

Photocatalytic activity of TiO₂-Cu-metal-organic framework (MOF)

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The accumulation of greenhouse gases including carbon dioxide (CO₂) in the atmosphere has greatly increased with industrialization and creates serious problems on our environment such as global warming, melting of glaciers, sea level rise, and extinction of species. One of the solutions is to reduce the level of CO₂. CO₂ conversion can be achieved in a sustainable and environmentally safe way by a light-based photocatalytic method.

In this study, a titanium dioxide doped copper metal organic framework (TiO₂/Cu-MOF-NH₂) based photocatalyst was prepared for the photocatalytic reduction of CO₂. MOFs are effective photocatalysts after surface modification, structuring with other semiconductors, and doping with metal nanoparticles. The activity of the photocatalyst (TiO₂/Cu-MOF-NH₂) was determined by means of synthetic dye reduction reaction. In order to determine the effect of TiO₂ on the MOF structure, characterization of TiO₂/Cu-MOF-NH₂ and Cu-MOF-NH₂ was done. The photocatalysts were characterized using Fourier transform infrared spectroscopy, scanning electron microscopy, and X-ray diffraction tests. As a result, 17% of adsorption and 31.7% adsorption-photocatalysis were achieved by TiO₂/Cu-MOF-NH₂ photocatalysis.

Keywords: CO₂ Reduction, Metal-organic framework (MOF), Photocatalyst, Photocatalytic activity

INTRODUCTION

Due to the rapid increase in global population and industrialization, the rate of energy consumption is rapidly increasing. The energy demand has rapidly increased over the years, however, clean and sustainable energy resources are limited. Although the renewable energy sources such as wind energy and solar energy are gaining importance, most of the energy is still provided by fossil fuels such as coal and oil. The use of fossil fuels causes significant accumulation of greenhouse gases such as carbon dioxide (CO₂) in the atmosphere. Therefore, this accumulation causes serious problems on the environment such as global warming, melting of glaciers, rising sea level and extinction of species [1]. The increased amount of CO₂ should be reduced to an appropriate level. In order to prevent the rising of CO₂, different chemical and physical techniques are used [2, 3]. Cryogenic techniques, membrane separation techniques, natural cyclic cycles are some physical techniques that allow carbon dioxide to be removed before or after combustion. However, the removal of carbon dioxide by converting it into more valuable chemicals is the most beneficial approach both environmentally and economically. Catalytic, biocatalytic and photocatalytic conversion of carbon dioxide to chemicals such as methanol, ethanol,

formic acid, dimethyl ether has come to the fore in recent years. Among these techniques, photocatalytic carbon dioxide conversion is the most effective one because of its low energy consumption and safe process.

Photocatalysts are semiconductor materials that are activated under light and cause catalytic reactions. Photocatalysts increase product efficiency as they have high surface area for small particle size. They have advantages such as non-toxic nature and possibilities of environmentally friendly process design. They also increase selectivity for a single chemical synthesis [4]. Photocatalyst classification defined by Nikokavoura & Trapalis [5] is as follows:

- Inorganic: single metal oxides, mixed metal oxides, metal oxide composites, layered double hydroxides and salt composites;
- Carbonaceous: graphene (GR), carbon nanotubes (CNTs) and g-C₃N₄ composites;
- Hybrid organic-inorganic photocatalytic materials.

Low-band gap photocatalysts are preferred as they are easily excitable under visible light. It is common to use additives or incorporate noble metals into the material to create a visible photosensitive catalyst. In addition, physical changes can be made to the catalyst and its support to adjust the photocatalytic performance [6, 7].

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To summarize the ways to develop an effective catalyst, there are two critical points. The first is to increase the visible light absorption by reducing the band gap. The second is to limit the recombination of photoinduced charge carriers [8].

Many photocatalysts have been studied by researchers. It has been reported that semiconductors such as TiO₂, ZnO, CdS and Fe₂O₃ are used as photocatalysts [9]. TiO₂ is the most widely used photocatalyst due to its non-toxicity, high activity and stability. ZnO and CdS are less photoactive than TiO₂ and have some disadvantages such as releasing Cd²⁺ and Zn²⁺ ions into the solution [10].

There are many studies in the literature on the use of TiO₂ as a photocatalyst. The main purpose here is to increase the photocatalytic activity. For this, the surface area of the catalyst must be increased using some supports. In this way, both the photocatalytic surface area and the reaction capacity increase, that is, the conversion efficiency increases. Many materials can be used as supports, such as clays, zeolites, polymers are some of them. In recent years, metal organic cages are preferred as support layers due to their favorable properties.

MOFs are formed by the bonding of metal ions with organic ligand groups. Researches are carried out in many application areas such as gas storage, separation, catalysis, drug release with MOFs. The main features of MOF-based materials are high porosity, high surface area, tunable structure, and multiple active sites. When synthesizing MOFs, they can be designed depending on the way metal ions and organic ligands come together in their structures. Thus, the structures and properties of MOFs can be adjusted during synthesis. Post-synthesis modifications are also possible [11].

Many MOF materials have been used in the literature for carbon dioxide removal. These materials consist of different metal groups [12-15]. In particular, MOF materials containing copper bonded group were found to be successful in chemical reduction. For example, in a study performed by Wang *et al.* [16], CTU/TiO₂ composite photocatalysts were successfully prepared. The resulting composites exhibited significantly improved photocatalytic activity for CO₂ reduction compared to pure TiO₂ or CTU. The outcome of this work has provided new insights into the design of MOF-based hybrid nanomaterials for efficient photoreduction of CO₂ [16]. However, the production values are still not at the desired levels. In particular, the success of the structures with NH₂ end groups in carbon dioxide adsorption has been observed [17-19].

In this study, a TiO₂-supported NH₂ end group copper-based MOF material (TiO₂/Cu-MOF-NH₂) was synthesized for the photocatalytic conversion of carbon dioxide to more valuable chemicals. Basic characterization tests of the synthesized MOF material were carried out. Afterwards, synthetic dye removal studies were carried out to determine its photocatalytic activity.

EXPERIMENTAL

Materials

Aminoterephthalic acid, copper (II) nitrate trihydrate, methylene blue were purchased from Sigma Aldrich. N,N-dimethylformamide (DMF) and methanol solvents were purchased from Merck Chemicals, Turkey.

MOFs preparation

Cu-MOF-NH₂ synthesis. 0.724 g of copper (II) nitrate trihydrate and 1.644 g of aminoterephthalic acid were dissolved in a mixed solvent of DMF and methanol (36/4 ml) under magnetic stirring for 30 minutes. The solution was kept under magnetic stirring at 180 °C for 72 hours. Then it was filtered and washed 3 times with DMF and methanol. Finally, the obtained product was dried in an oven at 80 °C.

TiO₂/Cu-MOF-NH₂ synthesis. 0.7 g of TiO₂, 0.724 g of copper (II) nitrate trihydrate and 1.644 g of aminoterephthalic acid were dissolved in a mixed solvent of DMF and methanol (36/4 ml) under magnetic stirring for 30 minutes. The solution was kept under magnetic stirring at 180 °C for 72 hours. Then it was filtered and washed 3 times with DMF and methanol. Finally, the obtained product was dried in an oven at 80 °C.

Synthetic dye reduction reaction experiment. Methylene blue (MB) was used in the reduction reaction experiment of synthetic dye. The reaction conditions are given in Table 1.

Table 1. Reaction conditions

Reaction conditions	
C _{MB}	10 ppm
V _{reaction}	25 mL
m _{cat}	0.05 g
W _{UV}	46 W
t _{light}	120 min
t _{dark}	120 min

The synthetic dye removal reaction was carried out both in the dark and in the light. For this, two 10 ppm 25 mL dye solutions were prepared at the same time. 0.05 g of photocatalyst was added to the

solutions. One of the solutions was left under UV light and the other in the dark for two hours. Then, the products were centrifuged at 3000 rpm for 4 minutes. Finally, measurements were made by UV-Vis spectroscopy (Shimadzu 1280) at 665 nm.

In order to determine the concentration of MB before and after reaction, a calibration curve was drawn by measuring the absorbance value at different concentrations of MB from 1 ppm to 16 ppm. The curve is given in Fig 1.

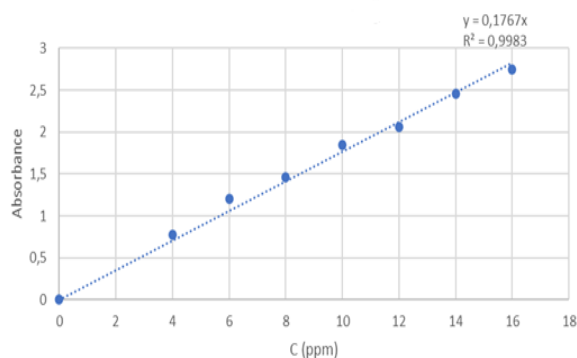


Fig. 1. Methylene blue (MB) calibration chart

The measured values were used in the yield calculation. The equation used to calculate the yield is given below:

$$\% \text{ Yield} = \frac{A_l - A_d}{A_l} \times 100 \quad (1)$$

where A_l is the 'measured' value determined from the methylene blue calibration chart for the absorbance value under light. A_d is the 'measured' value determined from the methylene blue calibration chart for the absorbance value in the dark. Thus, the catalytic efficiency of the photocatalysts was calculated.

In the first stage of the study, the catalyst was prepared with and without TiO₂ and was characterized and compared.

The photocatalyst with TiO₂ was named TiO₂/Cu-MOF-NH₂ and the catalyst without TiO₂ was named Cu-MOF-NH₂. X-ray diffraction test (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) analysis were done. XRD was used to determine the phase structure of photocatalysts (TiO₂/Cu-MOF-NH₂ and Cu-MOF-NH₂), FTIR was used to identify organic functional groups, SEM was used to examine the material surface.

XRD analysis

XRD patterns of TiO₂/Cu-MOF-NH₂ and Cu-MOF-NH₂ photocatalysts are shown in Fig. 2. It is seen that MOF and TiO₂ MOF have crystalline structure and well match with the same family groups of MOFs in the literature. It can be observed that the XRD pattern of TiO₂/Cu-MOF-NH₂ shows diffraction peaks at around 10°, 20°, 24°, 26°, which are corresponding to the MOF structure. The peaks of anatase of TiO₂ are seen around 36°. According to the literature, the 10.30°, 11.84°, 16.82°, 20.67° and 24.73° diffraction peaks of the Cu-MOF-NH₂ photocatalyst at 2θ indicate a crystal structure [20]. Therefore, it can be said that Cu-MOF-NH₂ photocatalysts are in crystalline form. When the XRD pattern of Cu-MOF-NH₂ photocatalysts and TiO₂/Cu-MOF-NH₂ photocatalysts are compared, first large refractions occurred in the Cu-MOF-NH₂ XRD pattern and then the diffractions decreased to a large extent. In TiO₂/Cu-MOF-NH₂ XRD pattern although the diffractions decreased, they were still present. In addition, TiO₂/Cu-MOF-NH₂ photocatalyst has not been synthesized before in the literature. For this reason, there is no source that we can directly compare.

RESULTS AND DISCUSSION

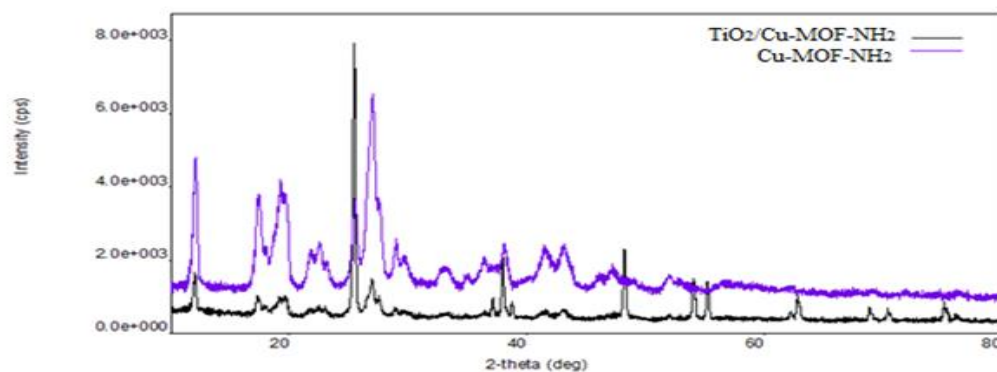


Fig. 2. XRD analysis of TiO₂/Cu-MOF-NH₂ and Cu-MOF-NH₂ photocatalysts.

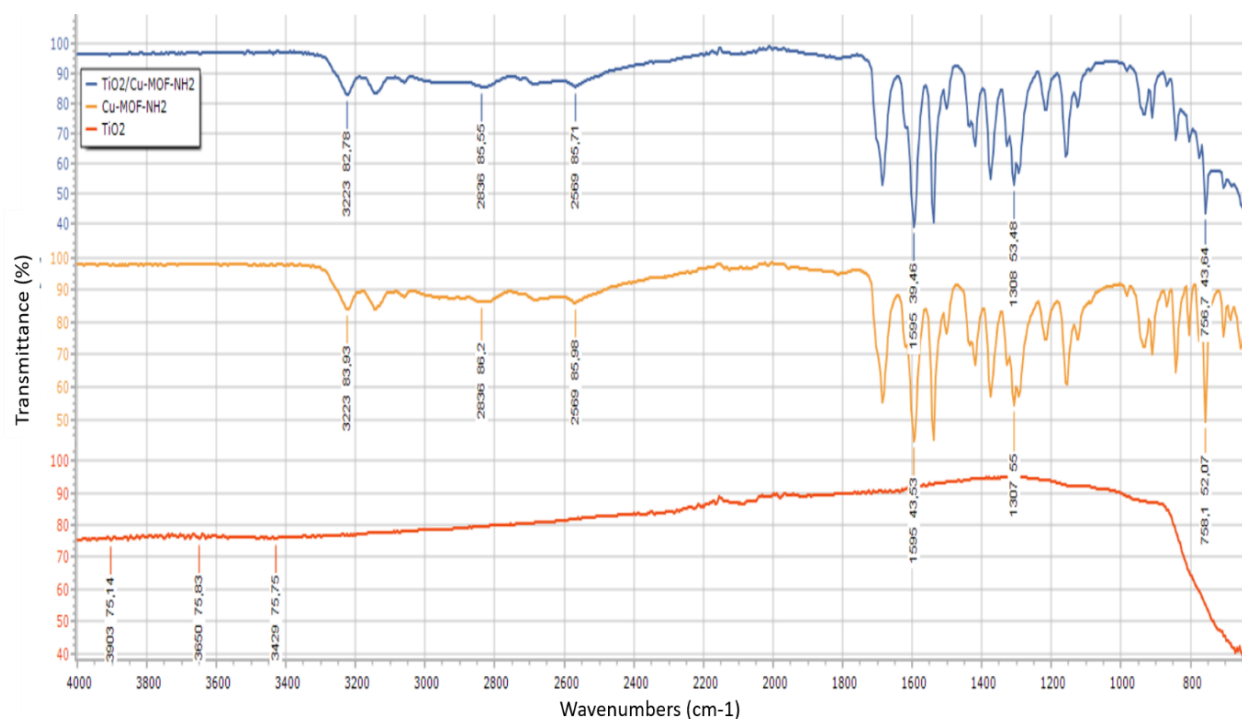


Fig. 3. FTIR analysis of TiO₂/Cu-MOF-NH₂, Cu-MOF-NH₂ and TiO₂.

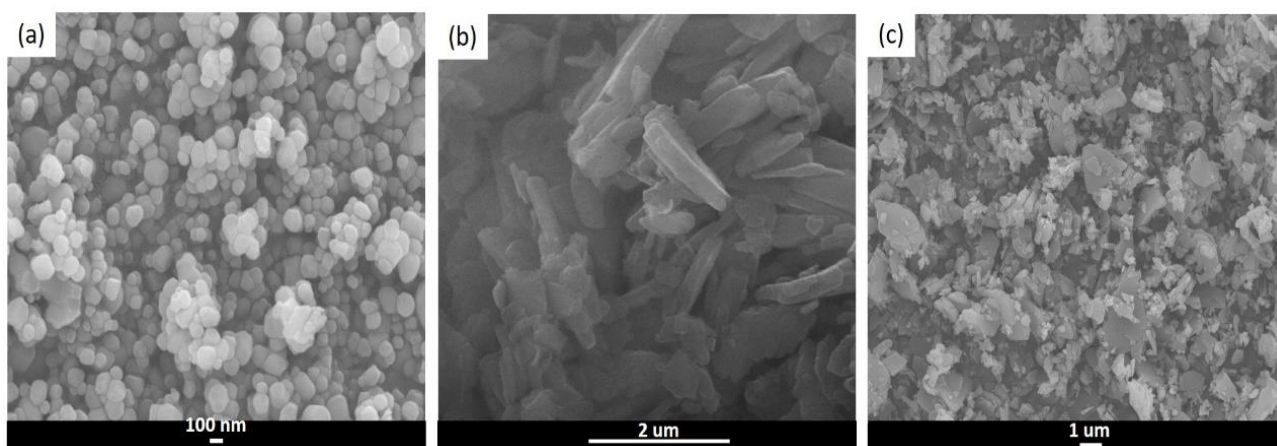
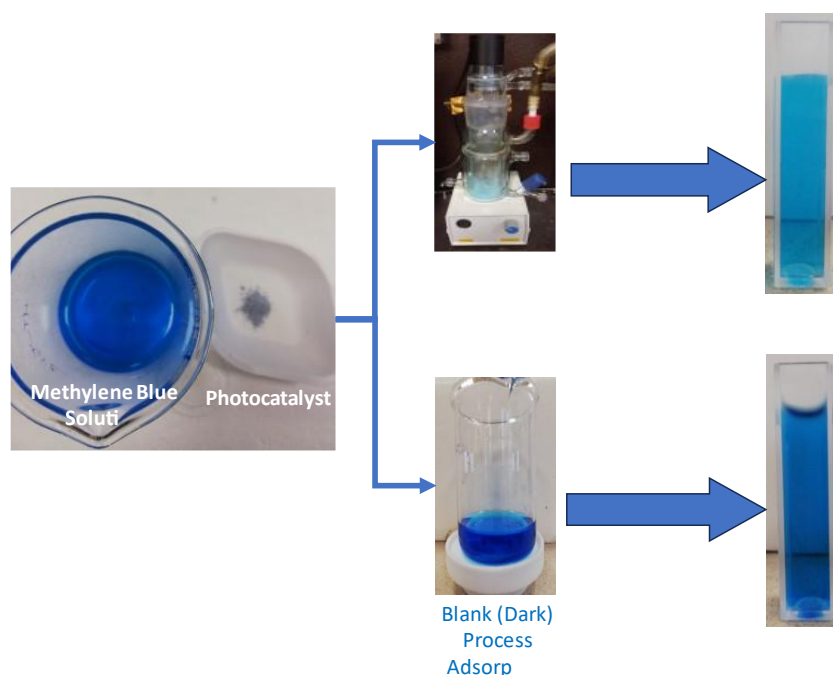


Fig. 4. SEM images of TiO₂ (a), Cu-MOF-NH₂ (b) and TiO₂/Cu-MOF-NH₂ photocatalysts

Table 2. Results of synthetic dye reduction reactions for TiO₂/Cu-MOF-NH₂

	Absorbance value (abs)	Measured (ppm)	Absorbed in the Cat (ppm)	Removal (%)	Reaction yield (%)
TiO ₂ /Cu-MOF-NH ₂ in the dark	1.467	8.30	1.70	17	
TiO ₂ /Cu-MOF-NH ₂ under UV light	1.206	6.83	1.70	31.7	17.79



Scheme 1. Scheme of synthetic dye reduction reaction experiment.

FTIR analysis

FTIR results of TiO₂, Cu-MOF-NH₂ and TiO₂/Cu-MOF-NH₂ photocatalysts are shown in Fig. 3. There are several characteristic peaks of MOF materials in the first two lines. For example; the N-H stretching vibration gives peaks around 3223 cm⁻¹ for both MOFs. The symmetric and asymmetric stretching vibrations of C-H are revealed in the range of 2836 cm⁻¹ and 2569 cm⁻¹, respectively. The C=O stretching vibration peak is seen around 1595 cm⁻¹. The sharp peak at 1307 cm⁻¹ is corresponding to the C-C vibration. The characteristic peak of Cu-O bonding can be seen at around 750 cm⁻¹ for both MOF materials. Since the device used experimentally was ATR (Cary 630 FTIR spectrometer – Agilent), it can measure up to 600 cm⁻¹. TiO₂ bonds are seen below 500 cm⁻¹. Therefore, even if it is not possible to see the direct TiO₂ bonds, it is possible to see the effect below 700 cm⁻¹. A change was observed at the peaks below 700 cm⁻¹ of and TiO₂/Cu-MOF-NH₂ material. In the literature, in MOFs that are directly treated with TiO₂ without modification, an O-H bond at around 3400 cm⁻¹ is observed. In this study, TiO₂ was used after the thermal treatment, therefore, these bonds have disappeared.

SEM analysis

The morphological structures of TiO₂, Cu-MOF-NH₂, and TiO₂/Cu-MOF-NH₂ photocatalysts are seen in Fig. 4. As seen in Figure 4a, TiO₂ particles are completely spherical, homogeneous and nanosized. The structure of the Cu-MOF-NH₂

material has a layered arrangement. Geometric structures are mostly roughly quadrangular. However, there are also round structures. Their length and width are micro sized and their thickness is in the nanoscale (Figure 4b). TiO₂/Cu-MOF-NH₂ material appears as a mixture of TiO₂ and Cu-MOF-NH₂. Both structures can be seen. TiO₂ particles were found to adhere to MOFs throughout all particles. This is an important finding that shows that photocatalysis can do its task. Cu-MOF-NH₂ keeps carbon dioxide in its structure, while TiO₂ provides photocatalytic activity. In this way, it is seen that the catalyst-substrate contact can increase and this can significantly affect the reaction efficiency.

Results of synthetic dye reduction reactions

The photocatalytic activity of the synthesized samples was calculated by measuring the absorption value of methylene blue as it was decomposed by photocatalysts under UV light and the absorption value of the sample in the dark. Thus, the catalytic efficiency of the photocatalysts was found. The absorbance values and photocatalytic efficiency of the photocatalysts are shown in Table 2.

The table shows the results of the experiments carried out in both dark and light conditions. Since there is no photocatalytic reaction in the experiments carried out in the dark, the separation result depends on the adsorption ability of the photocatalyst, while the result seen in the light includes both adsorption and photoreaction. MOF is a microporous material with a very wide active adsorption area. In the BET analyzes performed, the surface area was found to be close to 480 m²/g. This indicates that it is prone to

dye adsorption due to its large surface area. There are already many studies in the literature in which copper-based MOF materials are used as adsorbents [21-24].

In the experiments carried out in the light, both the adsorption and reaction results of the synthesized MOF are included. Since there is also a catalytic effect here, it is not possible to determine how much of the separation value obtained is adsorption. For this reason, 1.7 ppm, 17% separation, which is the value in the dark, was taken as the same type and used at the same rate. The rest of the total separation value of 31.7% was realized as a result of the photocatalytic reaction. This result can be seen in Scheme 1. The color of the dye solution obtained in the experiments performed under UV light is much lighter. As seen in the studies in the literature, the MOF-supported photocatalyst acts as a multifunctional material by performing simultaneously both adsorption and reaction [25-27]. As seen in the table, the photoreaction efficiency was calculated as 17.79%.

CONCLUSION

The accumulation of carbon dioxide (CO₂) creates serious problems in our environment. A solution is needed and one of the solutions developed is CO₂ reduction by a photocatalytic reduction method. Photocatalysis is a method based on the use of catalysts and light. Photocatalysts are very important for the photocatalysis method and new photocatalysts need to be developed. Therefore, we synthesized TiO₂/Cu-MOF-NH₂. The photocatalyst was characterized using FTIR, SEM and XRD tests. According to the results the TiO₂/Cu-MOF-NH₂ was successfully synthesized. The results of the synthetic dye reduction showed that the TiO₂/Cu-MOF-NH₂ photocatalyst has photocatalytic activity. Photocatalytic efficiency of the photocatalyst is 17.79%. Therefore, this study encourages the use and development of TiO₂/Cu-MOF-NH₂ as a photocatalyst.

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