

Mesoporous Carbon Nitride as Visible Light-Driven Photocatalyst for Removal of Salicylic Acid

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ABSTRACT: Mesoporous carbon nitride has been recognized as a potential visible light-driven photocatalyst. In the present study, mesoporous carbon nitride (mp-C₃N₄) was synthesized using urea as the precursor. In order to study the effect of the initial mass ratio of urea to silica, various ratios from 3 to 6 were used. Based on the results obtained from X-ray diffraction (XRD) and Diffuse Reflectance (DR) UV-Visible spectroscopy, it was revealed that the mp-C₃N₄ can be successfully prepared using the present method, regardless of the ratio of urea to silica. There was no linear relationship between the initial mass ratio of urea to silica and BET specific surface area. While the surface area of mp-C₃N₄ (4) and mp-C₃N₄ (5) was similarly high (ca. 200 m²g⁻¹), the surface area was low on mp-C₃N₄ (3) and mp-C₃N₄ (6) samples. It can be suggested that when the mass ratio of urea to silica was too low, the pore walls of the formed MCN would be thin and very susceptible to collapse when silica was removed during the washing process, which resulted in the low surface area. Since surface area has been proposed to play an important role in the photocatalytic activity, as representative, the mp-C₃N₄ (4) that has the highest specific surface area was further tested in the photocatalytic removal of salicylic acid. It was obtained that under visible light irradiation, salicylic acid can be removed up to 89.7% after 6 h-reaction.

KEYWORDS: carbon nitride, mesoporous, photocatalyst, salicylic acid, visible light

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I. INTRODUCTION

Carbon nitride is a metal-free semiconductor. It is used widely for photocatalytic applications such as for photocatalytic hydrogen production [1-3], photocatalytic degradation of pollutants [4,5] as well as for catalytic applications [1,6]. Several studies showed the superior photocatalytic activity of mesoporous carbon nitride than the non-porous ones [7-10]. While mesoporous carbon nitride can be prepared by a soft template, it can be also prepared by using silica as hard template which is heated together with its precursor. Organic precursors such as cyanamide, dicyandiamide, melamine, urea, and thiourea can be used to prepare the carbon nitride [11].

The demand to reduce environmental problems by employing a clean and green process is still emerging. Photocatalytic technology is believed to be one alternative method to produce clean energy and also to solve environmental problems such as organic pollutant decomposition [12-14]. For further use of sunlight energy in the future, photocatalysts shall be able not only to absorb UV light but also visible light. Carbon nitride is filling this requirement as it is yellow and can absorb visible light well.

On the other hand, salicylic acid is found as an organic pollutant in wastewater [15,16]. Salicylic acid and its derivatives are widely used in pharmaceuticals and cosmetics such as for anti-tumor, anti-bacterial, anti-fungal, and anti-viral [17]. The pharmaceuticals-based pollutants shall be treated well as they could lead to toxicity if the amount is too large. In this work, we reported the activity of mesoporous carbon nitride for photocatalytic removal of salicylic acid under visible light irradiation.

II. EXPERIMENTAL SETUP

2.1. Preparation of mp-C₃N₄

The mp-C₃N₄ was prepared using urea as the precursor and the silica with particle size of 7 nm as the template. Initial mass ratio of urea to silica was varied from 3 to 6, which the mesoporous materials were labelled as mp-C₃N₄ (x) and x indicates the initial mass ratio of urea to silica. Urea was added into the 7 mp-colloidal silica particles, followed by addition of double distilled water until urea was dissolved. The solution mixture was then stirred at 363 K until all water was evaporated. The resulting white powder was ground before heat treatment. The white powder was heated at a rate of 2.2 K min⁻¹ to reach a temperature of 823 K, and was

tempered at this temperature for 4 h. The resulting yellow powder was treated in 4 M ammonium hydrogen to remove the silica template. The powders were filtered and washed with distilled water and ethanol for several times. Finally, the obtained powders were dried at 353 K in an oven overnight.

2.2 Characterizations of mp-C₃N₄

A Pelkin-Elmer Diffuse Reflectance (DR) UV-visible spectroscopy (Lambda 900) was used to determine absorption spectra of the samples. X-ray Diffraction (XRD) was used to investigate the structure of the samples (Bruker AXS Diffrac plus release 2000). Brunauer-Emmett-Teller (BET) specific surface area of the MCN samples were calculated from nitrogen adsorption-desorption isotherm obtained at 77 K by using BELSORP-Mini instrument, BEL Japan.

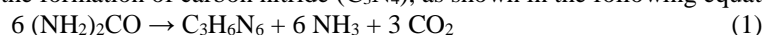
2.3. Photocatalytic Activity Test

The photocatalytic removal of salicylic acid was conducted by adding catalyst (0.05 g) in 50 mL of 100 μ M salicylic acid in a beaker containing a magnetic bar. Then, the beaker was placed on a stirring plate in a closed box in the dark for 1 h to reach the adsorption equilibrium. The system was then irradiated at room temperature with halogen fiber optic illuminator (MI-150, 150 Watt) equipped with an infrared cutoff filter for 6 h. After separation of the catalyst by centrifugation, the filtrate was then analyzed by using the gas chromatography with flame ionization detector (GC FID, Agilent 7820A).

III. RESULTS AND DISCUSSION

3.1. Preparation of mp-C₃N₄

Since cyanamide is harmful and toxic chemical, in the present study, urea precursor was used to prepare the mp-C₃N₄. Urea has both carbon and nitrogen, therefore, it is a good potential precursor to synthesize carbon nitride. In the case of using cyanamide, cyanamide is converted to dicyanamide, which then is transformed to melamine and melem before it becomes carbon nitride (C₃N₄). In the case of using urea as precursor, during the heating process at 550 °C, the decomposition of urea will result in melamine, which is the intermediate product for the formation of carbon nitride (C₃N₄), as shown in the following equation.



In the above mentioned reaction, there are two steps reaction. First step is decomposition of urea into cyanic acid and ammonia. Second step is polymerization of cyanic acid to form melamine and carbon dioxide. Melamine is then transformed to C₃N₄.



3.2. Characterizations of mp-C₃N₄

In order to study the absorption band of the prepared mp-C₃N₄, the optical absorption properties of the samples were investigated by DR UV-visible spectroscopy. The recorded DR UV-visible spectra are shown in Figure 1. All samples exhibited almost similar absorption up to 450 nm in blue light region. It was found that the absorption properties of the mesoporous materials were not influenced by the initial mass ratio of urea to silica, thus, all samples would be potential for photocatalytic reactions under visible light.

As shown in Figure 2, the prepared mp-C₃N₄ (x) series existed in amorphous form. All of the samples showed similar diffraction patterns, suggesting that all samples possess similar structure. Typical (002) peak at 27.6° indicated the graphite-like stacking of the conjugated aromatic units of CN with a distance of 0.32 nm. On the other hand, diffraction peak at 13.0° corresponding to a distance of 0.68 nm that could be assigned to the in-plane structural packing motif, such as hole-to-hole distance of the nitride pores. These results are in good agreement with the case of using other precursor to prepare mp-C₃N₄.

From BET specific surface area analyzer, it was also confirmed that the prepared mp-C₃N₄ samples showed various specific surface area depended on the initial ratio of urea to silica. There was no linear relationship between the initial mass ratio of urea to silica and BET specific surface area. While the surface area of mp-C₃N₄ (4) and mp-C₃N₄ (5) was similarly high (*ca.* 200 m²g⁻¹), the surface area was low on mp-C₃N₄ (3) and mp-C₃N₄ (6) samples. It can be suggested that when the mass ratio of urea to silica was too low, the pore walls of the formed mp-C₃N₄ would be thin and very susceptible to collapse when silica was removed during the washing process, which resulted in the low surface area.

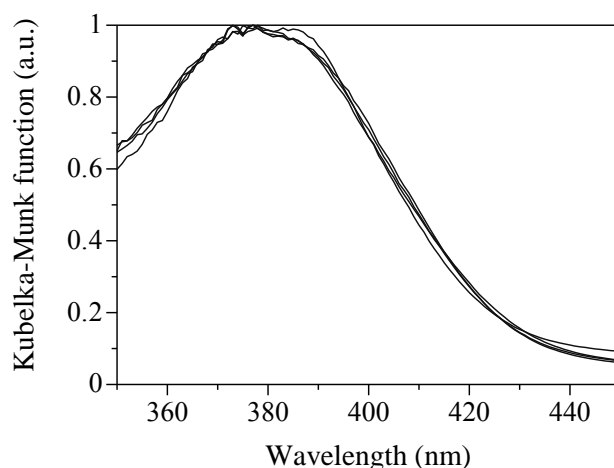


Fig 1. DR UV-vis spectra of all MCN samples

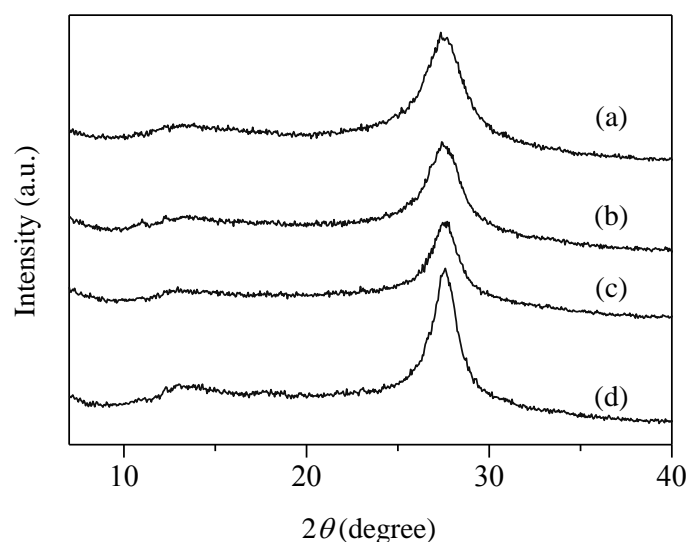


Fig 2. XRD patterns of (a) mp-C₃N₄ (3), (b) mp-C₃N₄ (4), (c) mp-C₃N₄ (5), and (d) mp-C₃N₄ (6).

3.1. Photocatalytic Activity of mp-C₃N₄

In order to check the photocatalytic activity of the prepared mp-C₃N₄, before reaction, the standard solution of salicylic acid with various concentrations was prepared. The typical chromatogram for 100 μM of salicylic acid as the standard solution is shown in Figure 3 as the representative. The large and broad peak *ca.* 0.75 min corresponds to the acetonitrile as the solvent, while the peak at *ca.* 1.8 min corresponds to the salicylic acid.

Analysis of the standard solution was made by plotting the peak area obtained from GC-FID to the concentration of the salicylic acid solution. The calibration curve of the prepared standard solution is shown in Figure 4. As can be seen from the calibration curve, the linear relationship with regression linear ($r^2 = 0.9904$, $r = 0.9952$) was obtained, thus, the quantitative analysis can be carried out.

Generally, material with high specific surface area will provide high active sites, thus, gives high activity in the catalytic reactions. Therefore, in the present study, in order to check the photocatalytic activity of mp-C₃N₄ prepared by urea, photocatalytic removal of salicylic acid was carried out using mp-C₃N₄ (4) that has the highest specific surface area among all the prepared samples. After adsorption equilibrium for 1 hour in the dark, the reaction was carried out under irradiation of visible light for 6 hours. The obtained chromatogram is shown in Figure 5. It can be observed that peak corresponding to salicylic acid decreased. It was obtained that the salicylic acid decreased from 100 to 10.2 μM, suggesting the percentage removal of 89.7%. New peaks were observed suggesting that salicylic acid might be converted to other oxidized compounds before it is fully decomposed to carbon dioxide and water.

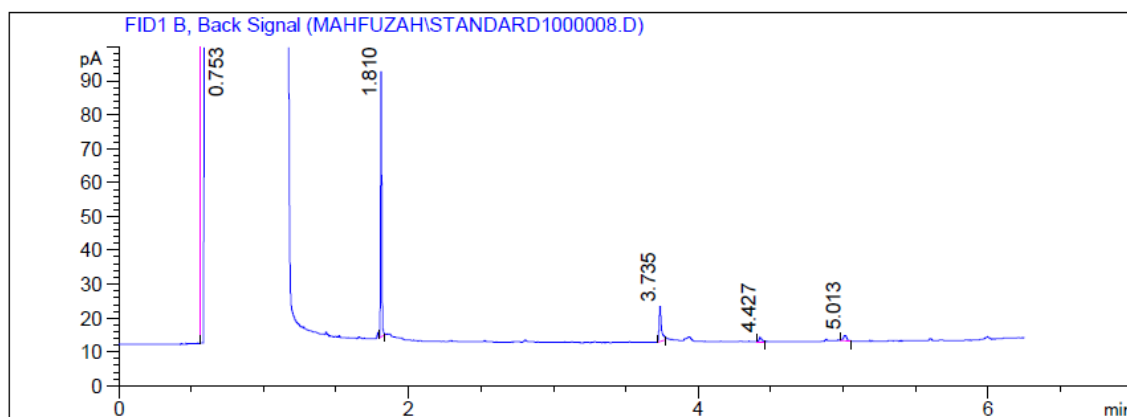


Fig 3. Typical chromatogram of salicylic acid in acetonitrile solvent. The salicylic acid used was 100 μM .

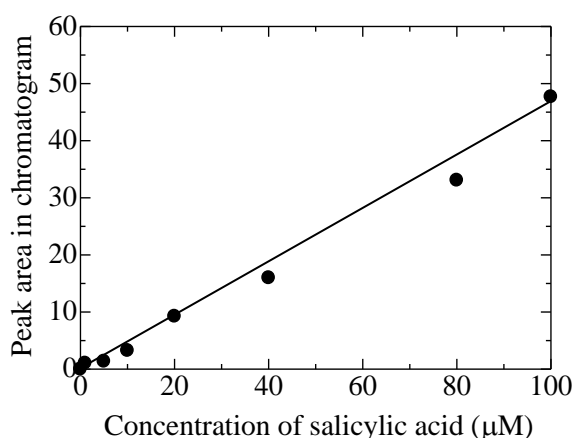


Fig 4. Calibration curve of salicylic acid with various concentrations.

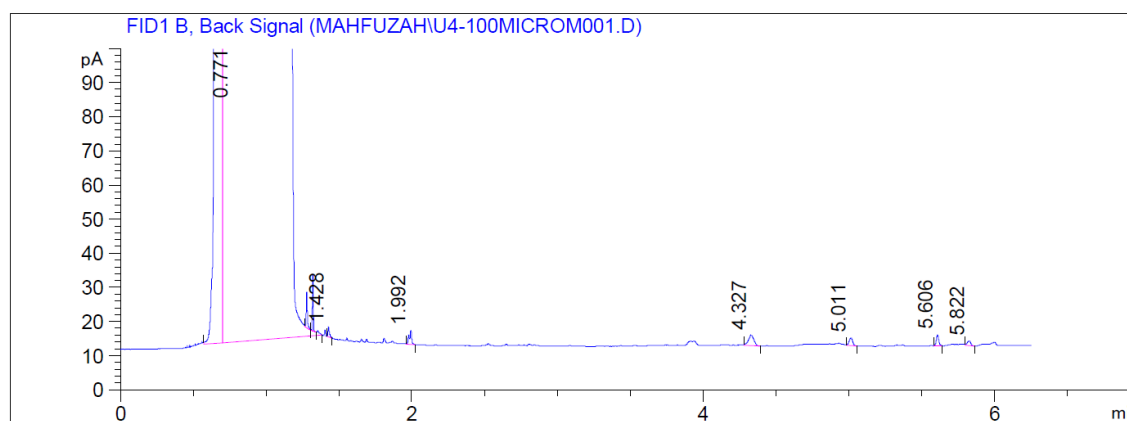


Fig 5 Chromatogram of salicylic acid in acetonitrile solvent after photocatalytic reaction under visible light irradiation for 6 h. The initial salicylic acid used was 100 μM .

IV. CONCLUSION

It was demonstrated that the series of mp-C₃N₄ was prepared successfully through thermal polymerization of urea precursor by hard template approach using silica nanospheres. From DR UV-vis spectroscopy and XRD patterns, it can be concluded that the prepared mp-C₃N₄ have the characteristics of carbon nitride. The different mass ratio of urea to silica only greatly affected the specific surface area of the samples. It was obtained that the mp-C₃N₄ (4) and mp-C₃N₄ (5) have high specific surface area while mp-C₃N₄ (3) and mp-C₃N₄ (6) showed low specific surface area that would be due to the collapse during the silica dissolving or formation of bulk C₃N₄. The photocatalytic activity testing of mp-C₃N₄ (4) for removal of

salicylic acid under visible light irradiation for 6 hours gave a percentage removal of 89.7%.

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