Origin of Visible Light Photoactivity of Reduced Graphene Oxide/TiO$_2$ by in Situ Hydrothermal Growth of Undergrown TiO$_2$ with Graphene Oxide

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ABSTRACT: Graphene-related—TiO$_2$ (G—TiO$_2$) nanocomposites show enhanced photocatalytic performance, not only due to promoting photogenerated electrons migration but also by extending optical absorption to the visible light range. However, little is known about the origin of the visible light activity, which seems to depend much on the precursor of the titanium source. In this study, an efficient visible light active G—TiO$_2$—413 was prepared by hydrothermally treating a graphene oxide (GO) suspension and TiO$_2$ sol with undergrown TiO$_2$ nanoparticles at 413 K. According to XRD, DRS, TEM, FTIR, Raman, and ESR analyses, when in situ growing TiO$_2$ nanoparticles from hydrolyzed titanium alkoxides in hydrothermal conditions, a strong chemical interaction appears at the interface of GO sheets and the underdeveloped loosely packed polymeric Ti—O—Ti skeletons, so as to facilitate retaining more alkoxyl groups, inducing crystal disorders, and creating oxygen vacancies. All of these contribute to the significantly enhanced visible light activity of G—TiO$_2$—413. This sheds new light on the development of visible light responsive TiO$_2$-based photocatalysts via surface modification approaches.

1. INTRODUCTION

Semiconductor photocatalysis utilizing solar energy has been regarded as a potential technology to deal with both environmental and energy problems. The fundamental requirement of this process is to develop a photocatalyst with an optical absorption covering as much of the visible light range as possible and with the ability to efficiently convert the absorbed photon energy. However, the inherent problems of TiO$_2$, one of the best photocatalysts, are the mismatch of its optical absorption and the solar spectrum and its low quantum yield due to significant recombination of photogenerated charges. Such disadvantages restrict the large-scale industrial applications of TiO$_2$. A large amount of effort has been taken to challenge such limitations, including doping with nonmetal elements, surface modifying with photocatalysts with narrow band gaps such as CdS, self-doping with Ti$^{3+}$, creating crystal disorder structure, and so on. Exploring a viable approach to synthesize visible light photoactive TiO$_2$ with stable and highly active performance under solar irradiation is still urgently demanding.

With the recent explosive growth of interest in graphene (GR), which is an atomic sheet of sp$^2$-bonded carbon atoms in a honeycomb structure, a great deal of attention has been paid to the GR related semiconductor nanocomposites. Due to the unique structural and electronic properties of GR, such as excellent electron conductivity, high specific surface area, and giant 2D morphology, GR offers an exciting opportunity for fabricating photocatalytic nanocomposites with desirable performance for diverse applications, such as organic pollutants removal, water splitting, and CO$_2$ photoreduction. The present strategies to synthesize Graphene-related TiO$_2$ (G—TiO$_2$) nanocomposites are either to deposit directly TiO$_2$ nanocrystallites with well-defined structure, such as Degussa P25, to the surface of graphene oxide (GO) during the process of GO reduction or to grow in situ TiO$_2$ nanocrystallites over a GO sheet with a titanium precursor, such as titanium chlorides or alkoxides, accompanied by the reduction process. Although some publications indicate that in such TiO$_2$—carbon composites the function of GR is the same as other carbon materials such as carbon nanotubes or fullerene, it has been strongly agreed that the presence of GR would facilitate the migration of photogenerated electrons and suppress the recombination of charges, so as to contribute to an enhanced photocatalytic activity. On the other hand, extended optical absorption and visible-light-driven photocatalytic activity is another advantage of G—TiO$_2$ photocatalysts. The origin of visible light activity has been tentatively attributed to a sensitizer mechanism in Xu’s recent work. However,
the performance of G–TiO₂ in the visible light range seems dependent on the synthetic methods, because the G–TiO₂ composites synthesized with TiO₂ having a well-defined structure always exhibit poor visible light activity, while those synthesized with titanium alkoxide as the precursor show efficient visible light activity. This phenomenon seriously challenges the sensitizer mechanism. More recently, Park et al. developed a G-wrapped anatase TiO₂ that has a low band gap of 2.80 eV and attributed the visible light activity to the downshift conduction band.25 However, there is no further explanation on this, in spite of calcination during the synthesis perhaps making carbon doping happen.

Carbon-modified TiO₂, including carbon-doped TiO₂, TiO₂ coated with carbon-related compounds, and TiO₂ nanoparticles loaded on carbon materials,26 has attracted continuous attention in the field of photocatalysis. The basic format of modified TiO₂ with GR-related materials could be categorized as one of the three modifications, which offers further hints at the origin of the visible light activity. The hydrothermal method is frequently employed for the in situ synthesis of GR–semiconductor nanocomposites. Herein, to understand the essential origin of the visible light response of hydrothermally grown TiO₂ modified by GO, a visible light active G–TiO₂ was prepared by hydrothermally treating undergrown TiO₂ nanoparticles and GO suspension, and a comprehensive mechanism has been proposed according to the presence of alkoxyl groups, crystal disorders, and oxygen vacancies.

2. EXPERIMENTAL SECTION

Materials. Tetrabutyl titanate [Ti(OBu)₄, CP], graphite (Spec. pure), and methyl orange (MO) were purchased from Sinopharm Chemical Reagent Co., Ltd. Commercial anatase TiO₂ was provided by Heihai Nanometer Science and Technology Co., Ltd. All other chemicals involved were of analytical-grade, obtained commercially from Sinopharm Chemical Reagent Co., Ltd., and used as received.

Synthesis of Graphene Oxide. Graphite oxide was prepared by a modified Hummers’ method.27 Briefly, graphite powder was first oxidized into graphite oxide by KMnO₄/H₂SO₄ and NaNO₃ and then exfoliated into GO suspension by using a JY92-2D ultrasonic crasher (Ningbo Scientz Biotechnology Co. Ltd.) for 30 min. Unexfoliated graphite oxide in suspension after ultrasonication was removed by centrifugation at 3000 rpm for 5 min. The obtained suspension of graphene oxide with a concentration of 10 g/L was then used for the following syntheses.

Synthesis of TiO₂ Sol. TiO₂ sol with undergrown TiO₂ nanoparticles was obtained by a modified method from a previous report.28 In a typical synthesis, 6 mL of tetrabutyl titanate dispersed in 20 mL of absolute ethanol was added dropwise into 30 mL of 0.08 M HNO₃ under a vigorous stirring. The amorphous TiO₂ suspension was kept stirring at 343 K for about 45 min in an uncovered beaker to ensure complete hydrolysis. Then, 80 mL of 0.08 M HNO₃ was added and the mixture was continuously stirred under 343 K for 4 h under air-proof conditions. The semitransparent sol was diluted with water to 100 mL, in which the concentration of TiO₂ is about 1.4 g TiO₂/100 mL.

Synthesis of G–TiO₂. The hydrothermal process was employed for the further crystallization of TiO₂ and the reduction of GO. The mixture of a just prepared TiO₂ sol and GO suspension with a certain ratio was sonicated for 30 min, and its pH value was adjusted to 2.0. Then the mixture was transfer into a Teflon-lined stainless steel vessel for hydrothermal treatment for 24 h. The resulting powder was collected and washed with a large amount of water and dried at 60 °C. The modified TiO₂ is assigned as G–TiO₂–T, where T is the hydrothermal temperature. For comparison, a well-defined TiO₂ structure, anatase TiO₂ with a high crystallinity, was used as the precursor for the hydrothermal treatment with GO suspension at 413 K, and the obtained sample is assigned as G–anatase.

Photocatalytic Activity. The optical system for photocatalytic reaction consists of a 1000 W xenon lamp and a cutoff filter with larger than 90% transmission (λ > 400 nm). In a typical photocatalytic activity test, 0.05 g of prepared catalyst was added into a 50 mL of MO solution (10 mg/L), and then the dispersion was kept in the dark for 10 min to obtain an equilibrium adsorption state. During the irradiation, samples were taken at 0.5-h intervals, filtered, and then analyzed by a UNICO UV-2102 spectrometer at 464 nm.

Characterization. The crystal phase of samples was characterized by powder X-ray diffraction (XRD, D/Max-2200/PC, Rigaku Corp.), operating at 40 kV and 30 mA, where λ = 0.15418 nm for the Cu Kα line. Diffuse reflectance spectra (DRS) were obtained on a Lambda 950 UV/vis spectrophotometer (PerkinElmer Instrument Co., Ltd.), and the reflectance was converted to F(Rₚ) values according to the Kubelka–Munk method. The nanometric structure and the morphology of the catalysts were observed by a transmission electron microscope (TEM, JEM-2100F, JEOL). Fourier transform infrared spectroscopy (FTIR) was performed at a scanning range of 4000–370 cm⁻¹ on an EQUINOX-55 infrared-Raman spectroscope (Bruker Co.) with a DTGS detector. Carbon contents of samples were studied by a PE-2400 II CHNS/O analyzer (Perkin-Elmer Co.). Raman spectra were obtained on a Renishaw InVia reflex Raman microscope (Renishaw) with a 532 nm laser source. Electron spin resonance (ESR) spectra were measured at room temperature with an EMX-8 ESR spectrometer (Bruker BioSpin Corp.). About 0.02 g of catalyst powder was applied for each test. The settings for the ESR spectrometer wereas follows: center field, 3523.92 G; sweep with 400 G; modulation frequency, 100 kHz; microwave frequency, 9.87 GHz; power, 1.99 mW.

3. RESULTS AND DISCUSSION

TiO₂ sol with undergrown nanoparticles was prepared with a typical hydrolysis–peptization method at about 343 K. A series of G–TiO₂ nanocomposites was synthesized by hydrothermally treating TiO₂ sol and GO suspension with various ratios and temperatures at a pH value of 2.0. At this pH value, ζ-potentials of TiO₂ sol and GO solution are determined to be +27.16 and −16.14 mV, respectively. By electrostatic interaction, GO can easily adsorb and wrap TiO₂ nanoparticles, so as to offer an opportunity for close contacts between the two components. XRD patterns were measured to investigate the crystal phase structure of various G–TiO₂ nanocomposites, as shown in Figure 1. TiO₂ obtained by directly drying TiO₂ sol, named TiO₂-sol, is employed as the comparison. The presence of characteristic peaks at about 25.3°, 37.9°, 47.8°, and 54.4° are observed for all diffraction patterns, which are identical to the standard cards (JCPDS, No. 21-1272) of anatase TiO₂. Meanwhile, the weak peak at 2θ = 30.7° in all samples suggests the presence of a small quantity of brookite TiO₂, which is frequently observed as a byproduct of anatase when prepared at low temperature in acid solution.29 The powder obtained
is the X-ray wavelength, the fast photogenerated charge separation is an important factor for a higher photocatalytic activity, owing to the presence of G–TiO_2 nanocrystals and adsorbed impurities on the surface of the TiO_2 nanoparticles. The size of the nanocrystallites is calculated, and the selected results are listed in Table 1. The diameter of TiO_2 nanocrystallites is calculated, and the selected results are listed in Table 1. The diameter of TiO_2 nanocrystallites is calculated, and the selected results are listed in Table 1.

Table 1. A Comparison of TiO_2 Nanoparticles from XRD Patterns and Elementary Analyses

<table>
<thead>
<tr>
<th>catalysts</th>
<th>TiO_2-sol</th>
<th>G-TiO_2-413</th>
<th>G-TiO_2-483</th>
</tr>
</thead>
<tbody>
<tr>
<td>size (nm)</td>
<td>3.6</td>
<td>4.7</td>
<td>8.9</td>
</tr>
<tr>
<td>RCD</td>
<td>1</td>
<td>1.87</td>
<td>3.15</td>
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<tr>
<td>carbon amount (wt %)</td>
<td>0.34</td>
<td>0.64</td>
<td>0.35</td>
</tr>
</tbody>
</table>

sol is calculated as only 3.6 nm. After hydrothermal treatment, nanocrystallines grow and develop into a more defined crystal structure with fewer defects. Perfect crystalline structure is one important factor for a higher photocatalytic activity, owing to the fast photogenerated charge separation efficiency. The sizes of G–TiO_2 nanocrystals increase to 4.7 and 8.9 nm after hydrothermal treatment at 413 and 483 K, respectively. The relative crystalline degree (RCD), which is denoted by the relative peak height of the anatase (101) plane, an average diameter of the nanocrystallites is calculated, and the selected results are listed in Table 1. The diameter of TiO_2 nanocrystallite in TiO_2-483 has almost the same absorption curve as the pure anatase TiO_2. This indicates that when the precursor solution was treated at a high enough temperature, the addition of GO had almost no influence on the optical absorption property of TiO_2. The lower carbon amount in G–TiO_2-483 also suggests that there is very little RGO remaining in the final powder. For comparison, TiO_2-413 is synthesized by hydrothermally treating TiO_2 sol without the addition of GO at 413 K. A comparison of the optical absorption property of TiO_2-483, G–anatase, TiO_2-413, and G–TiO_2-413 is shown in Figure 2B. Assuming the catalysts to be indirect semiconductors, like TiO_2, a plot of the modified Kubelka–Munk function versus the energy of photon energy affords band gap energies of 2.87, 3.07, 3.07, and 3.14 eV for G–TiO_2-413, G–anatase, TiO_2-413, and G–TiO_2-483, respectively (inset in Figure 2B). G–TiO_2-413 shows an obvious narrowed band gap. Considering the absorption tail above 400 nm, G–TiO_2-483 has significant absorption in the visible light range. Meanwhile, the blue-grayish G–anatase, which is obtained from the well-defined crystallized anatase TiO_2 also has a flat absorption tail above 400 nm. However, such an absorption tail is similar to that of simple mixtures of TiO_2 and carbon materials and does not seem to contribute much to the band gap narrowing.

The TEM image of GO shown in Figure 3A displays typical flake-like shapes and the crumpled nanostructure of GR, which is attributed to the thin and large sheet of GR. The morphology of G–TiO_2-413 is characterized as well-dispersed, spherical nanoparticles. The average sizes of these nanoparticles are estimated to be 5–8 nm, which is in good correspondence with the value calculated from XRD pattern. The interplanar spacing of crystallites marked in Figure 3B is about 0.35 nm, corresponding to the (101) plane of anatase. However, the decomposition of GO under the hydrothermal conditions with higher temperatures and pressures, like being burned out. Another reason could be that, at high temperatures, TiO_2 nanoparticles grow into more defined crystals and the more deeply reduced GO is hydrophobic; therefore, the reduced GO (RGO) is more likely to detach from the TiO_2 nanoparticles.

The UV–vis DRS is measured to evaluate the optical absorption properties of the catalysts, as shown in Figure 2. The appearance of G–TiO_2-413 is dark gray and becomes lighter and lighter upon increasing the hydrothermal temperature. G–TiO_2-413 has an extended long absorption tail from 400 to 800 nm, which is the strongest absorption above its band gap absorption edge in all catalysts. Wave splitting of the transformed Kubelka–Munk function versus the energy of light absorbed.

![Figure 1. XRD patterns of synthesized G–TiO_2 (0.8 wt %) and TiO_2-sol.](image1.png)

![Figure 2. (A) UV–vis DRS of G–TiO_2 (0.8 wt %) and pure anatase TiO_2. (B) Comparison of UV–vis DRS and digital pictures of G–anatase, G–TiO_2-413, G–TiO_2-483, and TiO_2-413. The inset is the plot of the transformed Kubelka–Munk function versus the energy of the light absorbed.](image2.png)
margin of each crystalline is not clear enough, indicating the existence of lattice disorder in the brink region.

The visible-light-driven photocatalytic activity of G–TiO$_2$ was evaluated by degradation of MO under the irradiation from a Xe lamp ($\lambda > 400$ nm). The effect of GO dosages was investigated for the catalysts that were hydrothermally treated at 433 K. As expected, pure anatase TiO$_2$ has negligible activity under visible light irradiation, with less than 5% MO reduced after 2 h illumination. Without the addition of GO, TiO$_2$ obtained by hydrothermally treating precursor sol at 433 K shows a low activity for MO degradation, about 36% of MO was reduced. The slight activity in visible light could be attributed to the presence of surface states that originated from the surface defects or residual alkoxyl groups.\(^{3,5}\) Catalysts generated by hydrothermal treatment of the TiO$_2$ precursor sol in the presence of GO show dramatically enhanced visible light activity. More than 96% MO was removed after 2 h irradiation over G–TiO$_2$ with 0.8 wt % GO addition. Further increases of GO dosage do not contribute to a higher activity, which could be explained by the fact that more carbonaceous substance existing over the surface of G–TiO$_2$ nanoparticles would induce a shielding effect or promote charge recombination. Moreover, the role of adsorption is negligible, because 30 min of stirring in the dark was carried out to reach an adsorption balance before each photocatalytic reaction. The low amount of carbon materials and negatively charged G–TiO$_2$ nanoparticles under the conditions also rationalize their poor MO adsorption capability.

The effect of hydrothermal temperatures on the activity of G–TiO$_2$ is shown in Figure 4B. The optimized temperature is 413 K, where MO is almost 99% removed after 2 h irradiation. Moreover, more than 80% MO has been reduced in the first 0.5 h. However, upon a further increase of the temperature, the activity decreased gradually, and the MO reduction is only 41% for G–TiO$_2$-483. According to these results, the contribution of brookite to visible light activity can be ignored because the ratios of brookite in all samples are almost the same and the crystallization of brookite is also improved at a higher hydrothermal temperature. Although the crystallinity of G–TiO$_2$ increases with hydrothermal temperatures, which contributes to the faster migration of photogenerated charges, the grown nanocrystallite with fewer defects and the loss of carbon (as shown in Table 1) at higher hydrothermal temperature result in a decrease of visible light activity. This indicated that the presence of certain carbonaceous species and the characteristic nanocrystal structure of G–TiO$_2$ play important roles for an efficient visible light activity.

To understand the mechanism of the high visible light activity of G–TiO$_2$-413, several control tests were done, and results are shown in Figure 5. It has been reported that GO could be photoactive for water splitting under visible light irradiation.\(^{34}\) To assess the role of GO in TiO$_2$ photocatalysis, 0.8 wt % of GO was added into the anatase TiO$_2$ suspension for photocatalytic reaction. The MO degradation was not obviously improved, which suggests that there is no interparticle charge transfer between GO and TiO$_2$.\(^{35}\) and that GO is not a suitable sensitizer for TiO$_2$ in the present reaction. Two comparison samples, TiO$_2$-483 (curve b) and TiO$_2$-413 (curve d), were obtained by hydrothermal treatment of TiO$_2$ sol without the addition of GO. A 23% and 56% reduction of MO is reached after 2 h irradiation over TiO$_2$-483 and TiO$_2$-413, respectively. Moreover, G–anatase has achieved 45% MO reduction after 2 h irradiation, a much improved activity compared to its precursor, the crystallized anatase TiO$_2$. These control samples exhibit little visible light activity for MO reduction, far lower than that of G–TiO$_2$-413, suggesting that the crystal structure of the precursor TiO$_2$ and the presence of GO have critical influences on the visible light activity of the final catalysts.

The characterizations of FTIR, ESR, and Raman spectra have been taken to further investigate the origin of efficient visible light activity of G–TiO$_2$-413. FTIR spectra were employed to characterize the carbon species in the catalysts. A typical FTIR spectrum of GO is employed for comparison. Many clear strong absorption peaks corresponding to oxygen functional groups can be observed for GO (Figure 6A,B), including water OH stretching ($3400$ cm$^{-1}$), carboxylates or ketones C=O stretching ($1730$ cm$^{-1}$), water OH bending and C=C stretching ($1615$ cm$^{-1}$), alcoholic C=OH stretching ($1420$ cm$^{-1}$), epoxide C–O–O or phenolic C–OH stretching ($1260$ cm$^{-1}$), and C–O stretching ($1110$ cm$^{-1}$).\(^{19–21,36}\) Most of those oxygen-containing groups have decreased significantly in G–TiO$_2$ not only due to the reduction of GO but also to the low GO dosage in the synthesis. However, the diffused band between 2400 and 3600 cm$^{-1}$ and the band at 1630 cm$^{-1}$, which correspond to the stretching and bending vibration of...
OH in adsorbed water molecules, are still remarkable in G–TiO2. Both G–TiO2 samples have a wide peak centering at 620 cm$^{-1}$, which is ascribed to the stretching vibration of Ti–O–Ti bonds in crystalline TiO2.$^{37}$ For G–TiO2-413, the obvious bending vibration of $\delta$(CH–) at 1387 cm$^{-1}$ and the in-plane deformation vibration of H atom in the CO–H group at 1410 cm$^{-1}$ indicate the presence of significant alkoxyl group in this catalyst.$^{38,39}$ The discernible band at around 720 cm$^{-1}$ corresponding to the out-of-plane bending of $\chi$(CH–) or carbonyl is another proof.$^{40}$ In our previous report, we have found that visible light activity of TiO2 seems to correlate with the intensity of the bands at 1380 cm$^{-1}$, which is the signal of alkoxyl groups.$^{40}$ These bands dramatically decrease for G–TiO2-483 due to the carbon loss. The intensity of the peak at about 1380 cm$^{-1}$ is even comparable to that of anatase TiO2 in Figure 6C, which could be regarded as a background value. The peak at this point for G–anatase is also small, while it is much stronger for TiO2-413. This suggests that alkoxyl groups retained in the catalysts come from the titanium alkoxide, Ti(OBu)$_4$. Moreover, the intensity of the band at around 1380 cm$^{-1}$ for G–TiO2-413 is obviously stronger than that of TiO2-413, which indicates that the presence of GO assists in the retaining of alkoxyl groups in the final products. In fact, under the catalysis of protons in the solution, the abundant carboxylate or ketone groups in GO are ready to react with the hydrolyzed alkoxyl groups at the end of the three-dimensional polymeric Ti–O–Ti skeletons or the adsorbed alkoxyl groups over the surface of such frameworks, so as to hold them on the surface of nanocrystalline G–TiO2. The high content of alkoxyl groups within the $\pi$–$\pi$ conjugate system of RGO could be one reason for the visible light activity of G–TiO2.

Raman spectroscopy is a powerful and nondestructive method to characterize the order and disorder/defect structures in nanocrystalline. Figure 7 is the Raman spectra of G–TiO2-483, G–TiO2-413, and G–anatase. Four characteristic Raman peaks of anatase TiO2 can be observed at around 444 cm$^{-1}$ ($E_{1g}$), 400 cm$^{-1}$ ($B_{1g}$), 518 cm$^{-1}$ ($A_{1g}$+$B_{1g}$), and 638 cm$^{-1}$ ($E_{1g}$) modes for all three catalysts. Besides the above four Raman modes of anatase TiO2, obvious Raman-active modes for brookite TiO2 can be resolved in both Raman spectra of G–TiO2-483 and G–TiO2-413, such as the bands at about 245 cm$^{-1}$ ($A_{1g}$), 320.5 cm$^{-1}$ ($B_{1g}$), 363 cm$^{-1}$ ($B_{2g}$), 545 cm$^{-1}$ ($A_{1g}$), and 585 cm$^{-1}$ ($B_{2g}$).$^{41}$ The existence of brookite phase in G–TiO2 corresponds to the result of XRD patterns. However, there are many more new Raman modes in G–TiO2-413, including bands at around 307, 435, 576, 698, 819, 846, and 858 cm$^{-1}$, which cannot be ascribed to any of the three TiO2 polymorphs, but some have been reported in the black hydrogenated TiO2.$^6$ This indicates that, in G–TiO2-413, disorders in crystal lattice break down the Raman selection rules to generate some new active modes. $^{42}$ It is also supported by the HRTEM images. The emergence of disorder can be attributed to the chemical interaction between RGO and the surface of TiO2 skeletons, which disturbs the growth of TiO2 nanoparticles during the hydrothermal process, as shown by the above analyses of the FTIR spectra. Moreover, besides Raman bands of anatase TiO2, G–anatase has no others below 900 cm$^{-1}$. This indicates that the ordered anatase nanostructure is more stable and unlikely to be modified and disturbed. This is reasonable because it is more possible to interfere and reorganize the nanoskeleton of insufficiently developed and loosely formed Ti–O chains. Moreover, the disorder nanocrystalline could be self-adjusted to be ordered at higher hydrothermal temperatures, as there is no signal of uncertain active mode for G–TiO2-483. Such crystal disorder could be another reason for the visible light activity of G–TiO2.

On the other hand, both G–TiO2-413 and G–anatase have characteristic D and G bands at around 1350 and 1595 cm$^{-1}$, respectively. However, there is no signal of RGO for G–TiO2-483, which is in accord with the carbon analyses. The D band is corresponding to the $\kappa$-point phonons of $A_{1g}$ symmetry, which is a common feature of sp$^2$ defects in carbon and usually can be associated with the structural defects, amorphous carbon, or edges that break the symmetry and selection rule, while the G band is common to all sp$^2$ carbon, which can provide information on the in-plane vibration of sp$^2$-bonded carbon domains.$^{17,36}$ It is notable that the D band peak for G–TiO2-413 extended to 1380 cm$^{-1}$, larger than the general D band position of 1340–1350 cm$^{-1}$ for GO or RGO.$^{17,43}$ It can be attributed to the overlap of the D band and the symmetric deformation mode of $\chi$(CH–) group, as shown in the FTIR results (Figure 6B). The larger ratio of the two bands, $I_D/I_G$, indicates more disorder/defect carbon in the catalysts.$^{45}$ According to results in Figure 7C, the ratios of $I_D/I_G$ are calculated as 0.89 and 1.49 for G–TiO2-413 and G–anatase, respectively. This suggests that, compared with G–anatase, there are less sp$^2$ defects and more sp$^3$ domains in the RGO of G–TiO2-413, and the reduction of GO is inhibited and incomplete when accompanied by the growth of TiO2 nanoparticles from the hydrolyzed titanium alkoxides. The possible reason for this can be ascribed to the strong interaction at the interface of TiO2 and RGO sheets, which is consistent with FTIR results.

The ESR spectra were employed to detect the oxygen vacancy or $T_{1g}$ in catalysts, as shown in Figure 8. No observable signal can be observed for TiO2-sol, TiO2-413, and anatase TiO2 (curves d–f), indicating there is no oxygen vacancy or $T_{1g}$ in these TiO2 powders, which is consistent with the previous reports that there is no ESR signal for pure
However, G–TiO2–413, which has the highest visible light activity, gives rise to a sharp symmetrical ESR signal at \( g = 2.004 \) (curve a). When G–TiO2 is synthesized at a higher hydrothermal temperature, the signal decreases and almost disappears for G–TiO2–483 (curve c), which has very poor visible light activity. Nakamura et al. attributed the ESR signal at this position to an oxygen vacancy, which has been regarded as the origin of visible light activity for the plasma-treated TiO2.46 Such an oxygen vacancy has also been frequently reported in the ESR spectra of reduced TiO2.47,48 Moreover, no other detectable signal, such as Ti^3+ \( (g = 1.960) \) or O^2− \( (g_0 = 2.025, g_1 = 2.009, g_2 = 2.003) \),49 appears in our tests. A low ESR signal also appears at \( g = 2.004 \) for G–anatase, suggesting the existence of a low content of oxygen vacancy in this catalyst. Considering that TiO2–413 has a significant alkoxyl group but no oxygen vacancy and that the inverse is true for G–anatase, the emergence of the oxygen vacancy is independent of the alkoxyl group but dependent on the presence of GO in synthesis. The oxygen depletion in an oxide lattice can be induced by thermally driven catalytic oxidation of organic adsorbates.50 Panayotov et al. has revealed an oxygen vacancy formation in TiO2 by organic adsorbate reacting with thermally activated bridging lattice oxygen.51 In our hydrothermal synthesis, the oxygen-containing groups of GO would deoxygenate and become the corresponding reduced form. Simultaneously, with the dynamic growth of TiO2 nanoparticle, the surface lattice oxygen atoms tends to diffuse out, chemically interact with RGO, and balance the deoxgenization process (eqs 1–3). Therefore, oxygen vacancies, which could remain stable in the presence of GO, generate in nanocrystalline G–TiO2–413. However, because of the detached carbonaceous materials at higher temperatures, the oxygen vacancy could be filled and disappear again. The presence of oxygen vacancy in TiO2 lattice is one of the most important reasons for visible light activity owing to the new states emerging below the conduction band.

\[
\begin{align*}
\text{GO(s)} & \rightarrow \text{RGO(s)} + \text{oxygen-containing substance} \\
\text{O}_2^\bullet + \text{RGO(s)} & \rightarrow \text{V}_2^\bullet + \text{RGO–O(s)} \\
\text{RGO–O(s)} & \rightarrow \text{RGO(s)} + \text{oxygen-containing substance}
\end{align*}
\]

According to the above analyses, the functional of GO to the origin of visible light activity of G–TiO2–413 is revealed. The presence of alkoxyl groups is one reason for the weak visible light activity of TiO2 during MO reduction. For example, TiO2–413, TiO2–483, and G–TiO2–483 have the signal of alkoxyl groups in their FTIR and show improved activity for MO reduction under visible light. However, the retained alkoxyl groups contribute little to the narrowed band gap. Oxygen vacancy in the TiO2 lattice could induce a lower band gap, which emerges from the chemical interaction of adsorbed RGO and lattice oxygen, in spite of the source of TiO2. This is the reason for the visible light activity of G–anatase, which has few alkoxyl groups and no crystal disorder. During in situ growth of TiO2 from titanium alkoxides or undergrown TiO2 nanoparticles, the underdeveloped and loosely packed polymeric Ti–O–Ti skeleton offers the opportunity to bring about strong chemical interactions at the interface of TiO2 and GO, which makes the disturbed crystal growth and depletion of lattice oxygen possible. Therefore, the presence of GO under such conditions helps the nanocomposites to hold alkoxyl groups, to induce crystal disorder, and to create oxygen vacancies, resulting in the significantly enhanced visible light activity of G–TiO2–413.

### 4. CONCLUSIONS

An efficient visible light active photocatalyst G–TiO2–413 was synthesized by hydrothermally treating undergrown TiO2 nanoparticles with a GO suspension at 413 K. Elevating the hydrothermal temperature, treating the well-defined structural anatase TiO2 with GO, or avoiding the addition of GO causes the visible light activities of the resulting catalysts to decrease dramatically. By forming a strong chemical interaction at the interface of the underdeveloped polymeric Ti–O–Ti skeletons and GO sheets, GO helps to retain alkoxyl groups, inducing crystal disorders and creating oxygen vacancies. All of these contribute to the efficient visible light activity of G–TiO2–413 or nanocomposites like RGO/TiO2. This work could provide new insight into the strategy to synthesize visible light active TiO2 by a molecular-scale chemical interaction at the interface of nanocomposites.

### ASSOCIATED CONTENT

Supporting Information
Complete author list of refs 7 and 22. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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