Enhanced Photocatalytic Activity and Stability of Bi$_2$WO$_6$–TiO$_2$-N Nanocomposites in the Oxidation of Volatile Pollutants

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Abstract: The development of active and stable photocatalysts for the degradation of volatile organic compounds under visible light is important for efficient light utilization and environmental protection. Titanium dioxide doped with nitrogen is known to have a high activity but it exhibits a relatively low stability due to a gradual degradation of nitrogen species under highly powerful radiation. In this paper, we show that the combination of N-doped TiO$_2$ with bismuth tungstate prevents its degradation during the photocatalytic process and results in a very stable composite photocatalyst. The synthesis of Bi$_2$WO$_6$–TiO$_2$-N nanocomposites is preformed through the hydrothermal treatment of an aqueous medium containing nanocrystalline N-doped TiO$_2$, as well as bismuth (III) nitrate and sodium tungstate followed by drying in air. The effect of the molar ratio between the components on their characteristics and photocatalytic activity is discussed. In addition to an enhanced stability, the composite photocatalysts with a low content of Bi$_2$WO$_6$ also exhibit an enhanced activity that is substantially higher than the activity of individual TiO$_2$-N and Bi$_2$WO$_6$ materials. Thus, the Bi$_2$WO$_6$–TiO$_2$-N composite has the potential as an active and stable photocatalyst for efficient purification of air.

Keywords: photocatalysis; VOC oxidation; UV; visible light; composite photocatalyst; N-doped TiO$_2$; Bi$_2$WO$_6$; stability test

1. Introduction

Photocatalytic oxidation is a convenient method for removing volatile contaminants from air via their complete degradation. TiO$_2$ is the most used photocatalyst for the oxidative degradation of pollutants due to its high activity, stability, and safety for living organisms [1,2]. A high activity of TiO$_2$ results from the positions of its valence band (VB) and conduction band (CB) that are appropriate for the generation of charge carriers with high redox potentials, an extended surface area, and surface chemistry [3,4]. The potentials of photogenerated electrons and holes are high enough for the formation of reactive oxygen species, which can provide oxidative degradation of various types of pollutants [5,6]. The degradation of aromatics, ketones, aldehydes, alcohols, carboxylic acids, alkanes, alkenes, and heterocompounds was investigated and discussed in the previously published papers [7–14]. However, a wide band gap of TiO$_2$ (3.0–3.2 eV) does not allow for efficient utilization of sunlight because TiO$_2$ can absorb radiation with wavelengths shorter than 400 nm (i.e., UV light) that corresponds to less 5% of the total solar light [15]. Room light sources also have a low impact on TiO$_2$ because they emit photons in the visible region of spectrum. Therefore, the development of active and stable photocatalysts, which can efficiently utilize light in a wide range, is important for environmental protection and human safety.
One of the promising photocatalysts for pollutant degradation both under UV and visible light is TiO$_2$ doped with nitrogen [16–19]. Energy levels of nitrogen impurities are located in the band gap of TiO$_2$ above its VB and lead to a reduction in the energy required for the excitation of electrons [20]. The potential of photogenerated holes localized in nitrogen levels is still high enough for the direct oxidation of organic molecules adsorbed on the surface of the photocatalyst [21]. As a result, N-doped TiO$_2$ is able to completely oxidize organic pollutants under radiation with wavelengths up to 500–530 nm and exhibits high values of quantum efficiency [22]. N-doped TiO$_2$ can be prepared using inexpensive inorganic precursors through simple routes that make it significant for practical application [23].

However, the efficiency of light utilization by N-doped TiO$_2$ in the visible region of the spectrum is still far from the corresponding value for the utilization of the UV light attributed to the band-to-band excitation of electrons in TiO$_2$ [19,24]. An increase in the values of quantum efficiency in the visible region is required for better utilization of solar light by this type of photocatalysts. It stimulates further studies on the modification of N-doped TiO$_2$ to enhance its photocatalytic activity. Another aspect of N-doped TiO$_2$ is that a gradual decrease in its visible-light activity occurs under long-term irradiation. This deactivation results from the oxidation of nitrogen species in the TiO$_2$ lattice by the photogenerated holes that do not migrate to the surface of the photocatalyst and do not participate in the redox reactions with adsorbed molecules [25]. Fast transfer of holes from the TiO$_2$ phase may help to prevent the degradation of nitrogen species and deactivation of the photocatalyst.

The surface modification of N-doped TiO$_2$ may solve both the mentioned problems via an enhanced interface transfer of photogenerated charge carriers that would improve their separation and prevent fast recombination. Surface modification with transition metals, especially noble metals, is an efficient way to suppress the recombination of charge carriers [26]. However, this approach commonly affects the pathway of photogenerated electrons only because an interface transfer of electrons from the CB of TiO$_2$ to the metal species occurs in the metal-modified photocatalyst. As a result, the modification with metals leads to an increase in the efficiency of light utilization but it has a low effect on the stability of N-doped TiO$_2$ [27].

Another approach to enhance the separation of charge carriers is the combination of TiO$_2$ with other semiconductors. When two semiconductors are in contact, different types of heterojunctions can occur [28–30]. The type of heterojunction depends on the characteristics of semiconductors that include their band gaps, potentials of VB and CB, and work functions [31,32]. A good cocatalyst for N-doped TiO$_2$ would be a semiconductor with a band gap that is narrower than the band gap of TiO$_2$, while the position of its VB would be close to the VB of TiO$_2$. These parameters would give a possibility to obtain a composite material, which is able to generate holes with a potential high enough for the formation of OH$^-$ species and direct oxidation of organic compounds [4].

Bismuth and tungsten oxides with a band gap of 2.6–2.8 eV correspond to the mentioned requirements [33]. Both type II [34] and S-scheme [35] heterojunctions were proposed for the composite Bi$_2$O$_3$–TiO$_2$ system. Similarly, a heterojunction of type II [36] or Z-scheme [37] was proposed for the WO$_3$–TiO$_2$ composite. An increased photocatalytic activity in all cases was attributed to an enhanced separation of charge carriers due to interface transfer.

Bismuth tungstate (Bi$_2$WO$_6$) is also regarded as one of the promising semiconductors which can enhance the characteristics of TiO$_2$ and N-doped TiO$_2$ on the efficiency of light utilization. Bi$_2$WO$_6$ absorbs light with wavelengths up to 450 nm and has a photocatalytic activity in the oxidation of organic pollutants both under UV and visible light [38]. On the other hand, the potential of photogenerated electrons in Bi$_2$WO$_6$ is not high enough for efficient transfer to oxygen molecules if compared with TiO$_2$-based photocatalysts. As a result, pristine Bi$_2$WO$_6$ does not exhibit superior values of photocatalytic activity in the degradation of pollutants. The composite Bi$_2$WO$_6$–TiO$_2$ photocatalysts was previously
shown to exhibit substantially higher activity than parent semiconductors [39–42]. In contrast to photocatalytic activity, no information concerning the effect of Bi$_2$WO$_6$ on the stability of N-doped TiO$_2$ was found by the authors during the literature review. It was our motivation to perform this study and investigate the stability of Bi$_2$WO$_6$–TiO$_2$-N composites under long-term exposure to powerful radiation.

In this paper, we show the effect of the ratio between Bi$_2$WO$_6$ and N-doped TiO$_2$ components on the activity of the composite system and its stability during long-term experiments. The synthesis of bismuth tungstate and composites with N-doped TiO$_2$ was performed using the hydrothermal method. The experimental data shows that the combination of N-doped TiO$_2$ with bismuth tungstate via this method results in a stable composite photocatalyst due to the prevention in the degradation of nitrogen species in TiO$_2$ during the photocatalytic process. In addition to an enhanced stability, the composite photocatalysts with a low content of Bi$_2$WO$_6$ also exhibit an enhanced activity that is substantially higher than the activity of the pristine N-doped TiO$_2$ and Bi$_2$WO$_6$ photocatalysts.

### 2. Materials and Methods

#### 2.1. Synthesis of Photocatalysts

High purity grade titanium(IV) oxysulfate (TiOSO$_4$), bismuth(III) nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O), and sodium tungstate dihydrate (Na$_2$WO$_4$·2H$_2$O), purchased from Sigma-Aldrich (Saint Louis, MO, USA), as well as reagent grade ammonium hydroxide solution (NH$_4$OH, 25%) and nitric acid (HNO$_3$, 65%) purchased from AO Reachem Inc. (Moscow, Russia), were used for the synthesis as received without further purification.

N-doped TiO$_2$ (TiO$_2$-N) was prepared from an aqueous solution of TiOSO$_4$ via the precipitation using ammonia according to our previously published technique [22]. Briefly, the solutions of titanium oxysulfate (1 M, 150 mL) and ammonium hydroxide (4 M) were simultaneously added dropwise to deionized water (200 mL) under vigorous stirring. The pH during the precipitation was adjusted at 7 by tuning the flows of reagents. After storing for 48 h in mother liquor, the precipitate was separated by centrifugation and washed with deionized water. Finally, it was calcined in air at 450 °C for 3 h and grinded using an agate mortar. Large particles were separated using a sieve to get a fraction of fine particles.

The synthesis of Bi$_2$WO$_6$ and its composites with N-doped TiO$_2$ was performed via the precipitation from an acidic solution of Bi(NO$_3$)$_3$ using Na$_2$WO$_4$ followed by the hydrothermal treatment. The molar ratio between the components was varied in a wide range. Table 1 shows the mass values of all the precursors used during the synthesis of samples. Bismuth nitrate (m(X) g) was dissolved in nitric acid solution (1 M, 40 mL) and ammonium hydroxide (4 M) were simultaneously added dropwise to deionized water (200 mL) under vigorous stirring. The pH during the precipitation was adjusted at 7 by tuning the flows of reagents. After storing for 48 h in mother liquor, the precipitate was separated by centrifugation and washed with deionized water. Finally, it was calcined in air at 450 °C for 3 h and grinded using an agate mortar. Large particles were separated using a sieve to get a fraction of fine particles.

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#### Table 1. Content of precursors during the synthesis of photocatalysts.

| Bi$_2$WO$_6$:TiO$_2$-N (Molar Ratio) | m(X), g (Bi(NO$_3$)$_3$·5H$_2$O) | m(Y), g (Na$_2$WO$_4$·2H$_2$O) | m(Z), g (TiO$_2$-N) |
|-------------------------------------|----------------------------------|----------------------------------|---------------------|
| 1:0 (Bi$_2$WO$_6$)                  | 2.42 (2.5 mmol)                  | 0.82 (1.25 mmol)                 |                    |
| 1:1                                 | 3.03 (6.25 mmol)                 | 1.03 (3.125 mmol)                | 0.25 (3.125 mmol)   |
Table 1. Cont.

| Molar Ratio | m(X), g (Bi(NO$_3$)$_3$·5H$_2$O) | m(Y)$_r$, g (Na$_2$WO$_4$·2H$_2$O) | m(Z)$_r$, g (TiO$_2$·N) |
|-------------|---------------------------------|---------------------------------|-------------------------|
| 4:10        | 1.21 (2.5 mmol)                 | 0.41 (1.25 mmol)                | 0.25 (3.125 mmol)       |
| 1:10        | 1.21 (2.5 mmol)                 | 0.41 (1.25 mmol)                | 1 (12.5 mmol)           |
| 5:100       | 0.6 (1.25 mmol)                 | 0.2 (0.625 mmol)                | 1 (12.5 mmol)           |
| 1:100       | 0.12 (0.25 mmol)                | 0.04 (0.125 mmol)               | 1 (12.5 mmol)           |

2.2. Characterization Techniques

Powder X-ray diffraction (XRD) was used for analysis of crystal phases in the prepared photocatalysts. The data were collected using a D8 Advance diffractometer (Bruker, Billerica, MA, USA), which was equipped with a CuK$_\alpha$ radiation source and a LynxEye position sensitive detector, in the 2$\theta$ range of 10–75° with a step of 0.05° and a collection time of 3 s. The average size of TiO$_2$ crystallites was estimated from the collected XRD patterns using TOPAS software (Bruker, Billerica, MA, USA). The specific surface area of the samples was determined by BET analysis of N$_2$ isotherms measured at 77 K using an Autosorb-6B-Kr (Quantachrome Instruments, Boynton Beach, FL USA). Before the measurements, the samples were outgassed in a vacuum at 150 °C for 17–23 h. The pore volume in the samples was estimated from the isotherms using the BJH method as a cumulative desorption pore volume. The morphology of individual components and composite photocatalysts was investigated using scanning electron microscopy (SEM). SEM micrographs were received using an ultra-high resolution Field-Emission SEM (FE-SEM) Regulus 8230 (Hitachi, Tokyo, Japan) at an accelerating voltage of 5 kV. The local structure was investigated by transmission electron microscopy (TEM) using a JEOL-2010 microscope (JEOL, Tokyo, Japan) at 200 kV and a resolution of 0.14 nm. The surface composition was investigated by X-ray photoelectron spectroscopy (XPS) using a SPECS photoelectron spectrometer (SPECS Surface Nano Analysis GmbH, Berlin, Germany) equipped with a PHOIBOS-150 hemi-spherical energy analyzer and an AlKx radiation source (hν = 1486.6 eV, 150 W). The scale of binding energy (BE) was pre-calibrated using the photoelectron lines of Au4f7/2 (84.0 eV) and Cu2p3/2 (932.67 eV) from metallic gold and copper foils. Peak fitting in the collected spectra was performed using XPSPeak 4.1 software (Informer Technologies Inc., Los Angeles, CA, USA). The optical properties of the samples were analyzed at room temperature using UV-Vis diffuse reflectance spectroscopy (DRS). The spectra were recorded in the range of 250–850 nm on a Cary 300 UV-Vis spectrophotometer from Agilent Technologies Inc. (Santa Clara, CA, USA) equipped with a DRA-30I diffuse reflectance accessory and special pre-packed polytetrafluoroethylene (PTFE) as a reflectance standard. The optical band gap was estimated using the Tauc method based on an assumption of indirect allowed excitations.

2.3. Photocatalytic Experiments

Long-term photocatalytic experiments were performed in a continuous-flow setup using acetone as a test volatile organic compound. The schematic diagram of this setup and details on the operation process can be found in Supplementary (Figure S1). Validation of the setup was previously performed during the investigation of functional properties of various photocatalytic systems [43–46]. The rate of air flow was 67 ± 1 mL min$^{-1}$ and the inlet concentration of acetone vapor was ca. 32 µmol L$^{-1}$. The relative humidity during experiments was adjusted at 19 ± 1% by tuning the flows of dry and humidified air. The experiments were performed with a thick layer of photocatalyst at a geometric area of 9.1 cm$^2$ and its area density was 20 mg cm$^{-2}$ to absorb the maximum number of photons. A UV light-emitting diode (LED) with a maximum at 371 nm and a blue LED with a maximum
specific radiation powers measured using an ILT950 spectroradiometer (International Light Technology, Peabody, MA, USA) were 10 and 160 mW cm\(^{-2}\) for UV and blue lights, respectively. Analysis of acetone and oxidation products in the gas phase was performed using in situ IR spectroscopy on an FTIR spectrometer FT-801 (Simex LLC, Novosibirsk, Russia) equipped with an IR long-path gas cell (Infrared Analysis Inc., Anaheim, CA, USA). The concentrations of volatile compounds were determined from the collected IR spectra using the Beer-Lambert law. The photocatalytic activity of materials was estimated as the steady-state rate of CO\(_2\) formation (\(\mu\)mol \(\times\) min\(^{-1}\)), which was the final oxidation product. Based on the statistics of many experiments, a relative error estimated using the confidence interval for the probability of 95% during the measurement of photocatalytic activity in the setup did not exceed 5%. This error value was used for all tested samples to evaluate statistically significant differences in their activity.

3. Results and Discussion

Composite photocatalysts containing Bi\(_2\)WO\(_6\) were synthesized using a wet process with the purpose to enhance the activity and stability of N-doped TiO\(_2\) as a photocatalyst for the degradation of volatile organic pollutants under visible light. Correlations between physicochemical characteristics of the materials and their functional properties are discussed below.

3.1. Characteristics

Phase composition, morphology, and textural and optical properties commonly have a strong effect on the photocatalytic ability of semiconducting materials. Therefore, these properties were investigated for the synthesized samples using corresponding techniques.

Figure 1a shows the XRD patterns of single photocatalysts and certain samples from a series of synthesized composites. TiO\(_2\)-N prepared from an aqueous solution of titanium oxysulfate had the crystal structure of anatase because all peaks in its XRD pattern are coincided with the reflexes attributed to anatase. Main reflection peaks at 2\(\Theta\) of 25.3, 37.8, 48.0, 53.9, and 55.1\(^{\circ}\) correspond to the (101), (004), (200), (105), and (211) diffraction planes of anatase TiO\(_2\), respectively. No peaks attributed to the rutile phase were detected. Formation of anatase phase at relatively low temperatures is typical for the preparation of TiO\(_2\) from the titanium oxysulfate precursor [47,48]. An averaged size of anatase crystallites in the TiO\(_2\)-N sample was estimated as 20 nm. SEM micrographs in Figure 2a illustrate this fact and show that large agglomerates in TiO\(_2\)-N consist of adherent nanosized spherical and oval particles, wherein the space between forms a porous structure. Consequently, this sample had a high surface area (98 m\(^2\) g\(^{-1}\)) and pore volume (0.54 cm\(^3\) g\(^{-1}\)) that positively affected its photocatalytic ability.

As expected, the applied technique via hydrothermal treatment of aqueous solutions of bismuth nitrate and sodium tungstate resulted successfully in a formation of orthorhombic bismuth tungstate (Bi\(_2\)WO\(_6\), PDF#39-0256). The main reflection peak at 2\(\Theta\) of 28.3\(^{\circ}\) corresponds to the (131) plane of orthorhombic Bi\(_2\)WO\(_6\), while the peaks with maxima at 32.9 and 47.2\(^{\circ}\) result from a series of reflexes: {(200), (002), (060)} and {(202), (260)}, respectively. No marked peaks attributed to the individual bismuth and tungsten oxides were detected. On the other hand, an asymmetry of peaks attributed to multiplied reflexes of Bi\(_2\)WO\(_6\) was observed in the XRD pattern of the synthesized Bi\(_2\)WO\(_6\) sample (Figure 1b). This fact indicates an anisotropy in the shape of its particles (see Supplementary for details). The results of microscopic study using the SEM technique confirms this statement. Figure 2b shows that the Bi\(_2\)WO\(_6\) sample has a lamellar structure and its agglomerates consist of adherent nanosized spherical and oval particles, wherein the space between forms a porous structure. Consequently, this sample had a high surface area (98 m\(^2\) g\(^{-1}\)) and pore volume (0.54 cm\(^3\) g\(^{-1}\)) that positively affected its photocatalytic ability.

At 450 nm (see Figure S2 in Supplementary) were used for the irradiation of photocatalysts and for the evaluation of their activity in both UV and visible regions, respectively. Specific radiation powers measured using an ILT950 spectroradiometer (International Light Technology, Peabody, MA, USA) were 10 and 160 mW cm\(^{-2}\) for UV and blue lights, respectively. Analysis of acetone and oxidation products in the gas phase was performed using in situ IR spectroscopy on an FTIR spectrometer FT-801 (Simex LLC, Novosibirsk, Russia) equipped with an IR long-path gas cell (Infrared Analysis Inc., Anaheim, CA, USA).
experimental pattern was observed for the model corresponding to a small thickness of disks (6.6 nm) but a large diameter (30 nm). These values characterize the relative sizes of crystallites in the Bi$_2$WO$_6$ sample at different crystallographic axes. Saha et al. [49] have recently shown using in situ X-ray techniques the mechanism of nucleation and growth of Bi$_2$WO$_6$ crystallites, describing the predominant formation of nanoplatelets.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of the synthesized TiO$_2$-N, Bi$_2$WO$_6$, and composite photocatalysts (a). Analysis (b) and simulation (c) of XRD pattern of Bi$_2$WO$_6$ sample.

![Figure 2](image2.png)

**Figure 2.** SEM micrographs of TiO$_2$-N (a), Bi$_2$WO$_6$ (b), and Bi$_2$WO$_6$–TiO$_2$-N (5:100) composites (c) at different magnifications.

In the case of Bi$_2$WO$_6$–TiO$_2$-N composites, the phase composition was influenced by the content of Bi$_2$WO$_6$. Only the peaks attributed to the anatase phase were observed in the XRD pattern of the sample with a Bi$_2$WO$_6$:TiO$_2$-N molar ratio of 1:100 and no
additional peaks were detected. Additionally, the volume of the TiO₂ unit cell did not change compared to pristine TiO₂-N, which indicates no doping TiO₂ lattice with Bi or W-species. This means that at low amounts of Bi and W-precursors, the formation of Bi₂WO₆ crystallites in a high number does not occur and they seem to be in the form of clusters on the extended surface of TiO₂-N particles.

An increase in the molar ratio up to 5:100 resulted in the appearance of the orthorhombic phase of Bi₂WO₆ in the composition (Figure 1a). This means that the amounts of Bi and W-precursors in this case are high enough for the formation of Bi₂WO₆ crystallites in a high number. Figure 2c shows a hybrid structure of the Bi₂WO₆–TiO₂-N (5:100) sample, where small TiO₂ nanoparticles are located on the surface of Bi₂WO₆ nanosheets of big size, and they together form large porous agglomerates. In addition, Figure 3 shows a local structure of the Bi₂WO₆–TiO₂-N (5:100) composite studied using the TEM technique. A high number of nano-crystallites with a lattice spacing of 0.35 nm attributed to the (101) plane of anatase TiO₂ was observed on the surface of sheet-like particles of Bi₂WO₆.

The results of XPS analysis also confirm the presence of bismuth and tungstate elements on the surface of the Bi₂WO₆–TiO₂-N (5:100) sample. According to the peak positions (Figure 4a,b), they have high charge states (i.e., +3 for Bi and +6 for W), which correspond to the states in the chemical composition of Bi₂WO₆. No additional lines attributed to the other charge states of these elements were detected in corresponding spectral regions. These data support the results of other characterization techniques on the formation of the Bi₂WO₆ semiconductor, which forms a composite system with TiO₂-N. The structure of the synthesized Bi₂WO₆–TiO₂-N composite indicates a possibility for a heterojunction of photogenerated charge carriers between the Bi₂WO₆ and TiO₂-N semiconducting components under irradiation and for an enhancement in its photocatalytic ability, as will be discussed later.
All samples with a molar ratio of higher than 5:100 had the crystal phases of both components (i.e., orthorhombic bismuth tungstate and anatase). An increase in the content of Bi$_2$WO$_6$ led to an increase in the fraction of the Bi$_2$WO$_6$ crystal phase and, consequently, to a decrease in the textural characteristics of composites because synthesized Bi$_2$WO$_6$ had substantially worse textural properties than TiO$_2$-N due to a lamellar structure. As mentioned above, the synthesized TiO$_2$-N sample had a high surface area (98 m$^2$ g$^{-1}$) and pore volume (0.54 cm$^3$ g$^{-1}$) due to an extended pore structure formed between adherent nanosized particles of TiO$_2$. The specific surface area and pore volume of Bi$_2$WO$_6$ were 34 m$^2$ g$^{-1}$ and 0.20 cm$^3$ g$^{-1}$, respectively, which corresponds to high values for the concerned material [41,42]. As the molar ratio between Bi$_2$WO$_6$ and TiO$_2$-N was increased, the textural characteristics of composites monotonically decreased down to the values attributed to pristine Bi$_2$WO$_6$ because the content of the superfine component was decreased (Figure 5). Commonly, photocatalysts with an extended surface area exhibit higher photocatalytic activity due to the higher number of sites for adsorption of oxidizing compounds. Therefore, the Bi$_2$WO$_6$–TiO$_2$-N composites with a low content of Bi$_2$WO$_6$ would be preferable in this aspect.

![Figure 5. Effect of Bi$_2$WO$_6$:TiO$_2$-N molar ratio on the textural characteristics of materials.](image-url)

It is important to note that in addition to the main elements (Bi, W, Ti, and O) in the chemical composition of Bi$_2$WO$_6$–TiO$_2$-N (5:100), XPS analysis of this sample shows a signal in the N1s spectral region at 399.8 eV attributed to nitrogen species (Figure 4c). We have previously shown [22] that this value of binding energy corresponds to nitrogen that is placed in an interstitial position in the TiO$_2$ lattice and has a weak positive charge due to interactions with lattice O atoms. The formed nitrogen species result in the appearance of additional energy levels ($\pi^*$ N-O) in the band gap of TiO$_2$, above its VB [50], and provide the absorption of light in the visible region of the spectrum due to the excitation of electrons from these levels to the CB of TiO$_2$. In the UV-vis spectrum of synthesized TiO$_2$-N (Figure 6a), it appears as a shoulder of absorption in the region of 390–530 nm in addition to fundamental (i.e., band-to-band) absorption in TiO$_2$-N. Approximation of the Tauc plot for this sample (Figure 6b) gives a value of 3.18 eV, attributed to the band gap of anatase, but light absorption also occurs in the low-energy region until 2.32 eV (i.e., 535 nm). This value corresponds to a minimum energy required for the photoexcitation of electrons in N-doped TiO$_2$ and can be used for an estimation of the position of nitrogen energy levels compared to the bands of TiO$_2$. 
Carbon dioxide was the major oxidation product but pathways of excitation are realized. Therefore, their photocatalytic activity was investigated pathways of excitation are realized. Therefore, their photocatalytic activity was investigated.

TiO2-N, which better absorbed light in this region. However, for all these composite photocatalysts, the minimum energy required for the photoexcitation of electrons was ca. 2.3 eV, which is similar to TiO2-N. This indicates that the proposed Bi2WO6–TiO2-N composite system has the potential to perform the photocatalytic reactions under solar radiation, which has the major content in the visible region.

In contrast to pristine Bi2WO6, UV-vis spectra of composite Bi2WO6–TiO2-N photocatalysts had a form that is similar to the spectrum of TiO2-N (Figure 6a). The samples with a low content of Bi2WO6 (i.e., molar ratio of 1:100 and 5:100) exhibited even higher absorption of blue light due to a combination with Bi2WO6 and a greater depth for the penetration of light. Further increase in the content of Bi2WO6 led to lower values of absorption due to a decrease in the content of TiO2-N, which better absorbed light in this region. However, for all these composite photocatalysts, the minimum energy required for the photoexcitation of electrons was ca. 2.3 eV, which is similar to TiO2-N. This indicates that the proposed Bi2WO6–TiO2-N composite system has the potential to perform the photocatalytic reactions under solar radiation, which has the major content in the visible region.

All synthesized photocatalysts absorb light both in UV and blue regions but different pathways of excitation are realized. Therefore, their photocatalytic activity was investigated independently in each region to correctly analyze the effect of composition on the functional properties of materials.

### 3.2. Photocatalytic Activity

TiO2-mediated photocatalytic oxidation of pollutants in oxygen-contained mediums has no selectivity due to the formation of reactive species on the irradiated surface of photocatalysts. As a result, almost all organic compounds can be photocatalytically oxidized. We selected acetone as a volatile organic compound for testing the synthesized materials because it does not cause itself the deactivation of photocatalysts and, consequently, is suitable for long-term experiments to evaluate their stability in the view of photocatalytic activity. In this case, a change in the rate of photocatalytic oxidation, that would be observed during experiments, can be reliably attributed to a change in photocatalyst itself due to its transformation.

Bismuth tungstate prepared via the hydrothermal method from bismuth nitrate and sodium tungstate was able to provide the oxidation of acetone vapor both under UV (371 nm) and visible light (450 nm). Carbon dioxide was the major oxidation product but small amounts of intermediate products, namely formaldehyde and formic acid, were also detected in the gas phase during experiments using IR spectroscopy. These products of incomplete oxidation have low threshold limits and are harmful for human health [12]. Formation of intermediates during the oxidation of pollutants over Bi2WO6 is a drawback in contrast to Bi2WO6, N-doped TiO2 prepared from titanium oxysulfate using ammonia as a nitrogen source resulted in the...
complete oxidation of acetone without the formation of gaseous intermediates under the radiation in both spectral regions. The photocatalytic activity of TiO$_2$-N under UV attributes to the excitation of electrons from VB to the CB of anatase TiO$_2$. Under visible light, the excitation occurs using intermediate energy levels of nitrogen species in the TiO$_2$ lattice that are located higher than the VB of TiO$_2$. Therefore, a lower energy of photons is required for the excitation of electrons compared to the band-to-band excitation. As mentioned above, the redox potentials of charge carriers photogenerated under visible light remain high enough to provide the complete oxidation of pollutants with a high rate. Considering single materials, TiO$_2$-N is more active than Bi$_2$WO$_6$ in both spectral regions: in four times under UV and in 1.6 times under blue light (Figure 7). A high surface area of TiO$_2$-N and a high amount of light absorbed in the visible region give positive effects on its activity and ability for complete oxidation. It should be noted that one of the best commercially available photocatalysts for visible light, namely KRONOClean®7000 from Kronos Worldwide Inc. (Dallas, TX, USA), exhibited the visible-light activity of 0.07 μmol min$^{-1}$ under the same conditions that is much lower than the corresponding values for Bi$_2$WO$_6$ (0.45 μmol min$^{-1}$) and TiO$_2$-N (0.70 μmol min$^{-1}$). This fact confirms the high level of activity achieved for the synthesized materials.

![Figure 7](image-url)  
**Figure 7.** Effect of Bi$_2$WO$_6$:TiO$_2$-N ratio on the photocatalytic activity of composites under UV and visible light.

An enhanced activity was achieved for the synthesized Bi$_2$WO$_6$–TiO$_2$-N composites compared to the parent single-phase materials. It corresponds to the previously published results on an enhanced activity of Bi$_2$WO$_6$–TiO$_2$ composites in the degradation of organic dyes, 2-nitrophenol, and acetaldehyde [51,52]. Similar trends both under UV and visible light were observed for the synthesized Bi$_2$WO$_6$–TiO$_2$-N samples. The photocatalytic activity increased as the content of Bi$_2$WO$_6$ in composites was increased, but at a further increase in the Bi$_2$WO$_6$ content, activity began to decrease until the level for single Bi$_2$WO$_6$. Figure 7 clearly shows this dome-shaped dependence with a maximum at the molar ratio of 5:100 between the components for both spectral regions. The UV-light activity of this composite was higher than the activities of single TiO$_2$-N and Bi$_2$WO$_6$ in 1.6 and six times, respectively. Under visible light, initial activity was increased in 1.4 and 2.2 times compared to TiO$_2$-N and Bi$_2$WO$_6$, respectively.

An enhanced activity of Bi$_2$WO$_6$–TiO$_2$-N composites results from the efficient separation of photogenerated charge carriers due to a heterojunction between the semiconductors. According to the estimations using an empirical equation based on the electronegativity and band gap of semiconductors, the energy bands of Bi$_2$WO$_6$ are located lower than the bands of TiO$_2$. As a result, the heterojunction of type II, when the electrons photogenerated in the CB of TiO$_2$ are transferred to the CB of Bi$_2$WO$_6$, while the holes migrate backwards...
from the VB of Bi$_2$WO$_6$ to the VB of TiO$_2$, is commonly proposed for the Bi$_2$WO$_6$–TiO$_2$ system [41,53]. An increase in the content of Bi$_2$WO$_6$ leads to an increase in the number of contacts between Bi$_2$WO$_6$ and TiO$_2$–N nanoparticles, which has a positive effect on the photocatalytic activity. At a high content, Bi$_2$WO$_6$ begins to prevail and the system goes to its characteristics that are substantially lower compared to TiO$_2$–N. Therefore, the Bi$_2$WO$_6$–TiO$_2$–N composites with a low content of Bi$_2$WO$_6$ exhibit the highest activity.

In addition to a high activity, the stability of photocatalyst under long-term irradiation is also important for its practical application. N-doped TiO$_2$ containing nitrogen impurities in the interstitial positions of the TiO$_2$ lattice has a drawback in this aspect because a gradual decrease in its activity occurs under highly powerful radiation. Figure 8 illustrates this behavior of TiO$_2$–N under visible light. The photocatalytic activity of pristine TiO$_2$–N decreased by 47% compared to the initial level after 16 h of irradiation with blue light having a specific radiation power of 160 mW cm$^{-2}$. This deactivation results from a partial oxidation of nitrogen species in the TiO$_2$ lattice by the photogenerated holes that do not migrate to the surface of the photocatalyst and do not participate in the redox reactions with adsorbed molecules [25]. It is important to note that after longer irradiation for 2–3 days, the activity of TiO$_2$–N reached a permanent level, namely 50% of the initial value, and did not change over further time (see Figure S4).

In contrast to TiO$_2$–N, the synthesized Bi$_2$WO$_6$ exhibited a high stability from the first moment because no decrease in the values of the oxidation rate was observed during the irradiation under the same conditions (Figure 8a). Stability of Bi$_2$WO$_6$ arises from the fact that, in contrast to TiO$_2$–N, it has a narrower band gap and the absorption of blue light corresponds to the band-to-band excitation of electrons. No substantial change in the chemical composition of semiconductors occurs in this situation. Similar behavior was achieved for the Bi$_2$WO$_6$–TiO$_2$–N composites. The visible-light activity of composites with the Bi$_2$WO$_6$:TiO$_2$–N molar ratio of 5:100 and higher did not decrease during long-term irradiation but even slightly increased similarly to Bi$_2$WO$_6$ (Figure 8a).

![Figure 8](image_url)

**Figure 8.** Effect of irradiation time on visible-light activity of the prepared materials in absolute (a) and relative (b) units.

Deactivation of TiO$_2$–N results from the oxidation of nitrogen species in the TiO$_2$ lattice by the photogenerated holes. Therefore, the fast transfer of holes from the TiO$_2$ phase may suppress the degradation of nitrogen species and, consequently, deactivation of the photocatalyst. An enhanced transfer of photogenerated holes can be realized in heterojunction systems when the position of VB in the second semiconductor is higher than the level of holes in TiO$_2$ (type II) or when the holes recombine with the photogenerated electrons of the second semiconductor (Z-scheme). As mentioned above, the heterojunction of type II is commonly proposed for the Bi$_2$WO$_6$–TiO$_2$ system (Figure 9a) but the energy bands of Bi$_2$WO$_6$ are located lower than the bands of TiO$_2$, which prevents the transfer of holes from TiO$_2$. At the same time, the energy levels of nitrogen species in TiO$_2$–N are located substantially higher than the VB of TiO$_2$ [54] and a Z-scheme heterojunction, when the photogenerated electrons from the CB of Bi$_2$WO$_6$ would interact with the photogenerated holes.
from nitrogen levels of TiO₂ (Figure 9b), can be proposed for Bi₂WO₆–TiO₂-N similarly to other systems [55–57]. Therefore, this junction can promote a removal of photogenerated holes from the nitrogen energy levels and suppress the degradation of nitrogen impurities by these holes.

![Proposed pathways of photogenerated charge carriers in Bi₂WO₆–TiO₂ (a) and Bi₂WO₆–TiO₂-N (b) systems.](image)

Figure 9. Proposed pathways of photogenerated charge carriers in Bi₂WO₆–TiO₂ (a) and Bi₂WO₆–TiO₂-N (b) systems.

In contrast to the samples mentioned above, the visible-light activity of the Bi₂WO₆–TiO₂-N composite with a lower content of Bi₂WO₆ (i.e., molar ratio of 1:100) decreased during long-term irradiation, but this effect was much weaker than for pristine TiO₂-N. For a detailed comparison, Figure 8b shows the relative values of activity, which were recalculated by normalization to the initial value of activity for each photocatalyst. After the first 9 h of irradiation, the activity of the Bi₂WO₆–TiO₂-N (1:100) sample decreased by 17% compared to the initial value, but no substantial change was observed after further irradiation. No crystal phase of Bi₂WO₆ in the samples with low Bi₂WO₆ content can be a reason for the lower stability of these samples. This once again underlines the importance of the efficient heterojunction of charge carries between the semiconducting components in the composite system. Considering the data on the activity and stability for composite photocatalysts, as shown in Figure 7 and 8, a molar content of ca. 5% can be selected as an optimum content of Bi₂WO₆ in this system because at this value, a high activity and a high stability are achieved simultaneously.

The results described above show that the Bi₂WO₆–TiO₂-N composite system exhibits an enhanced activity and stability compared to TiO₂-N photocatalysts alone and has the potential for application in air purification using the photocatalytic oxidation method.

4. Conclusions

N-doped TiO₂ (anatase, 98 m² g⁻¹) prepared from titanium oxysulfate using ammonia as a nitrogen source and bismuth tungstate (Bi₂WO₆, 34 m² g⁻¹) prepared via the hydrothermal method from bismuth nitrate and sodium tungstate are able to provide the complete oxidation of volatile organic compounds in air both under UV and visible light. N-doped TiO₂ is more active than Bi₂WO₆ in both regions. A combination of TiO₂-N and Bi₂WO₆ results in a synergistic effect because the composite with a low content of Bi₂WO₆ (5 mol.%) exhibits the photocatalytic activity that is substantially higher than activity of each component. A dome-shaped dependance of activity on the content of Bi₂WO₆ was
found and the Bi₂WO₆–TiO₂–N composite with a molar ratio of 5:100 had the highest activity among all the studied samples both under UV and visible light. In addition to an enhanced activity, Bi₂WO₆ in composites promotes N-doped TiO₂ and prevents the degradation of nitrogen impurities in the TiO₂ lattice by holes during the photocatalytic process. As a result, Bi₂WO₆–TiO₂–N composites exhibit stable values of photocatalytic activity under highly powerful radiation (160 mW cm⁻²), while the activity of N-doped TiO₂ is decreased by two times in 16 h under the same conditions. The enhanced activity and stability of Bi₂WO₆–TiO₂–N composites result from an efficient separation of photogenerated charge carriers due to a heterojunction between the semiconductors. Therefore, the Bi₂WO₆–TiO₂–N composite system has the potential for efficient purification of air using the photocatalytic oxidation method.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/nano12030359/s1, Figure S1: Schematic diagram of the set-up used for the photocatalytic experiments; Figure S2: Emission spectra of the diodes used for irradiation of photocatalysts; Figure S3: Analysis of XRD patterns; and Figure S4: Long-term stability of TiO₂-N under blue light of 160 mW cm⁻². References [58,59] are cited in the supplementary materials.

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Data Availability Statement: The data presented in this study are available upon request from the corresponding author. The data are not publicly available due to privacy.

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