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Synthesis of MoS₂/g-C₃N₄ as a Solar Light-Responsive Photocatalyst for Organic Degradation

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Abstract

Photocatalytic degradation of organic contaminants is an attractive chemical process owing to its potential for using solar light for environmental applications. In this study, a novel molybdenum disulfide (MoS₂) and graphitic carbon nitride (g-C₃N₄) composite photocatalyst was synthesized using a low temperature hydrothermal method. MoS₂ nanoparticles formed on g-C₃N₄ nanosheets in the composite and this MoS₂ incorporation greatly enhanced the photocatalytic activity of g-C₃N₄. The photocatalyst was tested for the degradation of methyl orange (MO) under simulated solar light. Composite 3.0wt% MoS₂/g-C₃N₄ showed the highest photocatalytic activity for MO decomposition. MoS₂ nanoparticles increased the interfacial charge transfer and thus prevented the recombination of photo-generated electron-hole pairs. The new MoS₂/g-C₃N₄ photocatalyst material also displayed good stability during the photo-reactions and the recycled catalyst showed little reduction in activity during repeated test runs. The novel MoS₂/g-C₃N₄ composite is therefore shown as a promising catalyst for photocatalytic degradation of organic pollutants using solar energy.

Key words: Decoloration, graphitic carbon nitride (g-C₃N₄), molybdenum disulfide (MoS₂), photocatalysis, methyl orange, organic degradation

24 1. Introduction

25 Much attention has been focused on the photocatalytic strategy for the removal of
26 environmental contaminants, as solar energy is an inexhaustible and environmentally friendly
27 energy resource.¹ A large number of semiconductor materials, such as metal oxides and metal
28 sulfides (e.g. TiO₂, WO₃, CdS, ZnS and ZnO), have been developed as active catalysts for
29 photocatalysis of organic pollutants.² Efforts have been made in recent years to use non-metal
30 materials in the synthesis of new photocatalysts with improved reactivity and stability.³ Wang
31 et al. reported a novel polymeric photocatalyst, graphitic carbon nitride (g-C₃N₄) that exhibits
32 excellent photocatalytic hydrogen production using solar energy.⁴ The metal-free g-C₃N₄
33 photocatalyst possesses a good electronic property as well as a high thermal and chemical
34 stability, making it a valuable material for photocatalytic applications.^{1, 5, 6} However, the
35 photocatalytic efficiency of bare g-C₃N₄ is still limited due to the high rate of recombination
36 of the photo-generated electron-hole pairs.⁷ For further improvement, co-catalyst materials,
37 including noble metals, semiconductors and carbon allotropes, have been combined with g-
38 C₃N₄ to fabricate new composite photocatalysts.^{1, 7-14}

39 It is well known that loading precious metals, such as Pt and Au, effectively enhances the
40 activity of photocatalysts. However, these metals are rare and expensive to apply.
41 Molybdenum disulfide (MoS₂) is an emerging photocatalytic cocatalyst material that may be
42 used as a substitute for noble metals in synthesizing photocatalysts. As an indirect-gap
43 semiconductor, MoS₂ has a rather narrow band gap (1.29 eV), and its conduction band (CB)
44 and valence band (VB) edge potentials (-0.1 and +2.0 eV) are more positive than most
45 photosensitive semiconductors.^{8, 9} The difference between the CB edge potentials of a
46 semiconductor and MoS₂ allows electron transfer from the semiconductor to MoS₂, which
47 would make the CB electrons more mobile and hence promote the separation of electron-hole
48 pairs on the semiconductor.^{8, 10} Metal oxides and metal sulfates show improved

49 photocatalytic activity when MoS₂ is added as a synergistic cocatalyst.^{11, 12} Recently, a g-
50 C₃N₄-MoS₂ composite was synthesized by mixing g-C₃N₄ and MoS₂ together, which was
51 found to be effective for photocatalytic H₂ generation.¹⁰ In this study, we prepared the g-
52 C₃N₄-MoS₂ composites using a facial low temperature hydrothermal method to deposit MoS₂
53 as nanoparticles on the g-C₃N₄ sheets. The resulting composite catalyst exhibited a high
54 photocatalytic activity and good stability for the degradation of methyl orange under
55 simulated solar light.

56

57 **2. Experimental**

58 **2.1 Synthesis of g-C₃N₄ from thiourea**

59 Ten grams of thiourea powder was put into an alumina crucible with a cover that was
60 placed in a tube furnace. The chemical was heated to 550 °C at a heating rate of 10 °C /min
61 and kept at this temperature for 2 h in air. The air exhaust released during the thermal
62 treatment was absorbed by a dilute NaOH solution (0.05 M). The resulting yellow powder
63 collected was g-C₃N₄.¹³

64 **2.2 Synthesis of g-C₃N₄ supported MoS₂ nanoparticles**

65 Half a gram prepared g-C₃N₄ was dispersed with sonication in 100 mL DI water with
66 ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O) and Na₂S·4H₂O. The mixture was stirred for 2
67 h to obtain a homogeneous solution. Ten mL 35% HCl solution was added and the solution
68 was heated to 90 °C. After 30 min, 1 g NH₂OH·HCl was added and the solution was kept at
69 this temperature for another 4 h to grow MoS₂ on g-C₃N₄.¹⁴ The composite, g-C₃N₄-MoS₂,
70 was washed thoroughly with DI water and then dried in an oven at 60°C for 12 h.

71 **2.3 Photocatalytic degradation of methyl orange**

72 Methyl orange (MO), one of important classes of commercial dyes, was selected as a
73 model chemical compound for photocatalytic experiments. Given the short life of its excited-
74 state and its high stability under visible and near UV irradiation, MO has often been used as a
75 model dye for testing photo-redox reactions that result in color reduction. For a typical MO
76 decomposition test, 50 mg of the photocatalyst powder was first dispersed in 50 mL of water
77 in a quartz photo-tube by sonication, followed by the addition of MO to an initial
78 concentration of 20 mg/L. Before exposure to light, the suspension was stirred in the dark for
79 10 h to allow adsorption of MO by the catalyst. Photocatalysis of MO was performed in an
80 XPA-7 photo-reactor (Xujiang Electromechanical Plant, Nanjing, China) with a 500 W xenon
81 lamp for the simulated solar (SS) light. During the photocatalytic test, 3 mL of the solution
82 was sampled from the photo-tube at regular time intervals to measure the MO concentration.
83 Each sample was filtered and its absorbance (ABS) was measured by a UV-visible
84 spectrophotometer (UV-vis lambda 25, Perkin Elmer) at 463 nm to determine the MO
85 concentration in the solution.

86 **2.4 Material characterization**

87 The crystal forms of the photocatalysts were analyzed from their X-ray diffraction (XRD)
88 patterns using a Bruker D8 Advance X-ray powder diffractometer. The morphology of the
89 catalysts was examined by transmission electron microscopy (TEM) (Philips Tecnai G220 S-
90 TWIN, Amsterdam, the Netherlands). Fourier transform infrared spectroscopy (FT-IR)
91 (Perkin Elmer, FT-IR Spectrophoeometer Spectrum One B) was used to characterize the
92 functional groups of different catalysts. The chemical states of MoS₂ nanoparticles were
93 detected by X-ray photo-emission spectroscopy (XPS) (PHI 5600 Multi-Technique XPS
94 System, Physical Electronics). The UV-vis diffusive reflectance spectra (DRS) of the
95 catalyst powders were recorded by a spectrophotometer (Hitachi U-3010). The surface area
96 and pore structure of catalyst powder samples was determined by a Beckman Coulter

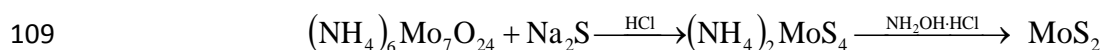
97 SA3100 surface area analyzer from the nitrogen adsorption-desorption isotherm at liquid
98 nitrogen temperature (77 K).

99

100 **3. Results and Discussion**

101 **3.1 Characterization of the photocatalysts**

102 The commonly used precursors for g-C₃N₄ are nitrogen rich compounds with a pre-
103 bonded triple or double C–N core structure, such as cyanamide and dicyandiamide, which are
104 unstable, highly explosive and toxic. In this study, a low cost, non-toxic chemical, thiourea,
105 was used as the raw material to produce g-C₃N₄. The process is simple and easy to perform
106 and can be completed in 2 h at 550 °C in the air atmosphere. MoS₂ nanoparticles were formed
107 and deposited on g-C₃N₄ by the reduction of molybdate with NH₂OH·HCl at 90 °C. The
108 reaction mechanisms for this process can be described as follows:



110 The composite sample was first characterized by XPS to verify its chemical composition.
111 As shown in Fig. S1a, the Mo3d spectrum exhibits two peaks at 229.4 eV (Mo3d_{5/2}) and
112 232.4 eV (Mo3d_{3/2}), indicating a +4 oxidation state for Mo in the composite. The peak at
113 163.2 eV in Fig. S1b can be attributed to S2p of S²⁻. These binding energies are all close to
114 the reported values for MoS₂.^{10, 15-17}

115 Fig. 1 presents the XRD patterns of the g-C₃N₄ and g-C₃N₄-MoS₂ samples. The g-C₃N₄
116 spectra show a strong peak at 27.4° corresponding to the tight inter-layer stacking distance
117 (0.325 nm) of the aromatic planes in g-C₃N₄. The other pronounced peak at 13.11°
118 corresponds to an in-plane structural repeating motif with a repeated distance of 0.675 nm.
119 Pure MoS₂ nanoparticles were prepared using the same method as described for the

120 composite, without the addition of g-C₃N₄. As shown in Fig. 1, the XRD profile for pure
121 MoS₂ displayed low and broad diffraction peaks. The pattern of broad peaks was likely
122 caused by the combination of small-size particles, disorder in crystallinity and strains in the
123 crystallites.¹⁶ The XRD pattern for g-C₃N₄-MoS₂ is nearly the same as that for g-C₃N₄, due to
124 the small percentage of MoS₂ and its low diffraction intensity. The FT-IR spectra also show
125 little difference between pure g-C₃N₄ and g-C₃N₄-MoS₂ (Fig. S2).

126 **Fig. 1.**

127 The optical absorption property of g-C₃N₄-MoS₂ composites with various MoS₂ contents
128 was analyzed. According to the DRS in Fig. 2, pure g-C₃N₄ displays absorption from UV
129 through the visible range up to 460 nm, which can be ascribed to the band gap of g-C₃N₄ (2.7
130 eV). In the UV (≤ 400 nm) region, the composites' absorption abilities follows the order g-
131 C₃N₄-0.03MoS₂ > g-C₃N₄-0.05MoS₂ > g-C₃N₄-0.01MoS₂ > g-C₃N₄. Generally, in the low
132 energy visible region, the DRS intensity strengthened with an increase of the MoS₂ content in
133 the g-C₃N₄-MoS₂ composite. The differences in optical adsorption agree well with the colors
134 of the catalyst powders, presented in Fig. 2, which range from yellow to brown. The DRS
135 features suggest that MoS₂ doping can enhance the response of the catalyst composite
136 towards solar light.

137 **Fig. 2.**

138 The TEM image of g-C₃N₄ in Fig. 3a shows a clear nanosheet structure similar to
139 graphene. The nanosheets are very thin and transparent to the electron beam. The TEM image
140 of pure MoS₂ in Fig. 3b shows aggregated nanoparticles in a wide size distribution. At a
141 higher magnification in Fig. 3c, a relatively weak crystallinity and strain of the MoS₂ in the
142 crystallites can be observed. The characteristic crystal lattice of MoS₂ (0.62 nm) can be
143 identified at the edge of the nanoparticles. The morphology and microstructure of the g-C₃N₄-

144 MoS₂ composite are shown in detail in the TEM image in Fig. 3d. MoS₂ nanoparticles on the
145 g-C₃N₄ surface can be seen at the edge of the composite, and the MoS₂ deposition does not
146 appear to disrupt the g-C₃N₄ nanosheets.

147 **Fig. 3.**

148 The specific surface area and pore volume of the catalyst samples were measured using
149 nitrogen adsorption (Fig. S3). The g-C₃N₄-MoS₂ composites have a larger surface area than
150 g-C₃N₄ (17.5 m²/g), but there is little difference between the composites with different MoS₂
151 loading percentages. The N₂ adsorption-desorption isotherms in Fig. S3a indicate that g-
152 C₃N₄-0.03MoS₂ has a greater N₂ adsorption capability than pure g-C₃N₄. The diameter of the
153 main pores increased with the MoS₂ content, from 18 nm for g-C₃N₄ to 30 nm for g-C₃N₄-
154 0.03MoS₂ (Fig. S3b), which is likely to be the cause of the composite's increased surface area.

155 **3.2 Photocatalytic decomposition of methyl orange**

156 The photocatalytic activity of the different catalysts was tested by the decoloring or
157 decomposition of 20 mg/L MO under simulated solar light. Prior to the photo-tests, the
158 changes in MO concentration caused by the adsorption of the catalyst materials were
159 determined in the dark. The adsorption capability of g-C₃N₄ clearly increased with MoS₂
160 deposition (Fig. S4). This is attributable to the increases in the surface area and pore size of
161 the composites (Fig. S3). After adsorption, the equilibrium MO concentrations were used as
162 the initial concentrations for the subsequent photocatalysis tests (Fig. 4). Composite g-C₃N₄-
163 MoS₂ exhibited a much greater photocatalytic activity than bare g-C₃N₄ for MO destruction.
164 The photocatalytic efficiency for MO decoloration under SS light follows the order g-C₃N₄-
165 0.03MoS₂ > g-C₃N₄-0.05MoS₂ > g-C₃N₄-0.01MoS₂ > g-C₃N₄. Integration of 1% MoS₂ into g-
166 C₃N₄ greatly increased its photocatalytic activity. Increase of the MoS₂ doping ratio to 3%
167 further increased the activity of the photocatalyst. However, when the MoS₂ ratio increased to

168 5%, the photo-activity of the catalyst decreased according to the MO degradation tests. The
169 half-time ($T_{1/2}$) of MO decoloring by the photocatalysts can be determined from the MO
170 reduction curves. Under SS light, the $T_{1/2}$ of MO for bare g-C₃N₄ was 1253 min, whereas the
171 $T_{1/2}$ for g-C₃N₄-0.03MoS₂ was only 213 min.

172 **Fig. 4.**

173 An unsuccessful attempt was made to further increase the activity of the photocatalyst by
174 annealing the g-C₃N₄-0.03MoS₂ composite at different temperatures. The photo-activity of
175 the catalyst actually decreased after the annealing treatment; even at the maximum annealing
176 temperature of 400 °C (g-C₃N₄ becomes unstable at 400 °C or higher). Detailed experiment
177 and results are reported in the Supporting Information (Fig. S5).

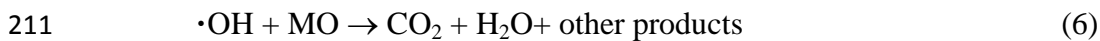
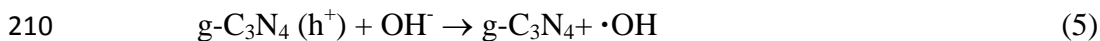
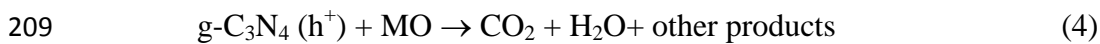
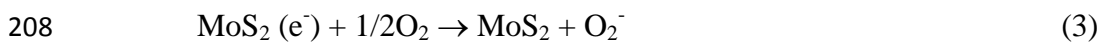
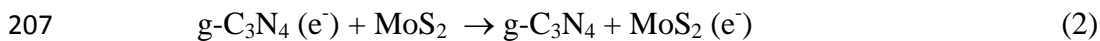
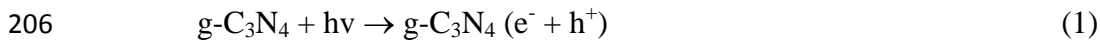
178 The stability of the g-C₃N₄-0.03MoS₂ composite as a photocatalyst was evaluated by
179 repeating the MO decoloration tests. As shown in Fig. S6, the adsorption capacity of g-C₃N₄-
180 0.03MoS₂ decreased after the first use, but little further decrease was observed in the
181 following test runs. The photo-activity of the catalyst was stable, as indicated by the repeated
182 MO decoloring tests (Fig. 5). No significant deactivation was found for the recycled
183 photocatalyst after four runs.

184 **Fig. 5.**

185 **3.3 Photocatalytic MO degradation mechanisms by g-C₃N₄-MoS₂**

186 The mechanisms of photocatalytic MO degradation by the g-C₃N₄-MoS₂ composite are
187 illustrated in Fig. 6. MO molecules are readily adsorbed via conjugation by the s-triazine
188 rings (C₃N₃) of g-C₃N₄, which is beneficial to the subsequent MO decomposition. Under SS
189 light, irradiation of photosensitive g-C₃N₄ leads to electron excitation and electron-hole pair
190 formation. The CB and VB edge potentials of polymeric g-C₃N₄ are reported at -1.13 and
191 +1.57 eV⁸. In comparison, the CB and VB edge potentials of MoS₂ are more positive, at -0.1

192 and +2.0 eV. The difference between the CB edge potentials of g-C₃N₄ and MoS₂ allows
 193 electron transfer from the CB of g-C₃N₄ to the CB of MoS₂, which is favorable to the
 194 separation of electron-hole pairs on g-C₃N₄.^{8, 10} Therefore, MoS₂ nanoparticles on the g-C₃N₄
 195 sheets apparently act as electron collectors, similarly to noble metals, conducting photo-
 196 generated electrons from the main photocatalyst and thus preventing the electrons from
 197 recombining with the holes. Moreover, the presence of MoS₂ could provide more active sites
 198 for MO adsorption and degradation. The electrons would eventually be accepted by dissolved
 199 oxygen in the aqueous phase to facilitate the electron-hole separation. The holes can directly
 200 oxidize MO molecules adsorbed on the catalyst surface, resulting in color reduction.
 201 Moreover, the holes react with water (or hydroxyl) to form hydroxyl free radicals ($\cdot\text{OH}$),
 202 which are a strong oxidant for MO decomposition^{2, 18, 2, 18}. The MO degradation in water
 203 results in decoloration of the solution and formation of CO₂ and intermediate products, such
 204 as phenolic compounds and carboxylic acids. The major reaction steps during the
 205 photocatalytic process may be described by the following equations (1–6):



212

213 **Fig. 6.**

214

215

216 **4. Conclusions**

217 Novel g-C₃N₄-MoS₂ composite photocatalysts were prepared using a facile, low
218 temperature hydrothermal method, with MoS₂ formed as nanoparticles on the g-C₃N₄
219 nanosheets. The composite catalysts exhibited much greater photocatalytic activity than pure
220 g-C₃N₄ for the decoloration and degradation of methyl orange under simulated solar light,
221 and the 3.0wt% MoS₂/g-C₃N₄ composite had the greatest activity. An annealing process
222 failed to further increase the activity of the photocatalysts. The enhanced photocatalytic
223 activity can be attributed to the synergetic function of MoS₂ in the composite catalyst. The
224 presence of MoS₂ nanoparticles apparently increased the interfacial charge transfer and thus
225 reduced electron-hole recombination. The photocatalyst also displayed good stability during
226 the photo-reactions and no obvious deactivation was found for the recycled catalyst after four
227 test runs. The MoS₂/g-C₃N₄ composite is thus a promising photocatalyst with a high
228 reactivity and stability for photocatalytic degradation of organic pollutants using solar energy.

229

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234

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263

264 **Figure Captures**

265

266 Fig. 1. XRD patterns of pure MoS₂, pure g-C₃N₄ and the g-C₃N₄-MoS₂ composite

267 Fig. 2. UV-vis diffusive reflectance spectra of g-C₃N₄ and g-C₃N₄-MoS₂ composites.

268 Fig. 3. (a) TEM image of pure g-C₃N₄, (b) TEM images of pure MoS₂, (c) HR-TEM images
269 of pure MoS₂ and (d) TEM image of g-C₃N₄-MoS₂ composite.

270 Fig. 4. Degradation of MO under simulated solar light by pure g-C₃N₄ and the g-C₃N₄-MoS₂
271 composites.

272 Fig. 5. Photocatalytic MO degradation by the recycled photocatalysts in repeated test runs.

273 Fig. 6. Schematics of the mechanisms of photocatalytic MO degradation by the g-C₃N₄-MoS₂
274 composite under SS light.

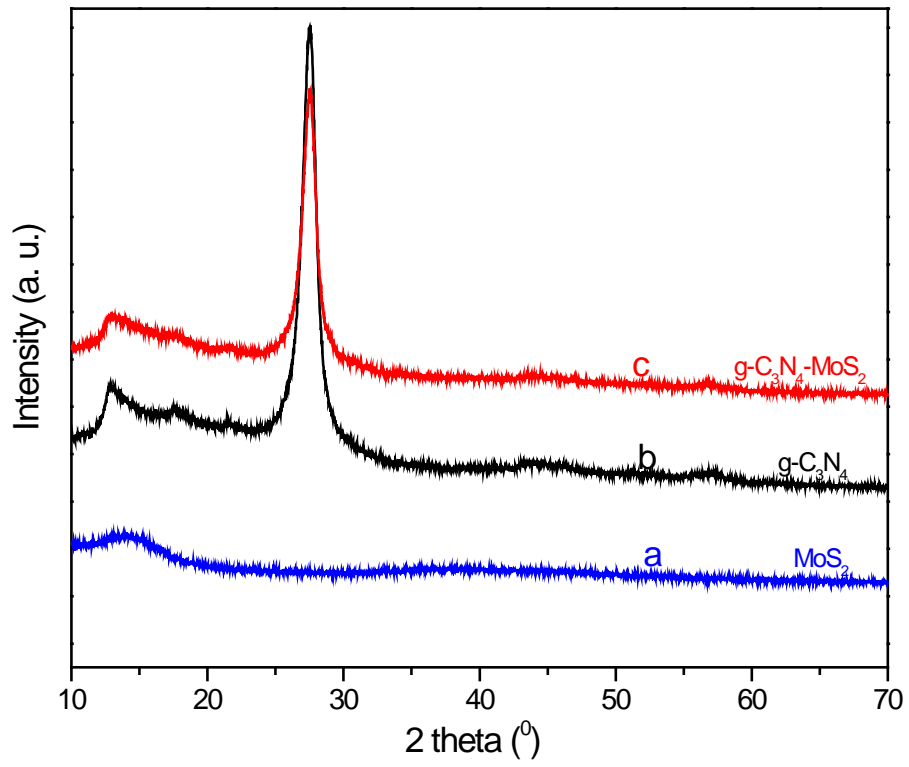


Fig. 1. XRD patterns of pure MoS₂, pure g-C₃N₄ and the g-C₃N₄-MoS₂ composite

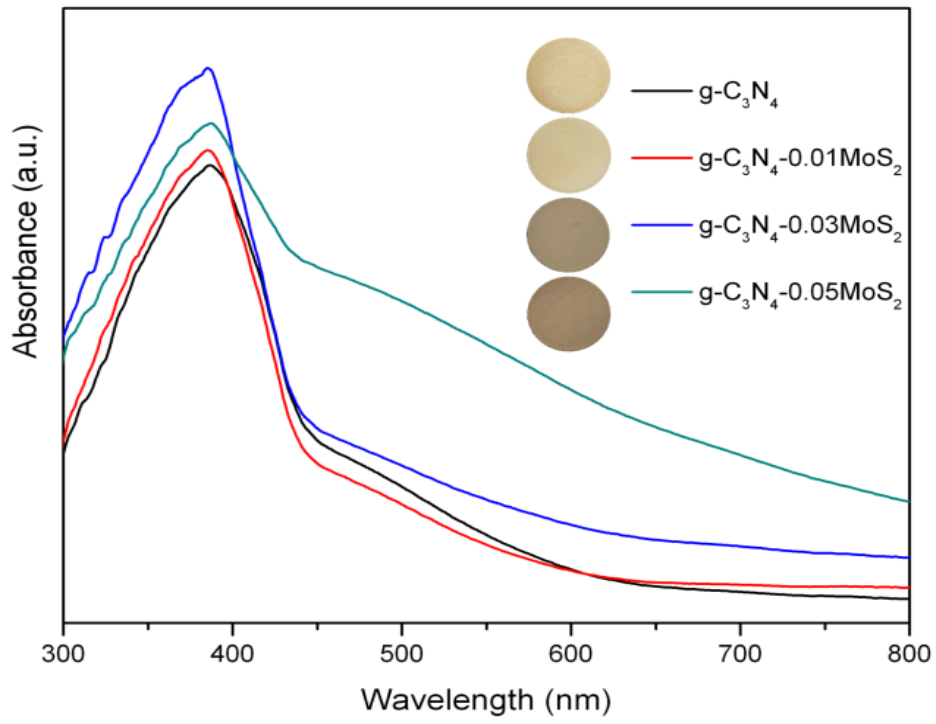


Fig. 2. UV-vis diffusive reflectance spectra of g-C₃N₄ and g-C₃N₄-MoS₂ composites.

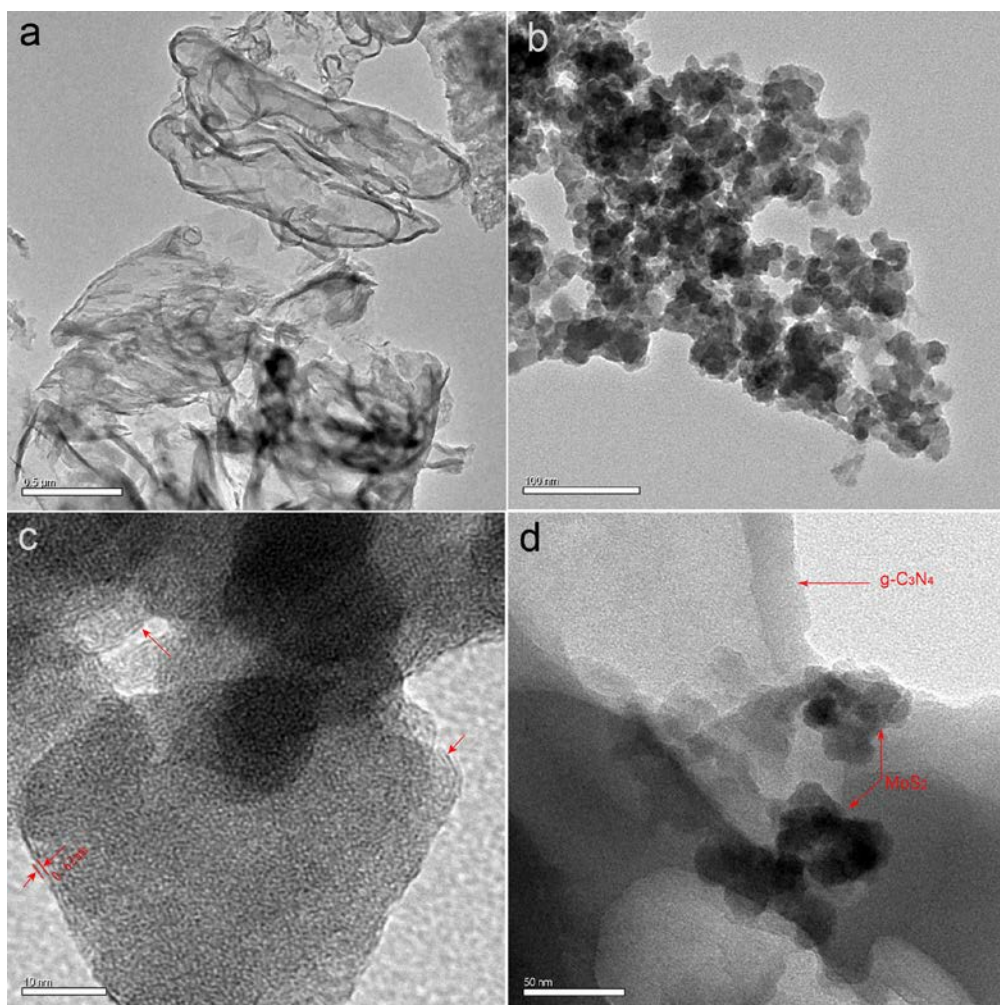


Fig. 3. (a) TEM image of pure g-C₃N₄, (b) TEM images of pure MoS₂, (c) HR-TEM images of pure MoS₂ and (d) TEM image of g-C₃N₄-MoS₂ composite.

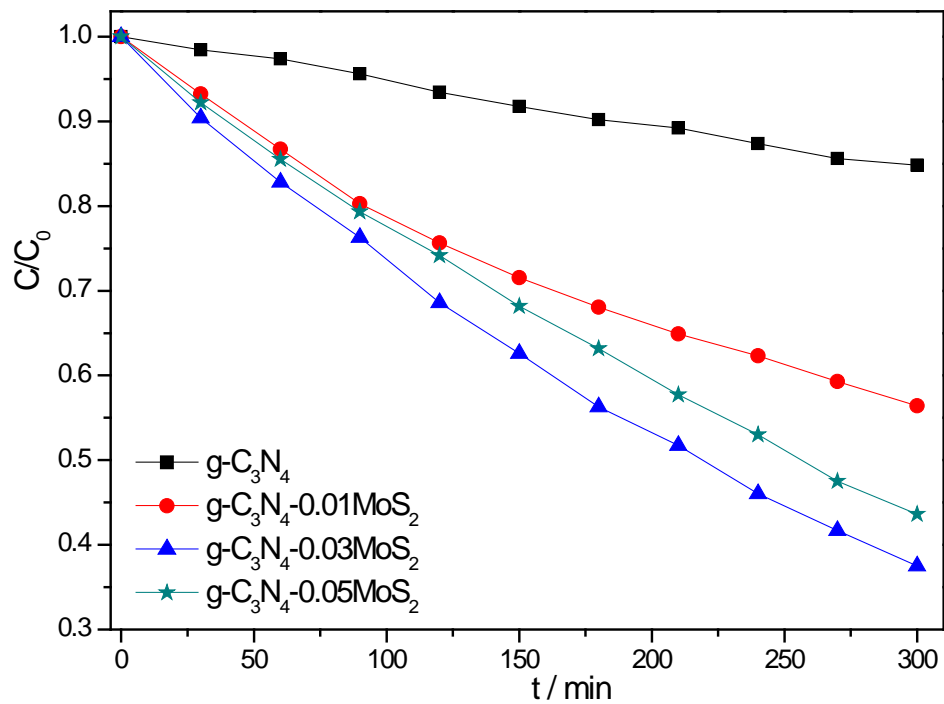


Fig. 4. Degradation of MO under simulated solar light by pure g-C₃N₄ and the g-C₃N₄-MoS₂ composites.

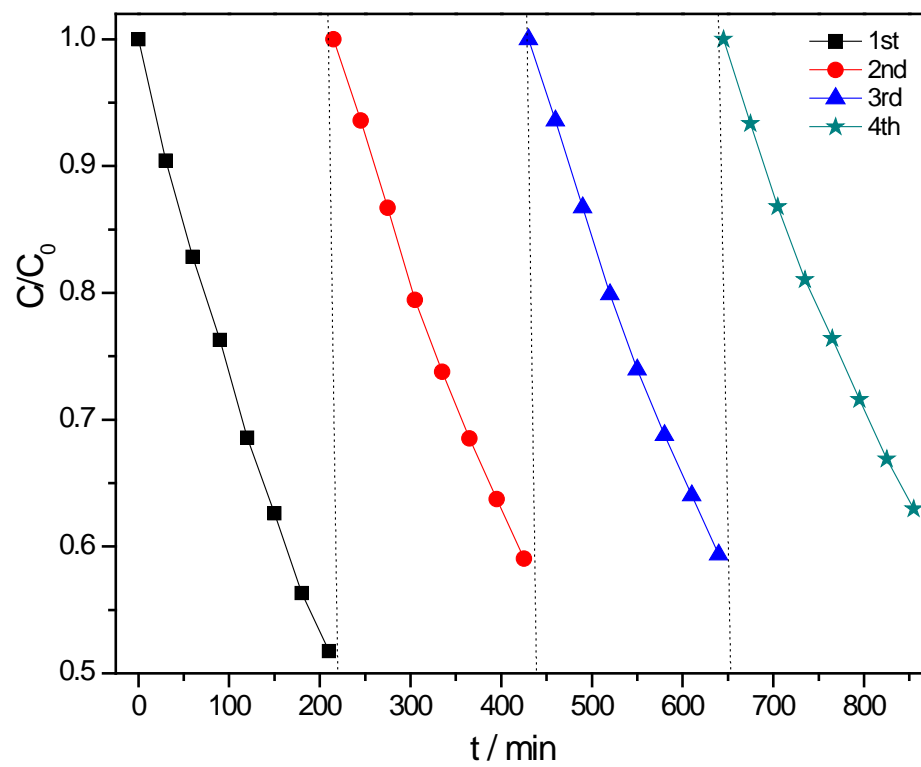


Fig. 5. Photocatalytic MO degradation by the recycled photocatalysts in repeated test runs.

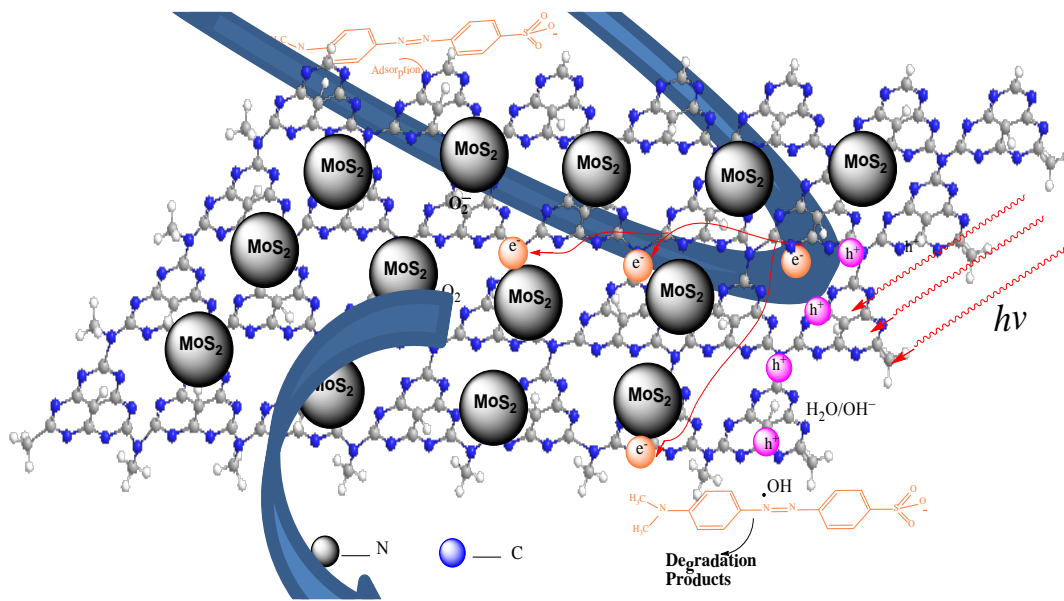


Fig. 6. Schematics of the mechanisms of photocatalytic MO degradation by the g-C₃N₄-MoS₂ composite under SS light.

Supporting Information

Synthesis of MoS₂/g-C₃N₄ as a Solar Light-Responsive Photocatalyst for Organic Degradation

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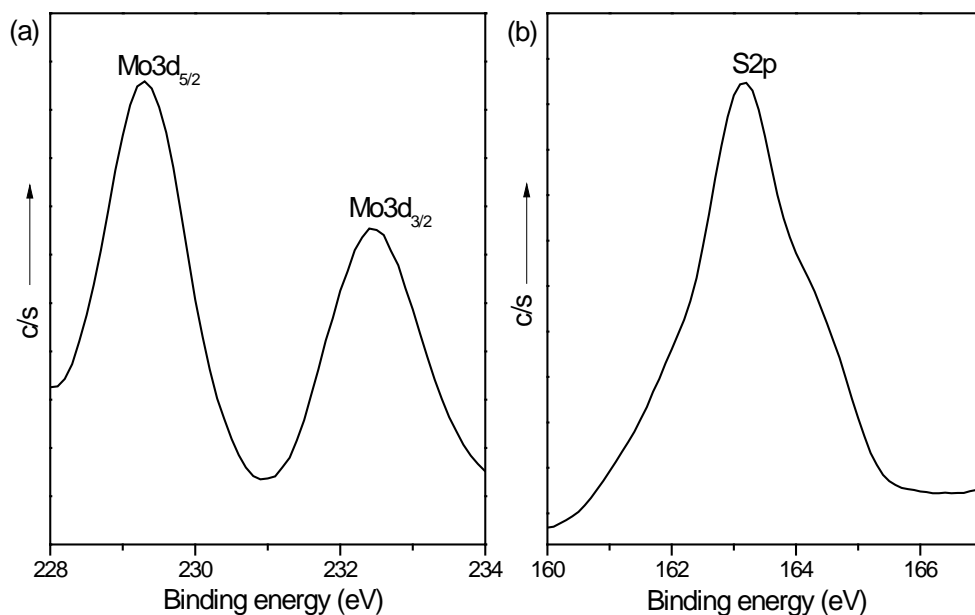


Fig. S1. XPS spectra of MoS₂ nanoparticles deposited on g-C₃N₄: (a) Mo (3d) spectrum and (b) S (2p) spectrum.

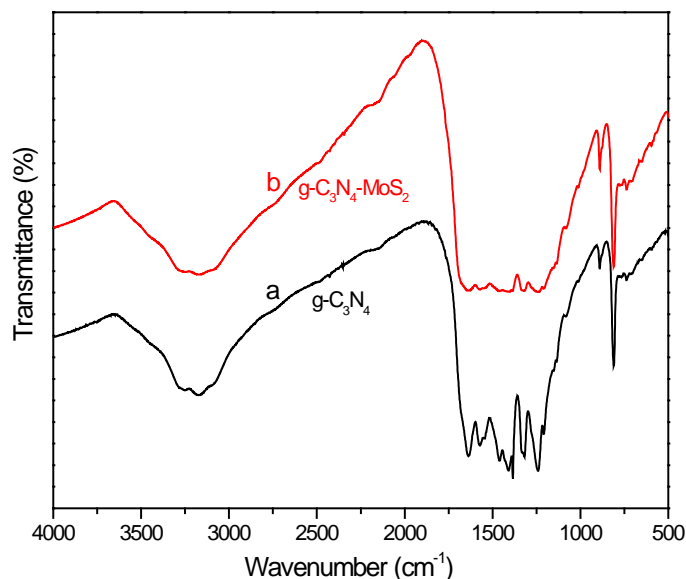


Fig. S2. FT-IR profiles of pure g-C₃N₄ and the g-C₃N₄-MoS₂ composite.

The FT-IR spectrum of pure g-C₃N₄ clearly shows several peaks at the frequency characteristic of the vibrational modes related to the chemical bonding between carbon and nitrogen. The adsorption peak at 810 cm⁻¹ corresponds to the breathing mode of the triazine units. Several strong bands in the 1240-1645 cm⁻¹ region can be attributed to the stretching modes of C-N heterocyclics (e.g. 1321 cm⁻¹ C-N stretching and 1641 C=N cm⁻¹ stretching). The broad absorption band at ~3200 cm⁻¹ can be assigned to the stretching modes of secondary and primary amines and their intermolecular hydrogen-bonding interactions. No major differences can be seen between the pure g-C₃N₄ and the g-C₃N₄-MoS₂ composite spectra. Therefore, MoS₂ doping did not change the functional groups of g-C₃N₄ and no new chemical bonds were generated during this process. However, the intensity of the peaks (1100-1750 cm⁻¹) for the g-C₃N₄-MoS₂ composite is relatively lower than those of pure g-C₃N₄. This was likely caused by the layer of MoS₂ on the g-C₃N₄ surface, which decreased the transmittance of infrared rays from g-C₃N₄.

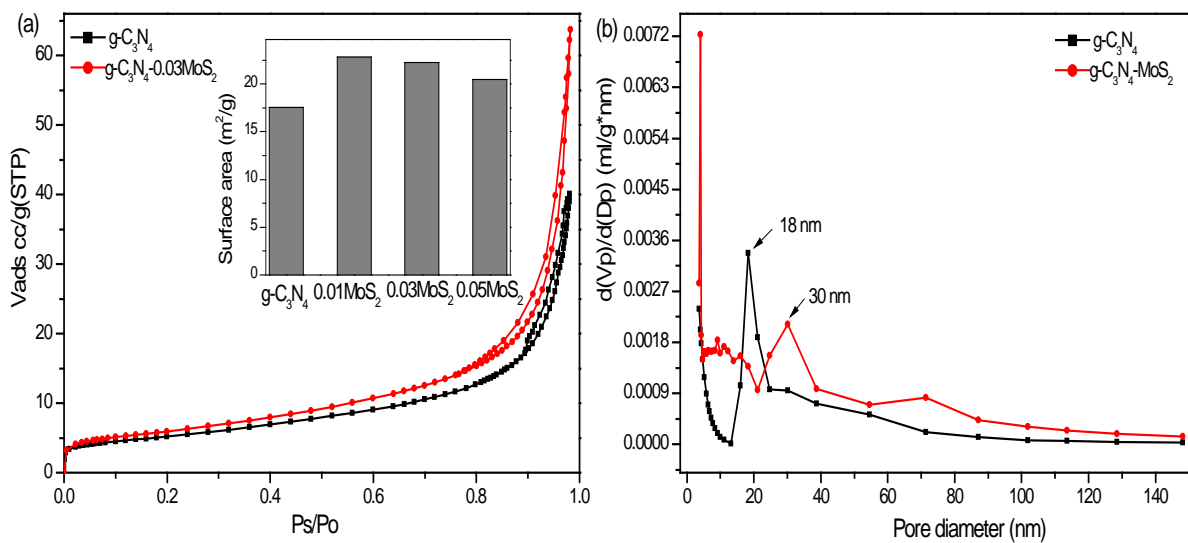


Fig. S3. (a) N_2 adsorption-desorption isotherms at 77 K and (b) pore size distributions of $g-C_3N_4$ and $g-C_3N_4-MoS_2$.

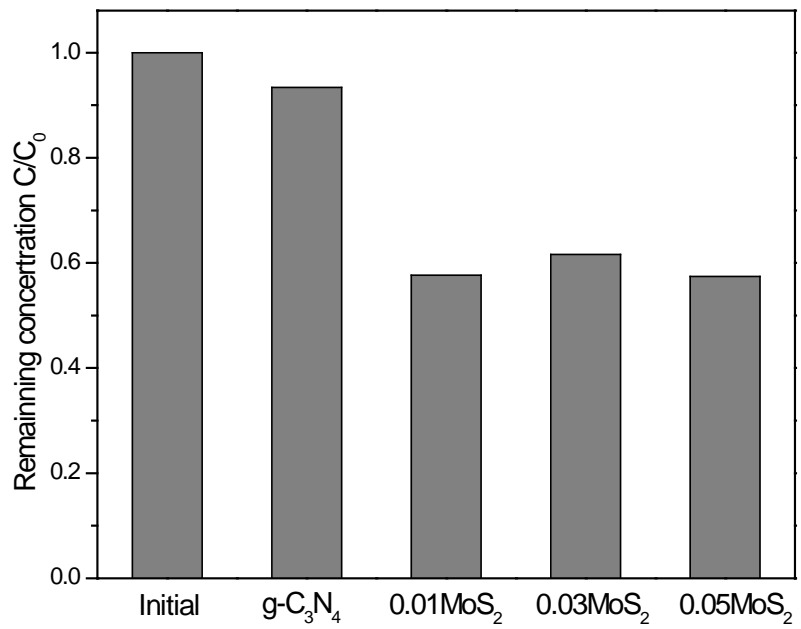


Fig. S4. Change in MO concentration after adsorption by the different catalyst materials ($g-C_3N_4$ and its composites with different amounts of MoS_2)

Thermal treatment of MoS₂/g-C₃N₄

The g-C₃N₄-0.03MoS₂ composite was placed in a crucible that was placed in a tube furnace. An N₂ flow (50 mL/min) was applied for 2 h to remove air from the furnace. The temperature was increased at a rate of 5 °C/min to the required temperature (200, 300 or 400 °C) and then maintained at that temperature for 2 h. A temperature higher than 400 °C will break the structure of g-C₃N₄, so this was set as the upper temperature limit. The furnace was cooled down naturally to room temperature to complete the annealing process.

The materials obtained were characterized by XRD and the results are shown in Fig. S5a. No major differences can be seen between the different samples. The catalysts were tested for photocatalytic MO degradation under the same conditions. Fig. S5b shows that their adsorption capacity decreased after the annealing treatment. In addition, the photo-activity of the thermally treated catalyst did not show any increase for MO degradation (Fig. S5c). The annealing process therefore did not enhance the photocatalytic activity of g-C₃N₄-0.03MoS₂.

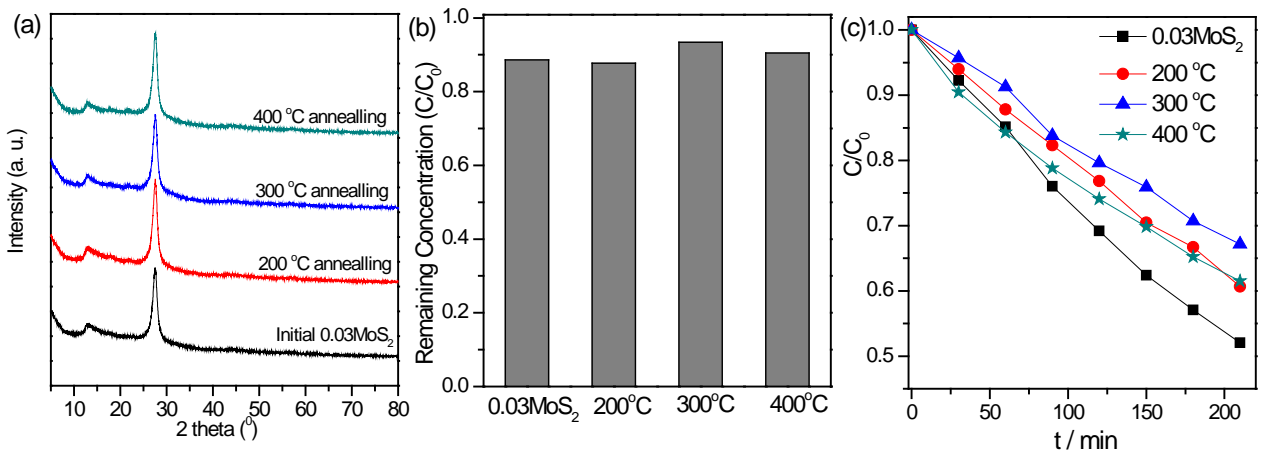


Fig. S5 (a) XRD patterns of $g\text{-C}_3\text{N}_4\text{-}0.03\text{MoS}_2$ annealed at different temperatures in the N_2 atmosphere, (b) the adsorption capability of the different catalyst materials and (c) photocatalytic degradation of MO by the different photocatalysts.

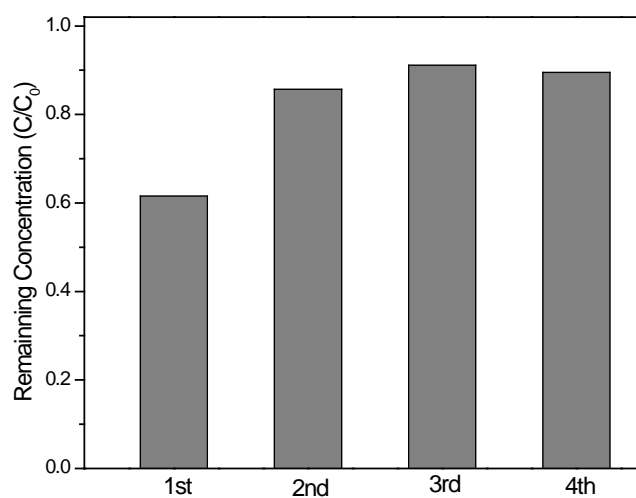


Fig. S6. The adsorption capacity of the recycled catalyst materials