

# Preparation, Synthesis and Characterization of WO<sub>3</sub>/AC from WO<sub>3</sub>/Polyaniline (PANi) for Photocatalytic Application under UV and Visible Irradiation

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**Abstract**—Regarding the possibility of photocatalytic improvement using a composite of tungsten trioxide (WO<sub>3</sub>), a different form of modified WO<sub>3</sub>, namely, WO<sub>3</sub>/Activated Carbon (AC), WO<sub>3</sub>/Carbon (C), and WO<sub>3</sub>/PANi were synthesized and compared. The WO<sub>3</sub>/Carbon composite was obtained by pyrolysis of WO<sub>3</sub>/PANi via *In-situ* polymerization method. The WO<sub>3</sub>/Activated Carbon (WO<sub>3</sub>/AC) obtained after treating WO<sub>3</sub>/Carbon with 1.0 M KOH solution followed by calcination at 450°C. X-ray powder diffraction (XRD), Fourier transform infrared (FTIR), and UV-Vis spectroscopy were used to characterize prepared samples. The evaluation of photocatalytic performance for the degradation of methylene blue under UV and visible light irradiation follow the trend: WO<sub>3</sub>/AC > WO<sub>3</sub>/C > WO<sub>3</sub>/PANi. The results of catalytic performance were higher under visible irradiation. Recyclability test demonstrated good performance for synthesized composite.

**Index Terms**—Photocatalyst, Activated carbon, WO<sub>3</sub>, Nanocomposite, Modification

## I. INTRODUCTION

Photocatalysis is an important solution to the problem of environmental contamination, and have recently been the center of attention. Research interest in this field involved enhancing catalytic activities. Taking into account both the advantages and disadvantages of photocatalyst, different strategies, such as surface and interface modification (including the control of morphology and particle size), composite materials, transition/noble metal doping, non-metal doping, noble metal deposition, and surface sensitization have been adopted for the purpose of modifying the catalytic activities of these materials. Considering WO<sub>3</sub> as an interesting photocatalyst and its recent modification

strategies developments [1], modification of composites has been the focus of many researchers.

Recently, activated carbon has been touted as a potential modification material for photocatalyst. This is most probably due to the fact that carbon possesses special characteristics that enhance photocatalysis performance. It is also proven that porous carbon layer can enhance the adsorption of substrate on the surface of catalyst [2]-[4].

In this study, the activated carbon was synthesized with polyaniline (PANi) as its source. WO<sub>3</sub>/PANi has been prepared via *In-situ* polymerization method, then this composite is pyrolyzed at 450°C under nitrogen gas flow for 1 hour to obtain WO<sub>3</sub>/Carbon. However, carbon without activation is not as highly porous compared to activated carbon. Hence, the WO<sub>3</sub>/Carbon composite was treated with KOH solution to produce WO<sub>3</sub>/Activated carbon. As a result of this, the composite of activated carbon over WO<sub>3</sub> photocatalyst could be developed in this work to increase the efficiency of photocatalyst. Meanwhile the catalytic performance for all different forms of modified WO<sub>3</sub>, namely, WO<sub>3</sub>/Activated Carbon (AC), WO<sub>3</sub>/Carbon (C), and WO<sub>3</sub>/PANi have been compared.

## II. MATERIALS AND METHODS

The WO<sub>3</sub> powder (purity ≥ 99.9%) was purchased from BDH Limited. Ethanol, 95% (v/v), Aniline hydrochloride, 99.995% and Ammonium peroxydisulfate, 98% was procured from Sigma Aldrich. Deionized water was used for the preparation of solutions. All the chemicals and solvents were used as is without further purifications.

### A. Preparation of WO<sub>3</sub>/PANi and WO<sub>3</sub>/Carbon

WO<sub>3</sub> powder was added to 0.2 mol/L aniline hydrochloride solution, prepared by adding 259 mg aniline hydrochloride into 5 ml distilled water while

stirring. 0.25mol.cm<sup>-3</sup> ammonium peroxydisulphate was prepared in aqueous solution by adding 571mg ammonium peroxydisulphate into 5ml distilled water. While stirring the mixture, the prepared ammonium peroxydisulphate solution was added to the aforementioned mixture under continuous stirring for 10 minutes at 60°C. The polymerization was completed in about 10 minutes. It was then left to cure at room temperature for 46 hours. The precipitate, in the form of fine powders, were obtained by centrifugation and washed several times with absolute ethanol, and distilled in order to remove any residuals, such as unreacted aniline monomer and other by-products. The product was dried in an oven for 24 hours at a temperature of 65°C to obtain WO<sub>3</sub>/PANi nanocomposite.

In order to decompose polyaniline to carbon in a WO<sub>3</sub> composite, the WO<sub>3</sub>/PANi composite is then pyrolyzed at a temperature of 450°C for 1 hour in nitrogen gas flow at a heating rate of 10°C min<sup>-1</sup> to produce WO<sub>3</sub>/carbon (WO<sub>3</sub>/C).

#### B. Chemical Activation for WO<sub>3</sub>/Carbon

Finally, the WO<sub>3</sub>/C composite obtained was treated with 1.0M KOH solution to produce porous carbon support and to activate the carbon on the WO<sub>3</sub>/Carbon composite. About 0.3g WO<sub>3</sub>/C was mixed into 2.5ml of 1.0M KOH solution. The mixture was heated at a temperature of 450°C under nitrogen gas flow for 1 hour. Then, the treated sample was washed with deionized water until it become neutral, and dried in an oven for 24 hours at a temperature of 100°C to prepare WO<sub>3</sub>/AC nanocomposite.

### III. PHYSICAL AND CHEMICAL CHARACTERIZATION

The crystallinity analyses of the samples were conducted using Bruker DB-Advance X-ray Diffractometer (XRD), Germany. The analyses utilized Cu K $\alpha$  radiation at 2 $\theta$ , ranging from 10° to 80° for a 1-gram sample. The functional groups of the samples were analyzed using Fourier Transmission Infra-Red (FTIR), while the photocatalytic performance was measured via the degradation of MB aqueous solution, and analyzed via UV-Vis spectrophotometer (Shimadzu, Model 2450).

The FTIR results (Fig. 1) for 15% WO<sub>3</sub>/PANi revealed two bands at approximately 1460 cm<sup>-1</sup> to 1480 cm<sup>-1</sup>, and 1550cm<sup>-1</sup> to 1580cm<sup>-1</sup>, which are assigned to benzenoid and quinoide rings, respectively. The band at 1290cm<sup>-1</sup> is related to the C–N stretching of a secondary aromatic amine. The band at approximately 1125cm<sup>-1</sup> originates from the plane bending vibration mode of C–H in the polymer. These bands indicated the presence of PANi in the synthesized sample. These peaks disappeared due to the decomposition of the PANi structure after the pyrolysis and chemical activation processes. The peak/shoulder appeared at approximately 800cm<sup>-1</sup>, and can be attributed to O–W–O bonding. The FTIR spectra of WO<sub>3</sub>/AC are shown Fig. 1 (a). The peak at about 3363 and 1600cm<sup>-1</sup> is indicative of the stretching vibrations of surface water molecules. Peaks at around 2900–3000cm<sup>-1</sup> were assigned to the molecular chemisorbed water and

the existence of hydroxyl groups. The peak/shoulder appeared at approximately 800cm<sup>-1</sup>, and can be attributed to O–W–O bonding [5].

The X-ray diffraction (XRD) measurements were performed on the synthesized samples, and the results are depicted in Fig. 2.

XRD patterns showed a sharp peak of bare WO<sub>3</sub> particles. It can be seen that the intensities of diffraction peaks WO<sub>3</sub> in 15% WO<sub>3</sub>/PANi are still sharp, but it decreased for 15% WO<sub>3</sub>/AC. This is due to the decomposition of Polyaniline to carbon amorphous covering the surface of WO<sub>3</sub>. It is also be seen that the amorphous structure of carbon appeared at about 2 $\theta$ =20°. The (JCPDF file no.01-072-0677) WO<sub>3</sub> particles are in the monoclinic system. Meanwhile, the estimation average of crystallite size of WO<sub>3</sub> using Sherrer's eq. and FWHM is about 31.9nm.

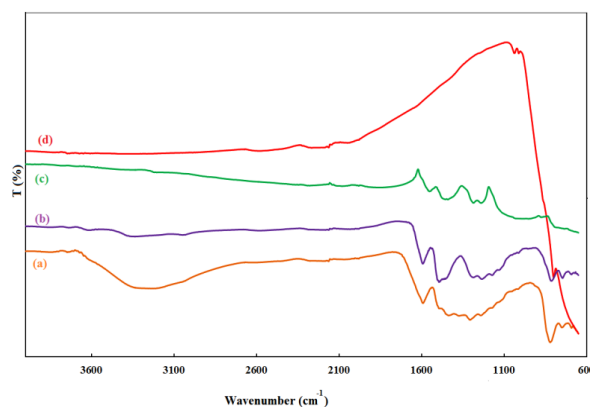


Figure 1. FTIR spectrum for (a) 15% WO<sub>3</sub>/AC, (b) 15% WO<sub>3</sub>/C, (c) 15% WO<sub>3</sub>/Pani and (d) WO<sub>3</sub> (bulk), respectively

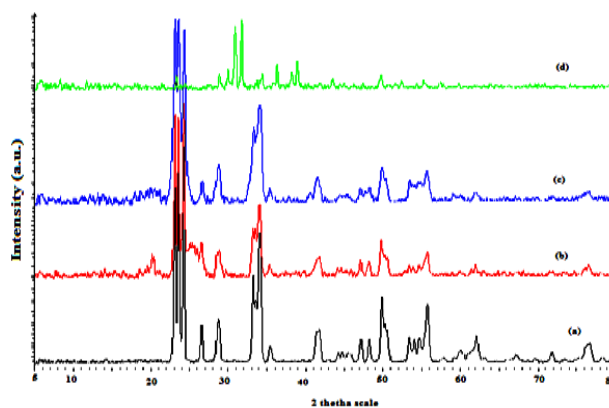


Figure 2. XRD patterns for (a) WO<sub>3</sub>-bulk, (b) 15% WO<sub>3</sub>/PANi, (c) 15% WO<sub>3</sub>/Carbon, (d) 15% WO<sub>3</sub>/AC.

### IV. PHOTOCATALYTIC ACTIVITY

The photocatalytic activity of all of the prepared catalysts was evaluated via photodegradation oxidation of Methylene Blue (MB) under UV and visible light irradiation. A 15-watt UV bench lamp was used as a light source. Prior to illumination, 20mg of catalyst was added to the MB aqueous solution (20ml, 0.05mM). The mixture solution is stirred in a dark place for 30 minutes to reach MB absorption-desorption equilibrium for the

commencement of the photocatalytic reaction. Then, the catalyst is exposed to the UV-lamp and visible light for 90 minutes irradiation. The rate of photocatalytic degradation was measured after 90 minutes.

The degradation efficiency of MB is analyzed using UV-Vis spectrophotometer. According to the Beer-Lambert Law, the concentration of MB is proportional to the absorbance of MB. Hence, the degradation of MB can be calculated using following equation:

$$R = (C_o - C_t) / C_o \times 100\% \quad (1)$$

where  $C_o$  is the initial concentration of MB solution and  $C_t$  is concentration of MB at irradiation time. The degradation of MB can also be calculated by the  $R = C/C_o$  equation.

#### A. Photocatalytic Activity of $WO_3$ -AC under UV and Visible Irradiation.

The photocatalytic activity of  $WO_3$  and its composites were evaluated after 90 minutes under both UV and visible light irradiation. The results have been depicted in Fig. 3 and Fig. 4, respectively. From the photocatalytic activity for both UV and Visible irradiation, 15%  $WO_3$ /AC had demonstrated the highest degradation of MB, which was 87.2% under UV irradiation, and 94.3% under visible irradiation. The increased activities indicate the presence of activated carbon support on  $WO_3$  composite, causing enhanced photocatalytic of  $WO_3$  composite compared to that of pure  $WO_3$  and  $WO_3$ /PANi.

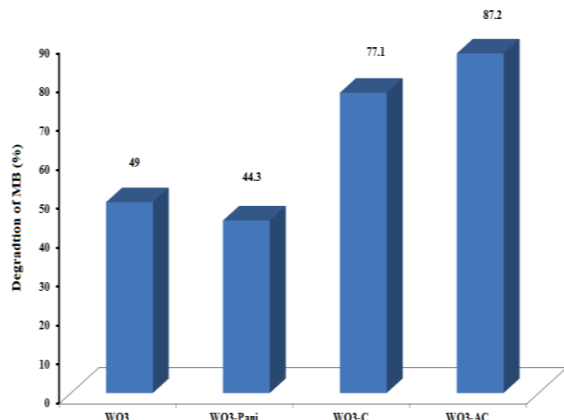


Figure 3. The degradation (%) of 0.05mM MB after 90min under UV light irradiation for  $WO_3$ ,  $WO_3$ /PANi,  $WO_3$ /C and  $WO_3$ /AC

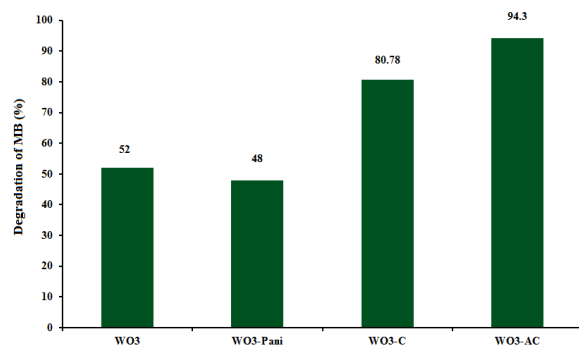


Figure 4. The degradation (%) of 0.05mM MB after 90min under Visible light irradiation for  $WO_3$ ,  $WO_3$ /PANi,  $WO_3$ /C and  $WO_3$ /AC

#### B. Recyclability of $WO_3$ /AC

Recyclability test was carried out for  $WO_3$ /AC up to five cycles. The results are depicted in Fig. 5, demonstrating excellent recyclability for the prepared composites.

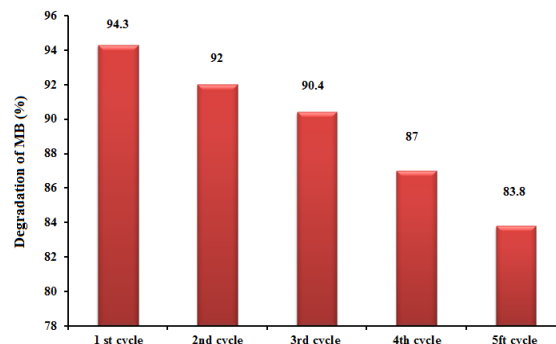


Figure 5. Recyclability of  $WO_3$ /AC was carried for 5 cycles used.

## V. CONCLUSION

Different  $WO_3$  composites have been synthesized, and their catalytic performance have been studied. It is observed that after chemical activation of  $WO_3$ /Carbon to  $WO_3$ /AC, the photocatalytic activity in MB aqueous solution was enhanced. The synthesized  $WO_3$ /AC demonstrated superior catalytic performance in both UV and Visible irradiations (87.1% and 94.3%, respectively). The recyclability test also demonstrated excellent results for the prepared composites.

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