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# [1+1] Copper(II) macrocyclic Schiff base complex on rGO as a photocatalyst for reduction of nitroaromatics compounds under visible-light irradiation



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# ABSTRACT

In this work, [1 + 1] macrocyclic Copper(II) Schiff base complex ([CuL](NO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O) was synthesized and grafted on reduced graphene oxide successfully. The novel prepared sample was characterized by physico-chemical techniques and used as a photocatalyst for the reduction of nitroaromatic compounds to their amine derivatives at room temperature under visible-light irradiation with hydrazine mono hydrate. From the prepared samples, reduced graphene oxide loaded with 30% [CuL](NO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O catalyst (rGO/CuM30) shows the best efficiency for converting different nitroaromatic compounds to the corresponding amino compounds using visible light. Asprepared catalyst illustrated excellent activity for the reduction of 2-nitrophenol to 2-aminophenol (100% conversion) in only 90 min. Finally, the catalyst could be recovered for five times and reused without decreasing of its efficiency.

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# 1. Introduction

Nitroarenes are one of the most important and the largest chemical compounds in use today. Nitroaromatics are relatively rare in nature and are produced mainly by human activities. Due to their environmental hazard, the U.S. Environmental Protection Agency added them to the list of perilous pollutants. Hence, the development of methodologies for their rapid conversion to non-hazardous compounds have become a prime necessity and became an important route for environmental protection [1].

Nitroaromatic compounds remain however important chemical reactants for many compounds such as pharmaceuticals, dyes, and agrochemicals synthesized via catalytic reduction of nitroaromatics [2–5]. The synthesis of amines follow mainly the Bechamp's method [6] and others: environmental toxic pollutants are produced. The development of more environmental friendly approach of the selective reduction of nitro compounds into their corresponding amines is looked for [7,8]. Photocatalytic reduction of nitroaromatic under UV irradiation is one possibility [9]. As UV light makes up less than 5% of electromagnetic

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waves spectrum and use of visible light irradiation would be more efficient [10,11].

Photocatalysts based on GO and rGO rather than semiconductors to reduce nitroaromatic have found wider applications [12,13]. Some of the recent research on graphene, GO and rGO based photocatalysts have shown noticeable performances, that make them utilizable in many cases. There are various ways to convert GO to rGO (solar light irradiation method, hydrazine, thermal processing, and green method) [14]. The high surface area and other properties of graphene oxide and reduced graphene oxide make the many metallic nanoparticles such as Au, Ag, Ni, Pd, and etc. are decorated on these materials [14].

Nanocomposite catalysts can be produced by radiation, green chemistry, wet chemical, co-reduction, and capillary and micro-reaction methods [15–19]. Among these, the radiation method is a clean, low-cost, and non-toxic method that does not require a large amount of reducing chemicals. Wu et al. [20] reported the photocatalytic performance Au–Ag decorated GO for reducing nitroaromatics. The photocatalytic performance of Au–Pt decorated rGO using the wet-chemical method to reduce p-nitrophenol has been reported by Song et al. [21]. The integration of macrocyclic complexes of transition metals on rGO photocatalysts might be an alternative [22].

In the present study, [1 + 1] Copper(II) macrocyclic complex ([CuL](NO<sub>3</sub>)<sub>2</sub>. H<sub>2</sub>O) was synthesized from reaction between 1,4-bis

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(2-formylphenoxy)butane, copper(II) nitrate and ethylenediamine in methanol and successfully grafted on to rGO. The prepared new heterogeneous sample (rGO/CuM) was used as catalyst for photoreduction of nitroaromatic compounds under visible-light irradiation. (Scheme 1).

#### 2. Experimental

## 2.1. Materials and instruments

The chemicals employed were received and used without further purification. Graphite flakes, sulfuric acid, potassium permanganate, hydrochloric acid, potassium carbonate, salicylaldehyde, 1,4dibromobutane, hydrazine monohydrate, hydrogen peroxide, para-hydroxynitrobenzene, nitrobenzene, para-methylnitrobenzene, para-chloronitrobenzene, 1,4-dinitrobenzene, para-Fluoronitrobenzene, para-nitroaniline, ortho-hydroxynitrobenzene, para-bromonitrobenzene, 2,4-dinitroaniline, orto-nitroaniline, and copper(II) nitrate trihydrate were purchased from Merck. Some substrates and solvents were obtained from Merck India Ltd. and others from Sigma Aldrich chemical Co. FT-IR spectra were measured on a Bruker Tensor 27 FT-IR spectrometer with KBr pellets as the sample matrix. Analysis of the changes in the concentrations of reaction materials was carried out by using gas chromatography-mass spectrometry (GC-MS) (Agilent 7890 A) with a capillary column and flame ionization detector (FID). Microscopic morphology of samples was obtained by FESEM (MIRA3 TESCAN-XMU). X-ray photoelectron spectroscopy (XPS) tests done with ESCALAB 250Xi. Surface Analyzer (BET Belsorp mini II,

Japan) was used to analyze the nitrogen adsorption-desorption analysis of the nanocomposites. Raman spectrums of samples were obtained using a model Takram P50COR10 laser Raman microscope.

### 2.2. Preparation of graphene oxide (GO)

Hummer method [23] has been used to prepare graphene oxide (GO) from graphene. For this purpose 68 mL sulfuric acid 98% and 1.5 g sodium nitrate were added simultaneously to 2.0 g of graphite in a round bottom flask and stirred in the ice bath for 10 min. Then 9.0 g potassium permanganate was added bit by bit to this blend and stirred for 5 days. Then 100 mL diluted  $H_2SO_4$  (5 wt%) was added to the mixture and heated at 85 °C for 120 min with continuous stirring. In the next step, 6 mL  $H_2O_2$  27% was added to the mixture and stirred for 120 min at 25°C. The prepared graphene oxide was separated by centrifugation (5000 rpm) from the mixture. In order to purify, the specimen was washed with HCl (2.5 wt%),  $H_2O_2$  (0.6 wt%) and  $H_2SO_4$  (2.5 wt%) respectively. Eventually, it was washed with double distilled water to rich the pH = 7.

## 2.3. Preparation of reduced graphene oxide (rGO)

rGO was obtained using the solvothermal method [24]. The synthesized GO flakes in the preceding step were sonicated after diluting (with a 10:8 proportion (wt/v)) in deionized water for 40 min. Amount 6 mL of H<sub>2</sub>SO<sub>4</sub> (97 wt%) was added and diluted to 120 mL with water and stirred at 25°C for 24 h. The suspension was washed with double



Scheme 1. Preparation of rGO/CuM30 photocatalyst

distilled (DD) water to adjust pH = 6. After that, the suspension was diluted with 20 mL of ethanol and placed in autoclave reactor at 170 °C for 24 h. To more purification, the obtained sample was washed several time with acetone and dried in oven at 90 °C.

## 2.4. Preparation of 1,4-bis(2-formylphenoxy)butane

1,4-bis(2-formylphenoxy)butane was synthesized according to the literature [25]. For this purpose 300 mmol 2-hydroxybenzaldehyde and 150 mmol K<sub>2</sub>CO<sub>3</sub> was stirred in 150 mL of DMF. Then 32.4 g (150 mmol) of 1,4-dibromobutane (dissolved in 60 mL DMF) was added dropwise to the desired mixture. The mixture was stirred for 12 h at 170 °C. Then the stirring was continued at 25°C for 6 h. Then 300 mL distilled water was added to mixture and placed in the refrigerator for 1 h. The formed solid was obtained via filtration and washed with 700 mL of distilled water. Finally the obtained solid was recrystallized in ethanol and dried in vacuum. Yield: 34.7 g (78%), m.p: 104–108°C, Color: Light brown. Mass percentage Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>: H, 6.08; C, 72.47. Found (%): H, 6.49; C, 71.9. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7–7.80 (m, 8H, aromatic), 10.52 (s, 2H, CH-O), 2.1 (t, 4H, C-CH<sub>2</sub>-C), 4.2 (t, 4H, aliphatic O-CH<sub>2</sub>-C) [26] (Fig. S1).

#### 2.5. Synthesis of Copper (II) macrocyclic Schiff base complex, CuM

Copper(II) macrocyclic Schiff base complex was synthesized according to the literature [25]. Amount 3.00 g (10 mmol) of 1,4-bis(2-formylphenoxy)butane and 2.42 g (10 mmol) of  $Cu(NO_3)_2.3H_2O$  were dissolved in 120 mL of CH<sub>3</sub>OH. To the stirred solution, 10 mmol of ethylenediamine (dissolved in 80 mL CH<sub>3</sub>OH) was added dropwise and stirred for 120 min. Finally, the obtained sample was filtrate and washed with CH<sub>3</sub>OH and dried at room temperature. Yield; 1.15 g (20%), [CuL](NO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O. Anal. calcd for C<sub>20</sub>H<sub>30</sub>CuN<sub>4</sub>O<sub>12</sub>: C 41.24, H 5.15, N 9.62; found C 41.33, H 5.63, N 9.95. IR (in KBr,  $\nu/cm^{-1}$ ) 3300 (H<sub>2</sub>O), 2954, 2887 (aliph-CH), 1626 (C=N), 1388, 1106 (NO<sub>3</sub><sup>-</sup>), 1240 (Ar–O), 1160, 1042  $\nu$ (R-O), 526 (Cu–O), 480 (Cu–N).

### 2.6. Preparation of photocatalyst

The rGO/CuMx composites were prepared using different amount of [CuL](NO<sub>3</sub>)<sub>2</sub>,H<sub>2</sub>O with rGO. In a typical synthesis of rGO/CuM30 (30% Cu macrocyclic complex on rGO), 85.7 mg of as synthesis of [CuL](NO<sub>3</sub>)<sub>2</sub>. H<sub>2</sub>O in 50 mL ethanol was added dropwise to the ultra-sonicated of 200 mg of rGO in 200 mL ethanol. The suspended mixture was stirred for 12 h and centrifuged and washed with ethanol for several times and dried at 70 °C for 12 h. For the preparation of catalysts with various amount of CuMx (x = 5, 10, 20, 25, 40 and 50) amount 10.5, 22.2, 50, 66.7, 133.3 and 200 mg of [CuL](NO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O was used with 200 mg of rGO by the same method mentioned, respectively. For the synthesis of Cu(II)/rGO, 35.6 mg of Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O was dissolved in 30 mL of ethanol and added dropwise to the ultra-sonicated of 200 mg of rGO in 200 mL ethanol. The suspended mixture was stirred for 12 h and centrifuged and washed with ethanol for several times and dried at 70 °C for 12 h. For the synthesis of Schiff base ligand/rGO, 51 mg of Schiff base ligand was dissolved in 50 mL of ethanol and added dropwise to the ultra-sonicated of 200 mg of rGO in 200 mL ethanol. The suspended mixture was stirred for 12 h and centrifuged and washed with ethanol for several times and dried at 70 °C for 12 h.

## 2.7. Photocatalytic reduction of nitroaromatic compounds

Catalytic activity tests were carried out by a LED lamp (Model No. HP-FL-25 W-F-Hope LED Opto-Electric Co., Ltd. (Shenzhen, China)). For this goal, 100 mg of rGO/CuMx was sonicated for 15 min in 10 mL of 1:1:1 mixed solvent (CH<sub>3</sub>OH/ dichloromethane/acetonitrile). Then 1 mmol of nitrobenzene and 10 mmol of N<sub>2</sub>H<sub>4</sub>H<sub>2</sub>O were added in mixture. Finally, the reactor of reaction was exposed under

visible light irradiation. Progress of the reaction was monitored by gas chromatography (GC-FID).

## 3. Results and discussion

#### 3.1. Characterization of photocatalyst

Fig. 1 shows the FT-IR spectrum of GO, rGO, CuM and rGO/CuM30. The bands at 1053, 1170, 1600, 1707, 2930, and 3400 cm<sup>-1</sup> that assigned to C-O-C, C-O, C=C, C=O, C-H, and O-H respectively for GO [27]. In the case of rGO, the broad peak of the O-H group decreased significantly. The peak at 1626 cm<sup>-1</sup> can attributed to the stretching vibration of C=N, in rGO/CuM30 and CuM30 (Fig. 1c and d) [28]. Bands around 2900, 485 and 525 cm<sup>-1</sup> are assigned to Alph-CH, Cu–O and Cu–N bands in the metal complex respectively [29].

Fig. 2 shows the survey X-ray photoelectron spectroscopy (XPS) of rGO/CuM30. Showing contributions of  $C_{1s}$ ,  $N_{1s}$ ,  $O_{1s}$ , and  $Cu_{2p}$  corresponding to the chemical composition of rGO/CuM30. The atomic percentages are 81.7, 14.49, 3.15, and 0.66 for C, O, N and Cu, respectively with a Cu/N ratio = 0.21, confirming the formation of the Cu complex. The  $C_{1s}$  peak (Fig. 2b.) deconvoluted into four peaks: 291.2, 287.9, 285.0 and 284.2 eV are dedicated to (O=C-OH), (C=O), (C-C/C-H) sp<sup>3</sup> and (C-C) sp<sup>2</sup> respectively [30]. The  $N_{1s}$  peak (Fig. 2c.) is deconvoluted into bands at 406.2 and 399.9 eV attributed to N–O and C=N-C respectively. The  $Cu_{2p}$  peak (Fig. 2d.) shows 2p3/2 and 2p1/2 peaks at 934.4 and 953.7 eV with broad satellite peaks characteristic of Cu<sup>2+</sup>.

Elemental mapping image (Fig. 3A) and EDAX spectrum (Fig. 3 B) of rGO/CuM30 provide the distribution almost uniformly of the C, O, N and Cu on the photocatalyst surface. This confirms that the Cu complexes have been well crafted onto the rGO surface.

Fig. 4 shows FESEM images of as-synthesized GO, rGO and rGO/ CuM30, showing that the surface morphology is similar to sheets with folds and wrinkles. These wrinkles can be attributed to the interaction of oxygen groups in the sheets. SEM images show of rGO structure is more compact than GO, which can be attributed to the decrease in the number of oxygen groups in rGO. The FESEM images show that Cu complex caused the surface of rGO to be compressed. This can be attributed to a good combination between the Cu Complex and rGO. The uniform distribution of Cu Complexes on reduced graphene oxide sheets indicates that the rGO/CuM30 nanocomposite has been successfully formed.

Fig. 5 (A) shows the nitrogen adsorption and desorption on the photocatalyst surface at different relative pressures. Due to the penetration of nitrogen in the capillary pores of the photocatalyst a type B (slits) hysteresis is formed. Using the BET equation the pore volume ( $Cm^3/g$ ),



Fig. 1. FT-IR spectra of (a) GO, (b) rGO, (c) rGO/CuM30 and (d) CuM.



Fig. 2. XPS analysis of rGO/CuM30: (a) survey spectrum (b) C<sub>1s</sub>, (c) N<sub>1s</sub> and (d) Cu<sub>2p</sub> of rGO/CuM30.

surface area (m<sup>2</sup>/g) and pore diameter (nm) [31] were determined (Table 1) with a surface area for rGO/CuM30 (74.9 m<sup>2</sup>/g) being higher than rGO (10.4 m<sup>2</sup>/g). The attachment of the Cu complex onto the rGO layers in terms of structural changes was studied by using Raman spectroscopy. The two main characteristic bands (D and G bands) show the sp<sup>2</sup> and sp<sup>3</sup> hybridization. Fig. 5 (B) shows the D and G bands of rGO/CuM30 and GO at 1366 and 1608 cm<sup>-1</sup>. In the presented work, the I<sub>D</sub>/I<sub>G</sub> ratio of rGO/CuM30, rGO and GO are 1.05 and 0.9 respectively. Increasing the I<sub>D</sub>/I<sub>G</sub> ratio in rGO/CuM30 indicates the removal of some disorders [32].

The optical absorption property of the photocatalyst is an important case for investigate photocatalytic activity (Fig. 6 (A)). The band gap of

rGO, CuM and rGO/CuM30 were calculated by the plot:  $\alpha h\nu = A(h\nu - Eg)^{\frac{\mu}{2}}$ . The band gap of the rGO, CuM and rGO/CuM30 obtained 2.15, 2.19 and 2.07 eV respectively. The influence of rGO, CuM and rGO/CuM30 on the recombination of electron-hole pairs were further confirmed by photoluminescence (PL), which are widely used to study the efficiency of charge transfer, migration and transfer in photocatalyst. Fig. 6 (B) shows the room-temperature photoluminescence spectra of pure CuM, rGO and rGO/CuM30 samples with an excitation wavelength of 350 nm. The spectra indicate a wide emission in the visible region (400–650 nm), which is related to photoluminescence from surface states due to the recombination electron-hole pairs. The addition of CuM on rGO leads to a significant decrease in the peak



Fig. 3. Elemental mapping image (A) and EDAX spectrum of rGO/CuM30 (B).

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Fig. 4. FE-SEM image of prepared (a) GO, (b) rGO, and (c) rGO/CuM30.

intensity. It indicates that the synergistic effect between two components can effectively decrease recombination rate of electron-hole pairs.

### 3.2. Reduction of nitrobenzene

Reduction of nitrobenzene was investigated under 25 W visible light irradiation using 100 mg of CuM, rGO, GO and the several rGO/CuMx (x = 5, 10, 20, 25, 30, 40, and 50), 1 mmole of Nitrobenzene, 5 mmole of N<sub>2</sub>H<sub>4</sub>H<sub>2</sub>O in 15 mL of the (1:1:1) mixture of acetonitrile, dichloromethane and methanol. The electrons and protons required for this reaction are supplied from the hydrazine monohydrate. The results of optimization experiments have summarized in Table 2. As considering of the Table 2, as-synthesized photocatalysts rGO/CuM5, rGO/CuM10, rGO/CuM20, rGO/CuM25, rGO/CuM30, rGO/CuM40, and rGO/CuM50 showed a photocatalytic reduction of nitrobenzene conversion about 71%, 74%, 85%, 87%, 100%, 67%, and 63% respectively in 3 h. The photocatalytic performance increased with increasing the mass percentage of the CuM from 5 to 30 (Table 2, entry 4-8) and decreased with increasing CuM content (Entry 8-11). As considering in Fig. 7, the photocatalyst rGO/CuM30 was selected as photocatalyst for reduction reaction. The catalytic activity of rGO/CuM30 was investigated under visible light conditions. Because it is believed in the dark environment the efficiency of the catalyst is significantly reduced [33].

In the following, the photocatalytic reduction reaction was generalized for other nitroaromatic compounds in the presence of 100 mg of

Table 1				
Characteristics of nitrogen adsorption	desorption	analysis of	the photocatal	vst precursor.

Precursor	Pore Volume (cm <sup>3</sup> /g)	Surface area $(m^2/g)$	Pore diameter (nm)
rGO	0.015	10.5	1.2
Cu Complex	0.008	4.55	1
rGO/ CuM30	0.281	74.95	1.2

rGO/CuM30 photocatalyst, 1 mmol nitroaromatic compounds and hydrazine monohydrate (5 mmol) as a reducing agent using 25 W- LED  $(\lambda > 400 \text{ nm})$  at 25 °C. Photoreduction results of catalyst was listed in Table 3. By focusing on the results of Table 3, it seems that the nitro compounds with NO<sub>2</sub>, F, Br, Cl and OH in ortho position need shorter times for photoreduction reaction.

As shown in Fig. 8, the catalyst was recycled for several times (five) without a significant decrease in the efficiency. For this purpose, the photocatalyst was centrifuged, washed with ethanol, dried at 70 °C and used for catalytic testing.

## 3.3. Mechanism of the reduction reaction

For verifying the reaction path, at first, light procreates e/h pairs in CuM and the excited electrons are transferred to the conduction band of reduced graphene oxide. The conjugated sp<sup>2</sup> carbons of the reduced graphene oxide supply excellent mobility of photogenerated electrons,



Fig. 5. (A) Nitrogen adsorption and desorption isotherms of reduced graphene oxide and rGO/CuM30, (B) Raman spectra of graphene oxide, and rGO/CuM30.



Fig. 6. (A) Tauc plot for the band gap energy of photocatalyst and (B) Photoluminescence spectra of CuM, rGO and rGO/CuM30 excited at 350 nm.

#### Table 2

Optimized results of nitrobenzene reduction reaction. The experiment condition: Nitrobenzene (1 mmol), N<sub>2</sub>H<sub>4</sub>H<sub>2</sub>O (5 mmol), photocatalyst (100 mg) with 25 W- LED ( $\lambda > 400$  nm) at 25 °C. 15 mL of the (1:1:1) mixture of acetonitrile, dichloromethane and methanol.

Entry	Photocatalyst	Time (h)	Conversion%
1	Cu complex	8	35
2	GO	8	17
3	rGO	8	25
4	Schiff base Ligand/rGO	8	24
5	Cu(II)/rGO	8	61
6	rGO/CuM5	3	71
7	rGO/CuM10	3	74
8	rGO/CuM20	3	85
9	rGO/CuM25	3	87
10	rGO/CuM30	3	100
11	rGO/CuM30	2	78
12	rGO/CuM40	3	67
13	rGO/CuM50	3	63
14	No catalyst	8	11
15	rGO/CuM30	3	27 <sup>a</sup>

<sup>a</sup> The reduction reaction was done in dark

which prevents the recombination of e/h pairs. So for the reduction of nitroaromatics to the corresponding amines, the photogenerated electrons are easily available. However, N<sub>2</sub>H<sub>4</sub>H<sub>2</sub>O is oxidized by the holes which generated in the valence band of rGO/CuM30. It acts as a sacrificial e and hydrogen donor for this reaction (Fig. 9-A). According to the

existed literatures, the exact mechanism of the reduction reaction is not fully known and for this reaction can be proposed two major pathways [34,35]. One of the paths is the direct path that consists of *N*-phenylhydroxylamine and nitrosobenzene intermediates, while the second path consists of a condensation of *N*-phenylhydroxylamine, and nitrosobenzene to give azobenzene, hydrazobenzene and azoxybenzene intermediates. For confirmation of the reaction mechanism, the mixture of reaction was monitored after 10 min under visibleirradiation by GC-Mass analysis. As illustrated in Fig. 9 B, there was no evidence of azoxybenzene, hydrazobenzene and azobenzene in the reaction mixture. Our progress indicates that the direct route as a reaction mechanism.

#### 4. Conclusion

In this present work, Copper macrocyclic complex  $([CuL](NO_3)_2 H_2O)$  was synthesized and grafted on rGO successfully. Results showed that the rGO was successfully decorated by Cu macrocyclic complex. Our research has shown that the rGO/CuM30 photocatalyst has a great ability to reduce nitroaromatic compounds under visible-light irradiation. The synthesized photocatalysts in this study provide a new insight into rGO-based photocatalysts to reduce environmental pollutants. The photocatalyst showed no decrease after five times of recovery and reuse. The photocatalytic reduction by using the rGO/Metal complex is a promising method for the reduction of nitroaromatic compounds.



Fig. 7. Comparison of photocatalytic performances of different rGO/CuM hybrids for the nitrobenzene reduction to aniline under vis light irradiation for 3 h.

#### Table 3

Photoreduction of various nitroaromatics using rGO/CuM30. The experiment condition: Nitroarenes (1 mmol),  $N_2H_4H_2O$  (5 mmol), photocatalyst (100 mg) with 25 W- LED ( $\lambda > 400$  nm) at 25 °C. 15 mL of the (1:1:1) mixture of acetonitrile, dichloromethane and methanol.

Reactant	Products	Time/h	Conversion (%)
		3	100
$O_2N$ $\sim$ $NO_2$		3	91
		2	98
	Br - NO <sub>2</sub>	3	86
$O_2 \overline{N}$		1.5	99
$H_2N$	_		
$O_2N$		3	97
$H_2N \longrightarrow NO_2$			
		2.5	99
$H_2N \longrightarrow NH_2$	OH	2.5	97.5
		3	96.5
Br NH <sub>2</sub>	H <sub>2</sub> N	2	98
	H <sub>2</sub> N –		
	O <sub>2</sub> N	3	96



## Credit author statement

Saeed Nasiri Ghalebin: Analysis and/or interpretation of data. Abolfazl Bezaatpour: Supervision, Investigation, Writing - Review & Editing;

Moayad Hossaini sadr:: Supervision, Investigation, Writing - Review & Editing.

Mirabdullah Seyed Sadjadi: Editing.

Mohammad Khodadadi Moghaddam: Review & Editing; Sabine Szunerits: Analysis and/or interpretation of data

## **Declaration of Competing Interest**

None.





Fig. 9. (A) and (C) Plausible mechanism for the rGO/CuM30 Photocatalyst, (B) GC-MS analysis from the reaction mixture after 10 min.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.molliq.2021.115338.

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