have been applied in water splitting, sensitized solar cells, fuel cells, the paint industry, and cosmetics, as well as in biomedical applications [21,22]. Despite these advantages, TiO$_2$ NPs suffer from some limitations: high bandgap energy pushes photocatalytic activity into the UV region of the electromagnetic spectrum, and a high electron-hole pair recombination rate limits the use of TiO$_2$ NPs in large-scale applications [23].

To surmount these drawbacks, researchers are applying different strategies, like metal doping [24], non-metal doping [25], nanocomposites with metal oxides, carbon nanostructures [26], and noble metal loading [27]. Among these strategies, non-metal doping, using carbon, nitrogen, iodine, boron, sulfur, surface treatment [28], and fabricated nanocomposites with carbon nanotubes (CNT) attracts grate attention. CNTs have an extraordinary property such as charge transmission, electron-conducting, high mechanical strength, hollow layered structure, and large surface. Due to this, it makes an auspicious candidate as dopants and supports various photocatalysts [29]. With these advantages, CNTs also have limitations, the strong van der Waals interactions and the hydrophobicity of CNTs lead to poor dispersion in solvents and this inadequate chemical compatibility highly restricts the variety of applications [30]. To overcome this limitation there is a way to covalent surface functionalization. Surfaces functionalization improve the solubility of CNTs in various solvents to help make hybrid composites with various materials [31,32]. Such as nanocomposites between TiO$_2$ and CNTs improved photocatalytic efficiency. Due to the formation of a heterojunction that reduces the $e^- - h^+$ pair recombination, generates $e^- - h^+$ pairs in presence of a photon, and helps to easy transfer of an electron to the conduction band of TiO$_2$. CNTs play a role as an impurity by forming Ti–O–C or Ti–C defect sites that permit visible light absorption [33]. Recently, boron doping in anatase TiO$_2$ has shown many advantages, since the presence of boron may help weaken the Ti–O bonds, making it easier to replace the oxygen with boron [34,35]. Anatase TiO$_2$ photocatalyst doped with boron exhibits a strong absorption band in the visible region, as well as the separation of electron-hole pairs. Hong et al. [36] doped with boron in an anatase TiO$_2$ host lattice to maximize the visible-light photocatalytic activity. Sopchenski et al. [37] prepared B-doped TiO$_2$ and applied it to the photocatalytic inactivation of *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

Besides, researchers have prepared nanocomposites of TiO$_2$ NPs with CNTs for photodegradation of organic pollutants [38,39]. CNTs improve the optical properties of TiO$_2$ NPs under irradiation with UV and visible light: the non-metal doping enhances the photocatalytic efficiency of TiO$_2$ by shifting the absorption band into the visible light region, and the CNTs provide strong, stable support that reduces nanoparticle agglomeration. Therefore, the present work focuses upon a one-pot synthesis of boron-doped TiO$_2$-CNT nanocomposites and studies their structural, morphological properties, then applies them toward the photocatalytic degradation of toluene gas and the photocatalytic inhibition of *Escherichia coli* (E. coli.)
2. Results and Discussion

2.1. X-ray Diffraction Studies

Figure 1 shows the X-ray diffraction (XRD) patterns of TiO$_2$ NPs, 3B-TiO$_2$, and B-TiO$_2$-CNT nanocomposites. The characteristic peak at 25.3° of anatase TiO$_2$ was observed in pure TiO$_2$ NPs as well as in B-TiO$_2$-CNT nanocomposites, as other peaks at 37.07°, 48.24°, 54.62°, 55.58°, 62.8°, 68.76°, 70.31°, and 75.03°. All peaks matched JCPDS card 21-1272 for anatase TiO$_2$ [40]. Doping with boron and forming nanocomposites with CNT, increases the intensity of XRD diffraction peaks, confirming heterogeneous nucleation between the TiO$_2$ and CNT [41]. The absence of peaks for brookite and rutile TiO$_2$ confirmed the boron doping, and the presence of CNTs did not affect the anatase TiO$_2$ phase. Moreover, the absence of peaks for boron or boron-containing phases confirmed that the boron dopants in TiO$_2$ were highly dispersed [42]. In the doping process, boron replaces the oxygen in the TiO$_2$ lattice, and in calculations at 450 °C, boron occupies interstitial positions in the TiO$_2$ lattice. Due to the very low concentration of CNT, it not showing any peak in the XRD patterns of nanocomposites. The crystallite size of the synthesized nanomaterials was calculated by Scherrer’s formula and is listed in Table 1.

![Figure 1. XRD patterns of TiO$_2$, 3B-TiO$_2$, and B-TiO$_2$-CNT nanocomposites.](image)

Table 1. Crystallite size and optical bandgap of synthesized nanomaterials.

| Samples       | Crystallite Size (D) in nm | Optical Band Gap (Eg) eV |
|---------------|---------------------------|--------------------------|
| TiO$_2$       | 10                        | 3.2                      |
| 3B-TiO$_2$    | 17                        | 2.7                      |
| 1B-TiO$_2$-CNT| 12                        | 3.0                      |
| 2B-TiO$_2$-CNT| 14                        | 2.8                      |
| 3B-TiO$_2$-CNT| 17                        | 2.6                      |
| 4B-TiO$_2$-CNT| 18                        | 2.6                      |

2.2. UV-Vis Diffuse Reflectance Spectroscopy

The influence of boron doping and the presence of CNT on the optical properties of TiO$_2$ NPs is shown in Figure 2a. 3B-TiO$_2$ and B-TiO$_2$-CNT nanocomposite samples show higher absorbance than pure TiO$_2$ NPs in the UV range, and also exhibit an absorption band in the visible range, above 400 nm. Moreover, the significant shift in the absorption edge of the nanocomposites towards higher wavelength confirmed a reduction in the bandgap [43]. A Tauc plot was used to determine the bandgap, as shown in Figure 2b, and values are listed in Table 1. B-TiO$_2$ shows a redshift compared to undoped TiO$_2$ since the p orbital of B is mixed with the 2p orbital of O [44–46]. The literature also reveals that...
non-metal doped TiO$_2$ shows enhanced activity toward visible light by the formation of stable oxygen vacancies on the TiO$_2$ surface [45]. Also, the presence of CNT in nanocomposites helps enhance the photocatalytic efficiency of B-TiO$_2$. Due to the lower Fermi level of CNT as compared to TiO$_2$ NPs, CNT may accept and store photogenerated electrons, as well as enhance the separation of electron-hole pairs [47].

![Figure 2](https://example.com/fig2.png)

**Figure 2.** (a) UV–vis DRS spectra of TiO$_2$, 3B-TiO$_2$, and B-TiO$_2$-CNT nanocomposites; (b) Tauc plots for bandgap energy estimation of TiO$_2$, 3B-TiO$_2$, and B-TiO$_2$-CNT nanocomposites.

2.3. Photoluminescence Analysis

Figure 3 shows the photoluminescence (PL) emission spectra of TiO$_2$, 3B-TiO$_2$, and B-TiO$_2$-CNT nanocomposites. PL analysis yields important information regarding the separation and recombination of electron-hole pairs [48]. For an excitation wavelength of 285 nm, the spectra showed two emission peaks at 400 nm and 464 nm, which can be attributed to emission by free TiO$_2$ excitons and surface Ti–OH bonds, respectively [49]. As shown in Figure 3, the TiO$_2$, 3B-TiO$_2$, 1B-TiO$_2$-CNT, 2B-TiO$_2$-CNT, and 4B-TiO$_2$-CNT samples exhibited high-intensity peaks, while 3B-TiO$_2$-CNT exhibited a low-intensity peak, confirming that 3B-TiO$_2$-CNT has reduced recombination of photogenerated electron-hole pairs and high photocatalytic activity. The peak for 3B-TiO$_2$ NPs shows lower intensity as compared to 1B-TiO$_2$-CNT it confirms the boron doping, as well as CNT, plays an important role in reducing the recombination rate of electron-hole pair and enhancing photocatalytic activity. UV-DRS data Figure 2b shows that the excess doping of boron in TiO$_2$ does not reduce the bandgap of TiO$_2$. Similar phenomena were observed by other researchers and it may be due to excess doping of boron in TiO$_2$ that could result in the aggregation of the particles which affect the optical properties of synthesized nanocomposites [43,50].

![Figure 3](https://example.com/fig3.png)

**Figure 3.** PL spectra of TiO$_2$, 3B-TiO$_2$, and B-TiO$_2$-CNT nanocomposites.
2.4. Transmission Electron Microscopy Analysis

Figure 4 shows transmission electron microscopy (TEM) images of bare TiO$_2$, 3B-TiO$_2$ NPs, 1B-TiO$_2$-CNT, and 3B-TiO$_2$-CNT nanocomposites. From Figure 4a, it is clear that the morphology of the pure TiO$_2$ NPs is spherical, with sizes ranging from 10 to 20 nm and slight agglomeration. Figure 4c shows the same morphologies as TiO$_2$ with slight increases in particle size due to 3 mole% boron doping TiO$_2$, the particle sizes observed in the range from 10 to 30 nm. Figure 4e,g shows TEM images of 1B-TiO$_2$-CNT and 3B-TiO$_2$-CNT respectively. Images clearly show the B-TiO$_2$ NPs decorated on the CNT surface. Confirming that CNT provide support to B-TiO$_2$ NPs, reduces the agglomeration of nanoparticle, and increases the reactive surface area of the nanoparticles to photocatalytic activity [51].

Also, CNT are highly conductive, they permit easy movement of photogenerated electrons within the nanocomposites, improving the optical properties of TiO$_2$ NPs [52,53]. Figure 4b,d,f,h shows lattice fringes for TiO$_2$, 3B-TiO$_2$ NPs, 1B-TiO$_2$-CNT, and 3B-TiO$_2$-CNT nanocomposites respectively. The interplanar distance for TiO$_2$ NPs is 0.35 nm while in the 1B-TiO$_2$-CNT is 0.36 and 3B-TiO$_2$ 0.37 nm it confirms the as the dopant concentration increases particles size increases this may be due to the atomic radius of boron (87 pm) replaces the oxygen (48 pm atomic radius) in the TiO$_2$ lattice. Boron present in TiO$_2$ distorts the lattice and thereby increases the interplanar distance. This same phenomenon was observed in earlier reports [54,55].

![Figure 4. TEM images of (a,b) TiO$_2$, (c,d) 3B-TiO$_2$, (e,f) 1B-TiO$_2$-CNT and (g,h) 3B-TiO$_2$-CNT nanocomposites.](image)

2.5. X-ray Photoelectron Spectroscopy Studies

Figure 5 shows the X-ray photoelectron spectroscopy (XPS) spectra of 3B-TiO$_2$-CNT nanocomposites. Figure 5a shows the survey spectrum which confirms the presence of Ti, O, C, and B elements in the synthesized nanocomposites. Figure 5b, Ti2p configuration, the spectra contain two symmetrical peaks centered at 458.20 eV and 464.01 eV, corresponding to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively, with a binding energy difference of 5.81 eV. It is recognized that the Ti element of nanocomposites exists in the Ti$^{4+}$ oxidation state [34,56]. It is generally found that non-metal doping in TiO$_2$ may be responsible for a change in the oxidation state from Ti$^{4+}$ to Ti$^{3+}$, but in the present research investigation, there is no Ti$^{3+}$ peak, as shown in Figure 5b. The deconvoluted C 1s spectra are shown in Figure 5c. The three intense peaks at 284.64 eV, 286.34 eV, and 288.66 eV are attributed to graphitic carbon (C=C bonds), the C-C bonds of CNT, C-O bonds, and COO$^-$ bonds, respectively [57]. The O 1s spectrum, shown in Figure 5d, contains two main peaks at 529.73 eV and 530.70 eV, which are respectively due to the oxygen in TiO$_2$ and the surface hydroxyl groups present on the surface of TiO$_2$ NPs [58]. Figure 5e shows the deconvoluted B 1s XPS spectrum of 3B-TiO$_2$-CNT nanocomposites, which mainly includes peaks for B-O-B and B-Ti-O bonds, located at 192.14 eV and...
189.66 eV, respectively [59–61]. The peak observed at 192.14 eV confirms that the boron dopant creates a band between the conduction and valence bands of pure TiO₂, and the doped boron interacts with O₂p orbitals of the TiO₂ valence band. Therefore, Ti-O-B may have formed, which would confirm the doping of boron in the TiO₂ host lattice [60].

**Figure 5.** XPS spectra of 3B-TiO₂-CNT nanocomposites (a) survey spectrum (b) Ti 2p, (c) C 1s, (d) O 1s and (e) B 1s configuration.

### 2.6. Photodegradation of Toluene Gas

The photocatalytic degradation of toluene gas, under UV radiation in the presence of TiO₂, 3B-TiO₂ NPs, and B-doped TiO₂-CNT nanocomposites, over a 120 min interval, is shown in Figure 6. Pure TiO₂ NPs show less photocatalytic activity as compared to 3B-TiO₂ and B-TiO₂-CNT nanocomposites. The highest photocatalytic degradation efficiency, obtained for 3B-TiO₂-CNT nanocomposites, was 96%, while pure TiO₂ NPs, 3B-TiO₂, 1B-TiO₂-CNT, 2B-TiO₂-CNT, and 4B-TiO₂-CNT, showed photodegradation efficiencies of 37%, 51%, 76%, 83%, and 93% respectively. The impact of UV light on the photodegradation of toluene gas was studied in an experiment with no catalyst; UV light alone showed photodegradation efficiency of approximately 12%. In synthesized nanocomposites, optimized boron doping, as well as the addition of CNTs, playing a very important role in enhancing photocatalytic efficiency [62].

Pseudo-first-order reaction kinetics were observed for the photodegradation of toluene, as shown in Figure 7. 3B-TiO₂-CNT nanocomposites showed the fastest photodegradation of toluene gas, having a rate constant \( k = 0.02528 \text{ min}^{-1} \), while TiO₂, 3B-TiO₂ NPs, 1B-TiO₂-CNT, 2B-TiO₂-CNT, and 4B-TiO₂-CNT had rate constants of \( k = 0.01950 \text{ min}^{-1} \), \( k = 0.02250 \text{ min}^{-1} \), \( k = 0.02130 \text{ min}^{-1} \), \( k = 0.02170 \) and, \( k = 0.02370 \) respectively. The photodegradation reaction with UV light alone had a rate constant \( k = 0.01490 \text{ min}^{-1} \).
In the photodegradation of toluene gas using B-TiO$_2$-CNT nanocomposites, when UV light irradiated the sample, CNT and boron absorb light and electron excited from CNT goes to the conduction band (CB) of TiO$_2$ while electron excited from valance band (VB) of TiO$_2$ goes to the hole of CNT and boron band [63]. The hole formed in VB of TiO$_2$ reacts with moisture to form hydroxyl radical and electron in CB of TiO$_2$ reacts with oxygen to form superoxide. From the generated ROS, hydroxyl radical reacts with the phenyl ring of toluene to form various intermediates such as phenol, benzaldehyde, benzoic acid, and are finally converted into CO$_2$ and H$_2$O [64]. A possible photocatalytic degradation mechanism is shown in Figure 8.

![Figure 6](image1.png)\[ Figure 6. Photocatalytic degradation of toluene gas under UV light irradiation. \]

![Figure 7](image2.png)\[ Figure 7. The pseudo-first-order kinetics of degradation of toluene gas with a time of UV light irradiation. \]
After every cycle, the catalyst was removed from the Teflon bag and regenerated with heat treatment at 100 °C for 2 h. Then the regenerated catalyst was used again for the photodegradation of toluene. The catalyst was recycled four times, and the results are shown in Figure 9. Only a 4%–5% reduction in photocatalytic activity was observed. This reduction in photodegradation efficiency may be due to the loss of catalyst in the regeneration process as well as in the transfer of catalyst powder from one place to another place. Overall, the experimental results show that the synthesized 3B-TiO$_2$-CNT nanocomposites were used as photocatalysts and irradiated with UV light for 120 min. After every cycle, the catalyst was removed from the Teflon bag and regenerated with heat treatment at 100 °C for 2 h. Then the regenerated catalyst was used again for the photodegradation of toluene. The catalyst was recycled four times, and the results are shown in Figure 9. Only a 4%–5% reduction in photodegradation efficiency was observed. This reduction in photodegradation efficiency may be due to the loss of catalyst in the regeneration process as well as in the transfer of catalyst powder from one place to another place. Overall, the experimental results show that the synthesized 3B-TiO$_2$-CNT photocatalyst was highly stable and exhibited the best photocatalytic activity of all tested compounds up to four cycles.

To determine the stability of the photocatalyst, a recyclability test was performed with the same experimental setup used for the photodegradation of toluene. In this recyclability test, the 3B-TiO$_2$-CNT nanocomposites were used as photocatalysts and irradiated with UV light for 120 min. After every cycle, the catalyst was removed from the Teflon bag and regenerated with heat treatment at 100 °C for 2 h. Then the regenerated catalyst was used again for the photodegradation of toluene. The catalyst was recycled four times, and the results are shown in Figure 9. Only a 4%–5% reduction in photodegradation efficiency was observed. This reduction in photodegradation efficiency may be due to the loss of catalyst in the regeneration process as well as in the transfer of catalyst powder from one place to another place. Overall, the experimental results show that the synthesized 3B-TiO$_2$-CNT photocatalyst was highly stable and exhibited the best photocatalytic activity of all tested compounds up to four cycles.

Figure 8. Possible photocatalytic degradation mechanism of toluene gas with B-TiO$_2$-CNT nanocomposites under UV light.

Figure 9. Recyclability of photocatalyst 3B-TiO$_2$-CNT nanocomposites.

2.7. Photocatalytic Inactivation of Bacteria

The photocatalytic inactivation activity of TiO$_2$, 3B-TiO$_2$, and B-TiO$_2$-CNT nanocomposites was exhibited in the photocatalytic killing effect of *E. coli*, which was determined through a reduction in the number of colonies formed on Mueller–Hinton agar plates. As shown in Figure 10, the *E. coli* were almost entirely inactivated within 240 min by 3B-TiO$_2$-CNT nanocomposites under visible radiation. Neither the photocatalyst by itself nor visible light alone affected the *E. coli* growth, therefore confirming...
that the observed inactivation is attributed to the photocatalytic reaction. The digital photographs of photoinactivation of $E. coli$ with 3B-TiO$_2$-CNT nanocomposite under visible light shown in Figure 11.

![Figure 10](image-url)  
*Figure 10. % survival of $E. coli$ with TiO$_2$, 3B-TiO$_2$ and B-TiO$_2$-CNT nanocomposites as a function of time.*

![Figure 11](image-url)  
*Figure 11. Photographs of photo-inactivation of $E. coli$ under visible light exposure.*

A possible mechanism of photocatalytic inactivation of $E. coli$ is as follows when visible light irritated on B-TiO$_2$-CNT nanocomposites. An electron from the CNT and boron band near to valance band of TiO$_2$ get excited and transferred to the conduction band of TiO$_2$. A hole formed on CNT attracts an electron from the valance band of TiO$_2$ and the hole formed in TiO$_2$ VB reacts with H$_2$O to
form hydroxyl radical. While electron present in CB of TiO$_2$ reacts with oxygen to form superoxide. These formed ROS, especially hydroxyl radicals react with the E. coli cell wall and destruct the bacterial membrane and DNA strand, leading to cell lysis (release of metabolites, protein, and RNA from the cell and at the cell death occurs) [65,66].

3. Materials and Methods

3.1. Materials

Titanium (IV) butoxide and multi-wall carbon nanotubes (MWCNTs) were purchased from (Sigma-Aldrich, Saint Louis, MO, USA). Acetylacetone, boric acid, ethanol, extra pure sodium lauryl sulfate, were purchased from (Duksan, Gyeonggi-do, South Korea), and 10 ppm toluene gas purchased from (Korea Petrochemical Ind Co LTD, Seoul, South Korea).

3.2. Preparation of Boron-Doped TiO$_2$-CNT Nanocomposites

A previously reported sol-gel method [49], with slight modifications, was used to prepare boron-doped TiO$_2$-CNT nanocomposites with varying concentrations of boron from 1 mol% to 4 mol%. A 1:1 proportion of titanium (IV) butoxide to acetylacetone was added to a beaker. To this solution, an aqueous solution of sodium lauryl sulfate (capping agent; 2 wt.%) and excess distilled water were added with continuous stirring. Afterward, a stoichiometric concentration of boron (1 to 4 mol%), as an aqueous boric acid solution, was added, and the solution was vigorously stirred for 1 h at room temperature. Then 0.5 wt. % of CNT in aqueous solution were added. Afterward, the pH was adjusted to 8 with an ammonia solution, and the reaction mixture was stirred at 60 $^\circ$C for 3 h, then allowed to cool to room temperature. The solution was filtered with Whatman filter paper, and the obtained precipitate was washed with ethanol and distilled water. The precipitate was dried in the oven and calcinated at 450 $^\circ$C for 3 h. Pure TiO$_2$ NPs and 3B-TiO$_2$ were synthesized using the same method, omitting the boric acid and CNT respectively. The synthesized nanocomposites were denoted as TiO$_2$, 3B-TiO$_2$ NPs, 1B-TiO$_2$-CNT, 2B-TiO$_2$-CNT, 3B-TiO$_2$-CNT, and 4B-TiO$_2$-CNT, where the number before the B denotes the mol% of B present in the nanocomposites.

3.3. Photodegradation of Toluene Gas

Toluene gas was photodegraded by following a previously reported experimental method [67,68]. In this method, catalyst powder is uniformly spread in a polycarbonate petri dish and this petri dish is inserted into a 2 L Teflon film bag. Afterward, toluene gas with 10 ppm concentration was filled into the bag. adsorption-desorption equilibrium is created by keeping the experimental setup in the dark for 30 min. Then two 6 W UV light tubes, providing a total incident intensity of 2 mW/cm$^2$ were used to irradiate the setup for a fixed time interval, after which 1 mL of toluene gas was withdrawn by syringe. The change in toluene gas concentration was examined using a gas chromatography (GC) system.

3.4. Photo-Inactivation of E. coli

The photocatalytic inhibition of E. coli was studied using a previously reported method [26], as follows. All glassware and samples were sterilized before use. E. coli (NCIM 2066) was cultured on a nutrient agar plate at 37 $^\circ$C for 24 h. A 5 mL saline solution was used to prepare a bacterial suspension with a concentration of 10$^8$ CFU mL$^{-1}$, and the photocatalyst concentration was 2 mg mL$^{-1}$. Photocatalytic inhibition was carried out using TiO$_2$, 3B-TiO$_2$, and B-TiO$_2$-CNT nanocomposites in the dark and under visible light. For visible light studies, a borosilicate glass reactor was illuminated with eight fluorescent tubes (Philips, 8 W, $\lambda > 400$ nm, light intensity ~0.5 mW cm$^{-2}$) [48,69]. At specific time intervals, 100 $\mu$L aliquots of the irradiated bacterial suspension were withdrawn and spread on Mueller-Hinton agar plates. These plates were incubated at 37 $^\circ$C for 24 h. The standard plate count method was used to determine viable numbers of cells in units of CFU mL$^{-1}$ [69].
3.5. Characterization

The synthesized pure nanoparticles and nanocomposites were characterized using various techniques. A Bruker D8 Advance X-ray diffractometer (XRD) with a Cu K-alpha source (\( \lambda = 1.5406 \ \text{Å} \)) (Bruker, Aubrey, TX, USA) was used to study the phase and various structural parameters of the synthesized nanomaterials. A UV-3600 UV-vis spectrophotometer (Shimadzu, Kyoto, Japan) was used to measure the optical properties of the nanomaterials. The effect of the boron doping concentration on the recombination rate of electron-hole pairs was studied by photoluminescence (PL) with a Hitachi F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). Transmission electron microscopy (TEM, Tecnai G2 Spirit TWIN, 120 kV, from FEI, Hillsboro, OR, USA) was used to study the morphological properties of the synthesized nanomaterials. The physical, chemical bonding, and elemental analyses of the nanocomposites were performed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Waltham, MA, USA). The change in toluene gas concentration was determined by gas chromatography (GC, Agilent Technology 7890A, Santa Clara, CA, USA).

4. Conclusions

Boron-doped TiO\(_2\)-CNT nanocomposites were synthesized successfully by the sol-gel method. It was observed that the fabrication of nanocomposites with CNT, coupled with boron doping in TiO\(_2\), positively affected the photocatalytic activity. XRD analysis confirmed that the anatase phase was present in the nanocomposites and yielded a calculated crystallite size of around 10–20 nm for B-TiO\(_2\)-CNT nanocomposites. The uniform decoration of B-TiO\(_2\) nanoparticles on the CNT surface was confirmed by TEM. The slight increase in interplanar spacing confirms the presence of boron in the TiO\(_2\) host lattice. UV-DRS studies show red-shifted absorption bands for the nanocomposites. A qualitative XPS analysis recognized the Ti\(^{4+}\) oxidation state of the elemental Ti in the nanocomposites, as well as the boron doping, which created an intermediate band between the valence and conduction bands of TiO\(_2\). PL study shows that boron doping, as well as CNTs, plays an important role in reducing the recombination rate of electron-hole pair and enhancing photocatalytic efficiency. The photocatalytic activity was tested using toluene gas degradation and photoinactivation of \( E. \ coli \); the results confirmed that the 3B-TiO\(_2\)-CNT nanocomposites had superior photocatalytic efficiency to bare TiO\(_2\), 3B-TiO\(_2\) NPs, 1B-TiO\(_2\)-CNT, 2B-TiO\(_2\)-CNT, and 4B-TiO\(_2\)-CNT. Recyclability studies confirmed that the 3B-TiO\(_2\)-CNT nanocomposites were highly stable after four cycles. Therefore 3B-TiO\(_2\)-CNT well suited for removing organic pollutants from the environment.

Author Contributions: J.-S.K. supervised the work. V.B.K. designed and performed the experiments. S.P.D. performed the antibacterial experiments. V.B.K., A.G.D., and S.-C.K. wrote the manuscript. All authors analyzed the results and reviewed the manuscript. All authors have read and agreed to the published version of the manuscript.

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