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1	Novel Magnetically Separable Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG Photocatalyst:
2	Synthesis and Photocatalytic Performance under Visible-light
3	Irradiation
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9	

5	10304 and wise <sub>2</sub> particles were coated on the surface of two. The samples were characterized by
4	XRD, SEM, TEM, XPS, VSM, UV-vis DRS, TOC, GC-MS techniques. The results showed that
5	the photocatalytic activity of Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG photocatalysts under visible-light illumination was
6	higher than that of WSe2/NG owing to the narrow band gap energy and delayed electron-hole
7	recombination, and Fe <sub>3</sub> O <sub>4</sub> can be used for the advanced oxidation processes (AOPs) to degrade
8	organic pollutants at pH 3 and $H_2O_2$ 3.0mM. Moreover, the mass fraction of $Fe_3O_4$ had a great
9	effect on the photocatalytic activity of Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG. Among the hybrid photocatalysts, 30
10	wt%Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG (30 wt% of Fe <sub>3</sub> O <sub>4</sub> ) exhibited the highest photocatalytic activity with a rate
11	constant of 0.05589 min <sup>-1</sup> for the degradation of the MB in aqueous solution under visible light
12	irradiation, and the removal efficiency reached 98.8% which was 1.6 times higher than that of
13	WSe <sub>2</sub> /NG. More importantly, the magnetic properties of 30 wt%Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG were measured
14	and its reusability was also investigated after four successive runs applying an external magnetic
15	field.
16	Keywords: Fe <sub>3</sub> O <sub>4</sub> ; WSe <sub>2</sub> ; graphene oxide; hydrothermal synthesis; photocatalytic degradation;

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2

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17 methylene blue

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Abstract: Visible light responsive Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG (Nitrogen doped graphene oxide) heterojunction nanocomposites were synthesized by a hydrothermal synthesis route, in which  $Fe_3O_4$  and  $WSe_2$  particles were coated on the surface of NG. The samples were characterized by , XPS, VSM, UV-vis DRS, TOC, GC-MS techniques. The results showed that activity of Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG photocatalysts under visible-light illumination was of WSe<sub>2</sub>/NG owing to the narrow band gap energy and delayed electron-hole d Fe<sub>3</sub>O<sub>4</sub> can be used for the advanced oxidation processes (AOPs) to degrade at pH 3 and H<sub>2</sub>O<sub>2</sub> 3.0mM. Moreover, the mass fraction of Fe<sub>3</sub>O<sub>4</sub> had a great tocatalytic activity of Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG. Among the hybrid photocatalysts, 30 NG (30 wt% of Fe<sub>3</sub>O<sub>4</sub>) exhibited the highest photocatalytic activity with a rate

## 1 1. Introduction

2	Common organic dye reagents have been widely used in printing and dyeing industries, and
3	the wastewater is often referred to as environmental pollutants. Their compositions are complex
4	and non-biodegradable, so it is necessary to find an effective way for treating dye wastewater. The
5	photocatalytic technology has gained greater attention ever since discovered of Water
6	decomposing under UV irradiation on the N-type semiconductor $TiO_2$ electrodes [1].
7	Recently, many semiconductors have been used to degrade organic contaminants, e.g. CdS
8	[2], Ag <sub>3</sub> PO <sub>4</sub> [3], ZnO [4] and TiO <sub>2</sub> [5,6], etc. Among these semiconductors, the two-dimensional

9	transition metal dichalcogenide (TMDC) semiconductor WSe <sub>2</sub> has attracted great attention [7,8].
10	Due to its electronic properties [9] and smaller bandgap of 1.35 eV [10]. But the photocatalytic
11	activity of pure WSe <sub>2</sub> is limited by its low efficiency of light absorption, low adsorption capacity
12	and high recombination rate of photoelectron hole pairs [11,12]. In order to promote the separation
13	of photoelectric charges of WSe2, heterojunction is usually used to change the photocatalysts
14	[13-16].

15 More recently, nitrogen doped graphene oxide (NG), a metal-free, stable, large surface area 16 and inexpensive polymer semiconductor, is attracting more and more attention [17-19]. What's 17 more, the modest bandgap energy of NG enables direct use of visible light. Nitrogen-doped 18 graphene oxide is synthesized by hydrothermal method from graphene oxide and urea, the 19 graphite type N in the nitrogen doped graphene oxide (NG) can increase the conductivity of GO 20 and improve the adsorption capacity of the dye molecules [20]. In addition, when NG modified 21 other materials to form heterojunctions, in the photocatalytic process, the transferred photoelectric 22 energy can participate fast in the reduction reaction and promote the separation of photoelectric

1	charges, thus significantly improve the photocatalytic performance of NG modified photocatalysts.
2	Recently, the improved photocatalytic properties of NG modified conventional semiconductor
3	have been studied, such as g-C_3N_4/Bi_2O_2CO_3[21], g-C_3N_4/BiIO_4[22], ZnO/g-C_3N_4[23] and
4	g-C <sub>3</sub> N <sub>4</sub> /Bi <sub>2</sub> MoO <sub>6</sub> [24]. Although photocatalysts compound can improve photocatalytic properties,
5	these improvements do not solve the issues of photocatalysts for separation and recovery. In
6	previous works, WSe <sub>2</sub> /NG photocatalyst was generally suspended in water for photocatalytic
7	reaction and was difficult to be separated, because the light and fine particles were difficult to
8	stabilize.
9	Magnetic separation is a very convenient and effective method for removing and recovering a
10	magnetic catalyst by applying an external magnetic field. Fe <sub>3</sub> O <sub>4</sub> has high super-magnetism for
11	effective recycling by magnet that aroused our attention [25-29]. He et al [30] used Ti (SO <sub>4</sub> ) $_2$ Ti as
12	the initial raw material, prepared the core-shell structure TiO2@Fe3O4 catalysts by precipitation
13	method, they had a high photocatalytic activity and easy recovery, but the The synthesis process
14	was cumbersome. Liu et al [31] composited $TiO_2/SiO_2@Fe_3O_4$ magnetic microspheres and used
15	them as photocatalytic degraded dyestuff. In this study, We have synthesized Fe $_3O_4$ -WSe $_2/NG$ by
16	a simple hydrothermal method and the difficult problem of recovery of photocatalyst would be
17	solved. What's more, $Fe_3O_4$ can also be used for AOPs, the characteristic is to produce high
18	activity hydroxyl radical (HO·), can unselectively degrade, have been successfully used in the
19	field of Many kinds of organic wastewater treatment [32-34]
20	In this artical, preparation of a high quality $Fe_3O_4$ -WSe <sub>2</sub> /NG nanocomposites was used by

20 In this artical, preparation of a high quality  $Fe_3O_4$ -WSe<sub>2</sub>/NG nanocomposites was used by 21 hydrothermal synthesis. Take advantage of the excellent performance and complementarity of the 22 three ingredient. Compared with WSe<sub>2</sub>/NG, in the presence of pH 3 and H<sub>2</sub>O<sub>2</sub> 3.0mM,

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Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposites exhibited great enhancement in photocatalytic degradation of

2	methylene blue (MB) under visible light irradiation. Fe $_3O_4$ -WSe $_2$ /NG as photocatalyst can
3	improve the photocatalytic efficiency effectively and the degradation of MB (32 mg/L) was
4	98.8%.
5	2. Experimental
6	2.1 Reagents and instruments
7	KMnO <sub>4</sub> was purchased from Sanhe Chemical Reagent Co. H <sub>2</sub> O <sub>2</sub> was brought from Tianjin
8	DingShengXin Chemical Co. LTD. FeSO4·7H2O, Na2WO4·2H2O, NaNO3, NH3, CO(NH2)2 and
9	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O were purchased from Tianjin BASF Chemical Co. LTD. FeCl <sub>3</sub> ·6H <sub>2</sub> O was purchased
10	from Tianjin Damao Chemical Reagent Factory. Se powder, P-25 and MB were obtained from
11	Aladdin Reagent Co. NaOH, HNO3(65 wt%), H2SO4 (98 wt%) and HCl (36~38wt%) were
12	supplied by Laiyang Fine Chemical Factory. Graphite powder was purchased from Sinopharm
13	Chemical Reagent Co. LTD. $\alpha$ -D-grucose was purchased from Tianjin Bodi chemical Co. LTD.
14	All chemicals are used without further processed. Doubly distilled water was used throughout all
15	of this work.
16	The general morphology and microstructure of the prepared catalysts were investigated using
17	a scanning electron microscopy (SEM, JEOL 6700-F) and a transmission electron microscope
18	(TEM, JEM 2100). The crystallographic structures of samples were examined by X-ray diffraction
19	(XRD) measurements using a D/Max-2400 powder diffractometer with Cu Ka X ray sources
20	(Japanese Physical Co.). The XPS analysis was performed on a Thermo Scientific Escalab 250xl.
21	T=300K magnetic-hysteresis (M-H) loops of the samples were obtained using vibrating sample

1 reactor (Qiaoyue Electronics Co.). UV-vis diffuse reflectance spectra of the samples were obtained 2 on a UV-vis spectrophotometer (TU-2600). Elemental analyses were obtained by a EuroEA 3 Elemental Analyser. Energy-dispersive x-ray spectroscopy (EDS) mapping was carried out to 4 verify the element distribution. Qualitative quantitative analyses of dye components after 5 degradation were provided by a GC-MS (Thermo Scientific Co. LTD.). The total organic carbon 6 (TOC) of dye was obtained on Total Organic Carbon Analyzer (SHIMADZU, SSM-5000A). 7 Adjustable pipettes and automatic dual water distiller were purchased from Brocade Equipment 8 Co. LTD. All measurements were recorded at room temperature.

## 9 2.2 Synthesis of GO

10 GO was prepared by using graphite powder as a precursor through the Hummers method 11 [35,36] with a minor modification. NaNO<sub>3</sub> (0.75 g) and concentrated H<sub>2</sub>SO<sub>4</sub> (33.75 ml) were 12 added into a 250 ml flask and the mixture was cooled to 0 °C using an ice bath. 1.0 g graphite 13 powder and 4.5 g KMnO<sub>4</sub> were added slowly into the mixture and the reaction temperature was 14 maintained below 20 °C, the reaction was then warmed (30 °C) with stirring for 1 h, the mixture 15 became a dark brown mushy material and was kept stirring slowly for 12 h. Then the above 16 mixture was poured into 46 mL deionized water. 30 min later, it was poured into 140 mL 17 deionized water containing 2.5 mL 30% H<sub>2</sub>O<sub>2</sub> in order to react with excess KMnO<sub>4</sub> and produced 18 MnO<sub>2</sub>, and the color of the mixture immediately turned bright yellow. The mixture was then 19 dialysed until the pH added to 7. At last, the resulting product was dried at 40 °C in a vacuum oven 20 for 12 h.

### 21 2.3 Synthesis of the WSe<sub>2</sub>

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WSe<sub>2</sub> photocatalyst was prepared by one-step hydrothermal method. In the classical

procedure, 0.66 g Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and 0.32 g Se powder were dissolved in 45 mL deionized water,

then 25 ml HCl and 10 ml $N_2H_4$ · $H_2O$ were poured into the solution successively, stirred for 2h.
Above suspension was transferred into an 80 mL Teflon-lined autoclave and was maintained at
200 °C for 48 h. After being cooled down naturally, then treated with 25% NaOH solution to
remove residual Se powder, the products were washed with ethanol and distilled water for six
times and dried at 105 °C in a vacuum oven for 12 h.
2.4 Synthesis of Fe <sub>3</sub> O <sub>4</sub> nanoparticles
$Fe_3O_4$ nanoparticles were synthesized by the classical liquid phase coprecipitation
method[37]. A certain amount of FeSO <sub>4</sub> ·7H <sub>2</sub> O, FeCl <sub>3</sub> ·6H <sub>2</sub> O, a-D-grucose dissolved in the second
distilled water respectively, FeCl <sub>3</sub> ·6H <sub>2</sub> O(5ml 0.3mol/L), FeSO <sub>4</sub> ·7H <sub>2</sub> O (11.25ml 0.1mol/L) and
a-D-grucose (5ml 0.05mol/L) mixture were added into 50ml dry three bottles and the mixture was
stirred at 80 °C for 20 minutes, then the temperature was adjusted to 60 °C, stirring rapidy while
dropping $1 \text{mol/L NH}_3 \cdot \text{H}_2\text{O}$ solution slowly, when the mixed solution PH was 10, then the solution
became black immediately, continue stirring for 30min, the nano-ferroferric oxide solution was
obtained, the whole reaction process were carried out in nitrogen protection. The product was
separated with a permanent magnet, the precipitate was washed with distilled water and ethanol
for several times and dried at 50 °C in a vacuum oven for 8h.
2.5 Synthesis of Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /GO, Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG nanocomposites and WSe <sub>2</sub> /NG
nanocomposites

A typical synthesis of  $Fe_3O_4$ -WSe<sub>2</sub>/NG nanocomposites was as follows. The prepared GO powder (0.25 g) was dissolved in 500 mL distilled water and was ultrasonicated for 3 h, then it was centrifuged and the GO supernatant was taken. 7.5 g CO(NH<sub>2</sub>)<sub>2</sub>, 0.25g Fe<sub>3</sub>O<sub>4</sub> and 0.25 g





## 14 2.6 Adsorption and photocatalytic performance measurements

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15 The adsorptive and photocatalytic performances for P-25, WSe<sub>2</sub>, WSe<sub>2</sub>/NG 16 nanocomposites and Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposites were assessed by calculating the adsorption 17 and photocatalytic degradation rate of MB solution in the dark and then under visible light

1	irradiation, respectively. A photocatalyst sample (50 mg) was distributed in 50 mL MB aqueous
2	solution (32 mg/L), add a certain amount of $H_2O_2$ and nitric acid, and stirred 30 min in dark to
3	achieve the adsorption-desorption equilibrium. Then, the suspension was under irradiation by a
4	500W Xe lamp with a cut-off filter (> 400 nm) as the visible light source. 5 mL sample solution
5	was taken at 10 min interval and remove the catalyst completely used a centrifuge, then the
6	supernatant was measured at 665 nm by UV-vis spectrophotometry. The removal efficiency of
7	MB was measured by $D = (C_0 - C_t) / C_0 \times 100\%$ , where D is the removal efficiency of MB,
8	$C_0$ is the starting concentration of MB; and $C_t$ is the MB concentration at time t.
9	Generally, the photocatalytic degradation of a dye followed the pseudo-first order kinetics and
10	rate constant is determined by $\ln(C_0/C) = kt$ ; k is calculated from a graph of $\ln(C_0/C)$
11	and time, where $C_0$ and C denote the MB concentrations at illumination time 0 and t, respectively.
12	Following the above procedure, different operating conditions such as initial concentration of
13	the H <sub>2</sub> O <sub>2</sub> and initial pH were investigated.
14	2.7 Total organic carbon experiments

15 The degree of mineralization for MB was calculated as: mineralization 16 degree =  $(TOC_0 - TOC_t)/TOC_0 \times 100\%$ , where  $TOC_0$  was the content of TOC (MB) in the 17 initial solution and  $TOC_t$  was the content of TOC (MB) after light irradiation at time t.

## 18 2.8 Recycling tests

In practical application, the photocatalysts' activity, stability and reusability are very
important [38]. Hence, the used catalysts were separated with a permanent magnet, washed with
ethanol and distilled water for several times, dried in vacuum at 50 °C for 8 h, and then four
consecutive recycling tests for MB degradation were finished by Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG.

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## 2 3.1 Characterization of Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG photocatalysts

3	The XRD analysis was used to study the crystalline structure of pure WSe2, WSe2/NG and
4	Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG nanocomposites. As shown in Fig. 2a, several major diffraction peaks are
5	observed in the pure WSe <sub>2</sub> , the feature peak of WSe <sub>2</sub> are at around $2\theta$ =13.54°, 31.44°, 37.78°,
6	41.64°, 47.28°, 55.92°, 57.74°, corresponding to the (002), (100), (103), (006), (105), (110) ,
7	(112)agreed well with the typical hexagonalstructure of WSe <sub>2</sub> (JCPDS No. 38-1388). From Fig. 2c,
8	it can be seen that the feature peak of Fe <sub>3</sub> O <sub>4</sub> are at around $2\theta$ =30.76°, 35.7°, 43.06°, 57.08° and
9	62.58°, corresponding to the(220), (311), (400), (511) and (420) planes were consistent with the
10	standard Fe <sub>3</sub> O <sub>4</sub> XRD spectrum (JCPDS No. 19-629). There are no other miscellaneous peaks on
11	the XRD spectrum, indicating that the prepared Fe <sub>3</sub> O <sub>4</sub> particles have higher purity. In addition, the
12	feature peak of NG are at around $2\theta$ =23.5°, 28°, 43.8° and 52° are attributed to the (002) , (100),
13	(004) in Fig. 2c. Fig. 2d compares with Fig. 2a, Fig. 2b and Fig. 2c, The XRD analysis of
14	Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG composite in Fig.2d contains all the feature peaks of WSe <sub>2</sub> , Fe <sub>3</sub> O <sub>4</sub> and NG,
15	implying that the Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG composite synthesized successfully.



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The TEM images of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposites are provided in Fig. 3(a) and 3(b). From Fig. 3(a), the Fe<sub>3</sub>O<sub>4</sub> nanoparticles are mostly spherical, due to the magnetic force between the particles and electrostatic force. Fig. 4(b) shows the particle size distribution of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles in Fig. 3(a). It exhibits that the particle size ranges from 9 to 16 nm, so the Fe<sub>3</sub>O<sub>4</sub> nanoparticles owned a small size distribution. As shown in Fig. 3(b), WSe<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> is successfully.





(contains a picture of a magnification)(d).

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2 Fig. 5. XPS spectra of Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposites and Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/GO nanocomposites.

3 Fig. 6 is the photo showing magnetic capture of the  $Fe_3O_4$  nanoparticle, the  $Fe_3O_4$ -WSe<sub>2</sub>/NG nanocomposites and their M-H curve at T=300K. A photo of  $Fe_3O_4$  with aqueous solution in 4 5 addition to magnetic field is as shown in Fig. 6a, it can be seen from the figure that the prepared 6  $Fe_3O_4$  nano-particles are greatly influenced by the applied magnetic field, which is beneficial for 7 recycling. Fig. 6b is a photo of  $Fe_3O_4$ -WSe<sub>2</sub>/NG with aqueous solution in addition to magnetic 8 field. It shows that the further preparation of Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG have good magnetic properties and 9 can be effectively recycled under the effect of magnetic field. From Fig. 6c, it shows that no 10 hysteresis loop is formed in the magnetization of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG particles, and the 11 magnetization curve and the demagnetization curve coincide perfectly. When external magnetic 12 field is at H = 0 Oe, the residual magnetization and coercivity of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG 13 particles are zero, displays the standard superparamagnetic characteristics. The results show that the prepared Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG particles have obvious super paramagnetic properties at 14 15 T=300K. What's more, the saturation magnetization of  $Fe_3O_4$  and  $Fe_3O_4$ -WSe<sub>2</sub>/NG particles are 16 60.5emu/g and 42.5 emu/g respectively.



5 3.2 Properties of Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposites

6 3.2.1 Visible light responsive property

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7 The visible light responsive properties of P-25, WSe<sub>2</sub>, WSe<sub>2</sub>/NG and 30
8 wt%Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG were expressed by UV-vis diffuse reflectance spectra in Fig. 7. From Fig. 7a,
9 P-25 showed an absorption edge at 420 nm and WSe<sub>2</sub> showed an absorption edge at 760 nm,
10 showing these two catalysts are ultraviolet light active and visible-light active semiconductors,

22

- 1 respectively. WSe<sub>2</sub>/NG presented a similar UV-vis spectrum as that of WSe<sub>2</sub> and showed an 2 absorption edge at 950 nm. It not only compensates for the absorption of WSe<sub>2</sub> in the ultraviolet 3 area, but also responds well in the visible region. With the addition of Fe<sub>3</sub>O<sub>4</sub>, the absorption edge 4 reaches to1300nm. For crystalline semiconductor, the bandgap can be derived from the Kubelka Munk equation:  $(ahv)^{\frac{1}{n}} = A(hv - Eg)$ , where a, v, Eg, and A stand for the absorption 5 6 coefficient, light frequency, band gap energy, and a constant, respectively [39]. The plots of  $(ahv)^2$ 7 and photon energy (hv) are exhibited in Fig. 7b; from which we can estimate the bandgap energy 8 of P-25, WSe<sub>2</sub>, WSe<sub>2</sub>/NG and 30 wt%Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG are 3.05, 1.35, 0.85 eV and 0.35ev, 9 respectively. They are consistent with the reported values [6,10].
- These results also demonstrated that the addition of NG and Fe<sub>3</sub>O<sub>4</sub> could narrow the
  bandgap of WSe<sub>2</sub>, which is attributed to the formation of Fe-W-Se-C-N chemical bonding in 30
  wt% Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG. Moreover, it can be observed that a broad absorption peak in the visible
  region for 30 wt% Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposites [6].



Fig. 7. UV-Vis absorption spectra (a) and estimated band gaps (b) of P-25, WSe<sub>2</sub>, WSe<sub>2</sub>/NG and

30 wt%Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposites.

According to previous work, the optimum synthesis ratio of WSe<sub>2</sub> and NG was 1:1. The photocatalytic performance of commercial P-25 was measured by the degradation of MB as a model reaction in dark and under ultraviolet light, the as-prepared WSe<sub>2</sub>, WSe<sub>2</sub>/NG and Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposites were also measured by degradation MB in dark and under visible light irradiation. The results are shown in Fig. 8.



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8 Fig. 8. The absorbance variation curves of MB over different  $Fe_3O_4$  photocatalysts in the dark (a)



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1	MB over different photocatalysts under visible light irradiation and P-25 under UV-light
2	irradiation (c). Photodegradation kinetics of different catalysts on MB (d).
3	As shown in Fig. 8a, the majority of Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG nanocomposites showed high adsorption
4	capacity, and the mass fraction of NG increases and the adsorption capacity of $\mathrm{Fe_3O_4\text{-}WSe_2/NG}$
5	nanocomposites also increases. The strong adsorption capacity of $Fe_3O_4$ -WSe <sub>2</sub> /NG
6	nanocomposites may be ascribed to the strong interactions between azo dye molecules and NG
7	[40]. Obviously, the concentrations of MB in all samples showed that there are almost no changed
8	after being stirring for 40 min in the dark, implying that adsorption-desorption equilibrium formed.
9	As shown in Fig. 8b, photodegradation curves of MB over different Fe <sub>3</sub> O <sub>4</sub> photocatalysts under
10	visible light irradiation. Most of them have high photodegradation efficiency of MB, it can be
11	attributed to the larger surface area and unique electronic structure of NG. The addition of $Fe_3O_4$
12	into WSe <sub>2</sub> /NG can promote the photocatalytic performance. With the mass fraction of $\mathrm{Fe_3O_4}$
13	increasing, the photocatalytic activity of $Fe_3O_4$ -WSe <sub>2</sub> /NG nanocomposites increases and then
14	decreases. The 30 wt%Fe $_3$ O4-WSe $_2$ /NG nanocomposites showed the highest photocatalytic
15	performance and the degradation rate of MB was 98.8% within 60 min under visible light
16	irradiation. At last, 30 wt% of $Fe_3O_4$ was chosen as the optimum mass fraction.

17 The Fig. 8c showed that MB aqueous solution without catalyst showed little change under visible light, the removal efficiency of MB was only 5% after 60 min, which exhibited that in the 18 19 absence of a photocatalyst, the degradation of MB is extremely slow under visible-light 20 illumination. We can see that the degradation performance of different photocatalysts decreases 21 follow this sequence of 30 wt% Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG > WSe<sub>2</sub>/NG > P25 > WSe<sub>2</sub>. Among them, the 30 22 wt% Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposites showed the highest photocatalytic performance. This is due

1 to the introduction of  $Fe_3O_4$  can be used for the AOPs in the presence of low pH and hydrogen

2 peroxide and can produce high activity hydroxyl radical(HO·) which is conducive to degradation

3 of organic pollutants.

4 In addition, the kinetics of MB degradation reactions are showed in Fig. 8d. In general, the 5 organic dyes conform to the obvious first-order kinetics which is in good consistency with a

6 general langmuir-hinshelwood mechanism,  $\gamma = -dC / dt = \frac{kKC}{1 + kC}$ , where,  $\gamma$  is the

7 degradation rate of the reactant (mg/L, min), C is the concentration of reactant (mg/L), t is the 8 illumination time, K is the adsorption coefficient of the reactant (L/mg) and k is the reaction rate 9 constant (mg/L·min). If C is very small then the above equation could be reduced to  $\ln(C_0/C) = kKt \approx k_{app}t$ . In general, a plot of  $\ln(C_0/C)$  and time represents a straight line and the 10 11 slope is equal to the apparent first order rate constant k<sub>app</sub>. From Fig. 8d, we can see that the largest obvious first-order reaction rate constant kapp is from 30 wt%Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG (0.05589 12 min<sup>-1</sup>), which is a few folds higher than others, including P-25. What's more, the first-order 13 14 reaction rate constant kapp of 30 wt%Fe3O4-WSe2/NG is much higher than that 30 15 wt%Fe<sub>3</sub>O<sub>4</sub>.WSe<sub>2</sub>/GO, it suggests that the N dopping content has very important effect on the 16 activity of photocatalyst.

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Fig. 9. The Photodegradation curves of MB over 30 wt%Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG photocatalysts

3 under different pH conditions (a) and under different  $H_2O_2$  conditions (b).

4 The dye industrial wastewater generally has a wide range of pH values. Furthermore, the 5 generation of hydroxyl radicals is a function of pH. Thus pH plays an important role in the 6 performance of photocatalytic process. Hence, photodegradation of the synthetic wastewater using 7 30 wt%Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG photocatalyst was investigated under different initial pH values (Fig. 9a). 8 The highest photodegradation rate was obtained at pH 3. H<sub>2</sub>O<sub>2</sub> also plays an important role in 9 photocatalytic process, which affects the amount of OH, From Fig. 9b, we can see that with the 10 concentration of H<sub>2</sub>O<sub>2</sub> increasing, the photocatalytic activity of 30 wt%Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG 11 composites increases and then decreases. The highest photodegradation rate was obtained at  $H_2O_2$ 12 3.0mM.

## 13 3.3 The reaction mechanism of Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG catalyzed MB degradation

A good photocatalyst not only has good photoactivity, but also the high conversion (mineralization degree) in its practical application which is very important. TOC of MB solution were analysed to characterize the mineralization degree of 30 wt%Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG

1	nanocomposites. The results of TOC analysis showed that 30 wt%Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG had the highest
2	mineralization degree of 87.7% under visible light irradiation. GC/MS analysis was used to
3	detect the intermediate compounds produced during the MB photodegradation for 30 wt%
4	Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG under visible light irradiation could help us to understand the photodegradation
5	process of MB. The result showed that MB had been almost completely mineralized to $CO_2$ and
6	$\mathrm{H}_{2}\mathrm{O}$ , and other products were isopropyl acetate and D-glucopyranuronic acid. This reveals that 30
7	wt%Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG has excellent photocatalytic performance.

8 Three typed of factors enable Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposites' generally high photocatalytic 9 activity for MB degradation. First, the efficient adsorption. Second, the efficient transport and 10 separation of charge carriers. Third, Fe<sub>3</sub>O<sub>4</sub> can be used for AOPs. The possible mechanism of 11 separation and transportation of electron-hole pairs at the Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG photocatalyst interface 12 under visible light and  $Fe_3O_4$  for AOPs are proposed in Fig. 10. Under visible light irradiation, 13 both WSe<sub>2</sub> and NG can absorb visible light to produce charge carriers. The valence band (VB) and 14 conduction band (CB) potentials of NG are 1.52 eV and - 0.9 eV [41]. Due to the CB edge 15 potential of WSe<sub>2</sub> (-1.04eV) is more negative than that of NG (- 0.9 eV) [42-44], the charge 16 transfer between WSe<sub>2</sub> and NG heterojunction causes that the CB electrons of WSe<sub>2</sub> are injected 17 into the NG via the well-developed interface, meanwhile the holes on the NG surface can migrate 18 to  $WSe_2$  in a similar way. NG acts as an electron trap that promotes the separation of 19 photogenerated electrons, and also facilitate the interfacial electron transfer process. The 20 separation of electron-hole pairs is also driven by the internal tectonic field, it reduces the 21 recombination of the electron-hole and results in the buildup of electrons and holes on the surfaces 22 of NG and WSe<sub>2</sub>, respectively [45,46]. Then the photogenerated electrons (e) react with oxygen to

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generate  $\cdot O^{2-}$  on the surface of NG,  $\cdot OH$  is formed on the surface of WSe<sub>2</sub> nanosheets by the 1 2 reaction of holes  $(h^+)$  with the adsorbed water, hydroxide, etc. These radicals initiate redox reactions with MB molecules, then are degraded [6,47]. The graphite type N can increase the 3 4 adsorption capacity of the reactants and improve the nanocomposite's conductivity [20], thus, NG 5 modified WSe<sub>2</sub> greatly improves the charge separation efficiency, while reduces the recombination 6 probability of photogenerated electrons and holes. In addition,  $Fe_3O_4$  for AOPs is as follows: the catalyzed decomposition of  $H_2O_2$  by  $Fe^{2+}$  to produce  $\cdot OH$  at low pH, Eq. (1), using 7 light-assisted  $\text{Fe}^{3+}$  regeneration  $\text{Fe}^{2+}$ , Eq. (2). [48-51], these  $\cdot \text{OH}$  initiate redox reactions with MB 8 9 molecules, then are degraded (3). Due to the synergy of these components, the photocatalytic 10 performance of Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposites are improved significantly.





Fig. 10. Proposed photocatalytic mechanism of Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG.

13 3.4 Recycling tests

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## Fig.11. Recovery (a) and recycling tests (b) for 30 wt%Fe3O4-WSe2/NG under visible light

## irradiation.

According to Fig. 11a, the average recovery rate of 30 wt%Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG is 90% after 4
recycling. The average recovery rate of WSe<sub>2</sub>/NG is only 70.3%, significantly lower than that of
30 wt%Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG. The results of four successive recycling tests for degradation of MB by
30 wt%Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG are shown in Fig. 11b. Each run was carried out under the identical
conditions. As displayed in Fig. 11b, after four times repeated use, the removal efficiency of MB
still preserved above 85%, which presented excellent magnetic property and good reusability of
the photocatalyst.

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## 12 4. Conclusions

Novel magnetically separable Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG nanocomposite photocatalysts were
 hydrothermally synthesized. Compared with WSe<sub>2</sub>/NG and P-25, Fe<sub>3</sub>O<sub>4</sub>-WSe<sub>2</sub>/NG
 nanocomposites exhibited excellent photocatalytic activity for degradation of MB under visible

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light irradiation, which is attributed to the superior adsorption performance for MB, the excellent

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electrical conductivity, the efficient transport and separation of charge carriers of NG, and $Fe_3O_4$
can be used for the AOPs to degradation of organic pollutants in the presence of pH 3 and $H_2O_2$
3.0mM. The 30 wt%Fe <sub>3</sub> O <sub>4</sub> -WSe <sub>2</sub> /NG nanocomposites degraded MB (32 mg/L) by 98.8% in 1
hour. Moreover, it showed higher magnetic property and good reusability, and the removal
efficiency of MB remained above 85% after four times repeated runs applying an external
magnetic field.
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