Removing lignin model pollutants with BiFeO$_3$–g-C$_3$N$_4$ compound as an efficient visible-light-heterogeneous Fenton-like catalyst

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ABSTRACT

BiFeO$_3$–g-C$_3$N$_4$ nanoscaled composite was prepared with a hydrothermal method and evaluated as a highly efficient photo-Fenton like catalyst under visible light irradiation. The BiFeO$_3$–g-C$_3$N$_4$ composite exhibited much stronger adsorption ability to lignin model pollutant (guaiacol) than that of BiFeO$_3$, which may be due to the higher specific surface area (BiFeO$_3$–g-C$_3$N$_4$: 35.59 m$^2$/g > BiFeO$_3$: 7.42 m$^2$/g) and the adsorption form of π–π stack between g-C$_3$N$_4$ and guaiacol. The composite exhibited excellent visible light-Fenton like catalysis activity, being influenced by the solution pH value and the proportions of BiFeO$_3$ and g-C$_3$N$_4$ nanosheets. Under optimal conditions with visible light irradiation, the BiFeO$_3$–g-C$_3$N$_4$ composite yielded fast degradation of guaiacol with an apparent rate constant of 0.0452 min$^{-1}$, which were 5.21 and 6.80 folds of that achieved by using BiFeO$_3$ and the mixture of BiFeO$_3$ and g-C$_3$N$_4$ nanosheets, respectively. The significantly enhanced visible light-Fenton like catalytic properties of the BiFeO$_3$–g-C$_3$N$_4$ composite in comparison with that of BiFeO$_3$ was attributed to a large surface area, much increased adsorption capacity and the semiconductor coupling effect between BiFeO$_3$ and g-C$_3$N$_4$ in the composite.

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Introduction

Carbon nitrides (CNs) are promising candidates to complement carbon in material applications due to the theoretical prediction of their unique electronic properties, remarkable mechanical properties and wide promising applications (Wang et al., 2012a; Zheng et al., 2012; Kawaguchi et al., 2004), in fields of organic catalysis (Su et al., 2010; Wang et al., 2011; Li et al., 2011), pollution control (Ishida et al., 2014; Oh et al., 2014; Pan et al., 2012; Wang et al., 2012b; Bai et al., 2013) and other domains. Among the allotropes of CNs, graphitic CN (g-C$_3$N$_4$) has been considered the most stable one under environmental condition. It possesses a stacked 2D structure, which can be regarded as an N-substituted graphite framework consisting of p-conjugated graphitic planes formed via sp$^2$ hybridization of carbon and nitrogen atoms (Zhang et al., 2011). It could be prepared economically and possess visible light catalytic activity. Due to the above properties, bulk g-C$_3$N$_4$ was used as catalyst carriers in the preparation of visible light catalysts (TaON/g-C$_3$N$_4$ (Yan et al., 2010), TiO$_2$/g-C$_3$N$_4$ (Yan and Yang, 2011), PANI/g-C$_3$N$_4$ (Ge et al., 2012), Au/g-C$_3$N$_4$ (Singh et al., 2012), Ag/g-C$_3$N$_4$ (Ge et al., 2011) and g-C$_3$N$_4$/BiFeO$_3$ (Fan et
Except bulk g-C3N4, researchers have prepared g-C3N4 with special structure. Jiang et al. (2014) have prepared 1-, 2-, and 4-layers g-C3N4 with significant improvements in the synthesis, structure, electronic and optical properties. Compared with bulk g-C3N4, few layer g-C3N4 nanosheets (NS) exhibited higher specific surface area and stronger visible light photocatalytic activity (Zhao et al., 2014). Therefore, few layer g-C3N4 NS may be excellent candidates as catalyst carriers.

Advanced oxidation processes which employed strong oxidative radicals (such as hydroxyl radicals and sulfate radicals) have been widely used for remove organic pollutants in water (Ren et al., 2015). Recently, increasing attention has been paid to heterogeneous Fenton-like process for water treatment in (AOPs). However, the catalytic efficiency of this process was not high enough to degrade stable pollutants. It was found that the association of visible light process and heterogeneous Fenton-like process could improve the catalytic efficiency (Yuan and Dai, 2014; Gao et al., 2015). Generally, some iron-contained catalysts possess Fenton or Fenton-like catalysis ability (Zhang et al., 2008; Feng et al., 2004; Neamtu et al., 2004; Deng et al., 2008; Guo et al., 2013; Guo and Zhang, 2016). BiFeO3 is a typical iron-contained catalyst, which possess relatively strong heterogeneous Fenton-like catalysis ability (Luo et al., 2010). However, BiFeO3 has weaker visible light catalysis performance (Liu et al., 2010; Li et al., 2009a).

To improve its weaker visible light catalysis performance, many efforts has been made by researchers (Guo et al., 2010; Li et al., 2009b). In our previous work, the surface modification of BiFeO3 with small molecule ligands could improve its visible light and heterogeneous Fenton-like catalysis ability. The oxidized species generated by the modified catalyst could degrade methyl violet efficiently during the visible light-heterogeneous Fenton-like process (An et al., 2013a). To further improve the catalytic performance of BiFeO3, we prepared the composite by growing BiFeO3 nanoparticles on graphene sheets, which were used to degrade tetrabromobisphenol A (An et al., 2013b). However, the preparation cost of graphene was high, it is necessary to develop a new low-cost carrier.

The pulp and paper industry is an almost global manufacture, being present in most developed and developing countries, which is very important to the development of economy and society. However, the industry is also considered as one of the largest contributor to industrial water pollution due to release of huge amount of dark colored effluent containing recalcitrant toxic compounds, which have an adverse effect on the environment (Pokhrel and Viraraghavan, 2004). The wastewater produced by the pulping process contains high levels of chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids (SS), and organic toxins (Catalaya and Kargj, 2008). Among these pollutants, the main compositions in the wastewater are degraded polysaccharide and lignin. The polysaccharide could be disposed by general technologies. However, the lignin is difficult to remove. And it is also the main source which generates the dark color and COD of the wastewater. Many efforts have been made to remove lignin in pulp and papermaking waste water. And the effect and shortcoming of these processes were showed in Table 1. As shown in the table, the most effective treatment technology to lignin is AOPs, which adopt strong oxidizing species (such as hydroxyl radicals) to degrade pollutants. And the efficiency of the Fenton process in AOPs is almost the highest. However, the homogeneous process produced abundant iron sludge, which is needed to be disposed with additional manpower and material resource. Therefore, the utilization of heterogeneous Fenton-like process to treat lignin is more welcomed. Lignin is a complex heteropolymer, composed of phenylpropanoid aryl-C3 units linked together via a variety of ether and C-C bonds. And the structure of softwood lignin was showed in Fig 1a. Considering the high complicated structure of lignin, many researchers choose some compounds which were similar with lignin in structure as lignin model compounds to evaluate the possibility of lignin degradation. Among them, guaiacol is considered a classic lignin model compound (Rittstieg et al., 2003), which is also an intermediate product in lignin degradation (Fig 1b). Therefore, guaiacol was chosen as a lignin model compound in this paper.

In order to further improve the adsorption and visible light-heterogeneous Fenton-like catalytic ability of BiFeO3, we prepared the composite of BiFeO3 and g-C3N4 NS by growing BiFeO3 nanoparticles on g-C3N4 NS in this paper. And guaiacol was chosen as an objective pollutant to evaluate the catalytic performance of the above composite. During the existence of visible light irradiation and H2O2, guaiacol was degraded by the generated strong oxidized species catalyzed with the composite. Through the study of guaiacol degradation, it may also provide a certain theoretical basis for the further degradation of lignin catalyzed by the composite in the future work.

### Table 1 – Effect and shortcoming of lignin removal process.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Process</th>
<th>Effect</th>
<th>Shortcoming</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical technology</td>
<td>Catalytic oxidation process</td>
<td>Could remove 90% lignin</td>
<td>Long disposal time; low degraded efficiency</td>
<td>Chang et al. (2004)</td>
</tr>
<tr>
<td></td>
<td>Electrochemical process</td>
<td>Change lignin to some small molecule phenols</td>
<td>High energy cost; rigorous reactive condition; low active ability</td>
<td>Parpot et al. (2000)</td>
</tr>
<tr>
<td>Biotechnology</td>
<td>White-rot fungus process</td>
<td>Could degrade lignin</td>
<td>High request for culture of bacterium; poor repeatability</td>
<td>Hakala et al. (2005)</td>
</tr>
<tr>
<td>Advanced oxidation</td>
<td>Homogeneous Fenton process</td>
<td>Could degrade lignin efficiency</td>
<td>Request narrow pH range; losing of Fe**</td>
<td>Torrades et al. (2011)</td>
</tr>
<tr>
<td>technology</td>
<td>Wet oxidation process</td>
<td>89% of lignin was removed</td>
<td>High disposal cost; high request for equipment</td>
<td>Banerjee et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>Photochemical oxidation process</td>
<td>Could degrade lignin efficiency</td>
<td>No obvious shortcoming</td>
<td>Makhotkina et al. (2008)</td>
</tr>
</tbody>
</table>
1. Experimental

1.1. Chemical reagents

Iron nitrate ($\text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}$), bismuth nitrate ($\text{Bi(NO}_3\text{)}_3 \cdot 5\text{H}_2\text{O}$), concentrated sulfuric acid (98.5%, $\text{H}_2\text{SO}_4$), 30% (W/W) hydrogen peroxide, nitric acid, tripolycyanamide, ethanol, potassium nitrate and potassium hydroxide were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Guaiacol was purchased from Shanghai kechang fine chemical Co., Ltd. (Shanghai, China). All chemicals were analytical grade reagents and used without further purification.

1.2. Preparation of $\text{BiFeO}_3 - g\text{-C}_3\text{N}_4$ composite

Iron nitrate (0.005 mol) and bismuth nitrate (0.005 mol) were dissolved in HNO$_3$ solution (3.2 mol/L). And a certain amount of $g\text{-C}_3\text{N}_4$ NS which prepared by sulfuric acid intercalating and liquid exfoliating of the bulk $g\text{-C}_3\text{N}_4$ in water (Jiang et al., 2014) was dispersed by ultrasonic treatment and added to above solution. KOH solution was added slowly to the above suspension, followed by stirring continuously to form precipitate of $\text{Fe}^{3+}$ and $\text{Bi}^{3+}$. The precipitate was washed and filtrated with deionized water several times. And $\text{K}^+$ and $\text{NO}_3^-$ ions in the precipitate were removed by dissolving to deionized water. Next, the precipitate was mixed with KOH solution (40 mL, 12 mol/L), followed by stirring for 5 min. Then the suspension was transferred into the polytetrafluoroethylene lining stainless steel reactor, followed by adding KNO$_3$ (0.1 mol). The reactor was sealed and heated at 200°C for 24 hr, followed by cooled naturally. The suspension was filtrated and washed several times with deionized water and absolute ethyl alcohol. At last, the product was obtained after being dried at 70°C for 4 hr.

1.3. Degradation experiment

The degradation experiment was carried out in a cylindrical Pyrex vessel (100 mL, Shenshi, China) at 25°C. Typically, a given amount of $\text{BiFeO}_3 - g\text{-C}_3\text{N}_4$ composite was dispersed in guaiacol solution (100 mL; 50 mg/L) by sonicating for 5 min, followed by adjusting the pH to 5.0 (Considering the adding of the $\text{BiFeO}_3 - g\text{-C}_3\text{N}_4$ composite will change the pH value of guaiacol solution slightly (from 7.28 to 7.33), the pH adjustment was carried out after the adding of the composite). The dispersion was magnetically stirred for 60 min to achieve adsorption–desorption equilibrium between the catalyst and pollutant. A small volume (1.5 mL) of the dispersion was sampled and immediately centrifuged at 14,000 r/min on an EBA-21 centrifuge (Hettich, Germany) to separate $\text{BiFeO}_3 - g\text{-C}_3\text{N}_4$ composite from the solution. The pollutant concentration in the supernatant was measured and taken as its initial concentration. After H$_2$O$_2$ was added to the solution, the photocatalytic degradation was initiated by switching on a 500 W halogen lamp with a cutoff filter ($\lambda > 420$ nm). At given time intervals, aliquots of the solution (1.5 mL) were sampled to centrifuge tubes containing a certain quantity of absolute ethyl alcohol (to quench $\text{HO}^\cdot$ radicals). After being centrifuged at 14,000 r/min, the remaining pollutant concentration in the supernatant was determined immediately.

1.4. Characterization and analytical methods

The morphology of the samples was observed on a Tecnai G2 20 transmission electron microscope (TEM, FEI, Holland). The phase composition of the materials were analyzed by X-ray diffraction (XRD) using a D8 Advance diffract meter (Bruker, Germany) with Cu Ka radiation and a diffracted beam graphite monochromator. All samples were characterized by N$_2$ adsorption at 77 K on a micrometers ASAP 2020 apparatus (BEL, Japanese) by applying Brunauer–Emmett–Teller (BET) equation to the N$_2$ adsorption isotherm. Raman spectra were recorded on a DXR Raman spectrometer (Thermo Fisher Scientific, America) with a 532-nm excitation at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Multilab 2000 X-ray photoelectron spectrometer (Thermo Fisher Scientific, America), using Mg Ka X-ray as the excitation source. Fourier-transform infrared spectroscopy (FT-IR) spectra of the samples in KBr pellets were recorded using a Spectrum...
The UV–vis diffuse reflectance spectrum (DRS) was recorded on an UV-3100 UV–vis spectrophotometer (Hitachi, Japanese) with an integrating sphere attachment. Photoluminescence (PL) spectra were recorded on a Jasco FP-6500 fluorescence spectrophotometer (Jasco, Japanese). Fe and Bi contents were monitored by a Analyst 300 atomic absorption spectroscopy (AAS, Perkin Elmer, America). The generation of \( \text{HO} \) was evaluated by using the coumarin probe method (Guan et al., 2008), in which the fluorescent intensity of product 7-hydroxycoumarin from the oxidation of coumarin (1 mmol/L) by attacking of \( \text{HO} \) radicals was recorded on a Jasco FP-6200 fluorescence spectrophotometer (Jasco, Japanese). The guaiacol concentration in the supernatant was determined by measuring the absorbance at about 274 nm on a Cary 50 UV–visible spectrophotometer (Varian, America).

2. Results and discussion

2.1. Characterization of catalysts

The morphology of g-C\(_3\)N\(_4\) NS and BiFeO\(_3\)-g-C\(_3\)N\(_4\) composite was observed with TEM. The TEM observation (Fig. 2a) indicated that g-C\(_3\)N\(_4\) displayed sheet-like structure. BiFeO\(_3\) nanoparticles (grain sizes <30 nm) were loaded on g-C\(_3\)N\(_4\) NS (Fig. 2b), and the sizes of BiFeO\(_3\) were much smaller than that (50–80 nm) in the previously reported graphene-BiFeO\(_3\) composite (An et al., 2013b). The reason may be the hydrothermal method favors producing BiFeO\(_3\) with smaller grain sizes (Wang et al., 2007).

Raman spectra are ideal methods to investigate the structure of carbon-contained material. The Raman spectra of BiFeO\(_3\) (prepared by hydrothermal method (Wang et al., 2007)), g-C\(_3\)N\(_4\) NS and BiFeO\(_3\)-g-C\(_3\)N\(_4\) composite were shown in Fig. 3a. It was found that a strong and wide vibrational band at the range of 1140–2400 cm\(^{-1}\) existed in the Raman spectra of g-C\(_3\)N\(_4\) NS. The G band and D band may be included in the wide vibrational band. Compared with that of g-C\(_3\)N\(_4\) NS, the obvious characteristic peak was not found in the Raman spectrum of BiFeO\(_3\). Moreover, an obvious characteristic peak at 1620 cm\(^{-1}\) was existed in the Raman spectra of BiFeO\(_3\)-g-C\(_3\)N\(_4\) composite, which may be corresponding to the symmetric vibration mode of g-C\(_3\)N\(_4\) NS (G band). This may indicate that the g-C\(_3\)N\(_4\) NS were successfully introduced to the composite.

FT-IR spectra of BiFeO\(_3\), g-C\(_3\)N\(_4\) NS and BiFeO\(_3\)-g-C\(_3\)N\(_4\) composite were showed in Fig. 3b. It was found that the adsorption peaks of g-C\(_3\)N\(_4\) NS were distributed in the three main regions: 810 cm\(^{-1}\), 1245–1647 cm\(^{-1}\) and 3160–3600 cm\(^{-1}\).
The adsorption at the range of 810 cm\(^{-1}\) and 1245–1647 cm\(^{-1}\) may be attributed to the bending vibration of Thiotriazinone. The wide and weak adsorption peak at the range of 3160–3600 cm\(^{-1}\) may be corresponding to the stretch vibration absorption of –NH\(_2\). And these adsorption peaks were also existed in the FTIR spectra of BiFeO\(_3\)-g-C\(_3\)N\(_4\) composite. Except that, the characteristic absorption peaks of BiFeO\(_3\) at the range of 400–850 cm\(^{-1}\) were also found in the spectrum of the composite. This further indicated that the BiFeO\(_3\) nanoparticles have been combined with g-C\(_3\)N\(_4\) NS.

In order to investigate the chemical composition of the composite and the interaction between BiFeO\(_3\) and g-C\(_3\)N\(_4\), the XPS analysis for BiFeO\(_3\)-g-C\(_3\)N\(_4\) composite, g-C\(_3\)N\(_4\) and BiFeO\(_3\) was carried out, which was shown in Fig. 4. The C1s and N1s envelop of g-C\(_3\)N\(_4\) was showed in Fig. 4a and b (curve 2), and their deconvolution was performed by using a Gaussian-Lorentzian peak shape after performing a Shirley background correction. The deconvolution of the C1s envelop of g-C\(_3\)N\(_4\) signed the existence of the carbon atoms with sp\(^2\) hybridization (N-C\(_\_\_\_\_\)C), carbon atoms with sp\(^3\) hybridization (C-(N)\(_3\)) and carbon atoms in C-N bonding at binding energies of 284.6, 286.0 and 287.9 eV. And the deconvolution of the N1s envelop of g-C\(_3\)N\(_4\) signed the existence of the nitrogen atoms with sp\(^2\) hybridization (C-N=C), nitrogen atoms connected with ring structure (N-C\(_3\)) or nitrogen atoms of amidogens at the edge of layer structure (C\(_2\)–N-H) and the nitrogen atoms connected with three carbon atoms in aromatic nucleus bonding at binding energies of 398.4, 399.5 and 400.8 eV (Yang et al., 2013). And the C1s and N1s envelop of BiFeO\(_3\)-g-C\(_3\)N\(_4\) composite was showed in Fig. 4a and b (curve 1). Similar with that of g-C\(_3\)N\(_4\), the deconvolution of the C1s and N1s envelop also signed the existence of corresponding carbon and nitrogen atoms. But the corresponding bonding energies were higher than those of g-C\(_3\)N\(_4\), which may be due to the formation of Fe-N coordination bond in BiFeO\(_3\)-C\(_3\)N\(_4\) composite. Fe atoms provide the unoccupied orbitals for the bond formation as well as N atoms provide the electrons for the

**Fig. 4 – XPS spectra for BiFeO\(_3\)-g-C\(_3\)N\(_4\) composite (1), g-C\(_3\)N\(_4\) (2) and BiFeO\(_3\) (3).** (a) C1s envelop, (b) N1s envelop, (c) O1s envelop, (d) Fe2p\(_{1/2}\) and Fe2p\(_{3/2}\) envelops, and (e) Bi4f\(_{5/2}\) and Bi4f\(_{7/2}\) envelops.
bond formation. These results reduce the density of electron cloud around the N atoms and C atoms connected with them. Therefore, the binding capacity of these atomic nucleuses to extranuclear electrons was improved, which resulted in the improvement of the corresponding energies of the C1s and N1s envelop in the composite. The formation of Fe–N bond was also confirmed by the comparison of the Fe2p XPS spectra between BiFeO3 and BiFeO3–g-C3N4 composite (Fig. 4d). Compared with that of BiFeO3 (Fe2p3/2: 725.1 eV; Fe2p1/2: 710.6), the elemental binding energy of Fe2p3/2 (725.7 eV) and Fe2p1/2 (711.1 eV) about BiFeO3–g-C3N4 composite was higher. This result is similar to previous report of Fe–N bond existed in the complex of Fe and g-C3N4 (Wang et al., 2009). The O1s and Bi4f envelop of BiFeO3 and BiFeO3–g-C3N4 composite were showed in Fig. 4c and e, respectively. And no obvious difference was found between that of BiFeO3 and BiFeO3–g-C3N4 composite.

The UV–Vis diffuse reflectance spectra of g-C3N4 NS, BiFeO3–g-C3N4 composite and BiFeO3 were shown in Fig. 5. The BiFeO3 nanoparticles were found to absorb light over the whole tested region ranging from 200 to 800 nm (curve 3 in Fig. 5). This is consistent with the previous observation that BiFeO3 nanoparticles showed photocatalytic performance under both UV and visible light irradiation (Liu et al., 2010), although the reported photocatalytic activity was rather low. And g-C3N4 NS absorbed light more strongly than that of BiFeO3 at the range of 200 to 430 nm, while it was lower than that of BiFeO3 as wavelength is above 430 nm. BiFeO3–g-C3N4 composite could absorb light more strongly than that of BiFeO3 at the whole tested range. The adsorption was also stronger than that of g-C3N4 NS at the range of 400 to 800 nm, although it was slightly weaker when the wavelength is below 400 nm. The corresponding values of the direct band gap of g-C3N4 NS, BiFeO3–g-C3N4 composite and BiFeO3 were evaluated by extrapolating the linear portion of (αhν)2 vs. (hν). The band gap energy of BiFeO3 and g-C3N4 NS was about 1.61 and 1.33 eV, respectively. The value of the band gap energy of BiFeO3–g-C3N4 composite was about 1.40 eV, lower than that of BiFeO3. This hints that the introduction of g-C3N4 NS can improve the UV and visible light absorption ability of BiFeO3.

PL can be used to investigate the efficiency of charge carrier trapping, immigration, transfer, and to understand the fate of e−/h+ pairs in semiconductor particles (Yu et al., 2003). In order to explore the recombination of e−/h+ generated by BiFeO3 and g-C3N4 NS under visible light irradiation, the PL spectra of g-C3N4 NS, BiFeO3, and BiFeO3–g-C3N4 composite were recorded with excitation at 375 nm (Fig. 5b). The g-C3N4 NS and BiFeO3 showed a stronger PL emission band with the emission maximum wavelength at around 460 and 468 nm, respectively.
respectively, whereas that of the BiFeO$_3$–g-C$_3$N$_4$ composite was much lower. Since the observed PL spectra can be attributed to the radiative recombination process of self-trapped excitons, the significant reduction of PL intensity indicates the decrease of radiative recombination process. Therefore, the recombination of e$^-$/h$^+$ produced by BiFeO$_3$ under visible light was able to be reduced by the introduced g-C$_3$N$_4$. The reason may be the semiconductor coupling effect between BiFeO$_3$ and g-C$_3$N$_4$. During the course of visible light photocatalysis, the excited electrons of BiFeO$_3$ could be rapidly transferred from the conduction band of g-C$_3$N$_4$ to that of BiFeO$_3$. While the photogenerated holes were transformed from the valence band of BiFeO$_3$ to that of g-C$_3$N$_4$. The above course effectively suppresses the recombination of photo-generated charge carriers (Fig. 5c).

The nitrogen sorption isotherms of BiFeO$_3$, BiFeO$_3$–g-C$_3$N$_4$ composite and g-C$_3$N$_4$ NS at 77 K were showed as Fig. 6a and Fig. S1a. The adsorption of the above samples at higher p/p$_0$ was characteristic of a Type H3 loop, indicating their meso- and macroporous characteristics. The BET analysis revealed that the specific surface area of BiFeO$_3$ was 7.42 m$^2$/g, being close to that previously reported (Luo et al., 2010), and that of BiFeO$_3$–g-C$_3$N$_4$ composite was 35.59 m$^2$/g, being much higher than that of BiFeO$_3$. The prepared g-C$_3$N$_4$ NS in the present work had a specific surface area of 36.36 m$^2$/g. The much increased BET area of the composite showed that g-C$_3$N$_4$ NS were excellent supports to immobilization BiFeO$_3$. The pore-size distribution of the samples was calculated by using the Barret–Juyner–Halenda (BJH) method (Fig. 6b and Fig. S1b). It was found that g-C$_3$N$_4$ NS involved much meso-pores with sizes of 5.292, 9.221 and 14.13 nm. Due to the introduction of g-C$_3$N$_4$ NS, the composite involved more meso-pores than that of BiFeO$_3$. Therefore, in comparison with BiFeO$_3$, the BiFeO$_3$–g-C$_3$N$_4$ composite involved more meso-pores with sizes of 3.55, 5.29, 6.93, 10.64, g-C$_3$N$_4$ NS 14.12 and 22 nm, which attributed to the much increased surface area of the composite.

The XRD patterns of g-C$_3$N$_4$ NS, BiFeO$_3$–g-C$_3$N$_4$ composite and BiFeO$_3$ were shown in Fig. 6c. The characteristic peak of g-C$_3$N$_4$ NS was located at 13.2° and 27.5°, respectively (curve 1). The (002) peak at 27.5° is very strong, which was attributed to the characteristic interlayer stacking structure. While the (100) peak at 13.2 reflected the interplanar structural stacking of g-C$_3$N$_4$ NS (Xu et al., 2013). The XRD pattern of BiFeO$_3$ (curve 3) showed a highly crystalline and single-phase perovskite structure (JCPDS File Nos. 20–169) and all the peak-splitting suggests that it was rhombohedral. Except that, it was found that the impurity phase of Bi$_2$Fe$_4$O$_9$ (JCPDS File Nos. 25–0090) existed in BiFeO$_3$ (such as the peaks located from 25° to 30°). The pattern of the composite (curve 2) also showed single-phase perovskite structure (JCPDS File Nos. 20–169), but its crystalline was higher than BiFeO$_3$. And through the comparison the peak strength from 25° to 30°, it was preliminary found the content of Bi$_2$Fe$_4$O$_9$ phase in the composite was smaller than that of BiFeO$_3$. The crystallite size of BiFeO$_3$ in the composites was obtained as 30.25 nm by using the Scherrer equation ($D = k\lambda/\beta\cos\theta$) being in good agreement with the TEM observation.

Fig. 6 – (a) Nitrogen sorption isotherms and (b) the corresponding pore-size distribution for (1) BiFeO$_3$–g-C$_3$N$_4$ composite and (2) BiFeO$_3$ at standard temperature and pressure (STP). (c) XRD patterns of (1) g-C$_3$N$_4$ NS, (2) BiFeO$_3$–g-C$_3$N$_4$ composite and (3) BiFeO$_3$. NS: nanosheets; XRD: X-ray diffraction.
2.2. Photo-Fenton like catalytic degradation of guaiacol by BiFeO$_3$–g-C$_3$N$_4$ composite

The degradation of guaiacol was carried out in the presence of H$_2$O$_2$ under visible light irradiation. The UV–vis adsorption spectra and the linear relationship between the absorbency and concentration of guaiacol ($y = 0.0187x + 0.03146$, $R^2 = 0.9857$) were shown as Fig. 7a and b, respectively. Under all the tested conditions, the guaiacol degradation approximately followed a pseudo-first order reaction in kinetics, which may be expressed as

$$\ln \left( c_0 / c \right) = kt + y$$

where, $y$ is a constant, $t$ (min) is the reaction time, $k$ (min$^{-1}$) is the apparent rate constant, and $c_0$ (mg/L) is the guaiacol concentrations at time of $t = 0$.

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![Fig. 7](https://example.com/fig7.jpg)

**Fig. 7** – (a) UV–vis adsorption spectra of guaiacol and (b) the linear relationship between the absorbancy and concentration of guaiacol. Degradation kinetics of guaiacol on BiFeO$_3$–g-C$_3$N$_4$ composite with the mole ratio of BiFeO$_3$ and g-C$_3$N$_4$ NS of (1) 1:1, (2) 3:1, (3) 11:1, (4) 9:1, (5) 5:1, and (6) 7:1 (c) and the effects of (d) the mole ratio of BiFeO$_3$ and g-C$_3$N$_4$ NS, (e) catalyst load, (f) initial H$_2$O$_2$ concentration and (g) pH on the apparent degradation constant of guaiacol. Reaction conditions: the mole ratio of BiFeO$_3$ and g-C$_3$N$_4$ NS 7:1 (e, f, g), catalyst load 0.5 g/L (c, d, f, g), guaiacol concentration 0.4 mmol/L, initial H$_2$O$_2$ concentration 15 mmol/L (c, d, e, g), pH 5 (c, d, e, f) and temperature 298 K. NS: nanosheets.
The effect of the proportions of BiFeO$_3$ and g-C$_3$N$_4$ NS in the composite on the degradation of guaiacol was investigated. The degradation kinetics of guaiacol on BiFeO$_3$–g-C$_3$N$_4$ composite with different mole ratios of BiFeO$_3$ and g-C$_3$N$_4$ NS was shown as Fig. 7c. It was found that guaiacol could almost be completely removed in 60 min on the optimal condition. And the apparent pseudo-first-order kinetics constants of degradation were also obtained, which were shown as in Fig. 7d. It was observed that the rate constant was improved from 0.0127 to 0.0452 min$^{-1}$ with the increasing of the mole ratio of BiFeO$_3$ and g-C$_3$N$_4$ NS from 1:1 to 7:1, and declined as the mole ratio increasing continuously. And the highest degradation efficiency was obtained at the mole ratio 7:1. This may be because BiFeO$_3$ was the main composition which possesses visible light catalytic and Fenton like catalytic performance. As the content of BiFeO$_3$ increases, the catalytic activity of the composite improved, which induces the higher efficiency of guaiacol degradation. And as the mole ratio was increased to 7:1, the best degradation efficiency was achieved. As the mole ratio further increases, the nanoparticles of BiFeO$_3$ may be excessive which induces that part of the nanoparticles could not grow on the g-C$_3$N$_4$ NS. This may reduce the catalytic activity of the composite, which result in the poor degradation efficiency of guaiacol.

The effect of catalyst load on the degradation of guaiacol was showed in Fig. 7e (also see Fig. S2). It was found that the k value firstly increased, passed a maximum at a catalyst load of 0.5 g/L, and then decreased with increasing catalyst load. The initially increased catalyst load led to the increased number of the reactive sites on catalyst surface, resulting in enhanced generation of hydroxyl radicals and faster degradation of guaiacol. However, superabundant catalyst may produce overmuch OH radicals, inducing hydroxyl radical scavenging effect which leads to the decline of the efficiency of OH radicals for the degradation of pollutants. Except that, the over high catalyst load increases light filtering effect, inducing lower efficiency of OH radical generation. Therefore, the optimal load of BiFeO$_3$–g-C$_3$N$_4$ composite was 0.5 g/L.

The effect of initial H$_2$O$_2$ concentration on the degradation of guaiacol was showed in Figs. S3 and 7f. Similarly, the k value of guaiacol removal was improved with increasing H$_2$O$_2$ concentration from 0 to 15 mmol/L, and then slightly decreased beyond 15 mmol/L. The slight decrease of guaiacol removal at higher H$_2$O$_2$ concentration is possibly related to the excessive H$_2$O$_2$ that can induce hydroxyl radical scavenging effect.

The effect of pH on the guaiacol degradation was shown in Fig. 7g. As pH was increased from 3 to 5, the k value was increased from 0.0139 to 0.0452 min$^{-1}$, and the removal of guaiacol was increased from 55% to 94% (Fig. S4). This may be because the adsorption of guaiacol on the composite was increased with increasing pH value, which induced the improvement of the contact between the pollutant and oxidizing species. As pH value was increased further (pH > 5), the degradation efficiency of guaiacol was decreased due to two reasons: one is the reduction of adsorption between the catalyst and pollutant, and the other is that the alkalinity condition was unfavorable to the generation of hydroxyl radicals. Therefore, the optimal pH value was 5.

The degradation of guaiacol by g-C$_3$N$_4$ NS, BiFeO$_3$ nanoparticles, BiFeO$_3$–g-C$_3$N$_4$ composite and the simple mechanical mixture of BiFeO$_3$ and g-C$_3$N$_4$ NS were investigated under the optimal conditions (Fig. 8a). It was observed that the degradation efficiency of guaiacol by g-C$_3$N$_4$ NS was the lowest. After 60 min, only about 10% of guaiacol was removed (curve 1) with a rate constant k of 0.00167 min$^{-1}$ (Fig. 8b). The degradation efficiency by the simple mechanical mixture of BiFeO$_3$ and g-C$_3$N$_4$ NS was higher than that of g-C$_3$N$_4$ NS. The k value was about 0.00662 min$^{-1}$. And the k value for the degradation by BiFeO$_3$ was higher than the above two catalysts (k = 0.00867 min$^{-1}$). All the above three catalysts could not degrade guaiacol effectively after achieving adsorption/desorption equilibrium. Compared with BiFeO$_3$–g-C$_3$N$_4$ NS and the simple mixture, BiFeO$_3$–g-C$_3$N$_4$ composite could catalyze H$_2$O$_2$ to generate hydroxyl radicals more effectively. After 60 min, about 94% of guaiacol was removed (curve 5). The corresponding k value was 0.0452 min$^{-1}$, being 27.1, 5.21 and 6.80 folds to that of g-C$_3$N$_4$ NS, BiFeO$_3$ and the simple mechanical mixture of BiFeO$_3$ and g-C$_3$N$_4$ NS. It was further observed that the total organic carbon (TOC) removal by BiFeO$_3$–g-C$_3$N$_4$ composite was achieved 74% after 120 min, being much higher than that by other catalysts (Fig. 8c, only 4.5% by g-C$_3$N$_4$ NS, 21.16% by the simple mixture and 30.23% by BiFeO$_3$). This indicated that the introduction of g-C$_3$N$_4$ NS could significantly enhance the catalytic activity of the composite.

The catalytic activity of the composite was compared with that of BiFeO$_3$–graphene and bulk g-C$_3$N$_4$/BiFeO$_3$ being prepared with a previously reported method (An et al., 2013b; Fan et al., 2015). It was found that the degradation efficiency and TOC removal catalyzed by the composite were higher than those of the other two composites.

2.3. Stability and reusability of BiFeO$_3$–g-C$_3$N$_4$ composite

During the guaiacol degradation, no leaching of Bi ions from BiFeO$_3$–g-C$_3$N$_4$ composite was detected at pH 5.0 by AAS, and the leaching of Fe ions was less than 1% of the iron element from the composite (Fig. S7a). The good chemical stability of the composite was further confirmed by the little degradation in the BiFeO$_3$–g-C$_3$N$_4$ leaching solution (Fig. S7b). The little degradation in the composite leaching solution demonstrated two aspects: one is that the catalytic effect of BiFeO$_3$–g-C$_3$N$_4$ comes from itself, but not from the Fenton reaction induced by the possible dissolved iron; the other is that BiFeO$_3$–g-C$_3$N$_4$ as the catalyst is very stable because little iron was dissolved from it. Therefore, the composite was stable and could be reused without loss of catalytic activity.

The recyclability of BiFeO$_3$–g-C$_3$N$_4$ composite was evaluated by six successive batches of guaiacol degradation. It was found that the composite was able to be reused with the catalytic activity as efficient as the fresh one (Fig. S5), yielding a guaiacol degradation rate constant of 0.0452, 0.0451, 0.0451, 0.0450 and 0.0449 min$^{-1}$ for the initial six cycles. This indicated that the composite could be efficiently reusable.

2.4. Contributions of g-C$_3$N$_4$ to catalytic performances of BiFeO$_3$–g-C$_3$N$_4$ composite

The functions of g-C$_3$N$_4$ in the composite as a catalyst could be summarized as follows:

The first one is that it’s providing more contact sites between the catalyst and the pollutant. The increased
adsorption performance to guaiacol may be firstly ascribed to the enough dispersed nanoparticles of BiFeO$_3$ on g-C$_3$N$_4$ NS. Except that, the large $\pi$ bonds similar to the structure of benzene rings existed in the molecule of g-C$_3$N$_4$. These large $\pi$ bonds are beneficial to adsorb the pollutants with the structure of benzene rings in the form of $\pi$–$\pi$ stack. Therefore, g-C$_3$N$_4$ could adsorb guaiacol more effectively. To confirm the contribution of adsorption to the catalytic performance of the catalyst, we made a comparison between the quantity of generated $\cdot$OH being evaluated by using the coumarin probe method (Fig. 8d), adsorption capacity ($q_e$, Fig. S6) and $k$ value for BiFeO$_3$ and BiFeO$_3$–g-C$_3$N$_4$ composite. The three factors had the same order of BiFeO$_3$–g-C$_3$N$_4$ > BiFeO$_3$, and the ratio of the $k$ value (5.21:1) for BiFeO$_3$–g-C$_3$N$_4$ to that of BiFeO$_3$ is very close to that of $q_e$ values (4.85:1), but not to that of the fluorescence intensity (1.95:1). This suggests that the adsorption of guaiacol on the catalyst dominates the visible light and heterogeneous Fenton-like catalytic degradation of guaiacol. It may be concluded that the adsorption is very important to the degradation of guaiacol.

The second one, the loading of BiFeO$_3$ disperses the nanoparticles more effectively, which enhance the contact chance between catalyst and H$_2$O$_2$ and result in the generation of more hydroxyl radicals (Fig. 8d).

The third one may be the semiconductor coupling effect between BiFeO$_3$ and g-C$_3$N$_4$ as discussed above. Thus, more charge carrier will be survived which further be formed to highly reactive species (such as $\cdot$OH radicals). Therefore, the efficiency of organic pollutant degradation was improved. These all induce the enhancement of the catalytic performance of the composite.

3. Conclusions

Using g-C$_3$N$_4$ NS as a support, we developed the hydrothermal method to synthesize the BiFeO$_3$–g-C$_3$N$_4$ nanoscaled composite. Through BET analysis, it was found that the BiFeO$_3$–g-C$_3$N$_4$ nanoscaled composite has a specific surface area of 35.59 m$^2$/g, being considerably larger than that of BiFeO$_3$ nanoparticles (7.42 m$^2$/g). The UV–vis diffuse reflectance spectrum analysis showed that the introduction of g-C$_3$N$_4$ could decrease the band gap energy of the composite, which favors the adsorption to visible light and producing higher visible light catalytic activity. The PL spectra investigation indicated that the recombination of $e^-/h^+$ produced by BiFeO$_3$ under visible light was able to be reduced by the introduced g-C$_3$N$_4$, which was benefit to generate strong oxidative species to degrade pollutants. As a result, the BiFeO$_3$–g-C$_3$N$_4$ nanoscaled composite exhibited excellent visible light-Fenton like catalytic activity toward the degradation of guaiacol. It was found that the catalytic activity of the composite was influenced by the solution pH value and the proportions of BiFeO$_3$ and g-C$_3$N$_4$ NS. Under the optimal conditions, the rate constant of guaiacol degradation with the BiFeO$_3$–g-C$_3$N$_4$ nanoscaled composite as catalyst was 0.0452 min$^{-1}$, being 5.21 or 6.80 folds of that obtained
with BiFeO$_3$ and the mixture of BiFeO$_3$ and g-C$_3$N$_4$ NS as catalyst, respectively. Excellent visible light-Fenton like catalytic properties of BiFeO$_3$–g-C$_3$N$_4$ nanoscaled composite were attributed to a large surface area, much increased adsorption capacity, and the semiconductor coupling effect between BiFeO$_3$ and g-C$_3$N$_4$ in the composite. The high efficiency of guaiacol degradation catalyzed by the composite indicated that the composite may be an effective candidate for the degradation of lignin in pulping and papermaking wastewater.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.01.024.

**REFERENCES**


