



Article Facile Synthesis of Hafnium Oxide Nanoparticle Decorated on Graphene Nanosheet and Its Photocatalytic Degradation of Organic Pollutants under UV-Light Irradiation

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Abstract: The HfO₂ nanoparticles and the nanocomposites of HfO₂-graphene (10, 30, and 50 wt%) were prepared via precipitation and simple mixing method. The XRD pattern confirmed the presence of monoclinic HfO₂ and hexagonal graphene in the nanocomposite. Raman spectroscopy studies revealed the formation of HfO2-graphene nanocomposite. According to SEM and TEM images the HfO₂, NPs are spherical, and their size is less than 10 nm, anchored on the surface of the graphene sheets. The EDX spectrum shows carbon, oxygen, and HfO₂ and reveals the formation of the HfO₂-graphene nanocomposite. The UV-vis absorption spectra show the optical properties of synthesized HfO2-graphene nanocomposite. The study examines the influence of different ratios of the addition of graphene on the photocatalytic activity of HfO₂-graphene. It was found that the HfO₂-graphene (50 wt%) 40 mg nanocomposite exhibits enhanced photocatalytic activity than the bare HfO₂ towards the methylene blue photodegradation, an aromatic pollutant in water under UV light irradiation, which can be applied optimally for individually wastewater management system. The HfO₂-graphene (50 wt%) photocatalyst degrades $81 \pm 2\%$ of tetracycline in 180 min, implying that tetracycline can be degraded more efficiently under UV light. The enhancement in photocatalytic activity under UV light illumination can be attributed to the effective separation of photogenerated electrons, inhibiting recombination in the HfO₂-graphene composite.

Keywords: HfO2; graphene; photodegradation; nanocomposites; tetracycline

1. Introduction

Accumulate persistent organic pollutants (POPs) in the food chain adversely affect human health and the environment. Industrial chemicals (e.g., textile dyes), pesticides, solvents, and pharmaceuticals (such as tetracycline) are the different types of POPs [1,2]. A prominent POP in this group is tetracycline, which is used extensively as an antibiotic in veterinary medicine and aquaculture [3,4]. Therefore, it is essential to find practical solutions to remove such POPs from the environmental [5,6]. Photocatalysis has gained recognition as an environmentally friendly technology at ambient temperature for efficiently mineralizing POPs [7–9].

This study uses methylene blue and tetracycline as a model of organic pollutants. It endangers aquatic biodiversity when used as a dye or a decontaminant, besides removing organic pollutants from organic solutions and releasing toxic compounds due



Citation: Jayaraman, V.; Mahalingam, S.; Chinnathambi, S.; Pandian, G.N.; Prakasarao, A.; Ganesan, S.; Ramasamy, J.; Ayyaru, S.; Ahn, Y.-H. Facile Synthesis of Hafnium Oxide Nanoparticle Decorated on Graphene Nanosheet and Its Photocatalytic Degradation of Organic Pollutants under UV-Light Irradiation. *Appl. Sci.* 2022, *12*, 11222. https://doi.org/ 10.3390/app122111222

Academic Editor: Lionel Maurizi

Received: 16 October 2022 Accepted: 3 November 2022 Published: 5 November 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). to chemical and biological reaction processes [10,11]. When irradiated using an appropriate catalyst, methylene blue has been noted as photobleached, photodegraded, and demethylated [12,13]. With its ability to decimate toxic environmental contaminants, photocatalysis has been given considerable attention. In ecological and biomedical applications, semiconducting metal oxide heterogeneous photocatalysts are exclusively used [14–17]. Owing to their similar bandgap, TiO_2 and ZnO semiconductors have been widely studied as effective photocatalysts for the photodegradation of organic pollutants [18–20]. MB also causes the depletion of the dissolved oxygen in water bodies. Different procedures have evolved over the years to enhance the photocatalytic performance of the semiconductor photocatalysts, such as noble metal loading and semiconductor composites and textural design [21]. The specific property of hollow nanostructures of the TiO_2 nanocrystals with internal pores is instrumental for their augmented photocatalytic activity compared to TiO_2 solid nanocrystals [22]. The higher charge carrier mobility of the anatase phase TiO_2 enables it to exhibit higher photocatalytic activity than the rutile phase [23,24]. Sangpour et al. demonstrated that noble metals, such as Cu, Au, and Ag, could increase the efficiency of photocatalysis [25]. Of late, graphene has emerged to hold a pivotal position in the environment and in energy [26,27]. Graphene, with the structure of a two-dimensional macromolecular sheet of carbon atoms, is an excellent electrical conductor with unique mechanical properties and has proved to be an efficient electron-transport material for photocatalytic processes, and it is better than the graphite-like Carbon, C60, polyaniline [28–30].

Graphene, due to its high surface area and excellent electrical and mechanical properties, is much sought after as a novel substrate for creating hybrid nanostructures in a combination of a variety of nanomaterials by incorporating graphene with metals, metal oxides, and polymers; new applications have been developed in recent times [31–34]. In the degradation of rhodamine B, the graphene/TiO₂ nanocrystal hybrid material exhibits excellent photocatalytic activity, unlike the other forms of TiO₂ [35]. The enhanced photocatalytic activity is more shown in the catalytic degradation of MB under UV light irradiation by the P25-graphene photocatalyst than by the bare P25 [36]. Similarly, rather than the pure SnO_2 nanoparticles, graphene-embedded SnO_2 nanoparticles exhibited an improved photocatalytic degradation activity with the MB under sunlight [37]. The graphene sheets/ZnO nanocomposites, which show photocatalytic activity, are eminently suitable for various applications in environmental protection [38].

The distinct physical and chemical properties of hafnium oxide (HfO₂) have made it considerably investigated as an essential dielectric material for a wide range of applications such as dosimeters, biosensors, radiosensitizers, and biomaterials [39–42]. It is common knowledge that TiO₂ and ZnO are conventional semiconductor photocatalysts. In group IV of the periodic table, hafnium has been included as the metal oxide along with titanium and zirconium. Enhanced photocatalytic activity is induced by hafnium-doped ZnO under sunlight irradiation for MB degradation, and it does so more effectively than the pure ZnO [43]. Cho et al. (2013) have reported that ZrO₂-Graphene (50 wt%) nanocomposites photodegrade the MB under ultra-violet irradiation [44]. Hence, HfO₂, belonging to the same category of ZrO₂, can also exhibit similar properties to ZrO₂. As such, motivating research towards the HfO₂-graphene nanocomposite enhances the photodegrade of MB dye under ultraviolet irradiation. It is well known that able intrinsic oxygen vacancies, with various defect levels in HfO₂, are used to utilize the electron-hole pairs more effectively [45,46].

There seems to be earlier studies on the synthesis, characterization, and photocatalytic activity of the HfO₂-graphene composite. By precipitation and chemical methods, HfO₂ nanoparticles and graphene were synthesized by the solution mixing method, and HfO₂-graphene composites that were prepared with different amounts of graphene (10, 30, and 50 wt%) were loaded on the surface of catalyst particles (HfO₂) to form HfO₂-graphene nanocomposites, and their photocatalytic activity was studied and evaluated.

2. Materials and Methods

2.1. Materials

Hafnium tetrachloride (HfCl4, 98%) and NaOH (sodium hydroxide, 97%) were purchased from Sigma-Aldrich, USA. Natural graphite powder (99.99%) was obtained from Alfa-Aesar. All the chemicals parched in the analytical grade were used without further purification. Hydrazine hydrate (H₆N₂O, 80%) was procured by Merck. Methylene blue (MB) was used as the model dye for photocatalytic studies.

2.2. Preparation of Hafnium Oxide Nanoparticle

The HfO₂ NPs were synthesized by the precipitation method (see Equations (1) and (2)) [47]. In brief, 0.4 M solution of NaOH was slowly added dropwise into 0.1 M solutions (HfCl₄) (that is, 100 mL of NaOH and HfCl₄ with a 4:1 volume ratio of each solution allowed for vigorous stirring for 8 h). Finally, the white-colored precipitate was obtained as a hafnium hydroxide. Then, we used deionized water to wash white precipitate and centrifuged at 4000 rpm. The product was dried at 100 °C for 3 h, then calcined at 500 °C for 2 h to get HfO₂ NPs.

$$Hf(Cl)_4 + 4NaOH \rightarrow HfO(OH)_2 + 4NaCl + H_2O$$
(1)

$$HfO(OH)_2 \to HfO_2 + H_2O \tag{2}$$

2.3. Preparation of Graphene

The typical GO synthesis was followed by the modified Hummer's method [48]. The prepared GO was reduced to graphene by successive chemical reduction methods [49]. The synthesized GO (200 mg) was dispersed in 100 mL of DI, and the solution was ultrasonicated for 1 h. We used a 100 °C oil bath to heat the GO solution. Later, 3 mL of hydrazine hydrate was added at constant stirring. The solid-state product was obtained by centrifugation and washed several times with DI and ethanol. At last, we used vacuum oven for 24 h at 60 °C to obtain the dried graphene.

2.4. Synthesis of HfO₂-Graphene Nanocomposite

To synthesize the HfO_2 -graphene nanocomposites with different wt%, a solution mixing method was performed using DI as a solvent. Initially, 90 mg of HfO_2 and 10 mg of graphene were sonicated separately in 50 mL of DI for 90 min. Afterward, the graphene solution was mixed dropwise into the HfO_2 solution and allowed constant stirring for 30 min. Then, the mixing solution was aged with constant stirring for 3 h to form a homogeneous suspension. The obtained suspension was then dried in the oven at 80 °C for 12 h. The same strategy was used to synthesize the remaining composites by changing the graphene content.

2.5. Characterization Methods

The X-ray diffraction (XRD) patterns were analyzed to identify the nanocomposites' crystalline phase with Rigakumultiflex using Cu k α (λ = 1.54 Å) radiation. Raman spectra were recorded using Lab Ram HR 800 Micro Raman spectrometer (Horibo Jobin-Yvon, Longjumeau, France), with Ar-ion Laser having an excitation wavelength of 514 nm. The particle size and surface morphology of HfO₂ NPs were evaluated by a scanning electron microscope (VEGA3 TESCAN, Germany), and the HR-TEM operated with an acceleration voltage of 120 kV (Hitachi H-7650, Singapore). The UV spectra of HfO₂ NPs were studied using a UV-Vis spectrometer (Lamda35, Perkin-Elmer, Waltham, MA, USA). The photocatalytic activity of the prepared catalysts was measured by the degradation of MB and tetracycline under UV light.

2.6. Photocatalytic Experiments

The methylene blue (MB) photodegradation was captured under UV light based on the absorption spectroscopic technique. For this analysis, 0.1 mmole of the MB dye was dispersed in 500 mL of the aqueous solution with the addition of 15 mg of HfO_2 -graphene composite. Before illumination, the prepared solution was homogenized under stirring for 30 min in a dark room to achieve adsorption-desorption equilibrium between the catalyst and dye. We used a 4 W UV lamp (Philips, TUV4 W/G4 T5) with 365 nm wavelength for the irradiation experiment. Later, we collected 3 mL of the sample with a particular time interval of UV illumination. Then, the sample was centrifuged at 3000 rpm for 5 min. The final sample absorption spectra were measured using a UV-Vis spectrophotometer.

For the tetracycline experiment, a 250 mL glass reactor was filled with 20 ppm aqueous tetracycline solution mixed with 15 mg of HfO₂-graphene (50 wt%) as a photocatalyst. Subsequently, the reaction mixture was stirred for 2 h in the dark to reach a complete equilibrium between adsorption and desorption. The solutions were then exposed to UV light irradiation while being stirred continuously over 180 min. At 30-min intervals, 3 mL of the suspension was taken to measure the degradation of tetracycline. Before examining UV-visible absorption, the suspension of the tetracycline solution was centrifuged to remove the catalyst. A control experiment without the photocatalyst was also conducted.

3. Results and Discussion

3.1. X-ray Diffraction

The prepared catalysts' crystallinity, purity, and particle size were characterized by powder X-ray diffraction. Figure 1 shows the XRD patterns of HfO₂, graphene, and HfO₂-graphene composites. The XRD pattern of pure HfO₂ (Figure 1) exhibited the monoclinic phase with a preferential orientation of the (111) plane. Debye Scherer's formula estimates the particle size (7 nm) of the HfO₂.

$$D = k\lambda/\beta cos\theta \tag{3}$$

where k = dimensionless constant (0.94). λ indicates X-ray wavelength, β peak full width half maximum, and θ represents Braggs angle.

The observed XRD pattern and its peaks are matched with the monoclinic HfO_2 phase (JCPDS card No: 06-0318). We don't find any other diffraction peaks, indicating the catalysts' successful preparation. A broad and robust peak appeared at a 20 value of 24 °C, which corresponded to the (002) plane of graphene (Figure 1b) [50].

In the XRD pattern of the graphene-HfO₂ nanocomposites (Figure 1c–e), it is observed that the Graphene-HfO₂ nanocomposites with different weight addition ratios (10, 30, and 50 wt%) of graphene exhibit similar XRD patterns. Notably, the peaks corresponding to graphene disappeared in the graphene-HfO₂ nanocomposites. The reason is that the main characteristic peak of graphene, that corresponds to (002) plane, might be shielded by the main peak of the monoclinic HfO₂ that belongs to the (-111) plane [51,52].

3.2. Raman Spectroscopy

Raman spectroscopic analyses were carried out to ratify the composite confirmation. Figure 2 compares the Raman spectra of HfO₂, graphene and graphene-HfO₂ nanocomposites. In Figure 2, the Raman peaks at 112, 142, 258, 502, and 576 cm⁻¹ could be attributed to the Ag modes of HfO₂, whereas the peaks at 330, 405,659, and 774 cm-1 are assigned to Bg modes of the HfO₂ monoclinic. These peaks are similar to reported values for monoclinic HfO₂ [53]. The unique peaks of graphene (Figure 2) can be found at 1357 and 1583 cm⁻¹, corresponding to D (where the D peak is a defect peak owing to intervallic scattering) and G (G refers to the graphene G peak) peaks [54]. In the Raman spectra of HfO₂-graphene nanocomposite, it is worth noting that the typical graphene peaks were also observed in addition to the monoclinic of HfO₂ peaks (Figure 2). The appearance of the D & G bands corresponds to graphene. Since the wt% of graphene increases, the corresponding D & G bands also increased. The calculated relative amplitude ratios of the "D" and "G" bands were similar, and the values of graphene and graphene–HfO₂ (10, 30, 50 wt%) were 0.86 and 0.85, respectively. These results reveal the successive decoration of the HfO₂ nanoparticles on the graphene sheets.



Figure 1. XRD pattern of (**a**) HfO₂ nanoparticles, (**b**) graphene, and (**c**–**e**) HfO₂-graphene (10, 30, and 50 wt%) nanocomposites.



Figure 2. Raman spectra of HfO2 nanoparticles, graphene, HfO2-graphene (10, 30, and 50 wt%) nanocomposites.

3.3. Morphology and EDX Analysis

The surface morphology of the HfO₂, graphene, and HfO₂-graphene nanocomposites were characterized by SEM. Figure 3a–d shows that the HfO₂ nanoparticles are densely attached to the surface of graphene sheets. The surface morphology of the HfO₂, graphene, and HfO₂-graphene nanocomposites was characterized by SEM and displayed in Figure 3a–d. Figure 3a shows HfO₂ particle aggregation due to the high surface interaction between nanoparticles with a large specific area and high surface energy [42]. Figure 3c,d shows that the graphene sheets are covered densely with the HfO₂ layer.



Figure 3. SEM images of (**a**) HfO₂ nanoparticles, (**b**) graphene, (**c**) HfO₂-graphene (10 wt%) nanocomposite, and (**d**) HfO₂-graphene (50 wt%) nanocomposites.

To further characterize the morphology of the HfO₂-graphene composites, HR-TEM was observed. The HR-TEM images confirm the present structure of the composites that contain graphene sheets covered with HfO₂. The HR-TEM images (Figure 4a,d) also revealed that the HfO₂ nanoparticles were densely bound on the surface of the graphene sheets. Similar results were observed by R.A. Dar et al., 2022 [55]. It can be seen from HR-TEM images the observed average size of the HfO₂ nanoparticles was around 10 nm. The HR-TEM image size also matched with XRD measurements. The EDX spectrum of the HfO₂-Graphene nanocomposite is shown in Figure 5. The results further confirm the presence of carbon (C), oxygen (O), and hafnium (Hf) elements in the HfO₂-graphene nanocomposite.



Figure 4. HR-TEM images of (**a**) HfO₂ nanoparticles, (**b**) graphene, (**c**) HfO₂-graphene (10 wt%) nanocomposite, and (**d**) HfO₂-graphene (50 wt%) nanocomposite.



Figure 5. EDX spectrum of HfO₂-graphene nanocomposite.

3.4. Optical Properties

UV absorption spectra of HfO₂, graphene, and HfO₂-graphene nanocomposites (10, 30, 50 wt%) are shown in Figure 6a. We observed a peak around 205 nm that is due to the absorption of HfO₂ nanoparticles [56]. The UV spectrum of graphene showed an absorption peak at 263 nm with a broad absorption spectrum [57]. The HfO₂-graphene (50%) nanocomposites shows broad absorption absorbed from 225 to 300 nm when compared to other composites. Figure 6b shows the band gap energy changes from 4.5 eV to 1.6 eV when graphene weight percentage increments.



Figure 6. (a) UV-Visible absorption spectra of HfO₂ nanoparticles, graphene, and HfO₂-graphene (10, 30, and 50 wt%) nanocomposites, (b) Variation of $(\alpha h\nu)^2$ with photon energy for graphene and HfO₂ and HfO₂-graphene (10, 30, and 50 wt%) nanocomposites.

3.5. Photocatalytic Activity

HfO₂-graphene nanocomposites are novel, and there are no earlier reports on their photocatalytic activity to date. The universal method of assessing a nanocomposite photocatalyst activity is by measuring the time dependence of the concentration loss of an organic compound such as MB dye under UV irradiation. To investigate the photocatalytic activities of the bare HfO₂ and HfO₂-graphene nanocomposites with varying amounts of graphene (10, 30, and 50 wt%) with different reaction times (0, 30, 60, 90, 120, 150, and 180 min), a photodegradation study was performed by using MB dye under UV light irradiation (Figure 7).

The prepared nanocomposite, before and after irradiation, was used to measure the degradation efficiency of MB dye (D%) by the following equation [58].

$$D\% = \times 100 \tag{4}$$

where $C_0 = MB$ initial concentration and C = the catalyst concentration at particular time interval after irradiation. Figure 7a gives the UV-Vis absorption spectra for HfO₂-graphene (50 wt%) 40 mg catalysts composite. Whereas out of various combinations of composites, Figure 7a shows that HfO₂-graphene (50 wt%), whereas 40 mg catalyst composites show a significant decrease in the absorbance and, hence, a sizeable photodegradation efficiency. Figure 7b depicted that the decomposition of MB dyes using HfO₂- graphene catalyst at various weight ratios, such as 10, 20, 30, 40, and 50 mg, and the corresponding decomposition efficiencies were 35%, 57%, 73%, 99%, and 94% at 180 min. The best performance of the loading catalyst is 40 mg for the maximum decomposition of HfO₂-graphene. The catalyst's ability to remove large amounts of MB dyes is 40 mh, and it is impaired by the



light reflection of the catalyst particles [56]. Degradation at different concentrations of MB dyes has been analyzed.

Figure 7. UV-vis absorption spectra of MB solution during the photodegradation under UV light. (a) HfO₂-graphene (50 wt%) nanocomposites, (b) different dosages of catalysts, (c) c/c_0 vs. time, (d) number of recycling tests, and (e) scavenger test photodegradation of MB solution by all the catalysts.

The variation of C/C_0 vs. time of exposure is depicted in Figure 7c, and it is observed that the photocatalytic efficiency increases with the increasing content of graphene. It is worth noting that the HfO_2 -graphene composites (50 wt%) of 40 mg show a significantly improved photodegradation efficiency related to MB dye compared to the rest of the composites, achieving complete degradation in 180 min under UV light irradiation with a sharp fall-off at 180 min marking 99% of degradation. This abrupt enhancement of photocatalytic activity in the HfO₂-graphene composites (50 wt%) may be due to the excellent distribution of HfO_2 particles in the graphene matrix. This may be due to the creation of intermediate energy levels, thus minimizing the bandgap. The recycled runs investigated the catalyst stability performance of the HfO₂- graphene nanocomposite in removing the MB dyes with the recovered catalyst, as shown in Figure 7d. It is essential to conduct the recyclability test of the prepared photocatalyst for practical applications. Under UV light irradiation, the synthesized HfO2-graphene nanocomposite assessment was made for the photodegradation of MB dye. The decrease in the effectiveness of degradation for the dye for three recycling tests was shown, thereby showing the repeatability of the photocatalytic activity and the notable stability of the HfO₂-graphene nanocomposite as a catalyst. The degradation performance for five cycles shows a small decrease, and the photocatalytic performance does not decrease significantly after five runs. The prepared catalyst was stable and reusable UV light illumination. The important reaction involved in MB dye decomposition, undergoing UV light illumination, was detected by scavengers' impact on the degradation of oxidizing species. The results are shown in Figure 7e. Different scavengers, such as benzoquinone for $O_2^{\bullet-}$, triethanolamine for h⁺, isopropyl alcohol for OH, and ethanol for e⁻, have been utilized to trap the active species for decomposition. The decomposition performance was low to a maximum extent for benzoquinone. This result depicted the significant key role of $O_2^{\bullet-}$ in the photodecomposition of MB dye. However, the decomposition is affected by triethanolamine, depicting the role of h⁺ in the decomposition. The photocatalytic degradation is mainly based on $O_2^{\bullet-}$, with HfO₂ under UV light illumination.

The following equations show attainable reaction steps of the photocatalytic degradation mechanism under UV light irradiation.

$$HfO_2 + h\nu \to HfO_2 (h^+ + e^-)$$
(5)

$$HfO_2 (e^-) + Graphene \rightarrow HfO_2 + Graphene (e^-)$$
(6)

Graphene (e⁻) +
$$O_2 \rightarrow O^{2^-}$$
 + Graphene (7)

$$HfO_2 (h^+) + OH^- \to HfO_2 + \bullet OH$$
(8)

$$HfO_2 (h^+) + \bullet OH + O_2 + dyes \rightarrow CO_2 + H_2O + mineralization product$$
(9)

The enhanced photocatalytic activity under UV light illumination can be attributed to the effective separation of photogenerated electrons inhibiting recombination in the HfO₂-graphene composite. Under UV illumination, e⁻ is excited from the VB to the CB of HfO_2 . As a result, the electron-hole pairs are generated on the HfO_2 surface (Equation (5)). These photogenerated electrons and holes play a crucial role in pollutant degradation. The previous report proposed graphene as an electron acceptor in the composite [59,60]. As a result, the negatively charged electron is transferred into the graphene through the percolation mechanism (Equation (6)). Then, these negatively charged graphene sheets can activate the dissolved oxygen to produce $O_2^{\bullet-}$ (Equation (7)). In addition, the positively charged holes present in the HfO_2 can react with the adsorbed water to form OH (Equation (8)). Finally, the reactive active species, such as holes, OH^{\bullet} , and O^{2-} , were directly involved in the oxidation processes, leading to the degradation of methylene blue (Equation (9)) [61]. Figure 8 shows the degradation of the photographic image of the MB dye solution under the UV-light irradiation. From Figure 8, it was found that the gradual degradation of MB dye takes place. At 180 min of irradiation, MB in the presence of HfO₂-graphene nanocomposite was completely degraded.



Figure 8. Photographic image of MB dye solution in the presence of HfO₂-graphene nanocomposite after 180 min of UV-light irradiation.

Seema et al. demonstrated that graphene-SnO₂ composites spent nearly 360 min, even for the partial photodegradation of MB dye under UV light illumination [37]. Hao Zhang et al. synthesized the P25-graphene composite that achieved 85% of the degradation of the initial MB dye under UV light irradiation, even for less than 60 min [36]. The graphene-TiO₂ composite displayed the degradation of methylene blue by 75% when illuminated with sunlight for 180 min. BiVO4-graphene catalyst degraded the methylene blue by 89% after illumination with visible light for 180 min [62]. Zhang et al. prepared TiO₂–Graphene nanocomposites that degraded the MB dye under sunlight irradiation for 180 min; the degradation achieved was 75%. Shanmugam et al. prepared G- α MoO₃ nanocomposite, and it degraded the MB dye under UV illumination, with a degradation percentage of 97% [63]. Atchudan et.al. prepared GO-TiO₂ under UV-light irradiation, and its degradation achieved was 75% [64]. The present results were compared with the existing results in Table 1.

Table 1. Comparison of photocatalytic MB dye degradation efficiency of HfO₂-graphene.

Nanocomposites	Irradiation Source	Dye	Irradiation Time (min)	Degradation (%)	References
P25-graphene	UV	MB dye	60	85	[36]
Graphene-SnO ₂	UV	MB dye	360	100	[37]
TiO ₂ -graphene	sunlight	MB dye	180	75	[50]
graphene-BiVO ₄	Visible light	MB dye	180	89	[62]
G- αMoO ₃	UV	MB dye	180	97	[63]
GO-TiO ₂	UV	MO dye	240	75	[64]
HfO ₂ -graphene	UV	MB dye	180	98.5	This work

To determine photocatalytic tetracycline degradation of HfO₂-graphene nanocomposites (50 wt%), 15 mg of HfO₂-graphene nanocomposites mixed with the 20 ppm tetracycline solution (100 mL, pH = 5.19) and treated under UV light irradiation. To prevent the physisorption of tetracycline on the photocatalysts during degradation, tetracycline solution and HfO₂-graphene nanocomposites were stirred in the dark for 2 h with a magnetic stirrer. Following that, the reaction mixture was then exposed to UV light irradiation with continuous stirring for 180 min to examine degradation. The characteristic absorption peak at 357 nm is used to measure tetracycline degradation concentrations [65]. As a result, HfO₂-graphene degrades tetracycline with high efficiency, as shown in Figure 9A. In the blank test, without the photocatalyst, tetracycline degradation efficiency was measured under UV light. The HfO₂-graphene (50 wt%) photocatalyst degrades 81 \pm 2% of tetracycline after 180 min, suggesting that tetracycline can be degraded more efficiently under UV light (Figure 9A).

The degradation kinetics of HfO₂-graphene under UV light were further investigated based on the pseudo-first-order kinetic model:

$$\ln \left(C_{\rm t} / C_{\rm o} \right) = -kt \tag{10}$$

where C_0 indicates initial tetracycline concentration, C_t represents its concentration as a function of degradation time t, and k represents the reaction rate constant. Based on the results, we have identified a pseudo-first-order kinetic model for tetracycline degradation in the presence of UV light (Figure 9B). To validate the HfO₂-graphene nanocomposite impact on the degradation of tetracycline, we conducted a photodegradation experiment without HfO₂-graphene. Nevertheless, it rarely shows any photodegradation of tetracycline without HfO₂-graphene (Figure 9A). According to these results, the synthesized HfO₂-graphene nanocomposite is an extremely photoactive material, and the degradation process takes place via photocatalysis.



Figure 9. Photocatalytic efficiency of tetracycline degradation as a function of irradiation time under UV light using HfO₂-graphene (**A**). Rate of degradation of tetracycline under UV light (**B**).

3.6. Photocatalytic Degradation Mechanism

The higher surface of the graphene comprises numerous functional groups such as hydroxyl and carboxyl groups. Under UV light irradiation, the HfO_2 -graphene nanocomposite generates excitons on the absorption of photons. The generation of the oxide radicals (O^{-2}) by reducing the conduction band is intensified by the interaction of the photoexcited e^- with the residual functional groups of graphene molecules. The recombination of the electrons decelerates, and the reduction reaction accelerates due to graphene's presence and its high conductivity. Figure 10 shows the simultaneous process of the increase in hydroxyl radicals (OH^-) triggered by the oxidation reaction of the valence band. A strong reaction decomposes the dye molecules due to the enormous activity of O^{-2} radicals and OH° . The result establishes the superiority of the HfO_2 -graphene nanocomposite compared to HfO_2 as a photocatalyst under UV light irradiation.



Figure 10. Proposed reaction mechanism for the photocatalytic dye degradation of MB dye by HfO₂-graphene (50 wt%) nanocomposites under UV illumination.

4. Conclusions

The simple solution mixing method using variable amounts of graphene content (10, 30, and 50 wt%), the HfO₂-graphene nanocomposite, was prepared. More than the HfO₂ nanoparticles, the HfO₂-graphene nanocomposite showed notably higher efficacy of photodegradation. By HR-TEM, it was confirmed that the HfO₂ nanoparticles had been distributed on the graphene sheets. The chemical composition of C, O, and Hf were analyzed by EDX. Using the HfO₂-graphene nanocomposite as a catalyst, the MB solution's degradation was analyzed through UV light irradiation. As a result, 99% of MB dye removal

was achieved. The HfO₂-graphene (50 wt%) photocatalyst degrades $81 \pm 2\%$ of tetracycline in 180 min. It reaffirms that the HfO₂-graphene nanocomposite can effectively degrade MB dye and tetracycline under UV light irradiation, which can be applied optimally for proper wastewater management.

Author Contributions: V.J., S.M., S.C., A.P., S.G., J.R., G.N.P., S.A. and Y.-H.A. conceived the project; S.M., S.C., A.P., S.G. and J.R., performed the experiments, generated datasets, and wrote the first draft of the manuscript; V.J., S.A. and Y.-H.A. supervised the project and edited and revised the manuscript; All authors have read and agreed to the published version of the manuscript.

Funding: Global Korea Scholarship (GKS) Program through the National Institute for International Education (NIED), funded by the Ministry of Education Republic of Korea. The authors thank the Core Research Support Center for Natural Products and Medical Materials (CRCNM) for technical support regarding the nanoindentation test.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: No data were used for the research described in the article.

Acknowledgments: This research was supported by the Global Korea Scholarship (GKS) Program through the National Institute for International Education (NIED), funded by the Ministry of Education Republic of Korea. The authors thank the Core Research Support Center for Natural Products and Medical Materials (CRCNM) for technical support regarding the nanoindentation test. The first author, Venkatachalam J., is grateful to the Korean Ministry of Education for awarding the GKS to support the research program. S.C. was supported by a Grant-in-Aid for Early-Career Scientists fund (KAKENHI No.22K15249) by Japan Society for the Promotion of Science.

Conflicts of Interest: The authors declare that they have no competing interests.

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