Low-Temperature Nitrogen Doping in Ammonia Solution for Production of N-Doped TiO₂-Hybridized Graphene as a Highly Efficient Photocatalyst for Water Treatment

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Supporting Information

ABSTRACT: To facilitate the potential application of TiO_2 as an efficient photocatalyst, the modulation of its band gap and electrical structure is of great significance. Herein, we report a very simple nitrogen (N)-doping method to obtain N-doped TiO₂, which is hybridized with graphene sheets at a temperature as low as 180 °C and using an ammonia solution as the N source and reaction medium. X-ray photoelectron spectroscopy analysis revealed that the atomic N level could reach 2.4 atomic percent when the reaction time was 14 h. Photoluminescence (PL) emission spectra indicated that N-



doped TiO₂/graphene composites have drastically suppressed TiO₂ PL intensity when compared to undoped TiO₂, confirming the lower recombination rate of electron—hole pairs in the N-doped TiO₂. Additionally, photodegradation data showed that the decomposition rate of methylene blue with our N-doped TiO₂/graphene photocatalyst is twice as fast as a commercial Degussa P25 catalyst. Furthermore, density functional theory (DFT) calculations demonstrate that N doping creates empty states in the band gap of the TiO₂ that are below the Fermi energy of graphene. Thus, when N-doped TiO₂ is brought into contact with graphene, these states become filled by electrons from the graphene, shifting the TiO₂ bands upward relative to the graphene. Such a shift in band alignment across the TiO₂/graphene heterojunction makes transfer of the photoexcited electron more energetically favorable. This work provides a very convenient chemical route to the scalable production of N-doped TiO₂/ graphene photocatalyst for potential applications in wastewater treatment.

KEYWORDS: Graphene, N-doped TiO₂, Low temperature doping, Ammonia solution, Photocatalyst, Wastewater treatment

■ INTRODUCTION

The potential of TiO₂ as a photocatalyst is well recognized and has been studied extensively over many decades. In addition to being photoactive, it is chemically stable, nontoxic, and inexpensive,¹⁻³ making it very attractive for industrial-scale water treatment and the degradation of recalcitrant environmental pollutants. In this application, absorbed ultraviolet (UV) radiation excites electrons from the TiO₂ valence band to the conduction band, thus forming electron-hole pairs. The holes subsequently react as oxidants on surface-adsorbed hydroxide ions to produce hydroxyl free radicals, which in turn are the main oxidizing agents responsible for photo-oxidation of organic contaminants.¹ However, despite the great potential of TiO₂ for water treatment, there are two obstacles that have hampered industrial-scale adoption. The first is that TiO₂ photocatalysts are not photoactive under visible light; the second is the fast recombination rate of electron-hole pairs, which results in the low efficiency of competing photoinduced chemical reactions.

During the past decades, N doping has been proven to be the most effective strategy for altering the electronic structure of TiO₂, enabling the response of photocatalytic activity in the visible light region. To date, many experimental approaches have been developed to produce N-doped TiO₂ with visible light sensitivity, including sputtering,^{4,5} thermal nitridation of TiO₂,⁶ direct amination,⁷ and pulsed laser deposition.⁸ All these N-doping procedures were carried out at high temperatures (>400 °C) or required complicated and expensive equipment. However, based on the density functional theory (DFT) calculations by Tsetseris,⁹ high temperatures may not be required if N dopants are introduced to anatase TiO₂ interstitially (N_i) rather than substitutionally (N_s) because the diffusion of N to N_i sites becomes operative at much lower temperatures (100–300 °C). Inspired by such theoretical results, in this work, we have developed a novel low-

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temperature (180 °C) doping process to synthesize N-doped TiO₂ hybridized graphene using a liquid ammonia solution as the nitrogen source. While the N doping alters the band gap to allow visible light absorption, the synergistic anchoring of the N-doped TiO₂ nanoparticles to graphene decreases the rate of electron–hole pair recombination and increases the rate of photo-oxidation, as described below. To our knowledge, no comparable low-temperature methodology for the preparation of N-doped TiO₂/graphene composites has been reported before.

It is well recognized that graphene acts as an electron acceptor due to its 2D $\pi - \pi$ conjugation, which may decrease the radiative recombination rate and increase the catalytic activity of nanoparticle photocatalysts anchored to the graphene surface. Taking advantage of the high electron mobility of graphene $(2 \times 10^5 \text{ cm}^2/\text{V s})$,¹⁰ if the TiO₂/ graphene interface is clean, the excited electrons of TiO₂ will transfer quickly from the conduction band of TiO₂ to graphene and, therefore, greatly delay the electron-hole recombination. Also, due to a high surface area $(2600 \text{ m}^2/\text{g})$,¹¹ graphene sheets will not only allow the TiO₂ nanocrystals (NCs) to be well dispersed on the surface but also facilitate attachment of aromatic organic contaminants in treated water solution because graphene is hydrophobic and lipophilic in water and can act as a selective adsorbent.¹² Overall, the combination of exfoliated crystalline graphene and N-doped TiO₂ is expected to simultaneously improve the performance of TiO₂ as a photocatalyst by (1) extending photosensitivity to the visible light range, (2) decreasing carrier recombination rates by increasing electron-hole separation, and (3) increasing pollutant degradation rates through favorable absorption of organic pollutants.

Recognizing the advantages of graphene-hybridized TiO₂, the initial report by Zhang et al. used a hydrothermal reaction to hybridize graphene oxide (GO) with commercial Degussa P25;¹³ afterward, a number of similar studies were reported.¹⁴⁻²⁵ Their experimental results suggest that graphene-TiO₂ composites have a better photocatalytic performance in comparison to TiO₂ catalysts alone. Although these results are promising, the use of GO as a precursor for the preparation of graphene-TiO₂ composites poses a significant disadvantage because there exists a high density of defects in the lattices of GO, leading to the severe disruption of graphene's intrinsic electronic transport property. To overcome this challenge, we selected and prepared highly crystalline graphene as a substrate instead of using GO. During the past two years, we have developed the "thermal expansion-liquid exfoliation-solvothermal reaction (TELESR)" process to hybridize high-quality exfoliated graphene with various transition metal (Fe, Mn, Co) oxides²⁶ and noble metal (Pt, Pd, and Pt-based alloys) nanoparticles.^{27,28} We have demonstrated the advantage of using the high-quality conductive graphene prepared in this way as a platform for anchoring nanoparticles to fabricate hybridized nanoparticle/graphene composites with superior properties.

In the present study, we used this TELESR process to successfully hybridize graphene with N-doped TiO_2 NCs at a low temperature of 180 °C for the purpose of overcoming the two main obstacles mentioned above. This was done using titanium(IV) butoxide and exfoliated graphene as precursors and an ammonia solution in isopropanol (IPA) as both the solvent and nitrogen source. Photodegradation testing demonstrated that graphene-supported N-doped TiO_2 showed

significant improvement for decomposing a representative dye, methylene blue (MB), when compared to both commercial Degussa P25 and the undoped TiO₂ prepared under the same conditions. Additionally, we have performed electronic structure calculations that provide mechanistic understanding of the synergy between N-doped TiO₂ and the graphene substrate. The simple and low-temperature nitrogen-doping method via a liquid ammonia solution to produce a N-doped TiO₂/graphene composite, which we have demonstrated here, could make large-scale production of these materials both economical and sustainable, finally unlocking the potential of TiO₂ as an efficient photocatalyst for wastewater treatment.

EXPERIMENTAL AND SIMULATION METHODS

Chemicals and Materials. 1-Methyl-2-pyrrolidone (NMP), anhydrous, 99.5%, Sigma-Aldrich; anhydrous isopropanol (IPA), 99.5%, Sigma-Aldrich; titanium(IV) butoxide, Ti(OBu)₄, 99.5%, Sigma-Aldrich; ammonia solution (2M) in IPA, Sigma-Aldrich. All of them were purchased and used as received. Commercially available expandable graphite (average diameter 300 μ m, 99% purity, Beijing Invention Biology Engineering & New Material Co., Ltd., China) was exfoliated as described below. Photodegradation performance was evaluated relative to commercially available AEROXIDE TiO₂ P25 (Evonik Degussa).

Thermal Expansion and Liquid Exfoliation Process To Obtain Few-Layer Graphene. In a typical synthesis, commercially available expandable graphite was rapidly heated to 1000 °C and maintained for 60 s under the atmosphere of forming gas (5% H₂ and 95% Ar). The resulting expanded graphite (EG) was mixed with NMP. The few-layer graphene sheets were then exfoliated from the EG through durative sonication for 60 min (Misonix Sonicator 3000, 700 W power), followed by centrifugation at 300 rpm (900 g) for 30 min, forming a sustainable gray suspension. Finally, the solid exfoliated pristine graphene sheets were collected by centrifugation at 15,000 rpm for 3 min and separated without any heat treatment, surface modification, or oxidation process, as shown in Figure S1 of the Supporting Information.

Production of Reduced Graphene Oxide. Graphene oxide was prepared from natural graphite powder by a modified Hummer's method.^{29,30} Graphite powder (1 g), NaNO₃ (0.5 g), and 23 mL of concentrated sulfuric acid were added into a 250 mL round-bottomed flask and stirred at room temperature for 24 h. Next, the flask was moved into an ice bath, and 3 g of KMnO4 was slowly added under vigorous agitation. The flask was then heated in a water bath at 38 °C for 2 h. A total of 46 mL of water was gradually added to the flask, and the suspension was allowed to stir for 15 min. The suspension was diluted by 140 mL of water, and the reaction was ended by addition of 10 mL of 30% H₂O₂. Ten minutes later, the bright yellow suspension was centrifuged and washed with 10% HCl solution twice. The precipitate was finally washed with DI water, collected by centrifugation, and dried in a vacuum oven at 70 °C overnight. Reduced graphene oxide (RGO) was then produced using hydrazine hydrate as a reducer.³¹ Briefly, 100 mg of the graphene oxide was dispersed in 100 mL of DI water, stirred for 30 min, and then 1.0 mL of N₂H₄·H₂O was added. The mixtures were heated at 95 °C using a water bath for 45 min, forming a black solid precipitate, and then finally were isolated by filtration and washed with DI water.

Solvothermal Reaction to Deposit N-doped TiO₂ NCs onto the Few-Layer Graphene Surface. The resulting few-layer graphene stacks (5 mg), Ti(OBu)₄ (0.02 g, 0.05 mmol), and ammonia solution (2M) in IPA (20 mL) were mixed and mechanically stirred for 30 min. The mixture was then transferred to a closed stainless-steel autoclave with a Teflon liner (25 mL in total capacity). The autoclave was heated to 180 °C and maintained at this temperature for time periods ranging from 7 to 21 h. Similarly, for producing an undoped TiO₂/graphene composite (as shown in Figure S2, Supporting Information), as well as for producing an undoped TiO₂/RGO composite, the precursors and reaction conditions were almost the



Figure 1. TEM analysis of N-doped TiO_2 /graphene prepared at a low temperature of 180° at varying reaction times of 7 h (a), 14 h (b), and 21 h (c). (d) HRTEM image of deposited N-doped TiO_2 NCs. (e) Corresponding SAED pattern. (f) Typical EDX pattern of deposited N-doped TiO_2 NCs.

same, except that IPA was used as the solvent instead of an ammonia solution of IPA. Because the precursor amount of graphene and titanium are the same for producing the N-doped $TiO_2/graphene$, undoped $TiO_2/graphene$, and undoped TiO_2/RGO , the ratio of graphene in these composites should also be the same. We calculated the addition ratio of graphene in all these composites, which is about 55.6%.

Structural and Properties Characterization. An FEI TECNAI F20 transmission electron microscope (TEM) with EDX and GIF systems, operating at an accelerating voltage of 200 kV, was used for analysis of the morphology and crystal structure of N-doped TiO₂/ graphene composites. ImageJ and Digital Micrograph programs were utilized to analyze the particle size and coating density based on 24 TEM images. Specifically, we adjusted the contrast and thresholds of the image until ImageJ was able to give a percentage of black vs white pixels. Raman spectra were collected with a HORIBA Jobin Yvon LabRAM Raman spectrometer using an Ar⁺ laser (532 nm). Photoluminescence spectra were acquired using a 15 mW 325 nm HeCd laser as the excitation source. Powder X-ray diffraction (XRD) studies were performed in the 20–70° 2θ range using a Rigaku Ultima IV X-ray diffraction system with graphite monochromatized Cu K_a radiation ($\lambda = 1.54187$ Å). Samples for X-ray analysis (as-prepared graphene, as-prepared N-doped TiO₂, and N-doped TiO₂/graphene composites) were dropped from ethanol and deposited as thin films on glass slides.

Photocatalytic Activity Measurements. The photocatalytic activity of N-doped $\text{TiO}_2/\text{graphene}$ composites as well as undoped $\text{TiO}_2/\text{graphene}$ and undoped TiO_2/RGO were evaluated by degradation of MB in an aqueous solution. Typically, 5 mg of photocatalyst was mixed with a 20 mg/L MB solution. The suspension was first stirred in the dark for 60 min to reach the adsorption–desorption equilibrium of MB dye. Afterward, the mixture was illuminated with a 150 W Xe lamp (Newport, Oriel Instrument, model 67005) under magnetic stirring. Aliquots (2.0 mL) were drawn out of the solution at 15 min intervals after the start of sample illumination. The MB solution aliquots were separated from the photocatalyst by centrifugation. The dye concentration in the supernatant was analyzed using a UV–vis-NIR 3600 spectrophotometer (Shimadzu).

Simulation Methods and Model Systems. To provide mechanistic insight into the superior photocatalytic performance of the N-doped TiO₂/graphene composites, DFT was used to compute

the electronic structure of the composite and its heterojunction. Calculations were performed using the SIESTA DFT package³² using the Wu-Cohen generalized gradient exchange-correlation functional,³³ with relativistic core-corrected pseudopotentials to treat the core electrons and an energy cutoff of 300 Ry. Atom positions were relaxed such that forces were less than 0.01 eV per Å. The nanoparticles were modeled as a small slab of TiO₂ consisting of six planes of TiO₂ in the [001] direction and three and six Ti layers in the [100] and [010] directions, respectively. The small slab contained 30 Ti and 54 O atoms, and the Ti atoms on the (001) surfaces were modeled as being passivated with OH. Such a model particle is not stoichiometric. But it is charge neutral, and its density of electronic states closely matches that of bulk anatase. The relaxed configurations and electronic structures of doped and undoped anatase particles were computed both in isolation and in contact with graphene. The graphene in these calculations was a 27.21 \times 17.15 Å² rectangular patch (176 C atoms), with the long direction parallel to $[21\overline{1}0]$ periodically repeated to form an infinite sheet. The anatase was placed with its narrow (100) face contacting the graphene. It was arranged initially with a 3–4 Å spacing across the contact, and the system was fully relaxed. Several different initial configurations were used, and all resulted in the same final configuration. In these calculations, the TiO₂ formed no covalent bonds with the graphene with the particle adhering to the graphene through van der Waals interactions. As there is no evidence of preferred orientation in the anatase portion of the powder X-ray diffraction pattern (Figure S3, Supporting Information), there is evidently no any preferred plane orientation relation between the anatase particles and the graphene sheets. Thus, the model particle was oriented with the graphene patch in such a way as to minimize the number of C atoms required in the calculation, while maintaining sufficient spacing between the periodic images of the TiO₂ nanoparticle. The model N-doped TiO2 NC was doped both substitutionally and interstitially with a single N atom, which gives a 1.1 atom % doping concentration-equivalent to the doping concentration achieved experimentally through the TELESR process in liquid ammonia solution for 7 h. Several different doping sites were tested, and each resulted in qualitatively similar results. In addition, the structure of a TiO₂ NC doped with N_i and N_s atoms simultaneously was also computed. It should be noted that DFT is well known to underestimate the electronic band gap, and thus, in these calculations, we are careful not to interpret the predicted band gap quantitatively



Figure 2. XPS spectra of N-doped TiO₂/graphene and undoped TiO₂/graphene hybrids. (a) XPS spectra of N-doped TiO₂/graphene hybrid prepared at 180 °C from 0–21 h, respectively. (b) Comparison of N 1s spectra between N-doped TiO₂/graphene obtained at 14 h and undoped TiO₂/graphene samples. The N 1s peak can be fitted by two Lorentzian peaks at 401.2 and 399.8 eV, which are labeled by blue and red lines, respectively. (c) Comparison of O 1s spectra between N-doped TiO₂/graphene obtained at 14 h and undoped TiO₂/graphene sample. (d) Comparison of Ti 2p spectra between N-doped TiO₂/graphene obtained at 14 h and undoped TiO₂/graphene sample.

but rather examine relative band alignment and the formation of defect states.

RESULTS AND DISCUSSIONS

Our unique reaction process (TELESR), which uses Ti(OBu)₄, IPA, NH₃·H₂O, and exfoliated highly crystalline graphene, facilitates the low-temperature growth of N-doped TiO₂ in a gentle nitrogen-doping process, utilizing dissolved ammonia as the N source and reaction medium. TEM images (Figure 1a-c) show the N-doped TiO₂/graphene hybrids prepared in the TELESR process using reaction times of 7 h (a), 14 h (b), and 21 h (c), respectively. These images indicate that the coating density can be easily tailored by varying the reaction time. When the reaction time was 7 h, the particle coating density was only about 20%-30% of the exposed surface. As the reaction time was increased to 14 h, the particle coating density was increased to about 30%-40%. As the reaction time was further extended to 21 h, the particle coating density further increased to nearly 90%. A high resolution TEM image (Figure 1d) shows that a typical N-doped TiO₂ NC is well crystallized with a lattice spacing of 0.35 nm, which corresponds to the (101) plane of anatase TiO₂. In addition, the corresponding selected area electron diffraction (SAED) pattern (Figure 1e) exhibited not only the typical 6-fold symmetric diffraction pattern ascribed to graphene, but also multiple diffraction rings that can be indexed with anatase TiO_2 [(101), (004), (220), (105), (211) and (204), from inner to outer, respectively]. Elemental identification of the attached NCs was performed

using energy-dispersive X-ray spectroscopy (EDX). The spectrum, shown in Figure 1f, revealed the presence of Ti and O in the hybrid (Cu in the spectrum was attributed to the copper TEM grid). Moreover, the XRD pattern of the N-doped TiO_2 /graphene composite confirms the anatase phase of the N-doped TiO_2 nanoparticles on the graphene surfaces, and no other crystalline phases are present (as shown in Figure S3, Supporting Information).

It is interesting to note that some of the attached TiO₂ NCs in the TEM images have nanocuboid habits. Considering that anatase TiO₂ adopts a tetragonal structure with lattice parameters a = b = 0.377 nm and c = 0.950 nm, the square surface of the nanocuboid particles can be assigned as {001} facets; it has been previously shown that the (001) surface of anatase TiO₂ is the most catalytically active.^{34,35} In the TELESR process, the graphene substrate may act as a morphactin, facilitating the growth of attached TiO₂ into nanocuboid shape. More systematic optimization of synthesis parameters is underway for the purpose of producing a high yield of particles with nanocubic morphology, as such a sample anchored to graphene would present more catalytically active {001} facets.

As to the possible reaction mechanism for loading N-doped TiO_2 NCs on highly crystalline graphene surfaces, we propose the following four steps of "decomposition–doping–adsorption–coalescence", analogous to the mechanism for decorating graphene with transition metal (Fe, Mn, Co) oxide NCs, as described in our previous work.²⁶ Briefly, first, a titanium

precursor $(Ti(OBu)_4)$ is rapidly decomposed at an elevated temperature, producing some TiO₂ monomers in the presence of solvents (IPA and NH₃·H₂O). Second, in the ammonia solution, oxygen vacancies are partially doped with nitrogen via atomic diffusion.^{9,36} Third, due to very high surface energy, these N-doped TiO₂ seeds are preferentially adsorbed onto the graphene surface, finally coalescing into well-dispersed Ndoped TiO₂ NCs. As we discussed in the Introduction, a solvothermal reaction at 180 °C can overcome diffusion barriers, enabling the diffusion of atomic N_i in anatase TiO₂.

High-resolution XPS spectra of the graphene supported Ndoped TiO₂ prepared using ammonia solution as the N source with reaction times varying from 0 to 21 h confirmed the presence of various N doping levels, as shown in Figure 2a-d. The peaks at 285.1, 400.1, 530.1, 531.5, and 565.4 eV (Figure 2a) can be assigned to C 1s, N 1s, Ti 3p, O 1s, and Ti 2s, respectively. In the as-prepared TiO₂/graphene (Figure 2a, undoped), the atomic N percentage is only 0.6 atom %, while in the N-doped TiO_2 /graphene (Figure 2a, doped 7–21 h), the atomic percentage of N ranges from 1.1 to 2.4 atom %, increasing at first from 7 h (1.1 atom %) to 14 h (2.4 atom %) reaction time and then decreasing from 14 to 21 h (1.3 atom %) reaction time. These results indicate that due to the dynamic equilibrium of atomic diffusion in the solution phase the concentration of N-doped atoms will first increase and then decrease as a function of reaction time,³⁷ reaching saturation when the reaction time is between 14 and 21 h.

The N 1s spectra of N-doped TiO₂/graphene (doped 14 h) and undoped TiO₂/graphene were compared, as shown in Figure 2b. A weak peak in the spectrum of undoped TiO₂ was observed and attributed to N₂ molecules adsorbed on the TiO₂. For the N-doped TiO₂ sample, a relatively strong peak was observed. After curve-fitting, we attributed the peak at 399.8 eV to anionic N in N–Ti–O bonds and the peak at 401.2 eV to oxidized N in Ti–O–N.^{38,39} Both are due to the filling of oxygen vacancies by interstitial N atoms in the anatase lattice, which is consistent with other reports.^{40,41} The XPS results support the success of the TELESR process with ammonia solution for effectively N-doping anatase TiO₂, although there was no obvious 396 eV band assignable to Ti-N bonds produced by replacement of oxygen with substitutional N atoms.^{4,42,43} In addition, there is a shift of the O 1s peak by 0.3 eV toward low energy in N-doped TiO₂ (Figure 2c), indicating the existence of concomitant oxygen deficiencies, 40,44 which resulted in increased outer electron density of O and, consequently, decreased binding energy. As for the Ti 2p, the typical binding energies of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ at 458.5 and 464.3 eV remain unchanged before and after doping (Figure 2d) because the amounts of doped nitrogen species were not high enough to affect their bands.

Photoluminescence (PL) emission spectra have been widely used to investigate the efficiency of charge carrier trapping, migration, and transfer, as well as to understand the fate of electron—hole pairs in semiconductors, because PL emission is highly sensitive to the abundance of surface states in the band gap.^{38,45,46} Figure 3 shows the PL spectra of the undoped TiO₂/graphene and N-doped TiO₂/graphene with different atomic N percentages. All samples exhibit a broad signal from 400 to 600 nm, attributed to surface defects, such as an oxygen vacancies,^{45,47,48} as well as to the recombination of carriers trapped in the localized surface states.^{49,50} Compared to the undoped TiO₂/graphene, the N-doped TiO₂/graphene produced with different reaction times (7, 14, and 21h) leads to



Figure 3. PL spectrum of four samples including undoped $TiO_2/$ graphene and N-doped $TiO_2/$ graphene prepared at different doping times at 7, 14, and 21 h, respectively.

drastic suppression of the PL signal with different efficiencies, which is probably ascribed to that the photoinduced electrons are trapped by the oxygen vacancies, and the holes are efficiently captured by the doped $\rm N_{i^{-}}^{38,51}$ Because the PL emission is the result of the recombination of excited electrons and holes, the lower PL intensity of the N-doped $\rm TiO_2/$ graphene samples confirms the lower recombination rates. 15,52

Raman spectroscopy has been accepted as a versatile, purely optical, high-throughput technique for evaluating structural defects, number of layers, and doping level of graphene. Six Raman active modes for anatase TiO_2 , 42,53,54 $A_{1g} + 2B_{1g} + 3E_{gr}$, could be detected at 151 cm⁻¹ (E_g), 199 cm⁻¹ (E_g), 397 cm⁻¹ (B_{1g}), 515 cm⁻¹ (A_{1g}), 524 cm⁻¹ (B_{1g}), and 639 cm⁻¹ (E_g), as shown in Figure 4a, which indicates that anatase is the sole TiO₂ phase. The Raman spectrum of graphene is characterized by three main features: G, D, and 2D modes, each having different physical origins. The peak at $\sim 1580 \text{ cm}^{-1}$ (G band), arising from emission of zone-center optical phonons, corresponds to the doubly degenerate E_{2g} mode of graphite and is related to the coplanar vibration of sp^2 -bonded carbon atoms. The peak at ~1347 cm⁻¹ (D band) is related to the occurrence of defects and disorders. The peak at $\sim 2700 \text{ cm}^{-1}$ (2D band) originates from second-order zone boundary phonons and varies with the number of graphene layers. For the substrate of exfoliated graphene, the intensity ratio of the D to G band $(I_D/I_G = 0.086)$ is very small, reflecting the very low defect density of graphene. Furthermore, the line shape of the 2D band can be investigated to determine the number of graphene layers.^{55,56} The single 2D peak of monolayer graphene splits in four components in the bilayer graphene, 2D_{1B}, 2D_{1A}, 2D_{2A}, and 2D_{2B}. For few-layer graphene, the four components evolve into only two components by decreasing the relative intensity of the lower frequency 2D₁ peaks. The 2D peak of a typical sample was fitted (Figure 4b), then compared with the results obtained by Graf et al.,⁵⁷ to identify the number of graphene layers as four-layer.

Furthermore, we also tested the UV–vis absorption spectra of six samples, including commercial Degussa P25, undoped TiO_2 /graphene, and N-doped TiO_2 /graphene prepared at different doping times of 7, 14, and 21 h, as well as N-doped TiO_2 without graphene (Figure 5). In the spectrum of the undoped sample, only absorption in the UV range (<400 nm) can be observed; but for the commercial Degussa P25 and Ndoped TiO_2 with and without graphene samples, an enhanced absorption in the visible range between 400 and 600 nm can be



Figure 4. Raman spectrum of a N-doped TiO_2 /graphene sample (a) with 2D peak fitting (b).



Figure 5. UV–vis absorption spectra of six samples, including undoped TiO_2 /graphene, Degussa P25, and N-doped TiO_2 /graphene prepared at different doping times of 7, 14, and 21, as well as N-doped TiO_2 without graphene prepared at 14 h.

observed. More specifically, both of our prepared N-doped TiO_2 /graphene samples (doped 7 h) and N-doped TiO_2 without graphene (doped 14 h) exhibited better absorption and a certain red shift in the absorption edge, compared with Degussa P25, which suggests that it is more sensitive to visible light. It has been shown that oxygen vacancies give rise to the local states below the conduction band, and the N_i atoms would induce the local states near the valence band edge.^{43,58} Therefore, the extension of absorption into the visible range can be definitely attributed to the introduction of N_i dopants and oxygen vacancies in the lattice of the anatase structure, therefore narrowing the bandgap of TiO₂.

To evaluate the potential application of N-doped TiO₂/ graphene composites as efficient photocatalysts for pollutant degradation, we conducted the photodegradation curves of MB as a model reaction under visible light. Figure S4 of the Supporting Information is a representative time profile of MB absorbance spectrum with our catalyst (N-doped TiO₂/ graphene). These results were compared with measurements of the Degussa P25 TiO₂ under the same conditions. Figure 6 shows time profiles of C/C_0 of MB, where C is the concentration of MB after the specific irradiation time, and C_0 is the concentration of MB in the absorption equilibrium before irradiation. These experimental results indicate that the N-doped TiO₂/graphene composite (doped 14 h) has the best



Figure 6. Photodegradation curves of MB on six samples of undoped TiO_2/RGO , undoped $TiO_2/graphene$, Degussa P25 TiO_2 , and N-doped $TiO_2/graphene$ prepared at 7, 14, and 21 h, as well as one blank test.

performance among tested samples. Note in Figure 6 that the MB absorption in the 14 h sample drops to the instrument detection limit after 45 min, twice as fast as Degussa P25 TiO₂. We also investigated the degradation curves of undoped $TiO_2/$ RGO and undoped TiO₂/graphene. The results indicated that after irradiation of 90 min, 50% of MB was degraded for the solution containing the undoped TiO₂/graphene sample, while only 30% of MB was degraded for the solution containing the undoped TiO₂/RGO sample. This suggests that photocatalytic performance of undoped TiO2/graphene is much better than undoped TiO₂/RGO. To confirm the crystalline graphene acting as an acceptor of the photoinduced electrons, we measured the sheet resistance of the exfoliated graphene sheet by a four-probe instrument, as we reported in our previous paper.²⁶ The resistance was ~850 Ω/sq , at least 3 orders of magnitude less than RGO. Both the photodegradation curves and sheet resistance can prove that the low-defect exfoliated graphene acts as an excellent conductive substrate for electron transfer in comparison with RGO. In addition, we carried out one blank test showing that the solution of MB without TiO₂ was irradiated for 90 min, and only 0.7% of MB degraded.

Furthermore, the durability of the N-doped TiO_2 /graphene catalyst was checked for the degradation of MB. The photodegradation of MB was monitored for three consecutive cycles, each lasting 90 min. After each cycle, N-doped TiO_2 /graphene was filtered and washed thoroughly with distilled

water, and fresh MB solution was added. There was no significant decrease in photodegradation rate during the three consecutive cycles, indicating the good stability of the asprepared N-doped TiO₂/graphene photocatalyst. We also noted that the pH value of the MB solution plays an important role in the whole photodegradation process. It was found that the decomposition rate of MB increased when the pH values increased, which is likely the result of enhanced adsorption capacity of graphene sheets with more aromatic MB via $\pi - \pi$ conjugation.¹²

In order to quantitatively elucidate the photocatalytic behavior of N-doped TiO₂ clusters, as well as the charge–transfer interaction between TiO₂ and graphene, we have used DFT to compute the electronic structure of N_s- and N_i-doped anatase NCs, both in isolation and contacting a graphene substrate. There are two central concepts to improve the photocatalytic performance of the TiO₂: (1) enabling photo-excitation by visible light and (2) extending the lifetime of the excited state to give holes more time to diffuse to a free surface and form an \bullet OH radical. The former function is achieved by narrowing the TiO₂ band gap by N doping. The purpose of the graphene substrate is to achieve the latter function by separating the electron hole pair but leaving the hole on the TiO₂ to form the radical, as shown in Figure 7. To optimize



Figure 7. Schematic illustration of the separation of a photoexcited electron hole pair in a TiO_2 NC.

photocatalytic performance the energy of the system is reduced by transferring the photoexcited electron to the graphene, leaving the hole on the TiO_2 where it diffuses to the surface and forms a hydroxyl radical. The horizontal lines over TiO_2 depict the valence and conduction band edges in TiO_2 . The crossed lined over the graphene depict the conical band structure of graphene around its Dirac point. As the graphene has no band gap, in order to favor transfer of electrons over holes, the TiO_2 band edges must be shifted up relative to the Dirac point.

The four projected density-of-states (PDOS) plots in left of Figure 8 clearly show that N doping performs as expected to narrow the effective band gap by introducing a doping level. While the TiO₂ NCs are in isolation, the N_i doping and N_s doping give qualitatively different electronic structures. N_s forms a partially filled shallow defect state, while N_i forms a midgap defect state and raises the Fermi energy. These results are in agreement with more accurate DFT+U calculations for N-doped bulk anatase with higher doping concentrations and so validate the level of theory used in our calculations.⁵⁹ In our calculations, the band structure and Fermi energy of Ns- and N_i-doped particles in isolation differ as shown from the second and third PDOS plots in Figure 8. However, when these differently doped particles are put in contact with graphene, the density of states become very similar-the TiO₂ bands are shifted up relative to the graphene with a shallow defect state at the Fermi energy that narrows the band gap, as shown in the fifth and sixth PDOS plots in Figure 8. The results of these calculations indicate that the photocatalytic potency of the TiO₂-decorated graphene is relatively insensitive to this type of N doping and thus permits the growth of a highly effective photocatalyst at low temperatures.

The PDOS plots in Figure 8 illustrate the band alignment across the TiO₂/graphene heterojunction. It it shown that without N doping the bottom of the TiO₂ conduction band is much closer to the Fermi energy than the top of the TiO₂'s valence band, and so energetically, it is more favorable to transfer the hole to graphene rather than the photoexcited electron. Doping TiO₂ with N creates empty states below the graphene Fermi energy. When the N-doped TiO₂ is brought into contact with graphene, these states withdraw 0.8–0.9 electrons from graphene to TiO₂ NCs. This charge transfer in the ground state shifts the TiO₂ bands upward relative to the graphene, pinning the highest occupied electronic state of TiO₂ close to the Fermi energy. This shift in band alignment across the heterojunction makes transfer of the photoexcited electron more favorable.



Figure 8. Projected density of electronic states for (from left to right) an undoped $TiO_2 NC$, N_s -doped $TiO_2 NC$, N_i -doped $TiO_2 NC$, $TiO_2 NC$, T

CONCLUSIONS

In summary, N-doped TiO₂ NCs have been successfully deposited on the surface of exfoliated crystalline graphene by a simple doping process in ammonia solution at a low temperature of 180 °C. Such N-doped TiO₂/graphene composites show excellent photocatalytic efficiency, far exceeding that of commercial Degussa P25. For the composite of graphene-supported N-doped TiO2, both the conductive carbon platform and the N-doped TiO2 play synergistic roles during the photodegradation of MB in three ways: (1) enhance the adsorption of aromatic dye on the catalyst via $\pi - \pi$ conjugation between MB and graphene and, therefore, the absorptivity of dyes is better in comparison with Degussa P25, (2) extend light absorption into the visible range by narrowing the bandgap of TiO_2 via N_i-doping, and (3) suppress charge recombination, using crystalline graphene as an acceptor of the photoinduced electrons of the TiO₂ and, therefore, an effective charge separation can be achieved. We believe that the work presented here reveals a new, simple, and scalable strategy for the production of a N-doped TiO₂/graphene composite, which shows great promise for applications as a highly efficient photocatalyst for wastewater purification.

ASSOCIATED CONTENT

S Supporting Information

Additional information about TEM images and XRD spectrum of exfoliated graphene, undoped $TiO_2/graphene$, and N-doped $TiO_2/graphene$ samples; time profile of MB absorbance spectrum; computed PDOS plotted relative to the vacuum level; and a cartoon of the band structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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