

## Copper modified TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> catalysts for photoreduction of CO<sub>2</sub> to methanol using different reaction mediums

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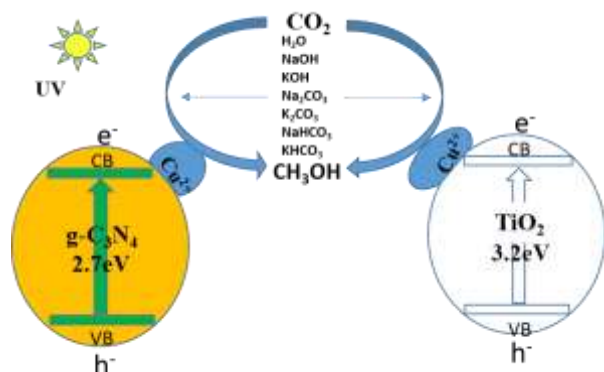
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### GRAPHICAL ABSTRACT

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### ABSTRACT

In this study, Cu/TiO<sub>2</sub> and Cu/g-C<sub>3</sub>N<sub>4</sub> catalysts were tested for CO<sub>2</sub> reduction to methanol. The catalysts were prepared by the wet impregnation method and, characterized by XRD and FESEM. The product identification and yield were determined using a GC with FID. The CO<sub>2</sub> photoreduction process was performed in each of the following reaction mediums: H<sub>2</sub>O, NaOH, KOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> and KHCO<sub>3</sub>. The efficiency was studied by comparing the methanol yield for each. A slurry type photoreactor with a UV lamp of 365 nm wavelength was used. CO<sub>2</sub> photoreduction to methanol using NaOH as the reaction medium registered the highest yield of 431.65 μmole/g-cat•hr. This is due to the higher solubility of CO<sub>2</sub> in the alkali as compared to that of the other reaction mediums, the ability of NaOH to serve as a hole scavenger owing to the formation of OH• ions and the higher selectivity of NaOH solution for CO<sub>2</sub> photoreduction to methanol. It was obvious the choice of reaction medium affected the photoreduction of CO<sub>2</sub> to methanol. The trend of results indicated the use of NaOH as a reaction medium improved the efficiency of the photoreduction process. The findings from this research could promote research in the field of photocatalysis by improving the yield which will encourage the support for methanol economy.

**Keywords:** methanol, titanium dioxide, carbon nitride, copper

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## 1. INTRODUCTION

The world today is experiencing two major problems global warming and the rising demand of energy. Global warming is due to the rapid increase of CO<sub>2</sub> in the atmosphere while the geometric progression of population growth in the world is the reason for the rising demand of energy. One of the most prominent strategies embraced by scientists is Carbon Dioxide Capture and Storage (CCS) which involves the storage of these captured CO<sub>2</sub> in deep oceans, depleted oil or gas wells etc. [1] Carbon dioxide Capture and Recycle (CCR) is the conversion/reduction of the captured CO<sub>2</sub> to hydrocarbon fuels. This is a better approach because it ends in a win-win situation. Since this initiative was executed in 1979 by employing semiconductors (TiO<sub>2</sub>, SiC, GaP, WO<sub>3</sub>) to photoreduce CO<sub>2</sub> to simple C<sub>1</sub> products (CH<sub>3</sub>OH, HCHO, HCOOH and trace amounts of CH<sub>4</sub>), researchers have focused more on it [2, 3]. Methanol is the most desired product from the photoreduction process of CO<sub>2</sub> amongst others because it can be easily/directly used as a liquid fuel [4].

The properties of methanol reveal numerous benefits which makes it a viable and prospective feedstock in industries [5]. The photoreduction process is dependent on some operating parameters which affects its efficiency and hence the yield and selectivity. One of the key parameters is type of reaction medium [6]. Researchers have used different types of reaction mediums such as H<sub>2</sub>O [7], NaOH [8], NaHCO<sub>3</sub> [9], and KHCO<sub>3</sub> [10] for CO<sub>2</sub> photoreduction. Water is the most abundant, readily available, inexpensive, and environment friendly of all the reaction mediums but it is faced with one draw-back which is its low solubility with CO<sub>2</sub> (2g/L) [11-13]. There is a need for reaction mediums (sacrificial electron donors) capable of improving the process efficiency.

In this paper, the efficiency of different reaction mediums used for CO<sub>2</sub> photoreduction is compared. Also, the efficiency of the two catalysts used is compared and the effect of reaction medium on the efficiency of the catalysts is discussed. Cu/TiO<sub>2</sub> has long been considered the best catalyst for methanol photosynthesis [14]. It is envisaged that doping TiO<sub>2</sub> with Cu<sup>2+</sup> could lower its band gap due to the lower redox potential of copper ions. The electron-hole

recombination rate could be effectively reduced [15].  $g\text{-C}_3\text{N}_4$  was selected because of its low band gap of 2.7 eV amidst its several other properties which makes it almost perfect as a metal free heterogeneous catalyst [16]. Meanwhile, the reaction mediums were  $\text{H}_2\text{O}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and  $\text{KHCO}_3$ . A slurry type photoreactor equipped with a UV light source of 365 nm was used for the process. The catalysts were characterized using XRD and FESEM while a GC with FID was used to separate and identify the products.

## 2. EXPERIMENTS

### 2.1 Catalyst Preparation

$\text{TiO}_2$  (anatase, Sigma Aldrich, >99% trace metals basis),  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Emory, 99%) the copper salt used for metal doping, and melamine (99% Sigma Aldrich) were used as the precursor for preparing carbon nitride. Both catalysts were prepared by the wet impregnation method. In a typical method, 4 g of  $\text{TiO}_2$  was dissolved in a solution of 0.456 g of copper nitrate  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . The mixture was stirred for 1h using a magnetic stirrer after which it was put in a water bath to evaporate the solvent at  $80^\circ\text{C}$  for 3h. The sample was oven dried at  $120^\circ\text{C}$  for 12h and then calcined for 5h at  $450^\circ\text{C}$  and grinded into powder form to give 3 wt % Cu doped  $\text{TiO}_2$  [17, 18].  $g\text{-C}_3\text{N}_4$  was synthesized by the thermal decomposition of melamine in a furnace at  $550^\circ\text{C}$  for 2h [19]. 3wt% Cu doped  $g\text{-C}_3\text{N}_4$  was synthesized by a method similar to that of  $\text{Cu}/\text{TiO}_2$  but with a slight modification where  $\text{TiO}_2$  was replaced with  $g\text{-C}_3\text{N}_4$ . 1 M of the different reaction mediums ( $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ ) were prepared conventionally.

### 2.2. Characterization

The crystalline structure of the as-prepared catalysts were determined with X-ray diffraction (XRD) recorded on a powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a  $\text{Cu K}\alpha$  radiation source in the range of  $2\theta = 5\text{-}80^\circ$  and a step size of  $0.05^\circ$  and counting time of 5s. The surface morphology was examined using field-emission scanning electron microscopy (FESEM JEOL model JSM-6700F, Japan).

### 2.3. Photocatalytic Activity Test

The photocatalytic reaction was conducted in a 1L jacketed Pyrex glass beaker mounted on a FAVORIT Stirring Hotplate HS0707V2. A 365nm UV lamp was used as the solar light source and a black casing was used for the reactor to shield against the radiation. 0.2g of the as-prepared powder form photocatalyst was placed in the slurry type reactor with 400ml of each reaction medium one after the other.  $\text{CO}_2$  gas was first injected into the solution for 30mins at a flow rate of 20 cc/min with the light off. This is to allow full adsorption of  $\text{CO}_2$  into the solution. The solution was then irradiated under the UV lamp light for 2h each. Sample was collected after 2h,

separated with a  $0.45\mu$  filter and analyzed using a GC with FID. Blank experiments were conducted to ensure that the product formed was due to the photoreduction of  $\text{CO}_2$ .

## 3. RESULTS AND DISCUSSION

Fig. 1 exhibits the XRD patterns of the  $\text{Cu}/g\text{-C}_3\text{N}_4$  and  $\text{Cu}/\text{TiO}_2$ . The wide-angle peak at  $27.5^\circ$  was characteristic of an interlayer stacking of conjugated aromatic systems. A minor diffraction peak was found at  $13.35^\circ$ , which was indexed to the (1 0 0) plane and assigned to the in-plane structural packing of aromatic systems. The presence of these two characteristic peaks confirmed the formation of  $g\text{-C}_3\text{N}_4$  framework. Nevertheless, there is no peak attributable to the Cu metal. This could be due to its low dopant percentage of just (3wt %) or that the metal dopant was firmly bonded to the  $g\text{-C}_3\text{N}_4$  support. This could be due to nucleophilic nitrogen surrounding the unique 2-dimensional layered structure of  $g\text{-C}_3\text{N}_4$ . This could have aided hybridization with other components. In the case of  $\text{Cu}/\text{TiO}_2$ , a single anatase phase  $\text{TiO}_2$  was formed. The peaks at  $2\theta$  values of  $25.26^\circ$ ,  $37.77^\circ$ ,  $48.0^\circ$ ,  $53.84^\circ$ ,  $55.02^\circ$ ,  $62.62^\circ$ ,  $68.67^\circ$ ,  $70.25^\circ$  and  $75.0^\circ$  were identified by comparing with literature data and confirming the particles are crystalline anatase  $\text{TiO}_2$  and Cu peak ( $43.2^\circ$ ). All peaks are in good agreement with the standard spectrum (JCPDS no 01-075-2246). From the XRD diffractograms, it is obvious that the Cu in  $\text{Cu}/\text{TiO}_2$  is more crystalline compared to the Cu in the  $\text{Cu}/g\text{-C}_3\text{N}_4$ . Graphitic carbon nitride is the most stable of all the allotropes of carbon nitride under ambient conditions. Its amorphous structure and high reactivity makes it an efficient photocatalyst for water splitting even without noble metal doping. It allows the transfer of charges maximally thereby reacting very well with the reaction mediums and stabilizing the electrons and holes.

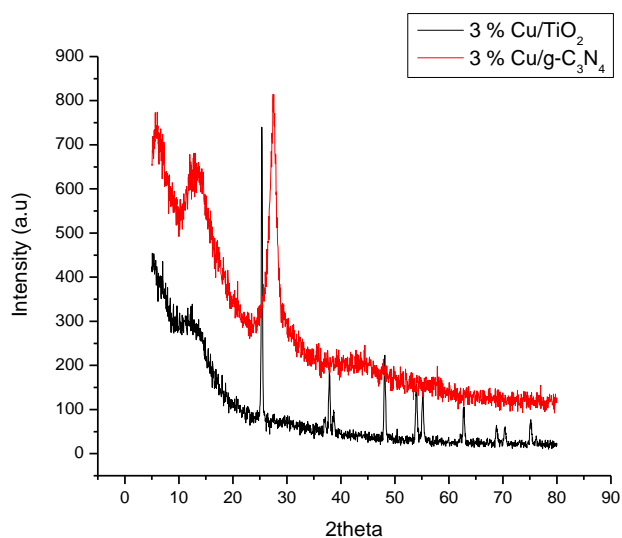


Fig. 1 XRD patterns of the samples

In order to investigate the morphology of the two photocatalysts used, FESEM analysis was performed. From Fig. 2a illustrates the Cu/TiO<sub>2</sub>, sample consists of agglomerated nanosized particles and the metal dopant was most probably incorporated into the support. In the case of Fig. 2b, Cu/g-C<sub>3</sub>N<sub>4</sub> image indicates lamellar structure with high porosity.

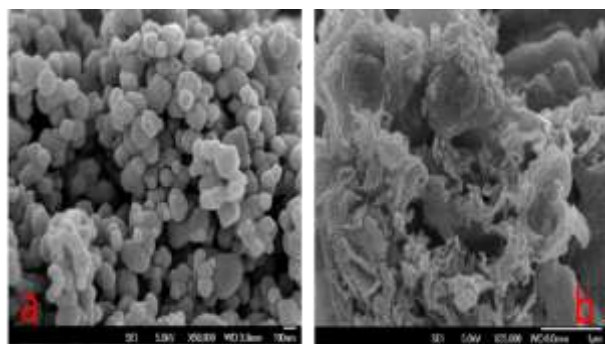


Fig. 2 FESEM images of (a) 3% Cu/TiO<sub>2</sub> and (b) 3% Cu/g-C<sub>3</sub>N<sub>4</sub>

From the results summarized in Table 1 and illustrated in Fig 3, it is obvious that in considering the reaction mediums and their yield of methanol, 1 M NaOH solution registered the best result and this can be traced to the solubility of CO<sub>2</sub> in NaOH. The solubility of CO<sub>2</sub> in water at room temperature is only 2g/L [15, 16]. More CO<sub>2</sub> is converted when NaOH was used as the reaction medium. This was seen during the process by observing the rapid flow of exit gas from the process while using water. This was due to the immediate formation of carbonic acid between water and CO<sub>2</sub> producing CO<sub>3</sub><sup>2-</sup> ions but in the case of NaOH the flow was rather slower because as more CO<sub>2</sub> was added to the NaOH solution the carbonic acid was converted to bicarbonate producing HCO<sub>3</sub><sup>-</sup> ions.

Table 1 Yield of methanol from CO<sub>2</sub> photoreduction using Cu/TiO<sub>2</sub> and Cu/g-C<sub>3</sub>N<sub>4</sub> using different reaction mediums

| Reaction medium                 | MeOH yield using Cu/TiO <sub>2</sub> (μmole/g cat·hr) | MeOH yield using Cu/g-C <sub>3</sub> N <sub>4</sub> (μmole/g-cat·hr) |
|---------------------------------|---|--|
| K <sub>2</sub> CO <sub>3</sub>  | 1.05  | 180.9  |
| KOH                             | 1.70  | 230.69   |
| NaHCO <sub>3</sub>              | 17.68   | 259.60   |
| KHCO <sub>3</sub>               | 41.89   | 271.70   |
| H <sub>2</sub> O                | 46.08   | 323.72   |
| Na <sub>2</sub> CO <sub>3</sub> | 61.39   | 375.65   |
| NaOH                            | 139.34  | 431.65   |

The potential can be lowered by nearly 0.7V when CO<sub>2</sub> was changed to CO<sub>3</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup> [20]. The HCO<sub>3</sub><sup>-</sup> (or CO<sub>3</sub><sup>2-</sup>) ions were anchored to the photocatalyst surfaces which efficiently received the electrons, and converted to CH<sub>3</sub>OH after protonation [21]. The use of water as a

reaction medium favors water splitting leading to H<sub>2</sub> production instead of CO<sub>2</sub><sup>•-</sup> radical anions which allows formation of the methoxy (•OCH<sub>3</sub>) radicals needed for CH<sub>3</sub>OH. This is because the electrode potential for water splitting is lesser than that of CO<sub>2</sub> reduction showing that water splitting is thermodynamically easier [6]. The NaOH also serves as a hole scavenger due to the formation of the OH• ions. CO<sub>2</sub> is also more soluble in Na<sub>2</sub>CO<sub>3</sub> compared to water and gave a better result [6]. The low yield of methanol in the case of the potassium salts may be attributed to the decrease in the ionization enthalpies of the alkali metals as the atomic number increases down the group of the periodic table due to decrease in lattice enthalpies. The removal of a valence electron from sodium is higher than that of potassium and since there is a need for electrons in the photoreduction process the sodium salts should give a better performance. KHCO<sub>3</sub> is an exception because its solubility is fairly higher compared to NaHCO<sub>3</sub> [22].

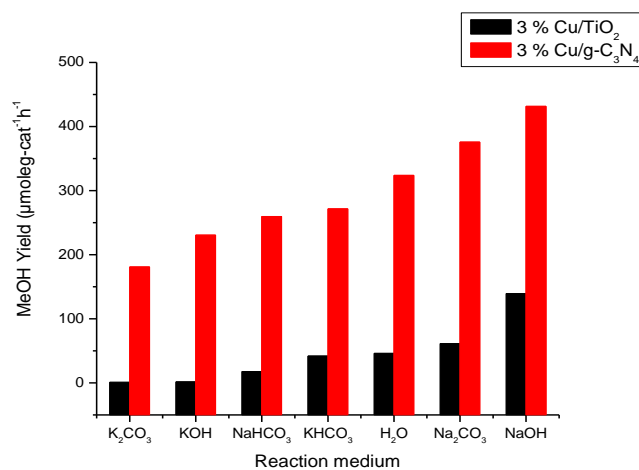


Fig. 3 Yield of methanol in various reaction mediums

The effect of doping on catalysts with Cu metal can be seen in Fig. 4. For both catalyst supports there is an increase in the efficiency of the process visible from the yield of methanol. This is obviously due to the ability of the Cu ions to act as electron trapping agents while still maintaining the mobility of photoelectrons. The yield of methanol from Cu/g-C<sub>3</sub>N<sub>4</sub> is more than 3 times higher than that of Cu/TiO<sub>2</sub> with NaOH as the reaction medium. This is so because of the suitable band gap of g-C<sub>3</sub>N<sub>4</sub> compared to that of TiO<sub>2</sub> and it is expected that the yield of methanol would be higher in the case of the former even after metal doping. The lamellar structure of the Cu/g-C<sub>3</sub>N<sub>4</sub>, as evident from FESEM, is characterized by a mesoporous morphology which is possibly responsible for the slight increase in its yield as compared to that of pure g-C<sub>3</sub>N<sub>4</sub>.

Another interesting observation from this study is the fact that the trend in the result obtained for both catalysts is similar. The results of the photocatalytic test indicated that for both catalysts, the methanol yield

prevailed in NaOH compared to the other reaction mediums. The concentration of the surface OH• groups was found to play a role in the selectivity for the formation of CH<sub>3</sub>OH [23]. The carbonate and hydrogen carbonates formed from the dissolution of CO<sub>2</sub> in NaOH assisted to increase the efficiency of the process.

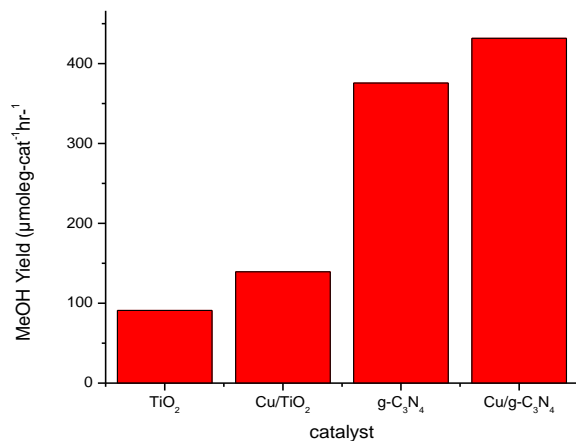


Fig. 4 Yield of methanol in NaOH reaction medium using different catalysts

#### 4. CONCLUSION

From the results, NaOH exhibits the highest yield of methanol and other reaction mediums spotted a similar trend for both catalysts. The Cu/g-C<sub>3</sub>N<sub>4</sub> gives a better yield compared to Cu/TiO<sub>2</sub> due to its suitable band gap for photocatalytic reactions even though the crystallinity of Cu on g-C<sub>3</sub>N<sub>4</sub> did not give much effect on its activity. It is evident that NaOH is a better reaction medium for CO<sub>2</sub> photoreduction to methanol due to the high solubility of CO<sub>2</sub> in NaOH and the selectivity of NaOH towards CO<sub>2</sub> photoreduction to methanol. The NaOH serves as a hole scavenger, its OH• radical helps foster the reduction of CO<sub>2</sub> by extending the decay time of electrons. Although the cost of using water as a reaction medium is cheaper compared to others, its solubility for CO<sub>2</sub> and the competition between water splitting and CO<sub>2</sub> reduction hampers its efficiency as a reaction medium for CO<sub>2</sub> reduction.

#### ACKNOWLEDGEMENTS

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