Preparation of non-polluting Tb-doped mesoporous carbon nitride photocatalyst and study on the efficacy and mechanism of degradation of antibiotics in water

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Abstract

Given that the biological treatment of antibiotic wastewater can easily induce resistant bacteria, the photocatalytic degradation of antibiotics is considered as a better method for treating antibiotic wastewater. Therefore, the ability to remove Tylosin (TYL) and Tetracycline (TC) in aqueous solution using rare earth element Tb-doped g-C₃N₄ under simulated natural solar radiation was investigated. A series of rare earth Tb³⁺ doped mesoporous g-C₃N₄ were successfully prepared by nitric acid treatment and Tb(NO₃)₃·5H₂O samples showed significantly higher degradation efficiency for TYL and TC than pure g-C₃N₄. Leaching toxicity experiments were carried out on the catalyst using chard seeds and demonstrated negligible toxicity of the leachate from the catalyst. The structure, elemental state, optical properties, morphology, and photogenerated carrier separation of the prepared xTCN catalysts were characterized by XRD, XPS, UV–Vis DRS, TEM, and PL. The results show that Tb doping enhanced the photocatalytic activity of the g-C₃N₄ catalyst by narrowing the band gap while improving the light-trapping ability; The separation and transport rate of photogenerated carriers were significantly increased after Tb doping. Finally, a simple, efficient, and non-polluting Tb-doped carbon nitride photocatalyst is successfully developed in this paper.

Keywords g-C₃N₄ · Photocatalysis · Rare earth elements · Mesoporous structures · Safety assessment · Chlorophyll

Introduction

With the rapid growth of the pharmaceutical industry, the production and use of antibiotics for humans and animals is increasing (Gao and Dai 2018; Wang et al. 2020). Although antibiotics can cure many diseases in a timely manner, large amounts of antibiotic wastewater are increasingly discharged. Because of its high organic content, deep color, the presence of a variety of inhibiting bacteria and the difficulty of biodegradation (Wang et al. 2018b) the wastewater is one of the most widespread environmental pollution, which seriously threatens the ecological environment and human health. For example, tetracycline antibiotics (TC) used in large-scale livestock, poultry and aquaculture have characteristics of good antibacterial activity and inexpensiveness, making them one of the most widely used antibiotic classes (Briones et al. 2016; Hu et al. 2011). However, the structural specificity of antibiotics makes it difficult for residual TC to degrade naturally in the natural environment, and in addition antibiotics inhibit or disrupt microbial growth, so the rate of biodegradation of most TC is much lower than the rate of abiotic degradation (Wang et al. 2017b). Thus there is an urgent need to develop more efficient and greener technologies for pharmaceutical wastewater treatment in order to meet the higher requirements for water safety (Hu et al. 2011; Karageorgou et al. 2014; Wen et al. 2018; Zhang et al. 2015).

Currently, due to the outstanding advantages of easy operation, high catalytic efficiency and low preparation cost, photocatalytic technology has shown great potential in water purification compared with traditional water treatment technology, so how to improve the photocatalytic degradation efficiency has become a research hotspot (Amandeep and Sushil Kumar 2016; Wan Kuen et al. 2018). Compared to other common semiconductor materials, g-C₃N₄ is a metal-free material for organic polymer semiconductors and has the advantages of low production cost, stable physicochemical...
properties, environmental friendliness, suitable forbidden band width and visible photocatalytic activity (Wang and Feng 2018; Fu et al. 2019; Ma et al. 2019; Yan et al. 2009), as well as showing efficient photocatalytic activity in the degradation of TC (Wang et al. 2018b), which is of wide interest to photocatalytic researchers. Nonetheless, for practical applications in energy and environmental photocatalysis, g-C3N4 still suffers from some unavoidable problems, such as fast photogenerated electron–hole complexation, low quantum efficiency and poor visible light absorption, which limit its photocatalytic activity in water decomposition (Li et al. 2017; Wang et al. 2018c, 2018d; Yan et al. 2019). Previously, Zhang et al. investigated the use of g-C3N4 to form a hetero-junction with TiO2 to suppress photogenerated electron vacancies and to provide significant photocatalytic performance for the degradation of TC (Zhang 2020; Zhang et al. 2021). Currently, various types of co-catalysts such as Ag, Mn, Fe, Bi, Cu, and Co and their compounds are doped in g-C3N4 to increase photocatalytic activity (Chen et al. 2009; Ding et al. 2010; Faisal et al. 2016; Jiang and Li 2017; Wang et al. 2017a). Among the metallic elements, the incomplete occupation of 4f and empty 5d orbitals by rare earth elements allows them not only to act as centres for electron capture, but also to increase the light absorption capacity and in the case of photocatalysts, to greatly increase their photoelectric activity (Cerrato et al. 2018; Gao et al. 2018; Zhang et al. 2018). In addition, rare earth ions can use 4f orbitals to interact with a variety of organic functional groups and thus form complexes with a variety of Lewis bases (organic acids, aldehydes, alcohols, and thiols), which can better aggregate organic matter onto the photocatalyst surface and thus improve photocatalytic degradation efficiency (Tang et al. 2013). At the same time rare earth elements are also a traditionally important upconversion luminescent material, but their application in photocatalysis is less reported (Sun et al. 2015; Vignesh et al. 2017; Zhu et al. 2019; Zou et al. 2018). Xu et al. doped Eu into g-C3N4 for the degradation of methylene blue, and the Eu/g-C3N4 catalyst showed well photocatalytic activity in the experiment (Xu et al. 2013). Li et al. prepared new catalysts by doping Er and Sm into g-C3N4 through direct thermal polymerization and characterized that the doping of Er and Sm changed the electronic and chemical properties of g-C3N4 and weakened the fluorescence emission intensity, thus enhancing the photocatalytic activity of g-C3N4 (Li et al. 2020a, 2020b). As a rare-earth element, it also possesses the properties of rare-earth elements, incomplete occupation as well as empty electron orbitals.

Recently, the impact of nanomaterials on the environment is also receiving increasing attention due to their special physical and chemical properties. Photocatalysts based on g-C3N4 as a common nanomaterial are environmentally friendly and free of secondary pollution. Nevertheless, the toxicity of rare-earth doped g-C3N4 has been relatively little studied; Degradation of contaminants in water is one of the main roles of photocatalysts and therefore the leaching toxicity of the catalyst samples in aqueous solution needs to be determined. No team has yet studied the effects of leaching solutions of rare earth doped g-C3N4 on plant growth and on physiology. The germination rate and rhizome length of plant seeds are important growth indicators to reflect the growth state of the plant. When plant seeds are under suitable conditions, they absorb water and swell to germinate, thus enzymatic activity is enhanced. If the leaching solution is toxic, it will inactivate the enzymes and inhibit seed germination, disrupting the germination process and thus affecting the germination potential and germination rate of the seeds (Mazumder et al. 2020). Plant chlorophyll is an important substance for photosynthesis by absorbing solar energy, and the level of chlorophyll in plant leaves is one of the most important physiological indicators of plant growth and development (Mishra et al. 2009; Mobin and Khan 2007; Tripathi et al. 2015).

In the present work, the photocatalytic degradation experiments of antibiotics by g-C3N4 doped with a small amount of Tb3+ ions under simulated solar radiation were investigated. We will prepare new porous nanophotocatalysts by doping terbium into g-C3N4 and protonating it with nitric acid and acting as a gas soft template. Meanwhile, the effects of terbium ion doping concentration on morphology, structure and photocatalytic activity are investigated in detail. The stability and recoverability of the samples were evaluated by repeated experiments of photocatalytic degradation of. The leaching toxicity of xTCN samples were evaluated by germination and growth experiments on cabbage seedlings, and growth indicators (seed germination and rhizome length) and physiological indicators (chlorophyll). In addition, a possible mechanism for the 0.01TCN catalyst to improve the photocatalytic degradation efficiency was proposed.

Materials and methods

Materials and reagents

Melamine (99%), Tb(NO3)3·5H2O (99.9%), TYL (≥ 800 units/mg), and TC (98%) were purchased from Aladdin Co. Nitric acid (AR) was obtained from Yaohua chemical reagent co. LTD (Tianjin, China). All materials do not require further purification and all water used throughout the experiments is deionized water. Cabbage seeds purchased from Farmers’ Market.
Preparation of photocatalyst

To begin with, dissolve an appropriate amount of Tb(NO₃)₃·5H₂O in 7.5 mL of dilute nitric acid (HNO₃), add 2 g of melamine after the sample has completely dissolved and mix well. After drying, the mixture was transferred to a semi-closed crucible with a lid and subsequently heated to 200°C at a rate of 5°C/min and then held for 2 h, then continued to 550°C and held for 2 h. After cooling, the prepared pale yellow fluffy sample was removed and ground well in an agate mortar and pestle. Depending on the molar percentage of Tb(NO₃)₃·5H₂O added to the prepared samples (0.005%, 0.01%, 0.02%), they were named 0.005TCN, 0.01TCN and 0.02TCN respectively. The product yield of xTCN is very stable and unaffected by the addition of Tb(NO₃)₃·5H₂O. Nitric acid treated g-C₃N₄ polymers, labelled HCN, were prepared under the same conditions without the addition of Tb(NO₃)₃·5H₂O.

Pure g-C₃N₄ was prepared according to previous reports. Briefly, 2 g of melamine powder was added to a semi-closed crucible and covered. The crucible was then placed in a muffle and heated to 550°C in air at a rate of 5°C per minute. After cooling to room temperature, the sample was removed and ground to a fine powder, noted as CN.

Characterization

The prepared catalysts were analyzed in crystalline phase using x-ray diffraction (XRD, RigakuD/migaku) of CuKα rays (λ = 1.5406 Å). XRD was performed with an operating current of 50 mA and an accelerating voltage of 40 kV. Chemical bonding in samples using Fourier transform infrared spectroscopy (FT-IR, Shimabu FT-IR8900, with potassium bromide as reference) in the range of 400–4000 cm⁻¹. The UV diffuse reflectance spectrum of the catalyst was obtained using a UV-2550 spectrophotometer (Shimazu) equipped with an integrated sphere using 100% barium sulfate as the reflected light sample. The surface properties of the photocatalysts were studied by x-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, ThermoFisher). The morphology and structure of the prepared samples were characterized using transmission electron microscopy (TEM, JEOL 2100, JEOL Ltd). The samples were characterized by photoluminescence (PL) using a steady-state transient fluorescence spectrometer with an excitation wavelength of 300 nm.

Evaluation of photocatalytic activity

The photocatalytic activity of the Tb-doped g-C₃N₄ catalyst was investigated using TYL and TC as representative antibiotics for degradation. For the experiments carried out simulating solar radiation, a 170 W xenon lamp was used, and the distance between the reactor and the lamp was kept at 2 cm. During photocatalytic degradation, 30 mg of the prepared samples were added to 60 ml of TYL solution (25 mg/L) or TC (25 mg/L), respectively. The prepared mixture is then magnetically stirred under continuous exposure to simulated solar irradiation. The photocatalytic reaction mixture is removed periodically for a certain period of light exposure. The obtained mixed solution was centrifuged at 8000 rpm for 5 min. The concentrations of TYL and TC in the centrifuged solutions were measured using a UV spectrophotometer at visible luminosity wavelengths of 290 nm and 357 nm respectively. For the reusability of 0.01 TCN for antibiotic removal, repeat durability experiments were conducted for antibiotic degradation. After each cycle of the experiment, the TCN was centrifuged, then washed with deionised water and anhydrous ethanol, dried at 60°C and then used for the next cycle of the experiment.

Leaching process and toxicity tests

Photocatalysts have excellent results in degrading wastewater, so we should investigate the leaching toxicity of photocatalysts. Twenty-five milligrams of catalyst was added to 50 mL of deionised water, stirred continuously with magnetic force for 8 h and left to stand for 16 h. The supernatant (leachate) was passed through a 0.45-μm filter membrane for use. Subsequently, 20 cabbage seeds were selected and placed in a Petri dish with filter paper and 5 mL of supernatant was added. Then, petri dishes were incubated in an incubator under dark conditions at a constant temperature of 25°C for 3 days. Three parallel experiments were carried out for each leaching solution using seeds cultured in deionised water as a control group. The final seed germination index (SGI) was obtained by the following equation (Wang et al. 2018a; Gao et al. 2010):

\[
\text{SGI} = \frac{\text{Averagerootlength}_{	ext{DW}} \times \text{Averagegerminationrate}_{	ext{DW}}}{\text{Averagerootlength}_{	ext{LC}} \times \text{Averagegerminationrate}_{	ext{LC}}} \times 100\%
\]

(1)

LC denotes leachate and DW denotes deionised water.

Physiological index test: Cabbage seeds were flotation with distilled water to remove dried out grains before germination, then placed in petri dishes lined with filter paper, 5 ml of deionized water was added and germinated in a constant temperature incubator at 25°C. After 24 h select those with normal germination for hydroponics, with Hoagland nutrient solution (pH = 6.8), with 5 ml of catalyst leachate added to the nutrient solution, and seedlings with deionised water added to the culture solution were used as a control group; they were incubated in a constant temperature light incubator, set at 25°C, for 10 days. Determination of chlorophyll content: weigh 0.1 g of cut cabbage leaves, put into a mortar, add a small amount of calcium carbonate and quartz sand and 5 ml 95% ethanol,
grind into a homogenous slurry, continue to grind until the tissue turns white, filter through filter paper; rinse the residue and filter paper repeatedly with ethanol until colourless, then fix the volume to 25 ml. use 95% ethanol as blank, measure the absorbance at wavelengths of 665 nm, 649 nm, 470 nm. The absorbance was measured at 470 nm. The formula was calculated as follows:

\[
C_a = 13.95A_{665} - 6.68A_{649} \\
C_b = 24.96A_{649} - 7.32A_{665} \\
C = (1000A_{470} - 2.05C_a - 114.8C_b)/245 \\
CLP = (C \times V)/1000W
\]

\[Ca, C_b, C, A, \text{ and } CLP\] denote chlorophyll a, chlorophyll b, chlorophyll concentration, absorbance and chlorophyll content (mg/g) respectively; V and M denote the volume of the extract and the fresh weight of the sample.

### Free radical capture experiments

Before the photocatalytic degradation experiment started, a certain amount of free radical scavengers was added to the solution. Ammonium oxalate (AO), p-benzoquinone (BQ), isopropyl alcohol (IPA), and ferrous sulfate-ethylenediaminetetraacetic acid disodium salt (Fe(II)/EDTA-2Na) were the scavengers of \(h^+, •O_2^-\), \(•OH\), and \(H_2O_2\). The distance between the reactor and the lamp was kept at 2 cm. The solution was subjected to a 30-min adsorption equilibrium prior to degradation. The UV spectrophotometer was model 752 N (China). The concentration of free radical trapping agent was 3.1 g/ml of ammonium oxalate, 0.027 g/ml of p-benzoquinone and 2% of isopropanol. 0.557 g of FeSO₄·7H₂O was weighed and dissolved in 8 ml of deionised water and 0.754 g of EDTA was weighed and dissolved in 10 ml of deionised water. EDTA was added to the ferrous sulphate solution with stirring until yellow, then 32 ml of deionised water was added stir well. respectively (Adam and Karthikeyan 2017; Wei Wang and Lu 2017). The addition of free radical scavengers would inhibit the degradation efficiency of antibiotics, and the degree of inhibition was proportional to the importance of the corresponding free radicals, that is, the greater the role played by the active species in the photocatalytic degradation process, the greater the degree of inhibition of the degradation effect of antibiotics after the addition of free radical scavengers.

### Results and discussion

#### Structure and composition

The crystal structures of the CN, 0.005TCN, 0.01TCN and 0.02TCN catalysts were tested by XRD. As shown in Fig. 1 at 13.0° and 27.2°, the 0.005TCN, 0.01TCN and 0.02TCN samples have the same profile as CN with two significant diffraction peaks. The dominant peak at 27.2° corresponds to the (002) crystal plane, which is due to the interlayer stacking reflection of the conjugated aromatic system. The peak at 13.0°is the (100) plane, caused by the periodic build-up of layers in the graphite structure (Han et al. 2018). Since no significant impurity peaks were observed in xTCN, the doping of Tb ions may not affect the crystalline phase of CN. The intensity of the diffraction peak of the 0.005TCN catalyst (27.2°) was significantly enhanced compared to CN, indicating that the participation of Tb enhanced the degree of polymerisation and crystallisation of the g-C₃N₄ interlayer network. However, the intensity of the 27.2° characteristic peak decreases with increasing Tb doping content, which may be due to the graphite diffraction intensity of the tri-s-triazinyl linker becoming weaker with increasing amounts of Tb incorporation (Jin et al. 2019).

The molecular structure information of the prepared CN, 0.005 TCN, 0.01 TCN and 0.02 TCN was investigated using FTIR spectroscopy. As shown in Fig. 2, the CN shows three main absorption regions at 805 cm⁻¹, 1200–1700 cm⁻¹ and 3171 cm⁻¹. The sharp characteristic peak at 805 cm⁻¹ is mainly caused by the bending vibration of the triazine unit. The series of peaks in the 1200–1700 cm⁻¹ range are the result of aromatic C-N stretching vibrations and the deposition of C = N bonds (Qi et al. 2016). The stretching
vibrations of the N–H group and the surface adsorption of water molecules give rise to a broad absorption band at 3171 cm\(^{-1}\). The FTIR profiles exhibited by xTCN and CN are essentially identical, except for the centre of the band between 2290 and 2390 cm\(^{-1}\) which is due to C≡N stretching vibrations, indicating that the C≡N triple bond is formed and not due to aromatic C–N stretching vibrations. The characterization results of the FTIR spectra can be explained by the addition of Tb ions breaking some of the triazine rings of g-C\(_3\)N\(_4\), transforming the sp2 C–N single bond into a C≡N triple bond (Wang et al. 2019).

The surface elemental composition and valence state of the 0.01TCN material was further confirmed by XPS analysis. The main peaks of the elements carbon, nitrogen, terbium and oxygen were observed through the measured spectra of 0.01 TCN, as shown in Fig. 3d. The high-resolution spectra of C1s at 284.8, 285.4, and 288.1 eV are attributed to sp2 hybridized C=C, C= and N–C=N, respectively, which are derived from coupled g-C\(_3\)N\(_4\). The peak carbon atom in a pure carbon environment is 284.8 eV. The peak of 0.01 TCN at 285.4 eV is the C-NH\(_x\) of the heptane molecule (x = 1, 2). The main peak of 0.01 TCN located at 288.1 eV was assigned to N–C=N, that further verifies the presence of C≡N, as the binding energy of C≡N is similar to that of C-NH\(_x\) (Fig. 3a). The high resolution profile of N1s can be fitted to three peaks at 398.4 eV, 399.9 eV and 400.9 eV respectively. The peaks at 398.7 eV and 400.6 eV can be identified as sp2 hybridized N, where 398.7 eV corresponds to N in the N=C bond and 400.6 eV belongs to N in the N-(C)\(_3\) bond. Due to the incomplete polymerization of melamine and the adsorption of surface water, the peak with binding energy at 400.6 eV belongs to the amino functional.
group (N-Hx,x = 1.2) (Fig. 3b) (Zhang et al. 2019). The positive charge localization in the heterocycle leads to the weakest peak at 404 eV. The peak around 158.8 eV in the Fig. 3c belongs to Tb4d5/2, indicating the presence of Tb3+ ions; the doped Tb is present in the form of Tb(III) (Fig. 3c) (Lu et al. 2017).

**Morphological analysis**

The microstructural features of CN, HCN, 0.005TCN, 0.01TCN, and 0.02TCN catalysts were analyzed by transmission electron microscopy. For HCN, it exhibits a completely different morphology from that of CN. It exhibits a typical lamellar porous structure and many pores of different diameters are observed in the layer structure. There are several reasons for this to happen: When nitric acid solution is added to melamine, the ionized H+ is transferred to the nitrogen atoms on the melamine triazine ring, which then causes the melamine to be protonated. In the heating process, the nitrate anion connected with the protonated melamine cation will decompose at high speed to produce a large amount of nitrogen. Nitrogen can be used as a bubble template to form mesoporous structures of CN. As shown in Fig. 4, 0.005TCN, 0.01TCN, and 0.02TCN have a microstructure similar to that of HCN (Fig. 4) (Liu et al. 2016; Xie et al. 2018).

The specific surface area of the sample has a significant impact on the photocatalytic performance of the catalyst, with a larger specific surface area facilitating both the adsorption of organic pollutants on the catalyst surface and providing more active sites. The specific surface areas of g-C3N4 and TCN were characterised using N2 adsorption–desorption isotherms, as shown in Fig. 5. The adsorption–desorption isotherms for both the g-C3N4 and TCN samples are typical Type IV adsorption curves with an H2-type hysteresis loop ((P/P0 > 0.4)), indicating that all samples are porous. g-C3N4 and TCN have specific surface areas of 21.9 and 34.5 m2·g−1, much larger than those reported in the literature for solid g-C3N4 polymers, due to their mesoporous structures have more geometrical surfaces compared to solid g-C3N4 polymers.

When the photocatalyst is energized by light, e− in the valence band is excited to jump into the conduction band, resulting in e− and h+ pairs. When e− and h+ are compounded in the bulk phase or surface of the photocatalyst, some energy is released in the form of fluorescence. Usually, the complication rate of photogenerated e− and h+ is proportional to the fluorescence intensity, and the PL characterization was performed to study the photogenerated carrier migration and separation of the prepared TCN samples by HCN and TCN samples, as shown in Fig. 6. From the figure, it can be seen that both HCN and TCN catalysts have a broad peak at around 460 nm, that belongs to the band photoluminescence specific to the photogenerated carriers of g-C3N4 polymer, and it can be found from the figure that the separation of photogenerated e− and h+ in the photocatalyst doped with Tb elements is significantly better than that of CN (Bui et al. 2020). The order of luminous intensity is: HCN > 0.02TCN > 0.005TCN > 0.01TCN. This implies that the separation and transport rates of photogenerated carriers are significantly increased after Tb doping, and the Tb element doping and mesoporous structure have a significant effect on improving the separation and transport of charges.

**Analysis of the light absorption properties of Tb/g-C3N4**

The light absorption ability of the prepared samples was measured by UV–Vis spectrophotometer, and the light absorption performance of the catalyst has a great influence on its degradation of organic pollutants. The absorption edge of pure CN can be obtained from Fig. 7a to be about 450 nm, which is consistent with the previous literature. However, the optical absorption edges of 0.005TCN and 0.02TCN were shifted to 475 nm, and 0.01TCN was further red-shifted to 490 nm (Bui et al. 2020). In addition, 0.005TCN, 0.01TCN, and 0.02TCN exhibit stronger light absorption than g-C3N4 in the visible range, which may be due to the synergistic effect of Tb doping into g-C3N4 to form a heterojunction. The Kubelka–Munk function gives the forbidden band width (Eg) of the catalyst:

\[
\alpha h\nu = A(h\nu - E_g)^{1/2}
\]

where \(\alpha, h, \nu, A\) denote the optical absorption coefficient, Planck’s constant, optical frequency and constant, respectively. The graph takes \(h\nu\) and \((\alpha h\nu)^{1/2}\) as the abscissa, and a tangent is drawn, the intersection between the tangent and the abscissa is the band gap energy. As shown in Fig. 7b. The band gap energies of the g-C3N4, 0.02TCN, 0.01TCN and 0.005TCN samples were determined to be 2.63 eV, 2.55 eV, 2.47 eV and 2.41 eV, respectively. This is due to the formation of a new impurity energy level between the valence and conduction bands of the g-C3N4 polymer, where the photogenerated e− can jump directly from the valence band of g-C3N4 to the Tb(III) impurity energy level, shortening the charge jumping distance (Zhang 2020).

**Photocatalytic performance**

In order to determine the optimal doping concentration of terbium in g-C3N4, the degradation experiments of TC (25 mg/L) and TYL (25 mg/L) using photocatalysts with different terbium doping concentrations under simulated solar irradiation were carried out. Figure 8 shows the photodegradation rate curves of the photocatalytic effect of

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solar simulated light expressed by CN, 0.01TCN, 0.02TCN and 0.005 TCN for TYL and TC, respectively. According to the blank test, TC and TYL could hardly be degraded under simulated solar irradiation without a catalyst, which means that it is difficult to photolyze TC and TYL without a photocatalyst. The photocatalytic activity of CN was relatively low after 90 min of simulated sunlight irradiation, degrading only 52.1% TYL and 64.1% TC. In order to make a more visual comparison of the photocatalytic activity of CN and xTCN; the results of the photocatalytic degradation of antibiotic by CN and TCN samples were investigated using quasi-level kinetics, the equations are as follows:

**Fig. 4** TEM images of 0.005TCN(a), 0.01TCN (b), 0.02TCN(c), HCN(d) and g-C3N4 (e)
where C is the concentration of TYL and TC at irradiation time t (min); $C_0$ is the initial concentration of TYL and TC; and k denotes the apparent reaction rate constant. CN degraded TYL and TC with k values of 0.0127 and 0.01055; 0.01TCN degraded TYL and TC with k values of 0.0271 and 0.0241.

It can be noted from the figure that the photocatalytic activity of xTCN increases and then decreases with the increase of the molar concentration of Tb doping, and the possible reasons for this situation are discussed below. As the rare earth trivalent cation (Tb$^{3+}$) has an incompletely occupied 4f orbital, it is thermodynamically feasible for Tb$^{3+}$ to be reduced by photogenerated electrons. Therefore, the use of Tb$^{3+}$ as a trapping agent is effective in trapping the electrons on VB and restoring them to Tb$^{2+}$. Subsequently, the Tb$^{2+}$ ion is oxidised back to Tb$^{3+}$ by O$_2$ in the ambient solution.

$$\ln(C/C_0) = kt \quad (7)$$

$$\text{Tb}^{3+} + e^- \rightarrow \text{Tb}^{2+} \quad (8)$$

$$\text{Tb}^{2+} + \text{O}_2 \rightarrow \text{Tb}^{3+} + \text{Â· O}_2^{-} \quad (9)$$

Therefore, by doping with an appropriate concentration of Tb$^{3+}$ ions can be used as an electron trapping agent, which not only promotes the rapid transfer of photogenerated electrons, but also reduces the complexation of electrons with holes, thus the quantum efficiency is increased. However, when the molar mass ratio of the doping of Tb(NO$_3$)$_3$·5H$_2$O exceeded the optimum value of 0.01%, the degradation rate

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**Fig. 5** N$_2$ adsorption–desorption isotherms

**Fig. 6** Photoluminescence spectra of g-C$_3$N$_4$, 0.005TCN, 0.01TCN, 0.02TCN and HCN

**Fig. 7** (a) UV–Vis diffuse reflectance spectra of CN, HCN, 0.005TCN, 0.01TCN and 0.02TCN, (b) the plots of $(\alpha h\nu)^{1/2}$ versus bandgap of CN, HCN, 0.005TCN, 0.01TCN and 0.02TCN.
of the antibiotic decreased, as shown in Fig. 8. This situation is explained by the reduction of Tb³⁺ to Tb²⁺ by electrons, which means that an excess of terbium ions acts as a complex centre for electron–hole pairs, reducing the number of photogenerated electrons that would otherwise react with oxygen molecules to form superoxide radicals. At the same time, too much terbium ions can occupy the active sites on the catalyst surface, which is not conducive to improving photocatalytic activity. Therefore, doping with the right amount of terbium ions can improve the photocatalytic activity of the photocatalyst.

**Stability evaluation**

For photocatalysts, their stability and reproducibility are important factors affecting their reagent application. The stability as well as the reproducibility of the prepared 0.01TCN catalysts were confirmed by running the degraded antibiotics three times under the same conditions. The relative concentration (C/C₀) of the antibiotics solution under simulated solar irradiation is shown in Fig. 9a as a function of time repeated over three cycles. The antibiotics photodegradation efficiency did not change significantly over the three cycles. The results show that the 0.01TCN photocatalyst has very good stability in the photocatalytic degradation process.

**Toxicity test of leaching solution**

The mean root length (AL) and seed germination rate (SR) of Chinese cabbage seeds were obtained by seed germination experiment, and the germination index was calculated according to formula 1. Figure 10a shows the germination conditions of different catalyst leaching solution as culture medium. In the seed germination experiment, the average root length (Al), germination percentage (Sr), and germination index (SGI) of Chinese cabbage seeds are shown in Table 1. It can be seen from Table 1 that the germination index of Chinese cabbage seeds cultivated with different catalyst leaching solutions fluctuated little, and the influence of different catalyst leaching solutions on the seed germination index was negligible. Figure 10b shows the growth of Chinese cabbage seedlings with different catalyst leaching solutions added to the culture medium. It can be seen from Fig. 10c that different catalyst leaching solutions have no inhibitory effect on Chinese cabbage seedlings and their chlorophyll content is almost the same, which does not affect the absorption and utilization of light. Therefore, it can be concluded that CN and TCN catalysts have little effect on seed germination.
Photocatalytic reaction mechanism

In general, the type of radicals originating from photoexcited electrons and holes directly determines the photocatalytic degradation mechanism. So we have revealed the mechanism of the photocatalytic reaction by examining the main oxides produced in the degradation reaction. ·O2, ·OH, H2O2 and h+ are the main substances involved in the photocatalytic reaction process. Therefore, in order to identify the active species that mainly participate in the reaction during catalysis, different bursting agents are added to the reaction solution to neutralise the free radicals (Jiang and Li 2017). The main active species during the degradation reactions were studied by using isopropyl alcohol (IPA), ammonium oxalate (AO), benzoquinone (BQ) and Fe(II)-EDTA as trapping agents for ·OH, h+, ·O2− and H2O2, as shown in Fig. 11. The degradation of TC decreased from 83.5% to 10.8%, 78.4%, 76.2% and 47.2% after the addition of BQ, IPA, AO and Fe(II)-EDTA respectively, indicating that the addition of BQ had the greatest effect on the degradation reaction of antibiotics, followed by Fe(II)-EDTA; finally AO and IPA had the least effect, thus indicating that ·O2− was the main active species. The slight decrease in degradation rate caused by IPA, Fe(II)-EDTA and AO implies that ·OH, H2O2 and h+ are also involved in the degradation reaction. The order of importance of the oxide species is: ·O2− > H2O2 > ·OH > h+; so ·O2− and H2O2 play an important role in the photocatalytic process and act as the main oxide species.

Based on the above photocatalytic performance tests, and free radical capture experiments, a preliminary explanation...
of the reaction mechanism of Tb³⁺/g-C₃N₄ photocatalysis is presented in Fig. 12. According to previous reports CN has a CB and VB of -1.4 eV and +1.3 eV (Guo et al. 2019) respectively. Since the reduction potential of photogenerated electrons is more negative than the redox potential of O₂/·O₂⁻ (-0.33 eV), O₂ is more easily reduced by electrons to form ·O₂⁻. The redox potentials of ·OH/OH⁻ (+1.99 eV) and ·OH/H₂O (+2.27 eV) are more positive than the potential of the highest occupied molecular orbital of CN (Yang et al. 2019), so h+ located in VB cannot oxidize H₂O or OH⁻ to produce ·OH that ·OH is produced from ·O₂⁻. During the photocatalytic degradation process, we found that during the adsorption equilibrium phase, TCN catalysts were able to provide a greater abundance of photocatalytic active

| Samples | AL (mm) | SR (%) | SGI |
|---------|---------|--------|-----|
| DW      | 27.5    | 95     | 1   |
| CN      | 28.7    | 90     | 0.989 |
| 0.005TCN| 27.7    | 92     | 0.975 |
| 0.01TCN | 27.3    | 92     | 0.961 |
| 0.02TCN | 27.9    | 95     | 1.014 |

Fig. 10 (a) Seed germination photos of different leaches; (b) Photos of seedling growth of Chinese cabbage with different leaching solutions; (c) The chlorophyll content of Chinese cabbage seedlings cultured in different leaching solutions

Fig. 11 Effect of several scavengers on the photocatalytic activity of 0.01TCN (a) catalyst; The value of the removal rate in the presence of as-prepared 0.01TCN (b) sample
sites compared to CN due to the mesoporous structure of the TCN catalysts enabling them to expose more geometric surfaces, resulting in a larger specific surface area. In addition, the presence of a mesoporous structure increases the specific surface area, which improves the adsorption and diffusion processes during the reaction. 0.01TCN catalysts with a high specific surface area enable molecules such as pollutants or oxygen to come into contact with the catalyst surface more effectively, while generating more efficient capture of photogenerated e− and h+ for oxidation or reduction reactions, thus improving the photocatalytic effect. The hollow pores in the mesoporous structure allow the incident light to be refracted and scattered several times inside the catalyst, allowing more contact with the incident light and improving the utilisation of the light. Mesoporous structures can also reduce carrier complexation by reducing the migration distances of electrons and holes and speeding up the transfer of photogenerated e− and h+ to locations at the edge of the catalyst surface (Xie et al. 2018). Based on the above analysis, a photocatalytic mechanism for the photocatalytic degradation of antibiotics by 0.01TCN catalyst is proposed. As shown in the figure, e− in the valence band of the 0.01TCN sample is excited to jump to the conduction band, forming e− and h+ pairs. When the g-C3N4 polymer is doped with Tb, a Tb impurity energy level is formed between its conduction band and valence band, which means that e- in the 0.01TCN sample can both jump to the Tb impurity energy level and transfer to the conduction band of g-C3N4, which facilitates the separation of e− and h+ (Zhou et al. 2019). A portion of the e− located in the conduction band and the Tb(III) impurity energy level then moves to the catalyst surface, which in turn reduces the O2 molecules adsorbed on the catalyst surface to ·O2−. Some of these ·O2− react with H+ to form H2O2 and ·OH. A series of free radicals are generated, which finally decompose pollutants such as TYC into H2O, CO2 (Shi et al. 2015) and other inorganic substances to reduce pollution. Compared to pure g-C3N4, the impurity energy level generated by Tb in the 0.01TCN sample provides an alternative transfer pathway for e−, which more effectively inhibits the compounding of photogenerated electron holes, thus improving the photocatalytic activity of the sample.

Conclusions

Overall, the new xTCN catalyst is a very promising photocatalyst, using a mixture of melamine and Tb(NO3)3 as precursor calcined at 550 °C for 2 h. The prepared xTCN samples showed very good photocatalytic activity for the degradation of antibiotics (TC and TYL) under simulated sunlight conditions and it has excellent stability. Through characterisation, photocatalytic performance testing and radical capture experiments, a potential mechanism for the improvement of photocatalytic efficiency of Tb/g-C3N4 materials is proposed. The improved photocatalytic performance is attributed to the wider visible light response range and the synergistic effect with terbium dopants, which inhibits electron–hole complexation and improves photocatalytic performance. In leachate toxicity experiments, it had little effect on the germination of plants and the chlorophyll content of seedlings, indicating negligible leaching toxicity of xTCN. This shows that Tb-doped g-C3N4 will provide a new aid to the photocatalytic degradation of effluents.

Acknowledgements

The authors want to thank Northeast Electric Power University for the support.

Author contribution

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Bing Wang, Qingtong Cao, Guomin Li and Jian Zhang. The first draft of the manuscript was written by Bing Wang and all
authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Data availability The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Approval was obtained from the ethics committee of Northeast Electric Power University. The procedures used in this study adhere to the tenets of the Declaration of Helsinki.

Consent for publication The participant has consented to the submission of the case report to the journal.

Competing interests The authors declare no competing interests.

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