Synergistic effect of citric acid and carbon dots modified g-C$_3$N$_4$ for enhancing photocatalytic reduction of Cr(VI)

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ABSTRACT

Carbon dot (CD)-modified graphitic carbon nitride (g-C$_3$N$_4$) photocatalysts were synthesized through a one-step homogeneous thermal pyrolysis. The synergetic effect of citric acid (Cit) and g-C$_3$N$_4$/CDs for high-performance visible light Cr(VI) photocatalytic reduction had been investigated. Cit was not only acted as a hole scavenger, but might also form surface charge transfer complexes (CTC) with g-C$_3$N$_4$ which delivered electrons on the Highest Occupied Molecular Orbital (HOMO) of Cit to the conduction band (CB) of g-C$_3$N$_4$. CDs decorated on g-C$_3$N$_4$ could provide channels for the preferential transfer of electrons on CTC to the CB of g-C$_3$N$_4$ as well as improved separation of the charge carriers. Owing to these synergistic effects, g-C$_3$N$_4$/CDs displayed much higher photocatalytic performance for the reduction of Cr(VI), which was 1.89 times higher than g-C$_3$N$_4$. Moreover, the synergetic photocatalytic reduction mechanisms of aqueous Cr(VI) were proposed to elucidate the active species formation and photogenerated electron transfer. The results suggested that the in situ generated hydrogen peroxide (H$_2$O$_2$) dominated the reduction of Cr(VI). The addition of Cit could trigger the in situ generation of H$_2$O$_2$ and the decorated CDs further enhanced the reaction. This work demonstrated the role of widely existed Cit on the photocatalytic reduction of Cr(VI) in natural aquatic environment.

Key words | CDs, chromium (VI), citric acid, g-C$_3$N$_4$, hydrogen peroxide (H$_2$O$_2$)

HIGHLIGHTS

- g-C$_3$N$_4$/CD photocatalysts were synthesized for Cr(VI) reduction.
- CDs promoted light harvest and improved the separation of charge carriers.
- Cit triggered the visible light photocatalytic reduction of Cr(VI) over g-C$_3$N$_4$/CDs.
- H$_2$O$_2$ is the main effective activator for Cr(VI) reduction in the g-C$_3$N$_4$/Cit system.
- The photocatalytic reduction pathways of Cr(VI) in the presence of cit were proposed.
GRAPHICAL ABSTRACT

INTRODUCTION

Chromium contamination in aquatic ecosystems is a critical issue owing to natural processes and the escalating worldwide use in many industrial and manufacturing processes, such as mining, electroplating, leather tanning, and pigmentation (Patnaik et al. 2018). Generally, chromium mainly exists as nontoxic trivalent chromium (Cr(III)) and highly toxic hexavalent chromium (Cr(VI)) in the aqueous environment (Rong et al. 2018). Cr(III) is a necessary trace element for human beings and has low solubility and toxicity in the environment (He et al. 2019). Further, Cr(VI) is a highly toxic contaminant that can greatly threaten human health (Xiao et al. 2018). Therefore, the reduction of Cr(VI) to Cr(III) is an effective way for the removal of Cr(VI) in aqueous solutions (Huang et al. 2017).

In recent years, the photocatalytic reduction technique, especially using visible light-driven catalysis, has drawn intensive attention due to its high efficiency, low cost, and nontoxicity (He et al. 2019). Various types of photocatalysts have been developed for the photocatalytic reduction of Cr(VI) under visible light irradiation. Among them, g-C₃N₄ has been widely studied as a metal-free semiconductor photocatalyst in the field of environmental photocatalysis due to its facile preparation, nontoxicity, low cost, and high thermal and chemical stability (Chen et al. 2019). However, the efficiency of photocatalytic reduction of aqueous Cr(VI) over g-C₃N₄ is poor in practical applications due to its low surface area, high recombination rate of the photogenerated carriers and bulk-layered structure, which limits the surface migration of photogenerated carriers and increases the mass transfer resistance in the photocatalytic reaction (Hu et al. 2014; Du et al. 2019). To improve the photocatalytic activity of g-C₃N₄, several strategies have been undertaken, including doping (Wang et al. 2015; Chen et al. 2017), coupling with other materials to form hybrids (Huang et al. 2017; Yang et al. 2018), modifying with carbon materials (Christoforidis et al. 2018; Wang et al. 2020), and morphology control (Deng et al. 2017; Wang et al. 2019). Nevertheless, the visible light photocatalytic activity of g-C₃N₄-based photocatalysts still needs to be improved in practical applications (Chen et al. 2019).

Carbon dots (CDs), as a new type of nanocarbon, have excellent up-conversion photoluminescence (PL) features and unique photoinduced electron transfer properties, all of which enable the photocatalysts to utilize the full spectrum of sunlight (Shen & Liu 2016; Xie et al. 2018). Due to these remarkable properties, CDs can be integrated with many semiconductors so as to design an efficient photocatalyst by broadening the photo-absorption region and reducing the photoinduced carrier recombination simultaneously (Dong et al. 2013; Lu et al. 2016; Xie et al. 2018). In particular, it has been proven that decorating g-C₃N₄ with CDs can efficiently facilitate the separation of photoinduced electron holes and could improve the photoelectrochemical performance (Wang et al. 2017). Recently, CD-decorated g-C₃N₄ has been employed for an efficient photocatalyst for H₂ evolution (Wang et al. 2017), the degradation of dyes (Zhang et al. 2019), and PPCPs (pharmaceutical and personal care...
products) (Xie et al. 2018). However, there are few reports on CD-doped g-C3N4 for highly efficient photocatalytic reduction of aqueous Cr(VI).

Carboxylic acid (CA) is a type of important natural organic matter. In the process of microbial degradation of root secretions and natural organic matter, CA is mainly released as a reaction intermediate or an end product (Jiang et al. 2019). CA has one or more carboxylic groups, such as malic acid, citric acid and formic acid (Gu et al. 2017; Jiang et al. 2019). It is found that the reactions of direct electron transfer from CAs to Cr(VI) are very slow, so that the half-lives of these reactions are very long. However, the reactions for Cr(VI) reduction can be catalytically facilitated with the addition of surface-bound/dissolved metals, such as TiO2 (Wang et al. 2010), Fe(II)/Fe(III), and Mn(II) (Mu et al. 2018). In such processes, CA not only serves as electron donors but also accelerates the electron transfer between the weak electron donors and Cr(VI) (Sun et al. 2017). Nevertheless, only a few studies have reported the synergetic performance and mechanism in the presence of CA in the g-C3N4 photocatalytic system.

In this study, g-C3N4/CD composites were successfully fabricated via a simple precursor pretreatment strategy using dicyandiamide co-pretreated with citric acid (Cit) as the raw material (Qu et al. 2018). The efficiency of the g-C3N4/CD composite on the photocatalytic reduction of Cr(VI) was quantified, and the effects of CDs were also evaluated. Moreover, Cit, which is a common CA, was induced as a green sacrificial agent in the g-C3N4 photocatalytic system. The roles of the citric acid were studied and the synergetic mechanism in the presence of the citric acid of enhanced photocatalytic activity was deduced. The study shows the potential for the remediation of both Cr(VI)-bearing effluents and natural Cr(VI)-contaminated waters under solar light.

**MATERIALS AND METHODS**

**Chemicals and materials**

Dicyandiamide, Cit, H2SO4, H3PO4, diphenyl carbonyl hydrazine, NaOH, acetone, ethanol (EA), and oxalic acid (OA) were supplied by the Chron Chemical Reagent Co., Ltd. Potassium titanium oxalate, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), catalase (CAT), Na2S2O8, benzoquinone (BQ), and tert butyl alcohol (TBA) were supplied by the Aladdin Industrial Corporation. All the reagents were used as received from commercial suppliers without further purification, and the experimental water used was ultrapure water.

**Preparation of catalysts**

g-C3N4 was prepared by directly heating dicyandiamide (Ong et al. 2016). Typically, 20 g of dicyandiamide was added to an alumina crucible with a cover and then heated to 550 °C at the heating rate of 5 °C per minute in a muffle furnace. After heating for 3 h, the sample was allowed to cool down to room temperature, and the final product was obtained.

The g-C3N4/CD composites were prepared by a one-step homogeneous thermal method (Qu et al. 2018). In typical synthesis, 20 g of dicyandiamide and a certain quality of citric acid were added to an alumina crucible with a cover and then heated to 550 °C at the heating rate of 5 °C per minute in a muffle furnace. After heating for 3 h, the sample was allowed to cool down to room temperature, and the final product was obtained. The g-C3N4/CD composites were prepared with different amounts of CDs (0.005, 0.05, 0.075, and 0.1 wt%) and were denoted to be CNC1–4, respectively. The pure g-C3N4 sample was simply denoted as CN.

**Experimental procedures**

The photocatalytic activities of the synthesized catalysts were evaluated by the reduction of Cr(VI) under visible light irradiation. A 300 W Xe lamp (Perfectlight) equipped with a UV cut filter was used as the visible light source (λ > 420 nm). In a typical experiment, 0.02 g of catalyst was added into a 150 mL mixture solution that included Cr(VI) (0.35 mM) and citric acid (3.5 mM). The solution pH was adjusted to 3 by H2SO4 (1 M) or NaOH (1 M) (Zhang et al. 2016). The suspension, including the Cr(VI) and catalyst, was ultrasonicated for 10 min and magnetically stirred in a dark condition for 30 min to establish adsorption–desorption equilibrium prior to visible light irradiation (Ong et al. 2016). The light source was then switched on, and fixed aliquots of the reaction solution were extracted at predetermined time intervals during irradiation. The concentration of Cr(VI)
was determined using the diphenylcarbazide photometric method at 540 nm by a spectrophotometer (Deng et al. 2017). The detailed determination method is shown in Supplementary Material S1 and S2. To quantify the H$_2$O$_2$ produced, samples collected at certain time intervals were analyzed by the titanium oxalate spectrophotometric method (Liu et al. 2019a, 2019b), and the detailed experimental procedures are shown in Supplementary Material S3. The detailed radical scavenging experiment procedures are shown in Supplementary Material S4. Besides, the electron spin resonance (EPR) measurement procedures are shown in Supplementary Material S5.

**Characterization**

Scanning electron microscopy (SEM) (Hitachi S-4700; Japan) with an acceleration voltage of 15.0 kV and transmission electron microscopy (TEM) (Tecnai G² F20 Super Twin; USA) were used to examine the morphologies and structures of the samples. X-ray diffraction (XRD, X’Pert-pro MPD; Holland Panalytical) with a Cu Kα radiation source was performed to characterize the crystal structure of the samples, with a scanned area of 2θ from 10° to 60°. The light absorption properties of the samples were determined by ultraviolet-visible diffuse reflectance spectroscopy (UV–vis DRS, Shimadzu UV-2600; Japan). The PL spectra of the samples were recorded by a fluorescence spectrophotometer (Hitachi F-7100; Japan). The excitation wavelength was 400 nm, the scanning speed was 1,200 nm min$^{-1}$, and the PMT (photomultiplier tube) voltage was 700 V. The width of excitation slit and emission slit were both 1.0 nm. The atomic surface concentration and valence states of the catalyst were analyzed using X-ray photoelectron spectroscopy (XPS) with a spectrometer (Thermo Scientific EscaLab 250Xi; USA) equipped with an Al Kα X-ray source. (1,486.6 eV) The molecular structural information was determined by Fourier transform infrared spectroscopy (FT-IR, Nicolet iS 10; USA). The surface area was calculated using the multi-point BET (Brunauer–Emmett–Teller) (NOVA 2000e, Surface Area & Pore Size Analyzer; USA) method.

Photoelectrochemical measurements were performed on an electrochemical analyzer (CHI770E, CHN) in a standard three-electrode electrochemical workstation composed of a Pt wire as the counter electrode and Ag/AgCl as the reference electrode. ITO coated with the prepared catalyst served as the working electrode. The reactive radicals formed were identified by EPR using DMPO as the spin-trapping agent. EPR spectra were obtained on a Bruker EMX plus X-band CW EPR spectrometer.

**RESULTS AND DISCUSSION**

Characterization of the photocatalysts

Figure 1(a) shows XRD patterns of the CNC photocatalysts with different contents of CDs and CN. Two distinct
Diffraction peaks at 27.5° and 13.0° were observed from the CNC photocatalyst XRD pattern which were well indexed to the pure g-C3N4 (JCPDS Card No.87-1526). However, the intensity of the (002) peak of CNCs was obviously higher than that of CN. These results indicate that the crystal structure of CN was well preserved (Jiang et al. 2017) and the crystal structure of CNCs tended to be more stable. It is noted that no diffraction peaks of CDs can be observed in the CNCs due to the low content of CDs.

Figure 1(b) displays the FT-IR spectra of the above prepared materials. It can be seen that the CN and CNCs displayed similar FT-IR spectra. In detail, the absorption peak at around 813 cm\(^{-1}\) can be attributed to the stretching vibration of triazine units (Zhao et al. 2012). The absorption peaks observed in the range of 1,200–1,700 cm\(^{-1}\) correspond to the C=N and CN stretching vibration modes (Zhao et al. 2012). The absorption peaks between 3,000 and 3,500 cm\(^{-1}\) can be ascribed to N–H stretching, with few hydrogenated N atoms shown in the CN (Li et al. 2016). Clearly, there are no obvious differences among the FT-IR spectra of the CNCs and CN, which indicate that the introduction of CDs does not change the chemical structure of the CN (Wan et al. 2017).

The surface elemental composition and the chemical bonding of CN and CNC2 were further analyzed by XPS. The survey XPS spectra (Figure 2(a)) reveal that CN and CNC2 contains C, N, and O components (Xing et al. 2015). The C 1s XPS spectra of the two samples display two peaks at 284.8 and 287.9 eV (Figure 2(b)). The peak at 284.8 eV can be attributed to the C–C–C bonds (Lv et al. 2016), whereas the peak at 287.9 eV can be identified as sp\(^3\)-hybridized carbon in an N-containing aromatic ring.

**Figure 2** XPS spectra of CN and CNC2: (a) survey, (b) C 1s, (c) N 1s, and (d) O 1s.
(N–C = N) (Zhang et al. 2015). From Figure 2(c), the N 1s XPS spectra of the samples can be deconvoluted into three peaks at 398.5, 400.0, and 404.4 eV, which can be assigned to N in triazine rings (C–N = C) at 398.5 eV and tertiary N (N–(C)₃) at 400.0 eV. The peak at 404.4 eV corresponds to the π excitations. As displayed in Figure 2(d), the peaks of O 1s at 532.6 eV correspond to the adsorbed water on the catalyst surface (Dong et al. 2013). By comparing the XPS results between CN and CNC2, it is found that the decorated CDs with CN does not change the chemical state of the element and content of CN.

The morphologies of the as-prepared CN and CNC2 were characterized by SEM and TEM, which are depicted in Figure 3. As seen clearly in Figure 3(a) and 3(b), CN and CNC2 form solid agglomerates with a size of several micrometers. Compared with CN, the particles of compound CNC2 were more concentrated, which can improve the catalytic efficiency. However, the presence of CDs can hardly be observed from the SEM images of CNC2, possibly due to the stacking of the CN sheets. Figure 3(c) and 3(d) show the TEM images of the CN and CNC2. The two samples exhibited a bulk-layered graphite-like structure (Liu et al. 2011). It can also be observed that CDs were mono-distributed with an average diameter of 5–7 nm on the surface of the CNC2 composites. The TEM images can fully prove that CN was effectively and completely coupled
with the negatively charged CDs via the homogeneous thermal pyrolysis process.

The N₂ adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore size distributions are displayed in Supplementary Material S6. The high Brunauer–Emmett–Teller (BET) surface area and pore volume of the prepared CNC2 composite were 8.725 m² g⁻¹ and 0.022 cc g⁻¹, while the surface area and the pore volume of CN are 6.055 m² g⁻¹ and 0.015 cc g⁻¹. The results reflect that the CDs have a relative effect on the BET-specific area of CN. The high surface area and pore volume of the CNCs imply that these were more active sites and shortened mass transfer distance, thus facilitating the photocatalytic activity of CNCs.

The optical absorption properties of the as-prepared photocatalysts were examined with UV–vis DRS and PL spectra. Figure 4(a) shows that CN exhibited an absorption edge at 457 nm with a calculated bandgap of 2.71 eV which agrees well with values in the literature (Fettkenhauer et al. 2015). With the increase of CDs, the visible light absorption of CN was enhanced. Particularly, the CNC composites had absorption edges at about 461, 464, 466, and 468 nm that corresponded to the bandgaps ($E_g$) of 2.69, 2.67, 2.66, and 2.65 eV, respectively (Figure 4(b)). The red shift of the adsorption edge means that the introduction of CDs might be favorable for absorption properties under visible light. The bandgap of CN decreased after coupling with CDs, implying that there may be sub-band energy levels between CN and CDs in the bandgap of CNC composites (Tang et al. 2016). These results suggested that CDs can serve as a light-harvesting component for CN so as to improve visible light utilization, which will enhance the photocatalytic performance of the CNC composites under visible light irradiation.

![Figure 4](http://iwaponline.com/aqua/article-pdf/70/4/570/898847/jws0700570.pdf)

**Figure 4** | (a) UV–vis diffuse reflectance spectra of CN and CNCs in the absorbance mode, (b) Tauc plots for estimating the bandgap ($E_g$) values of CN and CNCs and (c) photoluminescence spectra of the prepared samples.
The PL spectra of the obtained samples were obtained in order to investigate the separation and recombination behavior of photogenerated electrons and holes. The PL spectra of the obtained samples are shown in Figure 4(c). It can be seen that CN exhibited a strong emission peak at around 450 nm, which suggested the rapid recombination of photoinduced electron–hole (e−/h+) pairs. After the introduction of CDs, the intensity of the emission peak was significantly suppressed, suggesting that the separation of h+ and e− was improved by CDs modification. This further confirmed the role of CDs as an electron acceptor. The results suggest that CDs can improve the utilization of visible light and facilitate the separation of electron–hole (e−–h+) pairs, which would benefit the photocatalytic performance of the CNC composites under visible light.

**Photoelectrochemical measurements**

Electrochemical experimentation was conducted to further investigate the photoinduced charge transfer and separation behavior. As shown in Figure 5(a), the renewable photocurrent density during the four ‘on-off’ irradiation cycles showed the good stability of the two samples. In addition, the transient photocurrent density of CNC2 was 0.10 μA cm−2, whereas that of CN was less than 0.08 μA cm−2. The increasing photocurrent density indicates that the photoelectrochemical response is enhanced, which means the higher separation and transfer efficiency of the photoinduced carriers. The EIS Nyquist plots of the two samples under illumination conditions are presented in Figure 5(b). Classically, a smaller arc size in an EIS Nyquist plot indicates a more efficient charge-transfer process. The CNC2 electrode exhibited a smaller arc size than the CN electrode, implying that CNC2 is expected faster interfacial charge transfer than CN. Thus, decoration of CN with a suitable amount of CDs successfully made CN to be activated by the visible light in the solar spectrum and facilitated the separation of photogenerated electrons and holes by the built-in electric field, exhibiting excellent photoelectrochemical ability. This result confirmed the effect of CDs on promoting light harvest and electron separation as mentioned above and had good correspondence with PL test results.

**Photocatalytic activity**

The photocatalytic activity of the samples was evaluated by the degradation of Cr(VI) in the presence of citric acid under visible light irradiation. As shown in Figure 6(a), dark adsorption–desorption equilibrium between Cr(VI) and photocatalysts was obtained within 30 min, yet almost no obvious adsorption was observed. The poor adsorption capacity of CN or CNCs for Cr(VI) might be due to the weak electrostatic attraction between the anionic chromate species (HCrO4− and/or Cr2O72−) and the negative charge on the surface of CNCs at pH 3. It can be clearly seen that most of the CNCs showed higher photocatalytic activity than that of CN.
of pure CN and the photocatalytic activity of CNCs increased first and then decreased with an increase in the content of CDs. The zero-order rate constants $k$ of CNCs were calculated to be 0.0057, 0.006, 0.0108, 0.0089, and 0.004 min$^{-1}$, respectively (Figure 6(b)). In addition, CNC2 showed the highest photocatalytic reduction efficiency of Cr(VI), as the zero-order rate constant ($k$) for CNC2 was calculated to be 0.0108 min$^{-1}$, which was 1.89 times higher than that of CN. As described above, CDs on the surface of CN can both enhance the visible light absorption and improve the separation of $h^+$ and $e^-$. Therefore, the Cr(VI) photoreduction of CNC2 is obviously higher than that of CN. Although the hybrid structure of CDs and CN extensively improved the photocatalytic activity of CN, an excessive amount of CDs will inhibit the photocatalysis activity. Excessive CDs could aggregate without forming chemical bonds with CN and can act as charge-recombination centers rather than electron acceptors. As a result, the photocatalytic activity of CNC3 and CNC4 decreased (Pan et al. 2014). As shown in Supplementary Figure S2, the changes of Cr(total), Cr(VI) and Cr(III) during the reaction were also tested.

However, it is worth noting that neither CN nor CNCs alone showed significant photocatalytic reduction efficiency of Cr(VI) under visible light irradiation (Figure 6(c)). But the addition of citric acid (3.5 mM) into an aqueous solution of Cr(VI) (0.35 mM) in the presence of CN or CNCs can significantly accelerate the reduction rate, and it was also found that an increase in citric acid concentration led to faster Cr(VI) reduction (Supplementary Material S7). Moreover, as a common hole scavenger, the addition of ethanol could not accelerate the photocatalytic reduction of Cr(VI).
unlike previous reports (Figure 6(d)) (Du et al. 2019). All the results mean that citric acid can not only be used as a hole scavenger in the g-C₃N₄/CDs–Cit–Cr(VI) system, but the addition of citric acid can also trigger visible light photocatalytic reduction of Cr(VI) over g-C₃N₄/CDs.

**Photocatalytic mechanism for CNC composites**

To clarify the roles of the active species in the photocatalytic Cr(VI) reduction over CNC2 in the presence of Cit, capture experiments in regard to active species were conducted (Figure 7(a)). In detail, TBA (0.4 mmol L⁻¹), BQ (0.4 mmol L⁻¹), Na₂S₂O₈ (0.4 mmol L⁻¹), and CAT (0.07 mg L⁻¹) were introduced to capture ·OH, ·O₂⁻, e⁻, and H₂O₂, respectively. In addition, nitrogen gas was introduced to remove dissolved oxygen gas in the reaction solution to weaken the role of O₂. As shown in Figure 7(a), the efficiency of Cr(VI) reduction was significantly decreased by adding CAT and Na₂S₂O₈. Meanwhile, the Cr(VI) reduction efficiency decreased to some extent when ·OH and ·O₂⁻ were trapped. The k values for Cr(VI) reduction decreased from 0.0108 to 0.0068, 0.0079, 0.0051, and 0.0025 min⁻¹ by adding TBA, BQ, Na₂S₂O₈, and CAT, respectively (Figure 7(b)). On the contrary, the Cr(VI) removal efficiency was slightly enhanced when the solution was bubbling N₂ (k = 0.0121 min⁻¹), attributed to the decreased electron transport to O₂, highlighting the role of e⁻ in this system. In sum, all of the active radicals mentioned above played an important role in the photocatalytic reduction of Cr(VI), especially for the H₂O₂ and e⁻.

As a dominant active oxidative species in the Cr(VI) photoreduction system, the concentration of hydrogen...
peroxide (H$_2$O$_2$) was determined in this system (Figure 8(a)). No significant H$_2$O$_2$ was detected in pure CNC2 or CN systems. About 0.14 mM of H$_2$O$_2$ was generated in the CNC2–Cit system after 80 min of visible light irradiation. However, the generation of H$_2$O$_2$ was lower in the CN–Cit system under the same irradiation condition. This trend is consistent with the observed Cr(VI) photoreduction efficiency (Figure 6(a)). The results inferred that the generation of H$_2$O$_2$ was a crucial step in the photocatalytic reduction of Cr(VI) and the addition of citric acid could facilitate the generation of H$_2$O$_2$.

Firstly, photoexcited semiconductors produced e$^-$ and h$^+$ (Equation (1)) (Liu et al. 2014). Then, it was reported that H$_2$O$_2$ can be generated through water oxidation reaction by holes (i.e., H$_2$O $\rightarrow$ H$_2$O$_2$) (Equation (2)) or oxygen reduction reaction by electrons (i.e., O$_2$ $\rightarrow$ H$_2$O$_2$) (Equations (4)–(7)) in the photocatalytic systems (Qu et al. 2018; Hou et al. 2020; Zhao et al. 2020). The DMPO spin-trapping EPR spectra in Figure 7(c) and 7(d) (Buettner 1987) showed signals of ·O$_2$ in the g-C$_3$N$_4$ and g-C$_3$N$_4$/CD suspensions, confirming the oxygen reduction reaction for the production of H$_2$O$_2$. While in the CNC2–Cit system, the production of H$_2$O$_2$ was not completely suppressed under the N$_2$ atmosphere (Figure 8(b)). Moreover, it can be seen in Figure 7(a) that the generation of H$_2$O$_2$ played a more important role than e$^-$ and ·O$_2$. All the results demonstrated that the oxygen reduction reaction was not the only route for H$_2$O$_2$ generation and the water oxidation reaction might also exist simultaneously in this photocatalytic system. The poor production of H$_2$O$_2$ in the CNC2 or CN systems might be due to the fast charge recombination caused intrinsically by the π–π-conjugated electronic system and the

![Figure 8](http://iwaponline.com/aqua/article-pdf/70/4/570/898847/jws0700570.pdf)

**Figure 8**  | (a) The amount of H$_2$O$_2$ produced by the reaction of CN and CNC2 with Cit in air, (b) the amount of H$_2$O$_2$ produced by the reaction of CNC2 and Cit in air and nitrogen, and (c) the amount of H$_2$O$_2$ produced by the reaction of CNC2 with Cit and EA in air.
limited inhibition of the one-electron reduction of O\textsubscript{2} (Equation (3)) (Hou et al. 2020), while the addition of citric acid can prevent the recombination of electrons and holes and facilitate the generation of H\textsubscript{2}O\textsubscript{2}. The higher production of H\textsubscript{2}O\textsubscript{2} in the CNC–Cit system might be due to the roles of the CDs, which not only act as charge carriers but also hinder the decomposition of H\textsubscript{2}O\textsubscript{2} while promoting an increased production of H\textsubscript{2}O\textsubscript{2} (Hou et al. 2020).

\begin{align*}
g-\text{C}_3\text{N}_4 + \text{hv} &\rightarrow \text{h}^+ + \text{e}^- \quad (1) \\
2\text{H}_2\text{O} + \text{h}^+ &\rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad (2) \\
\text{H}_2\text{O}_2 &\rightarrow 2\text{H}_2\text{O} + \text{O}_2 \quad (3) \\
\text{O}_2 + \text{e}^- &\rightarrow \text{O}_2 \quad (4) \\
\text{O}_2^+ + \text{H}^+ &\rightarrow \text{HO}_2^- \quad (5) \\
\text{HO}_2^- + \text{H}^+ + \text{e}^- &\rightarrow \text{H}_2\text{O}_2 \quad (6) \\
\text{O}_2 + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{H}_2\text{O}_2 \quad (7)
\end{align*}

However, as a common electron donor, the addition of ethanol in the CNC2 suspension cannot produce H\textsubscript{2}O\textsubscript{2} under visible light (Figure 8(c)). It is found that aromatic alcohols and CAs are more able to form charge transfer complexes (CTC) with TiO\textsubscript{2} than aliphatic alcohols which are more sensitive to visible light irradiation and display much higher photocatalysis performance (Wang et al. 2010; Zhang et al. 2020). This phenomenon also exists in other organic substances. Liu et al. (2019a, 2019b) proposed a kind of photosensitization-like mechanism. The electrons on the DCF will be transferred to the g-C\textsubscript{3}N\textsubscript{4} modified by CDs under visible light irradiation, thereby improving the photocatalytic efficiency. Inspired by these studies, we consider that citric acid might form CTC with CNCs surface and play more diverse roles in the production of H\textsubscript{2}O\textsubscript{2}. To prove the possible formation of citric acid surface complexes, a series of tests were carried out on the samples before and after adsorption. Figure 9(a) shows the UV–vis diagram before and after citric acid adsorption. After citric acid is adsorbed on CNC2, the light absorption in the ultraviolet-visible region is significantly enhanced, and the absorption edge is obviously red-shifted. Figure 9(b) presents the PL diagram before and after citric acid adsorption. It is found that the peak of PL decreases after Cit addition, which indicates that Cit can accelerate the separation of e\textsuperscript{−} and h\textsuperscript{+}. However, no obvious change was found in the FT-IR results, and it may be due to the small adsorption capacity of Cit on CNC2 (Supplementary Material, Figure S4). These results indicate that citric acid in the system can transfer its own e\textsuperscript{−} to CNCs under visible light irradiation, thus enhancing the activity of CNCs. Besides, the formed surface complexes might initiate a direct electron transfer to the CNCs conduction band and facilitate the generation of H\textsubscript{2}O\textsubscript{2}. So, the addition of ethanol in the CNC suspension cannot generate H\textsubscript{2}O\textsubscript{2} which might be due to it not being
able to form surface complexes with CNC2. The detailed UV–vis DRS and PL test methods are shown in Supplementary Material S8.

The interaction between H$_2$O$_2$, Cr(VI), and citric acid was also investigated by adding 0.14 mM H$_2$O$_2$ instead of CNCs under visible light. As displayed in Figure 10(a), about 21% of Cr(VI) was removed within 80 min in the H$_2$O$_2$/Cr(VI) system, and the removal rate of Cr(VI) increased to 98% after the addition of citric acid, while the removal rate of Cr(VI) was only 24% in the Cit/Cr(VI) system. This implies that citric acid can greatly enhance the reduction of Cr(VI) by H$_2$O$_2$ under visible light.

According to previous studies, Cr(VI) tends to be reduced to Cr(III) by H$_2$O$_2$ at lower pH (Meichtry et al. 2007). Considering the reduction of Cr(VI) to Cr(III) is a three-electron transfer reaction, the Cr(VI) reduction generally proceeds via the one-, two-, or three-equivalent reduction reactions and thereby inevitably involves highly reactive Cr(V, IV) intermediates (Hu et al. 2014). To identify the intermediates during the photoreduction of Cr(VI), the EPR technique was used. From the EPR spectra in Figure 10(b), the signal centered at $g = 1.977$ was determined and assigned to Cr(V) (Wang et al. 2014). To further prove the production of Cr(V) intermediate, some experiments were carried out. As shown in Supplementary Material, Figure S5, the EPR test results and the reaction activity diagram can correspond. In the reaction between Cr(VI) and H$_2$O$_2$, Cr(VI) was reduced to multi-peroxochromate(V) by H$_2$O$_2$ (Equations (8) and (9)) and the formed peroxochromate(V) species spontaneously re-converted to Cr(VI) via the disproportionation reaction or was directly reduced to Cr(III) (Equations (10) and (11)) (Jiang et al. 2019). It is known that the Cr(V) species ($E^0$(Cr(V)/Cr(IV)) = 1.34 V/SHE) shows higher reduction activity toward Cr(III) than that of Cr(VI) species ($E^0$(Cr(VI)/Cr(V)) = 0.55 V/SHE). Furthermore, citric acid is capable of binding to Cr(V) intermediate during photoreduction of Cr(VI) (Wang et al. 2016; Jiang et al. 2019). When citric acid is introduced into the H$_2$O$_2$/Cr(VI) reaction system, activated citric acid mixed-ligand Cr(V) complexes may be produced through attack of the peroxochromium(V) species by citric acid. The mixed-ligand Cr(V) complexes readily decay via a one-step two-electron transfer reaction with the direct reduction of Cr(V) to Cr(III) instead of the re-conversion of Cr(V) to Cr(VI) (Wang et al. 2016; Jiang et al. 2019). This result can be proved by EPR (Supplementary Material S10). It was found that OH can be generated from the interaction between Cr(VI) and H$_2$O$_2$, but OH disappeared after the addition of citric acid (Wang et al. 2016, 2019). This indicates that the addition of citric acid might inhibit the generation of OH (Equation (10)) and promote the direct reduction of Cr(V) to Cr(III) (Equation (11)) (Wang et al. 2016). Moreover, it is interesting to note that O$_2$ was produced in the process of the Cr(VI)
reduction by H₂O₂, which could be reduced to H₂O₂ by e⁻ to further promote the reaction.

\[
[HCr^{VI}O_4]^- + H_2O_2 + H^+ \rightarrow [Cr^{V}O(O_2)(OH_2)]^+ + O_2 + H_2O \quad (8)
\]

\[
[Cr^{V}O(O_2)(OH_2)]^+ + H_2O_2 \\
\rightarrow [Cr^{V}O_2]_4^{3-} + H^+ + H_2O \quad (9)
\]

\[
[Cr^{V}(O_2)_4]^{3-} + H^+ \rightarrow [Cr^{VI}(O_2)_3(O)]^{2-} + OH \quad (10)
\]

\[
[Cr^{V}(O_2)_4]^{3-} + H^+ \rightarrow Cr^{III} + H_2O + O_2 \quad (11)
\]

In consideration of the above evidence, the mechanism of photocatalytic Cr(VI) reduction over CNCs in the presence of citric acid is proposed, as illustrated in Figure 11. Briefly, citric acid can form surface CTC with CNCs, and electrons on the Highest Occupied Molecular Orbital (HOMO) of citric acid are first activated by the visible light irradiation and further injected into the CB of CNCs. Subsequently, CB electrons can react with the adsorbed oxygen to produce H₂O₂ and the holes can also react with H₂O to form H₂O₂. Cr(VI) can be reduced to Cr(III) through photogenerated electrons on CB and by the generated H₂O₂ as well. Importantly, the enhanced photocatalytic activity of CNCs can be attributed to the CD-mediated efficient electron transfer from the CB of CN to the adsorbed O₂ and Cr(VI).

**Reusability**

The photocatalytic stability is very important for practical applications. Hence, the cycling stability of CNC2 was measured. As seen in Figure 12, CNC2 exhibited inappreciable loss of photocatalytic activity after four-cycle reaction processes. Furthermore, the CNC2 before and after the reaction was tested by XPS (Liu et al. 2014). It was found that the ratio of elements in CNC2 changes before and after the reaction, as shown in Supplementary Material, Table S2. The C element was reduced from 44.39% to 43.15%. The N element decreased from 51.18% to 45.6%, but the O element increased from 4.43% to 11.18%. The change in element ratio may be caused by the slight photodegradation of CNC2, but it does not affect the reuse of CNC2. Through the above test, the high stability of CNC2 composite material in the photocatalytic reaction process is demonstrated.
CONCLUSIONS

In summary, a novel visible light-induced, CD-decorated g-C_3N_4 catalyst has been successfully prepared. CD modification greatly enhances the photocatalytic activity of g-C_3N_4, while an excess amount of CDs blocks the light adsorption. Therefore, CNC2 exhibits the best photocatalytic performance, which is 1.89 times higher than g-C_3N_4 based on the zero-order rate constant (k) for Cr(VI) photoreduction in the presence of citric acid. The impregnation of CDs into g-C_3N_4 not only broadens the absorption spectrum of g-C_3N_4, but also acts as charge carriers for photogenerated electrons (e\(^{-}\)). Moreover, it is found that the generation of H_2O_2 is a crucial step in the photocatalytic reduction of Cr(VI) and citric acid plays an important role for Cr(VI) photoreduction in CNC suspensions. The critical roles of citric acid can be described as follows: (i) it works in sacrificial hole scavenging to deplete the photogenerated holes from the excited CNCs; (ii) it forms CTC with CNCs to enhance the absorption of visible light and accelerate H_2O_2 formation; (iii) it is capable of binding to the Cr(V) intermediate to enhance the reaction between Cr(VI) and H_2O_2. All in all, this paper provides new information that is beneficial for researchers in inspecting the natural attenuation of Cr(VI) contamination in environmental media and in treating Cr(VI) pollutants in industrial effluents.

ACKNOWLEDGEMENTS

This work was supported by the National Key Research and Development Program of China Air Pollution Causes and Control Technology Research (grant no. 2019YFC0214404), Sichuan Science and Technology Program (No. 2020YFG0065), and Science and Technology Major Projects in Sichuan Province (2019KJT0067–2018SZDZX0019).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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