Facile Synthesis of Metal Doped Graphite Carbon Nitride for Photocatalytic Degradation of Tetracycline Under Visible Light Irradiation

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Abstract

Using semiconductor photocatalysts for antibiotic contaminants degradation under visible light has become a hot topic in recent years. Herein, a novel cadmium doped graphite phase carbon nitride (Cd/g-C₃N₄) photocatalyst was successfully constructed via 60 °C oil bath method to degrade tetracycline. Experimental and characterization results revealed that cadmium was well doped at g-C₃N₄ surface and exhibited high intercontact with g-C₃N₄. Meanwhile, Cd/g-C₃N₄ presented excellent electrical conductivity and inhibited the recombination of electron-hole pairs. The introduction of cadmium significantly improved the photocatalytic activity and the degradation efficiency of 10 Cd/g-C₃N₄ reached to 89.09%, which was exceeded 2.0 times than pure g-C₃N₄ (43.99%). Additionally, the quenching experiments and electron spin-resonance tests exhibited holes (h⁺), hydroxyl radicals (•OH) and superoxide radicals (•O₂⁻) were dominated active species in TC degradation. Furthermore, the effects of various conditions on the reaction process, such as different pH, initial TC concentrations and catalyst dosage, were also researched. This work gives a reasonable point to synthesize high-efficiency and economic photocatalysts.

1. Introduction

For the past few years, researchers have been seeking suitable ways to solve the overwhelming environmental problems, especially caused by the continuous increase of population and energy-intensive industry (Abbott 2010, McCauley & Stephens 2012, Wang & Yang 2016). Photocatalysis, as an environmental-friendly process, has become the significant method applied in energy and environmental remediation field (Ge et al. 2011, Liu et al. 2016, Wang et al. 2008, Zhu et al. 2017). Undoubtedly, the most important tasks in photocatalysis research are designing high-efficient, stable and low-cost photocatalysts, which should include excellent light absorption capacity, non-toxic, narrow band gap, controllable morphology and good redox ability (Xiang et al. 2012). Recently, metallic oxides, metallic nitrides, metallic sulfides were developed as excellent photocatalytic material to remove organic pollutants (Chan et al. 2017, Shi et al. 2018, Song et al. 2019, Wang et al. 2018b, Xiao & Jiang 2017, Xu et al. 2019). Whereas, some obvious defects have hindered their further application. In comparison, more recently discovered carbon nitride in several covalent CN allotropes is considered as one of the most promising photocatalysts than metallic photocatalysts (Dong et al. 2012, Samanta et al. 2014, Wang et al. 2008).

Among the five phases (alpha, beta, cubic, quasi-cubic and graphite phase) of carbon nitride, graphite phase carbon nitride (g-C₃N₄) was widely used in organic pollutants degradation, owing to its high physicochemical stability, adjustable electronic structure and molecular tunability (Butchosa et al. 2014, Fan et al. 2016, Liu et al. 2015, Samanta et al. 2014). Particularly, g-C₃N₄, as a metal-free and environmentally benign conjugated catalyst (Lu et al. 2015, Zhou et al. 2013), possesses narrow diffusion length (Yan et al. 2009a), suitable specific surface area and appropriate band gap for absorbing blue light (Chai et al. 2012, Chen et al. 2020, Wang et al. 2020a, Wang et al. 2019, Wang et al. 2020b).

However, the disadvantages of g-C₃N₄ cannot be ignored, such as insufficient light absorption (Li et al. 2009a), and rapid recombination rate of photo-generated carriers (Chang et al. 2018, Zhang & Xia 2011).

Several strategies, including chemical doping, morphological control, electronic structural design and defects engineering have been explored to overcome inherent shortcomings of g-C₃N₄ and subsequently enhance the photocatalytic performance (Gao et al., Katsumata et al. 2014, Ou et al. 2015, Qi et al. 2018). Among these strategies, metal elements doping of g-C₃N₄ is regarded as a fungible and feasible method to improve the photocatalytic performance. And the reported researches have been commonly exhibited the advantages of metal elements doping g-C₃N₄, first of all, metal dopants can generate lone electron pairs in g-C₃N₄ as it interacts with the cations, thus enhancing its ability to capture electrons (Gao et al. 2013, Ong et al. 2016, Wang et al. 2009a). In addition, metal doping can effectively adjust the morphology and crystal phase of g-C₃N₄, thus introducing oxygen vacancies or constructing heterogeneous structures to enhance the photocatalytic activity of the catalyst. Meanwhile, metal doping can extend visible light absorption range, improve charge transfer efficiency, and enhance redox capacity (Fan et al. 2019, Huang et al. 2019, Jun et al. 2013, Liu et al. 2012, Samanta et al. 2014, Schwinghammer et al. 2014, Wang et al. 2018b, Zhao et al. 2014).

In addition, calcination is the most used method to obtain metal doped g-C₃N₄ (Thaweesak et al. 2017, Yan et al. 2010, Zhu et al. 2017), different forms of g-C₃N₄ were synthesized through calcination approach with different parameters (Yu & Wang 2015, Yuan et al. 2014), like nanotube (Gao et al. 2012), hollow sphere (Jun et al. 2013), nanofiber (Tahir et al. 2013), nanowire (Zhang et al. 2016c), nanoribbon (Zhao et al. 2014), nanosheet (Schwinghammer et al. 2014).

In this paper, different proportions of cadmium were introduced into porous g-C₃N₄ photocatalyst to degraded TC via oil bath and calcination method. To the best of our knowledge, there is rarely reported of cadmium doped g-C₃N₄ for photocatalytic degradation. The experimental results of photodegrading TC under visible light irradiation demonstrated that Cd/g-C₃N₄ possessed the higher photocatalytic performance in comparison with that of pure g-C₃N₄. This study offers an innovative viewpoint for g-C₃N₄ modification for further chemistry doped and elaborates the mechanism of cadmium doping for photoactivity improvement in detail.

2. Experiment Part

2.1. Chemicals

All the chemicals were of analytical grade. Cadmium chloride (CdCl₂), melamine, tetracycline (TC), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), anhydrous ethanol, isopropanol (IPA), 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPO), deionized water (H₂O), were employed without further purification.

2.2. Synthesis of g-C₃N₄

g-C₃N₄ was prepared via traditional calcination method and the specific steps were as follows (Wang et al. 2021): Weighing 10 g melamine into a porcelain alumina crucible, covered with tin foil, then the crucible was placed into muff furnace with a heating rate of 10°C /min and kept at 550°C for 3 h. After the porcelain alumina crucible was cooled down to room temperature, the obtained g-C₃N₄ powder was grounded and collected for further use.

2.3. Synthesis of Cd/g-C₃N₄

Cd/g-C₃N₄ was prepared through the thermal polymerization of melamine in the presence of CdCl₂. 1.0 g g-C₃N₄ sample was taken and dissolved in 20 mL of ethanol/H₂O solution (15/5, vol/vol), then put different amounts of CdCl₂ into the solution. After ultrasound for half an hour, the solvent evaporated in an oil bath under magnetic agitation at 60°C. The remaining solids were placed in a petri dish, covered with plastic wrap and dried in vacuum drying oven at 60°C for 24 h, when cooled to room temperature, the obtained samples were poured into a mortar to thoroughly ground. Then the samples were placed into muff furnace with a heating rate of 5°C/ min, kept at 550°C for 3 h. When the product was static cooled, Cd/g-C₃N₄ composite photocatalysts with different cadmium contents were prepared. The product was ground into powder and marked as X Cd/g-C₃N₄, (X = 3, 5, 7, 10, 15, 20, 30) according to different mass ratios.

2.4. Characterization

X-ray diffraction (XRD) of Cd/g-C₃N₄ was obtained by D8 advance via Cu-K α radiation. The scan ranges of 2 θ extended from 10 ° to 80 ° with a scan speed of 8°/min. The morphological structure was obtained on JSM-7800F scanning electron microscopy (SEM). Escalab 250Xi spectrometer via Al K α X-ray source was used to measure X-ray photoelectron spectroscopy (XPS). The morphologies of the catalyst were observed through Jeol 2100F transmission electron microscopy (TEM). The photoluminescence spectra (PL) spectra were investigated by Fluoromax-4 spectrofluorometer at 380 nm excitation wavelength. Fourier transform infrared spectroscopy (FT-IR) was measured by Bruker spectrometer, with the wavenumber ranging from 500 to 4000 cm⁻¹. Ultraviolet– visible diffuse reflectance absorption spectroscopy (UV-Vis DRS) was performed on Cary 300 UV-Vis spectrophotometer scanning from 200 ~ 800 nm. The Brunauer–Emmett–Teller (BET) surface area was carried out by Micromeritics ASAP2460. Electrochemical impedance spectroscopy (ESR) was analyzed by Bruker a300. The total organic carbon (TOC) was tested via Analytikjena multi N/C 2100. The chemical element compositions were also analyzed by the energy dispersive spectroscopy (EDS) mapping images captured on a Zeiss Sigma 300 atomic resolution analytical microscope.

2.5. Photocatalytic process

A 300 W Xenon lamp with 420 nm pass filter in the laboratory was employed to simulate sunlight for catalytic process. Typically, 0.04 g catalyst was weighed and put in a 100 mL beaker. Then 50 mL TC solution at 20 mg/L was poured in the beaker and put it on a blender and set the rotate speed at 450 rpm/s for photocatalysis studies. In order to eliminated the effect of adsorption, we placed the mixture

solutions in the dark and stirred for 0.5 hour until the adsorption-desorption equilibrium. During the light source was added, TC suspension was collected every 10 min with a syringe and filtered with 0.22 μm membrane. The samples were taken 6 times in an hour. Then the concentration of suspension was tested by UV-Vis spectrophotometer with wavelength at 357 nm.

2.6. Photoelectrochemical process

The photoelectrochemical test of catalyst was obtained from the instrument of CHI0-660D workstation. The PEC performance of the $\text{g-C}_3\text{N}_4$ and $\text{Cd/g-C}_3\text{N}_4$ electrodes was evaluated using a normal three-electrode system with 0.2 M Na_2SO_4 solution under illumination or in the dark. In the three electrodes system, Ag/AgCl electrode was reference electrode, Pt electrode was counter electrode and working electrode was 150 μL diluted catalyst adhered to fluorine-doped tin oxide (FTO). The load operation process was depicted as follows: FTO was firstly ultrasonic cleaned in ethanol, acetone and deionized water for three times, respectively. Secondly, 10 mg catalyst was uniformly imported into 150 μL naphthol for ultrasonic oscillation. Finally, 100 μL suspension was evenly dropped onto FTO and dried at 120°C . In the three-electrode system, a 300 W Xenon lamp with 420 nm pass filter in the laboratory was used as light source, then 0.2 M Na_2SO_4 aqueous solution was poured into the system until liquid passed through the catalyst as electrolyte.

3. Results And Discussion

3.1. Structure and morphology

Structure and crystalline phase of pure $\text{g-C}_3\text{N}_4$ and $\text{Cd/g-C}_3\text{N}_4$ were analyzed by XRD. Figure 1a showed two diffraction peaks appear at vicinity of 12.9° (100) and 27.5° (002), which were labeled as the typical graphitic carbon nitride in pure $\text{g-C}_3\text{N}_4$ and in good agreement with the standard XRD pattern of graphitic carbon nitride (JCPDS 87-1526). The in-planar tri-s-triazine structural ordering of the conjugated aromatic system was confirmed by the peak at 12.9° and the distance between the in-plane layers was about 0.69 nm. The peak at 27.5° represented the inter-planar periodic lamellar ordering of typical graphite-like carbon nitride, and the distance between the inter-planar layers was about 0.33 nm, calculated according to Bragg's Law (Lu et al. 2015, Zou et al. 2019). However, the intensities of both two peaks of $\text{Cd/g-C}_3\text{N}_4$ were significantly decreased with the increasing cadmium doping, and the (100) peak almost disappeared, indicating that the introduction of the Cd affected the chemical structure and reduced hydrogen bond effect in the intralayer of $\text{g-C}_3\text{N}_4$, thus decreasing the distance between the inter-planar layers and loose packing of layers in $\text{g-C}_3\text{N}_4$ (Thaweesak et al. 2017, Yu et al. 2016). It is worth noting that the (002) peak displayed a slight shift to higher angles in $\text{Cd/g-C}_3\text{N}_4$ samples, suggesting the decrease of interlayer distance in $\text{Cd/g-C}_3\text{N}_4$. Apparently, there were no peak of cadmium in any form in $\text{Cd/g-C}_3\text{N}_4$ composites compared with pure $\text{g-C}_3\text{N}_4$, which was due to the small content and high dispersion in solution (Jia et al. 2019, Wang et al. 2020b).

The possible functional groups in the g-C₃N₄ and Cd/g-C₃N₄ were determined by FT-IR spectroscopy. As illustrated in Fig. 1b, the Cd/g-C₃N₄ and g-C₃N₄ exhibited almost similar FT-IR features, indicating the primary framework of g-C₃N₄ well preserved after Cd doping. The peak at 809 cm⁻¹ was assigned to the typical out-of-plane bending vibration of tri-s-triazine-based structure (Liu et al. 2020), which verified the presence of triazine units (Yan et al. 2009b) and was consistent with previous findings (Wang et al. 2018a). Four characteristic peaks were found in the region of 1200–1600 cm⁻¹, which appeared at 1245, 1327, 1412 and 1573 cm⁻¹, respectively, indicating that the aromatic C–N heterocycle (C₆N₇) had a distinctive stretching mode (Park et al. 2011). In addition, the O–H bending vibration was observed in all samples at 1630 cm⁻¹ (Sobhana S S et al. 2011). Specifically, the peak at about 1645 cm⁻¹ were the stretching vibration of typical C = N units. The characteristic band at 2173 cm⁻¹ corresponded to terminal cyano groups (C ≡ N) (Yang et al. 2013). The wide region from 3000 to 3500 cm⁻¹ were ascribed to the stretching mode of the N–H in aromatic groups and O–H stretching vibrations, which may be due to partial hydrogenation of exposed nitrogen and the adsorption of water molecules on the surface of the catalyst (Tonda et al. 2014, Wang et al. 2018a, Yan et al. 2016). The spectra of Cd/g-C₃N₄ were basically as same as the pure g-C₃N₄, which confirmed that Cd doping did not change the functional group of g-C₃N₄.

The morphology and microstructure of g-C₃N₄ and Cd/g-C₃N₄ were examined by SEM, and the image of g-C₃N₄ without pre-treatment with CdCl₂ were presented in Fig. 2a and Fig. 2b, which displayed an aggregated, thick irregular platelets and scattered crystals particle structure stacking with bulky nanosheets. The image revealed the pure g-C₃N₄ was consists of randomly folded and stacked tri-s-triazine layers, which were piled up in an irregular manner to formed a porous structure (Narkbuakaew & Sujaridworakun 2020). After the Cd doping, great difference could be seen in Fig. 2c and Fig. 2d, Cd/g-C₃N₄ was composed of layer structure with some uniformly smaller particles on the surface. The thickness of the layer was thinner after employment of CdCl₂, revealing a certain degree of exfoliation of the aggregated thick nanosheets. Additionally, the porosity of the 10 Cd/g-C₃N₄ was obviously increased, which might be related to the produce of light layer cracks during crystal growth process and evaporation of chlorine gas during heating process. Consequently, the increased pores could provide more reaction active sites, thus enhancing the photocatalytic activity.

The detailed microstructure features and subtle morphologies of materials were further surveyed by TEM. As depicted in Fig. 3a and Fig. 3b, it could be clearly seen that the structure of pure g-C₃N₄ was transparent or non-transparent nanosheets because of ultrathin thickness or the overlap of a few nanosheets. Moreover, we could clearly observe a piece of a typical silk nanosheet with smooth external surface and flat layer structures of the obtained g-C₃N₄, which manifested that the graphene-like layers were uniformly distributed and like randomly oriented. Obviously, randomly folded and stacked layer were easily piled up in an irregular manner to an agglomerate. As shown in Fig. 3c and Fig. 3d, the 10 Cd/g-C₃N₄ exhibited a multilayered nanosheets structure and laminated crystallizes with abundant microporous. Further, the cadmium nanoparticles were well doped at g-C₃N₄ surface and exhibited high intercontact with g-C₃N₄, there were many small holes in the nanosheet, which was beneficial for

increasing the specific surface area significantly. Fig. S1 and Table S1 illustrated the weight ratio of Cd/g-C₃N₄ composites, elements C was 25.73%, N was 61.98% and Cd was 12.28%, which illustrated that the cadmium was well doped in the g-C₃N₄ with a slight atomic ratio. All these results proved that Cd/g-C₃N₄ composites were successfully constructed.

The specific BET surface area and the pore size distribution were investigated and depicted in Table S2 and Fig. S2. Obviously, the Cd/g-C₃N₄ sample obtained a larger specific surface area than the monomer g-C₃N₄. Table S2 illustrated the specific surface areas and pore volume of Cd/g-C₃N₄ was 16.46 m²/g and 0.123 cm³/g, whereas monomer g-C₃N₄ was 13.467 m²/g and 0.077 cm³/g. Undoubtedly, larger surface area and increased pore volume of Cd/g-C₃N₄ could increase the contact area and attachment active sites for pollutant, and accelerate the transfer of photogenerated carriers, thus achieving a more efficient degradation rate (Chang et al. 2015). The results of N₂ adsorption-desorption isotherm of g-C₃N₄ and Cd/g-C₃N₄ were exhibited that g-C₃N₄ and 10 Cd/g-C₃N₄ possessed a type IV curve with H3 hysteresis loop, which represented the presence of slit shaped mesoporous structure accumulation of particles (Iqbal et al. 2017). These results were consistent with the previous TEM images, further confirmed that Cd was successfully doped into g-C₃N₄.

The element chemical bonding states and electronic structure details of g-C₃N₄ and 10 Cd/g-C₃N₄ were investigated by XPS analysis. The full spectrum (Fig. 4a) indicated that the composite sample 10 Cd/g-C₃N₄ was consisted of Cd ions and pure g-C₃N₄, which could be seen from the strong peaks of C 1s, N 1s, Cd 3d and a small number of O element. C and N elements were mainly derived from g-C₃N₄, and the presence of Cd was caused by Cd doping. Carbon nitride thermal polymerization process and surface absorption of water and oxygen were the main sources of oxygen element (Chou et al. 2016, Fang et al. 2016, Xue et al. 2019). Additionally, there was no signal of Cl atom (around 200 eV), since Cl atoms were evaporated during heating process (Amirthaganesan et al. 2010).

Figure 4b depicted the peaks of Cd 3d, which were situated at 405.6 eV and 412.4 eV (Zhang et al. 2016a), indicating that the existence of Cd²⁺ in Cd/g-C₃N₄ and further proving the successful doping of Cd. Figure 4c showed the high-resolution C1s spectra, and the two sharp peaks were situated at 284.8 and 288.3 eV, respectively. The former peak at 284.8 eV was specifically on behalf of carbon atoms (C–C bonds), namely graphite or amorphous carbon (Liu et al. 2010, Takanabe et al. 2010), and the latter sharper peak at 288.4 eV resulted from *sp*² C atoms bonded with adjacent N atoms inside the aromatic structure (N–C = N) (Thomas et al. 2008). Three main peaks could be perceived from the high-resolution N 1s spectra (Fig. 4d), and the peak at 398.8 eV originated from *sp*²-bonded N atoms in triazine units (C = N–C) (Li et al. 2009b, Takanabe et al. 2010), and peak at 401.1 eV corresponded to amino groups (C–N–H) from the surface uncondensed bridging N atom (Liu et al. 2010, Thomas et al. 2008), which were similar to previously published literature (Chao et al. 2014, Matanović et al. 2015). The peak at 404 eV was assigned to the effects of surface charging or positive charge localization in the heterocycles (Kong et al. 2018, Zhang et al. 2014, Zhang et al. 2012), or the π – π^* excitations between the stacking interlayers

(Li et al. 2018). Both the high-resolution C 1s and N 1s spectra confirmed the presence of g-C₃N₄. Obviously, both C 1s and N 1s spectra of 10 Cd/g-C₃N₄ sample exhibited an upwards shifted to higher binding energies compared with pure g-C₃N₄. Remarkably, the peak at 404.4 eV of N 1s shifted to 405.6 eV and possessed higher intensity. All these positive shifts may be ascribed to the electrons transfer from g-C₃N₄ to doped Cd²⁺, further proving the strong interaction between Cd and g-C₃N₄ (Ji et al. 2019, Yan et al. 2019).

3.2. Optical properties

The optical absorption characteristics was an evaluation criterion to optical properties and electronic band structures of catalyst. Additionally, the absorption range and capacity of catalysts to light affected the photocatalytic performance. The UV–vis diffuse adsorption spectrum of g-C₃N₄ and Cd/g-C₃N₄ were revealed in Fig. 5. It can be found that there was a threshold value of 465 nm in the intrinsic absorption of bare g-C₃N₄, which was assigned to the bandgap of 2.57 eV (Kong et al. 2018, Wang et al. 2009b, Zhang et al. 2012), based on Tauc equation listed (Luo et al. 2017):

$$(ah\nu)^{1/2} = A(h\nu - E_g)$$

Where a is the absorptivity, h is the Planck's constant, ν is the light frequency, A is the constant. Obviously, the absorption edge of 10 Cd/g-C₃N₄ had a significantly redshift compared with bare g-C₃N₄, which illustrated that 10 Cd/g-C₃N₄ had a narrower band gap (2.29 eV), thus reducing the excitation energy for photogenerated carriers. Moreover, Cd/g-C₃N₄ extended the adsorption edge to near 700 nm and the intensity of light adsorption was significantly enhanced, leading to a significant improvement in the visible light response. The spectral range covered extension is conducive to increasing the generation of electron–hole pairs, which showed effective visible light absorption activity and meant that cadmium doping into g-C₃N₄ lattice greatly enhanced the optical response of g-C₃N₄.

The band gap (E_g) of 10 Cd/g-C₃N₄ was smaller than g-C₃N₄, which further confirmed the improvement of light absorption performance. The above analysis indicated that, with the doping of Cd, the light absorption performance was improved and the band gaps tended to be smaller. Based on this result, it can be inferred that doping g-C₃N₄ with Cd can significantly affect the electronic band structure of g-C₃N₄ and further improves the photocatalytic performance (Ge et al. 2012).

The charge separation, migration and recombination were analyzed by photoluminescence (PL) spectra. Commonly, the weakened PL intensity meant enhanced photoinduced charge carries separation and transfer efficiency. PL spectra of 10 Cd/g-C₃N₄ and g-C₃N₄ excited at 380 nm were indicated in Fig. 6a. Apparently, the strong absorption peak exhibited by pristine g-C₃N₄ at 460 nm was consistent with the absorption edge of the UV diffuse reflection spectrum, which indicated that the recombination of the photogenerated electron – hole pair was severe (Yu et al. 2013). Once cadmium was introduced, the highest intensity position showed a gradual red-shifted from 460 nm of g-C₃N₄ to 490 nm of Cd/g-C₃N₄, which was associated with the band gap narrowing effect (Zou et al. 2019)(Gu et al. 2018). Obviously,

the PL signals of Cd/g-C₃N₄ samples significantly fell with the doping of cadmium and 10 Cd/g-C₃N₄ was the lowest, which illustrated that Cd doping restrained the recombination of photoinduced charge carriers and further proved that 10 Cd/g-C₃N₄ composite possessed the best removing efficiency (Thomas et al. 2008). Figure 6b was a Mott-Schottky plots with flat band potentials at a frequency of 1000 Hz (conduction band potential is equivalent to flat band potential for an n-type semiconductor). Both g-C₃N₄ and 10 Cd/g-C₃N₄ displayed a positive slope, and the slope of 10 Cd/g-C₃N₄ was decreased compare with g-C₃N₄, indicating g-C₃N₄ and 10 Cd/g-C₃N₄ were both n-type semiconductors and the electron donor density in 10 Cd/g-C₃N₄ increased (Jun et al. 2013, Pan et al. 2018, Yang et al. 2013, Yuan et al. 2018, Zhou et al. 2014). Higher donor density is very helpful for improving photocatalytic performance because of the increased electrical conductivity and the mobility of charge carriers (Zhou et al. 2014). The conduction band potential of g-C₃N₄ and 10 Cd/g-C₃N₄ concluded from the Mott-Schottky plots was - 0.84 eV and - 1.02 eV, compared with Ag/AgCl electrodes, corresponding to -0.64 eV and - 0.82 eV vs normal hydrogen electrode (NHE).

Metal elements doping influenced the band edge of catalyst to a great extent, and the redox capacity of semiconductors were evaluated via the band edge position of conduction (E_{CB}) and the valence (E_{VB}), which were formed by N2p and C2p orbital of g-C₃N₄, respectively (Xiong et al. 2016). The E_{CB} and E_{VB} could obtained from following (Zhang et al. 2010):

$$E_{CB} = X - E^e - 0.5 E_g$$

$$E_{VB} = E_{CB} + E_g$$

Where X is electronegativity and E^e is 4.5 eV. Fig. S3 revealed the E_{VB} and E_{CB} positions of as-prepared materials. For pure g-C₃N₄, the E_{VB} was situated at 1.93 eV, on the basis of the experimental E_g (2.57 eV), the E_{CB} was - 0.64 eV. Meanwhile, the E_{VB} of 10 Cd/g-C₃N₄ decreased to 1.47 eV and the E_{CB} climbed to -0.82 eV.

Other photoelectrochemical techniques such as EIS and photocurrent response measurement have been employed to investigate the movement process of photoinduced electrons in prepared materials. Figure 6c revealed the photocurrent responses of g-C₃N₄ and Cd/g-C₃N₄ were repeatable and outstanding photostability under successive on/off illumination cycles. In addition, the photocurrent of g-C₃N₄ could be negligible, and significantly increased photocurrent response density of 10 Cd/g-C₃N₄ was observed, which indicated Cd doping increased the conductivity and separation of electron and hole of g-C₃N₄ (Ren et al. 2017). Electrochemical impedance spectroscopy (EIS) was another method to evaluated the separation and transfer efficiency of photoinduced carriers. The smaller arc radius suggested smaller transfer resistance, namely the better separation efficiency, which meant lower recombination of photoinduced carriers (Lu et al. 2017). The equivalent electrical circuit is illustrated in Fig. 6d, which contained electrolyte solution resistance (R_s), double-layer capacitance (CPE), and charge-transfer resistance (R_p) (Yang et al. 2002). As depicted in Fig. 6d, the arc radius of 10 Cd/g-C₃N₄ was smaller than

pristine g-C₃N₄, which reflected that the charge-transfer resistance of Cd/g-C₃N₄ was much lower than that of pristine g-C₃N₄, and Cd/g-C₃N₄ possessed high-efficiency photoinduced carriers separation ability and faster interfacial charge transport level (Zhu et al. 2015).

3.3. Photocatalytic activities

To test the effect of different content of Cd doping on the degradation performance of the catalyst, we carried out a group of comparative degradation experiments with only changing the content of cadmium under visible-light irradiation ($\lambda > 420$ nm) at room temperature. In this paper, TC was selected as the main contaminant due to the high stability under visible light irradiation. Undoubtedly, the more TC degraded, the better degradation performance of the catalyst. As illustrated in Fig. 7a, the degradation rate of TC without catalysts can be neglected. Furthermore, the adsorption capacity of the doped catalyst is slightly larger than that of pristine g-C₃N₄ during the dark stage, which corresponds to an increase in the specific surface area of the catalyst after doping with Cd. However, the photocatalytic activity of Cd/g-C₃N₄ composites first increases and then decreases with the increase of Cd content, which probably indicates that excessive Cd could serve as photo-carrier's recombination center and inhibited the photocatalytic performance. Moreover, the introduction of excessive Cd may reduce the photo-adsorption ability and cover the surface active site of catalyst, thus hindering the effective migration of charge carriers (Li et al. 2009a, Zhang et al. 2016b, Zhang et al. 2010). Obviously, Cd/g-C₃N₄ samples exhibits great increased photo-decomposition efficiency compared with pure g-C₃N₄ (45.1%) and the 10 Cd/g-C₃N₄ sample showed the greatest photocatalytic performance (89.09%) after an hour light irradiation, which can be attributed to the effective separation and transfer of photogenerated charges originating from the composite interface. All these results concluded that Cd load had significantly improved the photodegradation efficiency.

The pseudo-first-order kinetic model was an alternative analytical method, which could further investigate the performance of the catalyst, the formula is express as the following:

$$\ln (C_t/C_0) = - K_{app}t$$

C₀ is the initial concentrations and C_t is the concentrations at time t of TC, K_{app} is reaction rate constant (min⁻¹), respective. Fig. S4 presented the pseudo-first-order kinetic plots of Cd/g-C₃N₄ and pristine g-C₃N₄. Under the same condition, the degradation rate constant K_{app} of 10 Cd/C₃N₄ ($3.605 \times 10^{-2} \text{ min}^{-1}$) is about 3.6 times that of pristine g-C₃N₄ ($0.99 \times 10^{-2} \text{ min}^{-1}$), demonstrating that 10 Cd/g-C₃N₄ had the best photocatalytic performance, which consisted with the above experimental results. In conclusion, the introduction of cadmium could enhance photodegradation efficiency under light condition.

The effects of different reaction conditions, such as initial concentration of TC, different catalyst dosage and pH value, were studied to meet practical application. Figure 7b displayed the influence of different catalyst dosages on TC photodegradation. It was apparent that the removal rate of TC was enhanced

slightly as the dosages increased (0.4, 0.6, 0.8 and 1.0 g/L) and the catalyst dosages at 1.0 g/L showed the best photocatalytic performance.

The complete removal of TC in the photocatalytic process are crucial to prevent secondary pollution. Therefore, the ability of mineralization is also an important indicator of photocatalysts. Fig. S5 clearly indicated that the mineralization efficiency of TC reached to 34% within 60 min visible light irradiation, which confirmed that Cd/g-C₃N₄ could actually degrade TC into small molecule intermediate compounds or CO₂ and H₂O. The results indicated that Cd/g-C₃N₄ is an excellent photocatalyst for TC degradation.

In this experiment, diluted hydrochloric acid and sodium hydroxide were used to adjust the initial pH. Figure 7c indicated that 10 Cd/g-C₃N₄ performed well in wide pH range. Obviously, the degradation efficiency of TC was 77.2% at pH = 11. While the pH decreased to 7, the degradation efficiency got up to 79.9%, and while the pH decreased to 5, the degradation efficiency increased to 88.5%. It was concluded that photodegradation efficiency was higher in acidic environment than neutral environment and alkaline environment. Initial concentration of TC also had a strong effect on photocatalyst activities in practical application. It could be clearly detected that the removal rates of TC were 88.5%, 78.6%, 56.9% and 50.3% when the initial concentration of TC was 10, 20, 30 and 40 mg/L (Fig. 7d). This result indicated that the degradation rate was higher at low pollutant concentrations and then decreased with pollutant concentration increased. Two possible reasons could be proposed to elucidate this tendency. Firstly, high concentrations of contaminants might accumulate at the surface of catalyst, thus inhibiting the light absorption capacity. Secondly, intermediate products produced in the process of pollutant degradation might occupy the active site, so that pollutant had no contact with the catalyst.

Stability is an effective criterion to evaluated the practicability for semiconductor catalyst, thus, it is of great significance to assess stability of catalysts. The stability tests were carried out by reusing the catalyst under equal condition. It should be noted that the sample was cleaned with ethanol and deionized water, and then, it was dried in an oven at 60°C after each experiment. Figure 8a depicted that the TC degradation rates were slightly descending with the reuse of Cd/g-C₃N₄, which could be attributed to the small loss of sample during the collection after each cycle. The final removal efficiency still maintained at a relative high level, which was about 80.03%. Moreover, no obvious peak changes were found by XRD analysis of the used photocatalyst, indicating the outstanding stability of Cd/g-C₃N₄. Therefore, the Cd/g-C₃N₄ photocatalyst could be deemed as stable materials during the photocatalytic degradation of TC.

3.4. Mechanism

The trapping experiments was used to determine the decisive active species participating in the degradation process (Li et al. 2015). Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), anhydrous ethanol, isopropanol (IPA), 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPO) were added into reaction solution as scavengers to capture h⁺, •OH and •O₂⁻, respectively. Figure 9a and Fig. 9b illustrated that the degradation rate of TC was obviously suppressed by EDTA-2Na and descended from

~ 90 % to 75.38 %, indicating that h^+ was the main active species of Cd/g-C₃N₄ material. On the other hand, the degradation rates decreased slightly when the TEMPO and IPA were added, revealing that $\cdot O_2^-$ and $\cdot OH$ played auxiliary roles in photocatalytic degradation (Yan et al. 2010, Yu et al. 2018).

Electrochemical impedance spectroscopy (ESR) was carried out to verify the above results. As we could see from Fig. 9c and Fig. 9d, it is hard to see the ups and downs signals of free radicals under dark conditions in Cd/g-C₃N₄. However, a strong intensity signals of $\cdot OH$ and $\cdot O_2^-$ radicals could be found under the visible light illumination, which proved that light is prerequisite for catalyst to product active species.

According to all aforementioned results, the introduction of Cd speed up the transmission of electron-hole pairs and decrease the recombination rate of photogenerated charge carriers, providing more reactive sites and accelerating cross-plane diffusion in g-C₃N₄ nanosheets (Iqbal et al. 2017), thus achieving the enhanced photocatalytic property. A brief mechanism of TC degradation was summarized in Scheme 1. The electrons and holes were firstly generated under light irradiation, and the electrons transferred from valence band to conduction band spontaneously, thus leaving holes at valence band and electrons accumulated at conduction band (Eq. (1)). Then, the absorbed O₂ reacted with electrons to formed superoxide radical (Eq. (2)). Further, the surplus electrons reacted with superoxide radical to formed hydrogen peroxide (H₂O₂) (Eq. (3)). As listed in Fig. S3 the E_{CB} of Cd/g-C₃N₄ was - 0.82 eV, which were negative than redox potential of O₂/ $\cdot O_2^-$ (-0.33 eV vs NHE), thus the accumulated electrons could react with O₂ to formed $\cdot O_2^-$. But the E_{VB} of Cd/g-C₃N₄ was + 1.47 eV, which were negative than redox potential of OH⁻/ $\cdot OH$ (2.40 eV vs NHE), consequently, the accumulated holes could not react with OH⁻ to formed $\cdot OH$, which was not consistent with ESR result. Therefore the $\cdot OH$ probably derived from H₂O₂ decomposition (Eq. (4)). From what has been discussed above, $\cdot O_2^-$, $\cdot OH$ and h^+ were worked together to degrade TC into small molecules (Eq. (5)), which was in good agreement with ESR analysis and quenching tests. The reaction equations may be involved in the photocatalytic reaction process are shown below (Jia et al. 2020).

4. Conclusion

In summary, Cd/g-C₃N₄ composites were prepared by mixing dopant agent CdCl₂ with g-C₃N₄ in ethanol/H₂O solution. The degradation experiments demonstrated explicitly that the photocatalytic activity of g-C₃N₄ could be enhanced significantly with the doping of Cd elements, and the best removal efficiency was 89.09%, which was 2.0-times enhanced in comparison with pure g-C₃N₄ (45.1%). Based on the characterization analysis, the enhanced photocatalytic performance could be ascribed to the improved the migration and separation of the photogenerated carriers. Meanwhile, the increased surface area and mesoporous structure extended the photo-absorption region, accelerating the transfer efficiency of light-generated charges. Concurrently, the ultrathin structure and the increased surface area could provide more active sites along with a shortened electron-transfer pathway, which was conducive to inhibiting the recombination of the photogenerated electrons and holes. The present work is expected to provide a new way for metal doped photocatalyst.

Declarations

Authors contributions YZ: Responsible for writing papers, conducting experiments, drawing the chart and analyzing the characterization part. HQ, QL, ZW, HW, ZW, YH, QT, CW: Responsible for reviewing the article and providing suggestions for revisions. PX: Responsible for the revision and typesetting of the paper.

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Figures

Figure 1

(a) XRD patterns of pure g-C₃N₄ and Cd/g-C₃N₄ composites; (b) FT-IR spectra of pure g-C₃N₄ and Cd/g-C₃N₄ composites.

Figure 2

SEM images of g-C₃N₄ (a-b) and 10 Cd/g-C₃N₄ (c-d).

Figure 3

TEM images of g-C₃N₄ (a-b) and 10 Cd/g-C₃N₄ (c-d).

Figure 4

XPS spectra of pure $g\text{-C}_3\text{N}_4$ and $10\text{ Cd/g-C}_3\text{N}_4$. (a) full survey spectrum, (b) high-resolution Cd 3d, (c) high-resolution C 1s, (d) high-resolution N 1s.

Figure 5

(a) UV-vis diffuse reflectance spectra (DRS) and (b) band gap of g-C₃N₄ and 10 Cd/g-C₃N₄ composites.

Figure 6

(a) The PL spectra and (b) Mott-Schottky plots of pure $\text{g-C}_3\text{N}_4$ and $\text{Cd/g-C}_3\text{N}_4$ composites. (c) Photocurrent response spectra and (d) EIS Nyquist plots of pure $\text{g-C}_3\text{N}_4$ and 10 $\text{Cd/g-C}_3\text{N}_4$ composite.

Figure 7

(a) Degradation performance of catalysts curves with different amounts cadmium. Experimental conditions: [Cd/g-C₃N₄]₀ = 0.8 g L⁻¹, [TC]₀ = 20 mg L⁻¹, and T = 25 °C. (b) Degradation efficiency of different catalyst dosages. Experimental conditions: [TC]₀ = 20 mg L⁻¹, and T = 25 °C. (c) Degradation efficiency of Cd/g-C₃N₄ composites with different pH. Experimental conditions: [Cd/g-C₃N₄]₀ = 0.8 g L⁻¹, [TC]₀ = 20 mg L⁻¹, and T = 25 °C. (d) Degradation efficiency of catalyst with different initial TC concentrations. Experimental conditions: [Cd/g-C₃N₄]₀ = 0.8 g L⁻¹, and T = 25 °C.

Figure 8

(a) Degradation efficiency of TC over 10 Cd/g-C3N4 composite under four cycling tests. (b) XRD images of 10 Cd/g-C3N4 before and after four times used.

Figure 9

(a-b) Degradation efficiency of 10 Cd/g-C₃N₄ under different quenchers. ESR spectra for (c) DMPO- $\cdot\text{O}_2^-$ and (d) DMPO- $\cdot\text{OH}$ under dark and visible light condition.

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