Improved Photodegradation of Anionic Dyes Using a Complex Graphitic Carbon Nitride and Iron-Based Metal-Organic Framework Material

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Introducing heterostructure to graphitic carbon nitrides (g-C$_3$N$_4$) can improve the activity of visible-light-driven catalysts for efficient treatment of multiple toxic pollutants in water. Here we report for the first time that a complex material can be constructed from an oxygen-doped g-C$_3$N$_4$ and MIL-53(Fe) metal-organic framework using a facile hydrothermal synthesis and recycled polyethylene terephthalate from plastic waste. The novel multi-walled nanotube structure of the O-g-C$_3$N$_4$/MIL-53(Fe) composite which enables unique interfacial charge transfer at the heterojunction showed an obvious enhancement in separation efficiency of the photochemical electron-hole pairs. This resulted in narrow bandgap energy (2.30 eV compared to 2.55 eV in O-g-C$_3$N$_4$), high photocurrent intensity (0.17 mA cm$^{-2}$ compared to 0.12 mA cm$^{-2}$ and 0.09 mA cm$^{-2}$ in MIL-53(Fe) and O-g-C$_3$N$_4$, respectively), and excellent catalytic performance in the photodegradation of anionic azo dyes (95% RR 195 and 99% RY 145 degraded after 4 h, and only a minor change in the efficiency observed after four consecutive tests). These results demonstrate the development of new catalysts made from waste feedstocks that show high stability, ease of fabrication and can operate in natural light for environmental remediation.

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Improved photodegradation of anionic dyes using a complex graphitic carbon nitride and iron-based metal-organic framework material

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Abstract

Introducing heterostructure to graphitic carbon nitrides (g-C₃N₄) can improve the activity of visible-light-driven catalysts for efficient treatment of multiple toxic pollutants in water. Here we report for the first time that a complex material can be constructed from an oxygen-doped g-C₃N₄ and MIL-53(Fe) metal-organic framework using a facile hydrothermal synthesis and recycled polyethylene terephthalate from plastic waste. The novel multi-walled nanotube structure of the O-g-C₃N₄/MIL-53(Fe) composite which enables unique interfacial charge transfer at the heterojunction showed an obvious enhancement in separation efficiency of the photochemical electron-hole pairs. This resulted in narrow bandgap energy (2.30 eV compared to 2.55 eV in O-g-C₃N₄), high photocurrent intensity (0.17 mA cm⁻² compared to 0.12 mA cm⁻² and 0.09 mA cm⁻² in MIL-53(Fe) and O-g-C₃N₄, respectively), and excellent catalytic performance in the photodegradation of anionic azo dyes (95% RR 195 and 99% RY 145 degraded after 4 h, and only a minor change in the efficiency observed after four consecutive tests). These results demonstrate the development of new catalysts made from waste feedstocks that show high stability, ease of fabrication and can operate in natural light for environmental remediation.

Keywords

MIL-53(Fe) MOF; graphitic carbon nitride; O-g-C₃N₄; photodegradation; anionic dyes
1. Introduction

Water pollution from textiles, plastics and paper processing is a serious environmental problem because of non-biodegradable and highly carcinogenic aromatic amines in the organic dyes that are widely used in these industries.\textsuperscript{1,2} For example, anionic dyes (the most commonly-used dyes) containing azo groups (-N=N-) and sulphonate groups (-SO\textsubscript{3}\textsuperscript{-}),\textsuperscript{3} can cause direct destruction of aquatic creatures\textsuperscript{4} and can severely affect human health, being linked to issues such as cancer, jaundice, tumours and heart disease.\textsuperscript{5} As these dyes are highly soluble in water and resistant to chemical oxidation,\textsuperscript{6} these reactive dyes cannot be easily removed from industrial wastewater using conventional biochemical and physico-chemical methods,\textsuperscript{7} thus requiring some alternative processes such as photocatalysis,\textsuperscript{8–11} adsorption\textsuperscript{12–14} or biological treatment.\textsuperscript{15,16} Photodegradation, in which complex organics can be completely converted into simpler and less harmful compounds under solar irradiation, is one of the most cost-effective and green technologies for the removal of synthetic azo dyes in the aqueous phase. To achieve enhanced photodegradation efficiency, a number of studies have focused on developing new catalysts with relatively narrow bandgap energy, high surface area, high stability, low cost and ease of fabrication, which can operate in visible light.\textsuperscript{17–21}

Graphitic carbon nitrides (g-C\textsubscript{3}N\textsubscript{4}) have attracted much attention recently due to their photocatalytic activity over a wide range of wavelengths with a distinctive 2D structure and high stability.\textsuperscript{22,23} Most recent studies have been directed towards the development of g-C\textsubscript{3}N\textsubscript{4} with diverse morphologies such as nanoparticles,\textsuperscript{24} nanotubes,\textsuperscript{25} nanorods\textsuperscript{26} and nanowires.\textsuperscript{27} These different morphologies are achieved through use of various solvents such as water, acetone, N-methyl pyrrolidone and ethanol, or through the pyrolysis of various nitrogen-rich precursors such as urea, thiourea, cyanamide, dicyandiamide and melamine.\textsuperscript{28,29} Doping g-C\textsubscript{3}N\textsubscript{4} with non-metallic elements (such as O, S and P) has also been used to tune the electronic structure towards increased visible light absorption.\textsuperscript{30} In addition, creating defective frameworks can improve separation efficiency of the photochemical electron-hole pairs, thus improving the photocatalytic activity of this material.\textsuperscript{30–33} The synthesis of oxygen-doped graphitic carbon nitride (O-g-C\textsubscript{3}N\textsubscript{4}) was first reported by Li et al.,\textsuperscript{34} showing that the oxygen in the g-C\textsubscript{3}N\textsubscript{4} lattice could induce intrinsic electronic and band structure modulation, resulting in an absorbance edge of 498 nm and enhanced visible-light photoactivity. Pham et al. also reported the synthesis of an O-g-C\textsubscript{3}N\textsubscript{4}/H-ZSM-5 composite with improved catalytic performance for Reactive Red 195 (RR 195) dye photodegradation.\textsuperscript{35} The results show that with 40 wt.% doped oxygen, the composite had a comparatively high surface area of 259 m\textsuperscript{2} g\textsuperscript{-1}, narrow bandgap energy of 2.62 eV, enhanced photocatalytic activity (more than 96% of RR 195 removed after 5 h under natural light), remarkable stability and long-term recyclability (the photodegradation efficiency of RR 195 remained above 91% after 4 cycles).

The heterostructure construction created by the interface between g-C\textsubscript{3}N\textsubscript{4} and other porous materials can increase surface electrostatic interactions, achieve unique porosity and morphology, and can limit recombination of photogenerated electron-hole pairs, and is thus of broad and current interest.\textsuperscript{36–38} To this extent, metal-organic frameworks (MOFs) with diverse chemical compositions, exceptional surface areas and tuneable porosity,\textsuperscript{39–42} have gained
increasing attention in recent years. Heterojunctions in composites of g-C₃N₄ with MOFs, formed by the π-π interactions between the aromatic and the triazine rings, can accelerate charge transfer across the interface and shortens the charge transport distance, thus enhancing separation rates of photoinduced electron-hole pairs.⁴³ Huang et al. have reported a hybrid composite based on MIL-53(Fe) and g-C₃N₄, showing that the composite exhibited an enhanced separation and migration rate of photo-induced charges, resulting in excellent visible light-responsive photocatalytic activity for the reduction of Cr(VI).⁴⁴ MIL-101(Fe)/g-C₃N₄ heterojunction hybrids were also prepared via in-situ growth of MIL-101(Fe) onto a g-C₃N₄ surface.⁴⁵ These composites, with enhanced light absorption and efficient charge carrier separation, were employed as bifunctional photocatalysts for simultaneous reduction of Cr(VI) and degradation of bisphenol-A (BPA), exhibiting a clear enhancement in photocatalytic activity compared to either MIL-101(Fe) or g-C₃N₄ alone. Similar results were also reported on development of g-C₃N₄/NH₂-MIL-101(Fe) for Cr(VI) reduction and methyl orange degradation⁴⁶ and g-C₃N₄/NH₂-MIL-88B(Fe) for methylene blue degradation.⁴⁷ A direct excitation of the extensive iron-oxo (Fe-O) clusters in MIL-53(Fe), MIL-101(Fe) and MIL-88B(Fe) have demonstrated that these MOFs can be employed as exceptional candidates for preparation of visible-light-driven catalysts to generate holes and hydroxyl radicals for efficient treatment of multiple toxic pollutants in water.³⁸,⁴⁹

The aim of this work was to develop a novel and low-cost photocatalyst for removal of azo dyes. This involved the construction of a complex O-g-C₃N₄ and MIL-53(Fe) MOF material to take advantage of the excellent properties of both components in reducing the rate of electron-hole recombination in photocatalysis. The samples preparation was based on inexpensive chemicals including urea and abundant iron precursors. In this study, we also proposed the use of terephthalic acid (TPA or 1,4-benzenedicarboxylic acid) produced directly from polyethylene terephthalate (PET) in waste plastic bottles to explore new and cheaper sources of starting materials for the economical production of MOF materials. Degradation of two commercial textile anionic azo dyes (RR 195 and Reactive Yellow 145, RY 145) was subsequently used to investigate the photocatalytic activity of the O-g-C₃N₄/MIL-53(Fe) composite.

2. Experimental

2.1. Preparation of oxygen doped graphitic carbon nitride (O-g-C₃N₄)

The synthesis of graphitic carbon nitride (g-C₃N₄) and oxygen doped graphitic carbon nitride (O-g-C₃N₄) was carried out according to our reported procedure using urea ((NH₂)₂CO) as a precursor. Typically, 9 g of urea was directly heated at 550 °C for 2 h with a heating rate of 2 °C min⁻¹ to obtain g-C₃N₄. In the synthesis of O-g-C₃N₄, oxygen was doped following by the addition of hydrogen peroxide (H₂O₂), see Scheme 1. First, 9 g of urea was dispersed in 40 ml of H₂O₂, magnetically stirring at 300 rpm for 30 min at room temperature. After drying at 60 °C for 12 h, the solid was placed in a furnace and calcined under air at 550 °C for 2 h at a heating rate of 2 °C min⁻¹ to obtain O-g-C₃N₄.
Scheme 1. Synthesis of O\textsuperscript{g}-C\textsubscript{3}N\textsubscript{4} from urea and hydrogen peroxide. Structure of O\textsuperscript{g}-C\textsubscript{3}N\textsubscript{4} was proposed by Wei et al.\textsuperscript{50}

2.2. Preparation of terephthalic acid from plastic waste

In this study, PET water bottles randomly collected from recycling facilities were used as a source of plastic waste to prepare terephthalic acid. After removing caps and labels, these water bottles were cleaned, dried and cut into small pieces of 5x5 mm. TPA was synthesised by the alkali decomposition of waste PET with sodium hydroxide (NaOH) in ethylene glycol (EG), see Scheme 2. First, a mixture of 12 g waste PET, 22 g NaOH and 55 ml EG was added to a 500-ml 3-neck round-bottom flask with a serpentine condenser, then magnetically stirred at 300 rpm and heated at 190 ℃ for 3 h. After that, the reactor containing a milky solution was cooled down to 80 ℃ and 200 ml distilled water was added under stirring to dissolve completely the mixture. Unreacted plastic pieces were separated from the reaction by vacuum filtration with filter paper. The aqueous filtrate solution was acidified to pH 3 with 2 M sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) to achieve precipitation. The white solid was filtered and washed with distilled water 3 times to eliminate sodium sulphate, before drying in an oven at 60 ℃ to obtain pure TPA powder (dried weight = 6 g). The concentration of the final product was tested by high-performance liquid chromatography (HPLC).

\[
[-\text{O(CH}_2\text{)}_2\text{O-CO(p-C}_6\text{H}_4\text{)CO-}]_n + 2\text{NaOH} \xrightarrow{200 \circ \text{C}} \text{EG} \quad \text{HO(CH}_2\text{)}_2\text{OH} + p\text{-C}_6\text{H}_4(\text{COONa})_2
\]

Scheme 2. Alkali decomposition of polyethylene terephthalate with sodium hydroxide in ethylene glycol

2.3. Preparation of MIL-53(Fe)

MIL-53(Fe) MOF was prepared by a solvothermal reaction as illustrated in Scheme 3. First, 1.35 g of iron(III) chloride hexahydrate (FeCl\textsubscript{3}.6H\textsubscript{2}O) and 0.83 g of TPA were added in 25 ml of dimethylformamide (DMF), magnetically stirring at 300 rpm for 30 min at room temperature to obtain a stock solution. This mixture was then transferred to a 100-ml Teflon-lined stainless-steel autoclave and placed in an oven, heating at 150 ℃ for 15 h. After crystallisation, the resultant precipitate was separated from the solution by centrifugation (3,000 rpm for 10 min), washed three times with ethanol and dried at 60 ℃ for 12 h to obtain a yellowish-orange MIL-53(Fe) solid.
Scheme 3. Schematic illustration of MIL-53(Fe) synthesis. C atoms are represented by black spheres. O atoms are represented by red spheres. Iron clusters are represented by stripe-filled solids

2.4. Preparation of O-g-C₃N₄/MIL-53(Fe)

The O-g-C₃N₄/MIL-53(Fe) composite was prepared by adding 10 ml DMF solution containing 0.25 g of O-g-C₃N₄ to 25 ml of MIL-53(Fe) stock solution containing 1.35 g of FeCl₃.6H₂O and 0.83 g of TPA under stirring at 300 rpm for 30 min at room temperature. The mixture was transferred to the autoclave and subsequent steps followed the synthesis of MIL-53(Fe) in Section 2.3.

2.5. Photodegradation of anionic dyes

Photocatalytic activity of g-C₃N₄, O-g-C₃N₄, MIL-53(Fe) and O-g-C₃N₄/MIL-53(Fe) samples was assessed in the degradation of RR 195 and RY 145 under solar irradiation between 10 am and 2 pm at room temperature. In a typical experiment, 50 mg of the photocatalysts were dispersed in 40 ml of an aqueous solution containing anionic dyes (50 ppm). Prior to the reaction, the above mixture was magnetically stirred at 300 rpm under dark for 60 min to achieve the adsorption-desorption equilibrium, initial concentration (C₀) was taken at this point. After every hour (up to 5 h in this study), a small quantity of supernatant was taken and analysed under UV-Vis spectrometer to record the concentration (C) and calculate the dye degradation using Equation 2 in Supplementary Information. The degradation of RR 195 was tested without catalysts to estimate the baseline during the experiment. A xenon lamp (500 W) was also used in the removal of RR 195 over O-g-C₃N₄ to compare with the corresponding experiment under natural sunlight. The performance of O-g-C₃N₄/MIL-53(Fe) composite material in the photodegradation of anionic dyes was systematically investigated by varying the number of catalysts (25 - 75 mg) and the concentration of RR 195 and RY 145 (30 - 70 ppm) while other conditions maintained unchanged.

3. Results and discussion

3.1. Structural properties

Crystal and chemical structures of the synthesised materials including g-C₃N₄, O-g-C₃N₄, MIL-53(Fe) and O-g-C₃N₄/MIL-53(Fe) were revealed using powder X-ray diffraction (PXRD) and Fourier-transform infrared (FT-IR) spectroscopy. The results are shown in Figure 1.
As can be seen in Figure 1a, two typical peaks of graphitic carbon nitride, at 27 and 13 degrees 2-theta are observed in the g-C₃N₄ sample, corresponding to the stacking of carbon nitride sheets (002) and the in-plane ordering of polymeric melon units (100), respectively. In the oxygen doped sample (O-g-C₃N₄), the peak at 27 degrees 2-theta is much weaker and broader, indicating less long-range order of graphitic stacking. It can also be noticed that this peak is slightly shifted to a lower angle, which is due to the increase of interlayer distance in O-g-C₃N₄. Additionally, the peak at 13 degrees 2-theta almost disappears in this sample, which is ascribed to the decreased planar size of the layers. The FT-IR spectra (Figure 1b) demonstrate that the stretching vibration of N-H (evidenced by the broad absorption bands between 3100 and 3300 cm⁻¹), C= N (evidenced by the two peaks at 1574 and 1638 cm⁻¹) and C-N in the aromatic ring (evidenced by the further three peaks between 1200 and 1500 cm⁻¹) were retained in the structures of all graphitic carbon nitride samples. A sharp peak can also be noted at 891 cm⁻¹, indicating the appearance of the triazine ring in these samples. The peak at 1238 cm⁻¹ for the stretching vibration of C-O-C is overlapped with the peak at 1242 cm⁻¹ for the stretching vibration of C-N, thus is difficult to notice in O-g-C₃N₄. However, increased intensity of these peaks, together with a new peak at 1070 cm⁻¹, demonstrate the existence of C-O bonds in the oxygen-doped sample.

Figure 1. (a) PXRD patterns and (b) FT-IR spectra of g-C₃N₄ and O-g-C₃N₄. (c) PXRD patterns of simulated MIL-53(Fe), as-synthesised MIL-53(Fe) and O-g-C₃N₄/MIL-53(Fe). (d) FT-IR spectra of MIL-53(Fe) and O-g-C₃N₄/MIL-53(Fe)
In this study, TPA recycled from PET waste was used as the organic ligand in the synthesis of MIL-53(Fe). High-performance liquid chromatography (HPLC) result shows that the recovered TPA has a concentration of 99.85% (Figure S1 and Table S1), which is comparable to 99.96% in a standard TPA commercially sourced from Sigma-Aldrich, indicating that high purity terephthalic acid was successfully extracted by the alkali decomposition of plastic waste with sodium hydroxide in ethylene glycol. In the PXRD pattern (Figure 1c), all main peaks for simulated MIL-53(Fe), including those at 9, 13, 17, 19 and 26 degrees 2-theta, are observed in the synthesised MIL-53(Fe) and O-g-C₃N₄/MIL-53(Fe). This result demonstrates that MIL-53(Fe) crystals were successfully formed using the recycled TPA and the MOF crystallinity was maintained during the facile synthesis of the novel O-g-C₃N₄/MIL-53(Fe) composite. The FT-IR spectrum of the O-g-C₃N₄/MIL-53(Fe) composite (Figure 1d) confirms that all bonding groups of MIL-53(Fe) are retained, including the stretching vibration of C-H in the aromatic ring (731 cm⁻¹), COO⁻ in the dicarboxylate group (1685, 1540 and 1386 cm⁻¹), Fe-O in the bonding between Fe(III) and the carboxylic group (559 cm⁻¹). A decreased intensity of the peak at 1685 cm⁻¹ in O-g-C₃N₄/MIL-53(Fe) compared to MIL-53(Fe) might be due to the integration of the graphitic carbon nitride into the composite material. A similar result in MIL-101(Fe)/g-C₃N₄ was reported by Zhao et al.⁴⁵

Figure 2. XPS (a) survey scan, (b) C1s, (c) N1s and (d) O1s spectra of O-g-C₃N₄/MIL-53(Fe) composite

X-ray photoelectron spectroscopy (XPS) was conducted to investigate the elemental valence state and composition in the O-g-C₃N₄/MIL-53(Fe) composite sample (Figure 2a-d). In the high-resolution C1s spectrum (Figure 2b), three peaks at 284.8, 287.6, and 289.3 eV can be assigned to graphitic carbon (sp³ C), sp²-bonded carbon (N=C-N) and the C atoms bonded with
O (C-O), respectively. The N1s spectrum of this sample can be fitted using four peaks at 398.3, 399.9, 401.4, and 403.8 eV, which correspond to sp² N (C-N=C), tertiary N atoms (sp³ N), amino-functional groups (C₂-N-H) and π excitation, respectively. These results confirm that graphitic carbon nitride was formed and indeed combined intimately with the MOF. In addition, the O1s spectrum can be divided into two peaks at 531.5 and 532.5 eV, which correspond to the adsorption of water, and N-C-O, confirming that oxygen was successfully doped on the graphitic carbon nitride using urea and hydrogen peroxide as precursors.

### 3.2. Textural properties

Morphology and elemental composition of MIL-53(Fe), O-g-C₃N₄ and O-g-C₃N₄/MIL-53(Fe) composite were analysed by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM).

**Figure 3.** SEM images of (a) MIL-53(Fe), (b) g-C₃N₄, (c) O-g-C₃N₄/MIL-53(Fe) composite. (d) EDX spectra and elemental mapping of O-g-C₃N₄/MIL-53(Fe) composite. (e-g) TEM images of O-g-C₃N₄/MIL-53(Fe) composite.

Figure 3a shows that the MOF crystals are unevenly rod-shaped with the length varied between 0.5 and 2 µm, which is consistent with the observation of MIL-53(Fe) reported previously. Graphitic carbon nitrides (Figure 3b) were successfully combined with the MOF, as shown in
Figure 3c, which was further validated by the presence of both Fe and N in the EDX data of the composite material (Figure 3d and Table S2). Interestingly, TEM images of O-g-C₃N₄/MIL-53(Fe) (Figure 3e-g) disclose the appearance of multi-walled nanotubes with the onion-like walls annealed instantly under the beam, which is due to the integration of exfoliated graphitic carbon nitride nanosheets (Figure S2a and b) into the MOF material. Additional TEM images of this composite sample can be seen in Figure S2d-h.

The novel porous structure of O-g-C₃N₄/MIL-53(Fe) was further examined using a gas sorption technique. As shown in Figure 4a and Table S3, a hysteresis clearly emerges in the nitrogen isotherm of O-g-C₃N₄/MIL-53(Fe), following by a slightly larger surface area $S_{BET}$ (28.5 m² g⁻¹) and pore volume $V_p$ (0.136 cm³ g⁻¹) in this composite material compared to separated MIL-53(Fe) ($S_{BET} = 20.4$ m² g⁻¹ and $V_p = 0.052$ cm³ g⁻¹) and O-g-C₃N₄ ($S_{BET} = 22.1$ m² g⁻¹ and $V_p = 0.117$ cm³ g⁻¹) components. Figure 4b indicates that extra mesopores with a size of ~9 and ~22 nm were observed in the Barrett–Joyner–Halenda (BJH) pore size distribution, confirming the presence of nanotubes in the O-g-C₃N₄/MIL-53(Fe) composite material.

![Figure 4](image)

Figure 4. (a) N₂ adsorption-desorption isotherms and (b) Pore size distribution of MIL-53(Fe), O-g-C₃N₄ and O-g-C₃N₄/MIL-53(Fe) composite

### 3.3. Optical and photoelectrochemical properties

Optical properties of g-C₃N₄, O-g-C₃N₄ and O-g-C₃N₄/MIL-53(Fe) samples were assessed using ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS), see Figure 5a. In the pristine g-C₃N₄, a band edge is observed at 475 nm, which is consistent with previous reports.⁶¹ In the case of O-g-C₃N₄, the absorption edge shifts to a longer wavelength, indicating enhanced visible-light absorption in this sample. A small peak at ~500 nm found in O-g-C₃N₄/MIL-53(Fe) is attributed to the electronic transition of d-orbitals in Fe³⁺, with a similar result for Fe₂Ni-MIL-88B was previously reported by Vuong et al.⁶²,⁶³ Here, the estimated absorption edge for O-g-C₃N₄/MIL-53(Fe) is 540 nm, which is significantly higher than those for g-C₃N₄ (475 nm) and O-g-C₃N₄ (486 nm). The corresponding bandgap energies ($E_g$) of these samples were calculated using the Kubelka-Munk equation⁶⁴ (see Supplementary Information) and listed in Table 1. Photoluminescence spectroscopy (PL) was implemented to investigate the
carrier separation efficiency of g-C3N4, O-g-C3N4 and O-g-C3N4/MIL-53(Fe). The higher intensity in the emission peak the more rapid recombination of the photoexcited electron-hole pairs.65 As can be seen in Figure 5b, a PL emission peak at between 400 and 500 nm is observed in all samples with the highest intensity observed in g-C3N4, followed by O-g-C3N4 and O-g-C3N4/MIL-53(Fe), which is in good agreement with the analysis of UV-Vis DRS. These results indicate the enhanced separation rates of photoinduced electron-hole which is due to the effective charge transfer across the interface and the reduced charge transport distance at the heterojunction in the composite material.

![Figure 5](image-url)

Figure 5. (a) UV-Vis diffuse reflectance spectra and (b) photoluminescence spectra of g-C3N4, O-g-C3N4 and O-g-C3N4/MIL-53(Fe) composite. (c) Transient photocurrent response of g-C3N4, O-g-C3N4, MIL-53(Fe) and O-g-C3N4/MIL-53(Fe) composite. (d) Point of zero charge of O-g-C3N4/MIL-53(Fe)

Table 1. Optical properties of g-C3N4, O-g-C3N4 and O-g-C3N4/MIL-53(Fe) composite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption edge (nm)</th>
<th>Bandgap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-C3N4</td>
<td>475</td>
<td>2.60</td>
</tr>
<tr>
<td>O-g-C3N4</td>
<td>486</td>
<td>2.55</td>
</tr>
<tr>
<td>O-g-C3N4/MIL-53(Fe)</td>
<td>540</td>
<td>2.30</td>
</tr>
</tbody>
</table>
Transient photocurrent (TPC) response was carried out to investigate photoelectrochemical properties of g-C₃N₄, O-g-C₃N₄, MIL-53(Fe) and O-g-C₃N₄/MIL-53(Fe). As shown in Figure 5c, all of the samples exhibit rapid photocurrent responses when the light is turned on and off for 6 cycles within 400 s. The photocurrent remains relatively stable over the 6 cycles, indicating good reproducibility of the samples during the irradiation process. Further observation shows that the photocurrent of O-g-C₃N₄/MIL-53(Fe) (0.17 mA cm⁻²) is significantly higher than that of MIL-53(Fe) (0.12 mA cm⁻²), O-g-C₃N₄ (0.09 mA cm⁻²) and g-C₃N₄ (0.08 mA cm⁻²), demonstrating that the separation efficiency of the photoinduced electron-hole pairs in O-g-C₃N₄/MIL-53(Fe) is improved due to unique interfacial charge transfer at the heterojunction. As compared to pristine MIL-53(Fe), O-g-C₃N₄/MIL-53(Fe) exhibits higher photocurrent intensity, as the multi-walled nanotube structure exposes more active sites to restrain the recombination. In addition, a point of zero charge (pzc) was measured on the O-g-C₃N₄/MIL-53(Fe) composite under different pH conditions to investigate the surface charge of this sample. It is widely known that particles are positively charged at pH values below the pzc and negatively charged above this point. Figure 5d shows that the ΔpH values (ΔpH = pH₀ − pHᵢ) are negative over nearly the entire pH region studied and the pzc of O-g-C₃N₄/MIL-53(Fe) was determined to be 3.85. The various surface charges under different pH conditions are due to the diverse chemical interactions in O-g-C₃N₄, where the amine groups including C-NH₂, C₂-NH, C₃N can exhibit protonation and deprotonation in aqueous suspensions.

### 3.4. Photocatalytic testing

The photocatalytic performance of the synthesised samples was investigated in the removal of RR 195 and RY 145 under natural light. A pre-test experiment was carried out before introducing the catalysts (Figure S5a), confirming that almost no RR 195 was degraded (less than 2.5%) under sunlight over 4 h. Figure 6a shows that the degradation of RR 195 at the adsorption-desorption equilibrium point using MIL-53(Fe), g-C₃N₄, O-g-C₃N₄ and O-g-C₃N₄/MIL-53(Fe) is 16%, 13%, 17% and 28%, respectively. After 4 h of illumination, the O-g-C₃N₄/MIL-53(Fe) composite shows a relatively high photocatalytic efficiency in RR 195 degradation (95.1% compared to 49%, 66% and 76% using MIL-53(Fe), g-C₃N₄ and O-g-C₃N₄, respectively). A similar pattern is shown in the degradation of RY 145 (Figure 6b), where the catalytic activity of the samples after 4 h follows the order of MIL-53(Fe) (66%) < g-C₃N₄ (93%) < O-g-C₃N₄ (97%) < O-g-C₃N₄/MIL-53(Fe) (99%). The higher degradation efficiency of O-g-C₃N₄ compared to g-C₃N₄ is due to the defect formation in the graphitic framework upon oxygen doping (as shown previously in the PXRD result) which generates more excited electron-holes and increases visible light absorption. This result is in good agreement with the PL and TPC results discussed above. The highest photocatalytic activity observed in O-g-C₃N₄/MIL-53(Fe) is due to the heterojunction structure between O-g-C₃N₄ and MIL-53(Fe), along with the multi-walled nanotube structure, which can accelerate charge transfer
across the interface and shorten the charge transport distance, thus enhance separation efficiency of the photochemical electron-hole pairs in this composite material. Figure S5b shows that O-g-C$_3$N$_4$ was inactive in the dark, confirming the role of light in the removal of anion dyes. The photodegradation of RR-195 using O-g-C$_3$N$_4$ was also repeated using a xenon lamp 500 W (Figure S5c) to validate the stability of solar radiation during the experiment, indicating that no significant variation was observed between these two light sources. This result suggests the possible use of a sunlight simulator when the natural source is inaccessible.

The effect of O-g-C$_3$N$_4$/MIL-53(Fe) on the decomposition of RR 195 and RY 145 was further investigated by varying the initial concentration of the anionic dyes (30 - 70 ppm) and the amount of catalyst (25 - 75 mg) used in the photocatalytic reaction. Figure S4a and b show that a higher catalyst loading of up to 50 mg can facilitate improved degradation efficiency for both RR 195 and RY 145 dyes. When more catalyst was loaded after this point, the degradation remained almost unchanged, demonstrating that optimal efficiency to remove 50 ppm anionic dyes from water can be achieved using 50 mg of O-g-C$_3$N$_4$/MIL-53(Fe). The initial concentration of anionic dyes was also a factor, as demonstrated in Figure S4c and d. After 4 h reaction under natural light using 50 mg of O-g-C$_3$N$_4$/MIL-53(Fe), anionic dyes can be completely degraded in the contaminated water containing 30 ppm of RR 195 or 70 ppm of RY 145.

**Figure 6.** Photocatalytic degradation of (a) RR 195 and (b) RY 145 using g-C$_3$N$_4$, O-g-C$_3$N$_4$, MIL-53(Fe) and O-g-C$_3$N$_4$/MIL-53(Fe). The active species trapping experiments for degradation of (c) RR 195 and (d) RY 145 over O-g-C$_3$N$_4$/MIL-53(Fe) photocatalyst.
Here, trapping experiments were performed to identify the active species and understand the mechanism of the photocatalytic process over O-g-C₃N₄/MIL-53(Fe). As shown in Figure 6c and d, the decomposition rate of RR 195 and RY 145 decreases in the presence of tert-butyl alcohol (TBA), potassium dichromate (K₂Cr₂O₇), ammonium oxalate monohydrate (AO) and 1,4-benzoquinone (BQ), indicating that hydroxyl radicals (‘OH), electrons (ē), holes (h⁺) and superoxide radicals (‘O₂⁻) were formed during the photocatalysis. A significant reduction in degradation is observed after the introduction of BQ and AO compared to K₂Cr₂O₇ and TBA, demonstrating that superoxide radicals and holes act as the primary active species in O-g-C₃N₄/MIL-53(Fe) photodegradation. This result can be used to explain the enhanced photocatalytic performance of the composite material, in which the intrinsic electronic structure and multi-walled nanotube morphology were induced to enhance electron migration efficiency and decrease the recombination possibility of electron-hole pairs.

The recyclability properties of O-g-C₃N₄/MIL-53(Fe) in the photodegradation of RR 195 and RY 145 were also evaluated (Figure 7), showing that the catalytic activity of this sample exhibits only a minor change after four consecutive tests (from 95% to 94% for RR 195 and from 99% to 97% for RY 145) which might be due to the loss of catalyst during filtration after each cycle. The PXRD patterns (Figure S6) confirm that the crystallinity was still retained after four cycles, demonstrating the excellent stability of the synthesised O-g-C₃N₄/MIL-53(Fe) composite material during the photodegradation of anionic dyes.

![Figure 7. Recyclability of O-g-C₃N₄/MIL-53(Fe) in the photodegradation of (a) RR 195 and (b) RY 145](image)

4. Conclusions

In this study, a composite formed of a complex graphitic carbon nitride and a MOF material was successfully synthesised from O-g-C₃N₄ and MIL-53(Fe) using a facile hydrothermal approach. The novel multi-walled nanotube structure of O-g-C₃N₄/MIL-53(Fe) with intrinsic electronic modulation efficiently inhibited the recombination of the electron-hole pairs in photocatalysis. The composite material exhibited narrow bandgap energy (2.30 eV), high photocurrent intensity (0.17 mA cm⁻²) and enhanced catalytic performance in the removal of
two commercial textile azo-dyes (RR 195 and RY 145) under solar irradiation. The recycled PET used for the synthesis of MIL-53(Fe) in this study would allow for plastic waste to be economically valuable again and protect wildlife and the environment from further pollution.

**Conflicts of interest**

There are no conflicts of interest to declare.

**Acknowledgements**

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**References**


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1. Materials

Chemical reagents used in this study including urea ((NH₂)₂CO), hydrogen peroxide (H₂O₂), hydroxyl sodium (NaOH), sulphuric acid (H₂SO₄), ethylene glycol (EG), dimethylformamide (DMF), iron(III) chloride hexahydrate (FeCl₃.6H₂O), Reactive Red 195 (RR 195) and Reactive Yellow 145 (RY 145) were supplied by Sigma-Aldrich and used as received without further purification. Polyethylene terephthalate (PET) water bottles were used as a source of plastic wastes for the preparation of terephthalic acid (TPA).

2. Characterisation techniques

The crystal structure of synthesized samples was determined by X-ray powder diffraction (XRD) patterns using a D8 ADVANCE (Cu Kα₁ copper radiation, λ=0.154 nm, 3° min⁻¹ scanning speed, Bruker). The Fourier Transform Infrared (FT-IR) spectra were measured using a FTIR Affinity-1S (Shimadzu). The concentration of terephthalic acid (TPA) was determined using a high-performance liquid chromatographic (HPLC) assay with the
photometric detector (UV 255 nm) supplied by Shimadzu LabSolutions. Chromatographic experiments were performed with a flow rate of 1 ml min\(^{-1}\). Samples (10 µl, 0.3 mg ml\(^{-1}\)) were injected using an autosampler into a column (Heritage MA, 4.6 x 50 mm) stabilised at 20 °C by the passage of mobile phase (40% acetonitrile with 100 mM AmFm pH 3) for 1 h prior to measurements.

Scanning electron microscope (SEM) samples were coated with 15nm high purity graphite (Q150TES from Quorum Technologies Ltd, UK) for elemental analysis and to prevent charging. The micrographs and energy dispersive X-ray spectroscopy (EDS) maps were taken on a JSM-IT300 (JEOL, Japan), operated at 15kV, at a working distance of 10 mm, together with an X-max 80mm\(^2\) detector, run with Aztec software. Transmission electron micrographs were obtained from a JEM-2100F (JEOL, Japan) at 200kV, with the samples drop cast onto carbon (high purity)-coated copper grids.

The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution were determined using N\(_2\) adsorption-desorption at 77 K on a Micromeritics TriStar II Plus. All samples were degassed at 150 °C for 12 h prior to measurement. Surface areas were determined using a multipoint BET method using adsorption data in the relative pressure (P/P\(_0\)) range 0.05-0.3. Pore size distributions were determined using the Barrett–Joyner–Halenda (BJH) method.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis SUPRA XPS fitted with a monochromated Al k\(\alpha\) X-ray source (1486.7 eV), a spherical sector analyser and 3 multichannel resistive plates, 128 channel delay line detectors. All data was recorded at 150W and a spot size of 700 x 300 µm. Survey scans were recorded at pass energy of 160 eV, and high-resolution scans recorded at pass energy of 20 eV. Electronic charge neutralization was achieved using a magnetic immersion lens. Filament current = 0.27 A, charge balance = 3.3 V, filament bias = 3.8 V. All sample data was recorded at a pressure below 10\(^{-8}\) Torr and a room temperature of 294 K. Data was analysed using CasaXPS v2.3.20PR1.0 and the spectra were calibrated with C1s peak at 284.8 eV.

UV-Vis diffuse reflectance (UV-Vis DRS) and photoluminescence (PL) spectra were recorded on UV-2600 spectrophotometer (Shimadzu) and Cary Eclipse fluorescence spectrophotometer (Varian), respectively. The optical bandgap energy of the samples was estimated by using the following Kubelka-Munk equation\(^1\) as follows:

\[
\alpha h\nu = A(h\nu - E_g)^{1/2}
\]

where \(E_g\) is the bandgap energy, \(A\) is the absorption constant, \(h\) is Planck constant, \(\alpha\) and \(\nu\) represents the optical absorption coefficient and light frequency, respectively. \(n\) is determined by the transition modes of semiconductors (direct electronic transitions at \(n = 1\)),\(^2\) \(\alpha\) can be calculated from absorption constant \(A\) and thickness of the sample \(t\) using \(\nu = 2.303A/t\). \(h\nu\) can be calculated from wavelength using \(h\nu = 1240/\text{wavelength}\). Practically, the bandgap energies \(E_g\) of the samples were determined from a plot of \((\alpha h\nu)^{1/2}\) versus \(h\nu\) (Kubelka-Munk plot, see Figure S3), by extrapolating the straight-line portion of the curves to zero absorption coefficient value.
The point of zero charge (pzc) of O-g-C$_3$N$_4$/MIL-53(Fe) was measured by a salt addition method. Typically, 50 mg of each sample was dispersed in 50 ml KCl 0.1 M in six 100-ml glass Erlenmeyer flasks by magnetically stirring for 30 min. The initial pH values (pH$_0$) of the suspension were then adjusted to several values between 2 and 12 by adding 0.25 M HCl or NaOH solution, measured by a calibrated Hach pHC201 pH meter with accuracy = ±0.02. After shaking for 24 h in a revolving water bath to reach equilibrium, resulting pH values were measured and the difference between the initial and final pH values (ΔpH = pH – pH$_0$) against the initial pH was plotted. The pH value where ΔpH was zero was taken as the pzc.

The degradation experiments of RR 195 and RY 145 were carried out under solar irradiation. The sunlight intensity in the lab was measured with a pyranometer, showing the average solar flux is 700 lx. The concentration of the supernatant was analysed using the Shimadzu UV-2450 UV visible spectrophotometer (the absorption peak positions for RR 195 and RY 145 are at 541 nm and 419 nm, respectively). The dyes degradation was calculated using the following equation.

\[
Dye\ degradation\ (\%) = \frac{C_o - C}{C_o} \times 100\%
\]  

(2)

where $C_o$ (ppm) is the initial concentration and $C$ (ppm) is the calculated concentration of anionic dyes in the supernatant taken from the reaction after 1 - 5 h.

Trapping experiments were performed to indicate the active species involved in photodegradation of RR 195 and RY 145. ~40 µl of each 10⁻⁶ M scavenger (i.e. tert-butyl alcohol (TBA), potassium dichromate (K$_2$Cr$_2$O$_7$), ammonium oxalate monohydrate (AO) and 1.4-benzoquinone ($\text{O}_2^-$)) was added in the dyes solution (50 ppm of RR 195 or RY 145) containing 50 mg of O-g-C$_3$N$_4$/MIL-53(Fe). The photodegradation, in which hydroxyl radicals (•OH), electrons (ē), holes (h$^+$) and superoxide radicals (•O$_2^-$) were trapped by the scavengers, was calculated as above.
3. Additional information and results

![HPLC chromatogram of (a) commercial TPA and (b) prepared TPA](image)

*Figure S1. HPLC chromatogram of (a) commercial TPA and (b) prepared TPA*

**Table S1. The concentration of commercial TPA and recovered TPA (obtained from HPLC data)**

<table>
<thead>
<tr>
<th></th>
<th>Area of the peak at 3.1 min retention time</th>
<th>Total area</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial TPA</td>
<td>4,349,100</td>
<td>4,350,645</td>
<td>99.964</td>
</tr>
<tr>
<td>Recovered TPA</td>
<td>4,152,281</td>
<td>4,158,476</td>
<td>99.851</td>
</tr>
</tbody>
</table>
Figure S2. (a and b) TEM images of O-g-C₃N₄. (c) SAED spectra and (d-h) additional TEM images of O-g-C₃N₄/MIL-53(Fe) composite.
Table S2. EDX elemental composition of O-g-C₃N₄/MIL-53(Fe) composite analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%)</th>
<th>Atomic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>38.34</td>
<td>50.96</td>
</tr>
<tr>
<td>O</td>
<td>26.65</td>
<td>26.59</td>
</tr>
<tr>
<td>Fe</td>
<td>20.39</td>
<td>5.83</td>
</tr>
<tr>
<td>N</td>
<td>14.62</td>
<td>16.62</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table S3. BET specific surface (S_BET), pore volume (V_p) and pore size (D) of O-g-C₃N₄, MIL-53(Fe) and O-g-C₃N₄/MIL-53(Fe) composite

<table>
<thead>
<tr>
<th>Samples</th>
<th>S_BET (m²g⁻¹)</th>
<th>V_p (cm³g⁻¹)</th>
<th>D (nm)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-g-C₃N₄</td>
<td>22.1</td>
<td>0.117</td>
<td>21.21/23.64</td>
</tr>
<tr>
<td>MIL-53(Fe)</td>
<td>20.4</td>
<td>0.052</td>
<td>10.27/11.80</td>
</tr>
<tr>
<td>O-g-C₃N₄/MIL-53(Fe)</td>
<td>28.6</td>
<td>0.136</td>
<td>19.13/23.75</td>
</tr>
</tbody>
</table>

ᵃPore diameters calculated from the adsorption/desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method.

Figure S3. Kubelka-Munk plots of g-C₃N₄, O-g-C₃N₄, and O-g-C₃N₄/MIL-53(Fe) composite.
Figure S4. Photocatalytic degradation of (a) RR 195 and (b) RY 145 at the initial concentration of 50 ppm using different amounts of O-g-C₃N₄/MIL-53(Fe). Photocatalytic degradation of (c) RR 195 and (d) RY 145 at different initial concentrations using 50 mg of O-g-C₃N₄/MIL-53(Fe).
Figure S5. Photodegradation of RR 195 (a) without catalysts, (b) using O-g-C₃N₄ in the dark and (c) using O-g-C₃N₄ under natural sunlight and a xenon lamp 500 W
Figure S6. PXRD patterns of O-g-C₃N₄/MIL-53(Fe) before and after 4 degradation cycles

References
