An efficient eco advanced oxidation process for phenol mineralization using a 2D/3D nanocomposite photocatalyst and visible light irradiations

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Nanocomposites (CNTi) with different mass ratios of carbon nitride (C3N4) and TiO2 nanoparticles were prepared hydrothermally. Different characterization techniques were used including X-ray diffraction (XRD), UV-Vis diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), transmission electron spectroscopy (TEM) and Brunauer-Emmett-Teller (BET). UV-Vis DRS demonstrated that the CNTi nanocomposites exhibited absorption in the visible light range. A sun light - simulated photoexcitation source was used to study the kinetics of phenol degradation and its intermediates in presence of the as-prepared nanocomposite photocatalysts. These results were compared with studies when TiO2 nanoparticles were used in the presence and absence of H2O2 and/or O3. The photodegradation of phenol was evaluated spectrophotometrically and using the total organic carbon (TOC) measurements. It was observed that the photocatalytic activity of the CNTi nanocomposites was significantly higher than that of TiO2 nanoparticles. Additionally, spectrophotometry and TOC analyses confirmed that degraded phenol was completely mineralized to CO2 and H2O with the use of CNTi nanocomposites, which was not the case for TiO2, where several intermediates were formed. Furthermore, when H2O2 and O3 were simultaneously present, the 0.1% g-C3N4/TiO2 nanocomposite showed the highest phenol degradation rate and the degradation percentage was greater than 91.4% within 30 min.

Semiconductor photocatalysis is considered an alternative and environmentally benign technology in the field of wastewater treatment and for renewable energy sources. Although many semiconductors were tested as photocatalysts, TiO2 was intensively examined due to its nontoxicity, photostability, availability and low cost1–6. Nevertheless, there are several barriers concerning the use of TiO2 on a large scale. For example, TiO2 has a relatively high band gap energy (3.35 eV). This high band gap energy allowed the use of only UV radiation in photocatalysis, which is only 4% of the total solar energy7, 8. In addition, the high electron-hole recombination rate during the photocatalysis of TiO2 affects its activity. Therefore, numerous ideas and studies were developed to enhance its photocatalytic performance. These studies included changing the experimental conditions and synthesis methods of TiO29–11, metal particle loading5, 6, 14 and using a co-catalyst5, 6, 15. Considerable attention has been focused on utilizing carbonaceous nanomaterials as a support for TiO2 to improve its photocatalytic performance due to their unique electrical properties and controllable structures5, 16–21. An example of these supports is graphitic carbon nitride (g-C3N4), which can be obtained from the pyrolysis of nitrogen-rich organic precursors and is considered the most stable allotrope of carbon nitride14. Recently, Ong et al. reviewed numerous studies

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regarding g-C3N4-based photocatalysis. Additionally, several researchers have reported that coupling g-C3N4 with TiO2 may improve the photocatalytic behavior of TiO2 by lowering its band gap energy and slowing the electron-hole recombination rate. Phenol, among numerous organic pollutants found in wastewater, requires great attention due to its toxicity. Its existence has been confirmed in several industrial wastewaters, including chemical and petrochemical industries. Phenol treatment is expensive since it is unresponsive to traditional treatment techniques. Therefore, current investigations are directed at advanced oxidation processes (AOP) as a replacement for traditional techniques.

Although a few research studies targeted the use of g-C3N4/TiO2 composites in photocatalysis, most investigations were directed towards the degradation of dyes in the absence of oxidizing agents and using UV irradiation, which significantly increases the cost. In this work, the focus is on investigating the extremely enhanced kinetics of the advanced oxidation process in which the photocatalytic treatment of a high concentration of phenol (20 ppm), which is more difficult to mineralize than dyes, was done using a hydrothermally-prepared nanocomposite of 0.1% g-C3N4 nanosheets on top of TiO2 nanoparticles and a low-power Xe irradiation (mainly irradiates visible light) as a simulator for sunlight. Furthermore, the effect of the in-situ addition of eco oxidants e.g. hydrogen peroxide (H2O2) and/or ozone (O3) (generated using a home-made electrode) on the rate of photocatalytic degradation of phenol was also included, and to our knowledge, this work has not been previously addressed.

**Experimental Synthesis.** All chemicals were of analytical grade and no extra purification treatments were carried out. Graphitic carbon nitride (g-C3N4) was synthesized, as reported by Wang et al. Specifically, melamine (Alfa Aesar, 99% pure) was placed in a covered crucible and heated under stationary air conditions at 550 °C with a ramping rate of 2.5 °C min for 4 h. The resulting carbon nitride powder, which was pale yellow in color, was washed with deionized water and then dried under vacuum at 60 °C.

The g-C3N4–TiO2 nanocomposite (CNTi) photocatalyst was prepared by loading various mass ratios of CN on a commercial P25 TiO2 (Sigma Aldrich, 21 nm particle size) support as follows. TiO2 was added to an absolute ethanol/deionized water mixture at a 1:1 ratio and sonicated for 30 min. The same exact procedure was conducted with CN. Afterwards, the two aforementioned suspensions were mixed together, further sonicated for 30 min and nitric acid/ammonium hydroxide solutions were used to adjust the pH to 3.5. The resultant mixture was poured into a Teflon-lined stainless steel autoclave and left overnight at 120 °C. The suspension was centrifuged, and nitric acid/ammonium hydroxide solutions were used to adjust the pH to 3.5. The resultant mixture was then washed with hydrochloric acid (1 M) and then with deionized water. Lastly, the product was dried overnight at 80 °C. The loading percentages of C3N4 on TiO2 were designed to be 0.1, 0.5 and 1.0% and the corresponding names are 0.1CNTi, 0.5CNTi and 1CNTi, respectively.

**Characterization.** X-ray diffraction (XRD) measurements were conducted using a Bruker D8 diffractometer equipped with a Lynxeye detector and a Cu Kα, radiation source (λ = 15.406 × 10−2 nm). The diffractometer operated at 40 mA and 40 kV. The scanning was performed from 10–80° using a scan step of 0.015° and a step time of 0.2°. To determine the different phases, an automatic JCPDS library search and match was used. Additionally, standard SERACH and DIFFRACT AT (Australia) computer software packages were employed.

Raman spectra were obtained using an InVia Raman microspectrometer, which worked under macro conditions (λ = 3 cm) with a 785 nm excitation line and a laser control of approximately 2 mW. The measurements were conducted without prior treatment and average spectra were recorded from five registration scans. The spectra ranged from 100–3500 cm−1 with three accumulation numbers and a 10 s exposure time for each registration.

UV-Vis diffuse reflectance spectroscopy (DRS) was performed using a Cary 5000 UV-Vis-NIR (Agilent, Australia) equipped with an integrating sphere accessory. The test samples were supported by KBr, and the measured spectra were recorded at room temperature from 200 to 800 nm with a resolution of 0.05 nm.

The XPS spectra were obtained using Thermo Scientific ESCALAB-250Xi spectrometer. A monochromatic AlKα radiation source that operated at a power of 300 W (20 mA, 15 kV), was utilized. The vacuum in the analysis chamber was less than 7 × 10−10 Torr during the measurements. Carbon pollution that was referenced to C1s at 284.8 eV with a ±0.2 eV experimental error was taken as a base for elemental binding energies.

The amount of carbon, hydrogen and nitrogen were measured using a GmBH analyzer CHNS-O EA.

The BET (Brunauer-Emmett-Teller) surface areas were determined by an automatic ASAP 2010 Micromeritics sorpometer (USA) that was equipped with an outgassing platform and an online acquiring data and handling system, which functioned using numerous computer-run methods to examine the adsorption data.

Thermogravimetric analyses (TGA) were achieved utilizing a Perkin Elmer, USA/Pyris 1 TGA instrument. The air flow was heated at 5 °C min−1 to quantify the exact loading percentage of the carbonaceous material (CN) on the TiO2 support.

The CNTi nanocomposite was characterized using a Japanese JEOL 2100 F high-resolution transmission electron microscopy (HR-TEM) operating at 200 kV and coupled with an energy dispersive x-ray unit. The sample preparation was conducted by mixing a small quantity of sample with ethanol and sonicking for 15 min. The sample was then loaded onto the TEM grid.

A SiO2/Ti (300 nm)/Pt (100 nm)/TiOx (100 nm)/SnOx500 nm) electrode was used to generate ozone from a 0.5 M NaOH solution at 2 V versus the Ag/AgCl reference electrode. The electrode was manufactured at The Pennsylvania State University (USA) Materials Research Institute Nanofabrication Laboratory using a KJL CMS-18 sputtering system. The films were grown at room temperature on a quartz sample (SiO2) at 5 mTorr and 200 watts. The metallic films (Ti and Pt) were grown under an argon atmosphere, whereas the oxide films were grown in a mixture of 15% O2 in Ar. The generated ozone was transferred using Tygon tubing to the photocatalytic
reactor. The electrode had an ozone production efficiency close to 20% (excluding the dissolved ozone, which was not measured in the generating solution).

Photocatalytic experiments. For every photocatalytic run, 20 ppm of a phenol aqueous solution was prepared using deionized water. A 0.1 g catalyst was added to 100 mL of the phenol solution and stirred in the dark for 30 min until the adsorption equilibrium was achieved. The pH of the phenol solution was not adjusted. The photoreaction vessel was irradiated by a xenon lamp (150 W) without a cut-off filter at an integrated intensity of 12 mW cm\(^{-2}\) at 4.5 cm. The beginning of the experiment (time zero) occurred when the lamp was turned on. Samples were drawn every 5 min from the reaction vessel and filtered to dispose of the suspended catalyst particles through a nylon filter membrane with a 0.4 \(\mu\)m porosity. The UV-Vis spectrophotometer was used to determine the amount of phenol at a maximum absorbance of 298 nm. Experiments that involved O\(_3\), were electrochemically produced in an isolated cell that contained 0.5 M NaOH using a SiO\(_2\)/Ti (300 nm)/Pt (100 nm)/TiO\(_x\) (100 nm)/SnO\(_x\) (500 nm) electrode with a maximum current of 3000 mA at 8 V. The undissolved portion of the generated ozone was transferred to the photoreactor using a Tygon tube. A 4 ppm quantity of electrochemically generated ozone gas was used for each photocatalytic run. The photocatalysis system that included an O\(_3\) generating unit (electrochemical cell plus a potentiostat), an ozone meter, a UV lamp chiller and the photocatalytic reactor is shown elsewhere.

Finally, after photocatalytic experiments, the total organic carbon (TOC) for all phenol solutions were measured using a TOC-VPH analyzer, Shimadzu, Japan.

Results and Discussion

Characterization. Figure 1 displays a HR-TEM micrograph for the 1CNTi nanocomposite loaded on the TiO\(_2\) support. It is evident that the average particle size is approximately 20 nm and C\(_3\)N\(_4\) was uniformly distributed on TiO\(_2\). It also shows the lattice spaces of TiO\(_2\) (0.35 nm) and the lattice fringes of C\(_3\)N\(_4\).

To determine the C\(_3\)N\(_4\) contents in the final products, TGA was employed from 20 to 700 °C in air. Pure TiO\(_2\) shows almost no weight loss in the studied temperature range. However, pure C\(_3\)N\(_4\) experienced rapid weight loss from 550 to 640 °C, which indicates its decomposition. For the CNTi nanocomposite, the weight loss increased at temperatures above 500 °C. At the end of the analysis, the total combustion of CN was achieved. Therefore, the weight loss is related to the amount of CN in the composite. The results obtained from the TG studies indicated that the CN content in the respective composites corresponded to nominal values. For example, Fig. 2 shows the TGA of the 1CNTi composite.

Figure 3 displays FT-IR spectra of TiO\(_2\), CNTi and C\(_3\)N\(_4\). In Fig. 3a, a peak was detected at 1627 cm\(^{-1}\), which was ascribed to deformed water molecules or a Ti-O-Ti stretching vibration. Additionally, the low frequency strong and broad absorption band (below 1000) was assigned to the Ti-O-Ti vibration in TiO\(_2\). The broad band in the range of 3800 to 3000 cm\(^{-1}\) was designated as O-H stretching vibrations of C-OH groups (from carboxylic groups) or/and intercalated water molecules. The C\(_3\)N\(_4\) spectrum in Fig. 3d showed several strong bands from 1130 cm\(^{-1}\) to 1639 cm\(^{-1}\), which were associated with stretching and rotation vibrations of C-N and C= N in heterocycles. The band at 805 cm\(^{-1}\) was related to s-triazine ring vibrations and the wide absorption peak at 2000–3500 cm\(^{-1}\) was attributed to the N-H bond. The main characteristic peaks of C\(_3\)N\(_4\) were reduced and several peaks disappeared after loading on TiO\(_2\). These data indicated a low percentage of C\(_3\)N\(_4\) in the composites (Fig. 3b,c).

The XRD measurements for bare TiO\(_2\) (Fig. 4a) show diffraction patterns of both anatase and rutile phases. The peaks located at 25.4, 37.9, 48.0, 54.0, 55.1, 62.8, 69.1, 70.5 and 75.2° were assigned to the anatase phase (JPDs 21–1272), whereas the peaks assigned to the rutile phase were obtained at 27.5, 36.1 and 41.1° (JPDs 21–1276). Figure 4e shows two distinctive diffraction peaks: a strong peak located 27.4° with an interlayer spacing of 3.2 Å and a broad peak located at 13.1° with an interlayer spacing of 6.8 Å, which can be indexed to the hexagonal phase of graphitic C\(_3\)N\(_4\). The former peak was related to the (002) plane that was caused by the interlayer stacking of the conjugated aromatic system, whereas the latter peak was attributed to the (100) plane due to an in-plane...
structural packing motif. These two diffraction peaks are consistent with the results that have been reported in the literature. The diffraction patterns of CNTi composites (Fig. 4b–d) were similar to that of bare TiO₂ without the distinctive peaks of C₃N₄. This is can be ascribed to either (i) the low quantity of C₃N₄ in the composites or (ii) the peak overlap that relates to the interlayer stacking of the conjugated aromatic system with the peak at 27.5° for rutile TiO₂.

XPS measurements were performed to obtain information regarding the surface chemical composition along with their oxidation states. The survey spectra show Ti, C and O peaks in bare TiO₂ (Fig. 5Aa), C, O and N peaks in C₃N₄ (Fig. 5Ab) and C, N, Ti and O peaks in the CNTi composite (Fig. 5Ac). Figure 5B shows the C region of bare TiO₂, CN and CNTi. The deconvolution of the C region of bare TiO₂ (Fig. 5Bc) revealed three spectral peaks at 284.7, 286.2 and 288.8 eV, which were ascribed to adventitious carbon, -C-OH and -COOH groups, respectively. In the C₃N₄ spectrum (Fig. 5Bb), besides the spectral peak at 284.7 eV, which corresponds to C impurities, three peaks at binding energies of 286.6, 287.4 and 292.8 eV were allocated to the C-N-C, C-(N)₃ and C-NH₂ groups, respectively. The CNTi composite preserved all the carbon functional groups that existed in both TiO₂ and C₃N₄, as indicated in the devolution of its C region (Fig. 5Bc). However, a new peak at a lower binding energy of 281.1 eV appeared, which can be assigned to the C-Ti bond. The regional N 1s spectra for C₃N₄ and CNTi composites are presented in Fig. 5C. The spectrum of C₃N₄ (Fig. 5Ca) was deconvoluted into four peaks, which are attributed to N = C at 397.9 eV, N-(C)₃ at 399.1 eV, -NH- at 400.3 eV and -NH₂ at 403.8 eV. All the
N functional groups existed in CNTi and a new peak at a lower binding energy of 395.4 eV, which may be ascribed to an O-Ti-N bond (Fig. 5Cb). Figure 5D displays Ti 2P spectra of pure TiO₂ compared with that of the CNTi composite. The Ti 2p₃/2 and 2p₁/2 spin-orbit coupling peaks of bare TiO₂ appeared at 458.7 and 464.3 eV, respectively, with a spacing of 5.6 eV, which was ascribed to Ti⁴⁺ species in the TiO₂ cluster. However, this peak showed a broadening with a 0.2 eV shift of Ti 2p₃/2 to a lower binding energy, whereas the 2p₁/2 remained un-shifted after loading C₃N₄ on TiO₂. The deconvolution of the Ti region of the CNTi composite (Fig. 5Cd) revealed the existence of Ti-N or/and Ti-C (at 457.8 and 463.3 eV for Ti 2p₃/2 and 2p₁/2, respectively) with a spacing of 5.5 eV besides the TiO₂ main peak. Therefore, it can be concluded that the oxidation state of Ti (IV) did not change after the loading of C₃N₄ on TiO₂, and there is a chemical bond between the Ti and C and/or N of the C₃N₄. The negative shift in the Ti peak of CNTi due to electronic interactions between Ti and N atoms and/or C atoms caused an increase in the electron density on Ti. This was also supported by the presence of O-Ti-N in the N 1s region (Fig. 5Cb) and the peak of C-Ti in the C 1s region (Fig. 5Bc). The O 1s spectrum (Fig. 5Ea) of pure TiO₂ were fit into two peaks at binding energies of 529.87 and 531.42 eV that were assigned to oxygen in TiO₂ and the surface hydroxyl, respectively. In comparison with pure TiO₂, a negative shift of the main O 1s to 529.2 eV was observed for the CNTi composite. Note that this shift of 0.2 eV in O1s is similar to the shift found in Ti 2p₃/2 for the CNTi composite, which supports the suggestion of the existence of bonds between Ti and C and/or N and are in good agreement with previous reports. The XPS, XRD and FT-IR studies clearly revealed the successful preparation of nanocomposite material with chemically bound interfaces between C₃N₄ and TiO₂ rather than a physical mixture of two separate g-C₃N₄ and TiO₂ phases.

Argon bombardment was used to etch the CNTi nanocomposite to gain information regarding which material on top of the other. From Table 1, it is obvious that CN covered the TiO₂ surface since the quantity of TiO₂ increased while the quantity of carbon decreased with etching.

The elemental analysis of as-prepared C₃N₄ provided a C to N ratio of 0.53, which is less than the theoretical value of ideal carbon nitride (0.75 in C₃N₄). In addition to nitrogen and carbon, the elemental analysis also detected hydrogen. The presence of hydrogen in the form of N-H and NH₂ groups was established by FT-IR and XPS analyses, which describes the relatively low C to N ratio.

Figure 6 shows the Raman spectra of TiO₂, 0.1CNTi, 0.5CNTi and 1CNTi recorded with a 785 nm laser as the excitation source. The measured Raman spectrum of C₃N₄ (Fig. 6d) is similar to the one shown by Tonda et al. in which several characteristic peaks of C₃N₄ were revealed with strong peaks at 705 and 1232 cm⁻¹. Similar to the XRD results, the Raman spectrum of C₃N₄ loaded on TiO₂ did not show any characteristic peaks of C₃N₄. Only peaks corresponding to the anatase and rutile phases of TiO₂ were observed (Fig. 6a-c). This result was also observed by other researchers.

The band gap energies of TiO₂, 0.1CN, 0.5CN and 1CN were measured and the wavelengths at the absorption edge were calculated and recorded from the UV-Vis diffuse reflectance spectra (Fig. 7 and Table 2). The measurements revealed that the band gap energy of C₃N₄ equals 2.75 eV, as reported in the literature. Interestingly, the band gap energy of the CNTi composite increased as the C₃N₄ percentage in the composite increased but remained lower than that of the TiO₂. The composite with the lowest band gap energy (2.95 eV) was 0.1CNTi compared to 3.35 eV for TiO₂. Therefore, loading CN on TiO₂ shifted the TiO₂ absorption wavelength to the visible region and allowed the photocatalytic degradation of phenol using visible light or sunlight irradiation. Note that the BET surface area of 1CNTi composites (49.8–50.6 m² g⁻¹) and TiO₂ (51.1 m² g⁻¹) were similar. This proves that the surface area was not the controlling factor for this photocatalytic study.

**Photocatalytic applications.** Phenol degradation was studied using a xenon lamp photoexcitation source in the presence and absence of H₂O₂ and/or O₃. The % of phenol degradation was calculated using Equation 1.

\[
\text{Degradation} \% = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]
where $C_0$ is the adsorption equilibrium concentration of phenol before irradiation begins. $C_t$ represents the residual concentration of phenol after specific time $t$ of irradiation.

Apparent first order reaction rate law was found to fit the photocatalytic degradation of phenol with a perfect correlation constant ($R^2$) close to unity. The rate constant for the degradation, $K$, was obtained from the first-order plot (Equation 2).

$$\ln \frac{C_t}{C_0} = -Kt$$  

Figure 5. (A) XPS survey of (a) TiO$_2$, (b) C$_3$N$_4$, and (c) CNTi, (B) C 1 s region of (a) TiO$_2$, (b) C$_3$N$_4$, and (c) CNTi, (C) N 1 s region of (a) CN and (b) CNTi, (D) Ti 2 P region of (a) TiO$_2$ and (b) CNTi, (E) O 1 s region of (a) TiO$_2$ and (b) CNTi.
Table 1. Argon etching of 1CNTi at different times.

| Etching Time (s) | Etching Depth, (nm) | C(%) | Ti(%) |
|------------------|---------------------|------|-------|
| 0                | 0                   | 9.4  | 26.5  |
| 15               | 1                   | 2.4  | 29.2  |
| 40               | 3                   | 1.9  | 30.7  |
| 65               | 5                   | 1.4  | 31.5  |
| 90               | 7                   | 1.3  | 31.9  |
| 125              | 10                  | 1.2  | 32.0  |
| 230              | 20                  | 1.0  | 33.3  |

Figure 6. Raman spectra of (a) TiO₂, (b) 0.1CNTi, (c) 1CNTi, and (d) CN.

Figure 7. Band gap energies of TiO₂, 0.1CNTi, 0.5CNTi, 1CNTi and CN (C₃N₄) from UV-Vis DRS.

Table 2. Wavelengths at the absorption edge for TiO₂, 0.1CNTi, 0.5CNTi, 1CNTi and C₃N₄ and their corresponding band gap energies.

| Catalysts | Wavelength (nm) | Band Gap Energy |
|-----------|-----------------|-----------------|
| TiO₂      | 371             | 3.35            |
| 0.1CNTi   | 422             | 2.95            |
| 0.5CNTi   | 407             | 3.05            |
| 1CNTi     | 401             | 3.10            |
| C₃N₄      | 452             | 2.75            |
Note that in absence of the photocatalysts (CNTi or TiO₂ nanocomposites), there was no degradation of phenol, even in presence of C₃N₄ without the TiO₂ support. Furthermore, the C₃N₄ did not peel off the TiO₂ support during and after the photocatalytic experiments, which can be attributed to the chemical bond between C₃N₄ and TiO₂ during the synthesis process.

Figure 8 shows the degradation % (a, c and e) and reaction kinetics (b, d and f) for 20 mgL⁻¹ phenol using Ti, 0.1CNTi, 0.5CNTi and 1CNTi nanocomposite photocatalysts under 150 W Xe illumination in the absence (a and b) and presence (c and d) of 70µL of H₂O₂ and additional cases using 0.1CNTi in the presence and absence 70µL of H₂O₂ (e and f) and/or 4 ppm of O₃ (e and f).

Figure 8 shows the degradation % (a, c and e) and reaction kinetics (b, d and f) for 20 mgL⁻¹ phenol using Ti, 0.1CNTi, 0.5CNTi and 1CNTi nanocomposite photocatalysts under 150 W Xe illumination in the absence (a and b) and presence (c and d) of 70µL of H₂O₂ and additional cases using 0.1CNTi in the presence and absence 70µL of H₂O₂ (e and f) and/or 4 ppm of O₃ (e and f). The following conclusions were obtained from Fig. 8 and Table 3. First, in all cases, the photodegradation percentage increased with time regardless of the type of photocatalyst. Second, all CNTi composites showed better photocatalytic activity compared with bare TiO₂. An increase in the C₃N₄ percentage from 0.1 to 1% in the CNTi composites decreased the photocatalytic activity, and 0.1CNTi showed the best performance in terms of the phenol degradation rate. Furthermore, the phenol degradation rate
increased with the addition of H$_2$O$_2$ regardless of the photocatalyst type. This is mostly due to the increase in hydroxyl radical formation and retardation of the electron/hole (e/h$^+$) pair recombination due to the electron acceptor property of the C$_3$N$_4$ where electrons move from TiO$_2$ to the carbonaceous materials inhibiting the recombination between the electrons and the holes.

$$
\text{H}_2\text{O}_2 + \text{e}^-_{\text{CB}} \rightarrow \text{OH} + \text{OH}^- \\
\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}
$$

In the case of H$_2$O$_2$, the addition of O$_3$ to the reaction mixture increased the rate of phenol oxidation. However, the rate of phenol degradation in presence of H$_2$O$_2$ was higher than in the presence of O$_3$ regardless of the type of photocatalyst. In addition, the presence of both oxidants (O$_3$ + H$_2$O$_2$) greatly increased the photodegradation rate compared with the case where one oxidant was used. The 0.1CNTi composite demonstrated 91.4% phenol degradation within 30 min with rate of 0.08 min$^{-1}$ when both O$_3$ and H$_2$O$_2$ were used under a Xe illumination of 150 W. Miranda et al. obtained 85% conversion of phenol within 120 min under UV irradiation using g-C$_3$N$_4$/TiO$_2$ composite prepared by impregnation methods. Zhao and co-workers obtained 96.4% phenol degradation within 60 min under a Xe illumination of 500 W (20 ppm phenol and 1 gL$^{-1}$ CNTi). Zhou et al. tested TiO$_2$/Co-g-C$_3$N$_4$ catalyst for phenol degradation. The degradation of 10 ppm phenol reached 100% within 40 min under 300 W xenon illumination. Yao and his group tested TiO$_2$-CdS-gC3N4Ns composite for degradation of 10 ppm phenol under visible light irradiation. They obtained 80% degradation within 300 min. S. Obregón and G. Coloñ found that the modification of TiO$_2$/g-C$_3$N$_4$ composite with Pt and Mn improved the photocatalytic activity of phenol degradation under UV radiation. The best phenol rate was obtained $10.6 \times 10^{-8}$ mol/L/s over Pt-TiO$_2$/g-C$_3$N$_4$-MnOx composite.

Finally, a comparison of the phenol degradation % based on UV spectrophotometer and TOC measurements indicated similar results when the CNTi nanocomposite photocatalyst was used. By contrast, when TiO$_2$ was used, the phenol degradation % from the UV-Vis spectrophotometer measurement was higher than that from the TOC measurement. Therefore, it can be concluded that CNTi nanocomposites undergo complete oxidation in contrast to that of the TiO$_2$ surface where intermediates were formed. Su et al. reported 65.7% TOC removal.

### Table 3.

| Catalyst | $\tau$ | R$^2$ | % D | TOC |
|----------|-------|-------|-----|-----|
| TiO$_2$  | 0.021 | 0.99  | 49.1| 54.4|
| $+$H$_2$O$_2$ | 0.030 | 0.99  | 61.3| 57.8|
| 0.1% CNTi | 0.032 | 1.00  | 62.6| 63.1|
| $+$H$_2$O$_2$ | 0.056 | 0.99  | 81.2| 81.3|
| 0.5% CNTi | 0.030 | 1.00  | 60.7| 78.0|
| $+$H$_2$O$_2$ | 0.051 | 1.00  | 77.8| 49.9|
| 1% CNTi  | 0.023 | 1.00  | 60.7| 49.7|
| $+$H$_2$O$_2$ | 0.043 | 0.99  | 72.9| 73.0|
| 0.1% CNTi + O$_3$ | 0.038 | 0.99  | 69.1| 71.0|
| 0.1% CNTi + H$_2$O$_2$ + O$_3$ | 0.080 | 0.99  | 91.4| 92.1|

**Figure 9.** The cycling runs for the degradation of phenol (20 ppm) on 0.1CNTi in presence of H$_2$O$_2$ and O$_3$ under Xe illumination.
of phenol over carbon nitride quantum dots anchored onto TiO₂ nanotube arrays after 180 min reaction under solar light ⁵⁸.

Stability evaluation. Photocatalytic measurements of the 0.1CNTi nanocomposite, which yielded the best degradation rate of phenol (in this study) in the presence of both O₃ and H₂O₂ under Xe illumination, were repeated six times after isolating the photocatalyst. Figure 9 indicates that there was no obvious decline in the photocatalytic activity. In addition, XRD measurements both before and after the reaction was the same (the results are not shown). Therefore, the results demonstrated that the CNTi nanocomposite photocatalyst was stable under the abovementioned experimental conditions.

Conclusions
Coupling TiO₂ with C₃N₄ (visible light-sensitized semiconductors) has proved to be beneficial for improving the photocatalytic performance due to a synergism that was ascribed to improved light harvesting, enhanced photo stability and effective photexcited charge separation.

The addition of H₂O₂ or O₃ improved the photocatalytic degradation rate of phenol. However, the rate dramatically increased when a trace amount of O₃ gas (4 ppm) was added to H₂O₂ in the reaction mixture in the photocatalytic reactor, which was attributed to the increase in the rate of ozone degradation and, consequently, the rate of hydroxyl radical formation in the presence of H₂O₂.

The best C₃N₄ ratio in the CNTi composite, which yielded the highest degradation rate of phenol, was 0.1% C₃N₄. This photocatalyst was stable under experimental conditions, and its performance was drastically enhanced in the presence of both O₃ and H₂O₂.

Finally, based on the results, the CNTi nanocomposite photocatalyst can be considered to be a promising candidate for the treatment of wastewater contaminated with phenol, especially when H₂O₂ with traces of O₃ gas is used.

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Author Contributions
Dr. H. Al-kandari and Dr. Aboubakr M. Abdullah shared the idea of the work, wrote the manuscript, did some practical measurements, analyzed all data and prepared the figures. Dr. Yahia Ahmad and Dr. Siham prepared the carbon nitride and reviewed the article scientifically and linguistically. They did all the characterization to confirm the material is C$_3$N$_4$, but data is not included here. Dr. S. Al-kandari and Mr. Ahmed M. Mohamed participated in the practical work only.

Additional Information
Competing Interests: The authors declare that they have no competing interests.

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