

Article

Kinetic and Mechanistic Study on Catalytic Decomposition of Hydrogen Peroxide on Carbon-Nanodots/Graphitic Carbon Nitride Composite

Zhongda Liu, Qiumiao Shen, Chunsun Zhou, Lijuan Fang, Miao Yang * and Tao Xia *

School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Wuhan 430070, China; liuzhongda@whut.edu.cn (Z.L.); shen_qiumiao@163.com (Q.S.); zhouchunsun@whut.edu.cn (C.Z.); fanglijuan@whut.edu.cn (L.F.)

* Correspondence: yangmiao@whut.edu.cn (M.Y.); hsiatao@hotmail.com (T.X.); Tel.: +188-7225-6465 (M.Y.); +134-0714-2371 (T.X.)

Received: 12 September 2018; Accepted: 8 October 2018; Published: 11 October 2018



Abstract: The metal-free CDots/g-C₃N₄ composite, normally used as the photocatalyst in H_2 generation and organic degradation, can also be applied as an environmental catalyst by in-situ production of strong oxidant hydroxyl radical (HO·) via catalytic decomposition of hydrogen peroxide (H_2O_2) without light irradiation. In this work, CDots/g-C₃N₄ composite was synthesized via an electrochemical method preparing CDots followed by the thermal polymerization of urea. Transmission electron microscopy (TEM), X-Ray diffraction (XRD), Fourier Transform Infrared (FTIR), N₂ adsorption/desorption isotherm and pore width distribution were carried out for characterization. The intrinsic catalytic performance, including kinetics and thermodynamic, was studied in terms of catalytic decomposition of H₂O₂ without light irradiation. The second-order rate constant of the reaction was calculated to be $(1.42 \pm 0.07) \times 10^{-9} \,\mathrm{m \cdot s^{-1}}$ and the activation energy was calculated to be (29.05 ± 0.80) kJ·mol⁻¹. Tris(hydroxymethyl) aminomethane (Tris) was selected to probe the produced HO· during the decomposing of H_2O_2 as well as to buffer the pH of the solution. The composite was shown to be base-catalyzed and the optimal performance was achieved at pH 8.0. A detailed mechanism involving the *adsorb-catalyze* double reaction site was proposed. Overall, CDots/g-C₃N₄ composite can be further applied in advanced oxidation technology in the presence of H_2O_2 and the instinct dynamics and the mechanism can be referred to further applications in related fields.

Keywords: CDots/g-C₃N₄; H₂O₂; hydroxyl radical; Tris; advanced oxidation technology

1. Introduction

Advanced oxidation technology (AOT) is one of the most effective and economical approaches dealing with non-biodegradable organic pollutants (NBDOPs) in water, such as dyestuffs, pesticides, pharmaceutical and personal care products (PPCPs), synthetic chemicals and leachate of landfills [1–5]. In typical AOTs, different strategies like chemical, photochemical, sonochemical and electrochemical pathways, are employed to produce intermediate active oxidant radicals [1,6–8]. With an oxidation potential of 2.7 eV and nanosecond-level life time, hydroxyl radical (HO \cdot) is one of the most typical radicals, which can decompose NBDOPs non-selectively, forming CO₂, H₂O, inorganic ions or other biodegradable molecules [9–11]. It is worthy to note that the degradation of NBDOPs and the generation of HO \cdot take place simultaneously [12]. Thus, the core process of various AOTs is to improve the yield of HO \cdot , which mainly leads to the decomposition of NBDOPs.



The concentration of instantaneous HO· can be hardly determined directly but can be determined indirectly by probes like Rhodamine B [13], terephthalic acid [14], dimethyl sulfoxide [15], phenylalanine [16] and Tris(hydroxymethyl)aminomethane (Tris) [17]. Among the various probes, Tris can be applied in both homogeneous and heterogeneous systems as HO· scavenger and pH buffer at the same time [18]. Hydroxyl radical captures hydrogen atom from Tris, producing formaldehyde (CH₂O) and other compounds. Since the produced CH₂O can be quantified by the modified Hantzsch method [19], the concentration of HO· can be indirectly quantified. The detailed mechanism of the reaction between HO· and Tris was reported, involving the effects of O₂ and pH [17].

 H_2O_2 is one of the most common sources of HO· in the presence of metal salt solution, carbon-based species, metal or metal oxide via Fenton/Fenton-like reaction, electron-transfer mechanism or catalytic decomposition on the solid-liquid interface [18,20–24]. The well-known Fenton/Fenton-like reaction may occur in both homogeneous and heterogeneous system according to many works [18,20–23]. Similar to the Fenton reaction, HO· and HO₂· can be formed on the surface of carbon-based catalysts via the electron-transfer mechanism due to the donor-acceptor properties of the carbon surface. The redox cycle is necessary to keep the production of HO· and HO₂· species [24]. The catalytic decomposition of H_2O_2 on the surface of metal or metal oxides has also been studied to some extent in recent years, including Fe, W, Cu, UO₂, ZrO₂, CuO, CuO₂ and so on [18,22,25–27]. It is known that HO· and HO₂· will be formed as intermediates during the decomposition of H_2O_2 while the disproportion reaction of HO₂· ends up with H_2O_2 and O_2 . The disproportionation may also occur in the Fenton-like reaction and the reaction between H_2O_2 and carbon-based catalyst. From previous work, it is known that the reaction between scavenger and HO· will affect the production of O_2 [28].

Despite its high efficiency and effectiveness, the application of classic Fenton reaction faces the disadvantages of strict pH restrictions, iron precipitation and the cost for catalyst recycling [29–31]. The formation rate of HO· is strongly dependent on the pH value while the oxidation potential of HO· declines as the pH increases [31,32]. Furthermore, the generation of HO· is directly limited by the formation of iron sludge in alkaline condition [30]. Since iron precipitation remains the bottleneck of classic iron-based Fenton reaction, non-ferrous heterogeneous catalysts with multiple oxidation states and redox stability (Ce, Cu, Mn and Ru) [11] and transition metal substituted iron oxide (Cr, Co and Ti) [32], have been developed for the replacement. Nevertheless, the abovementioned metal materials still face the drawbacks of high cost, high toxicity and/or environmental unfriendliness. Hence, a number of metal-free catalysts have been developed for the generation and/or decomposition of H₂O₂ regarding to their high earth abundance, good biocompatibility and environment-friendly properties, including graphene [6], carbon nanotubes [33], activated carbon fibers [34], graphitic carbon nitride (g-C₃N₄) [35–38] and carbon nanodots (CDots) [39].

As a metal-free polymer semiconductor material with suitable band gap and band position, $g-C_3N_4$ has embodied its research value in the field of H_2 production, CO_2 reduction, selective oxidation of alcohols and pollutant degradation [40–43]. The combination of CDots and $g-C_3N_4$ was firstly introduced in 2015 by J. Liu and her co-workers for water splitting, solving the chock point that $g-C_3N_4$ is poisoned by in-situ generated H_2O_2 in hydrogen evolution [44]. H_2O can be catalytically split into H_2O_2 and H_2 by $g-C_3N_4$ in the presence of photo irradiation. However, with the two-dimensional structure and large accessible area on the surface of $g-C_3N_4$, the in-situ generated hydrogen peroxides are strongly bonded and difficult to remove, which leads to the poisoning of catalyst, thereby limiting the yield of H_2 [45–47]. CDots was introduced to solve this problem by decomposing the bonded H_2O_2 on the surface of $g-C_3N_4$ into H_2O and O_2 , thereby remitting the poisoning of $g-C_3N_4$. It is known that intermediate HO· will be formed via electron-transfer on the surface of carbon-based catalyst [24]. Inspired from these, it can be hypothesized that the CDots/ $g-C_3N_4$ composite can be used as a catalyst providing promising yield of HO· via decomposing adsorbed H_2O_2 on the surface of $g-C_3N_4$ composite of $g-C_3N_4$ by embedded CDots. To the best of our knowledge, the kinetics and mechanism of catalytic decomposition of H_2O_2 on CDots/ $g-C_3N_4$ composite has been rarely studied.

In this work, CDots/g-C₃N₄ composite was synthesized via an electrochemical method followed by a thermal polymerization process. The obtained composites were characterized by TEM, FTIR, Brunauer-Emmett-Teller (B.E.T) and XRD. The catalytic performance of CDots/g-C₃N₄ composite for H₂O₂ decomposition was also investigated. The second-order reaction rate constant of H₂O₂ decomposition and reaction activation energy were obtained by varying the dosage of composite and temperature. Furthermore, a detailed mechanism involving the *adsorb-catalyze* double reaction sites was proposed.

2. Results and Discussion

2.1. Morphology of the Catalyst

The obtained CDots/g-C₃N₄ composite was prepared via an electrochemical method followed by a thermal polymerization process. To confirm the modification of CDots on g-C₃N₄, FTIR spectra and XRD patterns of pure g-C₃N₄ and CDots/g-C₃N₄ composite were obtained and exhibited in Figure 1A,B. The influence of CDots modification on the specific surface area was investigated by the B.E.T. method with isothermal adsorption and desorption of high purity nitrogen. The N₂ adsorption-desorption isotherms and pore size distributions of g-C₃N₄ and CDots/g-C₃N₄ composite are shown in Figure 1C. The TEM images of CDots/g-C₃N₄ are shown in Figure 1D,E.



Figure 1. Cont.



Figure 1. (**A**) Fourier Transform Infrared (FTIR) spectra; (**B**) X-Ray diffraction (XRD) patterns; (**C**) N_2 adsorption/desorption isotherm and pore width distribution of pure g-C₃N₄ and CDots/g-C₃N₄ composite; (**D**,**E**) Transmission electron microscopy (TEM) images of CDots/g-C₃N₄ composite.

As can be seen in Figure 1A, the sharp peak for $g-C_3N_4$ at 810 cm⁻¹ is attributed to stretching vibration bond of tri-*s*-triazine [48]. Vibration peaks between 1200–1650 cm⁻¹ corresponds to the typical stretching modes of CN heterocycles [49]. A wider band can be seen at 3100–3300 cm⁻¹, which belongs to the stretching vibration modes for the unreacted –NH [50]. The same characteristic peaks are observed in CDots/g-C₃N₄ composite and the peak at 1405 cm⁻¹ can be seen as the indicator for the coupling of CDots and g-C₃N₄ [48].

XRD patterns of g-C₃N₄ and CDots/g-C₃N₄ are displayed in Figure 1B. The main diffraction peaks observed at 12.9° and 27.5° in both g-C₃N₄ and CDots/g-C₃N₄ composite are indexed to the (100) peak of the in-plane structure of tri-s-triszine unit and (002) crystal facets of the inter-layer stacking of aromatic segments [51,52]. The two patterns fit well with graphitic carbon nitride (JCPDS 87-1526) and no significant difference is observed, implying the low content of CDots in CDots/g-C₃N₄ composite. However, it is remarkable that the difference in relative intensity, together with the shift observed in the (002) peak location from 27.51° for g-C₃N₄ to 27.59° for CDots/g-C₃N₄, can be seen as the evidence of CDots introduction [45]. As can be seen in Figure 1C, the introduction of CDots in CDots/g-C₃N₄ leads to a 20% increase (from 120.92 to 145.24 m²/g) in specific surface area, which favors the decomposition of H₂O₂.

Figure 1D clearly shows the two-dimensional structure of $g-C_3N_4$ together with the embedding of CDots (the white circles). The close look of the CDots embedded in $g-C_3N_4$ matrix is given in Figure 1E. The CDots are non-uniformly distributed, ranging from 2 to 10 nm, which is in line with previous studies [45,51,53].

From the results and analysis above, it can be confirmed that CDots have been successfully decorated in $g-C_3N_4$ and the inlay of CDots brings an improvement in specific surface area of the composite.

2.2. Kinetic Study

The effect of CDots content in the catalyst has been investigated in several previous works proving that a certain amount of CDots can enhance the catalytic properties of the catalysts while an excessive loading may work opposite [45,51,53]. Thus, in this work the CDots/g-C₃N₄ composite was fabricated with a fixed fraction of CDots (1.26 wt.%) selected by preliminary experiments. It is known that the surface reaction is dominating in the present heterogeneous system, therefore surface area to solution volume ratio (SA/V) is used to represent the dosage of the composites other than the mass concentration, which has been applied in many reported works [17,18,22,27,28,54–56]. The SA/V value is obtained by combining the mass concentration (g/L) with specific surface area (m²/g) and can be normalized to m⁻¹.

To verify the synergistic effect of CDots and $g-C_3N_4$ in H_2O_2 decomposition, five samples were prepared according to the proportion of CDots and $g-C_3N_4$ in the composite. Sample 5 is the CDots/ $g-C_3N_4$ composite with SA/V of 4×10^5 m⁻¹. The pure $g-C_3N_4$ with the same SA/V value was identified as Sample 2. The single-component CDots solution containing the equivalent amount of CDots as Sample 5 (13.4 mg/L) was named as Sample 1 and it was obtained by directly diluting the originally prepared CDots solution. The physical mixture of Sample 1 and 2 is identified as Sample 3. Additionally, the originally prepared CDots solution with a high concentration (133 mg/L) was named as Sample 4.

Detailed descriptions of the samples are listed in Table 1. It should be noted that sample 1, 3 and 5 has equivalent amount of CDots and sample 3 is a simple mixture of CDots and g-C₃N₄ while sample 5 is the composite. The catalytic decomposition of H₂O₂ by each sample was investigated under the same experimental condition where initial concentration of H₂O₂ ($[H_2O_2]_0$) is 0.5 mM and the temperature is 298K. Normalized concentration of H₂O₂ ($[H_2O_2]/[H_2O_2]_0$) of each case is plotted against reaction time respectively (shown in Figure 2).

Sample	Description		
1	13.4 mg/L CDots		
2	$4 \times 10^5 { m m}^{-1} { m g-C_3N_4}$		
3	physical mixture of Sample 1 and Sample 2		
4	133 mg/L CDots		
5	$4 \times 10^5 \text{ m}^{-1} \text{ CDots/g-C}_3N_4$ composite		
1.0 0.8 1.0 0.8 1.0 0.8 1.0 0.8 1.0 0.8 1.0 0.0 1.0 0 0 0	-Sample 1 -Sample 2 -Sample 3 -Sample 4 -Sample 5 -Time / s		

Table 1. Samples prepared for the investigation of synergistic effect of CDots and g-C₃N₄.

Figure 2. $[H_2O_2]/[H_2O_2]_0$ ($[H_2O_2]_0 = 0.5$ mM) as a function of reaction time in the presence of sample 1–5 at 298 K.

As shown in Figure 2, Sample 4 (the originally prepared CDots, 133 mg/L) incurs a gradely decline in H_2O_2 concentration in darkness, demonstrating the inherent catalytic property of CDots for H_2O_2 decomposition. However, the catalytic performance becomes faint after diluting CDots to a 10.2% concentration when comparing sample 1 and 4, indicating that such catalysis process is strongly dependent on the applied CDots concentration, which is in accordance with reported work [57]. Sample 2 (pure g-C₃N₄) also incurs slight decline in H_2O_2 , which can be attributed to the adsorption of g-C₃N₄ and catalytic decomposition by carbon-based material through the delocalization of electrons on the surface [24]. However, the decomposition of H_2O_2 catalyzed by the pure g-C₃N₄ should not be considered as the main process in the system with CDots/g-C₃N₄ composite. It is remarkable that the consumption rate of H_2O_2 for sample 5 is much larger than sample 3, implying the thermal polymerization process gives rise to the remarkable synergy and the proximity between the CDots and the adsorption sites of H_2O_2 in g-C₃N₄ is necessary for the high efficiency of H_2O_2 decomposition [44].

It has been previously reported that [18,54], the catalytic decomposition of H_2O_2 in the heterogeneous system follows pseudo first-order kinetics with respect to H_2O_2 when solid is excess to H_2O_2 and the reaction rate equation can be described as $\frac{-d[H_2O_2]}{dt} = k_1 \times [H_2O_2]$, which can be integrated as

$$\ln \frac{[H_2 O_2]}{[H_2 O_2]_0} = -k_1 t \tag{1}$$

where k_1 is the pseudo first-order rate constant at a given temperature and dosage of the solid, t is the reaction time, $[H_2O_2]$ is the concentration of H_2O_2 at a time and $[H_2O_2]_0$ is the concentration of H_2O_2 at t = 0. When the solid catalyst is excess to H_2O_2 , the second-order rate constant in the system can be determined by studying the pseudo first-order rate constant (k_1) as a function of SA/V (surface area of solid to volume of solution). The second-order rate expression is given as

$$\frac{-d[H_2O_2]}{dt} = k_2 \times \frac{SA}{V} \times [H_2O_2]$$
⁽²⁾

where k_2 denotes the second-order reaction rate constant, SA denotes the surface area of the CDots/g-C₃N₄ and V is the volume of the reaction solution. The term SA/V has been applied to denote the catalyst concentration in a number of studies regarding the heterogeneous catalysis system [18,22,27,54].

According to the preliminary experiments, the lower limit of SA/V is 3.2×10^5 m⁻¹ after which it is excess to the fixed initial H₂O₂ concentration (0.5 mM). A series of experiments were carried out by varying the dosage of catalyst (SA/V) from 3.2 to 6.4×10^5 m⁻¹ under the same condition at 298 K to explore the kinetics of the present system. The logarithm of normalized H₂O₂ concentration is plotted as a function of reaction time (Figure 3A) and the slope of the linearly fitted curve of these plots (k₁) is plotted against SA/V accordingly (Figure 3B).



Figure 3. (A) $\ln([H_2O_2]/[H_2O_2]_0)$ ($[H_2O_2]_0 = 0.5 \text{ mM}$) as a function of reaction time with different SA/V values of catalyst (3.2–6.4 × 10⁵ m⁻¹) at 298 K; (B) pseudo first-order reaction rate constant as a function of SA/V at 298 K. The k₁ values were obtained from Figure 3A.

From Figure 3A, it can be seen that all the $ln([H_2O_2]/[H_2O_2]_0)$ plots are linearly fitted with reaction time which indicates it follows pseudo first-order kinetics at given dosage of the composite and the slopes of the fitted curves are denoted as k_1 . In addition, it is clearly that the observed decomposition rate of H_2O_2 increases with increasing the dosage of the composite. The key parameters of the fitted curves, including SA/V, slopes (k_1), standard deviation and R^2 , are listed in Table 2.

 $SA/V (10^5 m^{-1})$ $k_1 (10^{-4} s^{-1})$ Standard Deviation (10^{-4} s^{-1}) R² (%) 3.2 0.078 99.38 2.61 4.099.74 3.52 0.068 4.84.53 0.084 99.76 5.6 6.05 1.063 99.49 6.4 7.16 0.094 99.88

Table 2. The key parameters of the fitted curves with different SA/V values.

The obtained k₁ values from Table 2 were plotted in Figure 3B against SA/V. As can be seen from Figure 3B, k₁ is linearly correlated to SA/V in the range of $3.2-6.4 \times 10^5 \text{ m}^{-1}$ and the slope of the fitted curve is calculated as $(1.42 \pm 0.07) \times 10^{-9} \text{ m} \cdot \text{s}^{-1}$ which can be denoted as the overall second-order rate constant. This value is far from the rate constant of a diffusion controlled reaction in the order of $10^{-5} \text{ m} \cdot \text{s}^{-1}$ but still higher than some metal oxide catalysts like ZrO_2 ((2.39 ± 0.09) × $10^{-10} \text{ m} \cdot \text{s}^{-1}$), CuO ((1.23 ± 0.06) × $10^{-9} \text{ m} \cdot \text{s}^{-1}$) and Gd₂O₃ ((9.4 ± 1.0) × $10^{-10} \text{ m} \cdot \text{s}^{-1}$) [18,54].

Generally, the first-order rate constant k_1 is strongly related to the reaction temperature according to the Arrhenius equation:

$$k_1 = A e^{-E_a/RT}$$
(3)

where E_a denotes the activation energy for the reaction, R is the gas constant, T is the absolute temperature and A is the pre-exponential factor. The logarithm of k_1 obtained by plotting $ln([H_2O_2]/[H_2O_2]_0)$ against T (shown in Figure 4A) is plotted as a function of 1/T in Figure 4B so as to calculate E_a .



Figure 4. Cont.



Figure 4. (A) $\ln([H_2O_2]/[H_2O_2]_0)$ ($[H_2O_2]_0 = 0.5 \text{ mM}$) as a function of reaction time at different reaction temperatures (293–318 K) with the catalyst dosage of $4.0 \times 10^5 \text{ m}^{-1}$; (B) $\ln(k_1)$ as a function of (1/T) where k_1 were obtained from Figure 4A.

As shown in Figure 4A, $\ln([H_2O_2]/[H_2O_2]_0)$ declines with reaction time and the slope of the fitted curves increases as temperature increases. In addition, $\ln([H_2O_2]/[H_2O_2]_0)$ drops sharply in the initial period (~20 min) indicating the adsorption dominates this period, after which adsorbed H_2O_2 on the surface of the CDots/g-C₃N₄ composite reaches an equilibrium state and the decomposition of H_2O_2 catalyzed by embedded CDots turns the dominant role.

It can be seen from Figure 4B, $ln(k_1)$ is linearly dependent on 1/T and the slope of the fitted curve is obtained. Based on the slope, the activation energy of the reaction is calculated to be (29.05 ± 0.80) kJ·mol⁻¹, which is to some extent lower than a series of metal oxides developed before, including ZrO₂ ((33 ± 1) kJ·mol⁻¹), TiO₂ ((37 ± 1) kJ·mol⁻¹), Y₂O₃ ((47 ± 5) kJ·mol⁻¹), Fe₂O₃ ((47 ± 1) kJ·mol⁻¹), CuO ((76 ± 1) kJ·mol⁻¹), CeO₂ ((40 ± 1) kJ·mol⁻¹), Gd₂O₃ ((63 ± 1) kJ·mol⁻¹) and HfO₂ ((60 ± 1) kJ·mol⁻¹) [18,54,58].

The key parameters of the fitted curves, including T, pseudo first-order reaction rate constants (k_1) , standard deviation and R^2 , are listed in Table 3.

T(K)	k_1 (10 ⁻⁴ s ⁻¹)	Standard Deviation (10^{-4} s^{-1})	R ² (%)
293	3.02	0.071	99.61
298	3.52	0.068	99.74
303	4.50	0.088	99.74
308	5.37	0.090	99.80
313	6.27	0.104	99.81
318	7.44	0.129	99.80

Table 3. The key parameters of the fitted curves with different temperatures.

2.3. The Effect of pH

To investigate the mechanism of the present system containing H_2O_2 and $CDots/g-C_3N_4$ composite, it is significant to study the pH effect as well as quantify the in-situ produced hydroxyl radicals. Due to its scavenging capacity against HO· and pH buffering ability, Tris is chosen to carry out the mechanistic study. The pKa and the buffering range of Tris are 8.07 and 7.0–9.0 respectively, so the pH values were selected within this range. The decline of H_2O_2 together with the production of CH_2O against the reaction time with different pH are exhibited in Figure 5.



Figure 5. The concentration of H_2O_2 ($[H_2O_2]_0 = 5 \text{ mM}$) and CH_2O as a function of reaction time in the presence of Tris ($[Tris]_0 = 100 \text{ mM}$) with the catalyst dosage of $4.0 \times 10^5 \text{ m}^{-1}$ at 298.15K in pH from 7.0 to 9.0.

It can be clearly seen in Figure 5 that the decomposition rate of H_2O_2 increases with pH increases in the whole range. However, the formation of CH_2O shows a different trend. The evolution of CH_2O remains relatively low in neutral condition (pH 7.0), then it starts to accelerate until pH 8.0, after which the formation rate of CH_2O declines as pH increases. This indicates that the formation of CH_2O and probably the production of HO_2 are alkaline favored while the production is to some degree related to the pKa of Tris [54].

To figure out whether the production of HO· is also pH dependent, it is necessary to introduce the yield (Y) of CH_2O formed by HO· and Tris. Y is defined by the equation:

$$Y = [CH_2O] / [HO \cdot]$$
(4)

where [HO·] is the production of HO· and [CH₂O] is the accumulated CH₂O in H₂O₂ decomposition experiment. According to a previous study using γ -radiation in homogeneous system [17], the yield (Y) of CH₂O increases from 25% to 51% as increasing pH from 7.0 to 9.0. Provided that the yield (Y) in heterogeneous system is consistent with that in homogeneous system, the production of HO· in H₂O₂ decomposition on CDots/g-C₃N₄ composite can be estimated by this value together with the final concentration of CH₂O. The results are shown in Figure 6.



Figure 6. Final production of CH₂O and estimated production of HO· as a function of pH. The final productions of CH₂O were extracted from Figure 5. The estimated $[HO·] = [CH_2O]/Y$ and the yields (Y) were derived from a previous work [17].

As appeared in Figure 6, the plots of estimated production of HO· exhibit the similar tendency as that of final production of CH₂O and it still peaks at pH 8.0 with the maximum concentration of 2.10 mM ([HO·] = [CH₂O]/Y where Y = 37.5% at pH 8.0). This means the stoichiometry between H₂O₂ and CH₂O is approximately 1:0.158 and 42.1% of H₂O₂ ([H₂O₂]₀ = 5 mM, Tris is excess to H₂O₂) end up with HO· at the optimal pH. The efficiency of H₂O₂ consumption towards HO· is much higher as compared to that of the H₂O₂/ZrO₂/Tris system (13.4% at pH 8.0) [17]. Therefore, it can be concluded that the production of HO· is also pH-dependent and there is an optimal pH which may have something to do with the Tris [22].

Based on the results in present work, the intrinsic chemical catalytic properties of the synthesized CDots/g-C₃N₄ composite, other than the photocatalytic properties, have been revealed to some extent. The hypothesis in the introduction section could be confirmed as following: firstly, as demonstrated in Figure 2, the pure CDots synthesized via an electrochemical pathway showed excellent catalytic ability, in line with the literature [59]; secondly, similar as the reported property of g-C₃N₄ [60], Figure 2 also shows that the concentration of H₂O₂ in the solution decreases slightly in the presence of the pure g-C₃N₄ which indicates g-C₃N₄ does provide sufficient reaction site for H₂O₂ to adsorb; thirdly, by analyzing the results in Figures 2, 3, 5 and 6, it is known that hydroxyl radical can be formed during the decomposition of H₂O₂ catalyzed by the CDots/g-C₃N₄ composite in the heterogeneous system as hypothesized in the former section. Besides the strong affinity of g-C₃N₄ towards H₂O₂ and the catalytic property of CDots against the adsorbed H₂O₂ [47], the delocalization of the electrons on the surface of g-C₃N₄ may also leads to the decomposition of H₂O₂ via electron-transfer mechanism [24]. In conclusion, the synthesized CDots/g-C₃N₄ and catalytic decomposition of H₂O₂ by g-C₃N₄ and CDots producing hydroxyl radicals.

Based on the results and discussion above, the mechanism of catalytic decomposition of H_2O_2 in the heterogeneous system with CDots/g-C₃N₄ composite is proposed and illustrated in Figure 7.



Figure 7. The mechanism of catalytic decomposition of H_2O_2 on CDots/g-C₃N₄ composite.

Key of the mechanism is the so-called *adsorb-catalyze* double reaction sites. With plenty of accessible adsorption sites on the surface of $g-C_3N_4$, CDots/ $g-C_3N_4$ composite shows high selective adsorption ability towards aqueous H_2O_2 . From previous works studying similar heterogeneous system with H_2O_2 and solid catalyst [18,22,54], it is known that H_2O_2 concentration exhibits an initial drop indicating the adsorption on the surface of catalyst, after which the H_2O_2 decomposition obeys pseudo first-order kinetic when the surface reaches equilibrium state. As can be seen in Figure 3A, the H_2O_2 concentration follows the similar trend and kinetics. Hence, it can be demonstrated that the adsorption of H_2O_2 is also dominating in the initial short period. Tris was introduced

in the present work as a probe of hydroxyl radical and pH buffer. It is known that Tris can be partially oxidized to CH₂O and other byproducts and the ratio between the concentration of hydroxyl radicals and formed CH₂O is relatively fixed under given condition (pH and dissolved oxygen concentration) [17,27]. Therefore, the formation of CH₂O can be used to probe the formed hydroxyl radicals in the heterogeneous system containing H₂O₂ and CDots/g-C₃N₄ composite. It is in line with previous works that [17,18,22,27], CH₂O formation is reflected by the decomposition of H₂O₂ and is pH-dependent (Figures 5 and 6). Hence, it can be deduced that after the initial period, the adsorbed H₂O₂ catalyzed by embedded CDots on the surface sites turns the dominant role. During this procedure, large quantities of HO· was produced, exhibiting strong oxidation ability towards scavengers like Tris. It should be noted that the production of HO· is strongly pH dependent. To sum up, the CDots/g-C₃N₄ composite shows synergetic effect on the decomposition of H₂O₂ via *adsorb-catalyze* double reaction sites and more importantly, is proved to be a promising catalyst for the degradation of NBDOPs since it is a metal-free pathway of producing HO· efficiently.

3. Experimental Section

3.1. Instrumentation

The morphology and microstructure of samples were observed by JET-2100F (JEOL, Wuhan, China) transmission electron microscope (TEM). The Fourier transform infrared spectroscopy (FTIR) of the samples were recorded by Nicolet iS5 (Thermo Fisher Scientific, Wuhan, China) FTIR spectrometer with KBr pellets. The specific surface area of CDots/g-C₃N₄ composite and pure g-C₃N₄ were determined by the Brunauer-Emmett-Teller (B.E.T) method via isothermal adsorption and desorption of high purity nitrogen using a TriStar II 3020 (Micromeritics, Wuhan, China) instrument. X-ray diffraction (XRD) patterns were recorded with D8 advance (Bruker, Wuhan, China) diffractometer using Bragg-Brentano geometry in the 2 θ angle from 10° to 40° and Cu K α irradiation (λ = 1.54 Å). The samples were weighted to \pm 10⁻⁴ g in a ME104E (Mettler Toledo, Wuhan, China) microbalance. UV/Vis spectra were collected by V-5600 (METASH, Wuhan, China) and UV-5500PC (METASH, Wuhan, China) spectrophotometer. The pH of reaction solution was measured by PHS-3C (YOKE, Wuhan, China) pH meter with an accuracy of \pm 0.01 pH units.

3.2. Reagents and Experiments

All the solutions used in this study were prepared using deionized water.

Preparation of the catalyst: CDots were synthesized via an electrochemical method based on previous reported work [59]. In a typical preparation process, two graphite rods were insert parallel into 300 mL ultrapure water as electrodes with a separation of 7.5 cm and 4 cm depth under water. 60 V static potentials were applied to the rods by a direct-current (DC). After electrolyzing for 120 h, the anode graphite rod corroded and a dark brown solution was formed. The solution was filtered with slow-speed quantitative filter paper and then centrifuged at 10,000 rpm for 10 min. Finally, the soluble CDots was obtained and the concentration can be quantified by drying and weighting.

A thermal polymerization method was applied for the synthesis of pure g-C₃N₄ [61]. Typically, 40 g urea (CAS[57-13-6], 99%, Sinopharm, Wuhan, China) was dissolved in 40 mL ultrapure water in a quartz crucible, then heated to 550 °C with the rate of 7 °C/min in a muffle furnace and kept at 550 °C for 2 h. After naturally cooling down to room temperature, the resultant yellow product was collected and ground into powder to obtain pure g-C₃N₄. CDots/g-C₃N₄ composite was synthesized via in-situ thermal polymerization [51]. Following the same procedure, 40 g urea was dissolved in 40 mL CDots solution and calcined in muffle furnace. The dark gray product CDots/g-C₃N₄ was collected and ground for further use.

Kinetic studies: Hydrogen peroxide H₂O₂ (CAS[7722-84-1], 30 wt.%, Sinopharm, Wuhan, China), glacial acetic acid HAc (CAS[64-19-7], 99.5%, Sinopharm, Wuhan, China), sodium acetate NaAc

(CAS[127-09-3], 99%, Sinopharm, Wuhan, China), ammoniumdimolybdate ADM (CAS[27546-07-2], Mo 56.5%, Macklin, Wuhan, China) and potassium iodide KI (CAS[7681-11-0], 99%, Sinopharm, Wuhan, China) were used in kinetic studies. H_2O_2 decomposition experiments were performed in lucifugal bottles with different dosages of CDots/g-C₃N₄ composite and under variable temperatures. The suspension was dispersed with ultrasonic sound for 1 min before the reaction. Afterwards, H_2O_2 was added to the suspension to trigger the reaction. Samples were extracted with a syringe and a filter (220 nm, cellulose membrane) at fixed time intervals. The concentration of H_2O_2 as a function of time was determined by Ghormley triiodide method, where I⁻ can be oxidized to I_3^- by H_2O_2 in faintly acid conditions catalyzed by ADM [62,63]. In detail, 0.2 mL sample was added to 1.6 mL water, followed by the addition of 0.1 mL 1M KI and 0.1 mL 1M HAc/NaAc containing 0.03% ADM. The absorbance of produced I_3^- was measured at 350 nm by UV-vis spectrophotometer and the calibration curve of the absorbance of I_3^- as a function of H_2O_2 concentration was obtained with a linear correlation between absorbance and concentration in the range of 0.1–1 mM H₂O₂. The experimental error in the determination of H_2O_2 was less than 2%.

Mechanistic studies: Tris(hydroxymethyl) aminomethane Tris (CAS[77-86-1], 99%, Aldrich, Wuhan, China), acetoacetanilide AAA (CAS[102-01-2], 98%, Macklin, Wuhan, China), ammonium acetate NH₄Ac (CAS[631-61-8], 98%, Sinopharm, Wuhan, China) and formaldehyde CH₂O (CAS[50-00-0], Sinopharm, 37% wt.%, Wuhan, China) were used in mechanistic studies. The experiments were carried out by using Tris as HO· scavenger (forming CH₂O) to quantify the produced HO· indirectly. It is known that the amount of formed CH₂O is quantitatively correlated with that of HO· [17]. The decomposition experiments were carried out in 100 mM Tris solution with fixed quantities of CDots/g-C₃N₄ (SA/V = 4×10^5 m⁻¹, SA and V stands for the surface area of solid and the volume of solution) and H₂O₂ (5 mM). The pH values of solution were selected within the valid buffering range of Tris, namely pH 7.0–9.0 for investigating the effect of pH. The produced CH₂O was quantitatively determined by a modified Hantzsch method, where CH₂O reacts with AAA in the presence of NH₄Ac to form a dihydropyridine derivative with a maximum absorbance wavelength at 368 nm [19]. The calibration curve where the absorbance of produced dihydropyridine derivative was plotted as a function of CH₂O concentration with linear correlation was obtained at 368 nm in the range of 0.04–1.3 mM CH₂O for the conversion of absorbance to CH₂O concentration. The experimental error in the determination of CH₂O was less than 2%.

4. Conclusions

In this work, a promising catalyst CDots/g-C₃N₄ composite for degradation of non-biodegradable organic pollutants was synthesized via a two-step pathway including electrochemical exfoliation of graphite rod preparing CDots and thermal polymerization of CDots mixed urea. Through different characterization methods and kinetic experiments, it has been confirmed that CDots embed in g-C₃N₄ matrix and such structure accounts for the synergetic catalytic performance of the composite. Kinetics of catalytic decomposition of H₂O₂ on CDots/g-C₃N₄ composite were researched. The second-order rate constant (k₂) was measured to be $(1.42 \pm 0.07) \times 10^{-9} \text{ m} \cdot \text{s}^{-1}$ and the activation energy of the reaction was measured to be $(29.05 \pm 0.80) \text{ kJ} \cdot \text{mol}^{-1}$ under the applied conditions. The effect of pH (pH 7.0–9.0) on the production of HO· was also investigated by using Tris as a probe. It has been shown that the production of HO· is strongly alkaline dependent and the maximum reaches at pH 8.0 which is close to the pKa of Tris. A mechanism based on the *adsorb-catalyze* double reaction site theory has been proposed. This work implies that the photocatalyst (CDots/g-C₃N₄ composite) for water splitting or H₂ evolution may also be applied as an alternative catalyst in degradation of non-biodegradable organic pollutants. The instinct kinetics and the mechanism can be referred to for further applications in related fields.

Author Contributions: M.Y. conceived and designed the experiments; Z.L. and Q.S. performed the experiments; C.Z. and L.F. analyzed the data; T.X. contributed reagents/materials/analysis tools; M.Y. and Z.L. wrote the paper.

Funding: This work is supported by National Natural Science Foundation of China (21707108) and Independent Innovation Foundation of Wuhan University of Technology (20411057 and 20410962).

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. He, J.; Yang, X.F.; Men, B.; Wang, D.S. Interfacial mechanisms of heterogeneous Fenton reactions catalyzed by iron-based materials: A review. *J. Environ. Sci.* **2016**, *39*, 97–109. [CrossRef] [PubMed]
- 2. Nidheesh, P.V.; Gandhimathi, R.; Ramesh, S.T. Degradation of dyes from aqueous solution by Fenton processes: A review. *Environ. Sci. Pollut. Res.* **2013**, *20*, 2099–2132. [CrossRef] [PubMed]
- 3. Aval, A.E.; Hasani, A.H.; Omrani, G.A.; Karbassi, A. Removal of Landfill Leachate's Organic load by modified Electro-Fenton process. *Int. J. Electrochem. Sci.* 2017, 12, 9348–9363. [CrossRef]
- 4. Huang, J.; Shi, Q.; Feng, J.; Chen, M.; Li, W.; Li, L. Facile pyrolysis preparation of rosin-derived biochar for supporting silver nanoparticles with antibacterial activity. *Compos. Sci. Technol.* **2017**, *145*, 89–95. [CrossRef]
- Freyria, F.S.; Armandi, M.; Compagnoni, M.; Ramis, G.; Rossetti, I.; Bonelli, B. Catalytic and Photocatalytic Processes for the Abatement of N-Containing Pollutants from Wastewater. Part 2: Organic Pollutants. *J. Nanosci. Nanotechnol.* 2017, 17, 3654–3672. [CrossRef]
- Chen, C.Y.; Tang, C.; Wang, H.F.; Chen, C.M.; Zhang, X.Y.; Huang, X.; Zhang, Q. Oxygen Reduction Reaction on Graphene in an Electro-Fenton System: In Situ Generation of H₂O₂ for the Oxidation of Organic Compounds. *Chemsuschem* 2016, *9*, 1194–1199. [CrossRef] [PubMed]
- Santos, L.V.D.; Meireles, A.M.; Lange, L.C. Degradation of antibiotics norfloxacin by Fenton, UV and UV/H₂O₂. J. Environ. Manag. 2015, 154, 8–12. [CrossRef] [PubMed]
- Li, Y.G.; Hsieh, W.P.; Mahmudov, R.; Wei, X.M.; Huang, C.P. Combined ultrasound and Fenton (US-Fenton) process for the treatment of ammunition wastewater. *J. Hazard. Mater.* 2013, 244, 403–411. [CrossRef] [PubMed]
- 9. Nidheesh, P.V. Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: A review. *RSC Adv.* **2015**, *5*, 40552–40577. [CrossRef]
- Oller, I.; Malato, S.; Sanchez-Perez, J.A. Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review. *Sci. Total Environ.* 2011, 409, 4141–4166. [CrossRef] [PubMed]
- 11. Bokare, A.D.; Choi, W. Review of iron-free Fenton-like systems for activating H₂O₂ in advanced oxidation processes. *J. Hazard. Mater.* **2014**, 275, 121–135. [CrossRef] [PubMed]
- 12. Li, P.; Xie, T.; Duan, X.; Yu, F.B.; Wang, X.; Tang, B. A New Highly Selective and Sensitive Assay for Fluorescence Imaging of OH in Living Cells: Effectively Avoiding the Interference of Peroxynitrite. *Chem. Eur. J.* **2010**, *16*, 1834–1840. [CrossRef] [PubMed]
- 13. Cao, Y.Q.; Sui, D.D.; Zhou, W.J.; Lu, C. Highly selective chemiluminescence detection of hydroxyl radical via increased pi-electron densities of rhodamine B on montmorillonite matrix. *Sens. Actuators B Chem.* **2016**, 225, 600–606. [CrossRef]
- Jing, Y.; Chaplin, B.P. Mechanistic Study of the Validity of Using Hydroxyl Radical Probes to Characterize Electrochemical Advanced Oxidation Processes. *Environ. Sci. Technol.* 2017, *51*, 2355–2365. [CrossRef] [PubMed]
- 15. Yang, X.F.; Guo, X.Q. A novel fluorescence probe for the determination of hydroxyl radicals. *Chem. J. Chin. Univ.* **2001**, *22*, 396–398.
- 16. Fisher, S.C.; Schoonen, M.A.A.; Brownawell, B.J. Phenylalanine as a hydroxyl radical-specific probe in pyrite slurries. *Geochem. Trans.* **2012**, *13*, 1–18. [CrossRef] [PubMed]
- 17. Yang, M.; Jonsson, M. Evaluation of the O₂ and pH Effects on Probes for Surface Bound Hydroxyl Radicals. *J. Phys. Chem. C* **2014**, *118*, 7971–7979. [CrossRef]
- 18. Lousada, C.M.; Jonsson, M. Kinetics, Mechanism, and Activation Energy of H₂O₂ Decomposition on the Surface of ZrO₂. *J. Phys. Chem. C* **2010**, *114*, 11202–11208. [CrossRef]
- 19. Nash, T. The colorimetric estimation of formaldehyde by means of the Hantzsch reaction. *Biochem. J.* **1953**, 55, 416–421. [CrossRef] [PubMed]

- 20. Zheng, P.; Pan, Z.; Zhang, J. Synergistic Enhancement in Catalytic Performance of Superparamagnetic Fe3O4@Bacilus subtilis as Recyclable Fenton-Like Catalyst. *Catalysts* **2017**, *7*, 349. [CrossRef]
- 21. Yang, H.; Shi, B.; Wang, S. Fe Oxides Loaded on Carbon Cloth by Hydrothermal Process as an Effective and Reusable Heterogenous Fenton Catalyst. *Catalysts* **2018**, *8*, 207. [CrossRef]
- 22. Yang, M.; Zhang, X.; Grosjean, A.; Soroka, I.; Jonsson, M. Kinetics and Mechanism of the Reaction between H₂O₂ and Tungsten Powder in Water. *J. Phys. Chem. C* **2015**, *119*, 22560–22569. [CrossRef]
- 23. Hiroki, A.; LaVerne, J.A. Decomposition of Hydrogen Peroxide at Water–Ceramic Oxide Interfaces. *J. Phys. Chem. B* 2005, *109*, 3364–3370. [CrossRef] [PubMed]
- 24. Domínguez, C.M.; Quintanilla, A.; Ocón, P.; Casas, J.A.; Rodriguez, J.J. The use of cyclic voltammetry to assess the activity of carbon materials for hydrogen peroxide decomposition. *Carbon* **2013**, *60*, 76–83. [CrossRef]
- 25. Lousada, C.M.; Trummer, M.; Jonsson, M. Reactivity of H₂O₂ towards different UO2-based materials: The relative impact of radiolysis products revisited. *J. Nuclear Mater.* **2013**, 434, 434–439. [CrossRef]
- 26. Vilardi, G.; Di Palma, L.; Verdone, N. On the critical use of zero valent iron nanoparticles and Fenton processes for the treatment of tannery wastewater. *J. Water Process Eng.* **2018**, *22*, 109–122. [CrossRef]
- 27. Björkbacka, Å.; Yang, M.; Gasparrini, C.; Leygraf, C.; Jonsson, M. Kinetics and mechanisms of reactions between H₂O₂ and copper and copper oxides. *Dalton Trans.* **2015**, *44*, 16045–16051. [CrossRef] [PubMed]
- Lousada, C.M.; LaVerne, J.A.; Jonsson, M. Enhanced hydrogen formation during the catalytic decomposition of H₂O₂ on metal oxide surfaces in the presence of HO radical scavengers. *Phys. Chem. Chem. Phys.* 2013, 15, 12674–12679. [CrossRef] [PubMed]
- 29. Pignatello, J.J.; Oliveros, E.; MacKay, A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 1–84. [CrossRef]
- 30. Diya'uddeen, B.H.; Aziz, A.R.A.; Daud, W.M.A.W. On the Limitation of Fenton Oxidation Operational Parameters: A Review. *Int. J. Chem. React. Eng.* **2012**, *10*, 1498–1502. [CrossRef]
- 31. Garcia-Segura, S.; Bellotindos, L.M.; Huang, Y.H.; Brillas, E.; Lu, M.C. Fluidized-bed Fenton process as alternative wastewater treatment technology-A review. *J. Taiwan Inst. Chem. Eng.* **2016**, *67*, 211–225. [CrossRef]
- 32. Pouran, S.R.; Raman, A.A.A.; Daud, W.M.A.W. Review on the application of modified iron oxides as heterogeneous catalysts in Fenton reactions. *J. Clean. Prod.* **2014**, *64*, 24–35. [CrossRef]
- Yao, Y.J.; Chen, H.; Lian, C.; Wei, F.Y.; Zhang, D.W.; Wu, G.D.; Chen, B.J.; Wang, S.B. Fe, Co, Ni nanocrystals encapsulated in nitrogen-doped carbon nanotubes as Fenton-like catalysts for organic pollutant removal. *J. Hazard. Mater.* 2016, *314*, 129–139. [CrossRef] [PubMed]
- Zhou, F.Y.; Lu, C.; Yao, Y.Y.; Sun, L.J.; Gong, F.; Li, D.W.; Pei, K.M.; Lu, W.Y.; Chen, W.X. Activated carbon fibers as an effective metal-free catalyst for peracetic acid activation: Implications for the removal of organic pollutants. *Chem. Eng. J.* 2015, 281, 953–960. [CrossRef]
- 35. Zhu, Z.D.; Pan, H.H.; Murugananthan, M.; Gong, J.Y.; Zhang, Y.R. Visible light-driven photocatalytically active g-C₃N₄ material for enhanced generation of H₂O₂. *Appl. Catal. B Environ.* **2018**, 232, 19–25. [CrossRef]
- Jiang, G.D.; Yang, X.X.; Wu, Y.; Li, Z.W.; Han, Y.H.; Shen, X.D. A study of spherical TiO₂/g-C₃N₄ photocatalyst: Morphology, chemical composition and photocatalytic performance in visible light. *Mol. Catal.* 2017, 432, 232–241. [CrossRef]
- Yan, J.; Fan, Y.M.; Lian, J.B.; Zhao, Y.; Xu, Y.G.; Gu, J.M.; Song, Y.H.; Xu, H.; Li, H.M. Kinetics and mechanism of enhanced photocatalytic activity employing ZnS nanospheres/graphene-like C₃N₄. *Mol. Catal.* 2017, 438, 103–112. [CrossRef]
- Bicalho, H.A.; Lopez, J.L.; Binatti, I.; Batista, P.F.R.; Ardisson, J.D.; Resende, R.R.; Lorencon, E. Facile synthesis of highly dispersed Fe(II)-doped g-C₃N₄ and its application in Fenton-like catalysis. *Mol. Catal.* 2017, 435, 156–165. [CrossRef]
- Zhang, M.L.; Yao, Q.F.; Guan, W.J.; Lu, C.; Lin, J.M. Layered Double Hydroxide-Supported Carbon Dots as an Efficient Heterogeneous Fenton-Like Catalyst for Generation of Hydroxyl Radicals. *J. Phys. Chem. C* 2014, 118, 10441–10447. [CrossRef]
- 40. Wang, K.; Li, Q.; Liu, B.S.; Cheng, B.; Ho, W.K.; Yu, J.G. Sulfur-doped g-C₃N₄ with enhanced photocatalytic CO₂-reduction performance. *Appl. Catal. B Environ.* **2015**, *176*, 44–52. [CrossRef]
- Zhao, D.M.; Chen, J.; Dong, C.L.; Zhou, W.; Huang, Y.C.; Mao, S.S.; Guo, L.J.; Shen, S.H. Interlayer interaction in ultrathin nanosheets of graphitic carbon nitride for efficient photocatalytic hydrogen evolution. *J. Catal.* 2017, 352, 491–497. [CrossRef]

- Zhou, M.; Yang, P.J.; Yuan, R.S.; Asiri, A.M.; Wakeel, M.; Wang, X.C. Modulating Crystallinity of Graphitic Carbon Nitride for Photocatalytic Oxidation of Alcohols. *Chemsuschem* 2017, 10, 4451–4456. [CrossRef] [PubMed]
- 43. Lin, K.Y.A.; Lin, J.T. Ferrocene-functionalized graphitic carbon nitride as an enhanced heterogeneous catalyst of Fenton reaction for degradation of Rhodamine B under visible light irradiation. *Chemosphere* **2017**, *182*, 54–64. [CrossRef] [PubMed]
- 44. Liu, J.; Liu, Y.; Liu, N.Y.; Han, Y.Z.; Zhang, X.; Huang, H.; Lifshitz, Y.; Lee, S.T.; Zhong, J.; Kang, Z.H. Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. *Science* 2015, 347, 970–974. [CrossRef] [PubMed]
- Liu, Q.; Chen, T.; Guo, Y.; Zhang, Z.; Fang, X. Ultrathin g-C₃N₄ nanosheets coupled with carbon nanodots as 2D/0D composites for efficient photocatalytic H₂ evolution. *Appl. Catal. B Environ.* 2016, 193, 248–258. [CrossRef]
- 46. Oh, J.; Lee, J.M.; Yoo, Y.; Kim, J.; Hwang, S.J.; Park, S. New insight of the photocatalytic behaviors of graphitic carbon nitrides for hydrogen evolution and their associations with grain size, porosity, and photophysical properties. *Appl. Catal. B Environ.* **2017**, *218*, 349–358. [CrossRef]
- Liu, J.H.; Zhang, Y.W.; Lu, L.H.; Wu, G.; Chen, W. Self-regenerated solar-driven photocatalytic water-splitting by urea derived graphitic carbon nitride with platinum nanoparticles. *Chem. Commun.* 2012, *48*, 8826–8828. [CrossRef] [PubMed]
- Su, Y.H.; Chen, P.; Wang, F.L.; Zhang, Q.X.; Chen, T.S.; Wang, Y.F.; Yao, K.; Lv, W.Y.; Liu, G.G. Decoration of TiO₂/g-C₃N₄ Z-scheme by carbon dots as a novel photocatalyst with improved visible-light photocatalytic performance for the degradation of enrofloxacin. *RSC Adv.* 2017, *7*, 34096–34103. [CrossRef]
- 49. Fang, S.; Xia, Y.; Lv, K.L.; Li, Q.; Sun, J.; Li, M. Effect of carbon-dots modification on the structure and photocatalytic activity of g-C₃N₄. *Appl. Catal. B Environ.* **2016**, *185*, 225–232. [CrossRef]
- 50. Wang, X.F.; Cheng, J.J.; Yu, H.G.; Yu, J.G. A facile hydrothermal synthesis of carbon dots modified g-C₃N₄ for enhanced photocatalytic H₂-evolution performance. *Dalton Trans.* **2017**, *46*, 6417–6424. [CrossRef] [PubMed]
- 51. Wang, F.L.; Chen, P.; Feng, Y.P.; Xie, Z.J.; Liu, Y.; Su, Y.H.; Zhang, Q.X.; Wang, Y.F.; Yao, K.; Lv, W.Y.; et al. Facile synthesis of N-doped carbon dots/g-C₃N₄ photocatalyst with enhanced visible-light photocatalytic activity for the degradation of indomethacin. *Appl. Catal. B Environ.* **2017**, *207*, 103–113. [CrossRef]
- Dadigala, R.; Bandi, R.; Gangapuram, B.R.; Guttena, V. Carbon dots and Ag nanoparticles decorated g-C₃N₄ nanosheets for enhanced organic pollutants degradation under sunlight irradiation. *J. Photochem. Photobiol. A* 2017, 342, 42–52. [CrossRef]
- 53. Zhang, H.; Zhao, L.X.; Geng, F.L.; Guo, L.H.; Wan, B.; Yang, Y. Carbon dots decorated graphitic carbon nitride as an efficient metal-free photocatalyst for phenol degradation. *Appl. Catal. B Environ.* **2016**, *180*, 656–662. [CrossRef]
- 54. Lousada, C.M.; Yang, M.; Nilsson, K.; Jonsson, M. Catalytic decomposition of hydrogen peroxide on transition metal and lanthanide oxides. *J. Mol. Catal. A-Chem.* **2013**, *379*, 178–184. [CrossRef]
- 55. Yang, M.; Jonsson, M. Surface reactivity of hydroxyl radicals formed upon catalytic decomposition of H₂O₂ on ZrO₂. *J. Mol. Catal. A Chem.* **2015**, 400, 49–55. [CrossRef]
- 56. Fidalgo, A.B.; Dahlgren, B.; Brinck, T.; Jonsson, M. Surface Reactions of H₂O₂, H₂, and O₂ in Aqueous Systems Containing ZrO₂. *J. Phys. Chem. C* **2016**, *120*, 1609–1614. [CrossRef]
- 57. Pirsaheb, M.; Moradi, S.; Shahlaei, M.; Farhadian, N. Application of carbon dots as efficient catalyst for the green oxidation of phenol: Kinetic study of the degradation and optimization using response surface methodology. *J. Hazard. Mater.* **2018**, *353*, 444–453. [CrossRef] [PubMed]
- Lousada, C.M.; Johansson, A.J.; Brinck, T.; Jonsson, M. Mechanism of H₂O₂ Decomposition on Transition Metal Oxide Surfaces. J. Phys. Chem. C 2012, 116, 9533–9543. [CrossRef]
- Ming, H.; Ma, Z.; Liu, Y.; Pan, K.; Yu, H.; Wang, F.; Kang, Z. Large scale electrochemical synthesis of high quality carbon nanodots and their photocatalytic property. *Dalton Trans.* 2012, *41*, 9526–9531. [CrossRef] [PubMed]
- Wei, Q.Y.; Yan, X.Q.; Kang, Z.; Zhang, Z.; Cao, S.Y.; Liu, Y.C.; Zhang, Y. Carbon Quantum Dots Decorated C₃N₄/TiO₂ Heterostructure Nanorod Arrays for Enhanced Photoelectrochemical Performance. *J. Electrochem. Soc.* 2017, *164*, H515–H520. [CrossRef]

- Guo, F.; Shi, W.L.; Guan, W.S.; Huang, H.; Liu, Y. Carbon dots/g-C₃N₄/ZnO nanocomposite as efficient visible-light driven photocatalyst for tetracycline total degradation. *Sep. Purif. Technol.* 2017, 173, 295–303. [CrossRef]
- Hochanadel, C.J. Effects of Cobalt γ-Radiation on Water and Aqueous Solutions. J. Phys. Chem. 1952, 21, 587–594. [CrossRef]
- 63. Ghormley, J.A.; Stewart, A.C. Effects of γ-Radiation on Ice¹. J. Am. Chem. Soc. **1956**, 78, 2934–2939. [CrossRef]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).