Fabrication of covalently linked ruthenium complex onto carbon nitride nanotubes for the photocatalytic degradation of tetracycline antibiotic

Mohaddeseh Shahabi Nejad (✉ mshahabinejad@sci.uk.ac.ir)

<https://orcid.org/0000-0002-0560-6082>

Zahra Vakily

Ali Mostafavi

Hassan Sheibani

Research Article

Keywords: Graphitic carbon nitride nanotubes (g-C₃N₄ NTs), Dichloro(p-cymene)ruthenium(II), Photocatalyst, Tetracycline antibiotics.

Posted Date: May 16th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1016964/v2>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Due to the problem of direct disposal of effluents containing antibiotics to the environment and the emergence of resistant bacterial pathogens, the wastewater treatment of the pharmaceutical industry has been known as an important research background. In this study, the refinement and photodegradation ability of one of the most widely used antibiotics, "tetracycline" was investigated by ruthenium complex immobilized on the modified graphitic carbon nitride nanotubes. For this purpose, graphitic carbon nitride nanotubes (g-C₃N₄ NTs) were successfully synthesized by the hydrothermal method and functionalized with 1,10-Phenanthroline-5,6-dione ligand during another step. Then, the functionalized g-C₃N₄ NTs were reinforced with immobilization of dichloro(p-cymene)ruthenium(II) dimer. The structure and morphology of the prepared photocatalyst was studied by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), scanning, and transmission electron microscopy (SEM & TEM) analyses. In the following, the photocatalyst's ability to optically degrade the tetracycline antibiotics was performed in a suspension reactor equipped with a LED lamp (60 W), and effective parameters such as the amount of catalyst, and irradiation time, temperature, and pH were optimized. The results showed that the immobilization of Ru complex onto functionalized g-C₃N₄ NTs improved the photocatalytic activity and increased the degradation efficiencies to an amount of 43%. Furthermore, COD analysis has used the determination of the amount of mineralization and results showed that the mineralization of 10 mg/L tetracycline solution of about 90% can be performed using 20 mg of Ru (II) complex/ g-C₃N₄ NTs at pH = 7 after 480 min without any additive oxidant.

1. Introduction

Tetracyclines are known as a group of broad-spectrum antibiotics that have a common basic structure and one of the most widely used these antibiotics is tetracycline. This antibiotic is used to treat humans and stimulate the growth of livestock and birds [1]. According to the World Health Organization (WHO), the presence of this substance in nature is dangerous [2]. Tetracycline finds its way to surface and groundwater through domestic and hospital effluents so livestock and poultry farms that it enters the human food cycle by drinking water and consuming fruits and vegetables [3]. This antibiotic causes genetic resistance and accumulates in the skeletal tissues of the human body through the formation of a stable complex with calcium [4, 5]. Tetracycline is not biodegradable and disrupts in the biological treatment units, and also produces more toxic products in many chemical treatment processes such as chlorination and ozonation [6, 7]. On the other hand, the use of the surface adsorption technique only transfers tetracycline from one phase to another and does not eliminate its contamination [8]. Therefore, it can be said that the common removal methods of organic contaminations are inefficient and troublesome for this antibiotic [9]. Instead, the advanced oxidation processes, especially photocatalytic systems, are a good way to remove these compounds and are based on the production of hydroxyl radicals [10–12]. These radicals are able to oxidize all organic compounds to the stage of carbon dioxide and water production [13]. Most of the photocatalysts presented so far are efficient only in the ultraviolet range [14, 15], and since only a small percentage of sunlight is made of ultraviolet light and most of that

is visible light, so it needs to design and fabrication of the new generation of active photocatalysts in the visible range. In recent years, a lot of research has been done on semiconductors that have a suitable gap and can be used in the visible range [16–18]. Graphite nitride carbon is one of the semiconductors that has a smaller bandgap (~ 2.7 eV) than many other common photocatalysts such as titanium oxide and zinc oxide, and as a result, it is more efficient at absorbing sunlight [19, 20]. This substance is non-toxic, cheap and easy to prepare [21]. However, the most important weakness of $g-C_3N_4$, which reduces its performance in optical degradation, is the rapid recombination of electron-hole pairs [22, 23]. Increasing efficiency in the optical degradation operations depends on the degree of separation of electron-hole pairs. To produce active oxygen species, it is necessary that the electrons and produced holes can react separately with the water or oxygen molecules around them [24]. There are two major ways to solve this $g-C_3N_4$ problem and achieve maximum performance; First, changes in the morphology and particle size of the photocatalyst: The particle size of a photocatalyst has a large effect on the energy gap. As the particle size decreases along with increasing the width of the energy gap, and so its oxidation-reduction strength will increase [25]. Second, the decoration of $g-C_3N_4$ with other conductive and semiconductor metals; these metals increase the absorption of visible light and the efficiency of the photocatalyst by producing hot electrons and injecting them into the semiconductor [26].

In the present project, the above two techniques were used to fabricate an efficient photocatalyst in the visible range. In this regard, the $g-C_3N_4$ nanotubes were synthesized instead of $g-C_3N_4$ bulk and it cause to improve the energy band gap and reduce the recombination rate of the electron-hole pair. In addition, the use of $g-C_3N_4$ nanotubes increases the surface area and has a positive effect on photocatalyst performance. To implement the second approach and further enhance the photocatalytic properties, the surface of the nanotubes was decorated with a ruthenium complex. The ruthenium complexes have the ability to absorb light in the wavelength range of 400–800 nm and cause the formation and injection of electrons into the photocatalytic system. In the end, the photocatalytic ability of Ru(II)complex/ $g-C_3N_4$ NTs was investigated in the decomposition of tetracycline antibiotic under visible light and the effect of factors such as radiation time, amount of photocatalyst, pH, and temperature on degradation efficiency was investigated. The advantages of this method are maintaining the photocatalyst stability and reusability in the heterogeneous system.

2. Experimental

2.1. Material and methods

Cyanoric chloride (99%), and 1,10-Phenanthroline (99.5%) were purchased from Merck- Millipore chemical Co. and used as received. Melamine (99%), Dichloro(p-cymene)ruthenium(II) dimer (99%), and Tetracycline (98%) were obtained from Sigma-Aldrich. The prepared Ru(II)complex/ $g-C_3N_4$ NTs was characterized by fourier transform infrared (FT-IR, Bruker, Germany, RT-DLATGS detector) spectroscopy, scanning electron microscopy (FE-SEM, TESCAN-MIRA3), transmission electron microscope (TEM, EM10c-100 KV) and the concentration of tetracycline solutions have been monitored using Ultraviolet-

visible (UV-Vis) spectroscopy was performed in the range of 200–900 nm wavelength on a Cary 50 single detector double beam in time spectrophotometer (Varian, Australia).

2.2. Synthesis of g-C₃N₄ NTs

The preparation of g-C₃N₄ NTs was done in two separately steps. First, white crystals of melamine-cyanuric acid were prepared by a hydrothermal method briefly, 0.5 mmol of melamine and 0.5 mmol of cyanuric chloride were dissolved in 75 mL deionized water and kept stirring for 30 min. The resultant transport solution was transferred to an autoclave flask and maintained at 180°C for 6 h. After this time, the autoclave was cooled until to ambient temperature and the obtained white needle-like crystals were centrifuged and washed several times with deionized water to remove organic impurities and freezer dried for 24 hours.

The second step was the calcination process as follows the melamine-cyanuric chloride crystals were calcined at 450°C for 5 h with a heating rate of 1°C min⁻¹ under nitrogen inert atmosphere.

2.3. Functionalization of g-C₃N₄ NTs with phenantroline-5,6-dione

In order to functionalize graphitic carbon nitride nanotubes, 250 mg of g-C₃N₄ NTs along with 1 mmol of phenantroline-5,6-dione ligand were dispersed in 50 ml of acetonitrile and after equipping the reaction vessel with the condenser it was refluxed for 60 hours at 60 ° C. At the end of the reaction time, the functionalized g-C₃N₄ NTs were collected by centrifugation and dried at 50 ° C after washing several times with acetonitrile.

2.4. Synthesis of Ru (II) complex/ g-C₃N₄ NTs

A 250mL flask was charged with the g-C₃N₄ NTS bearing the phenantroline-5,6-dione ligand (250 mg), [RuCl₂(p-cymene)]₂ (0.2 mmol) and 200 mL anhydrous dichloromethane. The obtained suspension was refluxed for 2 h at 50°C. After that, the resultant product was separated through decanting of the solvent and the nanotubes were washed several times with dried dichloromethane to remove extra values of ruthenium moieties. according to ICP-OES analysis amount of Ru was 10% in the obtained photocatalyst.

2.5. Study of the photocatalytic activity of Ru (II) complex/ g-C₃N₄ NTs

All photocatalytic reactions were performed in a 50 ml beaker containing 25 ml of tetracycline solution (10 mg/L). During irradiation of visible photons, the sample containing the nanocomposite was stirred by a magnetic stirrer to homogenize the system and prevent photocatalytic precipitation. The 60-watt visible light source was placed directly on top of the beaker at a distance of 15 cm from and at a distance of 15 cm from it, and despite the heat generated by the lamp, no cover was used. At the beginning of the test, from the moment that the samples were immersed in the solution, placed in the dark for 30 minutes to

reach the adsorption /desorption equilibrium. The concentration of initial and residual tetracycline in the samples that irradiated by UV-Vis spectrometer at different times were measured after separating of nanocomposite by centrifuge and then the percentage of drug removal was calculated according to Eq. 1.

$$\text{Photocatalytic destruction (\%)} = (C_0 - C) / C_0 \times 100 \quad (1)$$

In this equation, C_0 is the initial concentration of tetracycline and C is the concentration of the tetracycline remaining in the solution, after the photodegradation reaction. It should be noted that all experiments were repeated twice and the average value was reported. In addition, the COD of the samples was measured every hour by FAS titration with potassium permanganate [27].

2.6. Adsorption kinetics study

The kinetic of photocatalytic degradation of pesticides in the heterogeneous oxidation systems with visible light follows the Langmuir-Hinslowood kinetic model (Eq. 2) [28–30].

$$r = \frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (2)$$

Where r , C , t , k and K are the oxidation rate (mg/L min), herbicide concentration (mg/L), irradiation time (min), reaction rate constant (1/min) and reaction adsorption coefficient (L/mg), respectively. At low initial concentrations of herbicides, Eq. 2 is changed to the quasi-first-order equation (Eq. 3).

$$\ln \left(\frac{C}{C_0} \right) = kKt = k_{app}t \quad (3)$$

By plotting $\ln (C/C_0)$ versus t , the slope of the diagram shows the apparent rate of photocatalytic degradation.

3. Results And Discussion

3.1. Investigation of Synthesis of Ru (II) complex/ g-C₃N₄ NTs

So far, various methods have been introduced for the synthesis of g-C₃N₄, all of which use nitrogen-rich precursors including cyanamide, dicyandiamide, melamine, urea, thiourea, triazine derivatives, and heptazine [31, 32]. One of the simplest and most common methods for synthesizing this substance is the condensation method [33–36]. In this method, the mentioned precursors are converted to g-C₃N₄ at 550 °C. But the main challenge of this method is the variable condensation efficiency, which leads to the production of a product with a small surface area and, of course, limits its application to photocatalytic processes [37]. However, the surface area of g-C₃N₄ depends on the type of precursor and synthesis

conditions, and by changing the above factors, a high surface area can be achieved. Typically, the use of melamine precursors results in the production of $g\text{-C}_3\text{N}_4$ with a high N/C ratio [38]. The higher the N/C ratio, the lower the energy bandgap and the higher the photocatalytic property. If melamine is used in combination with an oxygen-containing precursor to making $g\text{-C}_3\text{N}_4$, the product has more porosity and a higher surface area [39]. The use of chlorine-containing precursors has a similar effect, increasing the porosity and surface area, possibly due to the evaporation of chlorine ions in the form of HCl [40]. The second approach to achieve a high surface area is to change the synthesis conditions to create nanostructures. Most reports on nanostructures derived from graphite carbon-nitride are about nanoporous and nanoplate [41, 42]. In addition to these two structures, nanotubes have recently been introduced as a new morphology of $g\text{-C}_3\text{N}_4$, which, due to their high specific surface area, regular crystalline walls available for mass transfer, have desirable semi-conductivity properties [43]. There are two general methods for synthesizing $g\text{-C}_3\text{N}_4$ NTs: First method, hard templating method [44], which is done by polymerizing the precursors in the created space of the template (such as silica) and then removing the template by reagents that dissolve the silica. Although the $g\text{-C}_3\text{N}_4$ NTs obtained from this method has a high surface area, its crystallinity has decreased. Crystallinity is an effective parameter against the separation of excited charges in the photocatalytic process [45]. The second method is the soft templating [46], which its general mechanism is based on the polymerization of nitrogen-rich precursors in the space that has been created by soft template such as trithion X10, P12, and F124 [47]. The disadvantage of this method is the high polymerization temperature, which leads to the loss of the template before the complete formation of the nanotube. In the present project, $g\text{-C}_3\text{N}_4$ NTs were synthesized by the joint polymerization of nitrogenous (melamine) and chlorinated (cyanuric chloride) precursors through the hydrothermal process without the use of any template. The cyanuric chloride is unstable under aqueous conditions therefore; it was converted to cyanuric acid as an oxygenated precursor created melamine-cyanurate crystals through a series of hydrogen bonds with melamine. Finally, the growth of these crystals within 6 hours and calcination at 450°C , it cause to produce $g\text{-C}_3\text{N}_4$ NTs. Because of incomplete polymerization of melamine, there are free amine groups at the outer edges of the prepared $g\text{-C}_3\text{N}_4$ NTs and these defects in the structure cause to balance in the energy bandgap and also it facilitates the functionalization of the surface. So here, the functionalization was done in the through formation imine band between carbonyls of phenantroline-5,6-dione ligand and free amines of $g\text{-C}_3\text{N}_4$ NTs. In the end, the coordination of immobilized bidentate ligands with dichloro(p-cymene)ruthenium(II) led to the stabilization of the relevant complex on the outer edges of $g\text{-C}_3\text{N}_4$ NTs. Scheme1 depicted the steps of the synthesis of the photocatalyst.

3.2. Catalyst characterization

3.2.1. Fourier transform-infrared spectroscopy (FT-IR)

The functional groups of melamine-cyanuric acid, $g\text{-C}_3\text{N}_4$ NTs, Ru(II)complex/ $g\text{-C}_3\text{N}_4$ NTs samples were confirmed by FTIR spectroscopy. The melamine-cyanuric acid spectrum (Fig. 1a) is extremely crowded,

which can be attributed to the formation of a complicated network of hydrogen bonds. The appeared peaks at 3088, 3230, and 3391 cm^{-1} are due to the symmetric stretching vibrations of the amine groups of melamine cations that have shifted to shorter wavelengths (blue shift) than pure melamine [48–49]. The asymmetric stretching vibrations of the amine groups attributed to broad peaks around 2500–2700 cm^{-1} . In addition, the intense peak at 1731 cm^{-1} is assigned to carbonyl stretching vibrations of cyanurate anions which produced from hydrolysis of cyanuric chloride. The strong peaks in region 1400–1700 cm^{-1} corresponded to bending vibrations of N-H and stretching vibrations of C-N and C = N. These peaks in the assembly indicate the successful synthesis of melamine-cyanuric acid crystals. After pyrolysis treatment, the arrangement of the absorption bands was changed (Fig. 1b). For example, the intensity of absorption bands attributed to N-H groups dropped sharply in region $> 3000 \text{ cm}^{-1}$, and also the assigned peak of carbonyl at 1731 cm^{-1} disappeared which confirmed the release of NH_2 and H_2O during pyrolysis treatment to the formation of g- C_3N_4 . Figure 1c again shows the decreasing of the vibrations of the amino groups, which, together with the new appeared band at 1650 cm^{-1} , proves the chemical modification of the nanotubes through the formation of the imine band with phenantroline-5,6-dione ligand.

3.2.2. Ultraviolet and visible absorption spectroscopy (UV-Vis)

To get the UV-Vis absorption spectrum of g- C_3N_4 Nts, this material was dispersed in ethanol by ultrasonic bath for 20 minutes and then its adsorption was measured. As shown in Fig. 2, g- C_3N_4 NTs have maximum adsorption at 368 nm, which has a blue shift (the transition to a higher energy level or shorter wavelength) relative to the bulk sample [50]. In nanomaterials, the distance between the electron-hole is controlled by the particle size, so that as the particle size shrinks to the nanometer scale, the movement of excitons are limited and a transition in the optical spectrum is observed [51]. In general, the transfer of optical spectrum to higher energies due to the decreasing of particle size means an increase in the forbidden band energy. The energy difference (in units of electron volts) between the highest valence band and the lowest conduction band is called the energy bandgap [52]. To calculate the bandgap energy of a material, the absorption coefficient parameter of the material must first be obtained. The absorber coefficient is an important parameter in optical applications and is calculated for a transparent thin film from the following relation:

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \quad (4)$$

Here, d is the thickness of the thin film in nanometers and T is the percentage of light transmission. Since g- C_3N_4 has a direct energy gap, so by direct electron transfer between the capacitance band and the conduction band, the band gap energy (E_g) is obtained from the Tuac Eq. (5).

$$(\alpha h\nu)^{(1/n)} = A(h\nu - E_g) \quad (5)$$

Here, A is constant, α is the absorption coefficient, E_g is the width of the energy gap, and $h\nu$ is the energy of the emitting photon with respect to the absorption spectrum of the synthesized g-C₃N₄ NTs. Also, n for g-C₃N₄ NTs with a straight and permissible bandgap is equal to 1/2. According to Fig. 2, the energy gap of g-C₃N₄ NTs can be calculated by drawing $(\alpha h\nu)^2(\text{eV}\cdot\text{cm}^{-1})^2$ in versus of $h\nu$ (eV) and extrapolation its linear part. This energy gap was obtained 2.96 eV.

3.2.3. X-ray diffraction (XRD)

The prepared melamine-cyanuric acid sample and its Ru(II)complex/g-C₃N₄ NTs have been characterized by X-ray powder diffraction technique (Fig. 3). The presence of sharp diffraction peaks in the XRD of the synthesized melamine-cyanuric acid sample during the hydrothermal process confirms that the obtained product is highly crystalline [53]. The X-ray diffraction pattern changed completely after the pyrolysis process and the formation of g-C₃N₄ NTs nanotubes, followed by chemical modification.

New peaks have appeared around $2\theta = 13.1$ and 27.2 and confirm the formation of graphite nitride carbon phases in the sample [54]. An important point that can be seen in this image is the decrease in the intensity of the peaks after heat treatment, which indicates the percentage of crystallinity of the sample is reduced, or in other words, the long-range order of the structure is reduced.

During the heat treatment, the carbon nitride surfaces appear to be oxidized and the layers separated. Also, due to the oxidation process, the structure is defective and its effects in reducing the peak intensity of this material have appeared. Another reason for the low intensity of peaks is the modification process when an element enters the structure of the compound through chemical bonding, causing the corresponding peaks to flatten or shift and due to the stabilization conditions of the complex, there is no possibility of ruthenium phases in the final structure.

3.2.4. Scanning Electron Microscopy (SEM)

Scanning electron microscopy provides useful information from topography and morphology of the prepared photocatalyst. Scanning electron microscope images of the sample are shown in Fig. 5. These images were taken with different magnifications to determine the overall morphology of the sample and how the nanotubes are arranged. As you can see, the study sample contains clusters of orderly nanotubes and the amount of unwanted particles in that is very low.

To determine the composition of the elements in the prepared photocatalyst, the distribution of active sites, and to determine whether the ruthenium complex is embedded in the surface of the nanotube matrix or in the inner part of the matrix, two complementary analyzes of energy-dispersive X-ray pattern and element distribution map (EDS & Map) were used. The EDS spectrum confirmed the presence of the elements carbon, nitrogen, ruthenium, and chlorine with the appearance of the corresponding peaks and the mapping analysis of polymer shows uniform distribution and non-accumulation of elements that enhance the properties of the photocatalyst.

3.2.5. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images showed that the structure of g-C₃N₄ is in the form of hollow curved tubes with an outer diameter of less than 10 nm and a length of several hundred nanometers (Fig. 5). It appears that after chemical functionalization of nanotubes and loading of ruthenium (II) complex, failure has occurred in areas where defects such as pentagons and heptagons. In addition, the modification process has resulted further distance between the nanotubes, which has a constructive effect on increasing the surface area of the photocatalyst. The Ru(II) complex/g-C₃N₄ NTs show accumulations in some areas, which possibly due to the agglomeration of graphitic nanotubes. This re-stacking of graphitic nanotubes is dependent on strong van der Waals forces and π - π interactions of sp² structures and hydrogen bonding.

3.3. Investigation of effective factors in optical degradation of tetracycline

3.3.1. Influence of amount of photocatalyst

As shown in Fig. 6, the degradation efficiency of tetracycline increased with increasing photocatalyst concentration to 30 mg, after which the degradation efficiency remained almost constant. This can be attributed to the fact that when all the antibiotic molecules landed on the nanotubes, the excess amount of photocatalyst due to the lack of antibiotic molecules had no effect on the percentage of degradation and even slightly reduced the reaction rate. The decreasing in reaction rate at a dose of 40 mg was caused by two main factors. First; g-C₃N₄ nanotubes tend to agglomeration due to their nanometric size and high surface energy, and when the concentration of these nanotubes exceeds a certain limit, the activated nanotubes will be deactivated by contact with the base catalyst, and to follow it, the catalytic efficiency decreases. Second, with the increasing amount of photocatalyst, the turbidity increased and the light scattering occurs due to the collision of optical rays with the catalyst particles scattered in the solution and a number of light photons lose their energy and thus the efficiency of photocatalytic processes decreases.

3.3.2. Influence of irradiation time

To investigate the effect of irradiation time on degradation efficiency, a certain concentration of tetracycline was exposed to an optimized amount of photocatalyst (30 mg) and a frequency of 60 watts at different times. The results are shown in Fig. 7. As you can see, the percentage of antibiotic degradation increased with increasing reaction time, so that in 90 minutes, more than 99% of the tetracycline molecule was broken down into smaller components. This step was followed by monitoring the UV spectrum. But the degradation of the small organic components until producing carbon dioxide and water takes longer so that after 6 hours, 30% of the smaller molecules are still present in the solution. Chemical Oxygen Demand (COD) technique was used to determine the concentration of organic components in the second step. In this method, the sample is strongly refluxed by acidic solutions and a

certain amount of potassium dichromate ($K_2Cr_2O_7$). After digestion of the sample to determine COD, the residual and unoxidized amount of potassium dichromate is titrated with ammonium sulfate to determine the amount of potassium dichromate consumed and the oxidized material is calculated in the oxygen equations.

3.3.3. Influence of temperature

The influence of temperature on tetracycline degradation was shown in Fig. 8. Changes in process velocities in the range of 0 to 75 ° C indicate that degradation rate is directly related to reaction temperature (Fig. 8). In fact, the reaction temperature, on the one hand, contributes to the production of dissolved O_2 and the degradation of H_2O_2 , which ultimately leads to the production of active hydroxyl radicals, and on the other hand, it provides the activation energy for the reaction. Based on this, it can be said that the catalytic process is exothermic and by drawing $\ln k$ (rate constant) versus the inverse of the temperature (kelvin) and in accordance with Arrhenius equation [55] (Eq. 6), the activation energy of the reaction was obtained from the slope of the straight line. The value of the slope is equal to $-E_a/R$ where R is a constant equal to 8.314 J/mol K. (Fig. 9).

$$\ln k = \ln A - \frac{E_a}{RT} \quad (6)$$

The activation energy (E_a) of tetracycline degradation is estimated to be 0.94 kJ/mol.

3.3.4. Influence of pH

In optical degradation processes, pH can affect the desired decomposition rate of the contaminant. Previous studies have shown that pH plays an important role in the breakdown and elimination of antibiotics. As shown in Fig. 5, there is a significant difference between the percentage of tetracycline degradation at different pHs and the rate of decomposition at alkaline pH is significantly higher and optimized at pH = 9. The pH variable affects the adsorption and dissociation capacity of the target compounds, the electric charge distribution on the surface of the catalysts, and the oxidation potential of the conduction band.

Since the isoelectric point of $g-C_3N_4$ based materials is around pH = 9 [56] and the tetracycline antibiotic acidic, the effect of pH on the photocatalytic process can be justified by the presence of electrostatic forces between the surface of $g-C_3N_4$ NTs and tetracycline. Thus, at pHs > 9, the $g-C_3N_4$ NTs surface has a negative charge and the tetracycline molecules also have a negative charge, therefore, the force between them is repulsive and they don't have any reluctance to react and this cause to decrease resulting in the yield of photodegradation decreased at the pH = 11. At pHs < 9, the $g-C_3N_4$ NTs surface has a positive charge and the tetracycline molecules also have a positive charge due to protonation. Therefore, the electrostatic force between the photocatalyst and the tetracycline is the repulsive force, which leads to a decrease in degradation efficiency. Although, the highest percentage of pesticide degradation was obtained at an alkaline pH but, due to the economic aspect and ease of operation treatment at the neutral

pH, investigation of other parameters in photocatalytic degradation of the mentioned pesticides was performed at pH = 7

3.3.5. Effect of chemical scavengers

To probe role of reactive species in the photodegradation of tetracycline in the present Ru(II) complex/g-C₃N₄ NTs, trapping tests were investigated under optimal condonation. For this purpose, isopropyl alcohol as a hydroxyl radical scavenger, ethylenediamine tetra acetic acid as a hole scavenger and sodium sulphate as an electron scavenger were added separately to the reaction mixture and result compared to no scavenger addition. In all three cases, the addition of scavengers reduced the rate and degradation percentage. According to these results, it can be deduced that the hydroxyl radical (•OH) and species generated via hole carriers as key drivers are involved in the photodegradation of tetracycline.

3.3.6. Investigation of synergistic effect

In order to study the synergistic effect, tetracycline degradation reaction in the presence of g-C₃N₄ NTs and Ru(II) complex/g-C₃N₄ NTs was investigated separately and the results are reported in Table1. According to the results, g-C₃N₄ nanotubes alone are able to destroy 62% of tetracycline in 90 minutes. After loading the ruthenium complex, the degradation percentage was higher than 99% for the same period. It seems combining two photon-active substances; g-C₃N₄ NTs and Ru(II) complex has been able to optimize the prepared photocatalyst bandgap. Therefore, the synergistic effect of Ru(II) complex and g-C₃N₄ NTs enhances the photocatalytic properties.

Table 1
The kinetic parameters of photodegradation of tetracycline in the present of different catalyst components

Entry	Tetracycline		
	Photocatalyst components	Degradation(%)	k (1/min)
1	g-C ₃ N ₄ NTs	62	0.0109
2	Ru (II) complex/g-C ₃ N ₄ NTs	99	0.0417

Reaction condithion: tetracycline concentration: 10 mg/L; photocatalyst dosage: 30 mg; irradiation time: 90 min; light intensity: 60 Watt; temperature: 25°C; pH:7

4. Conclusions

In this study, Ru (II) complexes/g- C₃N₄ nanocatalyst was synthesized and its photocatalytic properties for the degradation of tetracycline antibiotic was investigated. The synthesized photocatalyst were evaluated by various methods such as Infrared spectroscopy, X-ray diffraction, scanning and transmission electron microscopy, and visible ultraviolet spectroscopy. The results showed the successful synthesis of graphite

nitride carbon nanotubes reinforced with ruthenium (II) complex. In general, one of the most important properties of a photocatalyst or a catalyst is its specific surface area. Therefore, the synthesis of g-C₃N₄ in the form of nanotubes had a significant performance in photocatalytic properties. In addition to increasing the specific surface area, the accessibility surface for light also increases automatically. Finally, since the bulk graphite carbon nitride alone is a suitable option for photocatalytic degradation of pollutants, the use of improved its, which has a higher specific surface area and better activity, is not far-fetched.

Declarations

Acknowledgments Thanks are due to the Iranian Nanotechnology Initiative and the research council of Shahid Bahonar university of Kerman and chemical engineering department for supporting of this work.

Data availability statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions

References

1. I. Chopra, M. Roberts. Tetracycline antibiotics: mode of action, applications, molecular biology, and epidemiology of bacterial resistance. *Microbiology and molecular biology reviews*. 2001 Jun 1;65(2):232 – 60
2. M. Conde-Cid, A. Núñez-Delgado, M.J. Fernández-Sanjurjo, E. Álvarez-Rodríguez, D. Fernández-Calviño, Arias-Estévez M. Tetracycline and Sulfonamide Antibiotics in Soils: Presence, Fate and Environmental Risks. *Processes*. **8**(11), 1479 (2020 Nov)
3. A. Fiaz, D. Zhu, J. Sun, Environmental fate of tetracycline antibiotics: degradation pathway mechanisms, challenges, and perspectives. *Environ. Sci. Europe* **33**(1), 1–7 (2021 Dec)
4. R.A. Smith, N.M. M'ikanatha, A.F. Read, Antibiotic resistance: a primer and call to action. *Health communication*. 2015 Mar 4;30(3):309–14
5. B. Zhu, Z. Zong, X. Zhang, D. Zhang, L. Cui, C. Bi, Y. Fan, Highly Selective and Stable Zn (II)-Based Metal–Organic Frameworks for the Detections of Tetracycline Antibiotic and Acetone in Aqueous System. *Appl. Organomet. Chem.* **34**(7), e5518 (2020 Jul)
6. S. Hariganesh, S. Vadivel, D. Maruthamani, M. Kumaravel, B. Paul, N. Balasubramanian, T. Vijayaraghavan, Facile large scale synthesis of CuCr₂O₄/CuO nanocomposite using MOF route for photocatalytic degradation of methylene blue and tetracycline under visible light. *Appl. Organomet. Chem.* **34**(2), e5365 (2020 Feb)
7. H. Park, Y.K. Choung, Degradation of antibiotics (tetracycline, sulfathiazole, ampicillin) using enzymes of glutathion S-transferase. *Human and Ecological Risk Assessment: An International Journal*. 2007 Sep 18;13(5):1147–55

8. V. Homem, L. Santos. Degradation and removal methods of antibiotics from aqueous matrices—a review. *Journal of environmental management*. 2011 Oct 1;92(10):2304-47
9. O.M. Rodriguez-Narvaez, J.M. Peralta-Hernandez, A. Goonetilleke, E.R. Bandala, Treatment technologies for emerging contaminants in water: A review. *Chem. Eng. J.* **1**, 323:361–380 (2017 Sep)
10. J. Xue, C. Huang, Y. Zong, J. Gu, M. Wang, S. Ma, Fe (III)-grafted Bi₂MoO₆ nanoplates for enhanced photocatalytic activities on tetracycline degradation and HMF oxidation. *Appl. Organomet. Chem.* **33**(11), e5187 (2019 Nov)
11. F. Al Marzouqi, N.A. Al-Balushi, A.T. Kuvarega, S. Karthikeyan, R. Selvaraj, Thermal and hydrothermal synthesis of WO₃ nanostructure and its optical and photocatalytic properties for the degradation of Cephalexin and Nizatidine in aqueous solution. *Mater. Sci. Engineering: B* **1**, 264:114991 (2021 Feb)
12. M.G. Bhosale, R.S. Sutar, S.S. Londhe, M.K. Patil, Sol–gel method synthesized Ce-doped TiO₂ visible light photocatalyst for degradation of organic pollutants. *Applied Organometallic Chemistry*:.e6586
13. Y.X. Zhang, Y. Jia, Synthesis of MgO/TiO₂/Ag composites with good adsorption combined with photodegradation properties. *Mater. Sci. Engineering: B* **1**, 228:123–131 (2018 Feb)
14. H.V. Vasei, S.M. Masoudpanah, M. Adeli, M.R. Aboutalebi, M. Habibollahzadeh, Mesoporous honeycomb-like ZnO as ultraviolet photocatalyst synthesized via solution combustion method. *Mater. Res. Bull.* **1**, 117:72–77 (2019 Sep)
15. M. Zhu, H. Chen, Y. Dai, X. Wu, Z. Han, Y. Zhu, Novel n-p-n heterojunction of AgI/BiOI/UiO-66 composites with boosting visible light photocatalytic activities. *Appl. Organomet. Chem.* **35**(5), e6186 (2021 May)
16. C. Zhang, Y. Zhou, Y. Zhang, S. Zhao, J. Fang, X. Sheng, The investigation of Ag decorated double-wall hollow TiO₂ spheres as photocatalyst. *Appl. Organomet. Chem.* **32**(3), e4160 (2018 Mar)
17. M. Zangiabadi, T. Shamspur, A. Saljooqi, A. Mostafavi, Evaluating the efficiency of the GO-Fe₃O₄/TiO₂ mesoporous photocatalyst for degradation of chlorpyrifos pesticide under visible light irradiation. *Appl. Organomet. Chem.* **33**(5), e4813 (2019 May)
18. N.P. de Moraes, C.M. Goes, D.C. Sperandio, R. da Silva Rocha, R. Landers, T. Paramasivam, L.A. Rodrigues, Development of a new zinc oxide/tin oxide/carbon xerogel photocatalyst for visible light photodegradation of 4-chlorophenol. *Mater. Sci. Engineering: B* **1**, 269:115183 (2021 Jul)
19. G. Dong, Y. Zhang, Q. Pan, J. Qiu, A fantastic graphitic carbon nitride (g-C₃N₄) material: electronic structure, photocatalytic and photoelectronic properties. *J. Photochem. Photobiol., C* **1**, 20:33–50 (2014 Sep)
20. R. Zhang, X. Zhang, S. Liu, J. Tong, F. Kong, N. Sun, X. Han, Y. Zhang, Enhanced photocatalytic activity and optical response mechanism of porous graphitic carbon nitride (g-C₃N₄) nanosheets. *Mater. Res. Bull.* **1**, 140:111263 (2021 Aug)
21. Z. Cui, H. Yang, X. Zhao, Enhanced photocatalytic performance of g-C₃N₄/Bi₄Ti₃O₁₂ heterojunction nanocomposites. *Mater. Sci. Engineering: B* **1**, 229:160–172 (2018 Mar)

22. H. Shi, J. Fu, W. Jiang, Y. Wang, B. Liu, J. Liu, H. Ji, W. Wang, Z. Chen, Construction of g-C₃N₄/Bi₄Ti₃O₁₂ hollow nanofibers with highly efficient visible-light-driven photocatalytic performance. *Colloids Surf., A* **20**, 615:126063 (2021 Apr)
23. G. Gebreslassie, P. Bharali, U. Chandra, A. Sergawie, P.K. Baruah, M.R. Das, E. Alemayehu, Hydrothermal synthesis of g-C₃N₄/NiFe₂O₄ nanocomposite and its enhanced photocatalytic activity. *Appl. Organomet. Chem.* **33**(8), e5002 (2019 Aug)
24. Z. Chen, S. Zhang, Y. Liu, N.S. Alharbi, S.O. Rabah, S. Wang, X. Wang, Synthesis and fabrication of g-C₃N₄-based materials and their application in elimination of pollutants. *Sci. Total Environ.* **5**, 139054 (2020 May)
25. M. Singh, M. Goyal, K. Devlal. Size and shape effects on the band gap of semiconductor compound nanomaterials. *Journal of Taibah University for Science.* 2018 Jul 4;12(4):470- 5
26. K.C. Devarayapalli, S.P. Vattikuti, T.V. Sreekanth, K.S. Yoo, P.C. Nagajyothi, J. Shim, Hydrogen production and photocatalytic activity of g-C₃N₄/Co-MOF (ZIF-67) nanocomposite under visible light irradiation. *Appl. Organomet. Chem.* **34**(3), e5376 (2020 Mar)
27. C.P. Goh, P.E. Lim, Potassium permanganate as oxidant in the COD test for saline water samples. *ASEAN J. Sci. Technol. Dev.* **25**(2), 383–393 (2008)
28. Q. Wang, P. Li, Z. Zhang, C. Jiang, K. Zuojiang, J. Liu, Y. Wang. Kinetics and mechanism insights into the photodegradation of tetracycline hydrochloride and ofloxacin mixed antibiotics with the flower-like BiOCl/TiO₂ heterojunction. *Journal of Photochemistry and Photobiology A: Chemistry.* 2019 Jun 1;378:114 – 24
29. J. He, Y. Zhang, Y. Guo, G. Rhodes, J. Yeom, H. Li, W. Zhang. Photocatalytic degradation of cephalexin by ZnO nanowires under simulated sunlight: Kinetics, influencing factors, and mechanisms. *Environment international.* 2019 Nov 1;132:105105
30. F. Wang, Y. Feng, P. Chen, Y. Wang, Y. Su, Q. Zhang, Y. Zeng, Z. Xie, H. Liu, Y. Liu, W. Lv, Photocatalytic degradation of fluoroquinolone antibiotics using ordered mesoporous gC₃N₄ under simulated sunlight irradiation: kinetics, mechanism, and antibacterial activity elimination. *Applied Catalysis B: Environmental.* 2018 Jul 5;227:114–22
31. A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.O. Müller, R. Schlögl, J.M. Carlsson, Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts. *J. Mater. Chem.* **18**(41), 4893–4908 (2008)
32. E. Alwin, K. Kočí, R. Wojcieszak, M. Zieliński, M. Edelmannová, M. Pietrowski, Influence of high temperature synthesis on the structure of graphitic carbon nitride and its hydrogen generation ability. *Materials.* **13**(12), 2756 (2020 Jan)
33. H. Zhao, X.L. Chen, C. Jia, T. Zhou, X. Qu, J. Jian, Y. Xu, T. Zhou, WITHDRAWN: A facile mechanochemical way to prepare g-C₃N₄. *Materials Science and Engineering: B.* 2005 Sep 25;122(3):226–30
34. Z. Jin, Q. Zhang, S. Yuan, T. Ohno, Synthesis high specific surface area nanotube gC₃N₄ with two-step condensation treatment of melamine to enhance photocatalysis properties. *RSC Adv.* **5**(6),

4026–4029 (2015)

35. C. Hu, Y.C. Chu, M.S. Wang, X.H. Wu, Rapid synthesis of g-C₃N₄ spheres using microwave-assisted solvothermal method for enhanced photocatalytic activity. *Journal of Photochemistry and Photobiology A: Chemistry*. 2017 Nov 1;348:8–17
36. Z. Chen, S. Zhang, Y. Liu, N.S. Alharbi, S.O. Rabah, S. Wang, X. Wang, Synthesis and fabrication of g-C₃N₄-based materials and their application in elimination of pollutants. *Sci. Total Environ.* **5**, 139054 (2020 May)
37. M. Ismael, Y. Wu, A mini-review on the synthesis and structural modification of gC₃N₄ based materials, and their applications in solar energy conversion and environmental remediation. *Sustainable Energy & Fuels* **3**(11), 2907–2925 (2019)
38. S.C. Yan, Z.S. Li, Z.G. Zou. Photodegradation performance of g-C₃N₄ fabricated by directly heating melamine. *Langmuir*. 2009 Sep 1;25(17):10397-401
39. X. Zhao, Y. Zhang, X. Zhao, X. Wang, Y. Zhao, H. Tan, H. Zhu, W. Ho, H. Sun, Y. Li, Urea and melamine formaldehyde resin-derived tubular g-C₃N₄ with highly efficient photocatalytic performance. *ACS applied materials & interfaces*. 2019 Jul 18;11(31):27934–43
40. G. Goglio, D. Foy, G. Demazeau, State of Art and recent trends in bulk carbon nitrides synthesis. *Materials Science and Engineering: R: Reports*. 2008 Jan 7;58(6):195–227
41. Q. Gan, W. Shi, Y. Xing, Y. Hou, A polyoxoniobate/g-C₃N₄ nanoporous material with high adsorption capacity of methylene blue from aqueous solution. *Frontiers in chemistry*. 2018 Jan 31;6:7
42. X. Bai, L. Wang, R. Zong, Y. Zhu, Photocatalytic activity enhanced via g-C₃N₄ nanoplates to nanorods. *J. Phys. Chem. C* **16**(19), 9952–9961 (2013 May) 117(
43. M. Yin, F. Jia, C. Wu, P. Zheng, Y. Fan, Z. Li, Coupling g-C₃N₄ nanobelts and Cu (OH) ₂ nanoparticles with TiO₂ for visible-light photocatalytic H₂ production. *Mater. Sci. Engineering: B* **1**, 223:35–42 (2017 Sep)
44. A. Fischer. "Reactive hard templating": from carbon nitrides to metal nitrides (Doctoral dissertation, Universität Potsdam)
45. X. Wang, L. Sør, R. Su, S. Wendt, P. Hald, A. Mamakhel, C. Yang, Y. Huang, B.B. Iversen, F. Besenbacher. The influence of crystallite size and crystallinity of anatase nanoparticles on the photo-degradation of phenol. *Journal of catalysis*. 2014 Feb 1;310:100-8
46. Y. Chen, B. Yang, W. Xie, X. Zhao, Z. Wang, X. Su, C. Yang. Combined soft templating with thermal exfoliation toward synthesis of porous g-C₃N₄ nanosheets for improved photocatalytic hydrogen evolution. *journal of materials research and technology*. 2021 Jul 1;13:301 – 10
47. R. Rastogi, R. Kaushal, S.K. Tripathi, A.L. Sharma, I. Kaur, L.M. Bharadwaj, Comparative study of carbon nanotube dispersion using surfactants. *Journal of colloid and interface science*. 2008 Dec 15;328(2):421–8
48. V. Sangeetha, N. Kanagathara, R. Sumathi, N. Sivakumar, G. Anbalagan, Spectral and thermal degradation of melamine cyanurate. *Journal of Materials*. 2013;262094

49. D. Luo, W. Duan, Y. Liu, N. Chen, Q. Wang, Melamine cyanurate surface treated by nylon of low molecular weight to prepare flame- retardant polyamide 66 with high flowability. *Fire Mater.* **43**(3), 323–331 (2019 Apr)
50. G. Xin, Y. Meng, Pyrolysis synthesized g-C₃N₄ for photocatalytic degradation of methylene blue. *Journal of Chemistry.* 2013 Jan 1;2013
51. X. Ren, X. Meng, J. Ren, F. Tang, Graphitic carbon nitride nanosheets with tunable optical properties and their superoxide dismutase mimetic ability. *RSC Adv.* **6**(95), 92839–92844 (2016)
52. A. Kumar, P. Kumar, C. Joshi, M. Manchanda, R. Boukherroub, S.L. Jain, Nickel decorated on phosphorous-doped carbon nitride as an efficient photocatalyst for reduction of nitrobenzenes. *Nanomaterials.* **6**(4), 59 (2016 Apr)
53. C. Liu, X. Dong, Y. Hao, X. Wang, H. Ma, X. Zhang, A novel supramolecular preorganization route for improving gC₃N₄/gC₃N₄ metal-free homojunction photocatalysis. *New J. Chem.* **41**(20), 11872–11880 (2017)
54. S.P. Pattnaik, A. Behera, S. Martha, R. Acharya, K. Parida, Facile synthesis of exfoliated graphitic carbon nitride for photocatalytic degradation of ciprofloxacin under solar irradiation. *J. Mater. Sci.* **54**(7), 5726–5742 (2019 Apr)
55. F. Jensen, Activation energies and the Arrhenius equation. *Qual. Reliab. Eng. Int.* **1**(1), 13–17 (1985 Jan)
56. B. Zhu, P. Xia, W. Ho, J. Yu, Isoelectric point and adsorption activity of porous g-C₃N₄. *Appl. Surf. Sci.* **30**, 344:188–195 (2015 Jul)

Figures

Figure 1

FT-IR spectra of melamine-cyanuric acid (a), g-C₃N₄ NTs (b), and Ru(II)complex/g-C₃N₄ NTs (c).

Figure 2

The spectrum of a) UV-Vis spectrum b) curve of $(\alpha h\nu)^2$ versus $h\nu$ of g-C₃N₄ NTs to bandgap estimation.

Figure 3

XRD patterns of a) Melamine-Cyanuric acid , b) Ru(II)complex/g-C₃N₄ NTs

Figure 4

Scanning electron microscopy (SEM) photographs (a), energy-dispersive X-ray pattern (b) and element distribution map (c) of Ru(II)complex/g-C₃N₄ NTs photocatalyst.

Figure 5

TEM images of Ru(II) complex/g-C₃N₄ NTs photocatalyst.

Figure 6

a) Influence of temperature on the photocatalytic degradation of tetracycline, b) Plot of $\ln(C/C_0)$ versus time to investigation of temperature effect on the degradation rate. Reaction conditions: drug concentration: 10 mg/L, irradiation time: 90 min, light intensity: 60 Watt, temperature: 25°C, pH: 7

Figure 7

Influence of irradiation time on the photocatalytic degradation of tetracycline in water. Drug concentration: 10 mg/L, Ru(II) complex/g-C₃N₄ NTs amount: 30 mg, light intensity: 60 Watt, temperature: 25 °C, pH: 7

Figure 8

a) Influence of temperature on the photocatalytic degradation of tetracycline in the first 30 minutes, b) Plot of $\ln(C/C_0)$ versus time to investigation of temperature effect on the degradation rate. Reaction conditions: drug concentration: 10 mg/L, Ru(II) complex/g- C_3N_4 NTs amount: 30 mg, irradiation time: 90 min, light intensity: 60 Watt, pH: 7

Figure 9

Plot of $\ln k$ versus $1/T$ to estimation of E_a .

Figure 10

a) Influence of pH on the photocatalytic degradation of tetracycline in the first 30 minutes, b) Plot of $\ln(C/C_0)$ versus time to investigation of pH effect on the degradation rate. Reaction conditions: drug concentration: 10 mg/L, Ru(II) complex/g- C_3N_4 NTs amount: 30 mg, irradiation time: 90 min, light intensity: 60 Watt, Temperature: 25°C