Visible-Light Responsive Cu–MOF–NH₂ for Highly Efficient Aerobic Photocatalytic Oxidation of Benzyl Alcohol

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Abstract—The current study focuses on the photocatalytic oxidation of benzyl alcohol in acetonitrile under air bubbling conditions comparing titania-based materials, Cu–MOF, and Cu–MOF–NH₂ as semiconductor photocatalysts. The catalysts were characterized by XRD, N₂ adsorption–desorption isotherm, FTIR, Raman spectroscopy, and TEM. The photocatalytic benzyl alcohol conversion reached ~100% after exposing the four prepared catalysts to a 125 W mercury lamp for up to 240 min. Benzaldehyde is formed with a moderate selectivity (after a reaction time of 60 min. ca. 30, 37 and 45% over the titania-based catalysts, Cu–MOF, and Cu–MOF–NH₂, respectively). The formation of electron-hole pairs at the surface of the semiconductor nanoparticles followed by oxidation reaction was the suggested mechanism. The initial rate of benzyl alcohol oxidation was 4.6 and 4.7 mmol g⁻¹ min⁻¹ for titania-based materials. Cu–MOF and Cu–MOF–NH₂ showed a higher initial rate of reaction of 6.1 and 9.1 mmol g⁻¹ min⁻¹. According to preliminary research, decorating MOF linker by amine (MOF–NH₂) could improve visible-light harvesting, charge separation, and electron transport of the catalyst, resulting in increased photocatalytic activity. The current work offers some directions for the development of MOF-based photocatalysts for organic synthesis.

Keywords: benzyl alcohol, benzaldehyde, benzyl benzoate, photocatalysis, selective oxidation, Cu–MOF, Cu–MOF–NH₂

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1. INTRODUCTION

Environmentally friendly photocatalytic processes using semiconductors can be considered an integral part of environmentally benign processing [1]. Selective photocatalytic conversion or partial photocatalysis can potentially be applied to the synthesis of fine chemicals, such as oxidation of aromatic alcohols to aromatic aldehydes [2], which are essential intermediates for the synthesis of numerous valuable chemicals. For instance, benzaldehyde is the simplest aromatic aldehyde [3], is used in various applications ranging from an industrial solvent to commercial food flavoring. Furthermore, benzaldehyde is an intermediate in the synthesis of different perfumes and dyes [4–6].

The photocatalytic oxidation of benzyl alcohol has two typical by-products: benzoic acid and benzyl benzoate [7]. The benzoic acid is typically present at a low concentration in the reaction medium (near or under detection limit), because benzoic acid may react with unconverted benzyl alcohol, resulting in the formation of benzyl benzoate [7]. Skupien et al. argued that benzyl benzoate is predominantly produced in the oxidative reaction under base conditions via the esterification of benzyl alcohol with benzaldehyde [8].

Titanium dioxide is a well-known photocatalyst, which has excellent potential as a tool in green organic synthesis [5], for instance, in the oxidation of benzyl alcohol to benzaldehyde [9–11]. The TiO₂ properties,
particularly their crystalline phase, and the mode of adsorption of organic molecules onto its surface are the main factors affecting selective photocatalytic activity [7, 8]. In most photooxidation applications, anatase, pure or mixed with rutile, has a higher photocatalytic activity than pure rutile and brookite [12]. The activity is attributed to a higher density of surface-adsorbed hydroxyl radicals and slower charge carrier recombination in anatase relative to rutile. Indeed, the anatase-rutile mixed-phase TiO₂ (anatase and rutile phases in a 4 : 1 ratio) such as commercial TiO₂ Degussa P25 exhibits the highest photocatalytic activity due to the synergistic effect between anatase and rutile, resulting in an effective separation of photo-induced electrons and holes [13].

Typically, titania absorbs light in the UV range as the band gap of anatase is 3.2 eV and that of rutile is 3.0 eV. Shifting the absorption from UV light to visible light would increase solar light utilization, since UV light accounts for only 4%. As a result, the presence of rutile in an anatase-forming mixture may be responsible for increasing the TiO₂ anatase phase towards light absorptivity in the visible range [14].

Metal-organic frameworks (MOFs) are an attractive class of porous crystalline materials consisting of metal ions and polyfunctional organic linkers that possess several desired properties, such as high specific surface areas, large pore volumes, and structural flexibility and adaptability. These properties allow MOFs to be used in different applications, including adsorption and separation [12], heterogeneous catalysis [12], drug delivery [15], and sensing [16]. Recently, MOFs were used as photocatalysts due to their tunable properties for light absorption and the capability to incorporate various functional components in a single MOF material. MOFs are regarded as semiconductor-like materials, with the metal cluster as the conduction band and the organic linker as the valence band [17]. Furthermore, for various photocatalytic reactions, the highly crystalline nature of MOFs results in a fast electron and energy transfer from the photoexcited MOFs to the active sites [18]. Cu–MOF was found as a UV-responsive photocatalyst, because it acts as a wide-band semiconductor [19]. A convenient and viable method to improve, enhance, boost, develop or reinforce the optical characteristics of MOFs is to decorate the organic linkers or metal centers, thereby controlling chemical and physical characteristics of photocatalysts at the molecular level. However, the photocatalytic efficiency of pure MOF is limited, so the decoration of linkers or metal centers with semiconductors and/or metal nanoparticles (NPs) is necessary. The amine group (NH₂) linker decoration has shown a beneficial photocatalytic activity to selectively oxidize organic compounds [18]. The linker decorating may modify the bandgap energy of MOFs to a certain level. For example, stronger electron-donating substitutes such as amines dramatically lower the bandgap, shifting the photo absorption edge from the ultraviolet to visible light area [20–23].

Here, we report on the selective photocatalytic aerobic oxidation of benzyl alcohol using TiO₂ (pure anatase), TiO₂ (anatase : rutile = 4 : 1), Cu–MOF and Cu–MOF–NH₂ catalysts under irradiation with visible light. In particular, we have focused on the mechanisms of the selective photocatalytic oxidation of benzyl alcohol to benzaldehyde and benzyl benzoate.

2. EXPERIMENTAL

2.1. Material Synthesis

2.1.1. Preparation of TiO₂ nanoparticles by sol–gel method. Titanium dioxide nano-catalysts were prepared by the sol–gel method using titanium tetraisopropoxide, TTIP (97%, Sigma–Aldrich). The TiO₂ : isopropanol (i-PrOH) : pH modifier molar ratio was 2 : 22.5 : 3. The pH value was adjusted by adding either glacial acetic acid until pH 3–4.5 or an ammonium hydroxide solution (ACS reagent, NH₄OH, 28.0–30.0%) until pH 7–9. The mixture was sonicated for 1 h. During this time partial hydrolysis and polymerization occurred producing a transparent, homogeneous, and stable solution. After gelation for 24 h, the final gel material was dried overnight at 110°C and subsequently calcined at 550°C for 4 h to produce the desired TiO₂ photocatalyst. The catalysts were designated according to the pH range: TiO₂(A) in the acidic medium and TiO₂(B) in the basic medium.

2.1.2. Synthesis of Cu₃(BTC)₂⋅3H₂O. 1,3,5-Benzene tricarboxylic acid (BTC, 21 mmol) and Cu(NO₃)₂⋅3H₂O (12 mmol) were dissolved in a mixture of 125 mL N,N-dimethylformamide (DMF), ethanol and deionized water (1 : 1 : 1) and sonicated for 15 min in a 300 mL glass jar. Then jar was transferred into the microwave (700 W), and the sample was irradiated for 4 min. Blue crystals were formed upon cooling the mixture to room temperature. The product was washed three times with DMF and then with chloroform three times. The product was dried under vacuum at 100°C overnight. The produced sample was coded as Cu–MOF.

2.1.3. Functionalization of Cu₃(BTC)₂⋅3H₂O by ethylenediamine (ED). Pristine Cu–MOF was dehydrated at 110°C for 24 h before the functionalization. The dehydrated Cu–MOF (0.5 g) was suspended in 30 mL of anhydrous toluene. Ethylenediamine (5 mmol) was added to this suspension, and then it was refluxed for 12 h under continuous stirring [20]. The product was filtered off and washed with deionized water. Eventually, the sample was then dried at 110°C overnight and coded as MOF–Cu–NH₂.

2.1.4. Characterization methods. Powder X-ray diffraction (XRD) analysis has been carried out with a X’Pert PRO instrument (PANanalytical, Netherlands) using CuKα radiation (λ = 1.540 Å) to investi-
gate crystal phase structure and crystalline domain size of the catalysts

The specific surface area was calculated from the \( \mathrm{N}_2 \) adsorption–desorption isotherms at liquid nitrogen temperature (−196○C) using a Nova 3200 S automated gas sorption apparatus (Quantachrome, USA). Before measurements, all samples were degassed overnight at 150○C and evacuated to \( 1.3 \times 10^{-3} \) Pa.

Raman spectra of as-prepared \( \mathrm{TiO}_2 \) (A and B) catalysts were evaluated from 10 to 2000 cm\(^{-1} \) at room temperature using a SENTERRA Dispersive Raman Microscope (Bruker, Germany) equipped with a diode Nd: YAG laser at 532 nm with a maximum laser power of 60 mW on the sample.

The Fourier-transform infrared (FTIR) spectra were recorded in the transmission mode between 500–4000 cm\(^{-1} \) with an FTIR spectrometer Perkin Elmer (model spectrum one FTIR spectrometer, USA). Samples were prepared using standard 1% KBr pellets.

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The UV–Vis diffuse reflectance spectra (DRS) of the samples over a range of 200–800 nm were recorded by a UV-2600 (Shimadzu, Japan) spectrophotometer with BaSO\(_4\) as a reference.

### 3. RESULTS AND DISCUSSION

#### 3.1. Catalysts Characterization

The XRD patterns of the synthesized titania are shown in Fig. 1. The mass fractions of anatase and rutile were estimated from the reflection of anatase (101) at \( \theta = 25.48^\circ \) and the (110) reflection of rutile at \( \theta = 27.58^\circ \) by the formula below [26]:

\[
\chi_{\text{rutile}} = \frac{I_{\text{rutile}}}{I_{\text{rutile}} + 0.79I_{\text{anatase}}},
\]

where \( \chi_{\text{rutile}} \) is the weight fraction of rutile in the \( \mathrm{TiO}_2 \), and \( I_{\text{rutile}} \) and \( I_{\text{anatase}} \) are the intensities of the X-ray diffraction lines for rutile and anatase, respectively. On the other hand, the size of the crystalline domain of each of the phases is calculated by using the Scherrer equation (4):

\[
D = \frac{0.9\lambda}{\beta \cos \theta},
\]

where \( D \) is the crystallite thickness, \( \lambda \) is X-ray wavelength, \( \beta \) is FWHM (full width at half max), and \( \theta \) is Bragg angle.

The XRD pattern of titania synthesized under acidic conditions \( \mathrm{TiO}_2(A) \) consists of 82.6 wt % anatase and 17.4 wt % rutile forms, while the XRD pattern for the titania synthesized under basic conditions \( \mathrm{TiO}_2(B) \) showed that it was pure anatase. The behavior can be explained by considering the effect of pH: in a strongly acidic medium, rutile dominates over anatase and brookite due to the change of surface properties [27]. In other words, the resistance of anatase transformation to rutile is stronger in a basic medium than in an acidic medium at the same calcination temperature (550○C) [28]. The average size of the anatase crystalline domain according to the Scherrer equation in \( \mathrm{TiO}_2(A) \) was 16.8 nm (using the reflection at \( \theta = 25.48^\circ \)); the average size of the rutile domain was similar (15.2 nm determined using the reflection at \( \theta = 27.58^\circ \)). The crystalline domain of anatase in the sample synthesized under basic conditions \( \mathrm{TiO}_2(B) \) was slightly smaller (13 nm). The difference in the average size of the crystalline domain is related to the growth mechanism: the preparation of \( \mathrm{TiO}_2 \) from TTIP
included two major steps, viz. hydrolysis, followed by condensation, which is also compatible with the preparation of silica from tetraethoxy silane [29]. The hydrolysis is acid catalyzed, whereas the condensation reaction seems to base-catalyzed. This means that the number of monomers is large under acidic conditions, and at basic conditions, the rate of crystal growth is large. Smaller crystals are more prone to sinter thus resulting after calcination at 550°C in a material with larger sizes of the crystalline domains.

Figure 2 displays simulated and measured XRD patterns of pristine Cu–BTC and Cu–MOF–NH₂. Materials Studio 7.0 software was used to build the XRD pattern for the simulated Cu–BTC [30]. Obviously, all diffraction peaks of the synthesized sample coincide with the simulated ones implying that the produced Cu–BTC is highly purified and crystalline [30]. Additionally, the XRD patterns of the Cu–MOF–NH₂ sample perfectly resemble the simulated pattern, indicating that the preparation procedure did not alter the framework topology or texture. However there are some slight variations of the Bragg intensities at 2θ = 14°, 16° and 40° produced by a structural damage [17, 21]. Furthermore, the unforeseen peak of 6° could be attributed to crystal defects forming during the reflex process [31].

The N₂ adsorption–desorption isotherms and pore size distribution of Cu–MOF and Cu–MOF–NH₂ are shown in Figs. 4a, 4b and the data is presented in Table 1. Cu–MOF has a type (I) isotherm, a feature of microporous substances without a significant contribution of meso and macroporosity. In comparison, the sample Cu–MOF–NH₂ shows a type (IV) isotherm with mesoporous substances. The BET surface area decreases from 1405 to 54 m²/g after NH₂ grafting, indicating that the pores become inaccessible upon modification with ethylenediamine. This is further exemplified by decreasing the total pore volume from 0.95 cm³/g (Cu–MOF) to 0.14 cm³/g (Cu–MOF–NH₂). That is in agreement with the previously reported data [20].

The Raman spectra of the prepared TiO₂(A) and TiO₂(B) are shown in Fig. 5 at the frequency range of 100–1000 cm⁻¹. In TiO₂(A) catalyst prepared in acidic medium, two peaks at 418.8 and 609 cm⁻¹ are observed, corresponding to the E_g and A_1g vibrational modes of rutile TiO₂. On the other hand, four peaks are at a high relative pressure \( P/P^0 = 0.47–0.93 \), thus indicating mesoporous materials [32]. The titania sample prepared under basic conditions, TiO₂(B), has a higher specific surface area (82 m²/g) and a higher pore volume (0.17 cm³/g) than titania prepared under acidic conditions, TiO₂(A) (S_BET = 65 m²/g and V_pore = 0.13 cm³/g). The difference seems to be related to the smaller crystalline domains obtained in TiO₂(B) compared to TiO₂(A).
appearing at 149.1 cm$^{-1}$ ($E_g$, main peak), 398.6 cm$^{-1}$ ($B_{1g}$), 516.2 cm$^{-1}$ ($A_{1g} + B_{1g}$), and 637.3 cm$^{-1}$ ($E_g$) are observed in TiO$_2$(B) samples which correspond to the symmetric modes for anatase phase of TiO$_2$ crystal [27]. This result agrees with the XRD data.

The FTIR experiment was carried out to investigate the intermolecular interactions between ED molecules and MOFs. Figure 6 shows FTIR spectra of the pristine Cu–MOF and the Cu–MOF–NH$_2$ samples. Note that the spectral band for both samples displays high homogeneity, and the major peaks of both samples agree well with the published FTIR spectra for Cu–MOF [24]. The FTIR patterns show absorption bands at 3368 and 2940 cm$^{-1}$ due to $\nu$(O–H) vibration of the absorbed water and $\nu$(CH$_2$) vibrations, and absorption at 3500–3000 cm$^{-1}$ is due to $\nu$(OH) or $\nu$(NH). The vibrational peaks between 2999 and 2850 cm$^{-1}$ are assigned to the C–H stretching vibrations in both materials. However, some variations are noticed, and by comparing with the FTIR of ethylene diamine [25], the spectrum of the Cu–MOF–NH$_2$ shows new absorption peaks at 3305 and 3215 cm$^{-1}$ which can be assigned to the asymmetric and symmetric stretching vibrations of the N–H bond [20] and peaks at 1033 and 1550 cm$^{-1}$ which can be attributed to the C–N group [26].

The TEM photographs obtained for both TiO$_2$ samples prepared at acidic and basic media are shown in Figs. 7a, 7b. It is seen that both samples exhibit particles mainly in the form of rhombohedral and hexagonal prisms with random shapes rather than regular spherical particles. Furthermore, the TEM image of TiO$_2$(A) shows the appearance of spotty sharp rings indicative of polycrystalline materials with the presence of the rutile phase.

Table 1. Average size of the crystalline domain, BET-surface area, pore volume and the adsorption capacity properties of the photocatalysts

| Sample         | $D_{XRD}^a$, nm | $S_{BET}^b$, m$^2$ g$^{-1}$ | $V_p^c$, cm$^3$ g$^{-1}$ | Adsorption capacity$^c$, % | Adsorption capacity/m$^2$ | d |
|----------------|-----------------|-----------------------------|--------------------------|----------------------------|---------------------------|---|
| TiO$_2$(A)     | 16.2 (An);      | 65                          | 0.13                     | 9.9                        | 0.15                      |   |
|                | 15.2 (Ru)       |                             |                          |                            |                           |   |
| TiO$_2$(B)     | 13 (An)         | 82                          | 0.17                     | 16.3                       | 0.20                      |   |
| Cu–MOF         | 8               | 1405                        | 0.95                     | 24.6                       | 0.02                      |   |
| Cu–MOF–NH$_2$  | 14              | 54                          | 0.14                     | 44.1                       | 0.82                      |   |

$^a$Average size of the crystalline domain as determined using the Scherrer equation (An – anatase phase, Ru – rutile phase). $^b$Surface area ($S_{BET}$) and pore volume ($V_p$) from BET-isotherm. $^c$Fraction of benzyl alcohol adsorbed from a benzyl alcohol solution ([Benzyl alcohol] = 500 mg/L solid content: 1 g/L). $^d$Adsorption capacity/m$^2$ = adsorption capacity %/surface area.
In the inset images for the selected area electron diffraction patterns (SAED) of TiO$_2$(A) and TiO$_2$(B) (Figs. 7a, 7b), there is five SAED rings that represent anatase phase indexed as (101), (004), (200), (105), and (211) (JCPDS no. 21-1272). Furthermore, in TiO$_2$(A), the appearance of one more ring points out to the presence of the rutile phase indexed as (110) in addition to five rings of anatase.

Figures 7c, 7d show the TEM images of Cu-MOF and Cu–MOF–NH$_2$. Cu–MOF has a distinct morphology, whilst the morphology of Cu–MOF–NH$_2$ seems to be an embedded material with small particles in a matrix. Zhong et al. attributed the morphological change to solvent squeezing during the reflux processes [24].

### 3.2. Photocatalytic Oxidation of Benzyl Alcohol

Prior to studying benzyl alcohol oxidation, its adsorption on all prepared samples was investigated by exposing the catalyst to benzyl alcohol solution in the dark (500 mg of benzyl alcohol per gram of solid) (see Fig. 8 and Table 1).

The data indicate that TiO$_2$(B) (pure anatase) has a higher adsorption capacity than TiO$_2$(A) (a mix of anatase and rutile) due to larger surface area, higher
surface hydroxyl group density [5] and smaller average size of the crystalline domains. However, the increase is stronger than that could be due to the increase in the surface area. The surface hydroxyl group density increases with increasing surface area [5] and this may lead to the enhanced adsorption of benzyl alcohol on TiO$_2$(B) in comparison to TiO$_2$(A). In addition, the adsorption capacity of rutile for organic compounds (e.g., benzyl alcohol) is lower than that of anatase [27].

Similarly, both Cu–MOF and Cu–MOF–NH$_2$ display a high capacity for adsorption owing to the porous-like heterostructure. However, the measured adsorption capacity of Cu–MOF–NH$_2$ is about double the measured adsorption capacity of the unmodified Cu-MOF, despite the much smaller surface area and pore volume. The average pore diameter of Cu–MOF is much smaller than the average pore diameter of Cu–MOF–NH$_2$ and this may induce diffusion limitations in the uptake measurement and the equilibrium may not have been attained in a contacting time of 30 min.

The photooxidation of benzyl alcohol was monitored on catalysts TiO$_2$(A), TiO$_2$(B), Cu–MOF, and Cu–MOF–NH$_2$ as a function of time under irradiation with visible light emitted from the mercury lamp at room temperature in the presence of O$_2$. This reaction was completed within 240 min in acetonitrile solution as a solvent. Figure 9 shows that all catalysts exhibit good catalytic performance in the photooxidation of benzyl alcohol to benzoic acid and benzyl benzoate as the main products. The only observed products were benzoic acid and benzyl benzoate (Figs. 10 and 11).

Extrapolation of the conversion time graph indicates that the intercept is below zero. Hence, the conversion as a function of time is increasing strongly in the first 15 min of reaction ($t < 15$ min). Such an increase is characteristic for an autocatalytic reaction. This may be caused by the reaction of the product (benzoic acid) with the reactant (benzyl alcohol) thereby enhancing the rate of benzyl alcohol conversion via the creation of benzyl benzoate [4].

Increasing the reaction time (up to 240 min) increases the benzyl alcohol conversion with a modest increase in the selectivity for benzyl aldehyde and accordingly a modest decrease in the selectivity for benzyl benzoate. This is not accompanied by an increase in the formation of benzoic acid, and hence the decrease in the selectivity towards benzyl benzoate is not due to the reverse esterification of benzoic acid with benzyl alcohol. Thus, the decrease in benzyl benzoate selectivity is attributed to an increase in the rate
of formation of benzaldehyde at the increased conversion of benzyl alcohol as the reaction period increases.

The difference in performance of catalysts TiO$_2$(A) and TiO$_2$(B) for the photocatalytic oxidation of benzyl alcohol in terms of activity and selectivity is negligible (Figs. 9–11) despite the difference in the phase composition and the available surface area. The obtained activity and selectivity may be attributed to the presence of acetonitrile (CH$_3$CN) as a solvent to prevent the generation of non-selective ·OH radicals. Superoxide anion radicals of ·O$_2^-$ are generated from O$_2$ according to the valence band potential of the catalysts. This radical attack on benzyl alcohol results in the formation of a carbon radical that reduces Ti(IV) to Ti(III) via electron transfer. Both radicales cause fast oxidation of benzaldehyde to benzoic acid and subsequent esterification to benzyl benzoate [8].

The performance of Cu–MOF and Cu–MOF–NH$_2$ in the photooxidation of benzyl alcohol yielding benzyl aldehyde and benzyl benzoate is quite different (especially at the beginning of the reaction up to 60 min). Cu–MOF–NH$_2$ exhibits a higher catalytic activity and selectivity towards benzaldehyde formation.

The reaction kinetics of the selective photocatalytic oxidation of benzyl alcohol to benzaldehyde is investigated to understand the intrinsic activities of the catalysts. The conversion rate in the first 60 min of the reaction is seemingly independent of the conversion, and hence the initial rates were determined from the
slope of the conversion-time graphs and the reaction appears to exhibit a first order kinetics (Eq. (5)).

\[ -r_{\text{benzyl alcohol}} = C_0 \left( \frac{dX}{dr} \right)_{\text{initial}} = -\left( \frac{dC}{dr} \right)_{\text{initial}}, \tag{5} \]

where \( C_0 \) is the initial concentration of benzyl alcohol and \( X \) is the conversion of benzyl alcohol. The initial activity of TiO\(_2\)(A) and TiO\(_2\)(B) are virtually the same (initial rates are 4.6 and 4.7 mmol g\(^{-1}\) min\(^{-1}\), respectively). Cu–MOF and Cu–MOF–NH\(_2\) have a higher initial rate of reaction (6.1 and 9.1 mmol g\(^{-1}\) min\(^{-1}\)). The higher reactivity of the MOFs compared to titania may be attributed to the change in the catalytic active surface area and to the difference in the band gap of the materials.

The band gap width for titania is ca. 3.0–3.2 eV. Figure 12 shows the UV–Vis diffuse reflectance spectra of Cu–MOF and Cu–MOF–NH\(_2\). The optical absorption edge for Cu–MOF is estimated at 320 nm, and the calculated optical band gap of Cu–MOF is 3.9 eV based on the relationship \( E_g = \frac{1240}{\lambda} \) [19]. This implies that Cu–MOF will absorb a smaller fraction of the light emitted by the mercury lamp compared to titania catalysts. This would imply a low reactivity of this material in the photocatalytic conversion of benzyl alcohol, but the much higher surface area counters this.

![Fig. 8. Adsorption of benzyl alcohol adsorbed from a benzyl alcohol solution ([Benzyl alcohol] = 500 mg L\(^{-1}\), solid content: 1 g L\(^{-1}\)) for prepared catalysts in the dark (equilibration time 30 min).](image1)

![Fig. 9. Photooxidation of benzyl alcohol on TiO\(_2\)(A), TiO\(_2\)(B), Cu–MOF, and NH\(_2\)–Cu–MOF as a function of time under irradiation with visible light at room temperature in the presence of O\(_2\) (150 mL of 500 mg L\(^{-1}\) of benzyl alcohol and 1 g L\(^{-1}\) of catalyst; bubbling air, 25 mL/min).](image2)

![Fig. 10. Selectivity of benzaldehyde as a function of reaction time (150 mL of 500 mg L\(^{-1}\) benzyl alcohol and 1 g L\(^{-1}\) of catalyst; bubbling air, 25 mL min\(^{-1}\); Hg-lamp).](image3)
A linker decoration such as an amine modifies the bandgap and therefore the absorption energy moves from the ultraviolet to the visible region. The amino decoration acts as an auxochromic and bathochromic group in the aromatic ring, leading to the absorption wavelength shift of Cu–MOF [12]. Thus, introducing NH2-groups reduces the bandgap from 3.9 to 2.6 eV, causing a red shift of absorption edges. This is in line with the predictions by Sliva et al. [33], who proved that inserting NH2 in UiO-66 decreased the band gap due to changes in the linker and the nonbonding oxygen near the metalloid cluster. The emitting radiation of the 125 W mercury lamp is in the range of 200 to 420 nm [30]. Therefore, only the light from 200 to 320 nm can be utilized for pristine Cu–MOF. For the Cu–MOF–NH2 catalyst, the light from 200 to 420 nm can be utilized.

Furthermore, the maximum emission of the mercury lamp is at 365 nm, i.e., the light source intensity is the strongest at around 365 nm, allowing a greater light utilization. Therefore, the Cu–MOF–NH2 can absorb more light than the pristine Cu–MOF. As a result, the amine linker decoration improved light utilization capability, which resulted in increased activity for the photocatalytic conversion of benzyl alcohol despite the decrease in the surface area.

MOFs can be used as conventional semiconductor photocatalysts that can be excited when irradiated to create electrons and holes. Decoration of MOF linker by NH2 can result in electron-rich clouds, which produce (e−−h+) pairs. It is suggested that accelerated electron migration and high photocatalytic activity are obtained for Cu–MOF–NH2 due to an amine group adjacent to the organic linker. The electron is placed in the Cu-oxo clusters, whereas the hole is located in the amino terephthalate unit, specifically, the amino group, which further enhances the electron transfer pathway in photo-excited Cu–MOF–NH2 [31, 36]. Liu et al. [37] showed that ZIF-8 MOF showed significantly higher photocatalytic activity in the photocatalytic reduction of Cr(IV) compared to titania due to the high Cr(VI) adsorption property of ZIF-8 and more efficient charge transfer compared to pristine TiO2 beads.

The MOF may absorb incident photons under visible light irradiation. The photogenerated carriers then migrate to the MOF surface and take part in the redox reaction. The adsorbed oxygen is reduced to superoxide radicals (’O2) by photogenerated electrons, and the photogenerated holes (h+) on the MOF surface induce benzyl alcohol to release protons directly under the help of (’O2) which results in benzaldehyde. In other words, the holes on the catalyst surface initially generate benzyl alcohol cation radicals [25]. Indeed,
the absence of benzoic acid in the GC analysis indicates that, once benzoic acid is formed, it reacts directly with benzyl alcohol which is present in much higher concentrations to form benzyl benzoate.

4. CONCLUSIONS

Photocatalytic oxidation of benzyl alcohol to carbonyl compounds using titania-based materials, Cu–MOF and Cu–MOF–NH$_2$ under mercury lamp irradiation in aerated acetonitrile has been carried out. The performance of different titania catalysts is virtually identical despite the differences in the phase composition and surface area. Cu–MOF is more active than titania, although the effectiveness of light adsorption from the mercury lamp on these materials is less than that on titania. The increased activity is attributed to the much higher surface area of this material which may compensate the reduced light absorption. Modification of Cu–MOF with ethylene diamine allows absorption of light at much higher wavelengths, thus increasing light absorption efficiency. This results in an increased activity despite a strong reduction in the surface area. These results made MOFs and functionalized MOFs promising materials for exceptional chemical preparation.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Jeong, N.C., Farha, O.K., and Hupp, J.T., Langmuir, 2011, vol. 27, no. 5, p. 1996.
2. Alenzi, N., Liao, W.-S., Cremer, P.S., Sanchez-Torres, V., Wood, T.K., Ehlig-Economides, C., and Cheng, Z., Int. J. Hydrogen Energy, 2010, vol. 35, no. 21, p. 11768. https://doi.org/10.1016/j.ijhydene.2010.08.020
3. Li, Q., Guo, B., Yu, J., Ran, J., Zhang, B., Yan, H., and Gong, J.R., J. Am. Chem. Soc., 2011, vol. 133, no. 28, p. 10878. https://doi.org/10.1021/ja2025454
4. Augugliaro, V., Kisch, H., Loddo, V., López-Muñoz, M.J., Márquez-Alvarez, C., Palmisano, G., Palmisano, L., Parrino, F., and Yurdaka, S., Appl. Catal., A, 2008, vol. 349, no. 1, p. 182. https://doi.org/10.1016/j.apcata.2008.07.032
5. Li, C., Xu, G., Zhang, B., and Ru, J., Appl. Catal., B, 2012, vols. 115–116, p. 201. https://doi.org/10.1016/j.apcatab.2011.12.003
6. Ling, C., Ye, X., Zhang, J., Zhang, J., and Zhang, S., Sci. Rep., 2016, vol. 7, p. 1. https://doi.org/10.1038/s41598-017-00055-5
7. Nagy, G., Gál, T., Sránkó, D.F., Sáfrán, G., Maróti, B., Sajó, I.E., Schmidt, F.-P., and Beck, A., Mol. Catal., 2020, vol. 492, p. 110917. https://doi.org/10.1016/j.mcat.2020.110917
8. Skupien, E., Berger, R.J., Santos, V.P., Gascon, J., Makkee, M., Kreutzer, M.T., Kooyman, P.J., Moulijn, J.A., and Kaptueijn, F., Catalysts, 2014, vol. 4, p. 89. https://doi.org/10.3390/catal4020089
9. Shiraishi, Y. and Hirai, T., J. Photochem. Photobiol., C, 2008, vol. 9, no. 4, p. 157. https://doi.org/10.1016/j.jphotchem.2008.05.001
10. Marci, G., García-López, E.I., and Palmisano, L., Fine chemistry by TiO$_2$ heterogeneous photocatalysis, in Metal Oxides, Parrino, F. and Palmisano, L., Eds., Amsterdam: Elsevier, 2021, p. 609.
11. Song, H., Liu, Z., Wang, Y., Zhang, N., Xu, X., Guo, K., Xiao, M., and Gai, H., Green Energy Environ., 2019, vol. 4, no. 3, p. 278. https://doi.org/10.1016/j.gene.2018.09.001
12. Tian, J., Zhao, Z., Kumar, A., Boughton, R.I., and Liu, H., Chem. Soc. Rev., 2014, vol. 43, no. 20, pp. 6920–6937. https://doi.org/10.1039/C4CS00180J
13. Kafizas, A., Kafizas, A., and Parkin, I.P., J. Am. Chem. Soc., 2011, vol. 133, no. 50, pp. 20458–20467. https://doi.org/10.1021/ja208633g
14. Coronado, J.M., Maira, A.J., Conesa, J.C., Yeung, K.L., Augugliaro, V., and Soria, J., Langmuir, 2001, vol. 17, no. 17, p. 5368. https://doi.org/10.1021/la010153f
15. Horcajada, P., Chalati, T., Serre, C., Gillet, B., Sebrie, C., Baati, T., Eubank, J.F., Heurtaux, D., Clayette, P., Kreuz, C., Chang, J.-S., Hwang, Y.K., Marsaud, V., Bories, P.-N., Cynober, L., et al., Nat. Mater., 2010, vol. 9, no. 2, p. 172. https://doi.org/10.1038/nmat2608
16. Lu, Z.-Z., Zhang, R., Li, Y.-Z., Guo, Z.-J., and Zheng, H.-G., J. Am. Chem. Soc., 2011, vol. 133, no. 12, p. 4172. https://doi.org/10.1021/ja109437d
17. Wang, D. and Li, Z., J. Catal., 2016, vol. 342, p. 151. https://doi.org/10.1016/j.jcat.2016.07.021
18. Wang, D. and Li, Z., Catal. Sci. Technol., 2015, vol. 5, no. 3, p. 1623. https://doi.org/10.1039/C4CY01464B
19. Chen, L., Tang, J., Song, L.-N., Chen, P., He, J., Au, C.-T., and Yin, S.-F., Appl. Catal., B, 2019, vol. 242, p. 379. https://doi.org/10.1016/j.apcatb.2018.10.025
20. Hoover, J.M., Ryland, B.L., and Stahl, S.S., J. Am. Chem. Soc., 2013, vol. 135, p. 2357. https://doi.org/10.1021/ja3117203
21. Ryland, B.L. and Stahl, S.S., Angew. Chem. Int., Ed. Engl., 2014, vol. 53, no. 34, p. 8824. https://doi.org/10.1002/anie.201403110
22. Taher, A., Kim, D.W., and Lee, I., RSC Adv., 2017, vol. 7, p. 17806. https://doi.org/10.1039/c6ra28743c
23. Hu, Q., Di, J., Wang, B., Ji, M., Chen, Y., Xia, J., and Li, H., Appl. Surf. Sci., 2019, vol. 466, p. 525. https://doi.org/10.1016/j.apsusc.2018.10.020
24. Zhong, R., Yu, X., Meng, W., Han, S., Liu, J., Ye, Y., Sun, C., Chen, G., and Zou, R., Chem. Eng. Sci., 2018, vol. 184, p. 85. https://doi.org/10.1016/j.ces.2017.12.040
25. Wu, L., An, S., and Song, Y.F., *Engineering,* 2021, vol. 7, no. 1, p. 94.  
https://doi.org/10.1016/j.eng.2020.07.025

26. Spurr, R.A. and Myers, H., *Anal. Chem.*, 1957, vol. 29, no. 5, p. 760.  
https://doi.org/10.1021/ac60125a006

27. Velardi, L., Scrimieri, L., Serra, A., Manno, D., and Calcagnile, L., *Appl. Phys. A,* 2019, vol. 125, no. 10, p. 735.  
https://doi.org/10.1007/s00339-019-3038-2

28. Abdel-Azim, S.M., Aboul-Gheit, A.K., Ahmed, S.M., El-Desouki, D.S., and Abdel-Mottaleb, M.S.A., *Int. J. Photoenergy,* 2014, vol. 2014, p. 687597.  
https://doi.org/10.1155/2014/687597

29. Mahshid, S., Askari, M., and Ghamsari, M.S., *Mat. Process. Technol.,* 2007, vol. 189, p. 296.  
https://doi.org/10.1016/j.matprotec.2007.01.040

30. Wang, Y., Cao, W., Wang, L., Zhuang, Q., and Ni, Y., *Mikrochim. Acta,* 2018, vol. 185, p. 315.  
https://doi.org/10.1007/s00604-018-2857-8

31. Abd El Salam, H.M., Younis, S.A., Ali, H.R., and Zaki, T., *Microporous Mesoporous Mater.,* 2017, vol. 241, p. 210.

32. El-Ashgar, N.M., El-Nahhal, I.M., Chehimi, M.M., Babonneau, F., and Livage, J., *Int. J. Environ. Anal. Chem.,* 2009, vol. 89, p. 1057.

33. Wickenheisser, M., Jeremias, F., Henninger, S.K., and Janiak, C., *Inorg. Chim. Acta,* 2013, vol. 407, p. 145.

34. Colmenares, J.C., Ouyang, W., Ojeda, M., Kuna, E., Chernyayeva, O., Lisovytksi, D., De, S., Luque, R., and Balu, A.M., *Appl. Catal., B,* 2016, vol. 183, p. 107.

35. Santaclara, J.G., Nasalevich, M.A., Castellanos, S., Evers, W.H., Spoor, F.C.M., Rock, K., Siebbeles, L.D.A., Kapteijn, F., Grozema, F., Houtepen, A., Gascon, J., Hunger, J., and van der Veen, M.A., *ChemSusChem,* 2016, vol. 9, p. 388.

36. Cliffe, M.J., Wan, W., Zou, X., Chater, P.A., Kleppe, A.K., Tucker, M.G., Wilhelm, H., Funnell, N.P., Coudert, F.-X., and Goodwin, A.L., *Nat. Commun.,* 2014, vol. 5, p. 4176.  
https://doi.org/10.1038/ncomms5176

37. Liu, X., Dang, R., Dong, W., Huang, X., Tang, J., Gao, H., and Wang, G., *Appl. Catal., B,* 2017, vol. 209, p. 506.