Enhanced visible-light-driven photocatalytic performance of porous graphitic carbon nitride

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ABSTRACT

In this study, a series of porous graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) materials were fabricated through a direct pyrolysis of protonated melamine by nitric acid solution. These as-prepared porous samples were characterized by a collection of analytical techniques. It was found that a proper concentration of nitric acid solution involved facilitated to generate samples in tube-like morphology with numerous pores, identified with X-ray diffraction patterns, FT-IR spectra, SEM, TEM, and BET measurements. These $g\text{-C}_3\text{N}_4$ samples were subjected to photocatalytic degradation of dye Rhodamine B (RhB) in aqueous under visible-light irradiation. Under identical conditions, those porous $g\text{-C}_3\text{N}_4$ samples showed significantly improved catalytic performance in comparison with the sample prepared without the introduction of nitric acid. In particular, the best candidate, sample M1:1, showed an apparent reaction rate nearly 6.2 times that of the unmodified counterpart. The enhancement of photocatalytic performance could be attributed to the favorable porous structure with the enlarged specific surface area and the suitable electronic structure as well. In addition, ESR measurements were conducted for the sake of proposing a photocatalytic degradation mechanism.

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1. Introduction

Polymeric $g\text{-C}_3\text{N}_4$ materials, regarded as a family of attractive non-metal semiconductors, possess two-dimensional π -conjugated structures that are composed of numerous tri-s-triazine units [1]. These units mainly consist of sp^2 -hybridized carbon and nitrogen atoms connected by covalence bonds, ensuring unique chemical and thermal stabilities. With favorable structural and electronic properties, $g\text{-C}_3\text{N}_4$ samples are able to catalyze the splitting H_2O to generate gaseous oxygen and hydrogen, and decompose various organic contaminants under visible-light illumination, hereby attracting intensive attention in fields of environmental remediation and energy storage [2–4].

However, the photocatalytic efficiency of $g\text{-C}_3\text{N}_4$ semiconductors is relatively low and still far from the level required for real applications, mainly owing to the small surface area values and high recombination rate of photogenerated electron-hole pairs [5–8]. As a result, many efforts have been devoted to modify synthetic procedures toward $g\text{-C}_3\text{N}_4$ to gain an efficient photocatalytic

system, such as doping with metal oxides or nonmetal elements [9–13], construction of porous or hierarchical nanostructures [14–16], and combining other semiconductors with suitable band structures [17–22]. Among strategies mentioned above, the fabrication of porous $g\text{-C}_3\text{N}_4$ from the precursor of protonated melamine is quite promising and possible to achieve satisfactory catalytic efficiency. Dong demonstrated the porous $g\text{-C}_3\text{N}_4$ produced from HCl-treated melamine possessed the extraordinarily large specific surface area and displayed excellent photocatalytic ability [23]. Yan reported the enhanced photocatalytic performance of porous $g\text{-C}_3\text{N}_4$ prepared by the pyrolysis of protonated melamine by H_2SO_4 solution [24]. Gao found that the nanotubular $g\text{-C}_3\text{N}_4$ by pyrolysis of HNO_3 -treated melamine displayed intense photoluminescence emission and reproducible photoconductivity [25]. Using a similar procedure, Tahir prepared porous $g\text{-C}_3\text{N}_4$ samples with the improved catalytic behavior under visible-light illumination [26]. Therefore, it is realized that the sintering of melamine pretreated in an acidic environment, especially in a nitric acid solution, tends to supply porous $g\text{-C}_3\text{N}_4$ materials with favorable physicochemical properties, thus guaranteeing excellent photocatalytic capability [26–28].

In this investigation, we dispersed the melamine powder in aqueous solution, instead of the generally used solvent ethylene

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glycol that was suspected to be of low toxicity [29]. After treated with nitric acid aqueous solution, the melamine was directly heated to produce porous $g\text{-C}_3\text{N}_4$ samples that were analyzed by various physicochemical techniques. The concentration of nitric acid added exerted an important role on the structure of obtained $g\text{-C}_3\text{N}_4$ samples. In the presence of an appropriate concentration of nitric acid, tube-like porous $g\text{-C}_3\text{N}_4$ samples with enlarged specific surface areas were achieved. These samples were then subjected to photocatalytic evaluation toward decomposition of RhB under visible light irradiation. As expected, modified samples showed the enhanced photocatalytic capabilities. In particular, the best candidate, sample M1:1, could show the apparent reaction rate nearly 6.2 times that of unmodified $g\text{-C}_3\text{N}_4$. The enhancement of photocatalytic efficiency could be ascribed to a synergistic effect of the porous microstructures with enlarged specific surface areas and suitable band gap energies. In addition, a possible mechanism was finally proposed basing upon ESR measurements.

2. Materials and methods

2.1. Reagents

Melamine ($\text{C}_3\text{H}_6\text{N}_3$, CP), isopropanol (IPA, AR), disodium ethylenediaminetetraacetate dehydrate (EDTA-2Na, AR), terephthalic acid (TA, AR), 1,4-benzoquinone (BQ, AR), Rhodamine B (RhB, AR), and other chemicals involved were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used directly for experimental without further purifications. All aqueous solutions throughout were prepared with the deionized water.

2.2. Preparation of porous $g\text{-C}_3\text{N}_4$ samples

In a typical procedure, a fixed amount of melamine was dispersed into deionized water (50 mL) and stirred for 1 h. A desired amount of concentrated nitric acid was dissolved into deionized water (30 mL) to make an aqueous solution that was then dropped slowly into the above the melamine aqueous suspension. The powder obtained by the filtration, rinse with water and absolute ethanol, and dryness at 60°C was transferred into a covered crucible and stood at 500°C for 4 h, with a heating rate of $10^\circ\text{C}/\text{min}$. After cooling down, these samples were collected and nominated as M6:1, M3:1, and M1:1, accordingly to molar ratios of melamine/ HNO_3 . $g\text{-C}_3\text{N}_4$ was prepared using a same procedure without addition of HNO_3 . Another sample was also synthesized. When the nitric acid solution was dropped into the melamine aqueous solution, a white precipitate was generated in a quite quick manner, resulting into a shaking white block in which the magnetic was covered. The white block was underwent a same procedure described above to supply a sample, named M1:3.

2.3. Characterization

X-ray diffraction patterns (XRD) were recorded on a Bruker D8 Advance X-ray diffractometer using a $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$). The general morphology of samples was measured on a scanning electron microscopy (SEM, XL-30, Philips) and transmission electron microscopy (TEM, JEOL JEM-2010, Japan) operated at 200 kV. The FT-IR spectra were conducted on a Bruker V-70 Fourier transformed infrared spectrophotometer using a KBr pellet as the reference. X-ray photoelectron spectroscopy (XPS) and the valence-band X-ray photoelectron spectroscopy (VB XPS) measurements were performed by using a Thermo ESCALAB 250Xi System. Binding energies were calibrated by using the containment carbon ($\text{C1s} = 284.8 \text{ eV}$). The specific surface areas were measured using the BET method by nitrogen adsorption–desorption isotherms at 77 K using an automatic surface area and size analyzer (3H-2000PS2). All

samples were degassed at 473 K for 2 h prior to analysis. Elemental analysis (EA) was carried out on an Elemental Vario III elemental analyzer. UV–vis diffuse reflectance spectra (UV–vis DRS) were obtained on a Hitachi U-4100 spectrophotometer using BaSO_4 as a reference.

2.4. Photocatalytic measurements

Photocatalytic capabilities of obtained samples were evaluated toward degradation of dye RhB under irradiation from a 300 W Xe lamp (CEL-HXF300, AuLight, Beijing) equipping with a 420 nm–780 nm cut-off filter at the light source. Typically, the photocatalyst (40 mg) was dispersed in an aqueous solution of RhB (8 mg L^{-1} , 80 mL) with a magnetic stirrer and the distance between the light source and the surface of reaction suspension was fixed at 20 cm. The suspension was magnetically stirred for 0.5 h in dark to ensure an adsorption–desorption equilibrium before exposing to the visible-light irradiation. At every 20 min intervals, 5 mL aliquot was sampled and centrifuged to remove suspended catalyst particles. The concentration of RhB was analyzed by a UV–vis spectrophotometer (Purkinje General T6) at 554 nm.

ESR signals of active radicals spin-trapped by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were examined with a JES-FA200 spectrometer. The settings for the spectrometer were: center field, 323.357 mT; microwave frequency, 9055.619 MHz; power, 0.998 mW.

3. Results and discussion

The crystallographic phase and compositions of as-synthesized $g\text{-C}_3\text{N}_4$ samples were analyzed by XRD, as depicted in Fig. 1a. It is obvious that melamine could be converted to $g\text{-C}_3\text{N}_4$ phase by means of pyrolysis whether the nitric acid was involved or not, which is proven by the presence of both characteristic diffraction peaks of pure $g\text{-C}_3\text{N}_4$. The intense peak centered at 27.7° is assigned to the crystallographic plane (002), an interlayer stacking of the conjugated aromatic segments. The calculated interlayer distance of aromatic units (0.322 nm) is relatively smaller than those of crystalline $g\text{-C}_3\text{N}_4$ reported [3]. A weak peak appears at around 13.2° and is attributed to the plane (100), relating to the in-plane structural repeating motif. Further observation of Fig. 1a indicates that the intensity of this reflection peak becomes gradually reduced as the concentration of HNO_3 solution increases, possibly owing to the reduced planar size of layers induced by the calcination process when HNO_3 molecules was present [8]. Gao reported that a white precipitate was formed as soon as the HNO_3 aqueous was charged into the ethylene glycol solution containing melamine. Components in the precipitate were determined as protonated melamine and NO_3^- species by means of elemental analyses [25]. In our case, we attempted a similar synthetic procedure except that the solvent ethylene glycol was replaced by deionized water, in the interest of avoiding the usage of low-toxic solvent. During reaction, a white precipitate was formed and increased with the increase of the nitric acid concentration. It is reasonable to deduce that the components in the white precipitate are the same as those in Gao's report. During sintering, the HNO_3 contained in precipitate activated the melamine to convert to $g\text{-C}_3\text{N}_4$ phase via releasing massive gaseous NH_3 and CO_2 . In addition, we speculate the HNO_3 molecules were unstable at high temperature and readily decomposed to various gases, like molecular oxygen and nitrogen oxides. These gases together with NH_3 and CO_2 could create an oxidative environment and partially destroy the microstructure of $g\text{-C}_3\text{N}_4$ to generate some randomly aggregated fragments or nanosheets, resulting into the destruction of in-plane structural repeating motif

Fig. 1. XRD patterns (a) and FT-IR spectra (b) of as-synthesized $g-C_3N_4$ samples.

and thus the low intensity of diffraction peak at 13.2° in XRD patterns, similar to the phenomenon in our previous work when the mixture of $NaNO_3$ and melamine was annealed [30]. The exact role of HNO_3 in the calcination process is not clear and need for further study.

FT-IR spectra of obtained $g-C_3N_4$ samples are shown in Fig. 1b. The intense adsorption band ranging from 1200 cm^{-1} to 1640 cm^{-1} is relevant to the typical skeletal stretching vibration of CN heterocycles. The sharp peak at 805 cm^{-1} is linked to the characteristic breathing mode of triazine units [31]. The wide adsorption band between 3000 cm^{-1} and 3500 cm^{-1} is indexed to the stretching vibration of residual N–H or the O–H bonds, originating from uncondensed amino groups or adsorbed water on surface [32]. The

presence of above characteristic peaks verifies the formation of $g-C_3N_4$ phase even the precursor melamine was treated with HNO_3 aqueous solution [33].

The surface chemical composition and valence band states of sample M1:1 were analyzed by XPS spectra, as shown in Fig. 2. The C 1s signal was calibrated at 284.8 eV. The survey spectrum reveals the existence of elements C, N, and O. The C 1s peaks can be fitted with three peaks at binding energies of 284.8, 286.2, and 288.2 eV, indicative of three different chemical environments of carbon. The two major peaks at binding energies of 284.8 and 288.2 eV correspond to the surface adventitious carbon and sp^2 -bonded carbon in N–C=N coordination [34]. Another weak peak at 286.2 eV is identified as sp^3 -coordinated carbon bonds from defects on $g-C_3N_4$

Fig. 2. XPS spectra of sample M1:1: (A) survey spectrum, high-resolution XPS spectrum of C1s, N1s, and O1s.

Fig. 3. SEM images of sample $g\text{-C}_3\text{N}_4$ and M1:1; enlarged SEM images of sample $g\text{-C}_3\text{N}_4$, M6:1, M3:1, and M1:1; TEM images of sample $g\text{-C}_3\text{N}_4$ and M1:1.

surface [35]. The N 1s spectrum shows three deconvoluted peaks at binding energies of 398.8, 400.6, and 404.4 eV. The first two signals are assigned to the nitrogen atoms in $\text{N}=\text{C}=\text{N}$ and $\text{N}(\text{C})_3$ moieties [24,35], and the last weak peak is attributed to charging effects [34,36]. The O 1s peak at 532.1 is relevant to the adsorbed H_2O on surface [6].

The morphology and microstructure of obtained products by SEM and TEM images are shown in Fig. 3. As can be seen, the sample $g\text{-C}_3\text{N}_4$ prepared without the addition of HNO_3 displays disorderly stacked large and irregular clusters formed as the result of the arbitrary aggregation of small particles. The enlarged SEM image of sample $g\text{-C}_3\text{N}_4$ shows that these large clusters have smooth surface without pores. The micropores and mesopores between nanosheets in sample $g\text{-C}_3\text{N}_4$ (as shown in Fig. 4) are possibly created by the evolution of massive gases and splitting of the large layers during calcinations. The micropores were constructed by

the aggregation of large clusters [33]. With the increase of HNO_3 addition, more oxidative gases generated to oxidatively destruct bulk clusters into small particles and further into segments and nanosheets, thus improving the porosity of samples. Therefore, the size of particles was gradually reduced and the surface became coarse, depicted in the enlarged SEM images from $g\text{-C}_3\text{N}_4$ to M1:1. In addition, some small particles in sample M1:1 are regularly aggregated to produce tube-like units that are further assembled into large clusters along the direction perpendicular to the axis, as seen in SEM image of M1:1. It is significant that sample M1:1 is full of numerous mesopores from the channels of tube-like units on surface, revealing the possible enlarged specific surface area. It was reported that the white precipitate, the protonated melamine, showed tubular structures in ethylene glycol, owing to the electrostatic attraction, π - π stacking interactions, and hydrogen bonding [25]. Upon pyrolysis, the tubular protonated melamine easily

Fig. 4. Nitrogen adsorption-desorption isotherms of as-prepared $g\text{-C}_3\text{N}_4$ samples.

converted to tubular $g\text{-C}_3\text{N}_4$. During preparation, tubular geometry of protonated melamine could be stabilized and maintained in ethylene glycol, and partially destroyed in water [25]. As a result, partially destroyed tubular protonated melamine was further oxidized and gradually destructed to generate π -conjugated matrix $g\text{-C}_3\text{N}_4$ with numerous pores on surface. Moreover, a lot of small pores generated in sample M6:1, M3:1, M1:1, and M1:3 (Fig. S1), instead of $g\text{-C}_3\text{N}_4$, might be from the evolution of molecular oxygen and nitrogen oxides in the presence of sufficient amount of HNO_3 at high temperature, since these gases likely oxidized and destroyed the microstructure surrounded. Besides, some arbitrary aggregated fragments were also identified by the quite transparent feature of the nanostructures in TEM image of sample M1:1.

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The elemental analysis data and specific surface areas of sample $g\text{-C}_3\text{N}_4$, M6:1, M3:1, M1:1, and M1:3 are listed in Table 1. The atomic ratio of C/N in sample $g\text{-C}_3\text{N}_4$ is 0.552 and much lower than the theoretical value 0.75, attributing to the incomplete condensation of amine groups and the presence of structural defects [24]. With the increase of HNO_3 addition, the atomic ratio of C/N in samples is slightly improved and then reaches to a maximum 0.562 when the molar ratio of melamine/ HNO_3 is set as 1. This result can be mainly relevant to the large N loss as the result of the generation of large amount of oxidative gases as soon as the HNO_3 addition is enhanced. However, when the molar ratio of melamine/ HNO_3 is beyond 1:1, the atomic ratio C/N is slight reduced and close to that of $g\text{-C}_3\text{N}_4$. A similar trend is also found in the variation of specific surface areas as below. As described in synthetic section, a white block was quickly formed. It is reasonable to speculate that some unreacted melamine were coprecipitated and might be enclosed by protonated melamine. Thereby, the produced sample M1:3 was $g\text{-C}_3\text{N}_4$ with a layer of modified $g\text{-C}_3\text{N}_4$, leading to a similar atomic ratio C/N and specific surface area to those of $g\text{-C}_3\text{N}_4$. The nitrogen adsorption-desorption isotherms of as-prepared $g\text{-C}_3\text{N}_4$ samples are displayed in Fig. 4 and can be classified as type

Table 1
Elemental analyses and specific surface areas of as-obtained samples.

Samples	C (at%)	N (at%)	C/N	S_{BET} (m^2/g)
$g\text{-C}_3\text{N}_4$	33.274	60.234	0.552	5.3
M6:1	32.198	58.830	0.547	4.1
M3:1	33.119	59.479	0.557	6.4
M1:1	32.187	57.283	0.562	11.8
M1:3	33.051	59.658	0.554	4.7

IV at the P/P_0 range of 0.4–1 with hysteresis loops of type H3 [37], revealing the presence of mesopores and slit-like pores with diameters about 2–50 nm and over 50 nm, respectively. These slit-like pores are associated to the aggregates of primary particles, which is accordance with SEM images. In addition, the adsorption ability of sample M1:1 is the strongest among those of all samples under identical conditions. Correspondingly, the specific surface area of sample M1:1 $11.8 \text{ m}^2/\text{g}$ is the largest one that is nearly twice as much as that of sample $g\text{-C}_3\text{N}_4$, possibly due to the greatly improved porosity of sample M1:1.

The optical property of obtained samples was measured by UV-vis DRS analyses, as shown in Fig. 5. It is clear that $g\text{-C}_3\text{N}_4$ samples are photoresponsive in both UV and visible light regions, with adsorption edges at about 450 nm–465 nm. The band gap energy (E_g) of these samples could be calculated by an empirical equation $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where α , $h\nu$, and A are absorption coefficient, photon energy, and a constant, respectively [38]. n was adopted as 4 because of the direct transition of $g\text{-C}_3\text{N}_4$ samples [14,39], by which E_g values were estimated ranging from 2.60 to 2.76 eV. Adsorption edge of sample M1:1 is slightly blue shifted in comparison with that of sample $g\text{-C}_3\text{N}_4$, corresponding to the slight expansion of band gap from $g\text{-C}_3\text{N}_4$ 2.64 to M1:1 2.67 eV, which is possibly attributed to the quantum size effect from the fragments generated in the oxidative environment [8] and some other effects, such as variable morphology, crystal size, and specific structure.

Photocatalytic evaluation of as-prepared $g\text{-C}_3\text{N}_4$ samples was conducted by means of dye RhB degradation under visible-light irradiation ($\lambda > 420 \text{ nm}$). As shown in Fig. 6a, the decrease of initial concentration of RhB by direct photolysis is negligible, indicating the sufficient stability of RhB at tested conditions. The sample $g\text{-C}_3\text{N}_4$ formed without HNO_3 during synthesis shows an unsatisfactory removal efficiency of 40% that is similar to that of M1:3 and far lower than those of samples M1:1 and M3:1. It is obvious that the introduction of HNO_3 in synthetic procedure is beneficial to construct samples with significantly improved photocatalytic capabilities. Especially, the addition amount of HNO_3 is increased and catalytic ability of samples is accordingly enhanced. The best candidate, sample M1:1, could completely remove RhB in aqueous solution after 100 min under visible light irradiation and correspondingly, the solution was decolorized. The experimental data were subsequently fitted by a pseudo-first-order model to study reaction kinetics of the RhB degradation and the corresponding apparent reaction constants (k) are shown in Fig. 6b. It is obvious that sample M1:1 owns the best catalytic degradation ability, with a k value 6.2 times that of unmodified $g\text{-C}_3\text{N}_4$ sample. However, the introduction of excess amount of HNO_3 would induce to generate samples, like M1:3, with relatively low catalytic capability. It is general that photocatalytic capability of materials is closely relevant to microstructures and band gap energies [40,41]. As discussed above, porous $g\text{-C}_3\text{N}_4$ samples with enlarged specific surface areas could be fabricated in presence of a proper concentration of HNO_3 solution. Below and over that concentration, the porosity and specific surface area of samples shrank. An enlarged specific surface area is able to increase the interfacial surface between catalysts and pollutant molecules and provide abundant active sites to contact with reactant molecules and hereby enhanced the visible-light harvesting [21]. In addition, the sufficient porosity of samples facilitates both the immigration of reactants and export of degraded products, and multiple scattering of visible light. The variation of band gaps of samples after pretreatment of HNO_3 solution is slight, ensuring those samples with appropriate electronic structures. With the improved porosity, the largest specific surface area, and the suitable band gap, the sample M1:1 exhibits the best photocatalytic behavior among all tested samples.

From the VB XPS analysis in Fig. 7a, the valence band maximum (E_{VB}) of sample M1:1 is estimated at 1.87 eV and correspondingly,

Fig. 5. UV-vis DRS spectra of g-C₃N₄ samples (a) and $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots of sample g-C₃N₄ and M1:1.

Fig. 6. Photocatalytic degradation of RhB by various g-C₃N₄ samples under visible light (a) and corresponding apparent reaction rates (b).

the conduction band minimum (E_{CB}) is calculated as -0.8 eV. A plausible photocatalytic degradation mechanism was proposed and displayed in Fig. 7b. Upon visible light irradiation ($420 \text{ nm} < \lambda < 780 \text{ nm}$), sample M1:1 is able to be excited to generate electrons and holes that stay at the bottom of conduction band and top of valence band, respectively. Since the E_{CB} (-0.8 eV) of sample M1:1 is more negative than $E(\text{O}_2/\text{O}_2^-)$ (-0.33 eV) [42], the electrons tend to react with adsorbed oxygen to produce O_2^- radicals through a one-electron reaction. However, the E_{VB} ($+1.87$ eV) is less positive than $E(\text{OH}/\text{OH}^-)$ ($+1.99$ eV) and $E(\text{OH}/\text{H}_2\text{O})$ ($+2.37$ eV) [33,43] and holes are insufficient to directly

oxidize surface water to form $\text{OH}^\bullet$ radicals. $\text{OH}^\bullet$ radicals can be formed through a two-electron oxygen reduction route instead [44]. The possibility of generating O_2^- and $\text{OH}^\bullet$ radicals were also measured by ESR with DMPO spin-trap analysis in Fig. 8. Signals of DMPO- $\text{OH}^\bullet$ adduct can be weakly detectable, and six characteristic peaks of DMPO- O_2^- adduct are easy to be observed, indicative of the formation of both O_2^- and $\text{OH}^\bullet$ radicals during catalytic reactions [45]. As a result, the formed O_2^- radicals together with photogenerated holes are deemed as dominant active radicals and $\text{OH}^\bullet$ radicals play minor roles for the degradation of RhB molecules.

Fig. 7. VB XPS analysis of sample M1:1 (a) and proposed mechanism upon visible-light irradiation (b).

Fig. 8. DMPO spin-trapping ESR spectra of sample M1:1 for DMPO-•OH (a) and DMPO-•O₂⁻ (b).

4. Conclusion

In this study, a series of porous g-C₃N₄ samples were constructed via a facile direct pyrolysis of HNO₃-treated melamine and subsequently characterized by various analytical techniques. Obviously, an appropriate amount of nitric acid involved facilitated to generate samples with the improved porosity and enlarged specific surface areas. These modified porous samples displayed quite higher catalytic removal efficiency than unmodified g-C₃N₄ under visible light irradiation. In particular, the best candidate M1:1 could completely decompose RhB after 100 min, with an apparent reaction rate approximately 6.2 times that of g-C₃N₄. The enhancement of photocatalytic performance mainly attributed to the porous structure with the enlarged specific surface area and the suitable band gap energy. Finally, a possible photocatalytic mechanism was proposed basing upon ESR measurements.

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