Photocatalytic conversion of carbon dioxide to methanol over different precursors of graphitic carbon nitride supported on fibrous silica iron

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Abstract. In this study, the graphitic carbon nitride (g-C₃N₄) was successfully synthesized through thermal polymerization under three different g-C₃N₄ precursors such as urea (U-g-C₃N₄), melamine (M-g-C₃N₄) and dicyandiamide (D-g-C₃N₄) and then doped into the fibrous silica iron (FSFe), denoted as U-g-C₃N₄/FSFe, M-g-C₃N₄/FSFe, and D-g-C₃N₄/FSFe, respectively. The synthesized catalysts were characterized using X-ray Diffraction (XRD), Fourier Transform Infrared Spectrometer (FTIR), and UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis/DRS) and also tested for photocatalytic conversion of carbon dioxide (CO₂) to methanol (CH₃OH). The study indicated that altering the precursors had a substantial impact on the physicochemical features of the FSFe, which in turn increased the catalytic performance of the conversion of CO₂ to CH₃OH. U-g-C₃N₄/FSFe exhibits the highest CH₃OH yield (2.3 x 10⁻⁵ µmol g⁻¹cat⁻¹) compared to bare FSFe, D-g-C₃N₄/FSFe and M-g-C₃N₄/FSFe under visible light irradiation within 240 min. The higher CH₃OH yield over U-g-C₃N₄/FSFe is mostly owing to the lower bandgap energy of U-g-C₃N₄/FSFe, as well as the advantageous interaction between g-C₃N₄ and FSFe.

1 Introduction

Carbon dioxide (CO₂) is the primary contributor to greenhouse effects, stemming from both natural and artificial processes. It’s acknowledged that CO₂ is essential for plant growth and various industrial applications [1]. However, it's imperative to maintain a balance between CO₂ emissions and consumption to preserve environmental stability. In reality, human industrial activities result in higher CO₂ emissions than consumption, disrupting the CO₂ equilibrium and exacerbating global warming [2]. To address this issue, numerous researchers have conducted studies. One potential solution is the conversion of CO₂ into valuable low-carbon fuels, such as methanol [3, 4].

In recent years, electrochemical catalyst approaches for CO₂ conversion have garnered significant attention due to their numerous advantages [5]. Nevertheless, the kinetics of CO₂ electroreduction remain suboptimal, even with high electrode reduction potential and the application of electrocatalysts. Another viable approach to converting CO₂ into methanol involves chemical, photochemical, photoelectrochemical, and photocatalytic reduction methods. Among these, photocatalytic conversion of CO₂ has been favored due to its high conversion efficiency, straightforward conversion procedures, and reasonable production cost [6]. In this process, a photocatalyst enhances CO₂ reduction by absorbing light, raising it to a higher energy level, and transferring this energy to a reacting substance to facilitate a chemical reaction [4].

In response to the escalating global environmental challenges, there is a strong need to develop efficient, cost-effective photocatalysts that are responsive to visible light for converting CO₂. A wide range of semiconductor materials, including titanium dioxide, zinc oxide, zirconium dioxide, iron oxide, graphitic carbon nitride (g-C₃N₄), and transition metal complexes, have been extensively studied for the photocatalytic conversion of CO₂ [3, 7, 8]. Among these, g-C₃N₄ has gained prominence as a highly promising photocatalytic material in recent years for CO₂ reduction under solar light exposure [9]. This is attributed to its affordability, unique chemical stability, environmentally friendly nature, and tunable microstructure [10].

Interestingly, g-C₃N₄ remains stable when exposed to light in both acidic and basic aqueous solutions due to the strong covalent bonds between carbon and nitrogen atoms [11]. It possesses an energy bandgap of 2.7 eV and can absorb the solar spectrum with a wavelength of less than 420 nm [12]. The g-C₃N₄ structure features interlayers with either a C₃N₃ ring or a C₃N₄ ring, and the graphite framework maintains a spacing of 0.326 nm between the two layers. These rings are connected by the N atom’s tail, forming an uninterrupted layer with planar extension.
Various synthesis methods, including thermal polymerization, solvent hot techniques, template-directed solid-state, soft-templating synthesis, and sonochemical processes, have been commonly employed to produce g-C₃N₄ [13]. However, its limited surface area (10 m²/g) and relatively low photocatalytic efficiency have made it less than ideal as a photocatalyst. Consequently, researchers have explored techniques such as coupling with other semiconductors or introducing co-catalysts to enhance the performance of g-C₃N₄. Moreover, the improved photocatalytic activity is associated with the specific structure resulting from different heat treatment temperatures, the quantity of g-C₃N₄, broad optical absorption range, effective separation and transport of electronic holes, and the composition of composite materials [14].

Numerous studies have investigated the synthesis of co-catalysts in conjunction with g-C₃N₄, but there has been a limited comparison of these synthesis methods. Common nitrogenous precursors include urea, dicyandiamide, and melamine, each having distinct structural characteristics. In this study, we opted for these structurally diverse nitrogenous precursors to produce g-C₃N₄ through fractional thermal polymerization, with the aim of conducting a comprehensive examination of the resulting g-C₃N₄ structures and properties. Finally, the synthesized g-C₃N₄ materials were doped into fibrous silica iron and assessed for their efficacy in the photocatalytic conversion of CO₂ to methanol.

2 Materials and methods

2.1 Materials

The chemicals used in the experiment were tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), butanol, urea, toluene, commercial iron oxide, Urea, melamine and which were purchased from Sigma-Aldrich, Malaysia. Other than that, the all reagents were prepared using deionized water.

2.2 Catalyst preparation

Graphitic carbon nitride was synthesized by using different type of precursors which is urea, dicyandiamide and melamine. In this study, for synthesis of g-C₃N₄ nanomaterial, 1 g of urea, dicyandiamide and melamine were put into a ceramic crucible separately. Then all the precursors in each crucible were calcined for 30 min at 620 °C under muffle furnace. The polymeric catalyst was then cooled to room temperature. In order to produce fine powder, the result of catalyst obtained was crushed for further purpose. Consequently, the resultant g-C₃N₄ obtained by urea, dicyandiamide and melamine precursors were denoted as U-gC₃N₄, D-gC₃N₄ and M-gC₃N₄, respectively.

Fibrous silica iron (FSFe) was synthesized by using microemulsion technique together with crystal-seed crystallization method. Firstly, 24.65 g of CTAB and 14.72 g of urea were mixed in 732 mL of distilled water, stirred for 5 min at vigorous stirring which is 850 rpm. Next, 624 mL of toluene and 37 mL of 1-butanol were added into the mixture and stirred for another 15 min at room temperature. After that, 3 g of iron seed was added into the mixture and stirred for another 30 min. Subsequently, 56 mL of TEOs was added drop wise and the mixture was stirred for 2 hours at room temperature. After 2 hours stirring, the resulting mixture was heated in oven for 6 hours at 120 °C. The heated product was dried overnight at 110 °C before calcination at 550 °C for 6 hours. A dry brown solid catalyst was obtained and it represented FSFe catalyst.

The preparation steps for g-C₃N₄/FSFe catalysts was started with dissolving 0.05 g of g-C₃N₄ from different precursor and 0.95 g of FSFe into 50mL distilled water. Then, the mixture was stirred for 30 min and then dried in oven at 110 °C overnight. Next, the mixture was transferred into microwave for 30 min at 450 W. Consequently, the resultant g-C₃N₄/FSFe obtained by urea, dicyandiamide and melamine precursors were denoted as U-gC₃N₄/FSFe, D-gC₃N₄/FSFe and M-gC₃N₄/FSFe respectively.

2.3 Characterization

The catalysts crystallinity were verified by D8 ADVANCE Bruker X-ray diffractometer. Meanwhile, the chemical properties of the catalysts was detected by the KBr method via Perkin Elmer Spectrum GX FT-IR. The optical properties of the catalyst were measured by using Agilent Technologies Cary 60 UV-Vis spectrometer with an integrating sphere.

2.4 Photocatalytic measurement

An amount of photocatalyst (0.06 g L⁻¹) was dispersed into 100 mL solution CO₂ which consist of distilled water and TEA (sacrificial agent). The photocatalytic conversion of CO₂ was conducted using a fixed batch reactor with a cooling system CO₂ was fed into the slurry photoreactor through a gas inlet pipe at the top. A 39 W metal halide lamp with a wavelength of 400 nm was used for visible light source. The solution was stirred in a dark for 60 min to achieve absorption equilibrium and then exposed under visible light for another 4 hours. The absorption equilibrium was determined by conducting a reaction in the dark for 60 min. During the process, 1 mL of solution sample was collected using a syringe for every 60 min in the dark and in every 30 min under visible light and then, centrifuged using Beckman Coulter Microfuge 16 Centrifuge at 14,000 rpm for 5 min. Then, the concentration of methanol was analyzed using Gas chromatography (GC) at the area peak of methanol 1.036.

3 Results and discussion

3.1 Crystallinity studies

The XRD patterns of the synthesized catalyst in the range of 2θ=10-80° are shown in Figure 1. Several peaks
At $2\theta = 24.19^\circ$, $30.03^\circ$, $33.07^\circ$, $35.50^\circ$, $40.84^\circ$, $43.30^\circ$, $49.57^\circ$, $53.89^\circ$, $57.34^\circ$ and $62.74^\circ$ was observed in fibrous silica iron (FSFe) corresponding to the planes (012), (220), (104), (110), (113), (202), (024), (116), (122) and (214) respectively, which attributed to the rhombohedral phase of $\alpha$-Fe$_2$O$_3$ (ICDD card no. 33-0664) [15]. The narrow and sharp peaks were observed due to its crystalline nature, implying that the high purity of synthesized FSFe is obtained by using microemulsion method. Meanwhile, the broad peak at $23.04^\circ$ was attributed to the amorphous silica framework of the materials [16]. For all catalyst of g-C$_3$N$_4$ synthesized from different precursor doped onto FSFe show similar diffractograms, with a slight decrease in intensity, particularly for U-g-C$_3$N$_4$/FSFe and D-g-C$_3$N$_4$/FSFe. In contrast, M-g-C$_3$N$_4$/FSFe showed the higher intensity compared to the FSFe, indicating the higher crystallinity might be due to the higher content of nitrogen [17]. Additionally, the obvious an additional peak at $27.5^\circ$, attributed to the (002) plane of g-C$_3$N$_4$ based on the JCPDS no.87-1526 [11].

![Fig. 1. XRD patterns of the FSFe and g-C$_3$N$_4$/FSFe under different precursors.](image)

For chemical properties studies, all the catalysts were then characterized by FTIR and the spectra in the region of 4000-400 cm$^{-1}$ are shown in Fig. 2. Typical bands for g-C$_3$N$_4$ were detected at 806 cm$^{-1}$ due to the vibration of triazine ring [18]. The U-g-C$_3$N$_4$ absorption band is more apparent than that of D-g-C$_3$N$_4$ and M-g-C$_3$N$_4$, owing to its more orderly polymeric melon unit packing (Fig. 2a-c) [17]. Also, the peaks at 1238 cm$^{-1}$ and 1322 cm$^{-1}$ are related to the typical stretching vibration of C-N heterocycles [12]. Meanwhile, major absorption bands for FSFe were spotted at 462 cm$^{-1}$, 800 cm$^{-1}$, 968 cm$^{-1}$, 1091 cm$^{-1}$, which were associated with the existence of M-O (M=Si and Fe), Si-OH external groups, symmetric Si-O-Si and asymmetric Si-O-Si stretching, respectively (Fig. 2d) [19]. The intensity of Si-O-Si bonds of FSFe was seems decreased when incorporation of g-C$_3$N$_4$, suggesting that Si-O-Si were isomorphously with C and N elements to form Si-O-C and Si-O-N, respectively. This result showed there is an interaction between g-C$_3$N$_4$ with SiO$_2$. Interestingly, the obvious peaks at 1322 and 1238 cm$^{-1}$ corresponding to the C-N heterocycles was observed in the U-g-C$_3$N$_4$, may be due to its orderly polymeric melon unit packing compared another precursor of g-C$_3$N$_4$.

![Fig. 2. FTIR spectra of (a) U-g-C$_3$N$_4$ (b) D-g-C$_3$N$_4$ (c) M-g-C$_3$N$_4$ (d) FSFe (e) U-g-C$_3$N$_4$/FSFe (f) D-g-C$_3$N$_4$/FSFe (g) M-g-C$_3$N$_4$/FSFe](image)

The optical behavior of photocatalysts results in an important impact on photocatalytic reactions. The UV–Vis's spectra for all photocatalysts was recorded in the spectral range 200-800 nm to investigate the optical properties of the catalyst as illustrated in Fig. 3. The bandgap of the samples was calculated using the equation of $E=1240/\lambda$, where $E$ is the band gap energy in eV and $\lambda$ is the wavelength in nanometres.

![Fig. 3. UV-Vis’s spectra of all catalysts.](image)

As seen, the absorption edges reached over 400 nm, indicating that all the synthesized catalyst could responds to the visible light. The summary of the band gap for all catalysts are stated in Table 1. The band gap energy of FSFe is 2.38 eV, and it altered the band gap
energy when g-C₃N₄ doped on FSFe. The band gap energy of D-gC₃N₄/FSFe (2.95 eV) and M-gC₃N₄/FSFe (3.18 eV) is higher compared to the FSFe, may be due to the quantum confinement effect[13]. Likewise, the U-gC₃N₄/FSFe (2.21 eV) showed the lowest bandgap among all catalyst. This result led to the potential use of it in visible light responsive photocatalytic reaction as the photogenerated electrons and holes were effectively separated due to lower bandgap, thus possibly induced charge-transfer transition between FSFe species and g-C₃N₄.

Table 1 Band gap energy of the catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Bandgap (eV)</th>
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<tbody>
<tr>
<td>FSFe</td>
<td>2.38</td>
</tr>
<tr>
<td>U-gC₃N₄/FSFe</td>
<td>2.21</td>
</tr>
<tr>
<td>D-gC₃N₄/FSFe</td>
<td>2.95</td>
</tr>
<tr>
<td>M-gC₃N₄/FSFe</td>
<td>3.18</td>
</tr>
</tbody>
</table>

The performance of the synthesized catalyst towards on the photoconversion of CO₂ to methanol was illustrated in Fig. 4, which the reaction was conducted under the visible light irradiation. As seen, U-gC₃N₄/FSFe exhibits the highest performance (2.3 x 10⁴ µmol g⁻¹cat⁻¹) compared to bare FSFe, D-gC₃N₄/FSFe and M-gC₃N₄/FSFe. The reason might be due to the lowest bandgap energy of U-gC₃N₄/FSFe. Notably, the interaction between g-C₃N₄ and FSFe could improve the generation of g-C₃N₄ and FSFe heterojunction in U-gC₃N₄/FSFe. Furthermore, the CH₃OH yield for all catalysts appears to be steady after 180 minutes, which can be attributed to the equal rates obtained between CH₃OH formation and CH₃OH re-oxidation.

Fig. 4. Catalytic performance of the catalyst towards conversion of CO₂ to methanol.

4 Conclusion

In this study, three different precursors of g-C₃N₄ which is urea, melamine and dicyandiamide were used to prepare the g-C₃N₄ by thermal polymerization, and denoted as U-gC₃N₄, M-gC₃N₄ and D-gC₃N₄, respectively. The resulting materials were then doped into fibrous silica iron (FSFe), designated as U-gC₃N₄/FSFe, M-gC₃N₄/FSFe, and D-gC₃N₄/FSFe, respectively. The synthesised catalysts were evaluated for their ability to photocatalytically convert CO₂ to CH₃OH. According to the research, changing the precursors significantly affected the physicochemical characteristics of the FSFe, which in turn improved the catalytic performance of converting CO₂ to CH₃OH. Under visible light irradiation for 240 minutes, U-gC₃N₄/FSFe shows the highest CH₃OH yield (2.3 x 10⁴ µmol g⁻¹cat⁻¹) when compared to bare FSFe, D-gC₃N₄/FSFe, and M-gC₃N₄/FSFe. The lower bandgap energy of U-gC₃N₄/FSFe and the beneficial interaction between g-C₃N₄ and FSFe are the main causes of the greater CH₃OH yield over U-gC₃N₄/FSFe.

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