

## Graphitic g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> Composite: Synthesis and Photocatalytic Properties

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Graphitic g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> composite was synthesized simply by decomposing melamine in the presence of WO<sub>3</sub> at 500 °C. The obtained material was characterized by XRD, SEM, IR and XPS. The results showed that the as-prepared composite exhibits orthorhombic WO<sub>3</sub> phase coated by g-C<sub>3</sub>N<sub>4</sub> and the g-C<sub>3</sub>N<sub>4</sub> decomposed completely with N-doped WO<sub>3</sub> remaining at elevated calcination temperatures. The photocatalytic activity of the composite was evaluated by the photodegradation of methylene blue under visible light. An enhancement in photocatalytic activity for the graphitic g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> composite compared to the conventional nitrogen-doped WO<sub>3</sub> was observed, which can be attributed to the presence of g-C<sub>3</sub>N<sub>4</sub> in the material.

**Key Words :** Tungsten oxide, Melamine, Photocatalysis, Degradation of methylene blue

### Introduction

Photodegradation of organic pollutants using semiconductors as heterogeneous catalysts has attracted much attention of researchers because of its efficiency and promises of economy.<sup>1,2</sup> Among the semiconductor materials, TiO<sub>2</sub> and ZnO have been widely investigated.<sup>3,4</sup> However, their technological application seems limited because they only work under ultraviolet (UV) light. As an alternative semiconductor, WO<sub>3</sub> with a band gap of *ca.* 2.7 eV can be capable of harvesting the blue part of the solar spectrum,<sup>5</sup> and is photostable in acid media, which makes it useful in photocatalysis for wastewater treatment in the presence of organic acids.<sup>6</sup> Therefore, tungsten oxide WO<sub>3</sub> is of particular interest in photocatalysts in the past decades.<sup>7</sup> However, it has some drawbacks in practical application because of its high solubility in water<sup>6</sup> and poor photodegradation of organic compounds under O<sub>2</sub> condition due to its conduction band edge with a position unfavorable for single-electron reduction of O<sub>2</sub>.<sup>8</sup> In order to overcome these limitations, a number of modifications such as size-controlling,<sup>9,10</sup> noble metal deposition<sup>11,12</sup> coupling with other semiconductors<sup>13-15</sup> have been tried. For reducing the solubility in water, some strategies have been developed to prepare tungsten oxides in composites with carbon.<sup>16</sup>

Recently, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has attracted much attention for application in photocatalytic water splitting and degradation of organic pollutants under visible light.<sup>17,18</sup> This material has some advantages such as band gap of 2.7 eV, production ability in large scale, non-toxicity. However, the pure g-C<sub>3</sub>N<sub>4</sub> exhibits high recombination rate of its photogenerated electron-hole pair.<sup>19</sup> To solve these drawbacks, several strategies have been applied to modify g-C<sub>3</sub>N<sub>4</sub> such as preparation of g-C<sub>3</sub>N<sub>4</sub> in mesostructure<sup>20</sup> and combination of g-C<sub>3</sub>N<sub>4</sub> with other materials by doping or grafting.<sup>21-37</sup> The obtained materials showed an improvement in photocatalytic performance.

More recently, g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> composites with enhanced photocatalytic activity have been reported.<sup>38-40</sup> However, in those works, the composites were prepared by mixing WO<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> in the two separate forms. In this work, g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> composite was synthesized directly in which g-C<sub>3</sub>N<sub>4</sub> formed in the presence of WO<sub>3</sub>. The presence of g-C<sub>3</sub>N<sub>4</sub> in the composite and its effect in photocatalytic activity of the material were demonstrated.

### Experimental

**Chemicals.** Tungsten trioxide (WO<sub>3</sub>), melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>) and methylene blue (C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>S) were purchased from Sigma Aldrich. All the chemicals were of reagent grade and used without further purification.

**Synthesis.** The samples were prepared by a simple method using commercial crystalline WO<sub>3</sub> powder and melamine as raw materials. First, a mixture of WO<sub>3</sub> and melamine with a weight ratio of 1:3 was well mixed and grinded with mortar. Then, the homogeneously mixed precursor was dried in an oven at 60 °C overnight. The as-prepared precursors were then transferred into alumina crucible, sealed with aluminum foil and calcined at different temperatures, 500, 600 and 700 °C, for 1 h under air atmosphere. The resulting samples were denoted as WM-500, WM-600 and W-700, corresponding to the heat-treatment temperatures, 500, 600 and 700 °C, respectively.

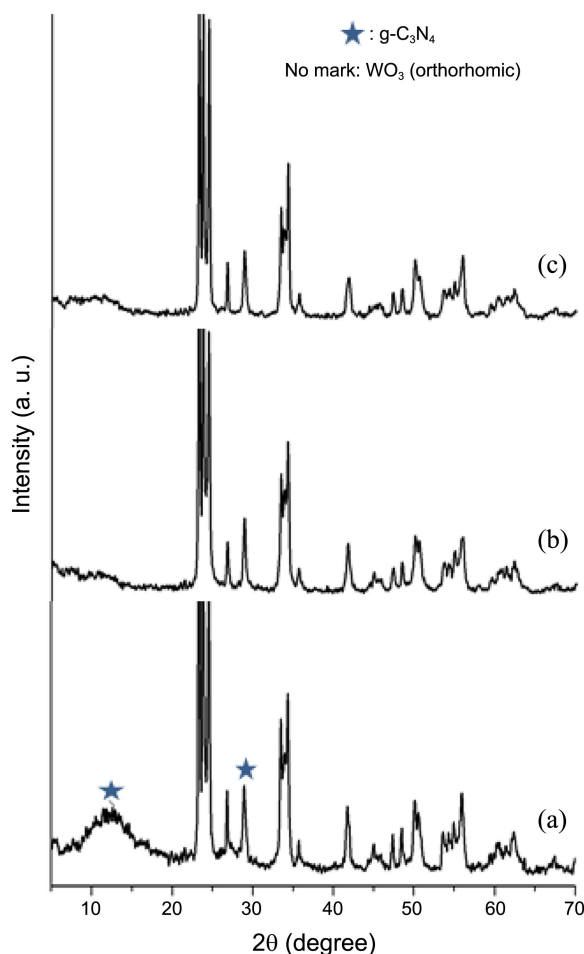
**Characterization.** Powder X-ray diffraction (PXRD) patterns were acquired using a Bruker diffractometer (D/max 2200), with Ni-filtered Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) from the powder samples, which were placed on a glass substrate. The morphology and the size of the synthesized samples were characterized by scanning electron microscopy (SEM, JEOL JSM-600F). Infrared (IR) spectra for the samples were recorded on a Thermo Nicolet spectrometer. Diffuse-reflectance UV-vis spectra were investigated on a Sinco S-4100 spectrometer. X-ray photoelectron spectroscopy

(XPS) was performed using an ESCALab spectrometer (Thermo VG, U.K.) with monochromated Al-K $\alpha$  radiation.

**Photocatalytic Activity.** In order to evaluate photocatalytic activity, methylene blue (MB),  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$  was selected as an organic pollutant. Into a 50 mg/L MB solution of 50 mL, the prepared sample of 0.05 g was dispersed under stirring and then the solution was kept in dark condition for 2 h. After then, the solution was irradiated by visible light source from a fluorescent lamp with a filter cutting UV rays. The degradation of MB was monitored by taking the suspension at the irradiation time intervals, 1 h. Each the suspension was centrifuged to separate the catalyst from the MB solution. Subsequently, the degradation rate was calculated as a function of irradiation time from absorbance change at a wavelength of 664 nm using a UV-vis spectrophotometer (Jenway 6800).

## Results and Discussion

**Characterization of Catalysts.** The X-ray diffraction patterns of the samples in Figure 1 show that as-prepared samples from thermal treatment of the mixture of  $\text{WO}_3$  and melamine at 500 °C, 600 °C and 700 °C contain mainly  $\text{WO}_3$  in orthorhombic phase. However, it is worth to note that a



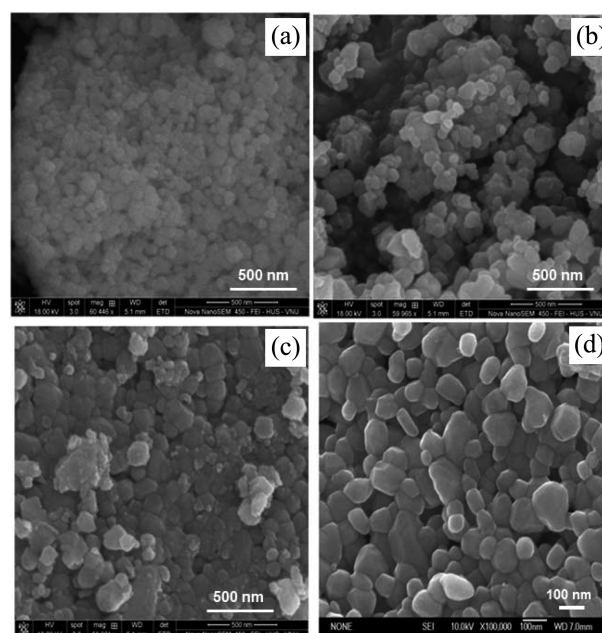
**Figure 1.** XRD patterns of WM-500 (a), WM-600 (b) and WM-700 (c).

board peak with  $2\theta$  value at about  $13^\circ$ , which can be attributed to  $g\text{-C}_3\text{N}_4$ <sup>38,39</sup> for WM-500. The formation of  $g\text{-C}_3\text{N}_4$  when heating melamine at temperature of about 500 °C was reported in several papers.<sup>39,40</sup> Meanwhile, this peak is not observable for the WM-600 and WM-700, implying that the further decomposition of  $g\text{-C}_3\text{N}_4$  with remaining  $\text{WO}_3$  phase occurs at elevated temperatures. This matches with the results in the papers.<sup>39,40</sup>

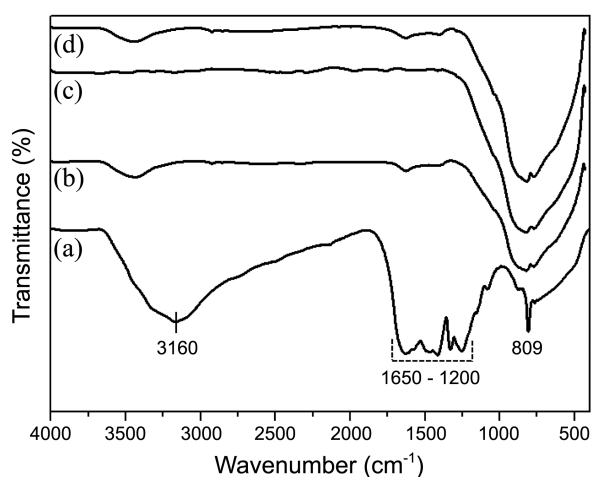
Morphology of the samples was investigated by SEM. From Figure 2(d), it can be observed that  $\text{WO}_3$  precursor exhibits the smooth particles with size of approximately 100–200 nm. The particle size nearly maintains for WM-500, WM-600 and WM-700. However, the treated samples exhibit a certain degree of particle agglomeration. This may be caused by the decomposition of melamine on surface of  $\text{WO}_3$ .

To further clarify the presence of  $g\text{-C}_3\text{N}_4$ , the materials were also characterized by IR and the results were presented in Figure 3. All materials have a board peak with strong intensity at about  $820\text{ cm}^{-1}$  which is assigned to stretching vibration of the W-O-W.<sup>38,39</sup> In addition to this peak, the spectrum for WM-500 has some additional peaks which are characteristic of  $g\text{-C}_3\text{N}_4$ . Indeed, peaks attributable to the vibration of the CN heterocycles can be clearly observed in the range of  $1200\text{--}1650\text{ cm}^{-1}$ ,<sup>38,39</sup> the characteristic breathing mode of the triazine units and the stretching vibration modes of NH were also observed at respectively around  $809\text{ cm}^{-1}$  and  $3160\text{ cm}^{-1}$ .<sup>38,39</sup> This observation supports strongly the presence of the  $g\text{-C}_3\text{N}_4$  in WM-500.

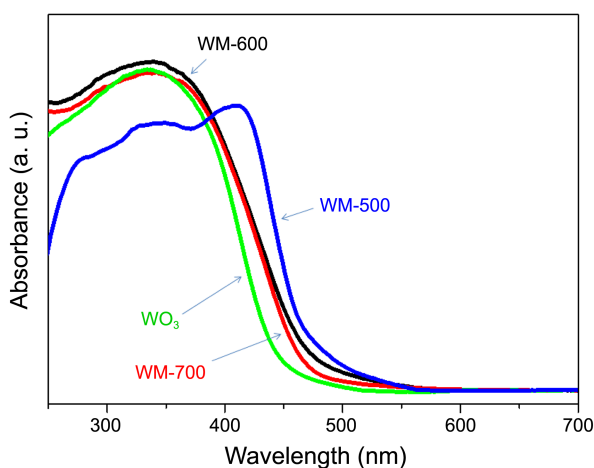
Optical absorptions of  $\text{WO}_3$ , WM-500, WM-600 and WM-700 were investigated by UV-vis diffuse reflectance spectra. Figure 4 shows that all samples exhibited absorbance in the visible light region. The absorption edges of the WM-500 and  $\text{WO}_3$  were located around 550 and 460 nm, respectively,



**Figure 2.** SEM images of WM-500 (a), WM-600 (b), WM-700 (c) and  $\text{WO}_3$  (d).



**Figure 3.** IR spectra of WM-500 (a), WM-600 (b), WM-700 (c) and WO<sub>3</sub> (d).

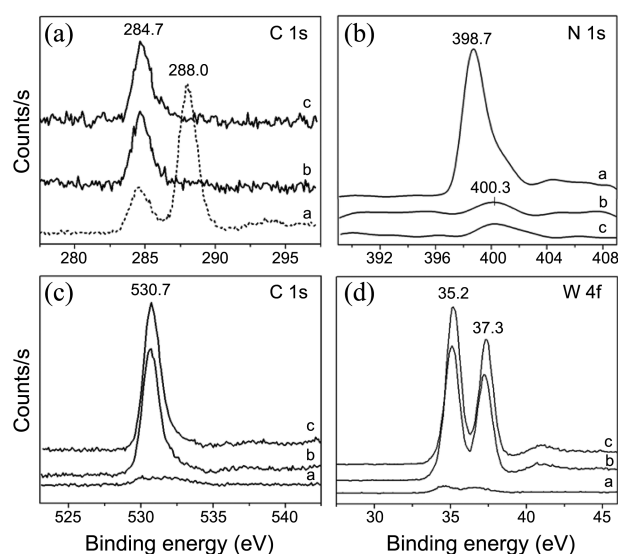


**Figure 4.** UV-vis spectra of WM-500, WM-600, WM-700 and WO<sub>3</sub>.

while the absorption edge of WM-600 and WM-700 occurred at 480 nm. This indicates a change in optical property of the materials during the thermal treatment with melamine.

The high-resolution XPS surface probe technique can further confirm the local structure of the g-C<sub>3</sub>N<sub>4</sub> in the materials (Fig. 5). Figure 5(a) shows the presence of the peak at 284.7 eV corresponding to the referenced C 1s for the three materials. Besides this peak, WM-500 exhibits the most intense peak at 288.0 eV which may be attributed to the carbon in the C-N-C configurations of g-C<sub>3</sub>N<sub>4</sub>.<sup>41,42</sup>

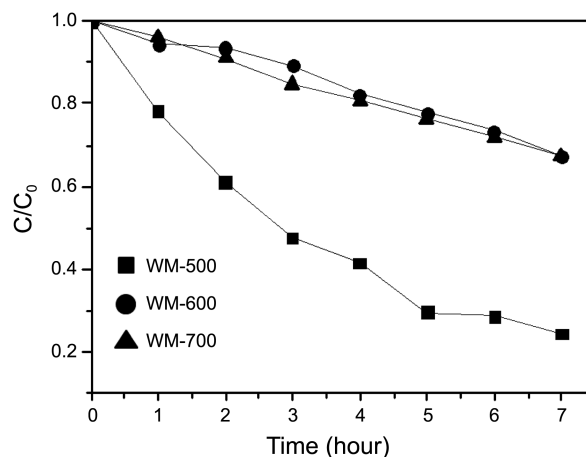
Figure 5(b) presents a difference in position and intensity of N 1s peaks for the three samples. Generally, it can be seen that content of N on surface of WM-500 is significantly higher than that of WM-600 and WM-700 samples. For WM-500, the most intense peak at 398.7 eV is assigned to sp<sup>2</sup> hybridized aromatic nitrogen atoms bonded to carbon atoms (C-N=C).<sup>43</sup> The weak peak at 400.3 eV for WM-600 and WM-700 samples may come from W-N bond in the N-doped WO<sub>3</sub>.<sup>44</sup> The XPS of the three samples in the O 1s binding energy regions were shown in Figure 5(c). A relatively low content of oxygen in WM-500 was observed.



**Figure 5.** XPS spectra of the materials: (a), (b), (c) are corresponding to WM-500, WM-600, WM-700, respectively, for all (a), (b), (c) and (d).

The intense peak at 530.7 eV for WM-600 and WM-700 samples can be attributed to O-W in WO<sub>3</sub>.<sup>44</sup> Figure 5(d) depicts W 4f XPS of the samples. The relatively low content of tungsten in WM-500 was also observed. The binding energy values of W4f7/2 and W4f5/2 in the WM-600 and WM-700 are observed at 35.2 eV and 37.3 eV, which are slightly lower than those for pure WO<sub>3</sub> (35.5 eV and 35.7 eV, respectively). Such a shift may be attributed to the presence of N-W in WM-600 and WM-700.<sup>38</sup> The obtained results show clearly that in WM-500, WO<sub>3</sub> is attached by a thin layer of g-C<sub>3</sub>N<sub>4</sub> on the surface to form g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> composite; and for the samples treated 600 °C and 700 °C, instead of disappearing g-C<sub>3</sub>N<sub>4</sub>, the presence of doping N in WO<sub>3</sub> were obtained. This may affect significantly their catalytic activity.

**Photocatalytic Test.** The photocatalytic activity of the samples was determined by the degradation of methylene



**Figure 6.** Photocatalytic activity of WM-500, WM-600, WM-700 toward the degradation of methylene blue.

blue in water under visible-light. Figure 6 shows the variation of methylene blue concentration ( $C/C_0$ ) with irradiation time on the three catalysts. It was reported that methylene blue can be easily absorbed on many materials and long time is required to reach adsorption equilibrium. Therefore, the adsorption of methylene blue on the materials by stirring in the dark for two hours was carried out. As seen in Figure 6, all materials can act as photocatalysts in the degradation of methylene blue under visible light. However, a difference in catalytic performance of the catalysts can be observed. On the WM-500 sample, the decrease in  $C/C_0$  is much faster than for the other materials. On the WM-600 and WM-700 samples, the decrease in  $C/C_0$  is slower under visible light. The good performance in photocatalytic activity for WM-500 may be due to the presence of g-C<sub>3</sub>N<sub>4</sub> in this material. Graphitic g-C<sub>3</sub>N<sub>4</sub> playing a key role in enhancement of photocatalytic activity for several composites was reported in the documents.<sup>38-40</sup> The enhanced photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> composites was discussed in several reports.<sup>38,39</sup> It can be seen in Figure 7 that the valence and conduction band potential of the pure g-C<sub>3</sub>N<sub>4</sub> are 1.57 eV and -1.13 eV, respectively.<sup>45</sup> These values for pure WO<sub>3</sub> are corresponding to 3.43 eV and 0.75 eV.<sup>37</sup> The band gaps of g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> are 2.70 eV and 2.68 eV, respectively. Therefore, the pure g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> can produce photogenerated electron-hole pairs under visible light irradiation. In g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> composite, the photogenerated electrons on the conduction band of the g-C<sub>3</sub>N<sub>4</sub> can directly inject into the conduction band of WO<sub>3</sub> and the photogenerated holes on the valence band of WO<sub>3</sub> can directly transfer to the valence band of g-C<sub>3</sub>N<sub>4</sub>. This phenomenon can lead to a significant decrease in the electron-hole recombination. As mentioned above, the pure g-C<sub>3</sub>N<sub>4</sub> exhibits high recombination rate of its photogenerated electron-hole pair.<sup>19</sup> Hence, this may contribute to the enhancement of photocatalytic reactivity.

To clarify further role of g-C<sub>3</sub>N<sub>4</sub>, we prepared WM-400 sample by heating the mixture of WO<sub>3</sub> and melamine with a weight ratio of 1:3 at 400 °C. The photocatalytic activity in degradation of methylene blue for this sample was insignificant (not shown). This may be attributed to no formation of

g-C<sub>3</sub>N<sub>4</sub> at this temperature. The preparation of g-C<sub>3</sub>N<sub>4</sub> from melamine at temperature of 500 °C or higher was reported.<sup>36,39,40</sup>

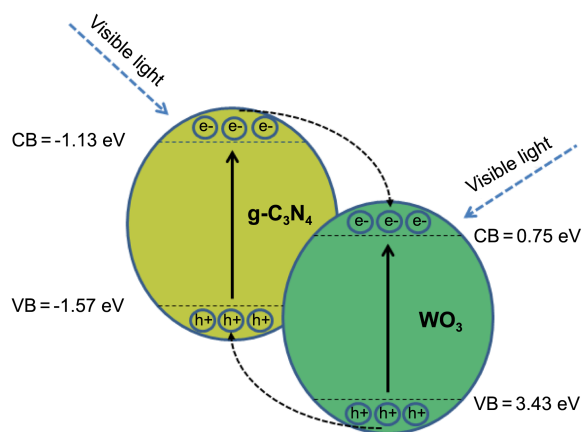
## Conclusion

A composite photocatalyst, WM-500, based on g-C<sub>3</sub>N<sub>4</sub> coated WO<sub>3</sub> was synthesized successfully by thermally decomposing melamine in the presence of WO<sub>3</sub> at 500 °C. The elevated calcination temperatures at 600 °C and 700 °C led to decomposition of the g-C<sub>3</sub>N<sub>4</sub> and formation of N-doped WO<sub>3</sub>. The composite demonstrates a high activity for degradation of methylene blue in aqueous solution under visible light irradiation. The presence of g-C<sub>3</sub>N<sub>4</sub> is believed to be beneficial for enhancement in photocatalytic activity of the g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> composite.

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**Figure 7.** Proposed mechanism for the photodegradation of methylene blue on g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> composite.

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