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# Identification of Intermediate Compound in Photodegradation of 1-Naphthol by $WO_3$-rGO Nanocomposites

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*ABSTRACT*

In this report, the degradation of 1-Naphthol was studied under xenon irradiation for 2 h using $WO_3$-rGO nanocomposite as photocatalyst. Raman spectroscopy and scanning electron microscopy demonstrated nanocomposite formation. Gas chromatography-mass spectrometry (GC-MS) technique which was utilized to analyze the degradation products, confirmed the formation of salicylic acid as an intermediate compound.

## 1. INTRODUCTION

Photocatalysis is an advanced oxidation process which has been the subject of a huge amount of studies related to air cleaning, odor control, sterilization, renewable energy, water purification, and environmental remediation [1, 2]. Interaction between semiconductor and light creates electron-hole pairs [2, 3]. Some of these carrier pairs diffuse out to the crystal surface and react with the adsorbed target materials during the reaction process [4]. Recently, graphene based nanocomposites have been the subject of many research activities due to their applications in different fields. Graphene is a two dimensional nanomaterial in which carbon atoms are arranged in a honeycomb lattice [5-7]. Various types of graphene–based nanocomposite including graphene oxide and reduced graphene oxide with different metal nanoparticles and semiconductor nanoparticles have been studied by researchers in the entire world. Tungsten trioxide ($WO_3$) is a semiconductor with a band gap of 2.8 eV [7] which has a potential to be used for different applications including sensor, coloration and photocatalysis [5, 7]. $WO_3$, individually, is not a good candidate for photocatalytic application; because the recombination time of electron-hole pairs is so short [8]. On the other hand, grapheme and reduced Graphene oxide (rGO) possesses high carrier mobility, high specific surface area and unusual band structure that make it an ideal candidate for photocatalysis [5]. Our literature survey demonstrated that there were few reports about $WO_3$ – rGO photocatalytic potentials. For examples photocatalytic dye removal has been reported by M. Zhou et al. [9] and S. Thangavel et al. [5] under UV irradiation via $WO_3$ – rGO nanocomposite. Gas sensing application of $WO_3$ nanorod – Graphene nanocomposite has been reported by X. An et al. [8]. Also photodegradation of 1-Naphthol by various oxide ceramics has been reported by Ch. Karunakaran et al. [4] under mercury lamp irradiation. Polycyclic aromatic hydrocarbons (PAHs), are among environmental pollutants. 1 – Naphthol is one of the

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PAHs compounds which is used for dye manufacturing, insecticides, etc. This hazardous compound affects the reproductive hormone levels in adult men [4] and also has carcinogenic effect on human body [10]. Our last work in this field showed that $WO_3$ is not a good candidate for photocatalysis reactions [11]. Also Farhadian et al. [12] indicated that nanocomposite fabrication of tugentan tioxide-multiwall carbone nanotube ($WO_3$-MWCNT) improved photocatalytic activity under visible light, because of reducing the recombination rate of electron-hole pairs in the semiconductor structure of nanocomposite. They also found that photodegradation of Naphthalene produced some intermediate compounds. In the current research, $WO_3$ – rGO nanocomposite was used as a photocatalyst under xenon lamp irradiation for 1-Naphthol degradation.

## 2. MATERIALS and METHOD

### 2.1. Materials

All the chemicals were purchased from Merck Company without any purification. Sodium tungstate dehydrate ($Na_2WO_4{\bullet}2H_2O$), Ethanol, Nitric acid (65%), Hydrogen peroxide (35%), Oxalic acid, Ammonia solution (37%), and 1-Naphthol were obtained from Merck (Germany). The water was employed in all the experiments is deionized.

### 2.2. Synthesis of graphene oxide

Graphene oxide was prepared by a modified Hummer's method. The full procedure has been addressed elsewhere [13].

### 2.3. Preparation of composite

In brief, 3 g of $Na_2WO_4.2H_2O$ was completely dissolved in 30 mL deionized water. Then nitric acid was added to the solution drop-wise until precipitation. The precipitate was centrifuged in room temperature with 4000 rpm for 10 minutes and washed by deionized water for several times. Then it was dissolved in 200 ml of 0.6 M oxalic acid solution completely. Certain amount of GO was then suspended in the above solution by ultrasonication in room temperature with frequency of 40 kHz for 5 minutes. Subsequently the sample was dried at 160°C for 2 h and annealed at 500 °C for 5 h in air atmosphere.

### 2.4. Photoreactor and photodegradation

Photodegradation of 1–Naphthol was carried out in a cylindrical Pyrex reactor. Top of the photoreactor was made of quartz so that the light could effectively enter the solution and excite the photocatalyst nanocomposite. Circulation of cold water was also performed to keep the temperature low during the reaction. Photoreactor design prevented evaporation of the solution. The target solution was stirred by a magnetic stirrer during photocatalysis reaction. The reactor was illuminated by a xenon lamp (570 W, Osram, Germany).

1-Naphthol solution (100 mL, 150 ppm) was prepared and used for the photodegradation study. Fifty mg of the nanocomposite was dispersed in the prepared solution and stirred in darkness for 1 h to ensure pre-adsorption of 1-Naphthol on the composite. The solution was then kept under illumination for 2 h. At the end of the photocatalytic reaction, 15 mL of solution was sampled and the catalyst powder was removed by centrifugation in room temperature with 4000 rpm for 5 minutes, and the supernatant was used for GC-MS analysis.

### 2.5. Characterization

Raman spectroscopy was performed by a Dispersive Raman Microscope (SENTERRA, 2009, Bruker). The morphology of samples was determined using Scanning Electron Microscope (SEM S360 Cambridge 1990 for GO images and SEM Philips XL30 for composites images). GC-MS analysis was performed by GC Agilent 6890N, Mass. 5973N. to investigate probable intermediates compounds.

## 3. RESULTS and DISCUSSION

### 3.1. Raman spectra analysis

Raman analysis was employed to determine the structure of $WO_3$-rGO composite. As shown in Fig. 1, the peaks located at 101 $cm^{-1}$, 130 $cm^{-1}$, 260 $cm^{-1}$, 328 $cm^{-1}$, 704 $cm^{-1}$,and 801 $cm^{-1}$ are ascribed to O –W –O stretching mode of $WO_3$. The band at 704 $cm^{-1}$, attributed to W=O bonds, was broadened and shifted to 695 $cm^{-1}$ for the $WO_3$ in the $WO_3$-rGO composite. It should be noted that C–O–W bonds could weaken the initial W=O bond as a reported by Zhu et al. [14]. After nanocomposite formation, there were local defects and disorders in the chemical adsorption of $WO_3$ and surface of the reduced graphene oxide. This chemical adsorption was related to C –O –W bond which means that $WO_3$ was grafted onto the surface of the reduced graphene layer by C –O–W bonds [15]. This structure is helpful when the light interacts with the photocatalyst and causes charge transfer. When rGO is introduced into a photocatalytic system, due to the higher conduction band level of $WO_3$ compared to Fermi level of the rGO, the photogenerated electrons are readily transferred from the semiconductor to the rGO by passing through the interface between them. On the other hand, rGO can reduce the recombination of the charge carriers. Nanocomposite formation can also cause a reduction in semiconductor bandgap.

These reasons are important for more effective photocatalytic process. More details about these reasons were reported in our previous work [11].

GO had two peaks around 1305 cm$^{-1}$ and 1595 cm$^{-1}$. The latter peak was characteristic of graphitic sheets, corresponding to a well-defined sp$^{2}$ carbon type structure, whereas the D band at around 1305 cm$^{-1}$ can be attributed to the defects in graphitic structure [14, 15]. The peaks at D band (1285 cm$^{-1}$) and G band (1570 cm$^{1}$) were also observed in the $WO_3$-rGO composite. This shift was reported as an evidence for chemical doping of carbon material by Gua et al. [15].

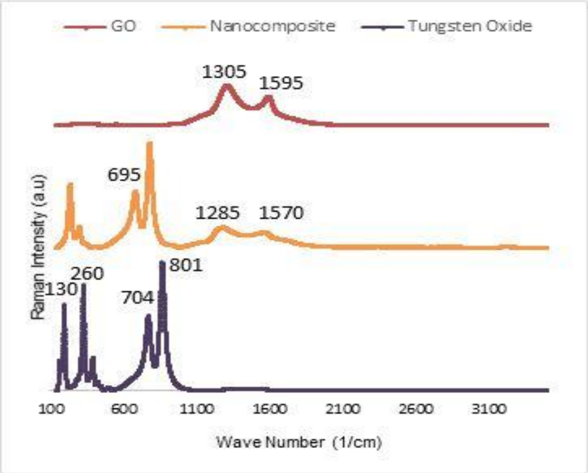


**Figure 1.** Raman spectroscopy Spectra of the synthesized $WO_3$, GO, and Composite sample (15% wt. of GO)

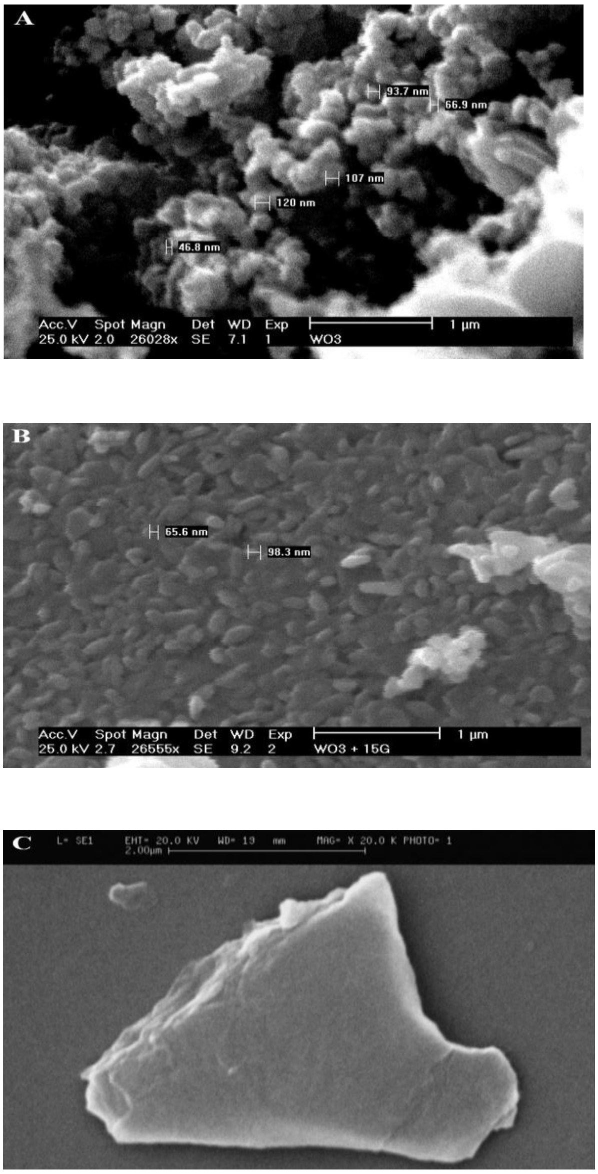
## 3.2. Morphological study

The surface morphology of the precursors and $WO_3$-rGO nanocomposite were examined by SEM technique. Fig. 2 shows the morphology of samples. During the nanocomposite synthesis process, tungsten oxide particles precipitated over the rGO sheets as shown in Fig. 2 (B).

## 3.3. GC-MS study

GC-MS of 1-Naphthol solution (150 ppm) as a blank (solution with no photocatalyst) and composite samples (containing 5%, 10%, and 15% wt. of GO) are shown in Fig. 3. Increasing GO content in the composite samples enhanced photocatalytic performance. Retention time of 1-Naphthol and salicylic acid were around 9.5 min and 8.1 min, respectively. GC-MS was utilized to determine the probable intermediate compounds. Since $WO_3$ is a weak photocatalyst under visible region, there was not any evidence of intermediate compound on GC-MS chromatograph and so, only one peak which was related to 1-Naphthol can be seen in Fig 3. (B). No significant peak was observed by increasing 5%W of GO into $WO_3$ matrix (Chromatograph (C), which means that the photocatalytic reaction was not effective. As another weak peak (retention time=8.1 min) was observed in GC-MS chromatogram D, it can be concluded that photocatalysis with nanocomposite (10 %wt. of GO) was more effective than photocatalytic reaction by $WO_3$ and nanocomposite with 5 %wt. of GO.

Photocatalysis by nanocomposite containing 15 % wt. GO was the most effective reaction in this study. There were two main peaks on chromatogram E that were related to1-Naphthol and salicylic acid. This means that there was an intermediate compound in the reaction solution caused by the photocatalysis with nanocomposite 15% wt. of GO.



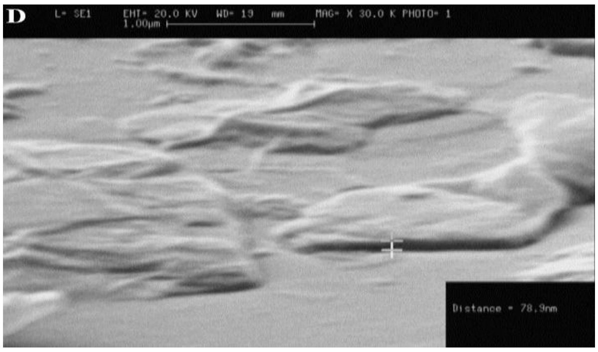


**Figure 2.** SEM images of A) synthesized $WO_3$, B) nanocomposite sample with 15% wt. of GO, C) synthesized GO, and D) cross section image of GO

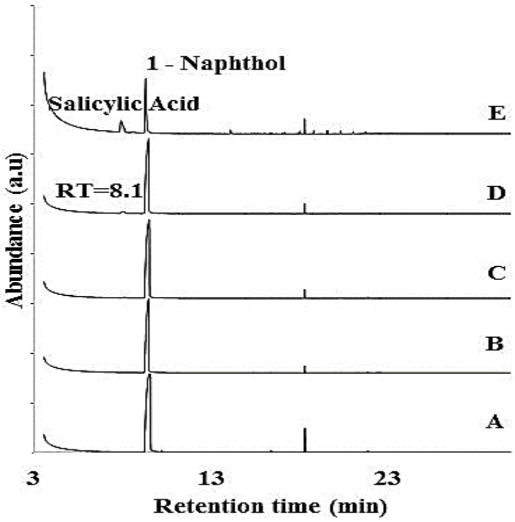


**Figure 3.** GC-MS chromatograms of A) 1-Naphthol as blank, B) 1-Naphthol after photocatalysis reaction with the synthesized photocatalysts, $WO_3$ , C) nanocomposite with 5% Wt of GO, D) nanocomposite with 10% of GO, and E) nanocomposite with 15% of GO

Analytical experiments by Karunakaran et al. [4], revealed adsorption of the 1-Naphthol on the $WO_3$. The acidic cationic sites on the surface may coordinate with the naphtholic oxygen. After light absorption by 1-Naphthol-adsorbed nanocomposite, an electron from the nonbonding orbital can be excited [4]. Migration of these carriers to the target leads to trapping of the holes by *OH* groups or by $H_2O$ to produce *OH* radicals and trapping of the electrons by the oxygen molecules to produce superoxide radical anion, and hydroperoxide radical.

In several papers *OH* radicals or hydroperoxide radicals were introduced to be responsible for photodegradation of organic compounds [4, 5, 16, 17]. These species can attack to organic molecules and finally transform the molecules to intermediate compounds. The graphene presented in nanocomposite play a beneficial role. It can delay recombination rate of electron – hole pairs and enhances photocatalytic efficiency. A perfect photocatalytic reaction can transform organic molecules to $CO_2$ and $H_2O$ [2]. The results showed that the intermediate organic species remained in the solution for several hours. Salicylic acid was identified by GC-MS library data. Other intermediates were not identified maybe due to their low concentration in the reaction mixture .

Different pathways were proposed for degradation of 1-Naphthol. Some of these pathways consist of several compounds such as 1,2 naphthalene diol, 1,2 naphthalene dione [18, 19], salicylic acid [14, 19], gentisic acid, catechol, phthalic acid, etc. [14, 20]. In this study, salicylic acid was observed as an intermediate product. More illumination may create different intermediates.

## 4. CONCLUSION

In this work, $WO_3$-rGO nanocomposite were synthesized which effectively catalyzes degradation of 1-Naphthol under visible irradiation for 2 h. Addition of GO in the composites had a great effect on the photocatalysis process. Graphene facilitated the transfer of electrons and diminished the band gap structure of the composites. So photocatalytic reaction can be effectively performed. In the presence of nanocomposite containing 15 %wt. of GO, results showed the best performance for synthesized nanocomposite and photocatalysis by $WO_3$ and nanocomposite containing 5% wt. of GO, indicated ineffective photocatalytic reaction.

## 5. ACKNOWLEDGEMENTS

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