Article

Graphene Oxide Hybridised TiO$_2$ for Visible Light Photocatalytic Degradation of Phenol

Guanyu Wang, Weijie Guo, Deping Xu *, Di Liu and Mengtao Qin

School of Chemical & Environmental Engineering, China University of Mining &Technology (Beijing), Beijing 100083, China; tbp150301010@student.cumtb.edu.cn (G.W.); tbp150303030@student.cumtb.edu.cn (W.G.); 201849@cumtb.edu.cn (D.L.); zqt1800303101g@student.cumtb.edu.cn (M.Q.)
* Correspondence: bqt1800303040@student.cumtb.edu.cn

Received: 24 July 2020; Accepted: 23 August 2020; Published: 26 August 2020

**Abstract:** In industrial pollutants, phenol is a kind of degradation-resistant hazardous compound. It is generated during industrial processes in factories and treatment at sewage plants. In this study, we analyse the photocatalytic activity of TiO$_2$ and rGO as a composite for the degradation of phenol. Hybridised titanium dioxide/reduced graphene oxide (TiO$_2$/rGO) nanocomposites were synthesised by a simple hydrothermal method using flake graphite and tetrabutyl titanate as raw materials. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Brunauer–Emmet–Teller (BET) specific area analysis, Fourier transform infrared spectroscopy (FTIR), Raman, X-ray photoelectron spectroscopy (XPS), photoelectrochemical analysis, and UV–vis diffuse reflectance spectra (DRS) were employed to characterise the physicochemical properties of the as-prepared nanocomposites. The results showed the TiO$_2$/rGO nanocomposites’ significant anatase phase and a small fraction of the rutile phase the same as that of the as-prepared TiO$_2$ nanoparticles. The spherical TiO$_2$ nanoparticles (diameter 20–50 nm) were agglomerated slightly and the agglomerates were anchored on the rGO sheets and dispersed symmetrically. The specific surface area of TiO$_2$/rGO-4% nanocomposites was 156.4 m$^2$/g, revealing a high specific surface area. Oxygen-containing functional groups that existed in TiO$_2$/rGO-4% nanocomposites were almost removed during hydrothermal processing. The photocurrent response of TiO$_2$/rGO-4% was strongest among the TiO$_2$/rGO nanocomposites, and the bandgap of TiO$_2$/rGO-4% was 2.91 eV, showing a redshift of absorption into the visible region, which was in favour of the high photocatalytic activity of TiO$_2$/rGO nanocomposites under visible light ($\lambda > 420$ nm). Moreover, the samples were employed to photodegrade phenol solution under visible light irradiation. TiO$_2$/rGO-4% nanocomposite degraded the phenol solution up to 97.9%, and its degradation rate constant was 0.0190 h$^{-1}$, which had higher degradation activity than that of other TiO$_2$/rGO nanocomposites. This is a promising candidate catalyst material for organic wastewater treatment.

**Keywords:** photocatalysis; titanium dioxide; reduced graphene oxide; visible light; phenol

1. Introduction

In recent years, wastewater treatment has attracted attention with the continuous deterioration of the global environment. Especially, the removal of toxic and refractory pollutant in coal-chemical wastewater has become a huge challenge [1–3]. Generally, coal-chemical wastewater, produced from gasification and coking, possesses high concentrations of contaminants, such as phenolic compounds, benzene, cyanide, aromatic organic, (oxygen, sulphur, and nitrogen)-heterocyclic compounds, and other harmful substances, which are posing a great threat to human health and sustainable development [4,5]. Phenol and phenolic derivatives are the most harmful among the common contaminants due to their high toxicity, long remaining ability, and poor biodegradation [6,7]. At present, well-established
techniques for the removal of phenol and phenolic derivatives include adsorption, coagulation, electrochemical, extraction, biological treatment, enzyme oxidation, and supercritical water oxidation. However, these methods cannot degrade them completely and even generate secondary pollution [8–11]. Compared to the techniques mentioned above, the method of photocatalysis is low-cost, highly efficient, and non-toxic; it is a novel strategy for the degradation of phenol and phenolic derivatives, as it can lead to fast and complete mineralisation of organic pollutants, without leaving harmful intermediates [12–18].

As a kind of semiconductor, TiO\textsubscript{2} has been widely applied in photocatalysis for wastewater and gas by using solar or artificial light irradiation due to its cheapness, environmental compatibility, and chemical stability [19–21]. Generally, as a kind of photocatalyst, TiO\textsubscript{2} is stimulated by UV light (~380 nm), which has higher energy than the band energy of TiO\textsubscript{2}. It generates electrons (e\textsuperscript{−}) in the conduction band and electron–holes (h\textsuperscript{+}) in the valence band to react with water into hydroxyl radicals (OH\textsuperscript{−}) and superoxide radicals (O\textsubscript{2}·\textsuperscript{−}) [22]. These potent oxidation radicals can mineralise organic pollution into water and carbon dioxide [23,24]. As is well known, the major drawback of TiO\textsubscript{2} is its high electron–hole recombination rate and poor absorption of visible light due to its low electron transfer mobility and narrow bandgap (3.2 eV for the anatase phase). Therefore, a great deal of effort has been directed to improve electron transfer mobility and extend the bandgap to one that can efficiently photodegrade organic pollution under nature or artificial light [25,26].

Sohrabi et al. synthesised nanostructured copper-doped titanium dioxide as a catalyst. They optimised the photocatalytic degradation of phenol under UV light irradiation with H\textsubscript{2}O\textsubscript{2}; the synergistic effect between TiO\textsubscript{2} and Cu exhibited better photocatalytic activity than that of pure TiO\textsubscript{2}. Moreover, the addition of H\textsubscript{2}O\textsubscript{2} can produce more strong oxidation radicals to mineralise organic pollution [29]. Almeida et al. synthesised TiO\textsubscript{2}/MgZnAl photocatalyst from ternary (Mg, Zn, and Al) layered double hydroxides hybridised with TiO\textsubscript{2} nanoparticles by the coprecipitation method at variable pH. The most efficient photocatalyst composite for the photodegradation of phenol was obtained at a 5% Zn\textsuperscript{2+}/Mg\textsuperscript{2+} molar ratio [30]. The methods mentioned above are all exciting, but some drawbacks still exist, such as small specific surface area, low degradation amount, and unavailability of visible light. Fortunately, graphene, as a kind of new multifunctional material that has been explored extensively due to its ability to mix with TiO\textsubscript{2}, can form nanocomposite films to improve electron transfer mobility due to its superior electrochemical activity and large specific surface area [19,31,32]. Malekshoar et al. synthesised graphene-based titanium dioxide and zinc oxide composites (TiO\textsubscript{2}-G, ZnO-G) using a hydrothermal process. Complete solar degradation of 40 ppm phenol was achieved with 60 min while using the coupled TiO\textsubscript{2}-G/ZnO-G photocatalysts at the optimum conditions [33]. Farzan Hayati et al. synthesised ZnO/TiO\textsubscript{2} anchored on a reduced graphene oxide (rGO) ternary nanocomposite heterojunction via hydrothermal, solvothermal, and sol–gel methods. With the addition of graphene oxide to the composite, a significant increase was detected in photocatalytic performance due to the higher available surface area and lower electron–hole recombination rate [34]. Ezzat Rafiee et al. made the TiO\textsubscript{2}/Gr nanocomposites modify with 12-tungstophosphoric acid (H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40}/TiO\textsubscript{2}/Gr/xPW). As a result, TiO\textsubscript{2}/Gr/xPW exhibited a higher visible light photocatalytic activity in comparison with TiO\textsubscript{2}/Gr.
and pure TiO$_2$, with the maximum degradation efficiency of 91%, 68%, and 15%, respectively [35]. Although there are many organic or inorganic materials doped or decorated TiO$_2$ as a photocatalyst for the degradation of phenol, the starting materials used in this work are new and rarely reported.

In this work, TiO$_2$ nanoparticles and TiO$_2$ nanoparticles hybridised with reduced graphene oxide (TiO$_2$/rGO) were successfully synthesised by the sol–gel and hydrothermal methods, respectively. TiO$_2$ nanoparticles were anchored on the rGO sheets and dispersed well. TiO$_2$/rGO nanocomposites exhibited excellent photocatalytic degradation of phenol under visible light irradiation due to their high specific surface area, low electron–hole recombination rate, and suitable bandgap energy. This work provides a novel way of phenol degradation and may be applied for organic wastewater treatment.

2. Experimental Setup

2.1. Materials and Reagents

Titanium butoxide, glacial acetic acid (17.5 mol/L), ethyl alcohol (95%), NaNO$_3$ (99.2%), KMnO$_4$ (99.3%), $\text{H}_2\text{SO}_4$ (99.8%), and $\text{H}_2\text{O}_2$ (35%) were purchased from Macklin Biochemical Co., Ltd., Shanghai, China. Crystalline flake graphite powder (99.5%, 325 mesh) was purchased from Sigma-Aldrich, Shanghai, China. Deionised water was used in all processes.

2.2. Synthesis of TiO$_2$ Nanoparticles

TiO$_2$ nanoparticles were prepared by the sol–gel method. Titanium butoxide (10 mL) was mixed with absolute ethyl alcohol (50 mL) under vigorous stirring for 30 min, to obtain solution A. Subsequently, deionised water (5 mL) was mixed with absolute ethyl alcohol (50 mL) and glacial acetic acid (6 mL) under rapid stirring for 30 min, to obtain solution B. Finally, solution A was added into solution B drop by drop under rapid stirring. Then, the TiO$_2$ gel was obtained. The gel was aged at room temperature for 24 h, followed by drying at 80 °C for 24 h. After calcination in air at 575 °C for 4 h, the obtained solid was ground into particles before use.

2.3. Synthesis of TiO$_2$/rGO Nanocomposites

Graphene oxide (GO) was fabricated from crystalline flake graphite through the modified Hummers method [36]. The rGO-decorated TiO$_2$ nanoparticles were obtained via a hydrothermal process. Next, 0.5 g as-prepared TiO$_2$ was ultrasonicated in a mixture of 120 mL deionised water and 60 mL absolute ethyl alcohol to disperse well. After 1 h, different weight addition ratios of GO (2%, 4%, 6%, 8%) were added to the above-mixed solution. Then, the mixed solution was aged with vigorous stirring for 2 h. After that, the grey mixed solution was added in a hydrothermal reactor and heated at 180 °C for 10 h in a dry oven. Finally, the mixed solution was treated by centrifugal separation, and the obtained solid was rinsed by deionised water several times. After drying at 40 °C for 6 h, the solid was ground into particles before use.

2.4. Characterisation

X-ray diffraction (XRD) pattern was performed on a diffractometer (Rigaku Miniflex, Tokyo, Japan) using Cu K$_\alpha$ radiation ($\lambda = 1.5406 \text{ Å}$) at a scan rate of 0.05 2θ/s. A scanning electron microscope (SEM), model JSM 6700F, at an accelerating voltage of 10 kV and a transmission electron microscope (TEM), model CM200 (Philips, Eindhoven, The Netherlands), at the opening voltage of 20–200 kV were used to investigate the morphology of the materials. An Autosorb-IQ-MP automatic gas analyser at 77 k was applied to calculate the specific surface area of the samples. Fourier transform infrared spectrometer (FTIR) was performed on a PerkinElmer Frontier FTIR spectrometer with a resolution of 1 cm$^{-1}$ between 500 and 4000 cm$^{-1}$ at RT. Laser Raman spectra were recorded on Renishaw in-Via Raman systems equipped with a 514 nm line of an air ion laser as the excitation source. X-ray photoelectron spectroscopy (XPS) spectra were acquired using an ESCALAB 250 photoelectron spectrometer (Waltham, MA, USA)
at 3.0 × 10^{-10} \text{ mbar} with monochromatic Al Kα radiation. UV–vis diffuse reflectance spectra (DRS) of photocatalysts were analysed by UV-2600 UV–vis spectrophotometers (Shimadzu, Kyoto, Japan).

2.5. Photoelectrochemical Analysis

Photoelectrochemical activity was measured on an electrochemical workstation (CHI-1140C, CH Instruments Ins) using 0.1 mol/L Na_{2}SO_{4} aqueous solution as the electrolyte in a three-electrode quartz cell. Platinum wire, mercurous sulfate (Hg_{2}SO_{4}) electrode, and TiO_{2}/rGO nanocomposites metal nets were used as the counter electrode, reference electrode, and working electrodes, respectively. The electrolyte consisted of Na_{2}SO_{4} solution deaerated with N_{2} for 30 min prior to use. The photocurrent of the samples with a light on and off was measured at 0 V using 500 W Xe lamp irradiation equipped with a UV/cutoff filter (λ > 420 nm).

The following is the preparation method of the working electrodes: 5 mg TiO_{2}/rGO nanoparticles, 4 mg acetylene black, and 1 mg polyvinylidene fluoride (PVDF) were mixed well with 2 mL ethyl alcohol. The obtained slurry was coated on the stainless-steel net (2 × 4 cm) and kept 0.09 g of the working electrode. After drying at 60 °C for 3 h, the working electrode was pressed at 10 MPa prior to use.

2.6. Photocatalytic Test

The photocatalytic experiments were carried out in a water-jacket reactor at a constant temperature of 10 °C and initiated under dark conditions for 30 min to establish an adsorption/desorption equilibrium for the model pollutant and dissolved oxygen on the surface of TiO_{2}. Then, the suspension was irradiated by a 500 W Xe lamp equipped with a UV/cutoff filter (λ > 420 nm) for 12 h. The distance between the water-jacket reactor and lamp was 15 cm. In each experiment, 50 mg of the test sample and 100 mL of 20 mg/L phenol aqueous solution were introduced into the reactor with magnetic stirring. A total of 4 mL of the irradiated solution was extracted from the reactor at specified intervals and centrifugally separated at 5000 r/min for 10 min. The concentration of phenol was analysed by a UV–vis spectrophotometer at λ = 270 nm. The degradation percentage of phenol was calculated by the equation:

\[
\text{Degradation rate} = \frac{C_0 - C_t}{C_0} \times 100\%
\]

where C_0 represents the initial concentration of the phenol and C_t is the concentration at time t.

3. Results and Discussion

The morphology of as-prepared TiO_{2}, rGO, and TiO_{2}/rGO-4% was observed by SEM and TEM. As shown in the SEM images (Figure 1a–c), the irregular TiO_{2} particles (Figure 1a) were aggregated into spherical particles (Figure 1c) after the hydrothermal process, and the reduced graphene oxide (Figure 1b) had an apparent layered structure. As seen from the TEM images (Figure 1d), the diameter of TiO_{2} nanoparticles was between 20 and 40 nm. Compared to the pure rGO sheets (Figure 1e), the as-prepared TiO_{2} nanoparticles were agglomerated slightly and the agglomerates were anchored on the rGO sheets and dispersed symmetrically (Figure 1f), owing to the electrostatic attraction between the monomeric titanyl ions (TiO^{+}) and the negative surface of graphene oxide. Besides, the π–π stacking between the rGO sheets was beneficial for sample synthesis [37]. The agglomerated TiO_{2} nanoparticles that dispersed symmetrically on the rGO sheets were beneficial for electron transport mobility, therefore, this reduced the electron–hole recombination rate.

XRD patterns for GO, TiO_{2}/rGO nanocomposites, and as-prepared TiO_{2} are shown in Figure 2. As for GO, the major diffraction peak at 9.4° was ascribed to the (002) crystallographic plane of GO and the interlayer space was 9.4 Å, larger than 3.4 Å of natural graphite, since many oxygen-containing function groups are introduced in natural graphite and extend the interlayer space by chemical process [38]. TiO_{2}/rGO nanocomposites with different ratios of rGO had similar XRD patterns and also had the same as that of as-prepared TiO_{2}. The XRD patterns of as-prepared TiO_{2} contained both the
anatase and rutile phases of TiO_2. The diffraction peaks at 25.3°, 36.9°, 37.8°, 48.0°, 53.9°, 55.0°, 70.3°, and 75.0° are ascribed to (101), (103), (004), (200), (105), (211), (200), and (224) of the anatase phase of TiO_2. The diffraction peaks at 27.4°, 36.0°, 39.1°, 41.2°, 56.6°, 62.7°, and 68.9° are ascribed to (110), (101), (112), (111), (200), (002), and (301) of the rutile phase (JCPDS 21-1272) [39]. The mixture of anatase and rutile phases was found to efficiently enhance the photocatalytic activity of the catalysts due to the synergic interaction between the two phases, which led to spatial charge separation and hindered electron–hole recombination [40]. In addition, the XRD pattern of TiO_2/rGO nanocomposites did not show any rGO phase and this can be attributed to its low concentration. Moreover, the characteristic peak of rGO at 24.5° may be screened by the main peak of anatase at 25.3° [41,42].

Figure 1. SEM images of (a) TiO_2, (b) rGO, and (c) TiO_2/rGO-4%. TEM images of (d) TiO_2, (e) rGO, and (f) TiO_2/rGO-4%.
As shown in Figure 3, the N\textsubscript{2} adsorption-desorption isotherms of TiO\textsubscript{2}/rGO and as-prepared TiO\textsubscript{2} belonged to the type IV isotherm. The BET surface areas of TiO\textsubscript{2}/rGO-4% and as-prepared TiO\textsubscript{2} were 156.4 and 65.3 m\textsuperscript{2}/g, respectively. It is evident that a hysteresis loop exists in the TiO\textsubscript{2}/rGO-4% isotherm when the relative pressure is between 0.4 and 0.8, meaning that mesopores exist in the TiO\textsubscript{2}/rGO-4% nanocomposites. In a solution, the high specific surface area can adsorb more substances targeted for degradation, improve the collision possibility between catalyst and substances targeted for degradation, and offer more photocatalytic activity sites and reaction centres. This is beneficial for the enhancement of photocatalytic performance [43].

Figure 2. XRD patterns for GO, TiO\textsubscript{2}/rGO nanocomposites, and as-prepared TiO\textsubscript{2}.

Figure 3. N\textsubscript{2} adsorption-desorption isotherms of TiO\textsubscript{2}/rGO-4% and as-prepared TiO\textsubscript{2}.

Figure 4 shows the FTIR spectra of GO and TiO\textsubscript{2}/rGO nanocomposites. In the FTIR spectra of GO, a broad adsorption band was observed near 3410 cm\textsuperscript{-1}, which is the characteristic adsorption peak of
absorbed water or the hydroxyl group in GO. The characteristic adsorption peak at 1735 cm\(^{-1}\) (C=O) is attributed to the carboxyl group stretching and the skeletal vibration of GO. Due to more moisture being absorbed in the GO, an adsorption band in the vicinity of 1634 cm\(^{-1}\) was observed, corresponding to the adsorption peak for the bending vibration of the water molecular OH. The peaks at around 1065 and 1220 cm\(^{-1}\) were related to the hydroxyl C-OH and alkoxy C-O stretching vibrations of GO sheets. These oxygen-containing functional groups provided anchoring sites for the adsorption of TiO\(_2\) on the GO sheets and also confirmed Hummer’s method was successful in bringing oxygen-containing functional groups into graphite flakes. TiO\(_2/rGO\) nanocomposites exhibited a similar FTIR spectrum. The adsorption peak at 480 and 1600 cm\(^{-1}\) was attributed to the vibration of Ti-O bonds in TiO\(_2\) and the skeletal vibration of graphene. Compared to the FTIR spectra of GO, the oxygen-containing functional groups were weak and almost disappeared. The only remaining adsorption peak of graphite and Ti-O proved that the GO was reduced to rGO by hydrothermal reaction and the existence of rGO in the TiO\(_2/rGO\) nanocomposites. The removal of oxygen-containing functional groups was beneficial for electron transport mobility, hindered electron–hole recombination, and improvement in the photocatalytic activity of the catalyst \[44,45\].

![FTIR spectra of GO and TiO\(_2/rGO\) nanocomposites.](image)

The Raman spectra of GO and TiO\(_2/rGO\) nanocomposites are shown in Figure 5. The D band (a common feature for sp\(^3\) defects in carbon) and G band (response of the in-plane stretching motion of symmetric sp\(^2\) C–C bond) were located at around 1356 and 1614 cm\(^{-1}\), respectively. As we all know, the intensity ratio of D to G usually reflects the order of defects in graphene, and the I\(_D/I_C\) ratios of GO, TiO\(_2/rGO\)-2%, TiO\(_2/rGO\)-4%, TiO\(_2/rGO\)-6%, and TiO\(_2/rGO\)-8% were 2.2, 1.7, 1.4, 1.5, and 1.6, respectively \[46\]. The I\(_D/I_C\) ratios of TiO\(_2/rGO\)-4% were the lowest, proving that oxygen-containing function groups that existed in TiO\(_2/rGO\)-4% were reduced and the number of graphene layers increased after the hydrothermal process, which was beneficial for the improvement in the photocatalytic activity of the catalyst due to the superior electron transfer mobility of rGO. Otherwise, the changes in I\(_D/I_C\) ratios also confirmed the presence of rGO in the nanocomposites.

GO and TiO\(_2/rGO\)-4% were investigated with the XPS technique. From the XPS spectra of the survey for TiO\(_2/rGO\)-4% (Figure 6a), C 1s was found and demonstrated the existence of rGO in the TiO\(_2/rGO\)-4% nanocomposites. In the deconvoluted C 1s spectra for GO (Figure 6b), the peaks at 284.5, 285.3, 286.7, 287.5, and 288.9 eV were ascribed to C–C, C–C, C–OH, O–C–O, and O–C=O, respectively. The apparent peaks at 286.7, 287.5, and 288.9 eV indicated the existence of oxygen-containing function groups, such as C–OH, O–C–O, and O–C=O in GO \[47,48\]. In comparison, the peaks of C–OH, O–C–O, and O–C=O remarkably decreased, as seen from Figure 6c, proving the hydrothermal reaction was a...
successful and effective transformation of GO to rGO. This is consistent with the results of FTIR and Raman spectra analysis.

To investigate the photogenerated electron transport mobility of the samples, the photocurrent responses of the TiO$_2$/rGO nanocomposites and as-prepared TiO$_2$ that covered the stainless-steel net as working electrodes were tested under a 500 W Xe lamp equipped with a UV/cutoff filter ($\lambda > 420$ nm) in 10-s on–off cycles. Figure 7 shows the fast and stabilised photocurrent response to each switch on and switch off. There were feeble photocurrent responses with TiO$_2$/rGO-2% and as-prepared TiO$_2$. The photocurrent of TiO$_2$/rGO-4% was approximately 2 and 3 times higher than that of TiO$_2$/rGO-6% and TiO$_2$/rGO-8%. A higher photocurrent curve responded with a higher efficient electron–hole separation [49]. Hence, TiO$_2$/rGO-4% showed the best efficiency of electron transport mobility and unusual photocurrent response activity.

Figure 5. Raman spectra of GO, TiO$_2$/rGO nanocomposites.

Figure 6. Cont.
The UV–vis diffuse reflectance spectra of TiO$_2$/rGO nanocomposites and as-prepared TiO$_2$ exhibited similar optical adsorption as seen from Figure 8a. As we all know, the wavelength distribution of the absorbed light is one of the important properties regardless of the quantum yield. The as-prepared TiO$_2$ showed intense adsorptions in the UV range (<420 nm), and this was ascribed to the intrinsic bandgap absorption of as-prepared TiO$_2$ (around 3.2 eV), caused by the excitation from the valence band to the conductance band of TiO$_2$. Moreover, the optical absorption of TiO$_2$/rGO nanocomposites increased with the increasing rGO amount. Additionally, this revealed the redshifts of the absorption edge from 420 nm to the entire visible region, which could be attributed to the visible light adsorption of black colour graphene. The band gaps were calculated according to the Kubelka–Munk method and the Tauc plot ($\chi h\nu$)$^{1/2}$ versus $h\nu$ for TiO$_2$/rGO nanocomposites and as-prepared TiO$_2$ is shown in Figure 8b, where $\alpha$, $h$, and $\nu$ are the adsorption coefficient, Planck constant, and light frequency, respectively. The band gaps of TiO$_2$/rGO-8%, TiO$_2$/rGO-6%, TiO$_2$/rGO-4%, TiO$_2$/rGO-2%, and as-prepared TiO$_2$ were 2.76, 2.84, 2.91, 2.98, and 3.22 eV, respectively. It can be found that the band gaps become narrower with the increasing rGO amount due to the interaction between unpaired $\pi$ and Ti atoms via chemical bonding in the Ti-O-C bond. Hence, the addition of rGO had a positive effect for enhancing the visible light photocatalytic activity.
Figure 7. Photocurrent response of TiO$_2$/rGO nanocomposites and as-prepared TiO$_2$ under Xe lamp irradiation.

Figure 8. UV–vis adsorption spectra of (a) TiO$_2$/rGO nanocomposites and as-prepared TiO$_2$. (b) The Tauc plot (ahv)$^{1/2}$ versus hv for TiO$_2$/rGO nanocomposites and as-prepared TiO$_2$. 
The photodegradation of phenol under visible light irradiation was chosen to evaluate the photocatalytic activity of catalysts. The time course of the decrease in the absorbance of phenol under visible light irradiation is shown in Figure 9a–d. It is crystal clear to see that the characteristic adsorption peak of phenol at around 270 nm steadily decreased with the increasing visible light irradiation time. Comparative studies of photocatalytic activity of catalysts are shown in Figure 9e. After 12 h, TiO$_2$/rGO-4% nanocomposite degraded the phenol solution up to 97.9%, and it was higher than that of TiO$_2$/rGO-2% (78.7%), TiO$_2$/rGO-6% (86.3%), TiO$_2$/rGO-8% (58.8%), and as-prepared TiO$_2$ (28.3%). When the rGO was introduced into TiO$_2$ nanoparticles, the absorbance edge of TiO$_2$ shifted to the wider wavelength region, which was in favour of TiO$_2$/rGO nanocomposites to absorb visible light. However, when the amount of rGO increased, such as TiO$_2$/rGO-6% and TiO$_2$/rGO-8%, the degradation of phenol decreased due to excess rGO being able to occupy some activity sites of TiO$_2$ and reduce the collision rate between TiO$_2$ activity sites and phenol molecules. Under dark conditions, there was a slight decrease in phenol concentration due to the absorption of phenol on the catalyst surface. The photodegradation kinetics of phenol on TiO$_2$/rGO nanocomposites and as-prepared TiO$_2$ were evaluated using the pseudo-first-order model: $-\ln(C/C_0) = k_{app}t$, where $C$ is the concentration of phenol at reaction time ($t$), $C_0$ is the initial concentration of phenol, and $k_{app}$ is the rate constant (h). The results (Figure 9f) show that TiO$_2$/rGO-4% exhibited the highest degradation rate constant 0.0190 h$^{-1}$, compared to TiO$_2$/rGO-2% 0.0038 h$^{-1}$, TiO$_2$/rGO-6% 0.0056 h$^{-1}$, TiO$_2$/rGO-8% 0.0014 h$^{-1}$, and as-prepared TiO$_2$ 0.0009 h$^{-1}$.
Symmetry 2020, 12, x FOR PEER REVIEW 13 of 18

(c)

(d)

(e)

Figure 9. Cont.
Increases the surface area for phenol adsorption via π-stacking interactions and prevents rapid electron hole recombination, leaving more charge carriers to form highly reactive species. Otherwise, incorporation of rGO increases the surface area for phenol adsorption via π-π stacking interactions and provides a suitable support substrate for the deposition of TiO₂ nanoparticles.

A schematic representation of the phenol degradation mechanism over TiO₂ dispersed on graphene sheets is shown in Figure 10. Under visible light irradiation, the electrons are excited by visible light and escape from the valance band to the conduction band. Subsequently, those excitation electrons migrate to the surface of the graphene sheets due to the superior electron mobility of rGO, which leads to the separation of the photoelectrons and holes. The excitation electrons react with H₂O to generate hydroxyl radicals and the electron holes react with dissolved oxygen to generate superoxide radicals. These strong oxidisability radicals can mineralise the phenol into water and carbon dioxide. The local work function of rGO is storing and shuttling electrons to the reaction sites due to its superior electron mobility work as a support and transmission unit. As electron acceptor material, rGO is a competitive candidate for the electron acceptor material due to its two-dimensional π-conjugation structure. The excited electrons from TiO₂ can quickly transfer from the conduction band of TiO₂ to the rGO and then, suppress in the electron–hole recombination, leaving more charge carriers to form highly reactive species. Otherwise, incorporation of rGO increases the surface area for phenol adsorption via π-π stacking interactions and provides a suitable support substrate for the deposition of TiO₂ nanoparticles.

**Figure 9.** Absorption spectra changes of phenol solution (20mg/L, 100mL) in the presence of photocatalysts (a) TiO₂/rGO-2%, (b) TiO₂/rGO-4%, (c) TiO₂/rGO-6%, and (d) TiO₂/rGO-8% under visible light (>420 nm) irradiation at 1 h interval. (e) Kinetic of phenol degradation upon irradiation, and (f) Photodegraded efficiencies for the TiO₂/rGO nanocomposites and as-prepared TiO₂, variation in –ln(C/C₀) as function of irradiation time and linear fits of photocatalysts.

![Figure 10. A plausible mechanism of photocatalytic degradation of phenol over TiO₂/rGO nanoparticles.](image-url)
4. Conclusions

TiO$_2$/rGO nanocomposites were successfully synthesised by hydrothermal methods and investigated as a new catalyst to degrade the phenol solution. The addition of rGO resulted in a reduction in the energy bandgap and enhanced absorption in the visible light region. Besides, the incorporation of rGO provided more activity sites and prevented rapid electron–hole recombination due to its high specific surface area and superior electron transfer mobility. The best system with TiO$_2$ nanoparticles hybridised with 4 wt% rGO was found to show very high activity 97.9%, 0.0190 h$^{-1}$ for 12 h of visible light irradiation of 20 mg/L phenol solution. To conclude, this study provided a facile method for enhancing the photocatalytic activity of TiO$_2$ under visible light irradiation and prepared TiO$_2$/rGO nanocomposites may be promising for practical applications in the field of environmental protection.

Author Contributions: G.W. and W.G. performed the experiment and wrote the paper; D.X. supervised the experiment; M.Q. contributed to the equation calculations and data curation. D.L. contributed to the fund acquisition. All authors contributed to the general discussion. All authors have read and agreed to the published version of the manuscript.

Funding: This research was founded by National Natural Science from China grand number 21806181.

Acknowledgments: The authors gratefully thank China University of Mining & Technology, (Beijing) for support of this work.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hasan, Z.; Jhung, S.H. Removal of hazardous organics from water using metal-organic frameworks (MOFs): Plausible mechanisms for selective adsorptions. *J. Hazard. Mater.* 2015, 283, 329–339. [CrossRef] [PubMed]
2. Ge, Q.L.; Yue, X.P.; Wang, G.Y. Simultaneous heterotrophic nitrification and aerobic denitrification at high initial phenol concentration by isolated bacterium Diaphorobacter sp PD-7. *Chin. J. Chem. Eng.* 2015, 23, 835–841. [CrossRef]
3. Antonopoulou, M.; Karagianni, P.; Giannakas, A. Photocatalytic degradation of phenol by char/N-TiO$_2$ and char/N-F-TiO$_2$ composite photocatalysts. *Catal. Today* 2017, 280, 114–121. [CrossRef]
4. Shannon, M.A.; Bohn, P.W.; Elimelech, M. Science and technology for water purification in the coming decades. *Nature* 2008, 452, 301–310. [CrossRef]
5. Ling, H.J.; Kyungduk, K.; Liu, Z.W. Photocatalytic degradation of phenol in water on as-prepared and surface modified TiO$_2$ nanoparticles. *Catal. Today* 2015, 258, 96–102. [CrossRef]
6. Eiroa, M.; Vilar, A.; Kennes, C. Effect of phenol on the biological treatment of wastewaters from a resin producing industry. *Bioresour. Technol.* 2008, 99, 3507–3512. [CrossRef]
7. Liu, Y.D.; Zhou, S.J.; Yang, F. Degradation of phenol in industrial wastewater over the F-Fe/TiO$_2$ photocatalysts under visible light illumination. *Chin. J. Chem. Eng.* 2016, 24, 1712–1718. [CrossRef]
8. Liu, Y.D.; Zhou, S.J.; Yang, F. Highly Efficient Oxidation of Gaseous Benzene on Novel Ag$_3$VO$_4$/TiO$_2$ Nanocomposite Photocatalysts under Visible and Simulated Solar Light Irradiation. *J. Phys. Chem. C* 2012, 116, 13935–13943.
9. Lim, J.; Monllor-Satoca, D.; Jang, J.S. Visible light photocatalysis of fullerol-complexed TiO$_2$ enhanced by Nb doping. *Appl. Catal. B-Environ.* 2014, 152, 233–240. [CrossRef]
10. Li, B.Z.; Sun, K.Q.; Guo, Y.B. Adsorption kinetics of phenol from water on Fe/AC. *Fuel* 2013, 110, 99–106. [CrossRef]
11. Ahmed, S.; Rasul, M.G.; Brown, R. Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review. *J. Environ. Manag.* 2011, 92, 311–330. [CrossRef] [PubMed]
12. Su, J.; Guo, L.; Bao, N.; Grimes, C.A. Nanostructured WO$_3$/BiVO$_4$ heterojunction films for efficient photoelectrochemical water splitting. *Nano Lett.* 2011, 11, 1928–1933. [CrossRef] [PubMed]
13. Dobrosz-Gomez, I.; Gomez-Garcia, M.A.; Lopez Zamora, S.M.; Gilpavas, E.; Bojarska, J.; Kozanecki, M.; Rynkowski, J.M. Transition metal loaded TiO$_2$ for phenol photo-degradation. *Comptes Rendus Chim.* 2015, 18, 1170–1182. [CrossRef]
14. Ali, I.; Kim, S.R.; Kim, S.P.; Kim, J.O. Andodization of bismuth doped TiO₂ nanotubes composite for photocatalytic degradation of phenol in visible light. Catal. Today 2017, 282, 31. [CrossRef]

15. Zhao, Z.G.; Miyawachi, M. Nanoporous-walled tungsten oxide nanotubes as highly active visible-light-driven photocatalysts. Angew. Chem. Int. Ed. 2008, 47, 7051–7055. [CrossRef] [PubMed]

16. Chen, X.; Burda, C. Photoelectron investigation of nitrogen-doped titania nanoparticles. Phys. Chem. B 2004, 108, 15446–15449. [CrossRef]

17. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. Nature 1972, 238, 37–38. [CrossRef] [PubMed]

18. Cong, Y.; Zhang, J.; Chen, F.; Anpo, M.; He, D. Preparation photocatalytic activity, and mechanism of nano-TiO₂ co-doped with nitrogen and iron (III). Phy. Chem. C 2007, 111, 10618–10623. [CrossRef]

19. Dong, L.; Cao, G.X.; Ma, Y.; Jia, X.L.; Ye, G.T.; Guan, S.K. Enhanced photocatalytic degradation properties of nitrogen-doped titania nanotube arrays. Trans. Nonferrous Met. Soc. China 2009, 19, 1583–1587. [CrossRef]

20. Nawi, M.A.; Zain, S.M. Enhancing the surface properties of the immobilised Degussa P-25 TiO₂ for the efficient photocatalytic removal of methylene blue from aqueous solution. Appl. Surf. Sci. 2012, 258, 6148–6157. [CrossRef]

21. Chen, X.; Mao, X.X. Titanium dioxide nanomaterials: Synthesis, properties, modification, and applications. Chem. Rev. 2007, 107, 2891–2959. [CrossRef] [PubMed]

22. Zhang, H.; Lv, X.; Li, Y.; Wang, Y.; Li, J. P25-Graphene composite as a high performance photocatalyst. ACS Nano 2010, 4, 380–386. [CrossRef]

23. Zhang, N.; Yang, M.Q.; Liu, S.; Sun, Y.; Xu, Y.J. Waltzing with the versatile platform of graphene to synthesis composite photocatalysts. Chem. Rev. 2015, 115, 10307–103717. [CrossRef]

24. Perera, S.D.; Mariano, R.G.; Vu, K.; Nour, N.; Seitz, O.; Chabal, Y.; Balkus, K.J. Hydrothermal synthesis of graphene-TiO₂ nanotube composites with enhanced photocatalytic activity. ACS Catal. 2012, 2, 949–956. [CrossRef]

25. Bell, N.J.; Ng, Y.H.; Du, A.; Coster, H.; Smith, S.C.; Amal, R. Understanding the enhancement in photoelectrochemical properties of photocatalytically prepared TiO₂-reduced graphene oxide composite. J. Phys. Chem. C 2011, 115, 6004–6009. [CrossRef]

26. Shao, X.; Lu, W.; Zahng, R.; Pan, F. Enhanced photocatalytic activity of TiO₂-C hybrid aerogels for methylene blue degradation. Sci. Rep. 2013, 3, 5018. [CrossRef]

27. Murcia, J.J.; Hidalgo, M.C.; Navio, J.A.; Arana, J.; Dona-Rodriguez, J.M. Study of the phenol photocatalytic degradation over TiO₂ modified by sulfation, fluorination, and platinum nanoparticles photodeposition. Appl. Catal. B Environ. 2015, 179, 305–312. [CrossRef]

28. Abdullah, A.M.; Al-Thani, N.J.; Tawbi, K.; Al-Kandari, H. Carbon/nitrogen-doped TiO₂: New synthesis route, characterisation and application for phenol degradation. Arab. J. Chem. 2016, 9, 229–237. [CrossRef]

29. Sohrabi, S.; Akhlaghian, F. Modeling and optimisation of phenol degradation over copper-doped titanium dioxide photocatalyst using response surface methodology. Process Saf. Environ. Prot. 2016, 99, 120–128. [CrossRef]

30. De Almeida, M.F.; Bellato, C.R.; Mounteer, A.H.; Ferreira, S.O.; Milagres, J.L.; Miranda, I.D.L. Enhanced photocatalytic activity of TiO₂-impregnated with MgZnAl mixed oxides obtained from layered double hydroxides for phenol degradation. Appl. Surf. Sci. 2015, 357, 1765–1775. [CrossRef]

31. Zhou, M.; Yu, J. Preparation and enhanced daylight-induced photocatalytic activity of C, N, S-tridoped titanium dioxide powders. Hazard. Mater. 2008, 152, 1229–1236. [CrossRef] [PubMed]

32. Williams, K.J.; Nelson, C.A.; Yan, X.; Li, L.S.; Zhu, X. Hot electron injection from graphene quantum dots to TiO₂. ACS Nano 2013, 7, 1388–1394. [CrossRef] [PubMed]

33. Malekshoar, G.; Pal, K.; He, Q.; Yu, A.; Ray, A.K. Enhanced Solar Photocatalytic Degradation of Phenol with Coupled Graphene-Based Titanium Dioxide and Zinc Oxide. Ind. Eng. Chem. Res. 2014, 53, 18824–18832.

34. Farzan, H.; Ali, A.I.; Moslem, F.; Bagher, A.; Sahand, J. Photocatalytic decontamination of phenol and petrochemical wastewater through ZnO/TiO₂ decorated on reduced graphene oxide nanocomposite: Influential operating factors, mechanism, and electrical energy consumption. RSC Adv. 2018, 8, 40035.

35. Ezzat, R.; Elham, N.; Ali, A.Z.; Hadis, Z. Photocatalytic degradation of phenol using a new developed TiO₂/graphene/heteropoly acid nanocomposite: Synthesis, characterization and process optimization. RSC Adv. 2016, 6, 96554–96562.
36. Chen, C.; Cai, W.; Long, M.; Zhou, B.; Wu, Y.; Wu, D.; Feng, Y. Synthesis of visible-light responsive graphene oxide/TiO$_2$ composites with p/n heterojunction. *ACS Nano* 2010, 4, 6425–6432. [CrossRef]

37. Patil, G.P.; Bagal, V.S.; Mahajan, C.R.; Chaudhari, V.R.; Suryawanshi, S.R.; More, M.A.; Chavan, P.G. Observation of low turn-on field emission from nanocomposites of GO/TiO$_2$ and rGO/TiO$_2$. *Vacuum* 2016, 123, 167–174. [CrossRef]

38. Agrawal, Y.; Kedawat, G.; Kumar, P.; Dwivedi, J.; Singh, V.N.; Gupta, R.K.; Gupta, B.K. High-performance stable field emission with ultralow turn on voltage from rGO conformal coated TiO$_2$ nanotubes 3D arrays. *Sci. Rep.* 2015, 5, 11612–11623. [CrossRef]

39. Huang, S.C.; Chen, Y.J. Enhanced field emission properties of titled graphene nanoribbons on aggregated TiO$_2$, nanotube arrays. *Mater. Res. Bull.* 2016, 79, 115–120. [CrossRef]

40. Zhu, W.D.; Wang, C.W.; Chen, J.B.; Yan, L.; Wang, J. Enhance field emission from Ti$_3^+$ self doped TiO$_2$ nanotube arrays synthesised by a facile cathodic reduction process. *Appl. Surf. Sci.* 2014, 301, 525–529. [CrossRef]

41. Peter, L.M. Band-edge tuning in self-assembled layers of BI2S3 nanoparticles used to photosensitise nanocrystalline TiO$_2$. *J. Phys. Chem. B* 2003, 107, 8378–8381. [CrossRef]

42. Du, J. Hierarchically ordered macro-mesoporous TiO$_2$-graphenen composite films: Improved mass transfer, reduced charge recombination, and their enhanced photocatalytic activities. *ACS Nano* 2010, 5, 590–596. [CrossRef] [PubMed]

43. Zhang, H. A facile one-step synthesis of TiO$_2$/graphene composites for photodegradation of methyl orange. *Nano Res.* 2011, 4, 274–283. [CrossRef]

44. Wu, Z.S. Graphene/metal oxide composite electrode materials for energy storage. *Nano Energy* 2013, 1, 110–116. [CrossRef]

45. Wang, D.; Choi, D.; Li, J.; Yang, Z.; Nie, Z.; Kou, R. Self assembled TiO$_2$-graphene hybrid nanostructures for enhanced Li-ion insertion. *ACS Nano* 2009, 3, 907–914. [CrossRef]

46. Fan, W.; Lai, Q.; Zhang, Q.; Wang, Y. Nanocomposites of TiO$_2$ and reduced graphene oxide as efficient photocatalysts for hydrogen evolution. *J. Phys. Chem. C* 2011, 115, 10694–10701. [CrossRef]

47. Zhang, X.; Sun, Y.; Cui, X.; Jiang, Z. A green and facile synthesis of TiO$_2$/graphene nanocomposites and their photocatalytic for hydrogen evolution. *Int. J. Hydrogen Energy* 2011, 37, 1–15. [CrossRef]

48. Xiang, Q.; Wu, J.; Jarovicj, M. Enhanced photocatalytic H$_2$-production activity of graphene-modified titania nanosheets. *Nanoscale* 2011, 3, 3670–3678. [CrossRef]

49. Cheng, X.; Liu, H.; Chen, Q.; Li, J.; Wang, P. Preparation of graphene film decorated TiO$_2$ nano-tube array photoelectrode and its enhanced visible light photocatalytic mechanism. *Carbon* 2014, 70, 249–257. [CrossRef]