Supporting information

1. Experimental section

1.1 Materials

Natural graphite powder (325 mesh) was commercially obtained from Alfa-Aesar, TiO₂ (P25, 20% rutile and 80% anatase) was purchased from Degussa, melamine were purchased from Aldrich. Concentrated sulfuric acid (98%, H₂SO₄) and potassium permanganate (KMnO₄) were purchased from Shanghai Chemical Reagent Co., Ltd (China). Sodium nitrate (NaNO₃), polyethylene glycol (PEG), potassium persulfate (K₂S₂O₈), phosphorus pentoxide (P₂O₅), hydrogen peroxide (30%, H₂O₂) and MB were purchased from Sinopharm Chemical Reagent Corp (China). Double distilled water was used during the experimental process. All reactants were of analytical purity and used as received without further purification.

1.2 Preparation of GO

GO was synthesized by the modified Hummers’ method.¹ In detail, 3 g of graphite was put into a mixture of 2.5 g of K₂S₂O₈, 12 mL of concentrated H₂SO₄ and 2.5 g of P₂O₅. The solution was heated to 80 °C and kept stirring for 4.5 h in oil bath. Then the mixture was diluted with 500 mL of water, and the product was obtained by filtering using 0.2 μm Nylon film and dried under ambient condition. Thereafter, 15 g KMnO₄ was added gradually with stirring, to prevent the temperature of the mixture from exceeding 10 °C. The ice bath was then removed and the mixture was stirred at 35 °C for 2 h. The reaction was terminated by adding 700 mL of distilled water and 20 mL of 30 % H₂O₂ solution. Finally, the GO was recovered by filtration and drying.
1.3 Synthesis of g-C$_3$N$_4$ nanosheet

Pure g-C$_3$N$_4$ nanosheet was synthesized by directly heating melamine. 5 g melamine powder was put into an alumina crucible and heated to 500 $^\circ$C for 2 h with a heating rate of 2 $^\circ$C/min. After cooling to room temperature, g-C$_3$N$_4$ was obtained in a powder form.

1.4 Preparation of GO/g-C$_3$N$_4$ hybrid

GO/g-C$_3$N$_4$ hybrid photocatalyst was prepared via sonochemical approach. Typically, 0.1 g GO were initially dissolved in 100 mL water. And then, a certain amount of g-C$_3$N$_4$ powder was added into the above solution. The suspension was ultrasonicated for 1 h and then dried at 60$^\circ$C for 6 h. With this method, GO/g-C$_3$N$_4$ composite photocatalysts was obtained. To investigate the effect of GO content on the photocatalytic performance rates of GO/g-C$_3$N$_4$ composites, the weight percentages of GO to g-C$_3$N$_4$ were varied from 0 to 7 (0, 1, 3, 5 and 7 wt%) by varying the weight of g-C$_3$N$_4$, and the samples were presented as x%GO/g-C$_3$N$_4$, where x is the weight content of GO. The physically mixed sample of 95% g-C$_3$N$_4$ nanosheets and 5% GO (presented as 5%GO+C$_3$N$_4$) was prepared by hand gridding GO and g-C$_3$N$_4$ powder.

1.5 Analytical and testing instruments

Scanning electron microscopy (SEM) images were recorded by Quanta 400FEG at an accelerating voltage of 30 kV. High resolution transmission electron microscopy (HRTEM) of samples was performed using Tecnai G2 F20 S-Twin with an accelerating voltage of 200 kV. Atomic force microscopy (AFM) was conducted using a Bruker Multimode8, the frequency is 0.801 Hz, the samples were prepared by
dropcasting dilute mixtures of samples in ethanol onto heated, freshly cleaved mica substrates. An etched silicon tip was used as a probe to image the samples. The X-ray photoelectron spectra (XPS) of GO/g-C₃N₄ hybrid were measured using a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer. X-ray diffraction (XRD) data for samples were collected using a Rigaku D/MAX 24000 diffractometer with Cu Kα radiation. The infrared absorption spectra were recorded over the frequency range from 400 to 4000 cm⁻¹ using a Nicolet 6700 FT-IR spectrophotometer. UV-vis diffuse reflectance spectroscopy (DRS) measurements were carried out using a Hitachi UV-3600 UV-vis spectrophotometer equipped with an integrating sphere attachment. The analysis range was from 250 to 800 nm, and BaSO₄ was used as reflectance standard. The photoluminescence (PL) spectra of the photocatalyst were measured by FLS920 combined fluorescence lifetime and steady state spectrometer with excitation wavelength of 325 nm. Wavelength of LED light was measured by PMS-50, light power was performed by UV-2000Z, voltage and current were performed by GPS-2303. The Brunauer-Emmett-Teller (BET) specific surface area values were determined by using nitrogen adsorption data at 77 K obtained by a Micromeritics ASAP 2010 system with multipoint BET method. The photoelectrochemical measurements were measured on CHI-660D electrochemical system, using a conventional three-electrode cell. The counter and the reference electrodes were platinum wire and saturated calomel electrode (SCE), respectively. The electrolyte solution was 1 M Na₂SO₄. The working electrodes were prepared as follows: the 0.1 g ground sample was mixed with 0.02 g PEG and 0.5 ml distilled water was added to
make slurry. The slurry was then injected onto a 1.0 cm × 1.0 cm ITO glass electrode and these electrolytes were dried at 60 °C for 2 h and then calcined at 250 °C for 4 h.

1.6 Measurement of photocatalytic activity

A 5×20 LED array was welded on copper clad laminate, and used as light source. The photocatalytic experiments were carried out in a reactor containing the 30 mL 10 mg/L aqueous solution of Methylene blue (MB) and 0.03 g photocatalysts. The distance between the LED light source and the reactor was 1 cm. Before irradiation, the suspension was magnetically stirred in the dark for 1 h to establish adsorption equilibrium under ambient conditions. Then, the mixture was exposed to the LED light irradiation. Then, the mixture was exposed to the LED light irradiation. At the given irradiation time, the concentration of MB was quantified by the absorbance, and the absorbance wavelength used in the spectrophotometer analysis to determine MB concentration was about 664 nm. The degradation efficiency was calculated as follows:

\[ \eta = \frac{C_0 - C}{C_0} \times 100\% \]  

(S1)

Where \( C_0 \) is the absorbance of original MB solution and \( C \) is the absorbance of the MB solution after UV light irradiation.

The decomposition behavior of MB by photocatalytic oxidative process can be described by Langmuir-Hinshelwood rate equation, equation S2 can be seen as follows:

\[ \frac{1}{r} = \frac{1}{k} + \frac{1}{kKC} \]  

(S2)
Where $C$ is the absorbance of the MB solution after LED light irradiation at time $t$; $k$, and $K$ are the rate constant, and the equilibrium adsorption constant, respectively. Integrating equation S3 gives

\[
\ln \frac{C_0}{C} = k_{\text{app}} t
\]  \hspace{1cm} (S3)

Where $C_0$ is the initial dye concentration in solution, $k_{\text{app}}$ is the apparent pseudo-first-order rate constant, and $t$ is the reaction time.

References

As indicated in Fig.S1, 5×20 LED arrays were used as the light source of the photocatalytic degradation device, the direct current of LED light is 0.4 A and the direct voltage is about 17.0 V. Fig.S1b shows the wavelength spectrum of the single LED at the condition of 20 mA and 25 °C. The result showed that the emission center wavelength of LED is 410 nm with very narrow wavelength range.

**Fig.S1** (a) photograph of LED arrays and (b) the wavelength spectrum of LED lamp
Fig. S2 Isotherms for N₂ adsorption-desorption

Table. S1 BET surface area of the as-prepared samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m²/g)</th>
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<tbody>
<tr>
<td>g-C₃N₄</td>
<td>14.3</td>
</tr>
<tr>
<td>Sonicated g-C₃N₄</td>
<td>16.4</td>
</tr>
<tr>
<td>1%GO/g-C₃N₄</td>
<td>48.6</td>
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<tr>
<td>3%GO/g-C₃N₄</td>
<td>112.4</td>
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<td>5%GO/g-C₃N₄</td>
<td>137.3</td>
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<td>7%GO/g-C₃N₄</td>
<td>161.1</td>
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<tr>
<td>5%GO+g-C₃N₄</td>
<td>62.4</td>
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