



## ENHANCED ACTIVITY OF $C_3N_4$ WITH ADDITION OF ZnO FOR PHOTOCATALYTIC REMOVAL OF PHENOL UNDER VISIBLE LIGHT

(Peningkatan Aktiviti  $C_3N_4$  dengan Penambahan ZnO untuk Fotomangkin Penyingkiran Phenol di bawah Sinaran Tampak)

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### Abstract

Phenol is a stable and hazardous compound that is commonly found as an industrial effluent. Phenol can be treated by photocatalysis using zinc oxide (ZnO) as a photocatalyst. Unfortunately, the use of ZnO in photocatalysis is limited due to the poor response to the visible light. On the other hand, carbon nitride ( $C_3N_4$ ) is able to absorb visible light. In the present study, a series of ZnO- $C_3N_4$  was prepared by impregnation method. The effect of zinc to carbon mol ratio (Zn/C) on the properties and photocatalytic activity was examined. X-ray Diffraction (XRD) patterns of the samples revealed that as the Zn mol ratio increased, the intensity of diffraction peaks for ZnO also increased but the intensity for  $C_3N_4$  decreased. All prepared composite materials have an extended absorption band in the visible light region due to the presence of  $C_3N_4$ , as supported by DR UV-Vis spectra. The prepared ZnO- $C_3N_4$  composites were further investigated in the photocatalytic removal of phenol under visible light for 5 hours. All ZnO- $C_3N_4$  samples showed higher activity than the bare ZnO with Zn/C mol ratio of 1% showed the highest photocatalytic activity for removal of phenol among all the samples. The high activity observed on the ZnO- $C_3N_4$  would be due to role of ZnO to suppress electron-hole recombination and  $C_3N_4$  to extend the absorption of ZnO in the visible light region.

**Keywords:** zinc oxide, carbon nitride, ZnO- $C_3N_4$  composites, impregnation method, phenol

### Abstrak

Fenol adalah sebatian stabil dan berbahaya yang sering dijumpai sebagai efluen industri. Fenol boleh dirawat dengan cara fotopemangkinan menggunakan zink oksida (ZnO) sebagai fotomangkin. Malangnya, penggunaan ZnO di dalam fotopemangkinan adalah terhad disebabkan sedikit respons terhadap sinaran tampak. Sebaliknya, karbon nitrida ( $C_3N_4$ ) mampu menyerap sinaran tampak. Dalam kajian ini, siri ZnO- $C_3N_4$  telah disediakan melalui kaedah pengisitepuan. Kesan nisbah mol zink kepada karbon (Zn/C) kepada ciri dan aktiviti fotomangkin telah diperiksa. Corak pembelauan sinar-x (XRD) daripada sampel – sampel membuktikan bahawa kesan nisbah mol Zn meningkat, keamatan puncak pembelauan untuk ZnO semakin naik tetapi keamatan untuk  $C_3N_4$  semakin kurang. Semua bahan komposit yang disediakan mampu memperluaskan jalur penyerapan di dalam kawasan sinaran tampak disebabkan kehadiran  $C_3N_4$  dan disokong oleh spectrum DR UV-Vis. Komposit ZnO- $C_3N_4$  yang disediakan selanjutnya dikaji di dalam fotomangkin penyingkiran fenol di bawah sinaran tampak selama 5 jam. Kesemua sampel ZnO- $C_3N_4$  mempunyai aktiviti yang tinggi berbanding dengan ZnO dengan 1% nisbah mol Zn/C menunjukkan aktiviti fotomangkin tertinggi dalam penyingkiran fenol. Aktiviti tinggi yang dilihat terhadap ZnO- $C_3N_4$  berkemungkinan disebabkan peranan ZnO untuk membantutkan penggabungan semula lubang elektron dan  $C_3N_4$  untuk memperluaskan penyerapan ZnO di dalam kawasan sinaran tampak.

**Kata kunci:** zink oksida, karbon nitrida, komposit ZnO- $C_3N_4$ , kaedah pengisitepuan, fenol

### Introduction

Zinc oxide (ZnO) is one of the crucial multifunctional oxide materials for various applications, such as in sensors, solar cells and photocatalysis [1 – 9]. The ZnO has been investigated due to its unique property of wide band gap (3.37 eV), excitation binding energy (60 meV) at room temperature and good activity for photocatalytic decomposition reactions. Unfortunately, since ZnO has wide band gap and absorption only in the UV region [10], it requires large amount of energy in order to be active as a photocatalyst.

There are various ways to extend the absorption of ZnO to the visible light, such as by incorporating the ZnO with transition metal doping [11 –13], dye sensitizer [14 –15], and CdS [16]. Another feasible modifier is metal free graphitic carbon nitride ( $C_3N_4$ ). The  $C_3N_4$  has relatively lower band gap energy (2.70 eV) compared to the ZnO (3.37 eV), thus it is also able to absorb visible light region. Furthermore, the  $C_3N_4$  has a strong covalent bond between carbon and nitrogen in the structure that makes it exhibit high stability under visible light irradiation, which can prevent photocorrosion effect that lead to the decreasing of activity. Due to these unique features,  $C_3N_4$  is used as a visible light driven photocatalyst and it can be combined with other photocatalysts for better photocatalytic activity in the complete spectral region [17]. However, only few reports emphasizing on the incorporation of ZnO with the  $C_3N_4$ . It was reported that the modification of ZnO with  $C_3N_4$  gave a promising result in the photocatalytic removal of methylene blue under visible light irradiation [18].

In this study, phenol was used as the model for organic pollutant. Phenol is considered as a toxic compound released from the industrial as an effluent. Moreover, phenol is very stable and it will remain in the waste water for a long term [19, 20]. Photocatalytic process is one of the available methods that offer both sustainable energy source and environmental friendly process. Since photocatalytic process involves minimum requirement of energy for decomposition of organic pollutant, it is believed that photocatalytic reaction is a green method for phenol decomposition. Moreover, it provides the possibility to utilize the solar light. Therefore, in this study, photocatalytic removal of phenol was investigated by applying visible light over the ZnO- $C_3N_4$  photocatalysts.

### Materials and Methods

#### Preparation of carbon nitride ( $C_3N_4$ )

Urea ( $CO(NH_2)_2$ , Merck, 99.5%) was used as a source of carbon and nitrogen for preparation of the  $C_3N_4$ . The urea (300 g) was calcined under air atmosphere at a rate of  $2.2\text{ }^{\circ}\text{C min}^{-1}$  for 4 h in order to reach a temperature of  $550\text{ }^{\circ}\text{C}$  and tempered for 4 h at this temperature. The resulting yellow solid was ground before using it as the photocatalyst.

#### Preparation of ZnO

Zinc acetate dihydrate ( $Zn(CH_3COO)_2 \cdot 2H_2O$ , 99.5%) was used as the precursor to synthesize the ZnO. The  $Zn(CH_3COO)_2 \cdot 2H_2O$  (15 g) was calcined at a rate of  $2.2\text{ }^{\circ}\text{C/min}$  and tempered for another 4 h. The resulted solid was white in colour and was ground before it was used.

#### Preparation of ZnO- $C_3N_4$

Various ZnO- $C_3N_4$  samples were prepared by impregnation method with ZnO to  $C_3N_4$  ratios were 1, 5, 10, 20, and 50 mol percentage (mol%). The samples were labelled as ZnO- $C_3N_4$  (x) with x shows the ratio of zinc present in the sample. For a typical synthesis of ZnO- $C_3N_4$  (1),  $Zn(CH_3COO)_2 \cdot 2H_2O$  (0.0716 g) was dissolved in methanol (20 mL). The  $C_3N_4$  (1 g) was then added slowly into the solution, stirred and dried at  $80\text{ }^{\circ}\text{C}$  on a hot plate until drying. The powder was then calcined at  $550\text{ }^{\circ}\text{C}$  for 4 h and tempered for 4 h, consecutively.

### Characterizations

X-ray Diffraction (XRD, Bruker AXS Diffrac plus release 2000) was used to identify the structure of the prepared photocatalysts. The X-ray diffractogram of the catalyst was analyzed at  $2\theta$  range of  $5\text{--}75^{\circ}$  with scan rate of  $0.05^{\circ}\text{ s}^{-1}$ . Diffuse reflectance Ultraviolet-Visible (DR UV-Vis, Shimadzu UV-2600) spectroscopy was used for measurement of absorption spectra of the prepared photocatalysts. Barium sulphate ( $BaSO_4$ ) was used as the background reference with the scan range of 200-800 nm. Nicolet iS50 Thermo Scientific Fourier Transform Infrared Spectroscopy (FTIR) was used to detect the presence of functional groups in the composites. The measured wavenumber was in the range of  $4000\text{--}400\text{ cm}^{-1}$  with the scan number of 32. Fluorescence spectroscopy (JASCO

Spectrofluorometer FP-8500) was used to obtain emission spectra of samples. The monitored wavelength was in the range of 200-600 nm. Potentiostat/Galvanostat/ZRA (Gamry Instruments Interface 100) was used for the photoelectrochemical studies. Typically, 0.01 g of  $C_3N_4$ , ZnO or ZnO- $C_3N_4$  composite was added to the solution containing of water (10 mL) and nafion (10  $\mu$ L). Then, the solution was sonicated for 10 min. Afterward, the prepared sample (20  $\mu$ L) was deposited onto the screen printed electrode (SPE) and then dried using a dryer for 10 min.  $Na_2SO_4$  (0.01 M) and  $K_3[Fe(CN)_6]$  (2.5 mM) aqueous solution was employed as an electrolyte. Before measurement, the prepared SPE was immersed in the electrolyte solution (6 mL) and the electrochemical impedance studies were conducted.

### Photocatalytic activity test

The photocatalytic removal of phenol was conducted at room temperature. The photocatalyst (0.05 g) was dispersed in 100 mL of jacketed-beaker containing of phenol (50 ppm, 50 mL). Then, the beaker was placed on a stirring plate with cooling water system in a closed box for 30 minutes to let the adsorption reach the equilibrium. The reaction was carried out for 5 hours under visible light irradiation (150 W,  $\lambda > 400$  nm, intensity of 100,000 lux). After reaction, the solution was taken and separated from the photocatalyst. The remaining phenol was measured by Gas Chromatography equipped with Flame Ionization Detector (GC-FID, Agilent 7820A).

## Results and Discussion

### Properties of $C_3N_4$ , ZnO and ZnO- $C_3N_4$

In order to reveal the structure of the prepared samples, the diffraction patterns of the samples were recorded. As can be seen from Figure 1(a), the prepared  $C_3N_4$  showed one intense peak at  $2\theta$  of  $27.65^\circ$ , which can be assigned as interlayer distances ( $d$ ) of 0.32 nm, corresponding to the graphite-like  $C_3N_4$  layer. An additional broad diffraction peak at  $2\theta$  of  $12.95^\circ$  with a  $d$  value of 0.683 nm showed a hole-to-hole distance of nitride pores, reflecting the geometric effect in pore walls of the prepared  $C_3N_4$  sample [21]. The  $d$  values were obtained from the Bragg's law as shown in Equation 1.

$$n\lambda = 2d \sin \theta \quad (1)$$

where  $n$  is a positive integer,  $\lambda$  is the wavelength of the incident wave,  $d$  is the interplanar distance, and  $\theta$  is the scattering angle. The presence of these diffraction peaks suggested that the  $C_3N_4$  was prepared successfully. As can be observed from Figure 1(g), the diffraction peaks of the prepared ZnO can be indexed as a wurtzite structure, according to JCPDS file (JCPDS 89-1397).

For the ZnO- $C_3N_4$  composite samples, there were different trends of the diffraction peaks. For samples with low amount of ZnO (1 – 10 mol %), the samples showed the similar pattern as  $C_3N_4$  with dominant peak at  $2\theta$  of  $27.75^\circ$ , suggesting the presence of  $C_3N_4$  in these samples (Figure 1(b)-(c)). On the other hand, the samples with high amount of ZnO (20-50 mol %) showed similar diffraction patterns to the ZnO sample. This was reasonable as the amount of ZnO was larger than the  $C_3N_4$ . With the increase of the ZnO, the peak intensity of the  $C_3N_4$  decreased. The XRD patterns clearly showed that the  $C_3N_4$  and ZnO can be detected on the ZnO- $C_3N_4$  composite samples, depending on the amount of  $C_3N_4$  and ZnO.

Figure 2 shows DR UV-Vis spectra for the ZnO and ZnO- $C_3N_4$  samples. For the  $C_3N_4$  sample, it showed three strong absorption peaks at 277, 330 and 370 nm, corresponding to the N=C groups of aromatic 1,3,5-triazine, uncondensed C=O group and the terminal N-C group of  $C_3N_4$ , respectively (Fig. 2(a)). It was obvious that the  $C_3N_4$  sample absorbed visible light up to ca. 450 nm. On the other hand, ZnO sample showed one absorption band centered at 320 nm due to the electron charge transfer in the Zn-O linkage, as shown in Fig. 2(g). For the ZnO- $C_3N_4$  samples, all samples showed the absorption peaks of both  $C_3N_4$  and ZnO (Fig. 2(b)-(f)). As the mol ratio of Zn/C decreased, the absorption edge of the samples showed blue-shifting from ca. 450 to ca. 380 nm. This was reasonable since when the amount of ZnO increased, the samples would behave like the ZnO, thus giving absorption spectra that were similar to that of the ZnO. From the DR UV-Vis measurements, it can be concluded that ZnO- $C_3N_4$  samples were successfully synthesized.

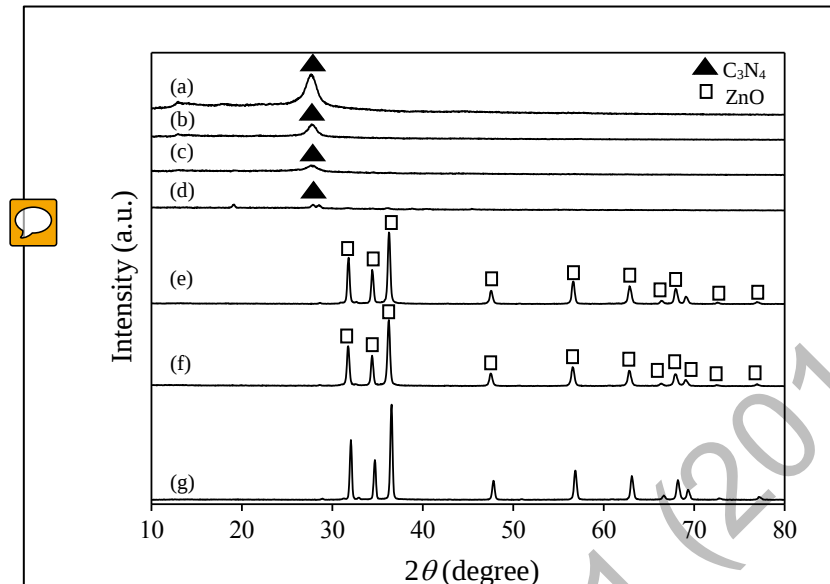


Figure 1. XRD patterns of (a)  $C_3N_4$ , (b)  $ZnO-C_3N_4$  (1), (c)  $ZnO-C_3N_4$  (5), (d)  $ZnO-C_3N_4$  (10), (e)  $ZnO-C_3N_4$  (20), (f)  $ZnO-C_3N_4$  (50), and (g)  $ZnO$ .

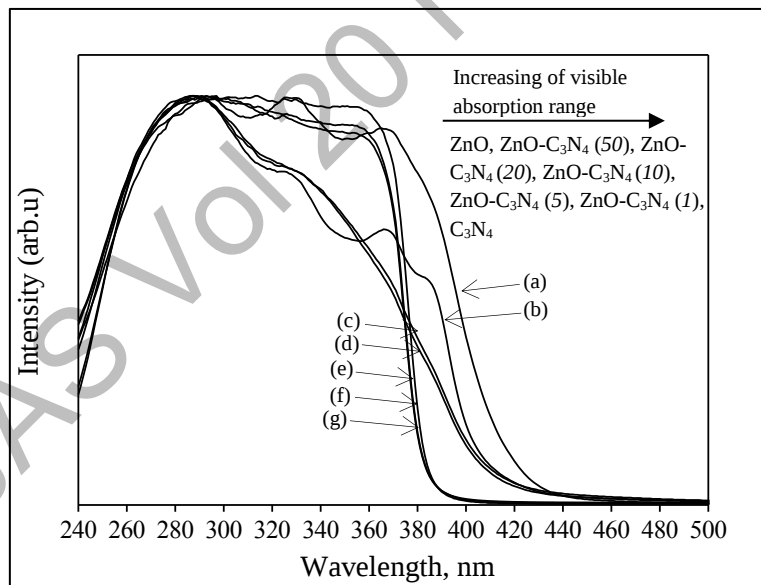


Figure 2. DR-UV Vis spectra of (a)  $C_3N_4$ , (b)  $ZnO-C_3N_4$  (1), (c)  $ZnO-C_3N_4$  (5), (d)  $ZnO-C_3N_4$  (10), (e)  $ZnO-C_3N_4$  (20), (f)  $ZnO-C_3N_4$  (50), and (g)  $ZnO$ .

Figure 3 shows the FTIR spectra of  $C_3N_4$ ,  $ZnO$ , and  $ZnO-C_3N_4$  samples. As shown in Figure 3(a), the  $C_3N_4$  showed several peaks due to the vibrations of some bondings occurred between carbon and nitrogen. The absorption peak at  $810\text{ cm}^{-1}$  corresponded to the triazine unit of  $C_3N_4$ , while peaks at  $1200-1600\text{ cm}^{-1}$  region corresponded to stretching modes of C-N heterocyclics. The absorption peaks at  $1340$  and  $1640\text{ cm}^{-1}$  were related to the C-N and

C=N stretching modes. The broad absorption band at  $3100 - 3300\text{ cm}^{-1}$  can be assigned as primary and secondary amines with their intermolecular hydrogen bonding interactions. All the observed peaks in the FTIR spectrum of  $\text{C}_3\text{N}_4$  were similar to the absorption peaks reported previously [22 – 24], supporting the successful transformation of the urea precursor to the  $\text{C}_3\text{N}_4$ . The prepared ZnO showed an intense peak in the range of  $400 - 500\text{ cm}^{-1}$  (Figure 3(g)), which was belonged to the Zn-O stretching. The FTIR spectra of the prepared ZnO- $\text{C}_3\text{N}_4$  samples are shown in Figure 3 (b)-(f). Similar to the results of XRD patterns and DR UV-Vis spectra, samples with low loading of ZnO showed the absorption peaks of  $\text{C}_3\text{N}_4$  as the dominant species. The peaks assigned to the  $\text{C}_3\text{N}_4$  decreased with the increase of Zn/C ratio. When the Zn/C ratio reached 50 mol%, the peaks related to the  $\text{C}_3\text{N}_4$  were completely disappeared and only ZnO peak could be observed on the ZnO- $\text{C}_3\text{N}_4$  (50) sample, as shown in Figure 3(f).

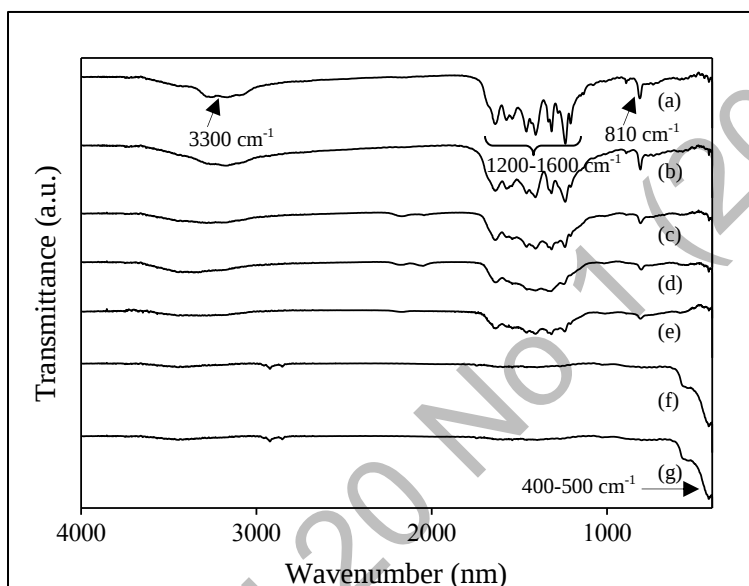


Figure 3. FTIR spectra of (a)  $\text{C}_3\text{N}_4$ , (b) ZnO- $\text{C}_3\text{N}_4$  (1), (c) ZnO- $\text{C}_3\text{N}_4$  (5), (d) ZnO- $\text{C}_3\text{N}_4$  (10), (e) ZnO- $\text{C}_3\text{N}_4$  (20), (f) ZnO- $\text{C}_3\text{N}_4$  (50), and (g) ZnO

Since the activity of the ZnO- $\text{C}_3\text{N}_4$  samples were evaluated under visible light irradiation, the charge transfer mechanism was investigated from the  $\text{C}_3\text{N}_4$  site. The  $\text{C}_3\text{N}_4$  exhibited two excitation peaks around 277 and 370 nm. The excitation peaks at 277 nm would be related to the N=C groups of aromatic 1,3,5-triazine, while the peak of 370 nm would be due to the terminal N-C group of  $\text{C}_3\text{N}_4$  [14, 22]. In order to investigate the effect of addition of ZnO on the emission of the  $\text{C}_3\text{N}_4$ , the emission spectra of the  $\text{C}_3\text{N}_4$  and the ZnO- $\text{C}_3\text{N}_4$  samples were measured at the excitation wavelength of 277 and 370 nm, as shown in Figure 4. For both excitation wavelengths, the  $\text{C}_3\text{N}_4$  showed two emission sites at 445 and 460 nm (Figure 4(a)). The emission intensity was found to decrease with the addition of ZnO (Figure 4(b)-(f)). The higher the amount of Zn/C ratio, the lower the emission intensity of the ZnO- $\text{C}_3\text{N}_4$  samples obtained. This result clearly suggested that there were interactions between the emission sites of  $\text{C}_3\text{N}_4$  and the added ZnO particles. Since the emission is the result of electron-hole recombination, the low emission intensity would suggest the suppression of the electron-hole recombination. It can be proposed here that the addition of ZnO was able to suppress the electron-hole recombination of the  $\text{C}_3\text{N}_4$ . Therefore, under visible light irradiation, it can be suggested that the electrons from the conduction band of the  $\text{C}_3\text{N}_4$  would be trapped by the ZnO, which would cause the less electron-hole recombination process. The mechanism of the electron charge transfer can be illustrated as in Figure 5.

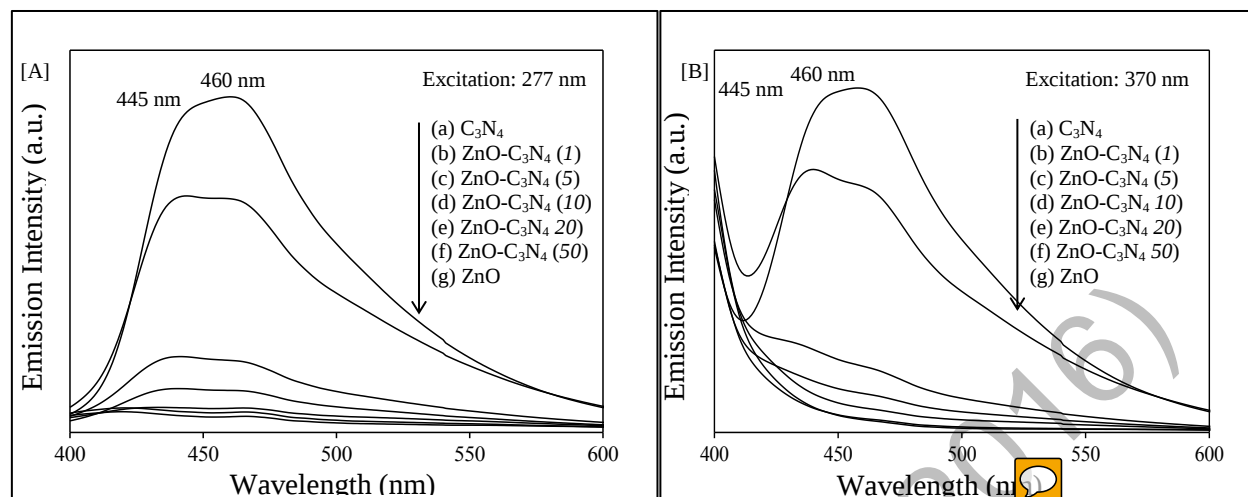


Figure 4. Emission spectra of (a)  $C_3N_4$ , (b)  $ZnO-C_3N_4$  (1), (c)  $ZnO-C_3N_4$  (5), (d)  $ZnO-C_3N_4$  (10), (e)  $ZnO-C_3N_4$  (20), (f)  $ZnO-C_3N_4$  (50) and (g)  $ZnO$  monitored at the excitation wavelength of [A] 277 and [B] 370 nm.

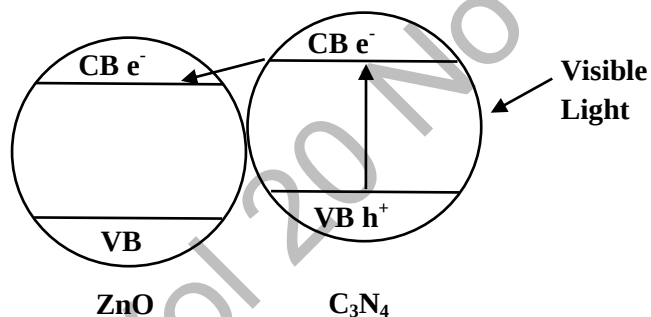


Figure 5. Schematic illustration of the electron charge transfer in the  $ZnO-C_3N_4$  composite. CB and VB are conduction and valence bands, respectively.

In addition to the reduced electron-hole recombination, the lower emission intensity especially for samples with high loading of  $ZnO$  would be also caused by the smaller amount of the  $C_3N_4$ . This factor would also affect the photocatalytic activity of the  $ZnO-C_3N_4$  composites under visible light irradiation.

#### Photocatalytic activity test

The  $C_3N_4$ ,  $ZnO$ , and the  $ZnO-C_3N_4$  samples were evaluated for the photocatalytic removal of phenol. Table 1 shows the percentage removals of phenol on the samples. The  $C_3N_4$  showed 34% removal of phenol (Entry 1), while the  $ZnO$  showed 15% (Entry 7). The  $ZnO-C_3N_4$  (1) showed 43% removal of phenol, which was three times higher than the activity of  $ZnO$  alone (Entry 7). It is worthy noted that the  $ZnO-C_3N_4$  (1) showed higher activity than either  $C_3N_4$  or  $ZnO$ . This result showed that there was a synergetic effect between the small amount of  $ZnO$  and the  $C_3N_4$ . As discussed previously, the small amount of  $ZnO$  would act to trap electron, thus inhibiting the electron-hole recombination process in the  $C_3N_4$  sample. The less electron-hole recombination would be the key factor to get the improved photocatalytic activity.

Unfortunately, when the Zn ratio was more than 1 mol%, the activity was found to be gradually decreased with the increase of the Zn ratio (Entries 3 – 6). Therefore, the ZnO-C<sub>3</sub>N<sub>4</sub> (1) showed the highest activity among the composite samples. As shown in the DR UV-Visible spectra, the ZnO-C<sub>3</sub>N<sub>4</sub> (1) showed the most intense absorption in the visible light. This property would be also one of the parameters that made it superior among the other composites. Moreover, as discussed in the characterization parts, samples with low loading of ZnO would behave like C<sub>3</sub>N<sub>4</sub>, while samples with high loading among would behave like ZnO. The ZnO-C<sub>3</sub>N<sub>4</sub> (50) showed activity closer to the activity of the ZnO (Entries 6 and 7). Even though the activity decreased with the increase of the ZnO loading, it is clear that all ZnO-C<sub>3</sub>N<sub>4</sub> composites showed better activities than the unmodified ZnO. This result strongly suggested that the activity of C<sub>3</sub>N<sub>4</sub> can be increased by the addition of ZnO.

Table 1. The percentages of phenol removal on ZnO and ZnO-C<sub>3</sub>N<sub>4</sub> samples after 5 hours reaction under visible light irradiation<sup>a</sup>

| Entry | Samples                                | Percentage of phenol removal (%) <sup>b</sup> |
|-------|----------------------------------------|-----------------------------------------------|
| 1     | C <sub>3</sub> N <sub>4</sub>          | 32                                            |
| 2     | ZnO-C <sub>3</sub> N <sub>4</sub> (1)  | 43                                            |
| 3     | ZnO-C <sub>3</sub> N <sub>4</sub> (5)  | 34                                            |
| 4     | ZnO-C <sub>3</sub> N <sub>4</sub> (10) | 33                                            |
| 5     | ZnO-C <sub>3</sub> N <sub>4</sub> (20) | 26                                            |
| 6     | ZnO-C <sub>3</sub> N <sub>4</sub> (50) | 21                                            |
| 7     | ZnO                                    | 15                                            |

<sup>a</sup>Photocatalyst used was 0.05 g in the 50 mL solution of phenol (50 ppm)

<sup>b</sup>Percentage removal of phenol was calculated from the percentage ratio of reacted phenol to the initial concentration of phenol

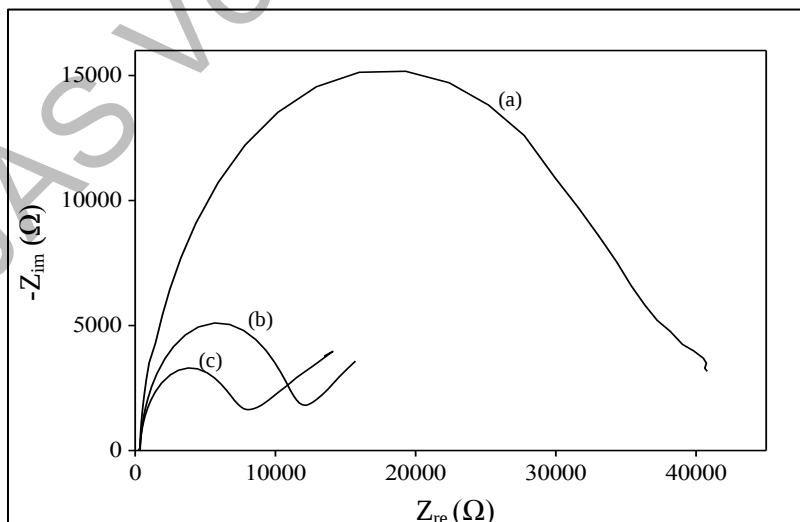


Figure 6. Nyquist plots of (a) ZnO, (b) C<sub>3</sub>N<sub>4</sub>, and (c) ZnO-C<sub>3</sub>N<sub>4</sub> (1).

In order to obtain more detail information on the charge transfer and further support the synergetic effect between the ZnO and the  $C_3N_4$ , the electrochemical impedance measurement was carried out. Nyquist plots of the  $C_3N_4$ , the ZnO and the ZnO- $C_3N_4$  (1) composite were plotted with an open circuit between 1 MHz and 0.1 Hz as shown in Figure 6. The ZnO- $C_3N_4$  (1) composite showed smaller semicircles compare to the bare ZnO and the  $C_3N_4$ , indicating the lower charge-transfer resistance on the surface of the composite [25]. With the suitable amount of ZnO, the charge transfer increased since  $C_3N_4$  can transfer the electron to the ZnO thus, preventing the rapid electron-hole recombination. This synergetic effect resulted in the higher activity in the photocatalytic reaction.

### Conclusion

The ZnO- $C_3N_4$  samples were prepared successfully by impregnation method. All the ZnO- $C_3N_4$  samples showed higher activity than the bare ZnO. The optimum amount of 1 mol% of Zn ratio gave *ca.* 3 times higher activity than unmodified ZnO. The ZnO- $C_3N_4$  (1) also showed higher activity than the  $C_3N_4$ . The synergic effect between the  $C_3N_4$  and the ZnO was proposed, where the addition of  $C_3N_4$  was able to extend the absorption of ZnO to visible light region and the small amount of ZnO would act to trap electron and suppress the electron-hole recombination.

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