# Insights into the mechanism of g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> microsphere heterogeneous activation of hydrogen peroxide under visible light

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**Abstract.** A-Fe<sub>2</sub>O<sub>3</sub> complex q-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> was successfully prepared by solvothermal method and used in optical Fenton photocatalytic process. Using experimental instruments such as XPS, XRD, DRS, TEM, FTIR, and photochemistry to characterize composite materials. According to the mechanism of the photocatalytic process, combining A-Fe<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> Fenton reagent with g-C<sub>3</sub>N<sub>4</sub> photocatalyst under visible light conditions can effectively accelerate the mineralization of pollutants. The photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> were evaluated by the decomposition of bisphenol A. When the content of a-Fe<sub>2</sub>O<sub>3</sub> is 15%, the photocatalytic efficiency of the composite is the highest. In addition, cyclic operation, iron leaching concentration, fresh and XRD pattern studies indicate that g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> composites are very stable and reusable. The results show that the decomposition of BPA by persulfate is a non-free radical reaction, but the coupling a-Fe<sub>2</sub>O<sub>3</sub> with q-C<sub>3</sub>N<sub>4</sub> can effectively activate the formation of persulfate free radicals and reduce BPA under visible light radiation. Studies showed that free radicals generated by electron holes and persulfate formed on catalysts were the main causes of BPA decomposition. Therefore, combined with previous research results, this paper proposed the mechanism of g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> composite photocatalytic reaction by photo-Fenton. More importantly, this work demonstrates a novel approach to activate persulfates that can efficiently degrade pops and gives some new ideas on the remediation of persulfates in contaminated Water.

**Keywords:** g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub>; Fenton photocatalytic process; persulfates; non-free radical reaction

# 1. Introduction

Due to their benefits of purity, energy efficiency, safety, and the absence of secondary pollution,  $AOH_2O_2$  based on the generation of reactive oxygen species, such as the Fenton reaction, photocatalytic oxidation, ozonation, etc., are regarded as efficient methods of degradation of harmful organic (and occasionally inorganic) pollutants in wastewater2, 3. As a result, numerous studies have been conducted in an effort to increase the treatment  $AOH_2O_2$  efficiency of  $AOH_2O_2$ , lower pollution, and improve performance. Heterogeneous is more of a worry than homogeneous  $AOH_2O_2$  due to its moderate reaction conditions and essentially nonexistent post-reaction sludge production4, 5.

Polymeric graphite-like carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), developed recently, has a moderately dense strip energy (~2.7 eV), a low cost, strong chemical and thermal durability, a straightforward synthesis procedure, and a two-dimensional metal-free structure with just carbon and nitrogen. It is a potentially useful solar photocatalytic substance6, 7. In contrast, the majority of metal oxide photocatalysts release poisonous metal ions and only can utilize ultraviolet light to generate conductive band electrons (e-) and valence band holes (h+) that can be used to degrade pollutants. Graphite carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), which only contains carbon and nitrogen, has been utilized in a number of photocatalytic applications9-11 under visible light to reduce environmental concerns and increase solar energy productivity. The polymeric semiconductor exhibits an intrinsic visible light response and is low-cost, very stable, and environmentally benign12.

Iron oxide (a-Fe<sub>2</sub>O<sub>3</sub>) is abundant in earth's surface soils, sediments, rocks, and water13. Due to its non-toxicity, low cost, availability and corrosion resistance, goethite (a-Fe<sub>2</sub>O<sub>3</sub>) has been widely

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used in rechargeable lithium-ion batteries, body sensing applications, organic pollutant degradation, water purification, magnetic components, electrode materials and other applications14-16. Many fellows have prepared manifold forms of a-Fe<sub>2</sub>O<sub>3</sub>, such as nanorods, sea urchins, nanospheres, arrays, and pancakes, and have assessed their photocatalytic activity17-19. Although exhibits high absorption capacity in the visible spectrum's reddish spectrum (1.9-2.2 eV), charge carrier recombination reduces the efficiency of a-Fe<sub>2</sub>O<sub>3</sub> as a photocatalyst. However, the drawback of pure g-C<sub>3</sub>N<sub>4</sub> is its limited specific surface area and high rate of photoinduced charge recombination6.

As a result, modifications are needed to dispel these inherent defects. The functionalization of metal nanoparticles20, 21, adulteration of metal<sub>20</sub> and non-metal components, increase of specific surface area21, 22, development of composite materials and heterostructures23-29, and control of shape are actions taken to improve the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> 30-32. Additionally, it has been demonstrated that the characteristics of the organic precursors as well as the actual heat treatment conditions (such as temperature, atmosphere) utilized to generate g-C<sub>3</sub>N<sub>4</sub> affect the activity of such photocatalysts (melamine, urea, etc.) 33-35. Therefore, different routes can prepare materials with various catalytic activities. linking with other semiconductors is of particular interest among the different approaches to improving g-C<sub>3</sub>N<sub>4</sub> activity. The coupling of different semiconductors and nanocomposites is an desired development of inexpensive materials with advanced performance. It is formed on the basis of abundant raw materials and can show distinctive performance not reflected in personal compound materials. Pure g-C<sub>3</sub>N<sub>4</sub>'s photocatalytic activity can be enhanced by recombination of g-C<sub>3</sub>N<sub>4</sub> with different metal oxides to enhances the e~/h+ separation effect and speeds up visible light absorption23, 24, 36-38. The strategy is to effectively separate photocarriers by choosing oxides with energy-matched conductance (CB) and valence band (VB) for g-C<sub>3</sub>N<sub>4</sub>, and is capable of controlling the separation and transfer of charges. Although  $H_2O_2$  can produce  $SO_4^{-}$  through ultraviolet radiation and thermal activation, the use of these techniques in practical applications is rather limited due to the high energy input required.36, 37 In recent years, transition excessive metals have been used to activate H<sub>2</sub>O<sub>2</sub> to degrade contaminants in water38, of which iron (usually dissolved Fe<sub>2</sub>+) is widely used due to its non-toxic, abundant and effective properties 39-42. However, because ferrous iron is inactivated due to rapid oxidation and deposition into ferrous iron, it also increases the operating costs of removing iron sludge from water for purification after reaction.

Although iron oxides exhibit good properties under laboratory conditions, leaching of harmful iron ions may have harmful side effects in industrial applications 43. Therefore, in order to use iron based AOH<sub>2</sub>O<sub>2</sub> for wastewater treatment, it is necessary to determine the mechanism of Fe<sub>2</sub>O<sub>3</sub> activation AOH<sub>2</sub>O<sub>2</sub> process and solve the problem of side effects. One concept is to use the high catalytic capacity of a-Fe<sub>2</sub>O<sub>3</sub> and the photocatalytic capability of g-C<sub>3</sub>N<sub>4</sub> to combine a-Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>. Therefore, g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> was prepared using a straightforward one-step approach in this study, and the activation of H<sub>2</sub>O<sub>2</sub> as a heterogeneous catalyst was investigated. Particular attention was paid to how pH affected the coupled process (g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) Instead of the electrostatic attraction between the matrix and the catalyst as was previously postulated, the considerable impact of the solution's pH on the functionality and stability of g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> may be mostly attributable to the leaching of iron ions. At last, catalyst's characterization and the experimental findings indicate that the g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> mechanism of the activated H<sub>2</sub>O<sub>2</sub> process is clearly understood. The activity of g-C<sub>3</sub>N<sub>4</sub> supported by 15% a-Fe<sub>2</sub>O<sub>3</sub> nanorods is raised by 3 times and 3.5 times when compared to pure g-C<sub>3</sub>N<sub>4</sub> and pure a-Fe<sub>2</sub>O<sub>3</sub> nanorods, respectively.Using various spectral methods, the excellent characteristics of the composite material  $a-Fe_2O_3(a)$  g-C<sub>3</sub>N<sub>4</sub> were obtained .

# 2. Materials and methods

# 2.1 Materials.

Both bisphenol A (99%) and 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) were purchased from Aladdin in China. The analytical grade isopropyl alcohol (IPA),  $Fe(NO_3)_{3}$ ·<sub>9</sub>H<sub>2</sub>O, NaOH, H<sub>2</sub>SO<sub>4</sub>, and urea were all purchased from Sinopharm Chemical Reagent Co. in China. Triethanolamine (TEOA) and zp-Benzoquinone (BQ) were supplied by Aladdin Ltd. (Shanghai, China). All of the materials utilized in the investigation were not deep purified, and Milli-Q water was used throughout.

# 2.2 Creation of g-C<sub>3</sub>N<sub>4</sub>.

By heating urea, graphitized carbon nitride  $(g-C_3N_4)$  was created<sub>26</sub>. Alumina crucible with a lid and 10 g of urea were used for the drying process, which took one hour at 80°C. The urea was subsequently heated to 520°C using a PID temperature controller in a reliable burner at a heating rate of 2.3°C/min1, and kept at this temperature for 3 hours. After waiting until it has reached room temperature, obtain a light yellow g-C<sub>3</sub>N<sub>4</sub> 3.

# 2.3 Hydrothermal synthesis of a-Fe<sub>2</sub>O<sub>3</sub> nanorods

 $Fe(NO_3)_3 \cdot 9H_2O$  diffluence was determined in 20 mL deionized water, and NaOH solution was added in with vigorous stirring to get pH to 12. The resultant solution was then hydrothermally treated at 180°C for 24 hours after being sealed in a Teflon autoclave. Centrifugation, washing in deionized water, and 24-hour drying at 60 °C

# 2.4 Hydrothermal synthesis of g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> composites

To create a well-separated mono-layer of  $C_3N_4$  in a classical experiment, the correct amount of  $g-C_3N_4$  was dispersed in 50 mL of deionized water and processed sonographically for two hours in an ultrasonic bath. The previously prepared Fe<sub>3</sub>+ precipitate was then added, and the yellow  $g-C_3N_4$  suspension was agitated for 30 minutes. The technique for creating  $a-Fe_2O_3$  nanorods after that is the same as what was previously stated. With values of 5, 10, 15, and 20 weight percent, different amounts of  $a-Fe_2O_3$  were loaded onto  $g-C_3N_4$ .

#### 2.5 Characterization

The Rigaku D/Max-Rb diffractometer was used to obtain powder X-ray diffraction (XRD) images of Cu-Ka radiation ( $\lambda$ =15418 a) in the 10-80°20 range. In the spectral region of 200–800 nm, ultraviolet–visible proliferating reflectance (DRS) spectrum data were collected using a PerkinElmer  $\lambda$  950 spectrophotometer at room temperature. Thermo Nicolet Avatar 370 FTIR spectrophotometer and the KBr pellet technique were used to determine the Fourier transform infrared spectrum. Perform scanning electron microscopy (SEM) and energy-dispersive X-ray spectra using a JEOL JEM-100C II electron microscope from Japan (EDX).

# 2.6 Experimental procedure and analyses

A UV filter ( $\lambda \ge 420$  nm) and a 500 W halogen tungsten light were both employed as sources of visible light. And use a cylindrical glass container with a glass casing to house the light. Under visible light, bisphenol A was degraded by photoreactor. In each experimentation, a water based solution of BPA (0.4 g/ L) was positioned in the reactor and the desired catalytic dose was added. The levitation is then mixed with a constant speed magnetic force for 30 minutes, and the lamp is turned on while the required volume of H<sub>2</sub>O<sub>2</sub> is put into the reaction kettle. To change the working solution's initial pH to the appropriate level, use HNO<sub>3</sub> or NaOH solution. The working settlement of the added material is mixed at room temperature with a magnetic stirrer for a preset period of time. The flow rate was 1 mL/min, the injection volume was 40 mL, and the analysis spectrum was

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278 nm. The flowing phase was a 70:30 mixture of methanol and water. To determine the pH of the fluid, a composite glass electrode was connected to a Mettler Toledo FE 20 pH meter. After combining 1,10-phenanthroline, an iron-phenanthroline complex is created. The amount of  $H_2O_2$  present was determined using an iodimetry titration, and the iron ion's dipping volume was determined using a spectrophotometer at 510 nm. Jena Multi N/C 3100 TOC analyzer was used to detect residual TOC in the aqueous solutions. Spectra of electron spin resonance (ESR) are maintained below. When employing the ESP 300E electronic paramagnetic resonance spectrometer with a xenon lamp (420 nm filter) as an illumination source, the spin signal of free radicals caught by DMPO was obtained.

After many applications, the stability of photocatalyst was studied. After each photocatalytic reaction, clean the solid photocatalyst and dry it with deionized water to ensure it can be reused.

#### 3. Results

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#### **3.1 XRD analysis**



Fig. 1 XRD patterns of (a) pure a-Fe<sub>2</sub>O<sub>3</sub>, (b) pure g-C<sub>3</sub>N<sub>4</sub>, (c) 0.5% a-Fe<sub>2</sub>O<sub>3</sub>@C<sub>3</sub>N<sub>4</sub>, (d) 1.0% a-Fe<sub>2</sub>O<sub>3</sub>@C<sub>3</sub>N<sub>4</sub> and (e) 2.0% a-Fe<sub>2</sub>O<sub>3</sub>@C<sub>3</sub>N<sub>4</sub>.

The structural features and elemental composition of pure  $a-Fe_2O_3$  nanorods and  $a-Fe_2O_3$  nanorods@g-C<sub>3</sub>N<sub>4</sub> nanocomposites were confirmed by the XRD patterns (Fig. 1). The orthogonal  $a-Fe_2O_3$  system in JCPDS document no. 81-0462 is related with the XRD peaks. There were no highly similar indexing surfaces or impurity correlation peaks to be seen. The produced photocatalyst exhibits a high purity of the crystal phase, and the relative widening of the reflection peak suggests the production of nanomaterials. For pure G-C<sub>3</sub>N<sub>4</sub>, what can be observed at  $2\theta=27.4^{\circ}$  is a strong diffraction peak, which is used as the diffraction plane (002) for graphite carbon nitride materials (JCPDS File No. 87-1526), famous as its melon nets27. On the (100) crystal plane of g-C<sub>3</sub>N<sub>4</sub>, there is another weak diffraction peak at  $2\theta=13.1^{\circ}$  that resembles the interplanar structural stacking of tris-triazine unit 28. The crystal phase of  $a-Fe_2O_3$  and the crystal plane of g-C<sub>3</sub>N<sub>4</sub> at  $2\theta=13.1^{\circ}$  that resembles the interplanar structural stacking of tris-triazine unit 28. The crystal phase of  $a-Fe_2O_3$  and the crystal plane of g-C<sub>3</sub>N<sub>4</sub> at  $2\theta=13.1^{\circ}$  vanishes. The mass fraction of  $a-Fe_2O_3$  is inversely correlated with the  $a-Fe_2O_3$  diffraction peak. Only the  $a-Fe_2O_3$  and g-C<sub>3</sub>N<sub>4</sub> phases were discovered in the composite since no other impurity peaks could be seen in the XRD pattern.

# **3.2 UV-vis diffuse reflectance spectra**





The equivalent DRS for the composite is displayed in Figure 2 to help with comprehension of the optic performance. All wavelength ranges of  $a-Fe_2O_3$  range were examined. Additionally, because  $a-E_2O_3$  has a larger absorption coefficient in the near-infrared region, the absorption of the composites at 600–800 nm is improved with an increase in  $a-Fe_2O_3$  mass fraction.

#### **3.3 TEM analysis**



Fig. 3 (A) and (B) HRTEM; (C) mapping images of 15% a-Fe<sub>2</sub>O<sub>3</sub>@C<sub>3</sub>N<sub>4</sub>

The morphological properties of  $a-Fe_2O_3$ , bare  $g-C_3N_4$ , and  $15\% a-Fe_2O_3@C_3N_4$  are shown in Figure 3. (Fig. 3A) show the canonical morphological characteristics of  $g-C_3N_4$  composited by

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melamine polymerization43. Fig. 3B shows the SEM image of a-Fe<sub>2</sub>O<sub>3</sub> microcrystals. As can be seen, many irregular nanorods self-assemble into rod-like upper Infrastructure. Fig. 3C show the morphology of 15% a-Fe<sub>2</sub>O<sub>3</sub>@C<sub>3</sub>N<sub>4</sub>. After g- combined with a-Fe<sub>2</sub>O<sub>3</sub>, the size of g-C<sub>3</sub>N<sub>4</sub> particles tended to become homogeneous and the lamellar structure decreased. Moreover, rod-like microcrystals are composed of irregular nanorods themselves.

#### 3.4 Performance of photo-Fenton photocatalysis

The photo-Fenton photocatalytic reaction of several catalysts was carried out under optical light treatment in the presence of  $H_2O_2$  in order to access the activity of the g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> composite, as shown in Fig. 4.  $H_2O_2$  degradation and direct photodegradation of BPA (blank) under optical light might both be disregarded. Pure a-Fe<sub>2</sub>O<sub>3</sub> has very little capacity to decompose when exposed to visible light without the aid of  $H_2O_2$ . However, the g-C<sub>3</sub>N<sub>4</sub> conjugation affects its capacity for degradation. The findings demonstrate that, within a particular range, the mass fraction of a-Fe<sub>2</sub>O<sub>3</sub> can enhance photocatalytic activity. The photocatalytic effect can be enhanced when the mass fraction of a-Fe<sub>2</sub>O<sub>3</sub> is less than 15%, but when the mass fraction of a-Fe<sub>2</sub>O<sub>3</sub> is increased to 20%, the degradation rate of BPA is lower than 15% of a-Fe<sub>2</sub>O<sub>3</sub> composite material. Therefore, in this study, 15% a-Fe<sub>2</sub>O<sub>3</sub> has the perfect photocatalytic viability. This may be because the surplus a-Fe<sub>2</sub>O<sub>3</sub> covering the surface provides a compound center for the electron-hole pair produced by light, thus preventing the effective utilization of optical light by g-C<sub>3</sub>N<sub>4</sub>. This will limit the contribution of g-C<sub>3</sub>N<sub>4</sub> to the Fenton reaction of a-Fe<sub>2</sub>O<sub>3</sub>, which means the promoting effect of g- C<sub>3</sub>N<sub>4</sub> on a-Fe<sub>2</sub>O<sub>3</sub> Fenton reaction cannot be fully demonstrated. Therefore, it is necessary to control a certain amount of a-Fe<sub>2</sub>O<sub>3</sub> in the composite catalyst to promote the photocatalytic efficiency of photo-Fenton.



Fig. 4 BPA breakdown over the various catalysts when exposed to visible spectrum and H<sub>2</sub>O<sub>2</sub>.

#### 3.5 Radical trapping experiments

We performed capture experiments to investigate the primary active components<sub>44</sub> in order to further clarify the photo-Fenton photocatalytic mechanism. IPA which may absorb •OH radicals, dramatically lowers the catalytic activity of a-Fe<sub>2</sub>O<sub>3</sub>@C<sub>3</sub>N<sub>4</sub> by 15%, as shown in Figure 5. The addition of triethanolamine (TEOA) also reduces the reaction rate and can capture the well. However, there was no discernible difference in the rate of degradation when the p-benzoquinone (BQ) scavenger was added. The photogenerated holes are the primary oxidizing agents in the photo phentonic photocatalytic process, according to the results of the capture experiment.

To support this finding, using EtOH—a radical scavenger for  $\bullet$ OH and  $\bullet$ SO<sub>4</sub>, in an EPR experiment with DMPO acting as the radical search agent to look for any radical formation. As

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shown in Fig. 5, the addition of ethyl acetate induces the formation of DMPO-SO<sub>4</sub> and DMPO-OH adduct signals, which are then amplified by the addition of 15% a-Fe<sub>2</sub>O<sub>3</sub>@C<sub>3</sub>N<sub>4</sub> (producing 15% Fe<sub>2</sub>O<sub>3</sub>@C<sub>3</sub>N<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>/Vis processes). This observation can be likened to systems that have been brightened by visible light, which indicates that more free radicals are generating. The findings demonstrated that exposure to visible light can cause the free radicals •OH and •SO<sub>4</sub> 37, which promotes BPA discoloration.



Fig. 5 Effect of the several scavengers on BPA decomposition exceeding 15% a-Fe<sub>2</sub>O<sub>3</sub>@C<sub>3</sub>N<sub>4</sub> in presence of H<sub>2</sub>O<sub>2</sub> under visible range radiation.

#### 3.6 ESR analysis

To investigate the effect for the active species due to the coupling of a-Fe<sub>2</sub>O<sub>3</sub> with the g-C<sub>3</sub>N<sub>4</sub>, ESR spin-trap experiments were carried out. To confirm this observation, we used EtOH, which is free radical scavenger •OH and •SO<sub>4</sub>, and DMPO as free radical scavenger to inspect free radical formation in EPR experiments. Fig. 6 a shows that the H<sub>2</sub>O<sub>2</sub>/dark process did not investigate a significant signal confirming that BPA depigmentation of H<sub>2</sub>O<sub>2</sub> alone was caused by a non-free radical reaction. The DMPO-OH adduct signal was muted when EtOH was introduced to the reaction system. In the procedure of H<sub>2</sub>O<sub>2</sub>/Vis, DMPO-OH adduct signals occurred, and the addition of 15% g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> amplified these signals, demonstrating the formation of additional free radicals. These findings imply that exposure to visible light may cause the production of •OH 37 radicals and hence accelerate BPA discoloration. The signals for different composites are displayed in Fig. 6b. The signal strengths are in the range of 15% g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> × a-Fe<sub>2</sub>O<sub>3</sub> × a-Fe<sub>2</sub>O<sub>3</sub> × a-Fe<sub>2</sub>O<sub>3</sub> was more effective at degrading the pollutants.



Fig. 6 Various processes' EPR spectra with and without BPA. g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> (0.4 g/L), H<sub>2</sub>O<sub>2</sub> (8.0 mmol/L), DMPO (18 mmol), starting pH 5.0, and photocatalytic reaction duration 5 min.

#### 3.7 Electrochemistry analysis

The photocurrent reaction of pure g-C<sub>3</sub>N<sub>4</sub> and composites made of 15% g-C<sub>3</sub>N<sub>4</sub>@a- Fe<sub>2</sub>O<sub>3</sub> and a-Fe<sub>2</sub>O<sub>3</sub> is shown in Fig. 7. When the light has been on, the current intensity is steady; when the light is out, it quickly returns to the electrically dark state. The photocurrent is created by isolating and sending the photoinduced charges to the active electrodes. When pure g-C<sub>3</sub>N<sub>4</sub>, a-Fe<sub>2</sub>O<sub>3</sub>, and 15% g-C<sub>3</sub>N<sub>4</sub>@a- Fe<sub>2</sub>O<sub>3</sub> are compared for photocurrent intensity, it is discovered that the 15% g-C<sub>3</sub>N<sub>4</sub>@a- Fe<sub>2</sub>O<sub>3</sub> compound has a higher current than the pure g-C<sub>3</sub>N<sub>4</sub> and a-Fe<sub>2</sub>O<sub>3</sub>. According to the findings, it is more effective at separating electrons and holes and has a longer carrier life than pure g-C<sub>3</sub>N<sub>4</sub> and a-Fe<sub>2</sub>O<sub>3</sub> (15 percent g-C<sub>3</sub>N<sub>4</sub>@a- Fe<sub>2</sub>O<sub>3</sub>).

EIS experiments were carried out in order to show how 15% g-C<sub>3</sub>N<sub>4</sub>@a- Fe<sub>2</sub>O<sub>3</sub> composite outperformed pure g-C<sub>3</sub>N<sub>4</sub> and a-Fe<sub>2</sub>O<sub>3</sub> for charge carrier transfer. The 15 percent g-C<sub>3</sub>N<sub>4</sub>@a- Fe<sub>2</sub>O<sub>3</sub> composite has a lower charge shift resistance and a more effective electron-hole pair isolation as seen by the smaller Nyquist circle trail of the compound than that of pure g-C<sub>3</sub>N<sub>4</sub>.



Fig. 7. (A) Transient photocurrent response of sample electrodes made from pure C<sub>3</sub>N<sub>4</sub> and composites made of 15 weight percent g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub>. (B) Nyquist plots of the sample electrodes of pure g-C<sub>3</sub>N<sub>4</sub> and <sub>15</sub> weight percent g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> composites from EIS.

# 3.8 XPS analysis

XPS investigation was carried out to further evaluate the surface state and chemical make-up of iron at 15% g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub>. In accordance with the EDX characterization, Fig. 8 a shows XPS examination spectrum at 15% g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> indicates the presence of C, O, Fe, and N. The faulty sp2 hybrid carbon atoms on the pure graphite sites in the carbon-carbon domain and CN matrix are what cause the sp2 hybrid carbon atoms on the C-C, C=N, and C=O bonds to have the combination energies of C 1s at 284.7, 287.9, and 288.9 eV, respectively23, 24. The combination energies of N 1s are 398.3, 399.5, and 400.7 eV, which, respectively, correspond to sp2 hybrid N atoms in C=N, sp3 hybrid N atoms in C-[N]3, and C- NHX. Deeper dissections of high resolution XPS spectra were performed at around 720.0 eV in the Fe 2P area (Fig. 8b) and 532.0 eV in the O<sub>1</sub>s area (Fig. 8c). According to Fig. 8b, the two peaks at 711.3 and 724.8 eV, respectively, are associated with the Fe 2p3/2 and Fe 2p1/2 core power levels, which is consistent with previously published findings on a-Fe<sub>2</sub>O<sub>3</sub> (711.4 and 724.6 eV) 45. An oxidation state of Fe<sub>3</sub>+ is present as evidenced by the 13.2 eV energy gap between the spin orbital dipoles. 46 Additionally, the satellite's peak at 719.1 eV provides additional evidence that Fe<sub>3</sub>+ species are present on 15% of the surface of g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub>. The high-resolution O1s spectra exhibited in Fig. 8c after the curve has been adjusted shows two peaks at 529.6 eV and 530.9 eV, which represent, respectively, C=O and sp<sub>2</sub>-hybridized O atoms in the oxygen of the a-Fe<sub>2</sub>O<sub>3</sub> lattice45, 47. The results support the conclusion that a-Fe<sub>2</sub>O<sub>3</sub> has been successfully loaded onto g-C<sub>3</sub>N<sub>4</sub> by SEM, EDX and XRD.



Fig. 8. XPS spectrum of the 15% g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> composites: Fe 2p (A), C 1s(B), N 1s(C), O 1s(D).

# 3.9 The regime of photo-Fenton catalytic reaction of g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> composite was presented

The formation of active •OH and •SO<sub>4</sub> species was confirmed by DMPO's ESR rotary pitfall technique. DMPO functions as a stable DMPO/  $0^{2\bullet-}$  or DMPO/•OH radical scavenger in general. Image displays a four-line spectrum with compared strength of 1:2:2:1 under visible light exposure, which we believe is the properties spectrum of DMPO/•OH and DMPO/•SO<sub>4</sub> adduct 48. On the

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contrary, when the situation is dark environment, we cannot investigate significant ESR signal. In addition, no DMPO/•OH signal was inspected under dark and visible light irradiation. It also displays that •OH is the major oxidizing lively matter.

Since IFCT is a surface phenomenon, so the number of excited electrons produced by light absorption is limited, so the excited electrons generated by g-C<sub>3</sub>N<sub>4</sub> can be separated into two categories after being exposed to visible light. The first kind of electron has the ability to enter transmission of G-C<sub>3</sub>N<sub>4</sub> zone and unite with dispersed  $S_2O_8^{2-}$  to create  $\bullet$ SO<sub>4</sub>; But because of the huge energy level difference and ease of the synthesis of  $\bullet OH$ , the CB electron of g-C<sub>3</sub>N<sub>4</sub> (-1.23V) cannot move energy to Fe (III) (0.77V). Interfacial charge transfer (IFCT) induced by visible light is the second sort of electrons produced by light in the g-C<sub>3</sub>N<sub>4</sub> price band49, 50, while the pores continue to be within the g-C<sub>3</sub>N<sub>4</sub> pricing range. This reduces the distance over which electrons must travel, making it simple to swiftly separate photogenerated holes from electrons, increasing the mobility of the holes and expanding the region of visible light absorption. Being unstable, Fe(II) is readily transformed to Fe(III) by persulfate in the presence of environmental factors, suggesting that Fe(III) is recycled and Fe(III)/Fe(II) maintains a dynamic equilibrium of H<sub>2</sub>O<sub>2</sub>. Oxygen ( $S_2O_8^{2-}$ ) is converted to  $SO_4$  (S<sub>2</sub>O<sub>8</sub><sup>2-</sup> + Fe(II)  $\rightarrow$  Fe(III) +  $SO_4 + SO_4^{2-}$ ,  $SO_4 + H_2O \rightarrow OH^+ + SO_4^{2-}$ )48. Fe (III)/Fe (II) can accomplish the multi-electron reduction of oxygen and enhance the electron transport, which improves the photocatalytic activity in comparison to the single-electron reduction of CB in g-C<sub>3</sub>N<sub>4</sub>. In addition, compared with the active substance of mild oxidant  $\bullet$ SO<sub>4</sub>, the pores in C<sub>3</sub>N<sub>4</sub> VB showed strong photooxidation ability, which made BPA have good mineralization51. In contrast, although holes are involved in photocatalytic reactions, as mentioned above, holes are also involved in other reactions.

Therefore, photodegraded BPA is not thoroughly transformed to  $CO_2$ . Thus, Combining the above factors, fast charge transfer improves carrier isolation by leaving pores in  $C_3N_4$  and Fe (III) BB, allowing IFCT to produce more efficient electrons to reduce oxygen, resulting in the optimal photocatalytic performance of 15% a-Fe<sub>2</sub>O<sub>3</sub>@C<sub>3</sub>N<sub>4</sub> composites. Through the coupling of C<sub>3</sub>N<sub>4</sub> and a-Fe<sub>2</sub>O, the distribution of a-Fe<sub>2</sub>O in the composite is good, the size is small, and the content is high, so the composite has more active sites than a single material. As a result, ternary photocatalysts have higher light intake and less charge reorganization, bringing about better photocatalytic activity.



Fig. 9 Proposed photo-Fenton photocatalytic reaction mechanism for 15% a-Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites

#### 4. Conclusions

In conclusion, I successfully used the hydrothermal approach to create the unique  $g-C_3N_4@a-Fe_2O_3$  spheres with various  $g-C_3N_4$  mass percents. Due to the interaction with the

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g-C<sub>3</sub>N<sub>4</sub> photocatalyst, the catalytic activity of Fenton's reagent a-Fe<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> under visible light and no-light irradiation is greatly increased. The g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> microspheres exhibit improved photocatalytic viability due to up visible light sensitivity and katabatic reorganization of photoinduced vectors. Besides, g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> spheres are extremely steady and reusable in photo-Fenton photocatalytic reactions. It was suggested that the photo-Fenton photocatalytic reaction of g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> spheres was the mechanism used to explain the synergistic impact of a-Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>. The findings demonstrate that g-C<sub>3</sub>N<sub>4</sub>@a-Fe<sub>2</sub>O<sub>3</sub> microspheres, a novel form of photocatalyst, can consistently remove non-biodegradable organic contaminants in wastewater.

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