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# Complete oxidation of acetaldehyde over a composite photocatalyst of graphitic carbon nitride and tungsten(VI) oxide under visible-light irradiation

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## Abstract

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was prepared by heating melamine and then its specific surface area was enlarged by hydrothermal treatment in aqueous sodium hydroxide solution. The g-C<sub>3</sub>N<sub>4</sub> samples were blended with tungsten(VI) oxide (WO<sub>3</sub>) using a planetary mill in order to improve photocatalytic activity. The composite photocatalyst with optimized amounts of these contents showed higher photocatalytic activity for decomposition of acetaldehyde under visible-light irradiation than did original samples. From the results, we concluded that the composite photocatalyst utilizes both high oxidation ability of WO<sub>3</sub> and high reduction ability of g-C<sub>3</sub>N<sub>4</sub> by Z-scheme charge transfer.

Keyword: g-C<sub>3</sub>N<sub>4</sub>; WO<sub>3</sub>; photocatalysis; planetary mill; Z-scheme.

## 1. Introduction

Titanium(IV) oxide ( $\text{TiO}_2$ ) is the most widely used photocatalyst because of its excellent oxidation ability, availability and stability [1]. However, there are two major problems with a conventional  $\text{TiO}_2$  photocatalyst: it is inactive under visible-light irradiation and it has low quantum efficiency due to a high recombination rate of photogenerated electron-hole pairs. There have been numerous studies on  $\text{TiO}_2$  with impurity doping [2, 3], co-catalyst loading [4] and shape control [5, 6] for improvement of visible-light response and reaction efficiency of electrons and holes, though these methods still have limitations for improvement of solar energy conversion efficiency.

It is rather challenging to design a semiconductor photocatalyst fulfilling the multiple requirements. Actually, a single semiconductor with large visible-light absorption has difficulty in exhibiting both high reduction and oxidation abilities due to its narrow bandgap structure. Therefore, a composite photocatalyst consisting of different kinds of semiconductors has been studied in recent years. Some studies showed that an appropriate composition of two kinds of photocatalyst enhanced photocatalytic activity as a result of charge separation between two semiconductors [7-12]. This mechanism employs interparticle electron transfer to one semiconductor with a more positive conduction band (CB) potential and hole transfer to the other semiconductor with a more negative valence band (VB) potential. Thus, this kind of composite photocatalyst cannot utilize both high reduction and oxidation abilities. In contrast, another reaction mechanism for a composite photocatalyst, namely, Z-scheme reaction mechanism, has been suggested in several reports [13-17]. This mechanism enables a composite photocatalyst to utilize both reduction ability for one semiconductor with more negative CB potential and oxidation ability for another semiconductor with more positive VB potential as a result of two-step excitation. Thus, a Z-scheme composite photocatalyst is one means for utilizing both high oxidation and reduction abilities under visible-light irradiation if appropriate semiconductors are used.

In our previous study, a composite of graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ), which is an organic semiconductor with visible-light absorption, high reduction ability and high chemical stability [18], with sulfur-doped  $\text{TiO}_2$  was made [19]. In that study, the composite sample prepared by a planetary mill showed high photocatalytic activity for acetaldehyde decomposition under visible-light irradiation as a result of

Z-scheme charge transfer. Thus, the sample showed both high oxidation ability of sulfur-doped TiO<sub>2</sub> and high reduction ability of g-C<sub>3</sub>N<sub>4</sub>. However, it was concluded that photoabsorption of sulfur-doped TiO<sub>2</sub> and small specific surface area of g-C<sub>3</sub>N<sub>4</sub> are bottlenecks for further enhancement of photocatalytic activity.

Tungsten(VI) oxide (WO<sub>3</sub>) may be ideal for a combination pair with g-C<sub>3</sub>N<sub>4</sub> in the Z-scheme reaction because it is well known as an oxidation part photocatalyst for Z-scheme photocatalytic water splitting [14]. Moreover, it has larger visible-light absorption than that of sulfur-doped TiO<sub>2</sub>. WO<sub>3</sub> without a co-catalyst is thought to be inappropriate for organic decomposition due to inferior reductive potential of the CB for one-electron reduction of oxygen (O<sub>2</sub>). Therefore, a co-catalyst metal for multi-electron reduction of O<sub>2</sub> [20, 21] or a reduction part semiconductor with sufficient negative CB potential for one-electron reduction of O<sub>2</sub> in the Z-scheme reaction [15-17] is necessary for complete oxidation of organic compounds over WO<sub>3</sub>. Although there have been some reports of composite photocatalysts with g-C<sub>3</sub>N<sub>4</sub> including g-C<sub>3</sub>N<sub>4</sub>/WO<sub>3</sub> [7, 9-11, 22-24], a charge separation mechanism was employed in those photocatalysts, and explanation of the mechanism was not sufficient. Complete oxidation of organic compounds into carbon dioxide (CO<sub>2</sub>) was not discussed in photocatalytic evaluation.

In this study, a composite of g-C<sub>3</sub>N<sub>4</sub>, which was prepared by heat treatment of melamine [25], and WO<sub>3</sub> was prepared by using a planetary mill and its photocatalytic activity for acetaldehyde decomposition was discussed from the viewpoint of complete oxidation into CO<sub>2</sub>. Moreover, g-C<sub>3</sub>N<sub>4</sub> with a large specific surface area, which was obtained by hydrothermal treatment of original g-C<sub>3</sub>N<sub>4</sub> in sodium hydroxide (NaOH) solution [26], was used for the composite photocatalyst in order to improve photocatalytic activity.

## **2. Experimental**

### **2.1. Materials**

All chemicals were reagent grade and used without further purification. g-C<sub>3</sub>N<sub>4</sub> powder was synthesized by heating 30 g of melamine at 823 K at a heating rate of 9 K·min<sup>-1</sup>, followed by heating for 4 hours at that temperature. The product was collected and ground into powder. WO<sub>3</sub> powders were commercial samples (Kojundo Chemical Laboratory Co.).

### **2.2. Hydrothermal treatment of g-C<sub>3</sub>N<sub>4</sub> in NaOH solution**

The specific surface area of g-C<sub>3</sub>N<sub>4</sub> was enlarged by hydrothermal method [26]. One gram of as-prepared g-C<sub>3</sub>N<sub>4</sub> powder was added to 50 mL of 0.1 M aqueous NaOH solution. The suspension was ultrasonicated for 10 min to completely disperse the g-C<sub>3</sub>N<sub>4</sub>, and then it was heated in a Teflon-lined autoclave at 373 K for 24 hours. After the treatment, the precipitates were centrifuged and washed with deionized water several times to remove Na<sup>+</sup> ion and then dried in a vacuum drying oven at 333 K overnight. This sample is denoted as HT-g-C<sub>3</sub>N<sub>4</sub>.

### 2.3 Preparation of a composite photocatalyst by a planetary mill

The composite sample of WO<sub>3</sub> and original g-C<sub>3</sub>N<sub>4</sub> was prepared as follows. One gram of WO<sub>3</sub> and original g-C<sub>3</sub>N<sub>4</sub> powder and 20 mL of deionized water were added to a 50 mL agate bowl containing 50 g of yttrium-stabilized zirconia grinding beads (Nikkato Co., = 0.6 mm). Then the agate bowl was put on a planetary mill (Fritsch Japan Co., Planetary Micro Mill pulverisette 7) and the planetary mill was operated at 750 rpm for 10 min. After removing the beads by screening, the sample was separated by filtration, washed with deionized water several times, and dried in a vacuum drying oven at 333 K overnight. This composite sample is denoted as CNW<sub>x</sub>, where x is the weight percent of WO<sub>3</sub> included in the composite sample. The composite sample of WO<sub>3</sub> and HT-g-C<sub>3</sub>N<sub>4</sub> was prepared by the same procedure as that for CNW<sub>x</sub>. This composite sample is denoted as HTW<sub>x</sub>. As a reference, each sample, i.e., original g-C<sub>3</sub>N<sub>4</sub>, HT-g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub>, was treated by the same procedure. These composite samples are denoted as CNW<sub>0</sub>, HTW<sub>0</sub> and PM-WO<sub>3</sub>, respectively.

### 2.4. Characterization

Crystal structures of the obtained samples were characterized by an X-ray diffractometer (Rigaku, MiniFlex II) equipped with a Cu K $\alpha$  irradiation source. The morphology of prepared particles was observed by field emission scanning electron microscopy (FE-SEM; JEOL, JSM-6701FONO). Diffuse reflectance spectra (DRS) were measured using a UV-vis spectrophotometer (Shimadzu, UV-2600) equipped with an integrating sphere unit (Shimadzu, ISR-2600 Plus). Specific surface area ( $S_{\text{BET}}$ ) was determined with a surface area analyzer (Quantachrome, Nova 4200e) by the Brunauer-Emmett-Teller method. Functional group vibrations were confirmed by using a Fourier transform infrared spectrometer (FTIR; JASCO, FT / IR

4200) with a diffuse reflectance accessory (JASCO, DR-81). Fluorescence spectra were obtained using a photoluminescence spectrometer (JASCO, FP-8500).

## 2.5. Photocatalytic measurement

Before evaluation of the photocatalytic activity, each sample was irradiated with UV light using black light (UVP, XX-15BLB) in order to remove organic contaminants on the sample. The photocatalytic activity of the composite sample was evaluated by CO<sub>2</sub> liberation from photocatalytic mineralization of acetaldehyde. One hundred milligrams of powder, which has complete extinction of incident radiation, was spread on the bottom of a glass dish, and the glass dish was placed in a Tedlar bag (AS ONE Co. Ltd.). Then 125 cm<sup>3</sup> artificial air containing 1000 ppm of acetaldehyde was injected into the bag. Photoirradiation was performed at room temperature after the acetaldehyde had reached adsorption equilibrium. A light-emitting diode (LED; Epitex, L435-30M32L), which emitted light at wavelengths of ca. 435 nm, was used as a light source, and its intensity was controlled by 1.0 mW cm<sup>-2</sup>. The concentration of CO<sub>2</sub> was observed by gas chromatography (Shimadzu GC-8A, FID detector) equipped with a Porapak N packed column and a methanizer (GL Science, MT-221) as a function of irradiation time.

## 3. Results and discussion

### 3.1. Characterization of g-C<sub>3</sub>N<sub>4</sub> and HT-g-C<sub>3</sub>N<sub>4</sub>

Figure 1A shows X-ray diffraction (XRD) patterns of original g-C<sub>3</sub>N<sub>4</sub> and HT-g-C<sub>3</sub>N<sub>4</sub> samples. The original g-C<sub>3</sub>N<sub>4</sub> had two peaks at 13.1° and 27.6°, which can be indexed as (100) and (002) diffraction planes (JCPDS 87-1526). Similarly, the XRD pattern of HT-g-C<sub>3</sub>N<sub>4</sub> also had characteristic peaks at 27.6°, suggesting that HT-g-C<sub>3</sub>N<sub>4</sub> has the same crystal structure as that of original g-C<sub>3</sub>N<sub>4</sub> (Fig. 1C). The low-angle reflection peak at 13.1° becomes less pronounced due to decreased planar size of the layers during NaOH solution etching of original g-C<sub>3</sub>N<sub>4</sub> [26, 27]. Functional groups of original g-C<sub>3</sub>N<sub>4</sub> and HT-g-C<sub>3</sub>N<sub>4</sub> were confirmed by FT-IR spectroscopy. As shown in Fig. 1B, the characteristic IR spectrum of HT-g-C<sub>3</sub>N<sub>4</sub> was similar to that of original g-C<sub>3</sub>N<sub>4</sub>: a peak at about 810 cm<sup>-1</sup> originating from the heptazine ring system and peaks in the region from 900 to 1800 cm<sup>-1</sup> attributed to either trigonal C-N(-C)-C or bridging C-NH-C units

were observed in both samples. UV-vis **DRS** are shown in Fig. 1C. Compared with the spectrum of original g-C<sub>3</sub>N<sub>4</sub>, the spectrum of HT-g-C<sub>3</sub>N<sub>4</sub> was shifted to longer wavelengths. A similar blue shift of peak wavelength was observed in fluorescence emission spectra (Fig. 1D). These results are presumably due to decrease in particle size [27, 28]. Actually, the S<sub>BET</sub> of g-C<sub>3</sub>N<sub>4</sub> was enlarged from 11 m<sup>2</sup> g<sup>-1</sup> to 50 m<sup>2</sup> g<sup>-1</sup> by hydrothermal treatment. Fig. 2 shows SEM images of original g-C<sub>3</sub>N<sub>4</sub> and HT-g-C<sub>3</sub>N<sub>4</sub> samples. The original g-C<sub>3</sub>N<sub>4</sub> was plate-like particles (Fig. 2A), while HT-g-C<sub>3</sub>N<sub>4</sub> had an uneven surface (Fig. 2B). This indicates that the surface of g-C<sub>3</sub>N<sub>4</sub> particles was etched by hydrothermal treatment in NaOH solution, resulting in enlargement of S<sub>BET</sub> without any change in crystal structure. These results coincide with the results of **reported study** [26].

Photocatalytic activity of original g-C<sub>3</sub>N<sub>4</sub> and HT-g-C<sub>3</sub>N<sub>4</sub> was evaluated by CO<sub>2</sub> liberation from decomposition of acetaldehyde. Figure 3 shows the time courses of CO<sub>2</sub> liberation over original g-C<sub>3</sub>N<sub>4</sub> and HT-g-C<sub>3</sub>N<sub>4</sub>. Although HT-g-C<sub>3</sub>N<sub>4</sub> showed smaller visible-light absorption than that of original g-C<sub>3</sub>N<sub>4</sub>, it showed 3-times greater CO<sub>2</sub> liberation due to large S<sub>BET</sub>, which increase in adsorption, reduction and oxidation sites. However, CO<sub>2</sub> liberation for 48 hours was much smaller than 2000 ppm, which means complete decomposition of acetaldehyde into CO<sub>2</sub>, due its low oxidation ability [19].

### 3.2. Characterization of CNW<sub>x</sub> and HTW<sub>x</sub>

Powder XRD patterns of CNW<sub>x</sub> samples are shown in Fig. 4A. XRD patterns showed only peaks attributed to g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub>, and peaks attributed to other components were not detected. Although a peak at 27.6°, which was attributed to (002) of g-C<sub>3</sub>N<sub>4</sub>, was observed in XRD patterns of CNW<sub>x</sub> (x < 50) samples, XRD patterns of CNW<sub>x</sub> (x > 50) samples showed no appreciable peak around 27.6° due to weak diffraction intensity of g-C<sub>3</sub>N<sub>4</sub>. On the other hand, peaks attributed to WO<sub>3</sub> could be observed in all CNW<sub>x</sub> samples (x > 0), and no changes in peak pattern and width of the peak at 24.3° were observed, compared with original WO<sub>3</sub> (Fig. 4, S1). This is reasonable since PM-WO<sub>3</sub> showed the same pattern and width of peak at 24.3° as original WO<sub>3</sub>. In contrast, CNW<sub>0</sub> showed a larger peak width at 27.6° than that of original g-C<sub>3</sub>N<sub>4</sub>. This result coincides with enlargement of S<sub>BET</sub> by planetary mill treatment (Fig. 5). A similar result was obtained for HTW<sub>x</sub> samples (Fig. 4B).

Figure 6 shows SEM images of PM-WO<sub>3</sub>, CNW<sub>x</sub> and HTW<sub>x</sub>. PM-WO<sub>3</sub> showed aggregated particles with

particle size of a few hundreds of nanometers (Fig. 5), and the morphology and  $S_{\text{BET}}$  of  $\text{WO}_3$  particles were slightly changed by planetary mill treatment (Fig. 5). On the other hand, plate-like particles were pulverized into small particles by the planetary mill treatment in SEM images of CNW0 and HTW0 samples (Fig. S2). This agreed with increase in  $S_{\text{BET}}$  (Fig. 5). For CNW $_x$  ( $x > 0$ ) samples, it seemed that  $\text{WO}_3$  particles attached to the surface of g- $\text{C}_3\text{N}_4$  increased with an increase in  $\text{WO}_3$  content. When the  $\text{WO}_3$  content was above 80 wt%, the g- $\text{C}_3\text{N}_4$  particles were almost completely covered by  $\text{WO}_3$  particles. The same result was also found in HTW $_x$  ( $x > 0$ ) samples.

Figure 7 shows UV-vis **DRS** of PM- $\text{WO}_3$ , CNW $_x$  and HTW $_x$ . **DRS** of CNW0 and HTW0 were blue-shifted compared with those of original g- $\text{C}_3\text{N}_4$  and HT-g- $\text{C}_3\text{N}_4$  (Fig. S3). This blue shift is presumably due to decrease in particle size by planetary mill treatment [27, 28], as observed in  $S_{\text{BET}}$ . Photoabsorption at the wavelength of 435 nm of HTW $_x$  samples increased with increase in  $\text{WO}_3$  content, and it was smaller than CNW $_x$  (Fig. 8A). This is because PM- $\text{WO}_3$  has the largest photoabsorption at the wavelength of 435 nm, followed in order by CNW0 and HTW0. On the other hand, photoabsorption at a longer wavelength of 500 nm, which was observed in the **DRS** of  $\text{WO}_3$ , was suppressed by composition with a small amount of g- $\text{C}_3\text{N}_4$ . Figure 8B shows relative reflectance of CNW $_x$  and HTW $_x$  samples at the wavelength of 800 nm as a function of  $\text{WO}_3$  content. CNW $_x$  and HTW $_x$  samples showed no linear relationship between relative reflectance at the wavelength of 800 nm and  $\text{WO}_3$  content. Since photoabsorption at a longer wavelength of 500 nm is attributed to the  $\text{W}^{5+}$  state in  $\text{WO}_3$ , which is generated by electron accumulation in  $\text{WO}_3$  and reduction treatment of  $\text{WO}_3$  [29-31], a nonlinear relationship means that electron accumulation in  $\text{WO}_3$  was decreased by composition with g- $\text{C}_3\text{N}_4$ . A similar phenomenon was observed in the Z-scheme composite photocatalyst of  $\text{WO}_3$  and  $\text{CaFe}_2\text{O}_4$  [13].

### 3.3. Photocatalytic activity for acetaldehyde decomposition

The photocatalytic activities of the prepared samples were evaluated by  $\text{CO}_2$  liberation from photocatalytic mineralization of acetaldehyde. Figure 9A shows the time courses of  $\text{CO}_2$  liberation of the CNW $_x$  samples and PM- $\text{WO}_3$ .  $\text{WO}_3$  showed a high  $\text{CO}_2$  liberation rate at the beginning of photoirradiation, but  $\text{CO}_2$  liberation stopped with longer photoirradiation before reaching 2000 ppm, which means complete decomposition of 1000 ppm acetaldehyde.  $\text{WO}_3$  can partially decompose acetaldehyde to formaldehyde or



formic acid with CO<sub>2</sub> liberation [15], but it cannot completely decompose these molecules to CO<sub>2</sub> without efficient electron consumption [16]. In contrast, almost all of the composite samples showed no saturation tendency of CO<sub>2</sub> liberation with irradiation time and a larger amount of CO<sub>2</sub> liberation for 48 hours. This implies that electron consumption in WO<sub>3</sub> was promoted by composition with g-C<sub>3</sub>N<sub>4</sub>, as observed in WO<sub>3</sub> composed with other semiconductors or metals [15-17, 20, 21]. Actually, results from UV-vis **DRS** of CNW<sub>x</sub> and HTW<sub>x</sub> samples indicate that electron accumulation in WO<sub>3</sub> is suppressed by composition of g-C<sub>3</sub>N<sub>4</sub> (Fig. 8B). Since g-C<sub>3</sub>N<sub>4</sub> is a semiconductor with more negative CB potential than that of WO<sub>3</sub> and one-electron reduction potential of O<sub>2</sub>, a plausible mechanism is Z-scheme reaction accompanied by electron transfer from the CB of WO<sub>3</sub> to the VB of g-C<sub>3</sub>N<sub>4</sub> (Fig. 10). Thus, all WO<sub>3</sub> particles are required to be attached on all g-C<sub>3</sub>N<sub>4</sub> particles for efficient charge transfer. Otherwise, acetaldehyde on non-composite g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> remained without being decomposed completely into CO<sub>2</sub>. This is the reason why CNW<sub>x</sub> with a large amount of WO<sub>3</sub> showed a saturation tendency and CNW<sub>x</sub> with a small amount of WO<sub>3</sub> showed a low rate of CO<sub>2</sub> liberation.

Figure 9B shows the time courses of CO<sub>2</sub> liberation of the HTW<sub>x</sub> composites and PM-WO<sub>3</sub>. HTW<sub>x</sub> samples also showed similar enhancement for CO<sub>2</sub> liberation by the composition as observed in CNW<sub>x</sub> samples. However, HTW<sub>x</sub> ( $x > 0$ ) samples showed slightly larger CO<sub>2</sub> liberation than that of CNW<sub>x</sub> ( $x > 0$ ), though CO<sub>2</sub> liberation of HTW<sub>0</sub> was twice larger than that of CNW<sub>0</sub> for 48 hours. This can be explained as follows. g-C<sub>3</sub>N<sub>4</sub> in composite samples predominantly works as not an adsorption and oxidation site for organic compounds but a reduction site for O<sub>2</sub>, while adsorption, oxidation and reduction must all proceed on single g-C<sub>3</sub>N<sub>4</sub>. Therefore, enhancement of S<sub>BET</sub> of g-C<sub>3</sub>N<sub>4</sub> in a composite sample is thought to show no direct contribution to oxidation of acetaldehyde because acetaldehyde is hardly decomposed over g-C<sub>3</sub>N<sub>4</sub> in the composite photocatalyst.

Figure 9C shows CO<sub>2</sub> liberation for 48 hours of CNW<sub>x</sub> and HTW<sub>x</sub> samples as a function of WO<sub>3</sub> content. A volcano-like relationship was observed in both CNW<sub>x</sub> and HTW<sub>x</sub> samples, but HTW<sub>x</sub> samples with a larger amount of WO<sub>3</sub> showed larger CO<sub>2</sub> liberation because larger S<sub>BET</sub> of g-C<sub>3</sub>N<sub>4</sub> in HTW<sub>x</sub> samples increased contact points between g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub>. However, optimized HTW<sub>x</sub> showed slightly larger CO<sub>2</sub> liberation than that of CNW<sub>x</sub>, and the optimum ratio of WO<sub>3</sub> in HTW<sub>x</sub> samples was the same as that in CNW<sub>x</sub> samples despite larger S<sub>BET</sub>. This is due to smaller photoabsorption of HTW<sub>0</sub> than that of CNW<sub>0</sub>, as

seen in Fig. 8A.

Figure 9D shows UV-vis DRS of PM-WO<sub>3</sub>, CNW50 and HTW50 before and after photocatalytic reaction. After photocatalytic reaction, photoabsorption of PM-WO<sub>3</sub> at wavelengths from 500 nm to 800 nm showed greatly increased, which is attributed to the partial reduction of W<sup>6+</sup> to W<sup>5+</sup> by photoexcited electrons. In the case of CNW50 and HTW50, no obvious changes can be found from DRS of the composite photocatalysts before and after photocatalytic reaction. The results indicate that the self-reduction process by photogenerated electrons in WO<sub>3</sub> are prevented after composite with g-C<sub>3</sub>N<sub>4</sub> or HT-g-C<sub>3</sub>N<sub>4</sub>, because photogenerated electrons in CB of WO<sub>3</sub> should be efficiently consumed by the reaction with photogenerated holes in VB of g-C<sub>3</sub>N<sub>4</sub> or HT-g-C<sub>3</sub>N<sub>4</sub>. This means that the composite photocatalysts follow Z-scheme charge separation mechanism.

Larger CO<sub>2</sub> liberation over composite samples may be attributed to decomposition of g-C<sub>3</sub>N<sub>4</sub>. Therefore, we confirmed stability of g-C<sub>3</sub>N<sub>4</sub> in the prepared samples by a self-decomposition test. Figure S4 shows the time courses of CO<sub>2</sub> liberation over CNW50 and HTW50 in the presence and absence of acetaldehyde. Although slight CO<sub>2</sub> liberation was observed in CNW50 and HTW50 samples, it was much smaller than CO<sub>2</sub> liberation in the presence of acetaldehyde. This confirmed that enlargement of CO<sub>2</sub> was not due to decomposition of g-C<sub>3</sub>N<sub>4</sub>. In the HTW50 sample, 1600 ppm of CO<sub>2</sub> was observed after 48 hours of photoirradiation, indicating that at least 600 ppm of acetaldehyde had been completely decomposed into 1200 ppm of CO<sub>2</sub>. This “partial complete oxidation” is also collateral evidence for Z-scheme charge transfer in the composite photocatalyst because complete oxidation of acetaldehyde into CO<sub>2</sub> cannot occur over WO<sub>3</sub> without a metal co-catalyst or semiconductor for Z-scheme charge transfer.

#### 4. Conclusions

In this study, a highly active photocatalyst under visible-light irradiation for organic decomposition was synthesized by a composite of g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> using a planetary mill. UV-vis DRS and photocatalytic evaluation indicated that the composite photocatalysts show high activity as a result of Z-scheme reaction. The optimized composite samples prepared in the present study showed complete oxidation of “most of all” acetaldehyde into CO<sub>2</sub> by Z-scheme reaction, unlike previously reported composite photocatalysts [22-24]. For further enhancement of photocatalytic activity under visible-light irradiation, a composite photocatalyst

with both large visible-light absorption and a large number of contact points between g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> is needed.

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## Figure Captions

Fig. 1 (A) XRD patterns, (B) FTIR spectra, (C) UV-vis **DRS** and (D) fluorescence emission spectra under excitation at the wavelength of 365 nm of original g-C<sub>3</sub>N<sub>4</sub> and HT-g-C<sub>3</sub>N<sub>4</sub>.

Fig. 2 SEM images of (A) original g-C<sub>3</sub>N<sub>4</sub> and (B) HT-g-C<sub>3</sub>N<sub>4</sub>.

Fig. 3 Time courses of CO<sub>2</sub> liberation from acetaldehyde decomposition over original g-C<sub>3</sub>N<sub>4</sub> and HT-g-C<sub>3</sub>N<sub>4</sub>.

Fig. 4 XRD patterns of original WO<sub>3</sub>, PM-WO<sub>3</sub>, CNW<sub>x</sub> and HTW<sub>x</sub> samples.

Fig. 5 S<sub>BET</sub> of original g-C<sub>3</sub>N<sub>4</sub>, HT-g-C<sub>3</sub>N<sub>4</sub>, original WO<sub>3</sub>, PM-WO<sub>3</sub>, CNW<sub>x</sub> and HTW<sub>x</sub> samples as a function of WO<sub>3</sub> content.

Fig. 6 SEM images of original WO<sub>3</sub>, PM-WO<sub>3</sub>, CNW<sub>x</sub> and HTW<sub>x</sub> samples with 250 nm size bar.

Fig. 7 UV-vis **DRS** of (A) CNW<sub>x</sub>, (B) HTW<sub>x</sub> and PM-WO<sub>3</sub> samples.

Fig. 8 Relative reflectance of CNW<sub>x</sub> and HTW<sub>x</sub> samples at the wavelengths of (A) 435 nm and (B) 800 nm as a function of WO<sub>3</sub> content.

Fig. 9 Time courses of CO<sub>2</sub> liberation from acetaldehyde decomposition over (A) CNW<sub>x</sub> and (B) HTW<sub>x</sub> samples. (C) CO<sub>2</sub> liberation over CNW<sub>x</sub> and HTW<sub>x</sub> samples for 48 hours of photoirradiation as a function of WO<sub>3</sub> content. (D) **UV-vis DRS of PM-WO<sub>3</sub>, CNW<sub>50</sub> and HTW<sub>50</sub> before and after photocatalytic reaction.**

Fig. 10 Schematic band structure of g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub>. The literature values for the band structure of g-C<sub>3</sub>N<sub>4</sub> [32] and WO<sub>3</sub> [33] were used.

Figure

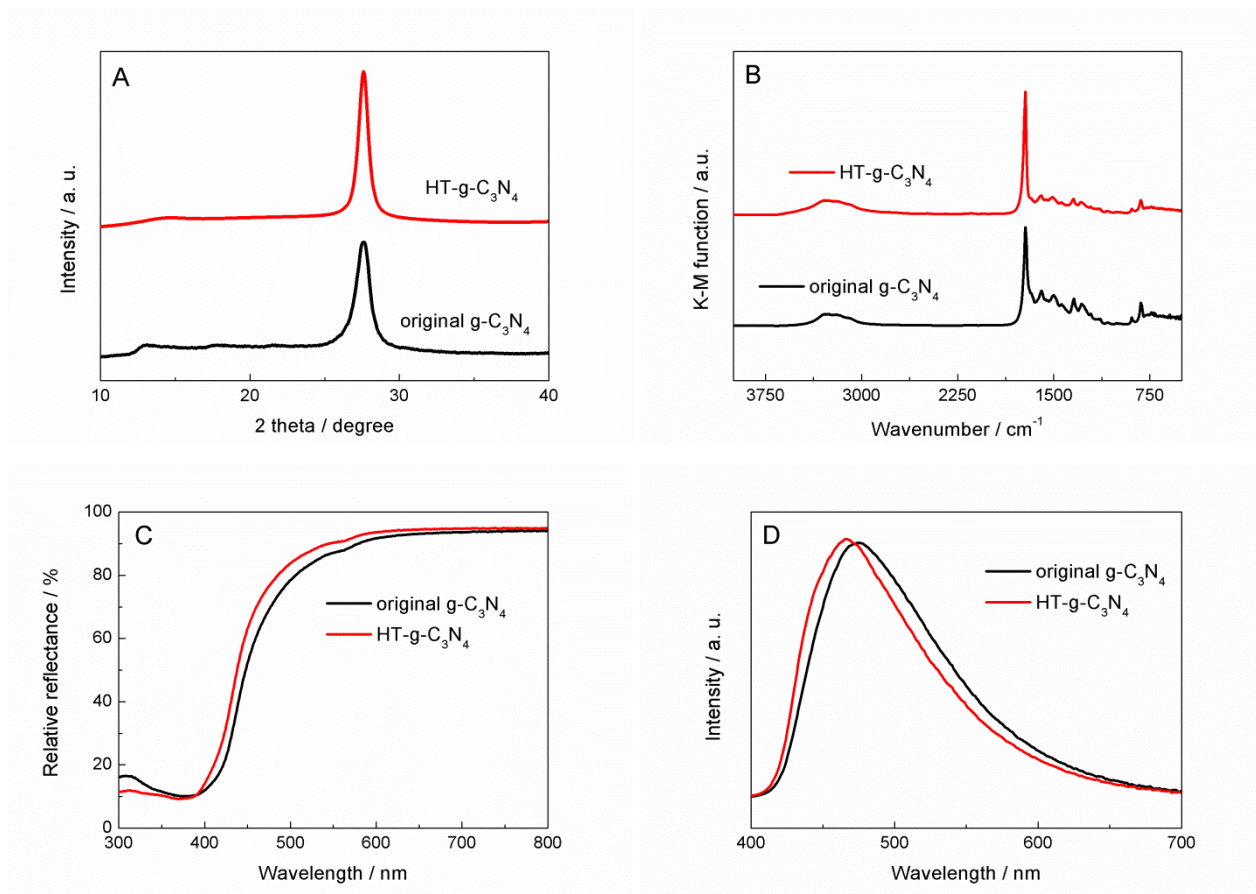


Fig. 1 (A) XRD patterns, (B) FTIR spectra, (C) UV-vis DR spectra and (D) fluorescence emission spectra under excitation at the wavelength of 365 nm of original  $g\text{-C}_3\text{N}_4$  and HT- $g\text{-C}_3\text{N}_4$ .

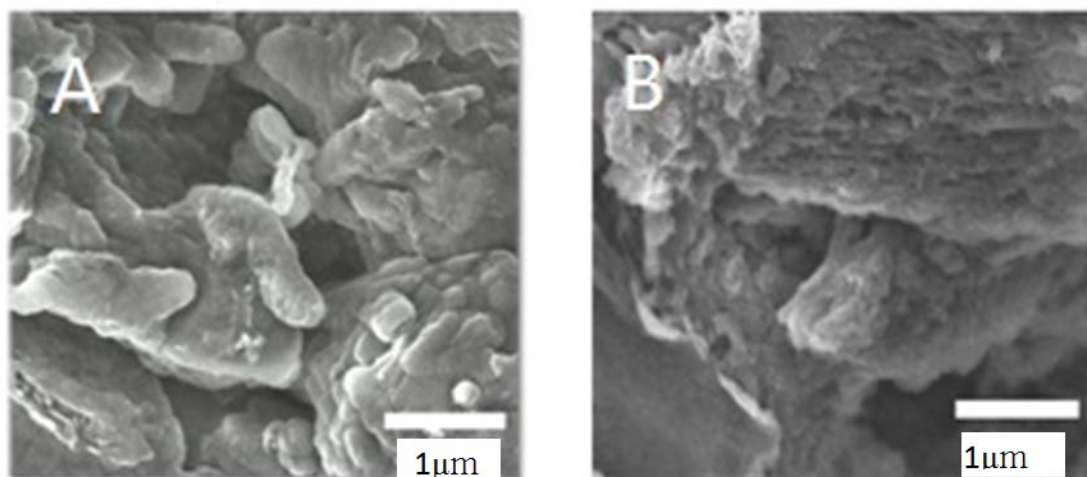


Fig. 2 SEM images of (A) original  $g\text{-C}_3\text{N}_4$  and (B) HT- $g\text{-C}_3\text{N}_4$ .



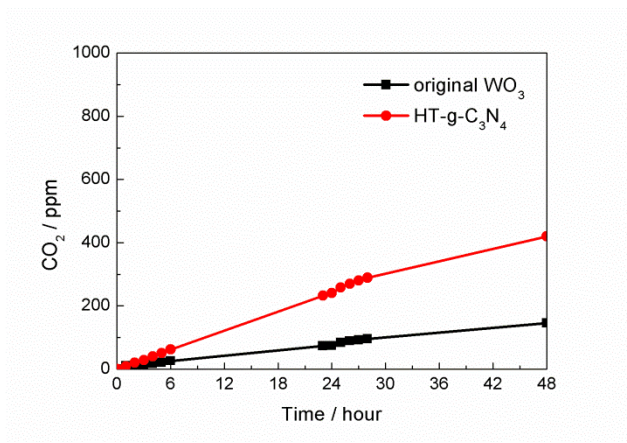


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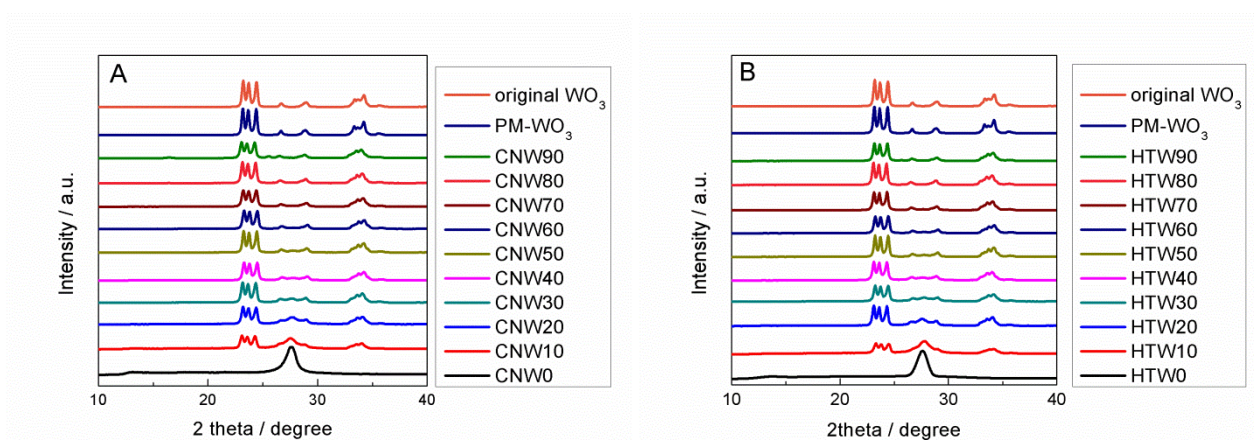


Fig. 4 XRD patterns of original WO<sub>3</sub>, PM-WO<sub>3</sub>, CNW<sub>x</sub> and HTW<sub>x</sub> samples.

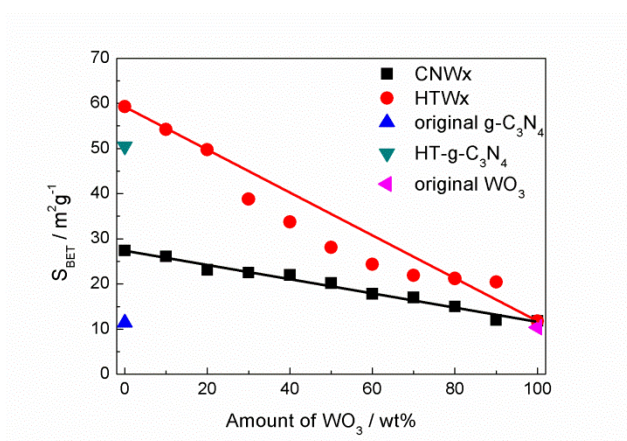


Fig. 5  $S_{\text{BET}}$  of original g-C<sub>3</sub>N<sub>4</sub>, HT-g-C<sub>3</sub>N<sub>4</sub>, original WO<sub>3</sub>, PM-WO<sub>3</sub>, CNW<sub>x</sub> and HTW<sub>x</sub> samples as a function of WO<sub>3</sub> contents.

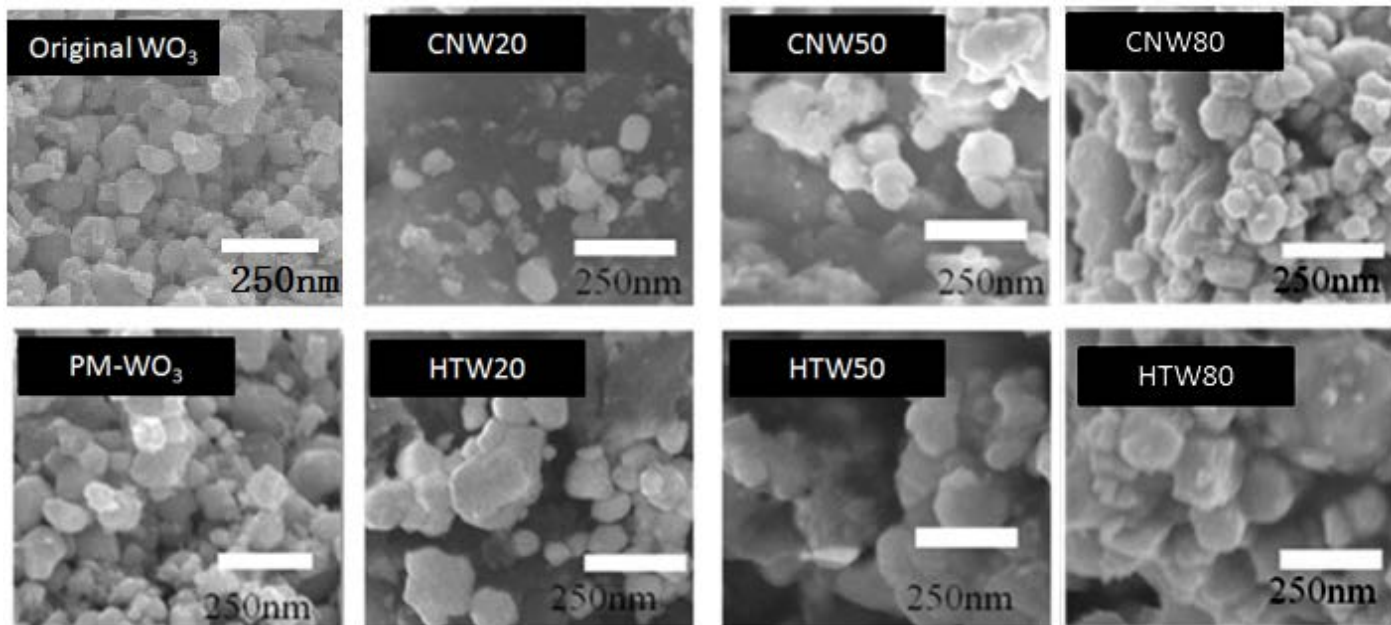


Fig. 6 SEM images of original  $\text{WO}_3$ , PM- $\text{WO}_3$ , CNW $_x$  and HTW $_x$  samples with 250 nm size bar.

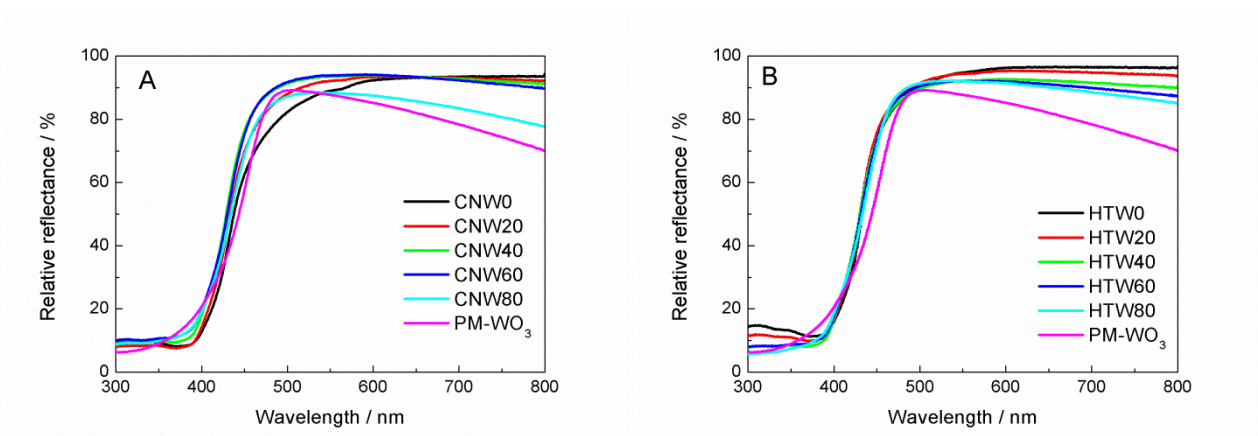


Fig. 7 UV-vis DR spectra of (A) CNW $_x$ , (B) HTW $_x$  and PM- $\text{WO}_3$  samples.

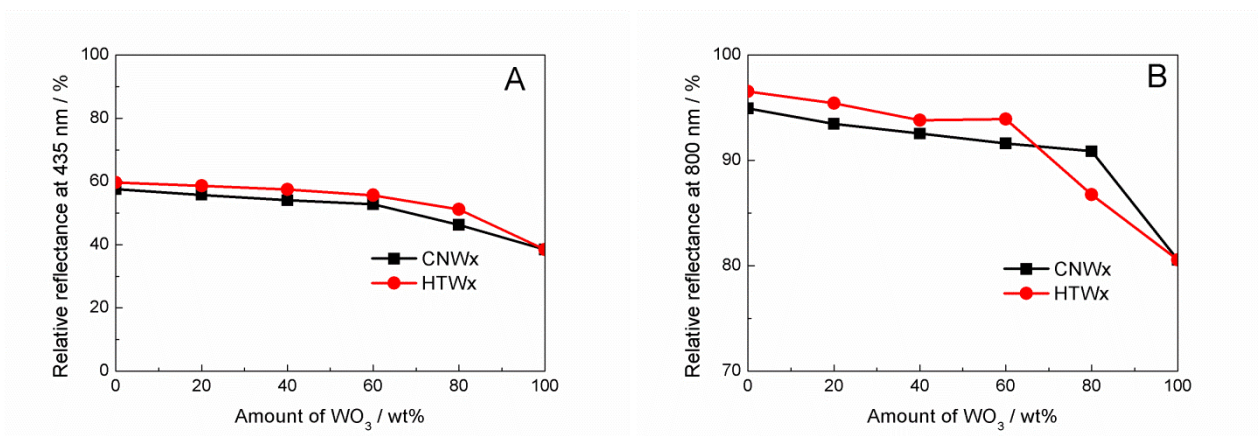


Fig. 8 Relative reflectance of CNW $_x$  and HTW $_x$  samples at the wavelength of (A) 435 nm and (B) 800nm as a function of  $\text{WO}_3$  contents.

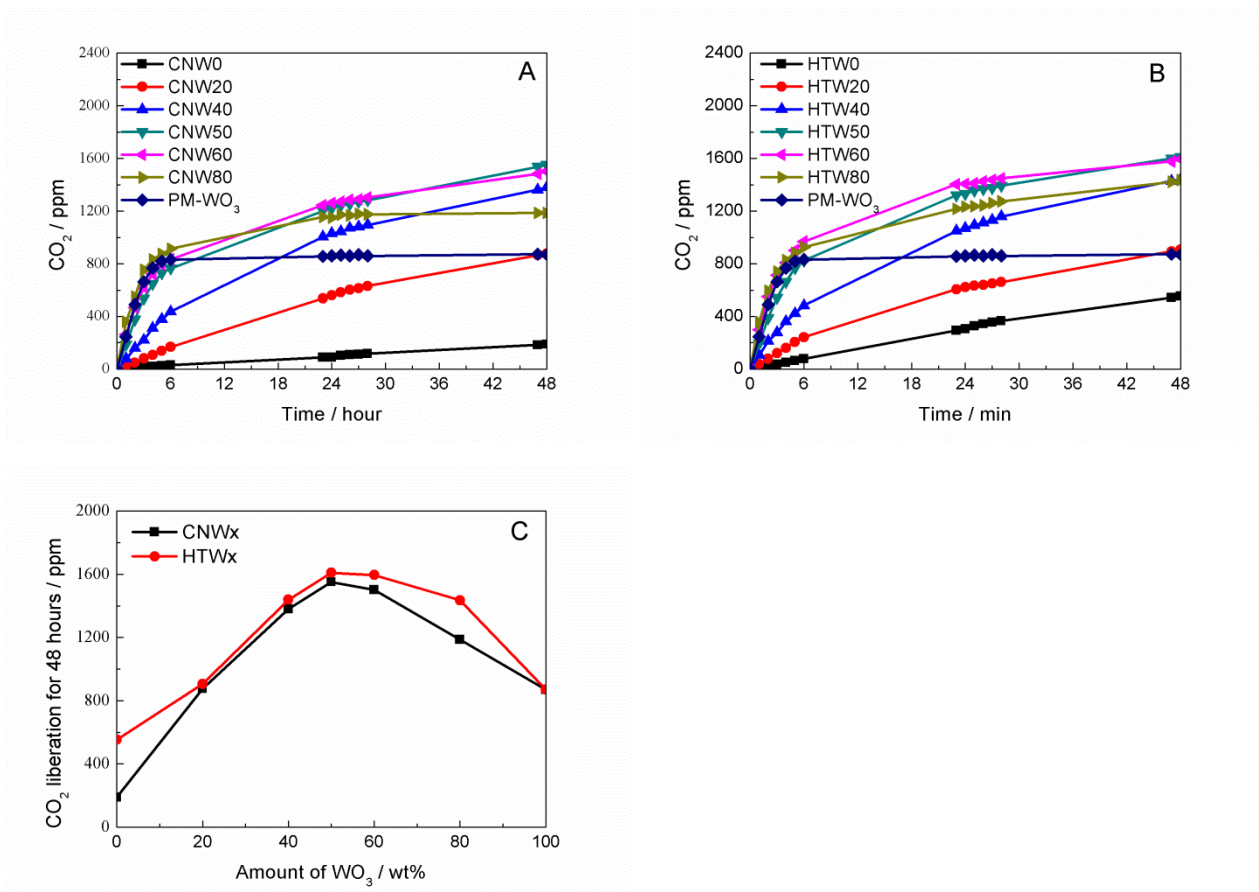


Fig. 9 Time courses of CO<sub>2</sub> liberation from acetaldehyde decomposition over (A) CNW<sub>x</sub> and (B) HTW<sub>x</sub> samples. (C) CO<sub>2</sub> liberation over CNW<sub>x</sub> and HTW<sub>x</sub> samples for 48 hours of photoirradiation as a function of WO<sub>3</sub> contents.

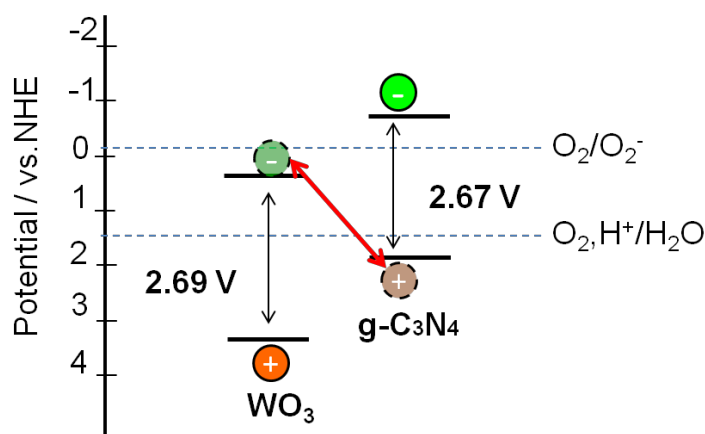


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