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Article

Effect of high-voltage discharge non-thermal plasma on g-C₃N₄ in a plasma-photocatalyst system

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ABSTRACT

The synergistic effect of high voltage discharge non-thermal plasma (NTP) and photocatalysts on contaminant removal has repeatedly confirmed by plenty of researches. Most previous plasma-photocatalyst synergistic systems focused on the utilization of the ultraviolet light but ignored the visible light generated by high voltage discharge. Graphitic carbon nitride (g-C₃N₄), a metal-free semiconductor that exhibits high chemical stability, can utilize both the ultraviolet and visible light from high voltage discharge. However, the synergistic system of NTP and g-C₃N₄ has been researched little. In this paper, the effect of NTP generated by dielectric barrier discharge (DBD) on g-C₃N₄ is studied by comparing the photocatalytic activities, the surface physical structure and the surface chemical characteristics of pristine and plasma treated g-C₃N₄. Experimental results indicate that the DBD plasma can change the physical structure and the chemical characteristics and to further affect the photocatalytic activity of g-C₃N₄. The effect of NTP on g-C₃N₄ is associated with the discharge intensity and the discharge time. For a long time scale, the effect of NTP on g-C₃N₄ photocatalysts presents a periodic change trend.

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1. Introduction

Non-thermal plasma (NTP) produced by high-voltage electrical discharge is an alternative approach to environment pollution control. NTP can be obtained by electrohydraulic discharge, gas discharge, and hybrid gas-liquid discharge with various discharge reactors and electrode configurations [1]. Based on different discharge reactors and power supplies, different discharge types such as corona discharge, streamer discharge, glow discharge, spark/arc discharge, and dielectric barrier discharge (DBD) can be yielded [1,2]. The electrical discharge can generate various physical and chemical effects

such as high-energy electron (e^{*}), electric field, UV radiation, visible light, and active species (like •OH, H•, O•, •O₂⁻, O₃, N•, etc.) [3]. Almost all of these discharge effects are directly or indirectly responsible for the surface treatment of materials and the degradation of pollutants in wastewater and exhaust gas. However, most of the applications of NTP in pollution control were concentrated on the generation and utilization of active species [4–6]. The physical effects were not much concerned because of their small direct contribution on pollutant removal.

To improve the efficiency of pollutant removal by NTP, the combination of NTP with other technologies were conducted

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by researchers. Plasma-photocatalyst technology was one of the most successful applications. Wang et al. [7] used TiO_2 to enhance the plasma degradation of phenol in wastewater. The plasma- TiO_2 system consists of a needle-to-plate discharge electrode and TiO_2 -loaded glass beads in the electrode gap. Their experimental results indicated that the plasma- TiO_2 system generated more oxidative species and enhanced the phenol decomposition. However, they did not clearly explain the influence of discharge on the photocatalyst. Zhang et al. [8] also employed a plasma- TiO_2 system to treat phenol containing water. Their experimental results verified the synergistic effect of plasma and TiO_2 photocatalyst. In addition, the effects of electrical discharge on the behavior of TiO_2 were studied preliminarily. The results showed that the generation of the rutile phase decreased the photocatalytic activity if the TiO_2 film was coated on the surface of the electrodes. However, no obvious change was observed on the TiO_2 film when the TiO_2 film was set away from the discharge electrodes. Mizuno et al. [9] also synergized pulsed streamer corona discharge and TiO_2 to remove acetaldehyde in indoor air, and yielded an improved energy efficiency. Chen et al. [10] designed a coaxial DBD reactor with nano- TiO_2 coated on the high-voltage electrode to purify toluene containing waste gas. A 24.7% improvement in toluene conversion was yielded in comparison with the untreated electrode. These studies illustrated that plasma and photocatalysts have synergistic effects during the pollutant degradation progress, and the high-voltage discharge has certain impacts on the photocatalysts. However, the details about the impact of high-voltage discharge on the photocatalysts remain obscure.

For a plasma-photocatalyst system, DBD might be more suitable than other discharge types. DBD with dielectrics covered on the electrodes or suspended between the electrodes can discharge at atmospheric pressure, and can lead to a uniform discharge and a high electron density [3,11]. Benefitting from the protective effect of dielectrics, the destruction of the electrodes can be greatly relieved and the adverse effects between the direct contact electrodes and catalysts can be weakened. In addition, the dielectrics can limit the charge transmission and the energy dispersion, which can improve the energy efficiency of discharge. Therefore, DBD has been widely applied to material modification and pollution control. Many researchers have used DBD plasma to modify solid materials such as polymers [12], carbon nanotubes [13,14], and graphite [15].

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) photocatalysts have been studied for environmental and energetic applications. This metal-free semiconductor exhibits high stability even in strong acids (HCl , $\text{pH}=0$) or in alkalis (NaOH , $\text{pH}=14$), a high bearing temperature (up to 600°C), and non-toxicity. $\text{g-C}_3\text{N}_4$ can utilize the visible and UV radiations generated during the discharge process [16–18]. Thus, $\text{g-C}_3\text{N}_4$ is conducive to the application of the plasma-photocatalyst system in water or air. Nonetheless, currently, the related studies about the plasma- $\text{g-C}_3\text{N}_4$ system for contaminants removal are few but plasma modification on $\text{g-C}_3\text{N}_4$ has emerged. For example, Hu et al. [19] used a coaxial DBD reactor to synthesize $\text{Mn}_3\text{O}_4/\text{g-C}_3\text{N}_4$ composite under a 10-min plasma treatment. Their results demonstrated that plasma had enlarged the surface area and the pore volume of

the composite. Mao et al. [20] reported that the modified $\text{g-C}_3\text{N}_4$ by the DBD system within a 5-min treatment had a higher photocatalytic performance than the pristine sample. However, the enhancement in the photocatalytic performance decreased when the treatment time exceeded 5 min. The improved photocatalytic performance was attributed to the generation of $-\text{OH}$ and $-\text{COOH}$ groups on the surface of $\text{g-C}_3\text{N}_4$. However, they did not demonstrate the influence of the treatment time and the discharge intensity on $\text{g-C}_3\text{N}_4$.

For a plasma- $\text{g-C}_3\text{N}_4$ system, the discharge effects including active species, energized electron, localized high temperature, and pressure and electric field may influence the morphology, photocatalytic structure, and chemical property of $\text{g-C}_3\text{N}_4$. To our knowledge, few have investigated about the detailed influence of discharge on $\text{g-C}_3\text{N}_4$, especially for a long-time-operating plasma- $\text{g-C}_3\text{N}_4$ system. Therefore, it is necessary to study and understand how the discharge affects $\text{g-C}_3\text{N}_4$ during a long-time discharge, to avoid some negative factors and optimize the plasma- $\text{g-C}_3\text{N}_4$ system. Thus, in this work, the research on the influence of DBD on $\text{g-C}_3\text{N}_4$ at different treatment time and applied voltage was conducted. The results may be favorable for the future applications of the plasma- $\text{g-C}_3\text{N}_4$ system on pollution control and material modification.

2. Experimental

2.1. Experimental apparatus and setup details

The DBD plasma reactor consisted of a power supply with an output of 0–2000 W (CTP-2000, Nanjing Suman Electronics Co., Ltd, Nanjing, China) and a plasma reactor composed of two parallel circular stainless steel plane electrodes and a quartz sample container between the electrodes (Fig. 1). The quartz sample container consisted of a concave quartz plate (external diameter of 145 mm, internal diameter 60 mm, external depth of 10 mm, internal depth of 8 mm) and an upper quartz cover (diameter of 150 mm, thickness of 2 mm). The discharge plasma was initiated at room temperature and atmospheric pressure without air flow. The $\text{g-C}_3\text{N}_4$ samples placed in the quartz reactor were treated under different treating time and discharge voltages. The voltage and current supplied to the dis-

Fig. 1. Schematic diagram of plasma- $\text{g-C}_3\text{N}_4$ reaction system.

charge reactor at a frequency of 10.37 kHz were monitored by a digital oscilloscope (Tektronix TDS 2014C, USA) with a 1:1000 high voltage probe (Tektronix P6015A, USA) and a current probe (Tektronix A622, USA).

2.2. Sample preparation

The g-C₃N₄ photocatalysts were prepared by directly heating melamine in a muffle furnace for 6 h. The melamine placed in alumina crucibles was heated at 520 °C. The resultant yellow powder (g-C₃N₄) was collected for subsequent use.

2.3. Discharge treatment

The prepared g-C₃N₄ photocatalysts were treated by DBD at different discharge peak voltage and treatment time duration. The peak voltages supplied to the reactor were 18.4, 19.2, 20.0, 20.8, and 21.6 kV respectively. The treatment time duration was change from 3 to 90 min. The signs of these samples were denoted as x kV-y min (x, y represents the peak voltage and the discharge treatment time duration respectively).

2.4. Sample activity determination

The photocatalytic activity of the treated g-C₃N₄ photocatalysts were tested by the photocatalytic degradation of methylene blue (MB) in water with 1 h of visible light irradiation. Before exposure to light, the mixed solution was stirred for 30 min in darkness. In each experiment, 50 mg of treated g-C₃N₄ was dispersed into 50 mL of MB solution with a concentration of 10 mg/L. Further, the MB solution on the magnetic stirrer was top-irradiated by a 120-W LED above the water surface. The temperature was maintained at the room temperature (26 °C) and the solution pH was maintained at the initial state of the MB solution. Subsequently, the solution was centrifuged to remove g-C₃N₄ and to obtain the supernatant. The residual concentration of MB was measured using a UV-1102 spectrophotometer (Shimadzu Inc., Japan) at 662-nm

wavelength. Parallel experiments were simultaneously operated to ensure the rigorism, and the data reported were obtained from more than two independent parallel experiments.

2.5. Sample characterization

The surface morphologies and the chemical properties of g-C₃N₄ before and after DBD treatment were compared by sample characterization. The crystal phases of the samples were analyzed by an X-ray diffraction using Cu K_α radiation (XRD, D8 Advance, Bruker Co., Germany). The Brunauer-Emmett-Teller (BET) specific surface area was determined using a nitrogen adsorption apparatus (ASAP 2020, Micromeritics). Before measuring the BET specific surface area, all samples were degassed at 120 °C for 4 h. The surface chemical function groups and the chemical bonding substance were measured using a Fourier transform infrared spectroscope (FT-IR, IRPrestige-21, Shimadzu Inc., Japan) and an X-ray photoelectron spectroscopy (XPS, Thermal Fisher Scientific ESCALAB 250Xi, America), respectively. The UV-Vis diffuse-reflectance spectrometry (UV-Vis DRS) of dry-pressed disk samples was performed using a scanning UV-Vis spectrophotometer (TU-1901, China). The charge transfer properties were investigated using a photoluminescence spectrophotometer (PL: F-7000, HITACHI, Japan).

3. Results and discussion

3.1. Influence of g-C₃N₄ on discharge

The influence of g-C₃N₄ on the discharge characteristics is shown in Fig. 2. In general, the discharge characteristic is consistent with the typical atmospheric gas-phase DBD, as shown in Fig. 2(a). The filaments on the current waveform indicate the ignition of the streamer or the corona discharge in every half-cycle of the sine voltage [21].

As shown in Fig. 2(b), the discharge characteristics with and without g-C₃N₄ in the DBD system are different. For example, in

Fig. 2. Discharge voltage and current waveforms. (a) Typical discharge waveforms of the DBD reactor; (b) Influence of g-C₃N₄ on the discharge.

the 10-min discharge, the addition of g-C₃N₄ in the DBD system enhances the discharge intensity (both the voltage and current increase in Fig. 2(b)). This enhancement may be ascribed to the high adsorption of g-C₃N₄ on the space charges that can reduce the density of free charges in the discharge gap. The reduced free charge density leads to a higher resistance and discharge voltage in comparison with no g-C₃N₄ in the DBD reactor. However, when the applied voltage goes to the reversed half-cycle, the direction of the applied electric field is the same as that of the absorbed charges. Consequently, the discharge current increases accordingly.

In addition, it is also indicated in Fig. 2(b) that the discharge intensity increases when prolonging the discharge time. This can be ascribed to the enhancement in the hydrophilicity of g-C₃N₄ (the details will be described in the following content), which improves the absorption of space charges and water. Consequently, the discharge density increases with the discharge time. Moreover, the absorbed water on the surface of g-C₃N₄ can be decomposed to •OH, •H or acts as a reactant under a high-voltage discharge [22].

3.2. Influence of DBD on the photocatalytic activity of g-C₃N₄

As shown in Fig. 3, the photocatalytic activity of the DBD-treated g-C₃N₄ is influenced by the discharge voltage and treatment time. In general, with the two parameters increasing, the photocatalytic activity is first enhanced at a short-time discharge (MB removal up to 52.5%). Subsequently, the photocatalytic activity is weakened (MB removal down to 20.11%), such as the process of 20.8 kV. The variation trend agrees with the previous experimental result from other researchers [20]. However, the photocatalytic activity is recovered partly when further prolonging the treatment time. Subsequently, the photocatalytic activity changes oscillatorily with the treatment time.

We found that the photocatalytic activity also changes oscillatorily with the voltage. At low discharge voltages such as 18.4

kV, the influence of discharge on the photocatalytic activity is not obvious because the weak discharge cannot change the surface properties. However, when increasing the discharge voltage, the influence of DBD treatment on the photocatalytic activity becomes apparent. At higher discharge voltages, the transformation of the increasing and decreasing processes of the photocatalytic activity becomes frequent. Moreover, the DBD treatment time required to create an obvious change in the photocatalytic activity is shortened when increasing the discharge voltage.

The high voltage discharge can induce complex chemical and physical effects. All the chemical and physical effects may influence the surface properties of g-C₃N₄. Therefore, the reasons why the discharge voltage and treatment time influence the photocatalytic activity of g-C₃N₄ must be analyzed with the surface characterization.

3.3. Physical characteristics of g-C₃N₄

The crystal structures of the as-treated g-C₃N₄ are elucidated in Fig. 4(a). The two characteristic diffraction peaks at 13.0° (100) and 27.51° (002) of pure g-C₃N₄ represent the in-plane structural repeating tri-s-triazine ring structure and the inter-layer reflection of conjugated aromatic rings, respectively [23]. The similar XRD patterns of all samples in Fig. 4(a) show that the electrical discharge does not disrupt the crystal structure of g-C₃N₄. Consistent with Table 1, the two slightly shifted-to-the right peaks from 0 min to 20 min denote the decrease in the planar size of the layers and the long-range order structure, respectively [23,24]. Therefore, the plasma process could shorten the gallery distance and change the degree of condensation of g-C₃N₄ similar to a thermal treatment [25]. The lowest crystallinity and the weak (100) diffraction peak of the 21.6 kV, 20-min sample demonstrates that it possesses more defects and that the intralayer structure is destroyed [26]. Further, the returned crystallinity and (100) diffraction peak of a longer-time discharge shows that the defects are purified. As

Fig. 3. Photocatalytic activity of DBD-treated g-C₃N₄. The degradation rate after (a) 30-min photocatalytic reaction and (b) 60-min photocatalytic reaction.

Fig. 4. Physical changes of treated g-C₃N₄ samples. (a) XRD pattern, (b) N₂ absorption-desorption isotherms; (c) Pore-size distribution curves.

Table 1

Interlayer distance, SSA, pore volume, peak pore diameter, MB removal ratio of all the as-treated g-C₃N₄ samples.

Sample	Inter-layer distance (nm)	SSA (m ² /g)	Pore volume (cm ³ /g)	Peak pore diameter (nm)	MB removal ratio (%)
0kV-0min	0.3242	7.82	0.057	27.78	41.00
21.6kV-10min	0.3233	11.02	0.068	24.13	26.19
20.8kV-20min	0.3228	10.37	0.064	24.87	20.11
21.6kV-20min	0.3233	8.39	0.069	34.05	32.01
21.6kV-60min	0.3241	9.25	0.074	32.28	49.25
21.6kV-90min	0.3231	11.17	0.066	24.16	40.39

shown, the single layer on the surface of bulk g-C₃N₄ may be undulated but could be planarized by further discharge treatments [27]. However, compared to a strong oxidizing solution, the DBD is sufficiently mild that it cannot significantly destroy the structure of bulk g-C₃N₄ [26–29]. Consequently, the periodic process may contribute to the layer-by-layer destruction of g-C₃N₄ and lead to the generation of smaller particles or nanosheets by the NTP.

The texture properties of samples accessed by nitrogen absorption-desorption isotherms and the Barrett-Joyner-Halenda (BJH) pore-size distribution curves are displayed in Fig. 4(b), (c) and Table 1. According to the IUPAC classification, all isotherms belong to type IV that is caused by the weak adsorption-desorption interaction [30]. Further, the type H3 hysteresis loops at high P/P_0 is typically related to the capillary condensation in mesopores and reflects the formation of slit-shaped pores from aggregates of plate-like particles [18,31]. DBD treatments can cause the disintegration of large particles and slightly enhance the surface specific area (SSA) of g-C₃N₄ under a 10-min treatment [19]. However, the SSA also changes periodically when prolonging the discharge time. Consistent with the XRD result, the undulated and planarized structure may cause the change of SSA in cycles (Table 1).

The pristine g-C₃N₄ prepared from melamine has a smaller SSA (7.82 m²/g) than from other precursors (like e.g., urea, dicyandiamide, thiourea) because of its higher crystallinity and thicker layered agglomerated sheets of g-C₃N₄ [28–33]. Therefore, the DBD air plasma is insignificant in the changes of SSA and volume of g-C₃N₄, as reported previously [19]. The periodic exfoliation process is reflected not only in XRD but also in the pore-size distribution curves, SSA, and pore volume. However, the 21.6 kV/10 min and 20.8 kV/20 min with high SSA and more defects have low photocatalytic performances. This may

contribute to the nonselectively physical effect by the NTP, unlike the selective destruction of strong oxidizing solvents [34]. Furthermore, DBD plasma oxidation could be dominated by physical attacks [35], and may produce some negative chemical components on the surface of g-C₃N₄.

3.4. Chemical functional groups and chemical bonding species of treated g-C₃N₄

NTP technology can produce various active species such as e⁺, •OH, H•, O•, •O₂⁻, O₃, N•, NO_x. Further, bulk g-C₃N₄ with regularly spaced triangular holes is a piezoelectric material and the discharge voltage may enhance the generation of reactive oxygen species [36,37]. These species may react with the defects. To determine the chemical changes on the as-treated g-C₃N₄, the chemical compositions and bonding characteristics of the photocatalysts are detected using FT-IR and XPS respectively, as is shown in Fig. 5.

The FT-IR spectra (Fig. 5(a)) show that all the g-C₃N₄ samples exhibit broad peaks assigned to the –NH groups (uncondensation) between 2900 and 3400 cm⁻¹, –OH group between 3400 and 3700 cm⁻¹ [19,25], characteristic stretching modes of CN heterocycles containing connected units C–(N)₃ (1321 cm⁻¹) and C–NH–C (1244 cm⁻¹) of aromatic rings, heptazine-derived repeating units from 1200 to 1650 cm⁻¹ [38], and the typical breathing mode of the tri-s-triazine ring system at 810 cm⁻¹. These indicate their similar chemical structures. The C–C, C–O, and C–N bonds own similar force constants; however, Liao et al. [39] reported that weak peaks at 1060 cm⁻¹ and 1410 cm⁻¹ were attributed to the C–O covalent bond in the C–O–C and C–OH groups, respectively. The fairly weak peak between 1660–1760 cm⁻¹ (Fig. 5(b)) belongs to the C=O functional group in carbonyl and carboxylic [27,40]. It is difficult to dis-

Fig. 5. Chemical changes of the treated g-C₃N₄ samples. FT-IR spectra. (a) 500–4500cm⁻¹ and (b) 600–2500cm⁻¹.

tinguish the C–O and C=O groups because of the small amount of oxygen-containing groups on the surface treated by discharge plasma, i.e., only 5.19% in the air atmosphere on carbon particles and only 7.47% in the pure dry oxygen atmosphere on carbon nanotubes [13,41]. A new weak peak occurs at 1387 cm⁻¹ on the treated g-C₃N₄, which is ascribed to the symmetric –NO₂ group, consistent with the following XPS spectra in N 1s [42–44]. The existence of the –NO₂ group in the oxidation process of g-C₃N₄ has not been reported even in strong oxidizing solvents such as KMnO₄+H₂SO₄. However, Xiao et al. [45] reported that the •OH radical could tear the heptazine unit from g-C₃N₄ to form cyameluric acid (C₆H₃N₇O₃) and the acid would be further oxidized to CO₂, H₂O, and NO₃⁻ in the aqueous phase. This is confirmed in that the –NO₂ could be generated on the surface by DBD air plasma.

Significant parallels of primary oxidative products exist on g-C₃N₄ between the DBD plasma and the strong oxidizing solvents such as the two methods to oxidize carbon nanotubes [14,27]. Carbonyl and carboxylic can be generated on carbon nanotubes oxidized by a relatively mild oxidation such as O₃ [46] and KMnO₄+NaOH [47]; however, carbonyl is absent under stronger oxidations such as H₂SO₄+HNO₃ and HNO₃ [41]. Thus, different oxidants contribute significantly to the degree of oxidation. Many –COOH and C–OH groups on g-C₃N₄ were generated in strong oxidizing solvents such as H₂SO₄+HNO₃ [48], H₂SO₄+KMnO₄ [49], K₂Cr₂O₇+H₂SO₄ [50], and H₂O₂ [18,51]. Moreover, the stronger the oxidizing ability of solvents, the more destructive is the g-C₃N₄ structure. Although O₃ is the primary production from the DBD generator and cannot oxidize g-C₃N₄ without structure defects, it should selectively oxidize the defects produced by the DBD system to C=O and C–OH groups, and even CO₂ gas emission above 25 °C [40]. Thus, these O-containing groups with low concentrations could be generated and transformed on the surface with the physical changes.

The XPS measurements were applied to determine the

chemical state of the elements. Fig. 6(a) displays the full survey spectra of all the g-C₃N₄ samples. As shown, the intensities of the O 1s spectrum of the as-treated g-C₃N₄ are stronger than those of the pristine, and signals of C, O, and N elements are represented in Fig. 6(b)–(d). The C1s peaks in Fig. 5(b) located at approximately 284.9 eV, 286.6 eV, and 288.32 eV are associated with *sp*² C–C bonds, C–O bonds (containing C–O–C, C–OH, C–O–N bonds), and *sp*²-bonded carbon in N-containing aromatic rings (N=C=N), respectively [32,43]. The weak peaks centering at 289.1 eV can be attributed to residual O–C=O or C=O bonds [42,45], and the pristine g-C₃N₄ possesses the bond by the heating treatment with air [52]. O 1s XPS can be fitted into several peaks (Fig. 5(c)), and can be ascribed to absorbed water at 532.7eV, O–C=O bond in –COOH groups at approximately 530.6 eV, C=O bonds at approximately 531.8 eV, and C–OH bond at 533.1eV, respectively [42–45,53]. The O of –NO₂ in the O 1s spectra, according to the NIST XPS database and the relative peak intensity in Table 3, is located at approximately 531.8 eV. The emergence of C=O bonds in the O 1s spectrum is consistent with the bonds (289.1 eV) in the C 1s spectrum. Moreover, the decline of the O–C=O bonds at 10 min suggests their transformation to CO₂ gas [41]. All the oxygen obviously comes from the heating treatment and discharge in the presence of air. In the N 1s region of all the g-C₃N₄ (Fig. 5(d)), four primary peaks can be observed. Peaks at approximately 398.8, 400.2, 401.4, and 404.74 eV could correspond to C=N–C (*sp*²-hybridized aromatic N), N–(C)₃ (tertiary nitrogen), C–N–H groups, and charge effects, respectively [44]. The types of chemical bonds for 5–90 min are similar to pure g-C₃N₄, but the –NO₂ bonds centered at 406.6 eV emerge on the surface after the DBD treatment [54,55]. Owing to a small amount of –NH₂ on the surface, the –NO₂ may originate from the oxidation of defects [39]. That all the peaks slightly shift the wave number or the large full width at half maximum (FWHM) along with prolonged treatment duration can be attributed to the chemical environment change of the electron withdrawing group of

Fig. 6. Chemical changes of the g-C₃N₄ samples in the XPS profiles (a) Survey spectra, (b) C 1s spectra, (c) O 1s spectra, and (d) N 1s spectra.

-NO₂, and the generation of other O-containing groups [48,56].

The oxygen content on the treated g-C₃N₄ is higher than that of the pure after a treatment by a plasma system (Table 2). Further, the 21.6 kV/10 min possesses the highest oxygen content. When the discharge time is prolonged, the O content and peak intensity of -NO₂ become lower and the photocatalytic performance begins to improve. Except for the destruction of the surface structure, the strong ability of attracting electron and hydrophilicity of the -NO₂ group may decrease the photocatalytic performance. The improvement in the C/N ratio and O content and the decreased relative intensity of the -NH_x bond at 5 min reveal that the -NH_x groups are successfully transformed to the O-containing groups such as the -OH and COOH groups on the surface of g-C₃N₄. Subsequently, the ratio of C=N-C to N-(C)₃ bonds declines from the initial 3.66 to 3.41 and the -NH_x intensity enhanced slightly. These changes show that DBD may break the aromatic units, and that the destruction of -N=C bonds achieves the electrophilic addition and oxidation reaction to produce N-H, C-N, -NO₂, C=O, and C-O

bonds [37]. The relative intensity of C=O/-NO₂ bonds in O 1s is consistent with the relative intensities of -NO₂ bond in N1s and the O intensities on the g-C₃N₄ surface (Table 2, 3). It can be indicated that the O content primarily originates from the C=O and -NO₂ groups under a long-time discharge. The C-OH bonds and the C intensity reduce under the long-time treatment because the hydroxyl groups may be converted into quinone groups and carboxylic acid; further, the -COOH could be oxidized to CO₂ and H₂O [14,41,44]. Undoubtedly, the lay-

Table 2

Relative peak intensities of C, O, and N for the g-C₃N₄ samples (obtained from XPS).

Sample	C (%)	O (%)	N (%)	C/N
0kV-0min	40.67	3.15	56.18	0.724
20kV-5min	40.74	3.59	55.67	0.732
21.6kV-10min	39.59	6.14	54.27	0.730
21.6kV-20min	39.39	5.8	54.81	0.719
21.6kV-60min	39.35	5.59	55.07	0.715
21.6kV-90min	39.54	5.99	54.47	0.726

Table 3Relative peak intensities of C, O and N with different chemical states for the g-C₃N₄ samples (obtained from XPS).

Sample	C (%)				O (%)			N (%)			
	C–C	N–C=N	C–O	C=O	O–C=O	C=O /–NO ₂	C–OH	C=N–C	N–(C) ₃	–NH _x	–NO ₂
0kV-0min	12.4	68.3	4.7	11.9	0.0	45.5	0.0	72.8	19.9	5.29	0.0
20kV-5min	11.6	68.8	4.1	11.9	19.3	17.0	10.7	74.7	18.4	4.69	0.4
21.6kV-10min	12.2	69.5	5.0	10.4	7.5	37.8	8.0	70.7	19.9	5.42	2.1
21.6kV-20min	13.0	70.9	5.3	7.4	0.0	33.6	12.8	70.7	20.6	5.20	2.0
21.6kV-60min	13.1	74.7	3.4	5.3	5.5	31.2	8.3	70.8	20.5	5.44	1.6
21.6kV-90min	12.9	77.2	2.8	3.3	0.0	30.4	4.8	70.3	20.6	5.68	1.9

er-by-layer exfoliation with the periodic physical changes could lead to continuous oxidation defects such as the appearance of –OH and –COOH groups at 60 min (Table 3).

3.5. Optical and photoelectrochemical properties

The UV-vis diffuse-reflectance spectra were adopted to investigate the photoelectric property of the g-C₃N₄ samples. As shown in Fig. 7(a), little changes in the absorption edges are shown under the short-time plasma treatment. This can be explained by that defects such as carbon or nitrogen vacancies inconspicuously occur on the surface of treated g-C₃N₄ samples [32]. Further O-doped g-C₃N₄ has no contribution in the valance band and can lead to the blue shift in UV-vis and PL spectrums [57]. It is interesting that the long-time discharge (20–90 min) also ultimately lead to the slight hypsochromic shift of the bandgap (Fig. 7(b)) because of the quantum confinement effects induced by nanosized particles [58–60]. Tuning the discharge time on g-C₃N₄ is also an approach similar to altering the microstructure and bandgap, such as the change in the pyrolysis time on the photocatalyst. Owing to the low O content on the catalytic surface and the slight layer-by-layer physical destruction, these changes are not obvious.

The separation efficiency of photogenerated carriers and the recombination behavior were measured by PL spectra (Fig. 6(c)). The intensity of all modified g-C₃N₄ samples is lower than the pristine g-C₃N₄. Therefore, the electric discharge enhances the separation of the photogenerated electrons and holes. Further, the catalytic activities of the 5–10 min samples are consistent with the separation efficiency reflected in Fig. 6. The

surface hydroxyl content and –NO₂ groups favor the trapping of photogenerated holes and electrons, respectively, thus preventing electron-hole recombination [32,61]. However, the lower intensity does not determine the enhancement in the photocatalytic performance under a long-time discharge; however, physical and chemical effects must be considered. These effects cause the shift in the bandgap and the change in the PL intensity.

3.6. Proposed mechanisms

DBD treatment can nonselectively induce layer-by-layer exfoliation during the transformation of an undulated and planarized structure. The discharge would not destroy the crystal structure of g-C₃N₄ under the 5–90 min discharge treatment and higher discharge voltages (Fig. 4(a)). The periodic physical changes in crystallinity and SSA from Fig. 4(a) and Table 1 verify the result. The NTP system can generate chemical effects in air, such as e[–], •OH, H•, O•, •O₂[–], O₃, N•, NO_x. Moreover, the addition of g-C₃N₄ in the DBD system can enhance the generation of active species and change the discharge intensity. Compared with strong oxidizing solvents, DBD air plasma induces different O-doped processes. At low discharge voltages, the applied voltage neither yields enough energy and plasma to collide and transform the surface groups nor evokes useful physical and chemical effects to change the photocatalytic performance. The typical effect mechanism of the DBD system on g-C₃N₄ is shown in Fig. 8. The 20 kV/5 min sample with a nearly complete structure possesses surface hydrophilic –OH functional groups of g-C₃N₄ [20], revealing a promising effect on the synergies

Fig. 7. Optical properties and band gap of the g-C₃N₄ samples for different parameters. (a) UV-Vis DRS, (b) plots of $(\alpha h\nu)^{1/2}$ vs photo energy; (c) Room temperature PL spectra.

Fig. 8. Schematic illustration for the mechanism of treating the g-C₃N₄ by DBD system.

between plasma and photocatalysts. The exposed O atoms on the g-C₃N₄ could enhance the absorption efficiencies and photocatalytic activity [62,63]. However, an undesirable result occurs in that the photocatalytic activities undergo a declining process, as shown in Fig. 2. The samples under a higher voltage and a short-time treatment such as 21.6 kV/10 min contain surface structure defects and the highest O content with poor photocatalytic performance illustrating the chemical instability of g-C₃N₄ by plasma. This may be attributed to the continuous exfoliation and destruction to g-C₃N₄ by high electrons with a high-temperature (10^4 – 10^5 °C), streamer and other species ($\bullet$ H, $\bullet$ O, $\bullet$ O₂[−], $\bullet$ OH, $\bullet$ N, NO_x) [3,19]. However, the photocatalytic performance of long-time treatment samples such as 21.6 kV/60 min also showed an improvement. This may be ascribed to the partly purified chemical components and the improvement in the physical structure of g-C₃N₄ (Fig. 4 and 5). However, the physical and chemical effects of the DBD system cannot significantly change the optical and photoelectrochemical properties of g-C₃N₄.

The previous oxidation position was reported on the defects or in the aromatics of g-C₃N₄ in that the O replaced the N in the C=N=C bonds under strong oxidizing solvents based on the charge distribution [43,45]. The DBD plasma, as a mild modified method, nonselectively destroy the surface structure of carbonaceous materials layer by layer. Moreover, the plasma primarily oxidizes the defects and induces coupling reactions. Table 3 shows that the primary defects occur on the C=N bonds. Thus, various bonds such as C=O, O–C=O, C–O, –NH–, and –NO₂ can be generated on the g-C₃N₄ surface by an electrophilic addition and oxidation reaction on the defects [37]. Moreover, the chemical attack, a highly selective process with various energy of active species, can produce and eliminate some positive function groups (e.g., –OH, –COOH) and negative groups (e.g., –NO₂). However, it is easy to control the electrical parameters and change the type of gas inlet to the plasma-photocatalyst system to weaken these adverse effects [27]. Although the $\bullet$ OH can tear the heptazine unit from g-C₃N₄, it perfectly reacts with pollution [39]. These virtues can contribute to the application of the plasma-g-C₃N₄ system.

4. Conclusions

In conclusion, the DBD is sufficiently mild that it cannot sig-

nificantly destroy the structure of g-C₃N₄. Based on the results above, the DBD plasma oxidation can change the physical structure and the chemical characteristics, and further affect the photocatalytic activity of g-C₃N₄. Our experimental results indicate that the effect of NTP on g-C₃N₄ photocatalysts presents a periodic change trend during a long time scale. Further, it is possible to adjust the electrical parameters, avoid the discharge gap, and alter the type of gas inlet into the plasma-catalytic system to avoid some undesirable effects. Thus, the synergistic effect of plasma and g-C₃N₄ photocatalysts under a long-time operation is promising and attractive for future applications of plasma-g-C₃N₄ systems in environment pollution treatment and material surface treatment.

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Graphical Abstract

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Effect of high-voltage discharge non-thermal plasma on g-C₃N₄ in a plasma-photocatalyst system

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The periodic oxidation and exfoliation on g-C₃N₄ photocatalysts under long-time DBD treatment is reported. Further, chemical and physical changes on g-C₃N₄ influence the photocatalytical activities.

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高压放电-光催化剂体系中低温等离子体对g-C₃N₄的影响

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摘要: 高压放电能产生物理和化学效应,如高能电子(e^{*})、电场、紫外光、可见光和活性物质(•OH, H•, O•, •O₂⁻, O₃, N•, NO_x)等,这些放电效应直接或间接应用于污染物的去除和材料的表面改性. 在环境领域中,很多研究都关注于高压放电体系中活性物质的产生和利用,而忽视了物理作用,致使处理污染物的能量利用效率不高. 近年来,为了提升能量效率,在放电系统中添加光催化剂的研究越来越多. 放电产生的物理和化学效应提升了活性物质的产量,从而增强污染物的去除效率. 然而,关于高压放电产生的活性物质和物理效应对光催化剂的影响缺乏研究. g-C₃N₄光催化剂是无毒、耐高温、低成本的非金属半导体,在环境与能源方面应用较广,但至今研究g-C₃N₄与低温等离子体协同处理污染物较少. 为了使等离子体-g-C₃N₄系统能在环境中得到应用,首要解决的是高压放电对光催化剂影响的问题,从而为后期的研究奠定基础.

本研究选用放电均匀、稳定、能产生高电子密度的介质阻挡放电(DBD)对g-C₃N₄进行处理. 在不同电气参数(放电电压和放电时间)对g-C₃N₄进行处理,用处理前后的g-C₃N₄光催化降解10 mg/L的亚甲基蓝检测其光催化活性,并对其表面的物理结构和化学特征进行表征. 结果发现在低放电电压的长时间放电会降低g-C₃N₄的催化活性,而在高放电电压的较短时间内会增强光催化剂的催化性能,随着放电时间的延长,催化活性会先降低再上升. 根据XPS表征结果,放电处理后的g-C₃N₄表面有化学键的破坏和新键的形成. 在放电处理过程中,加入光催化剂会增强放电强度,而且亲水官能团(-OH, -COOH, -NO₂)的增加也会使放电强度增强,这与光催化剂对放电间隙的空间电荷吸附量有关. 结合g-C₃N₄表面表征结果,发现g-C₃N₄的表面物理结构随着放电时间的延长层层破坏,其表面化学官能团也发生周期性变化,这些变化都会影响g-C₃N₄的光催化剂活性. 如果等离子体-g-C₃N₄系统要应用于环境治理,光催化剂需避免与放电间隙接触,使光催化剂既能利用高压放电产生的光和其他物理效应,也能不受到低温等离子体的影响.

关键词: g-C₃N₄; 低温等离子体; 光催化活性; 物理结构; 化学特性

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