Hydrothermal synthesis of N-doped TiO₂ nanowires and N-doped graphene heterostructures with enhanced photocatalytic properties

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ABSTRACT

N-doped TiO₂ nanowire/N-doped graphene (N-TiO₂/NG) heterojunctions are fabricated by a simple hydrothermal method in a solution containing urea. In this hybrid structure, a three-dimensional hybrid photocatalyst was fabricated by using one-dimensional N-doped TiO₂ nanowires penetrating through two-dimensional graphene nanosheets. Compared with TiO₂ nanowire/graphene and N-doped TiO₂ nanowire/graphene composites, the N-TiO₂/NG heterostructures demonstrate a better photocatalytic performance for the degradation of methylene blue under visible light irradiations, as well as displaying a better recyclability. It is found that the nitrogen atoms originated from the decomposition of urea were not only entered into the lattice of TiO₂ nanowires but also doped into the skeleton of graphene nanosheets. Results show that N doping expands the visible light absorption region of TiO₂, and N-doped graphene additionally improves the separation and transportation of photogenerated electron–hole pairs plus generating a higher photocurrent, which plays a critical role for enhancing the photocatalytic activity.

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1. Introduction

Since Fujishima and Honda found that the Titanium dioxide (TiO₂) can display photocatalytic activities under UV light in 1972 [1,2], numerous studies related to the photocatalytic performance of oxide semiconductor have been carried out [3–8]. Being a star semiconductor photocatalyst, TiO₂ has many outstanding advantages, such as long term stability, non-toxicity, low cost, and environmentally benign nature [9–12]. However, there are still some shortcomings of TiO₂ which significantly degrades its photocatalytic performance, including the too wide band gap, the fast recombination of the photogenerated electron–holes carriers, etc. [13,14]. In order to solve these demerits, researchers have tried some strategies such as doping, surface modification or amalgamation of other semiconductors to improve the performance of TiO₂

[15,16]. Among these methods, N doping has been proven to be an effective strategy for altering the electronic structure of TiO₂ because its p states contribute to the band gap narrowing by mixing O 2p, enabling the response of photocatalytic activity in the visible light region [17–19]. To date, many experimental approaches have been developed to produce N-doped TiO₂ with visible light sensitivity, including sputtering, thermal nitridation, direct amination, and pulsed laser deposition [15]. However, the synthesis of N-doped TiO₂ via a facile hydrothermal method has been scarcely reported. Hydrothermal reaction is a promising strategy of fabricating composites for its low cost, good dispersion of products, and easy operation of N doping at relatively low temperatures. Recently, one-dimensional TiO₂ nanostructures, such as TiO₂ nanotubes, TiO₂ nanowires (NWs) were studied extensively because they share both advantages of nanoparticles and two-dimensional (2D) nanosheets or thin films, such as large surface area and quantum confinement effects [14,20,21]. Moreover, TiO₂ NWs possess very high carrier transport speed along its axial direction, which is beneficial for carrier separation. Notably, the length of the 1D nanostructures imparts easy recyclability, which can be exploited in the

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preparation of nanostructured membranes for the creation of continuous photocatalytic devices [22]. So TiO_2 NW structures are the promising materials in environmental application areas. On the other hand, the combination of TiO_2 with nanostructured carbons, including zero-, one- or two-dimensional materials, offers broad potential applications such as photocatalysis, solar cells, etc. [23,24] Especially, the 2D graphene derivatives have been utilized as an important component for various functional composites [25–28].

Graphene, a 2D atomically thick carbon atom arranged in a honeycomb lattice, had captured the attention since its discovery by Geim et al. in 2004 because of its unique structure and property such as high electron mobility and high surface area [29]. It is well recognized that graphene can play as an efficient electron acceptor due to its 2D π – π conjugation, which may decrease the radiative recombination rate and increase the catalytic activity of nanoparticle photocatalysts anchored to the graphene surface. Additionally, chemical functionalization of graphene could potentially provide many localized highly reactive regions and thus improve its chemical actives [30–34]. Graphene nanosheets doped with nitrogen atom can greatly alter its electronic and chemical properties due to the comparable atomic size of nitrogen with carbon and the formation of strong valence bonds with the surrounding carbon atoms [35–40]. Moreover, after nitrogen doping in the graphene, the band gap between the conduction band and the valence band will be opened [41]. The doped nitrogen atoms can change the electronic structure of graphene and improve the free carrier density of graphene [42]. For instance, nitrogen-doped graphene can be fabricated through thermal reduction reaction of graphene oxide in NH_3 atmosphere, and the obtained nitrogen-doped graphene hybrids with CdS by consequent reaction enhance the photocatalytic hydrogen evolution from water under visible light irradiation [43].

Based on the above analysis, the combination of N-doped nanostructured TiO_2 NWs (N– TiO_2) and N-doped graphene (NG) would significantly improve the photocatalytic performance of TiO_2 . Therefore, in this study a novel N– TiO_2 NWs/N-graphene (N– TiO_2 /NG) composite was synthesized via a facile hydrothermal method using urea as the nitrogen source at relatively low N-doping temperature. During the hydrothermal reaction, N atoms originated from the decomposition of urea not only enter into the lattice of TiO_2 but also dope into the skeleton of graphene nanosheets. In order to comprehensively explore the effect of nitrogen-doping on the photocatalytic efficiency, we have measured the photocatalytic activity of samples by decomposing a representative dye, methylene blue (MB). Photodegradation testing demonstrated that N– TiO_2 /NG showed significant improvement for decomposing MB, when comparing with pure TiO_2 NWs, N– TiO_2 NWs, pristine TiO_2 NWs/Graphene composite (TiO_2 /G) and N– TiO_2 NWs/graphene composite (N– TiO_2 /G) under the same conditions.

2. Experiments

2.1. Preparation of samples

2.1.1. Preparation of TiO_2 NWs

TiO_2 NWs were synthesized by a hydrothermal method. Commercially available Degussa P25 was dissolved in 10 M KOH solution and the concentration of P25 was 7.5 mg/mL. The homogeneous suspension was obtained by sonicating for 10 min and magnetically stirring for 30 min. Then the mixture was transferred to a Teflon vessel held in a stainless steel vessel at 180 °C for 48 h. $\text{K}_2\text{Ti}_8\text{O}_{17}$ nanowire hydrogels were obtained and then ion-exchanged into $\text{H}_2\text{Ti}_8\text{O}_{17}$ by acid treatment (0.2 M HNO_3). After that, the hydrogen titanate nanowire materials were washed with excess deionized water until the filtrate became neutral and freeze-

dried for further use. Finally, $\text{H}_2\text{Ti}_8\text{O}_{17}$ NWs were transformed into anatase TiO_2 NWs by calcination at 600 °C for 4 h.

2.1.2. Preparation of graphene oxide (GO)

GO was prepared from natural graphite powder (Alfa Aesar, 325 mesh) by a modified Hummer's method [44]. Briefly, graphite powder (5 g) was added into solution of concentrated H_2SO_4 (15 mL), $\text{K}_2\text{S}_2\text{O}_8$ (2.5 g), and P_2O_5 (2.5 g) at 80 °C for 6 h. The mixture was diluted with 0.5 L de-ionized (DI) water, filtered and washed with excessive water several times to removal the acid. The pre-oxidized graphite powder was obtained by drying under ambient conditions. Then the powder was added into a cold concentrated H_2SO_4 (120 mL) solution for 10 min under stirring. KMnO_4 (17.5 g) was successively added and kept the temperature of the mixture under 15 °C by ice cooling. Deionized water (1000 mL) was injected into the suspension carefully in the ice water bath after the mixture was stirred at 35 °C for 2 h. Afterwards, the reaction was ended by addition of 20 mL of 30% H_2O_2 to removal redundant oxidizing agent. The mixture was washed with 1:10 HCl aqueous one time and finally washed with deionized water several times, collected by centrifugation. The jelly-like brown graphite oxide was transferred into dialysis bag to remove impurity ions for three days and then re-dispersed in deionized water and sonicated for 2 h, centrifuged to remove unexfoliated graphite oxide. The GO powder was collected by lyophilization for further experiments.

2.1.3. Preparation of N– TiO_2 /NG composites

The N– TiO_2 /NG hybrids were obtained by simple self-assembly of GO and TiO_2 NWs using urea as the nitrogen source under hydrothermal condition. In a typical synthesis, GO powder was added into 30 mL of deionized water by ultrasonic and magnetic stirring for 30 min to produce various concentrations of homogeneous GO solution. Then the prepared TiO_2 NWs (0.3 g) and urea (15 g) were added to the GO solution under stirring for 15 min. Subsequently, the mixtures were sealed in 50 mL of Teflon-lined autoclaves and hydrothermally treated 200 °C for 10 h. After the autoclaves were naturally cooled down to room temperature, the black cylinders were obtained. Finally, the samples were centrifuged and washed with deionized water three times and freeze-dried for further use. For the control experiments, N– TiO_2 NWs were synthesized via hydrothermal reaction under the same condition without GO. N– TiO_2 /G and TiO_2 /G composites were prepared via the same hydrothermal assemble route in the absence of urea. The different mass percentage of graphene in the hybrids was carried out to determine the optimal amount of graphene in displaying a better photocatalytic activity. Upon the result of photocatalytic activity measurement, the hybrids with 7 wt.% graphene showed better photocatalytic activity. Thus in this study, N– TiO_2 /7 wt.% graphene composite was selected as a representative for characterization. The following N– TiO_2 /NG refers N– TiO_2 /7 wt.% graphene composite.

2.2. Material characterization

The morphology of samples was characterized by FEI Quanta 200F scanning electron microscope (SEM) and the transmission electron microscope (Tecnai G2 F20) equipped with selected area electron diffraction (SAED) patterns. Thermal gravimetric analysis (TGA) was conducted in oxygen at a heating rate of 10 °C min^{-1} . The powder X-ray diffraction (XRD) measurements of as-prepared samples were recorded on the Bruker D8 Advance Germany using a graphite monochromator with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The specific surface area was measured by using a nitrogen gas sorption surface area tester (JW-BK222, Beijing JWGB) and calculated by the Brunauer – Emmett – Teller (BET) method. X-ray

photoelectron spectroscopy (XPS, Thermo Fisher K-Alpha American with an Al K α X-ray source) was used to measure the elemental composition of samples. Raman spectra were recorded at room temperature using (InVia Reflex, Renishaw, UK) with a 532 nm laser excitation in the range of 800–3500 cm⁻¹. The diffuse reflectance absorption spectra (DRS) of the samples were recorded by a UV–vis spectrophotometer in the range from 200 to 800 nm equipped with an integrated sphere attachment and with BaSO₄ as a reference standard. The photocurrents were detected by using a standard three-electrode cell with Ag/AgCl as reference electrode and Pt wire as the counter electrode in the KCl solution (3 M). Electrochemical impedance spectroscopy (EIS) and Cyclic voltammograms (CV) measurements were obtained using an electrochemical workstation (Corrtest corporation, Wuhan, China). EIS spectra were measured by applying 10 mV alternative signal versus the reference electrode (SCE) over the frequency range of 1 MHz–100 mHz. The CV spectra were measured in 0.1 M KCl solution containing 2.5 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) at 20 mV/s rate over a voltage range of -0.5–0.7 V versus the SCE. The working electrodes were made by mixing the as-prepared materials with binder which containing anhydrous terpineol (4 g), ethyl celluloses (0.562 g) and ethanol (6 mL), followed by stirring and sonication to form equally slurry. The obtained slurry was coated on the FTO glass by a screen printing technique. At last, the working electrodes were obtained after calcination in a tube furnace at 450 °C in Ar atmosphere for 30 min.

2.3. Measurement of photocatalytic activity

The photocatalytic activity of the N-TiO₂/NG was evaluated for the degradation of methylene blue (MB) (10 mg/L) in H₂O. Firstly,

80 mg of the catalyst was combined with the 100 mL of the dye solution in a 200 mL water-bath flask and placed inside in the dark for 60 min under stirring to establish adsorption–desorption equilibrium between the catalyst and MB dye at room temperature. After the adsorption–desorption equilibrium, the suspensions of catalyst and MB dye were irradiated equipped by a 300 W xenon lamp with a 420 nm cutoff filter ($\lambda > 420$ nm). During the illumination process, 4 mL sample solution was taken at a certain time interval during the experiment and centrifuged to remove the catalyst completely. The solution was analyzed on an UV–vis spectrophotometer (Japan Shimadzu UV–vis 1700). The percentage of degradation of MB is reported as C/C_0 . Here, C is the concentration of MB solution at each irradiated time interval, while C_0 is the initial concentration of MB solution after the adsorption–desorption equilibrium is reached. By comparison, the photocatalytic activities of TiO₂ NWs, N-TiO₂ NWs, TiO₂/G and N-TiO₂/G composites were also demonstrated with the same procedure.

A recycled photocatalytic activity for the used catalyst was estimated as follows. Typically, after reaction of the first run under visible light irradiation, the catalyst was separated by centrifugation from the suspension. After that the catalyst was washed with deionized water and ethanol for three times to fully remove the residual organic species, and reused for the next run.

3. Results and discussion

3.1. Crystal structure, Raman analysis and BET surface areas

Fig. 1a shows the X-ray powder diffraction (XRD) patterns of the TiO₂ NWs, N-TiO₂ NWs, TiO₂/G, N-TiO₂/G and N-TiO₂/NG. The diffraction peaks of TiO₂ NWs and N-TiO₂ NWs match well with

Fig. 1. (a) XRD patterns of the TiO₂ NWs, N-TiO₂ NWs, TiO₂/G, N-TiO₂/G and N-TiO₂/NG; (b) Raman spectra of GO, RGO, TiO₂/G, N-TiO₂/G and N-TiO₂/NG; (c) Nitrogen adsorption–desorption isotherms and (d) the corresponding pore-size distribution curves of TiO₂/G, N-TiO₂/G and N-TiO₂/NG.

the crystal structure of the anatase TiO_2 . The peaks at 2θ values of 25.3° , 37.8° , 48.0° , 53.9° , 55.0° , 62.9° , 68.8° , 70.3° , 75.0° can be well-indexed to (101), (004), (200), (105), (211), (204), (116), (200) and (215) crystal planes of anatase TiO_2 (PDF 21–1272), respectively. For the composites of TiO_2/G , $\text{N-TiO}_2/\text{G}$ and $\text{N-TiO}_2/\text{NG}$, all of the peaks are similar to TiO_2 NWs and N-TiO_2 NWs, indicating that TiO_2 crystal structure is not destroyed though hydrothermal reaction with graphene oxide and urea. It is worth to note that the characteristic peak for graphene nanosheet (26.5°) has not been observed, which is due to the weak intensity compared with TiO_2 and also demonstrates that TiO_2 NWs were efficiently deposited on the graphene surface, suppressing the stacking of graphene layers [38].

As shown in Fig. 1b, two typical Raman peaks can be observed for the sample of GO, RGO, TiO_2/G , $\text{N-TiO}_2/\text{G}$ and $\text{N-TiO}_2/\text{NG}$. One band located at around 1350 cm^{-1} (called the D-band) relates to the defects and structural disorder in graphene. The G-band at around 1588 cm^{-1} is due to the stretching of the sp^2 -hybridized $\text{C}=\text{C}$ [45]. The intensity ratio of D/G bands for GO and RGO is 0.85 and 0.92, respectively, while it is increased to 0.98, 0.95 and 1.07 for TiO_2/G , $\text{N-TiO}_2/\text{G}$ and $\text{N-TiO}_2/\text{NG}$. The D/G intensity ratios for the samples TiO_2/G , $\text{N-TiO}_2/\text{G}$ and $\text{N-TiO}_2/\text{NG}$ are higher than that of pure GO, which confirms the existence of graphene sheets in the graphene- TiO_2 composites [46,47] and indicates the reduction of the exfoliated GO [48]. In addition, the D/G intensity ratio of hybrids with NG is higher than others, thereby providing convincing evidence that N atoms dope into the skeleton of graphene nanosheets [44]. On the other hand, this result is consistent with the following XPS analysis.

Photocatalysts with high specific surface areas and large pore volumes are helpful for improving photocatalytic performance, due to enhanced adsorption of reactant molecules and fast transportation of reactant molecules and products [49,50]. The porous nature of $\text{N-TiO}_2/\text{NG}$ and $\text{N-TiO}_2/\text{G}$, TiO_2/G were compared by BET measurement, respectively (Fig. 1c). The adsorption–desorption isotherms of $\text{N-TiO}_2/\text{NG}$, $\text{N-TiO}_2/\text{G}$ and TiO_2/G exhibit typical IV nitrogen adsorption branches with a H3 hysteresis loop at a relative pressure between 0.5 and 1.0, indicating the presence of a mesoporous structure (2–50 nm) [46,49]. The pore size (Fig. 1d) distribution of $\text{N-TiO}_2/\text{NG}$ calculated by the BJH method derived from the desorption branch is centered around 3.9 nm, which is a little bigger than that of $\text{N-TiO}_2/\text{G}$ (3.7 nm) and TiO_2/G (3.7 nm). Remarkably, the specific surface area of $\text{N-TiO}_2/\text{NG}$ reaches up to $139.5\text{ m}^2\text{ g}^{-1}$, which is higher than that of $\text{N-TiO}_2/\text{G}$ ($119.8\text{ m}^2\text{ g}^{-1}$) and TiO_2/G ($106.5\text{ m}^2\text{ g}^{-1}$). This result demonstrates that the building up of porous frameworks by hydrothermal assembly is an effective way to achieve high surface area for hybrid materials [51,52].

3.2. FTIR spectra and thermogravimetric measurement

Fourier transform infrared (FTIR) spectra of the samples were employed to identify the different types of chemical bonds in the hybrids, as shown in Fig. 2a. The prominent absorption peaks of GO were observed at 3420 , 1732 , 1620 , 1401 , 1226 and 1050 cm^{-1} , which were attributed to O–H, $\text{C}=\text{O}$ in COOH, aromatic $\text{C}=\text{C}$, carboxyl $\text{C}=\text{O}$, epoxy $\text{C}=\text{O}$ and alkoxy $\text{C}=\text{O}$ stretches [23,53], respectively. The absorption peaks of most oxygen-containing functional groups are absent in the TiO_2 and graphene hybrid nanostructures obtained after hydrothermal reduction. Notably, the sharp peak at 1605 cm^{-1} contains the vibration of $\text{C}=\text{C}$ in the skeletal vibration of graphene sheet in TiO_2/G , $\text{N-TiO}_2/\text{G}$, and $\text{N-TiO}_2/\text{NG}$ [54]. Most characteristic absorption peaks of TiO_2 were appeared in the range of $500\text{--}1000\text{ cm}^{-1}$ indicating the Ti–O stretching mode in crystalline TiO_2 . Notably, a peak at 793 cm^{-1} related to Ti–O–C vibration of TiO_2 -graphene hybrids is observed,

Fig. 2. (a) FTIR spectra of the as-prepared photocatalysts; (b) TG curves of TiO_2/G , $\text{N-TiO}_2/\text{G}$ and $\text{N-TiO}_2/\text{NG}$ under an oxygen atmosphere.

indicating that there are TiO_2 NWs bound to the graphene surface [33].

Thermogravimetric (TG) measurement was carried out in an oxygen atmosphere to determine the mass percentage of TiO_2 in the hybrids at $10^\circ\text{C min}^{-1}$. As shown in Fig. 2b, the TG curve displays a significant weight loss at approximately 400°C and a constant weight above 500°C . The slight weight loss below 120°C can be ascribed to the evaporation of adsorbed water molecules. The major weight loss from 300 to 500°C was the combustion of graphene. Hence, the content of TiO_2 in the composites was calculated to be 93%.

3.3. Morphological characterization

Fig. 3 shows the typical microstructure of TiO_2 NWs and $\text{N-TiO}_2/\text{NG}$, respectively. The SEM image of TiO_2 NWs (Fig. 3a) confirms the formation of entangled one-dimensional nanostructures, with an average diameter of dozens of nanometers and length up to several micrometers. The morphology of TiO_2 in the $\text{N-TiO}_2/\text{NG}$ is similar to that of as-prepared pure TiO_2 NWs, as shown in Fig. 3b and c. During hydrothermal reaction with GO and urea, the majority of TiO_2 NWs kept original morphology except a little agglomeration, which may be due to that some TiO_2 NWs were wrapped up with RGO nanosheets. It is clear that the hydrothermal self-assemble reaction results in the uniform composite materials of micrometer-sized RGO sheets and TiO_2 NWs. In this case, parts of the RGO sheets are still exposed.

As shown in the TEM image (Fig. 3d), the diameter of pure TiO_2 NWs is around $60\text{--}80\text{ nm}$ and the length can be up to several micrometer. It is clearly visible that some TiO_2 NWs are located on the surface of 2D graphene nanosheets, while the distribution of TiO_2 is unordered, as shown in Fig. 3e. Furthermore, it is obvious

Fig. 3. SEM images of (a) TiO₂ NWs, (b, c) N–TiO₂/NG; TEM images of (d) TiO₂ NWs, (e) N–TiO₂/NG; (f) SAED pattern of N–TiO₂/NG.

that the morphology of TiO₂ NWs has changed with a little agglomeration after hydrothermal reaction. This phenomenon may be attributed to that graphene nanosheets crosslink and contraction to make TiO₂ NWs irregularly anchor on the surface of graphene during the hydrothermal self-assemble process. The SAED pattern of N–TiO₂/NG (Fig. 3f) contains a series of well-defined Debye–Scherrer rings which confirm their polycrystalline nature. The calculated *d*-spacing values of 3.52, 2.39, 1.89, 1.70 and 1.49 Å correspond to Miller indices (101), (004), (200), (105) and (204) of anatase TiO₂, being consistent well with the XRD pattern.

3.4. XPS analysis

In order to confirm that N atoms were doped into TiO₂ and graphene, X-ray photoemission spectroscopy studies were carried out. The survey scan spectrum from XPS analysis shows the composites contained C, O, N and Ti elements as shown in Fig. 4a. The Ti 2p_{3/2} (459.1 eV) and Ti 2p_{1/2} (464.9 eV) peaks are found in high resolution XPS spectrum of Ti 2p (Fig. S1a), being in agreement with the value of Ti⁴⁺ in TiO₂ lattice. The main C 1s peak located at 284.8 eV is assigned to the C=C bonds, with a tail at higher binding energies, indicating the existence of carbon atoms connected to N and O heteroatoms [55]. Peak deconvolution indicates that the left three peaks can be fitted to C=N & C–O (285.7 eV), C–N & C=O

(286.7 eV), Ti–O–C (287.9 eV) and N–C=O (289.5 eV), as shown in Fig. 4b. C 1s peak at 281 eV, characteristic of Ti–C bonds, is absent, indicating that carbon was not doped into the TiO₂ lattice [23,33,54]. The high-resolution O 1s XPS spectra of N–TiO₂/NG (Fig. 4c) present three peaks at 530.6, 531.4 and 532.9 eV. The main peak at 530.6 eV belongs to O 1s in the Ti–O linkage of TiO₂ and the peak at 532.9 eV corresponds to the residual oxygen-containing groups in graphene. It is important to note that the peak at around 531.4 eV can be ascribed to O–Ti–N, suggesting that nitrogen atom entered into the lattice of TiO₂ [56,57]. Moreover, the N 1s peak (Fig. 4d) can be resolved into four components centered at 398.2 eV, 399.6 eV, 400.9 eV and 402.8 eV, representing pyridinic N, pyrrolic N & O–Ti–N, quaternary N and N–O, suggesting that nitrogen atoms was doped into TiO₂ lattice as well as into graphene framework successfully [38,55,57]. The amount of N dopant is 4.64% based on the XPS analysis. In order to confirm that N atoms enter into the lattice of TiO₂ NWs by post-processing hydrothermal reaction with urea, XPS study of N–TiO₂ was also carried out. Fig. S1b shows that the high-resolution N 1s XPS spectra of N–TiO₂ can be resolved into three components at values of 396.3, 399.5 and 401.0 eV corresponding to Ti–N, O–Ti–N and molecularly chemisorbed γ-N₂ [16,38]. The above results demonstrate that N from the decomposition of urea by hydrothermal reaction can enter not only into the lattice of TiO₂ but also into the skeleton of graphene nanosheets.

3.5. UV–vis diffuse reflection spectra

Fig. 5a shows the UV–vis diffuse reflection spectra of TiO₂ NWs, N–TiO₂ NWs, TiO₂/G, N–TiO₂/G and N–TiO₂/NG. The pure TiO₂ NWs displayed an absorption band lower than 390 nm due to the charge from the O 2p valance band to the Ti 3d conduction band [58]. The introduction of nitrogen into the lattice of TiO₂ alters the electronic structure of TiO₂, resulting in the formation of N-dopant levels above the O 2p VB and enabling the adsorption of visible light. Meanwhile, the TiO₂/G, N–TiO₂/G and N–TiO₂/NG exhibited a broad absorption in the range of 400–800 nm due to the presence of black graphene, which is in agreement with the color change from white to yellow and black grey, pure TiO₂, N–TiO₂, TiO₂/G, N–TiO₂/G and N–TiO₂/NG, as shown in the inset of Fig. 5a. Therefore, the combination of the graphene and TiO₂ NWs can shift the optical response of TiO₂-base catalysts from the UV range to the visible spectral range, which shows the potential of the TiO₂/G and N–TiO₂ for the visible-light photocatalysis.

The band gaps of as-prepared samples, estimated by the extrapolated value from UV–vis diffuse reflectance spectroscopy of $[F(R) \cdot hv]^{1/2}$ versus photonenergy *hν* in Fig. 5b, are 3.23 eV for pure TiO₂, 3.08 eV for N–TiO₂, 3.01 eV for TiO₂/G, 2.91 for N–TiO₂/G and 2.82 eV for N–TiO₂/NG, respectively. It is noted that the band gap of N–TiO₂ is smaller than that of pure TiO₂, due to the N dopants introduced into the lattice of TiO₂. Furthermore, the narrow band gaps of TiO₂/G, N–TiO₂/G and N–TiO₂/NG can be attributed to the introduction of graphene, leading to a more efficient utilization of visible light. N–TiO₂/NG heterostructures own smaller band gap than N–TiO₂/G, signifying that the N dopants being introducing in the graphene sheets can narrow the band gap.

3.6. Photoelectrochemical measurements

To further explain the enhancement of photocatalytic properties of N–TiO₂/NG, the photo-electrochemical (PEC) performances of N–TiO₂/NG and other composites as comparison were carried out using a standard three-electrode cell. As shown in Fig. 6, the photocurrent responses of all samples were recorded under irradiation by an Xenon lamp. The photocurrent of the N–TiO₂/NG anode

Fig. 4. (a) XPS spectrum of N-TiO₂/NG; (b) C 1s, (c) O 1s and (d) N 1s XPS spectra of N-TiO₂/NG.

Fig. 5. (a) UV-vis diffuse reflection spectra of the as-synthesized TiO₂ NWs, N-TiO₂ NWs, TiO₂/G, N-TiO₂/G and N-TiO₂/NG samples (inset shows the colors of photocatalysts). (b) Corresponding plot of transformed Kubelka-Munk function versus the light energy. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is about $1.0 \mu\text{A cm}^{-2}$, while that of N-TiO₂/G, TiO₂/G, N-TiO₂, TiO₂ anodes are lower than N-TiO₂/NG. The photocurrent responses orders are as follows: N-TiO₂/NG, N-TiO₂/G, TiO₂/G, N-TiO₂, TiO₂. The higher photocurrent indicates that more electrons are transferred to the photoelectrode and a greater separation of the photo-induced electrons and holes. The photocurrents of all samples with graphene are obviously higher than the TiO₂ NWs and N-TiO₂ NWs. Meanwhile, N-doped composites show high photocurrents than pristine samples. There are three possibilities leading to this result: (1) N doping expands the visible light absorption region of TiO₂, (2) graphene nanosheets can drain excited electrons from the conduction band of TiO₂ to ITO base, (3) N-doped graphene accelerates electron transportation than undoped graphene.

Fig. 6. Photocurrent response of the photoanodes of TiO₂ NWs, N-TiO₂ NWs, TiO₂/G, N-TiO₂/G and N-TiO₂/NG samples.

Fig. 7. (a) The CV curves and (b) EIS curves of as prepared TiO₂ NWs, N-TiO₂ NWs, TiO₂/G, N-TiO₂/G and N-TiO₂/NG composites.

CV and EIS are widely used tools to reveal the transfer and separation efficiency of photogenerated charges, as shown in Fig. 7. The peak at positive potentials on the anodic (forward) sweep is around 0.2–0.3 V vs. SCE. N-TiO₂/NG presents smaller peak-to-peak separations (ΔE_p) than other samples, indicating highly improved reaction reversibility [28]. Meanwhile, N doped composites present smaller ΔE_p than undoped composites, which indicates that N doping can narrow ΔE_p whether N dopants enter into the lattice of TiO₂ or the skeleton of graphene nanosheets. Furthermore, the hybrids with graphene sheets display large current density, demonstrating a significantly enhanced rate of electron transfer attributed to the induction of the graphene. In the Nyquist diagram, the radius of each arc is associated with the charge transfer process. A smaller radius indicates a lower charge-transfer resistance. N-TiO₂/NG heterostructures exhibit the smallest charge transfer resistance among all photocatalysts, indicating the fast interfacial transfer of photogenerated charges and effective separation of photogenerated electron–hole pairs at the hybrid interfaces (Fig. 7b).

3.7. Photocatalytic activity

Relative photocatalytic activity of each synthesized material was comparatively investigated by evaluating the photodegradation rate of MB under visible light irradiation. As shown in Fig. 8a, MB hardly exhibits self-degradation under visible light, by contrast, in the presence of the TiO₂ and graphene hybrids, MB can be degraded

quickly. It was found that the TiO₂/G, N-TiO₂/G and N-TiO₂/NG showed that the concentration of MB was reduced by 59.8%, 71.1% and 87.9% after 180 min of irradiation, respectively, indicating a higher degradation rate to that found with TiO₂ NWs (19.8%) and N-TiO₂ NWs (32.9%). The photocatalytic activity of TiO₂ and graphene hybrids were higher than pure TiO₂ catalysts due to TiO₂ interacted with graphene surface –OH hydroxyl groups, resulting in forming Ti–O–C bonds through hydrothermal reaction [16].

To quantitatively evaluate the photocatalytic efficiencies of these catalysts, the corresponding apparent reaction rate constants (k) of the MB degradation calculated by using an equation $\ln(C/C_0) = kt$ based on the pseudo-first-order kinetic model is shown in Fig. 8b, where C_0 , C , k and t is the initial MB concentration, concentration after a certain reaction time, the rate constant and reaction time, respectively. For the blank experiment (without catalysts), the MB degrades at relatively slow reaction rate with $k = 0.000208 \text{ min}^{-1}$. Evidently, the apparent reaction constant of MB self-degradation was significantly lower than that of the photocatalytic degradation of MB with the assistance of TiO₂ NWs ($k = 0.00124 \text{ min}^{-1}$), N-TiO₂ NWs ($k = 0.00213 \text{ min}^{-1}$), TiO₂/G ($k = 0.00481 \text{ min}^{-1}$), N-TiO₂/G ($k = 0.00716 \text{ min}^{-1}$) and N-TiO₂/NG ($k = 0.0107 \text{ min}^{-1}$). The kinetic constants of the optimized N-TiO₂/NG for MB degradation was 8.6 times higher than that observed with TiO₂ NWs and 5.0 times than that observed with N-TiO₂ NWs, indicating that the RGO sheets on the TiO₂ NWs significantly enhanced the photocatalytic activity of the TiO₂. This is because that graphene has the special π – π conjugation structure and larger specific surface area of the porous layered structure which can strengthen dye adsorption capacity for gathering reactant to improve the reaction rate. Simultaneously, photocatalytic degradation of MB shows that N-TiO₂ NWs has higher activity than pure TiO₂ NWs under the irradiation of visible light. Because of the band gap modification upon N doping, N-TiO₂ NWs has a red shift of the band gap by modifying the valence band, and has a visible light response [16,19]. N-TiO₂/NG heterostructures show better photocatalytic performance than N-TiO₂/G, demonstrating that N dopants into graphene are favorable to enhancing photocatalytic activity. As shown in Fig. 8c, the degradation of MB is further carried out for different graphene mass percentage to optimize TiO₂ loading on graphene. It is found that N-TiO₂/NG hybrids show greater photocatalytic degradation of MB than N-TiO₂ NWs, which demonstrates that the introduction of graphene improves the photocatalytic activity. The photocatalytic performance enhancement for the degradation of MB is up to 7 wt.% graphene loading, after which it decreases. The result is inconsistent with other report [59] maybe because 0D TiO₂ nanoparticles are smaller and apt to agglomerate than 1D TiO₂ NWs, demonstrating that TiO₂ NWs are able to penetrate through more graphene sheets and can effectively prevent the restacking of GO sheets.

The stability and reusability are the important indicators to evaluate catalysts. So we performed another five cycles of sequential photocatalytic processes toward MB dye by using the recycled N-TiO₂/NG. In addition to the excellent photocatalytic degradation performance, the N-TiO₂/NG also exhibited good stability of photocatalytic activity during the degradation process of the MB solution, as shown in Fig. 8d. The photocatalytic activity of N-TiO₂/NG displays a little decrease (within 3%) after 5 cycles, indicating that the N-TiO₂/NG remained active for long-term service without obvious deactivation.

3.8. Possible photocatalytic mechanism

Based on the above results and discussion, we propose the mechanism for the visible light photocatalytic reaction over N-TiO₂/NG composites as shown in Fig. 9. The visible light

Fig. 8. (a) Degradation curves of the MB aqueous solutions containing different photocatalysts under visible light irradiation: without catalyst, TiO_2 NWs, N-TiO₂ NWs, TiO_2/G , N-TiO₂/G and N-TiO₂/NG. (b) Photodegradation rates for MB. (c) Photocatalytic degradation of MB by N-TiO₂/N-graphene composites with different graphene contents. (d) Cycling runs in photocatalytic degradation of MB in the presence of N-TiO₂/NG composite photocatalyst under visible light irradiation.

Fig. 9. (a) Schematic diagram of photogenerated electrons transfer between N-TiO₂ NWs and N-graphene materials. (b) Schematic diagram of photo-excited electrons and holes transfer among N-TiO₂ NWs and N-graphene nanosheets.

irradiation can excite the electrons from N 2p impurity energy level to the conduction band (CB) of N-TiO₂/NG, due to N 2p of N atoms doped into the lattice of TiO_2 , which is located above the valence band (VB) maximum (O 2p) and narrowing the band gap of TiO_2 . After that, the excited electrons on the CB of N-TiO₂ can be easily transferred to the NG sheets via the Ti–O–C bands due to the lower Fermi level of NG compared to N-TiO₂ [16]. Meanwhile, the incremental holes on the NG surface are transferred to the VB, which can separate electron–hole pairs and inhibit the recombination of charge carriers, leading to the enhanced photocatalytic activity. As a result, the electrons were gathered on the graphene sheets whereas holes were gathered on TiO_2 surface. The electrons can be scavenged by O_2 to intermediates (superoxide radical anions, O_2^-). The positive holes on TiO_2 VB can react with H_2O molecules, which lead to generation of many mobile free OH radicals and hydrogen ions [60]. Detailed free radical reaction process, as shown in Eqs. (1)–(5): the newly formed O_2^- from the CB of TiO_2 can further create the reactive hydroxyl radicals ($\cdot\text{OH}$).

In this process, electron acceptors (O_2 dissolved in the water) can restrain the electron–hole recombination on the graphene surface and then create highly reactive hydroxyl radicals ($\bullet OH$). A large number of generated mobile free OH radicals are powerful oxidizing agents for the degradation of MB into small molecules, such as CO_2 , H_2O , etc. under the visible light irradiation.

4. Conclusion

We demonstrated that N–TiO₂/NG, comprising N–TiO₂ NWs and N-doped graphene nanosheets, can be fabricated through a facile and efficient hydrothermal method. The success of N doping into both the lattice of TiO₂ and graphene was confirmed by the results of UV–vis absorption spectra, XPS spectroscopy and Raman spectroscopy. Comparing with pure TiO₂ NWs, N–TiO₂ NWs, TiO₂/G and N–TiO₂/G composites, N–TiO₂/NG indicates improved photocatalytic performance under visible light irradiation. Moreover, the N–TiO₂/NG exhibited good stability and reusability after several recycling. Our results suggest that the enhanced photocatalytic activity is attributed to the narrowing band gap of TiO₂ by N doping and rapid separation of photoinduced carriers through N-doped graphene. It provides a new strategy to improve the photocatalytic performance of N-doped TiO₂, which proposes a new thought to design and prepare other semiconductors for various applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jallcom.2015.09.211>.

References

- [1] A. Fujishima, K. Honda, *Nature* 238 (1972) 37–38.
- [2] D.A. Tryk, A. Fujishima, K. Honda, *Electrochim. Acta* 45 (2000) 2363–2376.
- [3] Y. Wang, J.G. Yu, W. Xiao, Q. Li, *J. Mater. Chem. A* 2 (2014) 3847–3855.
- [4] H. Zhang, X. Lv, Y. Li, Y. Wang, J. Li, *ACS Nano* 4 (2009) 380–386.
- [5] H.T. Wu, J. Fan, E.Z. Liu, X.Y. Hu, Y.N. Ma, X. Fan, Y.Y. Li, C.N. Tang, *J. Alloys Compd.* 623 (2015) 298–303.
- [6] P. Wang, J. Wang, T. Ming, X. Wang, H. Yu, J. Yu, Y. Wang, M. Lei, *ACS Appl. Mater. Interfaces* 5 (2013) 2924–2929.
- [7] X. Bai, X. Zhang, Z. Hua, W. Ma, Z. Dai, X. Huang, H. Gu, *J. Alloys Compd.* 599 (2014) 10–18.
- [8] K. Zhang, Q. Liu, H. Wang, R. Zhang, C. Wu, J.R. Gong, *Small* 9 (2013) 2452–2459.
- [9] O.K. Varghese, M. Paulose, T.J. LaTempa, C.A. Grimes, *Nano Lett.* 9 (2009) 731–737.
- [10] J. Yu, Y. Wang, W. Xiao, *J. Mater. Chem. A* 1 (2013) 10727–10735.
- [11] J. Yang, X. Zhang, B. Li, H. Liu, P. Sun, C. Wang, L. Wang, Y. Liu, *J. Alloys Compd.* 584 (2014) 180–184.
- [12] B. Qiu, M. Xing, J. Zhang, *J. Am. Chem. Soc.* 136 (2014) 5852–5855.
- [13] S. Neatu, J.A. Maciá-Agulló, P. Concepción, H. García, *J. Am. Chem. Soc.* 136 (2014) 15969–15976.
- [14] M. Xing, X. Li, J. Zhang, *Sci. Rep.* 4 (2014).
- [15] R. Asahi, T. Morikawa, H. Irie, T. Ohwaki, *Chem. Rev.* 114 (2014) 9824–9852.
- [16] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* 293 (2001) 269–271.
- [17] V. Balek, J. Šubrt, I.M. Bountseva, H. Irie, K. Hashimoto, *J. Therm. Anal. Calorim.* 92 (2008) 161–167.
- [18] M. Miyauchi, A. Ikezawa, H. Tobimatsu, H. Irie, K. Hashimoto, *Phys. Chem. Chem. Phys.* 6 (2004) 865–870.
- [19] H. Tokudome, M. Miyauchi, *Chem. Lett.* 33 (2004) 1108–1109.
- [20] X. Wang, Z. Li, J. Shi, Y. Yu, *Chem. Rev.* 114 (2014) 9346–9384.
- [21] Q. Zhang, N. Bao, X. Zhu, D. Ma, Y. Xin, *J. Alloys Compd.* 618 (2015) 761–767.
- [22] Y. Sang, Z. Zhao, J. Tian, P. Hao, H. Jiang, H. Liu, J.P. Claverie, *Small* 10 (2014) 3775–3782.
- [23] V. Etacheri, J.E. Yourey, B.M. Bartlett, *ACS Nano* 8 (2014) 1491–1499.
- [24] N.L. Yang, Y.Y. Liu, H. Wen, Z.Y. Tang, H.J. Zhao, Y.L. Li, D. Wang, *ACS Nano* 7 (2013) 1504–1512.
- [25] H.M. Jeong, J.W. Lee, W.H. Shin, Y.J. Choi, H.J. Shin, J.K. Kang, J.W. Choi, *Nano Lett.* 11 (2011) 2472–2477.
- [26] S.D. Perera, R.G. Mariano, K. Vu, N. Nour, O. Seitz, Y. Chabal, K.J. Balkus Jr., *ACS Catal.* 2 (2012) 949–956.
- [27] N. Farhangi, R.R. Chowdhury, Y. Medina Gonzalez, M.B. Ray, P.A. Charpentier, *Appl. Catal. B Environ.* 110 (2011) 25–32.
- [28] X. Pan, Y. Zhao, S. Liu, C.L. Korzeniewski, S. Wang, Z. Fan, *ACS Appl. Mater. Interfaces* 4 (2012) 3944–3950.
- [29] K.S. Novoselov, A.K. Geim, S. Morozov, D. Jiang, Y. Zhang, S. Dubonos, I. Grigorieva, A. Firsov, *Science* 306 (2004) 666–669.
- [30] X. Huang, X. Qi, F. Boey, H. Zhang, *Chem. Soc. Rev.* 41 (2012) 666–686.
- [31] D. Wu, F. Zhang, H. Liang, X. Feng, *Chem. Soc. Rev.* 41 (2012) 6160–6177.
- [32] H. Bai, C. Li, G. Shi, *Adv. Mater.* 23 (2011) 1089–1115.
- [33] Y. Tang, D. Wu, S. Chen, F. Zhang, J. Jia, X. Feng, *Energy Environ. Sci.* 6 (2013) 2447–2451.
- [34] G. Xie, K. Zhang, B. Guo, Q. Liu, L. Fang, J.R. Gong, *Adv. Mater.* 25 (2013) 3820–3839.
- [35] H. Wang, C. Zhang, Z. Liu, L. Wang, P. Han, H. Xu, K. Zhang, S. Dong, J. Yao, G. Cui, *J. Mater. Chem.* 21 (2011) 5430–5434.
- [36] X. Li, H. Wang, J.T. Robinson, H. Sanchez, G. Diankov, H. Dai, *J. Am. Chem. Soc.* 131 (2009) 15939–15944.
- [37] X. Wang, X. Li, L. Zhang, Y. Yoon, P.K. Weber, H. Wang, J. Guo, H. Dai, *Science* 324 (2009) 768–771.
- [38] Y. Li, Z. Wang, X.J. Lv, *J. Mater. Chem. A* 2 (2014) 15473–15479.
- [39] Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan, J.R. Gong, *J. Am. Chem. Soc.* 133 (2011) 10878–10884.
- [40] J. Zhang, J. Yu, M. Jaroniec, J.R. Gong, *Nano Lett.* 12 (2012) 4584–4589.
- [41] H. Wang, T. Maiyalagan, X. Wang, *ACS Catal.* 2 (2012) 781–794.
- [42] M. Wu, C. Cao, J.Z. Jiang, *Nanotechnology* 21 (2010) 505202.
- [43] L. Jia, D.H. Wang, Y.X. Huang, A.W. Xu, H.Q. Yu, *J. Phys. Chem. C* 115 (2011) 11466–11473.
- [44] Y. Zheng, Y. Jiao, L. Ge, M. Jaroniec, S.Z. Qiao, *Angew. Chem.* 125 (2013) 3192–3198.
- [45] Y. Wen, H. Ding, Y. Shan, *Nanoscale* 3 (2011) 4411–4417.
- [46] Y. Wang, J. Yu, W. Xiao, Q. Li, *J. Mater. Chem. A* 2 (2014) 3847–3855.
- [47] Q. Xiang, J. Yu, M. Jaroniec, *Nanoscale* 3 (2011) 3670–3678.
- [48] P.G. Ren, D.X. Yan, X. Ji, T. Chen, Z.M. Li, *Nanotechnology* 22 (2011) 055705.
- [49] J. Yu, J. Ran, *Energy Environ. Sci.* 4 (2011) 1364–1371.
- [50] S. Liu, J. Yu, M. Jaroniec, *J. Am. Chem. Soc.* 132 (2010) 11914–11916.
- [51] Y. Gong, S. Yang, Z. Liu, L. Ma, R. Vajtai, P.M. Ajayan, *Adv. Mater.* 25 (2013) 3979–3984.
- [52] L. Xiao, D. Wu, S. Han, Y. Huang, S. Li, M. He, F. Zhang, X. Feng, *ACS Appl. Mater. Interfaces* 5 (2013) 3764–3769.
- [53] H. Zhang, X. Lv, Y. Li, Y. Wang, J. Li, *ACS Nano* 4 (2010) 380–386.
- [54] F. Pei, Y. Liu, S. Xu, J. Lü, C. Wang, S. Cao, *Int. J. Hydrogen Energy* 38 (2013) 2670–2677.
- [55] Z. Lin, G. Waller, Y. Liu, M. Liu, C.P. Wong, *Adv. Energy Mater.* 2 (2012) 884–888.
- [56] P. Chen, T.Y. Xiao, H.H. Li, J.J. Yang, Z. Wang, H.B. Yao, S.H. Yu, *ACS Nano* 6 (2011) 712–719.
- [57] W. Yuan, J. Li, L. Wang, P. Chen, A. Xie, Y. Shen, *ACS Appl. Mater. Interfaces* 6 (2014) 21978–21985.
- [58] Q. Xiang, J. Yu, M. Jaroniec, *Phys. Chem. Chem. Phys.* 13 (2011) 4853–4861.
- [59] Y. Zhang, Z.-R. Tang, X. Fu, Y.-J. Xu, *ACS Nano* 5 (2011) 7426–7435.
- [60] Y.K. Lai, J.Y. Huang, H.F. Zhang, V.P. Subramaniam, Y.X. Tang, D.G. Gong, L. Sundar, L. Sun, Z. Chen, C.J. Lin, *J. Hazard. Mater.* 184 (2010) 855–863.