Article

**g-C₃N₄/MoS₂ Heterojunction for Photocatalytic Removal of Phenol and Cr(VI)**

Ilaeira Rapti¹, Feidias Bairamis¹ and Ioannis Konstantinou¹,²,*

¹ Department of Chemistry, University of Ioannina, 45100 Ioannina, Greece; il_rapti@windowslive.com (I.R.); bairamisfeidias@gmail.com (F.B.)
² Institute of Environment and Sustainable Development, University Research Center of Ioannina (URCI), 45110 Ioannina, Greece
* Correspondence: iokonst@uoi.gr

**Abstract:** In this study, molybdenum disulfide (MoS₂) decorated on graphitic carbon nitride (g-C₃N₄) heterostructure catalysts at various weight ratios (0.5%, 1%, 3%, 10%, w/w) were successfully prepared via a two-step hydrothermal synthesis preparation method. The properties of the synthesized materials were studied by X-ray diffraction (XRD), attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FT-IR), UV–Vis diffuse reflection spectroscopy (DRS), scanning electron microscopy (SEM) and N₂ porosimetry. MoS₂ was successfully loaded on the g-C₃N₄ forming heterojunction composite materials. N₂ porosimetry results showed mesoporous materials, with surface areas up to 93.7 m²g⁻¹, while determined band gaps ranging between 1.31 and 2.66 eV showed absorption over a wide band of solar light. The photocatalytic performance was evaluated towards phenol oxidation and of Cr (VI) reduction in single and binary systems under simulated sunlight irradiation. The optimum mass loading ratio of MoS₂ in g-C₃N₄ was 1%, showing higher photocatalytic activity under simulated solar light in comparison with bare g-C₃N₄ and MoS₂ for both oxidation and reduction processes. Based on scavenging experiments a type-II photocatalytic mechanism is proposed. Finally, the catalysts presented satisfactory stability (7.8% loss) within three catalytic cycles. Such composite materials can receive further applications as well as energy conversion.

**Keywords:** C₃N₄; MoS₂; composite; photocatalytic oxidation; Cr(VI) reduction

1. **Introduction**

Energy crisis and environmental pollution are currently among the most serious problems for humans [1]. Emerging and priority environmental pollutants comprise several chemical categories such as pharmaceuticals, pesticides and plasticizers. Phenol and in general phenolics may be present in several wastewater streams from different production processes as well as degradation products from the previously mentioned pollutants. In addition, toxic metal ions such as Cr (VI) may be present in combined wastewater streams; thus, treatment methods should be capable of removing both organic and inorganic pollutants. However, conventional treatment methods present either low removal of certain organic pollutants or are incapable of simultaneous removal of organics and toxic metal ions [2]. Therefore, there has been an increased interest in the development of more efficient and environmentally friendly methods for the removal of pollutants from wastewater, and for this reason the advanced oxidation processes (AOPs) are widely used. Their effectiveness for organics removal is based on the production of hydroxyl radicals, which are powerful oxidizing agents. Heterogeneous photocatalysis, which presents advantages over other removal techniques as it can be applied for both oxidation and reduction of pollutants in ambient conditions in the presence of solar radiation and for organic pollutants, can lead to complete mineralization [2–6].
Graphitic carbon nitride (g-C$_3$N$_4$) has drawn widespread attention and become a hotspot in various scientific disciplines as a metal-free semiconductor due to its advantages. It has an appealing electronic structure with a 2.7 eV band gap, it can be fabricated with low-cost precursors (e.g., urea, thiourea, melamine) [3,7,8] and it is environmentally friendly. However, the rapidly photogenerated electron–hole recombination diminishes the photocatalytic efficiency. The coupling of g-C$_3$N$_4$ with other semiconductors with an appropriate band gap was considered to increase photocatalytic efficiency.

Molybdenum sulfide (MoS$_2$) has attracted attention as an emerging photocatalytic cocatalyst material due to its distinctive features, such as high stability and hardness, reliability, non-toxicity and low cost. It possesses a narrow band gap (1.2–1.9 eV), which offers a wide spectral absorption range and provides high speed channels for the interfacial charge transfer in heterostructures [3]. Previous studies have explored the application of MoS$_2$ in Cr(VI) reduction. Photoreduction and chemical reduction (redox between MoS$_2$ and Cr(VI)) were determined through a collaborative contribution to reducing Cr(VI) by MoS$_2$ under light conditions [9–11]. The coupling of two semiconductors (MoS$_2$, g-C$_3$N$_4$) could significantly reduce the charge carrier recombination and highly improve photocatalytic activity compared to those bare materials. MoS$_2$/g-C$_3$N$_4$ has been synthesized and tested for energy conversion, as a supercapacitor and for organic dye degradation [3,12–15]; however, its application to the simultaneous oxidation/reduction of environmental pollutants has not been studied so far.

Based on the above, the present study deals with the preparation of a series of MoS$_2$/g-C$_3$N$_4$ heterostructure composite catalysts and their application for the removal of phenol and Cr (VI) for aqueous solutions. There are few works exploring the synthesis of MoS$_2$/g-C$_3$N$_4$ heterojunction structure via various methods such as hydrothermal treatment, impregnation–sulfidation and photodeposition [16–19]. Here, a two-step hydrothermal synthesis combined with a sonication–liquid exfoliation preparation method is proposed.

2. Materials and Methods
2.1. Materials and Chemicals

Urea (99.5%, M$_w$: 60.06 gmol$^{-1}$), thiourea (>99%, M$_w$: 76.12 gmol$^{-1}$) and 1,5-diphenyl carbazide (98% (M$_w$: 242.28) were obtained from Acros Organics (Geel, Belgium). Ammonium molybdate tetrahydrate (99%, M$_w$: 1235.86 gmol$^{-1}$) was supplied by Janssen Chimica. Potassium dichromate (KCr$_2$O$_7$, M$_w$: 294.18 gmol$^{-1}$) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Phenol (M$_w$: 94.11 gmol$^{-1}$) was purchased by Merck kGaA (Darmstadt, Germany). Methanol (MeOH), sulfuric acid >95% (H$_2$SO$_4$), methanol HPLC grade (MeOH, M$_w$: 32.04 gmol$^{-1}$) and water HPLC grade (M$_w$: 18.02 gmol$^{-1}$) were supplied by Fischer Scientific (Loughborough, Leics, UK). Distilled water was used throughout the experimental procedures of the study.

2.2. Preparation of g-C$_3$N$_4$, MoS$_2$ and Composite MoS$_2$/g-C$_3$N$_4$ Photocatalysts

2.2.1. Synthesis of Bare Carbon Nitride (g-C$_3$N$_4$) and Molybdenum Disulfide (MoS$_2$)

Graphitic carbon nitride (g-C$_3$N$_4$) was synthesized by thermal treatment of urea as a precursor compound. In a typical synthesis of g-C$_3$N$_4$, 30 g of urea was put in a crucible. After being dried at 90 °C it was heated to 500 °C at a heating rate of 10 °C/min and kept at this temperature for 4 h. The resulting yellow powder was collected and ground into a powder.

Molybdenum disulfide was prepared by hydrothermal synthesis. Hexaammonium heptamolybdate tetrahydrate and thiourea were dissolved in 10 mL of deionized water by stirring for 1 h at room temperature. The resulting solution was then placed in a Teflon-lined autoclave reactor and heated in an oven at 200 °C for 12 h.
2.2.2. Synthesis of MoS$_2$/g-C$_3$N$_4$ Heterostructure

MoS$_2$/g-C$_3$N$_4$ heterostructures with 0.5%, 1%, 3%, 10% (wt%) ratios were synthesized. An appropriate amount of bulk g-C$_3$N$_4$ was added in isopropanol into a beaker, and the mixture was sonicated for 2 h at room temperature. In a separate beaker, MoS$_2$ nanoparticles was added in a water/isopropanol (2:1) solution, and the mixture was sonicated for 2 h at room temperature. The solutions were mixed together and sonicated for another 2 h at room temperature. The product was cleaned with water and ethanol, collected by centrifuging and dried at 60 °C [18]. Then it was calcined in air at 200 °C for 4 h.

2.3. Material Characterization

The crystal forms of the photocatalysts were analyzed from their X-ray diffraction (XRD) patterns using a Bruker Advance D8 X-ray powder diffractometer (Billerica, MA, USA) working with Cu-Ka ($\lambda = 1.5406$ Å) radiation. Diffractograms were scanned from 20 $10^\circ$ to $90^\circ$. The patterns were assigned to crystal phases with the use of the International Center for Diffraction Data (ICCD).

Attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FT-IR) was conducted to characterize the functional groups of different catalysts. A Shimadzu IR Spirit-T spectrophotometer (Kyoto, Japan) with a QATR-S single-reflection ATR measurement attachment equipped with diamond prism was used. The photocatalysts were scanned in the range 4000–400 cm$^{-1}$.

The UV–Vis diffuse reflectance spectra (DRS) of the catalyst powders were recorded using a Shimadzu 2600 spectrophotometer bearing an IRS-2600 integrating sphere (Kyoto, Japan) in the wavelength of 200–800 nm at room temperature using BaSO$_4$ (Nacalai Tesque, extra pure reagent, Kyoto, Japan) as a reference sample.

The morphology of the catalysts was examined by scanning electron microscopy (SEM) using a JEOL JSM 5600 (Tokyo, Japan) working at 20 kV.

Nitrogen adsorption–desorption isotherms were collected by porosimetry using a Quantachrome Autosorb-1 instrument (Bounton Beach, FL, USA) at 77K. The samples (= 80 mg) were degassed at 150 °C for 3 h. The Brunauer–Emmet–Teller (BET) method was used to calculate the specific area (SSA) of each material at relative pressure between 0.05 and 0.3. The adsorbed amount of nitrogen at relative pressure P/P$_0$ = 0.95 was used in order to calculate the total pore volume (V$_{tot}$). The Barrett, Joyner and Halenda (BJH) method was used to determine the pore size distribution (PSD) of the photocatalysts.

2.4. Photocatalytic Experiments

Photocatalytic experiments were carried out using Atlas Suntest XLS+ (Atlas, Germany) solar simulator apparatus equipped with a xenon lamp (2.2 kW) and special filters in place to prevent the transmission of wavelengths below 290 nm. During the experiments the irradiation intensity was maintained at 500 W m$^{-2}$.

Aqueous solutions (100 mL) and the catalyst (10 mg) were transferred into a double-walled Pyrex glass reactor, thermostated by water flowing in the double-skin of the reactor. In binary systems the pH was adjusted to ca. 2 with sulfuric acid in order to achieve high adsorption efficiency of Cr(VI) onto the catalysts and avoid Cr(OH)$_3$ deposition on the catalyst surface, based on previous studies [11,20]. Before exposure to light, the suspension was stirred in the dark for 30 min to ensure the establishment of adsorption–desorption equilibrium onto the catalyst surface. The obtained aliquot (5 mL) was withdrawn at different time intervals and was filtered through 0.45 μm filters in order to remove the catalyst’s particles before further analysis. Quantification of phenol for the kinetic studies in aquatic solutions was carried out by high performance liquid chromatography (HPLC) (Shimadzu, LC 10AD, Diode Array Detector SPD-M10A, Degasser DGU-14A). The column oven (Shimadzu, CTO-10A) was set at 40 °C. The mobile phase used was a mixture of water HPLC grade (50%) and methanol HPLC grade (50%). The concentration of Cr(VI) was determined by the diphenylcarbazide colorimetric method.
measuring the absorbance at the wavelength of 540 nm using a UV–Vis spectrophotometer (Jasco-V630, Tokyo, Japan).

3. Results and Discussion

3.1. Characterization of the Prepared Photocatalysts

3.1.1. Structural Characterization

The XRD patterns for g-C₃N₄, MoS₂ and MoS₂/g-C₃N₄ composites are shown in Figure 1. For g-C₃N₄ two characteristic intense peaks were observed at 13.1° and 27.4°. A broad peak was observed corresponding to the (100) plane, arising from in-plane stacking of the tri-s-triazine motif, and to the (002) interlayer stacking of the conjugated aromatic rings. For MoS₂ three characteristic intense peaks at 13.4°, 33.5° and 57.8° were observed, which can be indexed to the (002), (100) and (110) planes, respectively, corresponding to the hexagonal phase of MoS₂ (JCPDS 87-1526) [21–24].

For the prepared composite catalysts no diffraction peaks corresponding to MoS₂ can be recognized, which may be because of the small quantity of MoS₂ contents and high dispersion in g-C₃N₄ photocatalysts.

![Figure 1. XRD patterns of (a) g-C₃N₄, MoS₂, (b) composite catalysts.](image)

The ATR-FT-IR spectra of g-C₃N₄, MoS₂ and g-C₃N₄/MoS₂ composite are shown in Figure 2. The prepared catalysts presented the main characteristic peaks of both g-C₃N₄ and MoS₂ suggesting the formation of composite heterostructures. The peaks of g-C₃N₄ can be observed at 1573, 1465, 1403, 1319 and 1241 cm⁻¹ confirming the stretching vibration of C–N (–C)–C or C–NH–C heterocycles. The broad peaks between 3300 and 3000 cm⁻¹ are related to the stretching vibration of N-H, and the peak at 1637 cm⁻¹ corresponds to the C=N bending vibration. The peak at 810 cm⁻¹ corresponds to heptazine ring vibration. The peak at 1400 cm⁻¹ confirms the presence of amino groups. The peaks of MoS₂ can be observed at 689 cm⁻¹, confirming the stretching vibration of Mo–O. The peak at 1112 cm⁻¹ corresponds to the stretching vibration of S=O [25].
Figure 2. ATR-FT-IR spectra of (a) g-C₃N₄, MoS₂, (b) composite catalysts.

3.1.2. Morphology Surface Analysis

The morphological evaluation of all catalysts was carried out by scanning electron microscopy (Figure 3). Figure 3a shows the morphology of g-C₃N₄ consisting of packed sheets. Figure 3b presents aggregation of flower-like spherical particles of MoS₂ [26]. Figure 3c (1MoS₂/g-C₃N₄) shows a morphology that seems to be close to that of g-C₃N₄; this may be because of the small quantity of MoS₂ contents on the surface of g-C₃N₄. The 10MoS₂/g-C₃N₄ (Figure 3d) reveals MoS₂ spheres attached on the surface of the g-C₃N₄ sheets.

Figure 3. SEM images of (a) g-C₃N₄, (b) MoS₂ and (c) 1MoS₂/g-C₃N₄ and (d) 10MoS₂/g-C₃N₄.
The nitrogen adsorption–desorption isotherms for the prepared photocatalysts are presented in Figure 4.

All composites samples exhibited typical type IV(a) adsorption and desorption isotherms with H3 hysteresis loop according to the IUPAC classification, suggesting mesoporous materials [27]. BET specific surface area ranged between 2.0 m²g⁻¹ for MoS₂ and 93.7 m²g⁻¹ for g-C₃N₄. MoS₂ presented a non-porous structure with some porosity owed to the aggregation of spherical particles. The calculated specific surface area, average pore diameter and total pore volume of the catalysts are shown in Table 1.

### Table 1. Specific surface area, average pore diameter and total pore volume of prepared catalysts.

| Catalyst                  | Specific Surface Area S_{BET} (m²g⁻¹) | Average Pore Diameter (nm) | V_{TOT} (cm³g⁻¹) |
|---------------------------|---------------------------------------|----------------------------|------------------|
| MoS₂                      | 2.0                                   | 31                         | 0.016            |
| g-C₃N₄                    | 81.3                                  | 8.3                        | 0.169            |
| 0.5% MoS₂/g-C₃N₄          | 93.7                                  | 10.2                       | 0.238            |
| 1% MoS₂/g-C₃N₄            | 62.2                                  | 9.5                        | 0.148            |
| 3% MoS₂/g-C₃N₄            | 90.2                                  | 10.9                       | 0.245            |
| 10% MoS₂/g-C₃N₄           | 92.1                                  | 10.5                       | 0.239            |

3.1.3. UV–Vis Spectroscopy and Band Gap Determination

The diffuse reflectance spectroscopy (DRS) results and the energy band gap (E_{g}) calculated with the Kübelka–Munk function, of all photocatalysts are presented in Figure 5. The absorption edge of MoS₂ was determined at 946 nm, while the absorption edge of g-C₃N₄ was at 480 nm indicating visible light response. The absorption edges of the prepared composite catalysts varied between 466–946 nm and the energy band gap 1.31–2.66 eV. The band gap energy and corresponding absorption edges are shown in Table 2.
MoS₂/g-C₃N₄ heterojunction samples presented enhanced light absorption in the visible region as compared to g-C₃N₄. The absorption intensity of the prepared samples strengthened with increasing MoS₂ contents, which agrees with the color of the prepared samples that vary from light yellow to grey.

The band edge position of conduction band (CB) and valence band (VB) of prepared catalysts was determined applying Equations (1) and (2).

$$E_{VB} = X - E_0 + 0.5E_g$$  \( (1) \)

$$E_{CB} = E_{VB} - E_g$$  \( (2) \)

where \( E_{VB} \) is the VB edge potential, \( E_{CB} \) is the CB edge potential, \( E_g \) is the band gap energy of the catalysts, \( X \) is the electronegativity of g-C₃N₄ (4.67 eV) and MoS₂ (5.33 eV) [28] and \( E_0 \) is the energy of free electrons on the hydrogen scale (4.5 eV). The \( E_{VB} \) and \( E_{CB} \) of g-C₃N₄ was calculated at 1.46 and −1.12 eV, respectively, while for MoS₂ the corresponding values were 1.48 and 0.17 eV.

Figure 5. (a) UV–Vis absorption spectra of prepared catalysts, (b) Kübelka–Munk plots for g-C₃N₄, MoS₂ and 1MoS₂/g-C₃N₄ for indirect band gap semiconductors.

Table 2. Energy band gap and absorption edge of prepared catalysts.

| Catalyst         | Energy Band Gap (eV) | Absorption Edge λ (nm) |
|------------------|----------------------|------------------------|
| g-C₃N₄           | 2.58                 | 480                    |
| MoS₂             | 1.31                 | 946                    |
| 0.5% MoS₂/g-C₃N₄| 2.56                 | 484                    |
| 1% MoS₂/g-C₃N₄  | 2.66                 | 466                    |
| 3% MoS₂/g-C₃N₄  | 2.64                 | 469                    |
| 10% MoS₂/g-C₃N₄ | 2.64                 | 469                    |

3.2. Photocatalytic Study

The photocatalytic performance of composite catalysts was studied against the oxidation of phenol (single system: \( C_{\text{Ph}} = 10 \text{ mg L}^{-1}, C_{\text{cat}} = 100 \text{ mg L}^{-1} \) ) as well as the simultaneous photocatalytic reduction of Cr(VI) and oxidation of phenol (binary system: phenol/Cr(VI) = 1/10, \( C_{\text{cat}} = 100 \text{ mg L}^{-1}, \text{pH} = 2 \) [29,30]) under simulated sunlight irradiation. The results of all photocatalytic experiments are shown in Figure 6 and Tables 3 and 4.

The first-order apparent reaction rates for phenol photocatalytic degradation in single system follows the sequence \( k_{\text{g-C₃N₄}} > k_{\text{MoS₂/g-C₃N₄}} > k_{0.5\text{MoS₂/g-C₃N₄}} > k_{1\text{MoS₂/g-C₃N₄}} > k_{3\text{MoS₂/g-C₃N₄}} > k_{10\text{MoS₂/g-C₃N₄}} > k_{\text{MoS₂}} \). In the binary system, reaction rates of phenol oxidation were as follows: \( k_{1\text{MoS₂/g-C₃N₄}} > k_{0.5\text{MoS₂/g-C₃N₄}} > k_{\text{MoS₂}} \).
$k_{g-C_3N_4} > k_{1MoS_2/g-C_3N_4} > k_{0.5MoS_2/g-C_3N_4} > k_{3MoS_2/g-C_3N_4} > k_{MoS_2}$ and as to the reduction of Cr(VI) it was as follows: $k_{g-C_3N_4} > k_{1MoS_2/g-C_3N_4} > k_{0.5MoS_2/g-C_3N_4} > k_{3MoS_2/g-C_3N_4} > k_{MoS_2}$.

In comparison, the prepared catalysts exhibit faster kinetics of phenol and Cr(VI) removal in binary than in single systems.

![Photocatalytic degradation kinetics of phenol and Cr(VI) in binary system under solar light irradiation.](image-url)

**Table 3.** Kinetic parameters (first-order kinetic constants ($k$), half-life ($t_{1/2}$) and correlation coefficients ($R^2$) of phenol in single system.

| Catalyst          | $k$ (min$^{-1}$) | $t_{1/2}$ (min) | $R^2$  |
|-------------------|------------------|-----------------|--------|
| $g$-C$_3$N$_4$    | 0.022            | 31.5            | 0.9401 |
| MoS$_2$           | 0.0002           | 3465.0          | 0.5016 |
| 0.5MoS$_2$/g-C$_3$N$_4$ | 0.006          | 116.0           | 0.9528 |
| 1MoS$_2$/g-C$_3$N$_4$   | 0.009           | 77.0            | 0.9940 |
| 3MoS$_2$/g-C$_3$N$_4$   | 0.005           | 139.0           | 0.9250 |
| 10MoS$_2$/g-C$_3$N$_4$   | 0.006           | 116.0           | 0.9158 |
Table 4. Kinetic parameters (first-order kinetic constants (k), half-life (t\(_{1/2}\)) and correlation coefficients (R\(^2\)) of phenol and Cr(VI) in binary system.

| Binary          | Ph (k (min\(^{-1}\)) | t\(_{1/2}\) (min) | R\(^2\) | Cr (k (min\(^{-1}\)) | t\(_{1/2}\) (min) | R\(^2\) |
|-----------------|-----------------------|-------------------|---------|----------------------|-------------------|---------|
| g-C3N4          | 0.068                 | 10.2              | 0.9978  | 0.003                | 231.0             | 0.9477  |
| MoS\(_2\)       | 0.002                 | 346.5             | 0.9373  | 0.002                | 346.5             | 0.9694  |
| 0.5MoS\(_2/g\)-C3N4 | 0.042                | 16.5              | 0.9738  | 0.002                | 346.5             | 0.9552  |
| 1MoS\(_2/g\)-C3N4  | 0.091                | 7.6               | 0.9246  | 0.003                | 231.0             | 0.9740  |
| 3MoS\(_2/g\)-C3N4  | 0.042                | 16.5              | 0.9513  | 0.002                | 346.5             | 0.9478  |
| 10MoS\(_2/g\)-C3N4 | 0.031                | 22.4              | 0.9374  | 0.003                | 231.0             | 0.9325  |

3.3. Photocatalytic Mechanism for the Composite Photocatalysts

Different photoinduced reactive species, such as hydroxyl radicals (\(\text{OH}^\cdot\)), superoxide radicals (\(\text{O}_2^\cdot\)) and holes (h\(^+\)), may be involved in the photocatalytic process after electron-hole pairs are generated. Thus, photocatalytic experiments in the presence of isopropanol (IPA), superoxide dismutase (SOD) and triethanolamine (TEOA) were used to scavenge •\(\text{OH}, \text{O}_2^\cdot\) and h\(^+\), respectively, during the photodegradation of phenol in order to investigate the photocatalytic mechanism [3]. As shown in Table 5, the degradation rate constant (k) for phenol was 0.009 min\(^{-1}\) after exposure for 120 min under simulated sunlight without scavenger addition, and this changed after adding, IPA, SOD and TEOA, to 0.003, 0.004 and 0.002 min\(^{-1}\), respectively. It is clearly observed that the degradation of phenol was inhibited with the addition of scavengers, though TEOA was the most obvious. The degradation kinetics of phenol in the presence of scavengers are shown in Figure 7 and Table 5.

Figure 7. Photocatalytic degradation kinetics of phenol in single system in the presence of scavengers and 1MoS\(_2/g\)-C3N4 photocatalyst under solar light irradiation.

Table 5. Kinetic parameters (first-order kinetic constants (k), half-life (t\(_{1/2}\)) and correlation coefficients (R\(^2\)) of phenol in scavenging experiments.

| Scavenger    | k (min\(^{-1}\)) | t\(_{1/2}\) (min) | R\(^2\)   |
|--------------|------------------|------------------|-----------|
| IPA          | 0.003            | 231              | 0.9742    |
| SOD          | 0.004            | 173.2            | 0.9590    |
| TEOA         | 0.002            | 346.5            | 0.9553    |
| no scavenger | 0.009            | 77.0             | 0.9940    |

According to the above analysis, the proposed photocatalytic mechanism (Type II), involving the carrier transfer and photodegradation of phenol was illustrated as shown
in Figure 8. The photogenerated electron–hole pairs were induced in the conduction band (CB) and valence band (VB) of g-C₃N₄ and MoS₂ under irradiation. The photogenerated electrons transferred from the CB of g-C₃N₄ to that of MoS₂, while holes moved from the VB of MoS₂ to that of g-C₃N₄, leading the photogenerated electron–hole pair to be separated and transferred effectively. The holes (h⁺) in the VB of g-C₃N₄ participate in the degradation process. Simultaneously, electrons (e⁻) in the CB together with H⁺ can reduce O₂ to H₂O₂, which forms hydroxyl radicals. The e⁻ on the CB of g-C₃N₄ and MoS₂ participates in the reduction of Cr (VI) to Cr(III). The proposed mechanism provides additional explanation for the better removal performance in the binary system. Regarding the reduction process, the electrons on MoS₂ have weaker reduction ability; consequently they can reduce strong oxidation agents such as Cr(VI), enhancing the target reduction reaction without other reactions, such as O₂ reduction. As far as the oxidation pathway is concerned, the enhancement is due to the better charge separation. The results of the present study indicate that the MoS₂ could be a promising candidate as a non-noble metal co-catalyst for g-C₃N₄ photocatalysts. The composite catalysts can receive further applications either for degradation of pollutants or in energy conversion.

**Figure 8.** Schematic illustration of carrier transfer in the MoS₂/g-C₃N₄ heterojunction.

### 3.4. Recyclability of the Composite Photocatalysts

The stability of the prepared photocatalysts was investigated by examining the photocatalytic activity of the most efficient photocatalyst (1MoS₂/g-C₃N₄) against oxidation of phenol in binary system for three continuous cycles (Figure 9). Reaction constants of phenol oxidation were 0.090, 0.089 and 0.083 min⁻¹ for the first, second and third cycle, respectively (Table 6). A total loss of photocatalytic activity about 7.8% after the third photocatalytic cycle showed the sufficient stability of the catalyst considering also the possible losses of catalyst particles during the recovery process after each cycle. In addition, the catalyst separated at the end of the third catalytic cycle was characterized by XRD, SEM and ATR-FT-IR (Figure 10a–c), revealing a nearly identical pattern to the starting material.
Figure 9. Reusability performance of 1MoS/g-C3N4 photocatalyst for three continuous cycles.

Table 6. Kinetic parameters (first-order kinetic constants (k), half-life (t1/2) and correlation coefficients (R²)) of phenol degradation by 1MoS/g-C3N4 catalyst after three consecutive cycles.

| Cycle | k (min⁻¹) | t1/2 (min) | R²  |
|-------|-----------|------------|-----|
| 1     | 0.09      | 7.7        | 0.9510 |
| 2     | 0.089     | 7.8        | 0.9453 |
| 3     | 0.083     | 8.3        | 0.9496 |

Figure 10. (a) SEM image, (b) XRD pattern, (c) ATR-FT-IR spectra of 1MoS/g-C3N4 photocatalyst after the third photocatalyst cycle.
4. Conclusions

In this work, mesoporous MoS$_2$/g-C$_3$N$_4$ heterostructures were successfully synthesized via a two-step hydrothermal synthesis at various weight ratios (up to 10% w/w of MoS$_2$) and assayed for the simultaneous oxidation of phenol and Cr(VI) reduction. Composite materials show higher photocatalytic activity under solar light in comparison with bare g-C$_3$N$_4$ and MoS$_2$ for both oxidation and reduction processes, while the material with 1% MoS$_2$ loading was found as the catalyst with the best efficiency. A considerable enhancement of the photocatalytic efficiency was observed for the binary system compared to the single component systems, indicating a promoting synergistic effect. The three cycling experiments indicated that the catalysts presented a good stability. Finally, type-II band alignment was proposed as the photocatalytic mechanism for the composed catalysts.

Author Contributions: Conceptualization, I.R. and I.K.; methodology, I.R. and I.K.; formal analysis, I.R. and F.B.; investigation, I.R. and I.K.; resources, I.K.; data curation, I.R.; writing—original draft preparation, I.R. and I.K.; writing—review and editing I.K., I.R. and F.B.; visualization, I.R.; supervision, I.K.; project administration, I.R.; funding acquisition, I.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors acknowledge the access in XRD and SEM units of the University of Ioannina. The authors would like to thank D. Petrakis for the collaboration in the Laboratory of Industrial Chemistry, Dept. of Chemistry, University of Ioannina.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jiménez-Rangel, K.Y.; Larutndo-Rojas, L.; García-García, A.; Cipagauta-Díaz, S.; Mantilla, A.; Samaniego-Benítez, J.E. Hydrothermal Synthesis of a Two-Dimensional g-C$_3$N$_4$/MoS$_2$/MnOOH Composite Material and Its Potential Application as Photocatalyst. J. Chem. Technol. Biotechnol. 2019, 94, 3447–3456, doi:10.1002/jctb.6088.
2. Antonopoulou, M.; Giannakas, A.; Konstantinou, I. Simultaneous Photocatalytic Reduction of Cr(VI) and Oxidation of Benzoic Acid in Aqueous N-F-Codoped TiO$_2$Suspensions: Optimization and Modeling Using the Response Surface Methodology. Int. J. Photoenergy 2012, 2012, doi:10.1155/2012/520123.
3. Zhang, X.; Zhang, R.; Niu, S.; Zheng, J.; Guo, C. Enhanced Photo-Catalytic Performance by Effective Electron-Hole Separation for MoS$_2$ Inlaying in g-C$_3$N$_4$ Hetero-Junction. Appl. Surf. Sci. 2019, 475, 355–362, doi:10.1016/j.apsusc.2018.12.301.
4. Cuerda-Correa, E.M.; Alexandre-Franco, M.F.; Fernández-González, C. Advanced Oxidation Processes for the Removal of Antibiotics from Water. An Overview. Water (Switz.) 2020, 12, 102.
5. Barrera-Díaz, C.; Cañizares, P.; Fernández, F.J.; Natividad, R.; Rodrigo, M.A.; Rosedal, E.; Toluca, E.; de México, M. Electrochemical Advanced Oxidation Processes: An Overview of the Current Applications to Actual Industrial Effluents. J. Mex. Chem. Soc. 2014, 58, 3.
6. Malato, S.; Fernández-Ibáñez, P.; Maldonado, M.I.; Blanco, J.; Gernjak, W. Decontamination and Disinfection of Water by Solar Photocatalysis: Recent Overview and Trends. Catal. Today 2009, 147, 1–59.
7. Zhang, G.; Zhang, J.; Zhang, M.; Wang, X. Polycondensation of Thiourea into Carbon Nitride Semiconductors as Visible Light Photocatalysts. J. Mater. Chem. 2012, 22, 8083–8091, doi:10.1039/c2jm00097k.
8. Bairamis, F.; Konstantinou, I. WO3 Fibers/g-C$_3$N$_4$ Z-Scheme Heterostructure Photocatalysts for Simultaneous Oxidation/Reduction of Phenol/Cr (VI) in Aquatic Media. Catalysts 2021, 11, 792; doi:10.3390/catal11070792.
9. Sun, K.; Jia, F.; Yang, B.; Lin, C.; Li, X.; Song, S. Synergistic Effect in the Reduction of Cr(VI) with Ag-MoS$_2$ as Photocatalyst. Appl. Mater. Today 2020, 18, 100453, doi:10.1016/j.apmt.2019.100453.
10. Sun, H.; Wu, T.; Zhang, Y.; Ng, D.H.L.; Wang, G. Structure-Enhanced Removal of Cr(VI) in Aqueous Solutions Using MoS$_2$ Ultrathin Nanosheets. New. J. Chem. 2018, 42, 9006–9015, doi:10.1039/c8nj01062e.
11. Wang, K.; Chen, P.; Nie, W.; Xu, Y.; Zhou, Y. Improved Photocatalytic Reduction of Cr(VI) by Molybdenum Disulfide Modified with Conjugated Polyvinyl Alcohol. Chem. Eng. J. 2019, 359, 1205–1214, doi:10.1016/j.cej.2018.11.057.
12. Fageria, P.; Sudharshan, K.Y.; Nazir, R.; Basu, M.; Pande, S. Decoration of MoS$_2$ on g-C$_3$N$_4$ Surface for Efficient Hydrogen Evolution Reaction. Electrochim. Acta 2017, 258, 1273–1283, doi:10.1016/j.electacta.2017.11.184.
