

Preparation and Characterization of CuFe₂O₄/TiO₂ Photocatalyst for the Conversion of CO₂ into Methanol under Visible Light

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I. INTRODUCTION

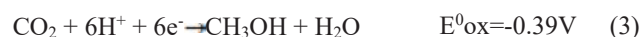
Abstract—A systematic study was conducted to explore the photocatalytic reduction of carbon dioxide (CO₂) into methanol on TiO₂ loaded copper ferrite (CuFe₂O₄) photocatalyst under visible light irradiation. The phases and crystallite size of the photocatalysts were characterized by X-ray diffraction (XRD) and it indicates CuFe₂O₄ as tetragonal phase incorporation with anatase TiO₂ in CuFe₂O₄/TiO₂ hetero-structure. The XRD results confirmed the formation of spinel type tetragonal CuFe₂O₄ phases along with predominantly anatase phase of TiO₂ in the CuFe₂O₄/TiO₂ hetero-structure. UV-Vis absorption spectrum suggested the formation of the hetero-junction with relatively lower band gap than that of TiO₂. Photoluminescence (PL) technique was used to study the electron-hole (e⁻/h⁺) recombination process. PL spectra analysis confirmed the slow-down of the recombination of electron-hole (e⁻/h⁺) pairs in the CuFe₂O₄/TiO₂ hetero-structure. The photocatalytic performance of CuFe₂O₄/TiO₂ was evaluated based on the methanol yield with varying amount of TiO₂ over CuFe₂O₄ (0.5:1, 1:1, and 2:1) and changing light intensity. The mechanism of the photocatalysis was proposed based on the fact that the predominant species of CO₂ in aqueous phase were dissolved CO₂ and HCO₃⁻ at pH ~5.9. It was evident that the CuFe₂O₄ could harvest the electrons under visible light irradiation, which could further be injected to the conduction band of TiO₂ to increase the life time of the electron and facilitating the reactions of CO₂ to methanol. The developed catalyst showed good recycle ability up to four cycles where the loss of activity was ~25%. Methanol was observed as the main product over CuFe₂O₄, but loading with TiO₂ remarkably increased the methanol yield. Methanol yield over CuFe₂O₄/TiO₂ was found to be about three times higher (651 μmol/g_{cat} L) than that of CuFe₂O₄ photocatalyst. This occurs because the energy of the band excited electrons lies above the redox potentials of the reaction products CO₂/CH₃OH.

Keywords—Photocatalysis, CuFe₂O₄/TiO₂, band-gap energy, methanol.

COMBUSTION of fossil fuel can be considered as the main power source for the growth of human civilization and no wonder, fossil fuel is the largest single source of energy consumed by the world's population. The reliance on fossil fuel for rapid industrialization cause unavoidable CO₂ emission [1]-[3]. CO₂ is the most concentrated greenhouse gas emitted by many industries, e.g. urea fertilizer industry, produce 100% CO₂ in flue gas [4], [5]. Therefore, carbon capture, storage and conversion into hydrocarbon technologies are drawing the attention of many researchers [3], [6].

Numerous methods have been explored to convert CO₂, such as hydrothermal, electrochemical and photochemical reduction of CO₂ to hydrocarbons. Hydrothermal reduction process requires high temperature (~450°C) and pressure (25 MPa), hence it is energy intensive and costly [5], [7], [8]. The reduction of CO₂ by photocatalysts is one of the most promising methods for CO₂ reduction into methanol, especially under visible light irradiation [9-12].

Titanium dioxide (TiO₂), the most commonly used photocatalyst, is active under UV-light due to its large bandgap (~3.2 eV). Various methods have been studied to reduce the bandgap of TiO₂, such as doping with metals, non-metals and composite semiconductors on to TiO₂ [2], [7], [13]. The pre-requisites for the visible light active catalyst for the selective conversion of CO₂ to methanol under visible light are as follows: increased visible light absorption by decreasing the band gap [1], efficient charge separation and most importantly, the shift of the conduction band (CB) to more negative regions than the standard potentials for CO₂ reduction reactions [1], [8], [14]. The following reactions occur in the aqueous phase during CO₂ reduction to methanol [3], [9], [11]:



So far, a variety of semiconductors including TiO₂ loaded composite and others catalysts like CdS/TiO₂, FeTiO₃/TiO₂, CuO-TiO₂, Pt-TiO₂/MgO, TiO₂/ZnO, AgBr/TiO₂, Cu/TiO₂, RuO₂/TiO₂ etc. have been reported as photocatalysts and these

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types of hetero-junction helps to enhance the CO₂ reduction in aqueous phase reaction [7], [9], [15]-[17].

In our recent work, we demonstrated that the nanostructured CuFe₂O₄ and its further combination with TiO₂ can efficiently reduce CO₂ to methanol under visible light [18]. However, the effect of TiO₂ loading in the CuFe₂O₄/TiO₂, light intensity and catalyst loading on methanol yield has never been reported. In this study, CuFe₂O₄/TiO₂ photocatalysts were synthesized with different CuFe₂O₄/TiO₂ ratio and their photocatalytic activity for CO₂ reduction under visible light was evaluated. The recyclability of the catalysts has also been investigated.

II. EXPERIMENTAL PROCEDURE

A. Materials

Copper nitrate, Cu(NO₃)₂·3H₂O (99%), iron nitrate, Fe(NO₃)₃·9H₂O (99%), Nitric acid, HNO₃ (65%), KOH, Agar, commercial TiO₂, KOH, and NaNO₂ were of analytical grade (R&M Marketing, Essex, UK) and used without further purification.

B. Catalyst Synthesis

CuFe₂O₄ photocatalyst was prepared using sol-gel method with slight modification of reaction conditions reported by [1]. For the preparation of CuFe₂O₄ catalyst, required amount of Cu(NO₃)₂·3H₂O and Fe(NO₃)₃·9H₂O were dissolved in 400 mL of water which contained HNO₃ (2M) and 4 g agar, and the solution was retained for 3 h under continuous stirring at room temperature. Thereafter, the temperature was raised to 90 °C and stirred for ~3 h, where a green gel was obtained. The gel was dried at 130 °C under vacuum for 24 h and grinded in a mortar. The powder was calcined at 900 °C with a heating rate of 10 °C/min for 14 h as recommended by [1], [8], [19]. To prepare CuFe₂O₄/TiO₂ photocatalyst, CuFe₂O₄ was dispersed in 50 mL distilled water using ultrasound bath (Brand: Elmasonic S; Model: S10/S10H) and thereafter required amount of commercial TiO₂ was added. The ultrasonication was continued for another 1 h. In further, the suspension was dried overnight at 100 °C in an oven. Afterward, the mixture was grinded and calcined at 700 °C for 3 h in tubular furnace under N₂ gas atmosphere.

C. Instrumentations

The XRD patterns of the powders were obtained at room temperature using Rigaku MiniFlex II at Bragg angle of 2θ = 3-80° with a scan step of 0.02°. The measurements were performed at 30 kV and 15 mA using Cu-Kα emission and a nickel filter. The crystallite size of the prepared nanocomposite was also determined from the XRD spectra and the size was calculated by using the Scherrer formula [20]:

$$D = \frac{K\lambda}{B \cos \theta} \quad (4)$$

where, D is the coherent scattering length (crystallite size), K is a constant related to crystallite shape whose value is

approximately 0.9 [20], λ is the X-ray wavelength of Cu-Kα radiation source = 0.15418 nm and B (in rad) is the full width at half-maximum (FWHM) of the peak, determined by Gaussian fitting. The morphologies of the prepared photocatalysts were observed by field emission scanning electron microscope (FE-SEM: model JEOL JSM-5410LV, Japan). Energy dispersive X-ray spectrometer (EDX) (5.0 kV) in connection with SEM was used to identify and analyze the elemental composition of photocatalysts. EDX patterns were also obtained using a JEOL JSM-7600, USA. UV-Vis absorption spectra of the samples were obtained by employing Shimadzu UV 2600 UV-Vis-NIR spectrophotometer. The N₂ adsorption-desorption experiments were conducted at 77 K in (Micromeritics ASAP 2020) Specific surface area (S_{BET}) of monolayer coverage was determined using Brunauer-Emmett-Teller (BET) method. Finally, the recombination rate of the photogenerated electron-hole pairs (e⁻/h⁺) was estimated using Perkin Elmer LS 55 Luminescence spectrophotometer. The catalysts are separated by centrifuging at 10000 rpm for 5 min using eppendorf centrifuge 5810 R.

Methanol in aqueous phase was analyzed by using Agilent gas chromatography (GC) with a flame ionization detector (FID) and the investigation was performed with Shimadzu, column DB-WAX 123-7033 (30 m×0.32 mm, 0.50 μm) and injected with a 7694 E headspace auto sampler.

D. Photocatalytic Activity

The photocatalytic reduction of CO₂ was performed in a continuous-flow reactor system as presented in Fig. 1. A reaction chamber was irradiated with a 500 W xenon lamp (light intensity 240 W/m²) located in the middle of a quartz cool trap. Sodium nitrite solution (2M) was circulated through the quartz trap to cut the UV light in the range of 320 nm and 400 nm [9], [21], [22]. Firstly, 300 mL of distilled water was poured into the reactor and 1.2 g of KOH was dissolved in it to raise the pH to 12. Required amount of catalyst was added into the reactor to maintain the catalyst loading in the range of 0.5-2 g/L. Ultrapure CO₂ gas was bubbled through the solution for at least 1 h to ensure that all dissolved oxygen was eliminated and the pH of the solution was recorded as ~5.9. Thereafter, the lamp was switched on to start the photoreaction. The CO₂ was continuously bubbled throughout the process (8 h). The liquid sample was withdrawn using the vacuum pump and centrifuged at 10000 rpm for 5 min using Eppendorf centrifuge 5810 R. The supernatant was analyzed by GC-FID method.

III. RESULTS AND DISCUSSION

A. XRD Analysis

The XRD patterns of as-prepared CuFe₂O₄ and CuFe₂O₄/TiO₂ photocatalysts are shown in Figs. 2 and 3, respectively. Fig. 2 illustrates that the diffraction patterns of the CuFe₂O₄ can be readily indexed as CuFe₂O₄ that has a good matching with JCPDS database (peak position of 101,112, 200, 202, 211, 220, 321, 224, 400, and 422). The spectra of the sample also indicate the presence of trace

amount of CuO (JCPDS 110, 200) phases. Fig. 3 illustrates the diffraction peaks of the CuFe₂O₄/TiO₂ photocatalysts that were calcined at 700°C and it also represents tetragonal,

anatase TiO₂ (JCPDS 111, 102, 021, 022, 230, 620, 502, 532), and tetragonal CuFe₂O₄ (JCPDS 112, 202, 402, 221, 200, 312, 321, 224, 116 and 422).

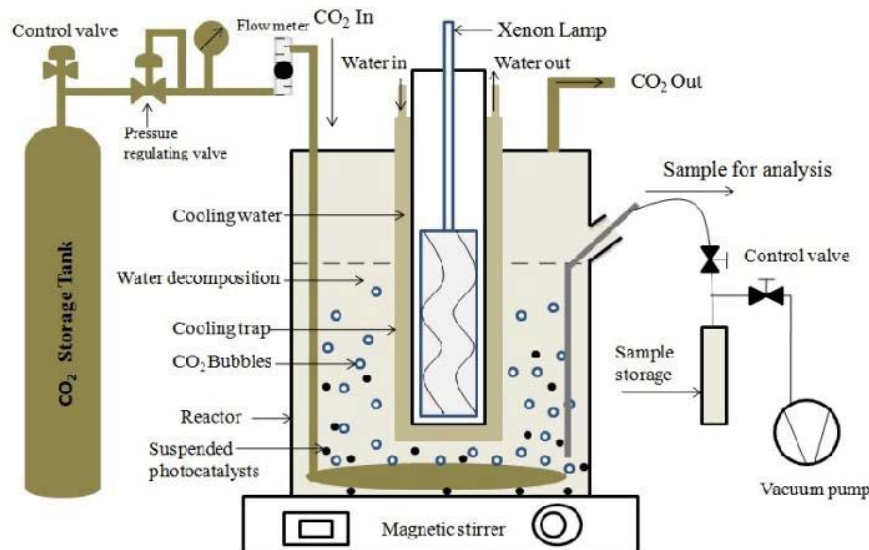


Fig. 1 Experimental setup for the photocatalytic conversion of CO₂ into methanol

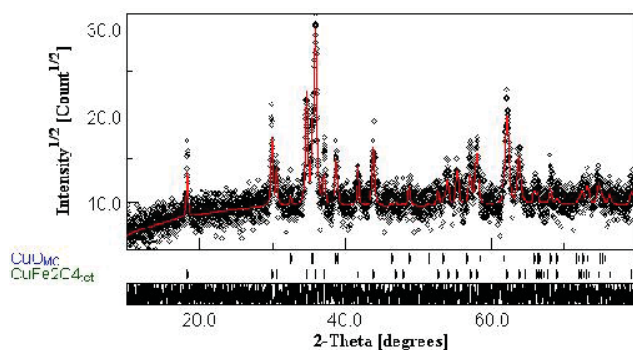


Fig. 2 XRD of as-prepared CuFe₂O₄

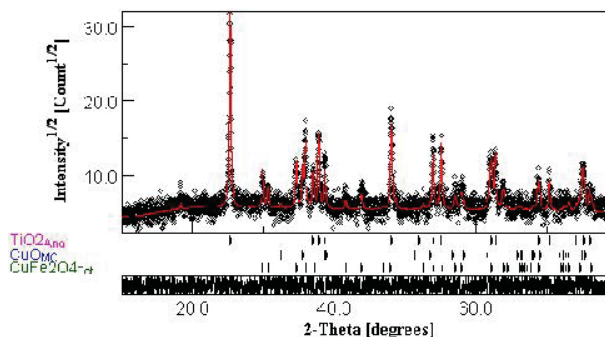


Fig. 3 XRD of as-prepared CuFe₂O₄-TiO₂

TABLE I
CRYSTALLOGRAPHIC PARAMETERS OF AS-PREPARED CuFe₂O₄ AND CuFe₂O₄/TiO₂ EXTRACTED FROM RIETVELD ANALYSIS

Sample	Phases	Composition (wt%)	symmetry	Space group	Lattice constant (Å)			Crystallite size (nm)	Microstrain	R%
					a	b	c			
CuFe ₂ O ₄	CuFe ₂ O ₄	85.33	Tetragonal	I41/amd:1	5.839	--	8.656	59	15.37E-4	16.65
	CuO	14.67	Monoclinic	C2/c:b1	4.688	3.425	5.135	67	4.02E-4	
	CuFe ₂ O ₄	18.06	Tetragonal	I41/amd:1	5.834	--	8.677	64	12.21E-4	
CuFe ₂ O ₄ /TiO ₂	CuO	9.34	Monoclinic	C2/c:b1	4.688	3.426	5.134	98	3.38E-4	19.55
	Anatase TiO ₂	72.60	Tetragonal	I41/AMDS	3.786	--	9.514	108	2.21E-4	

According to the Scherrer formula in (4) the crystallite size of CuFe₂O₄ and CuFe₂O₄/TiO₂ photocatalysts were to be ~59 nm and ~108 nm (TiO₂) evaluated at $2\theta = 36.161^\circ$ (maximum intense peak). The crystallite size of TiO₂ in prepared CuFe₂O₄/TiO₂ is higher (~19%) than that of CuFe₂O₄. A detailed description of phase constitution, lattice constants and micro structural parameters for as prepared samples is reported in Table I, as obtained from Rietveld refinement with a R% of about 16–20%. Together with the presence of tetragonal CuFe₂O₄ (85.33 wt%), the formation of a small

amount of monoclinic CuO (14.67 wt%) is observed. In both cases, the lattice constants of CuFe₂O₄ are very similar to those reported in the crystallographic database (ICDD 340425) and that of CuO (ICDD 10706830) is reported as $a_0 = 4.684$, $b_0 = 3.425$ and $c_0 = 5.129$ Å. Anatase phase of TiO₂ of space group I41/AMDS observed at room temperature diffraction pattern and crystallographic parameters are very close to available database (ICDD 211272, $a_0 = 3.789$ and $c_0 = 9.537$ Å). Rietveld refinement shows that the as-prepared nanocomposite is free from more stable rutile TiO₂. It is, in

general, accepted that anatase shows more activity than rutile, in most photocatalytic reaction systems [23], may be due to the fact that the Fermi level of anatase is higher than that of rutile and slow recombination of e^- and h^+ [24].

B. UV-Vis Spectroscopy

The UV-Vis spectroscopy of the as-prepared CuFe_2O_4 and $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ and commercial TiO_2 in the wavelength range of 250-1400 nm has been presented in Fig. 4 (a). Fig. 4 (a) shows transparency for wavelengths above 400, 480, 1010 nm which represents the visible light activity of the prepared photocatalysts. Plotting $(\alpha h\nu)^2$ versus $h\nu$ (Catalysts are presented as a direct transition) [25] based on the spectral response from Fig. 4 (a) gives the extrapolated intercept corresponding to the band gap energy value as shown in Fig. 4 (b), and Plotting $(\alpha h\nu)^{1/2}$ versus $h\nu$ (indirect transition) as shown in Fig. 4 (c). Figs. 4 (b) and (c) depict the band-gap of commercial TiO_2 (3.1 eV), $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ (2.61 eV), and CuFe_2O_4 (1.24 eV). The optical band gap energy of $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ is 2.61 eV which also display lower value compared to TiO_2 (3.1 eV). Kezzim et al. [1] reported the band gap of CuFe_2O_4 synthesized via sol-gel approach as 1.42 eV. Ahmed et al. [26] studied the suitable UV-visible light region (300-430 nm) for photocatalytic reduction of CO_2 into methanol. When a metal or composite is doped or loaded to the other composite, the previous band-gap was shifted to a new band-gap [2], [7]. In our prepared $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ catalyst, the absorption edge of TiO_2 shifted from 400 to 480 nm due to the loading effect. A small shoulder exists at 350 to 367 nm as shown in Fig. 4 (a) for the $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ photocatalyst; it may be due to the interaction of TiO_2 with CuFe_2O_4 . The band gap of the recycled (after 4-time use, e.g. 4th recycle) catalyst was found to be shifted towards higher band gap (2.71 eV), might be due to the leaching of CuO or CuFe_2O_4 from the hetero-junction, which could not be confirmed in the present paper.

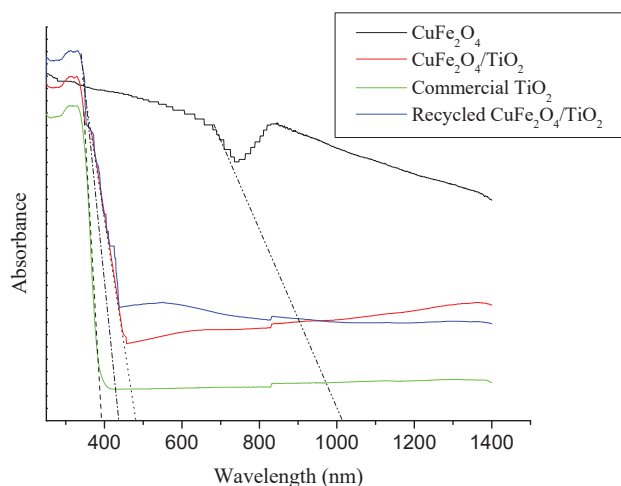


Fig. 4 (a) UV-Vis spectrum of prepared photocatalysts, the wavelength range was 250–1400 nm

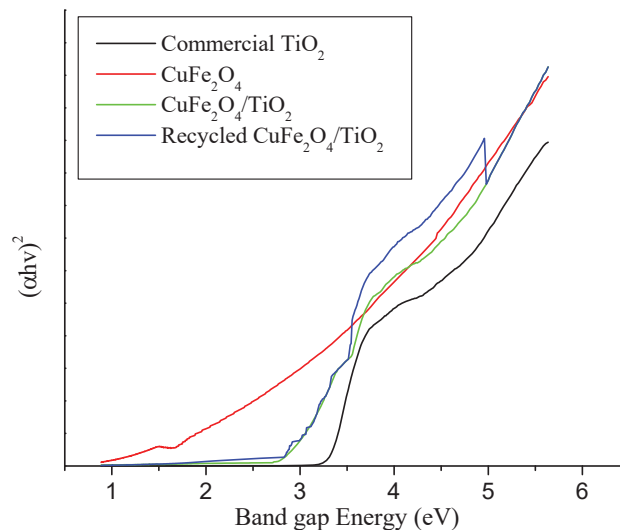


Fig. 4 (b) Band gap energy calculation of prepared photocatalysts (direct transition)

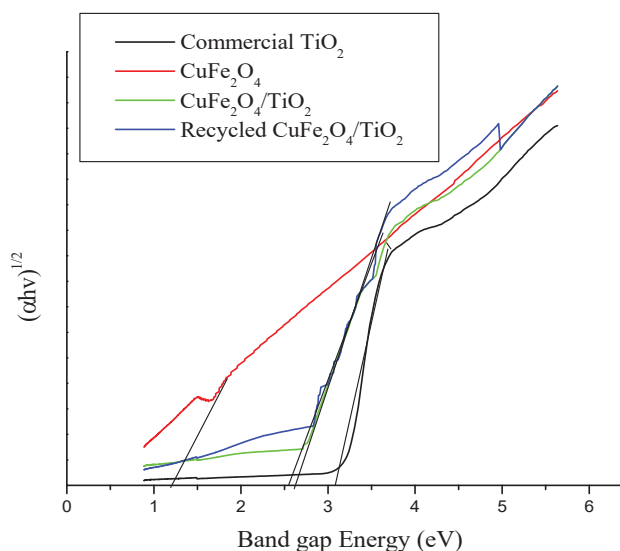


Fig. 4 (c) Band gap energy calculation of prepared photocatalysts (indirect transition)

C. PL Spectroscopy

The electron-hole (e^-/h^+) recombination process studied by PL spectroscopy. Fig. 5 compares PL spectra for CuFe_2O_4 and $\text{CuFe}_2\text{O}_4/\text{TiO}_2$, commercial TiO_2 and recycled $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ catalyst (after four cycle of recycling process). $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ photocatalyst exhibited a wide and strong PL signals in the range of 400-480 nm with the excited wavelength of 350 nm. The spectral peak located at 421 and 475 nm corresponds to anatase TiO_2 and effect of TiO_2 loading on CuFe_2O_4 while two peaks at 450 and 466 nm are attributed to the transition from the oxygen vacancies with two and one trapped electron to the CuFe_2O_4 conduction band (CB), respectively. However, TiO_2 band is more intense while the $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ band intensities gradually weakened suggesting the lowering of e^-/h^+ recombination due to the CuFe_2O_4 loading with TiO_2 . Furthermore, the recycled (after 4-time use, e.g. 4th recycle)

catalyst showed low PL intensity, but needed longer wavelength (very close to the TiO₂ spectrum), suggesting the loss of visible light active CuFe₂O₄ or CuO from the system. The result is consistent with the UV-Vis finding.

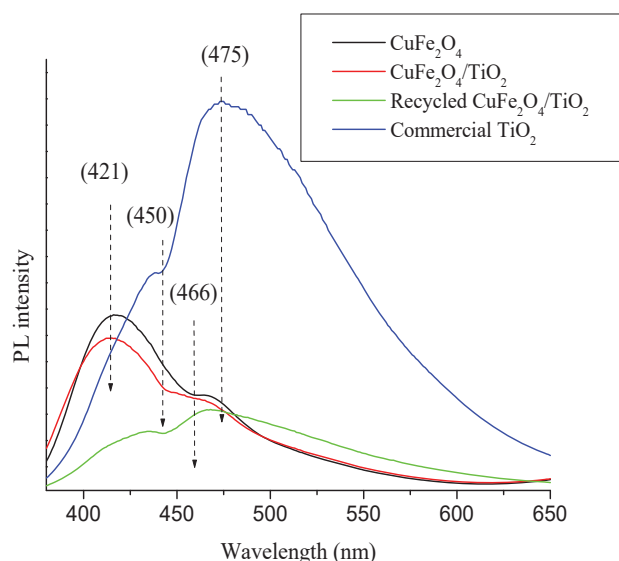


Fig. 5 PL emission spectra of CuFe₂O₄, CuFe₂O₄/TiO₂, commercial TiO₂ and recycled CuFe₂O₄/TiO₂ catalyst (after four cycle of recycling process) photocatalysts; Excitation at 350 nm

D. Adsorption Isotherms, Surface Area (BET) and EDX Analysis

BET and EDX analysis of CuFe₂O₄ and CuFe₂O₄/TiO₂ is presented in Table II. The BET method is widely used for measuring the specific surface area of catalyst as presented in Fig. 6. Fig. 6 exhibits the N₂ adsorption-desorption isotherms of CuFe₂O₄ and CuFe₂O₄/TiO₂ photocatalysts. The mesoporous structure of CuFe₂O₄ and CuFe₂O₄/TiO₂ samples without surface directing agents were evidently due to the controlled hydrolysis process. Furthermore, the initial part of the isotherms (at low P/P₀) is related to the monolayer-multilayer adsorption on the internal surface. However, at higher P/P₀, the steep increment in the adsorption volume is attributed to the capillary condensation as the pores were saturated with liquid. This finding indicated that capillary condensation of nitrogen was occurred within the pores of the catalyst. The obtained BET surface area, average pore diameter and specific pore volume of CuFe₂O₄ were 1.49 m²g⁻¹, 33.62 Å and, 0.0012 cm³g⁻¹, and the BET surface area, average pore diameter and specific pore volume of CuFe₂O₄/TiO₂ were 1.98 m²g⁻¹, 255.24 Å, and 0.013 cm³g⁻¹, respectively. The low surface area for metal ferrites was also reported in literatures. The BET surface area of NiFe₂O₄ was 2.13 m²g⁻¹ and Co and Mn ferrite BET surface area was 2 m²g⁻¹ [27]-[29].

TABLE II
SURFACE AREA AND EDX ANALYSIS OF BARE CuFe₂O₄ AND TiO₂ LOADED CuFe₂O₄/TiO₂ SAMPLES

Sample	Surface area(m ² g ⁻¹)	Average pore diameter (Å)	Specific pore volume (cm ³ g ⁻¹)	Surface elemental contents ^a (wt.%)			
				Cu	Fe	O	Ti
CuFe ₂ O ₄	1.48	33.62	0.0012	21	57	22	-
CuFe ₂ O ₄ /TiO ₂ (1:1 wt. ratio)	1.98	255.24	0.013	15.1	48.2	30.5	6.2

^a Surface elemental contents calculated using EDX

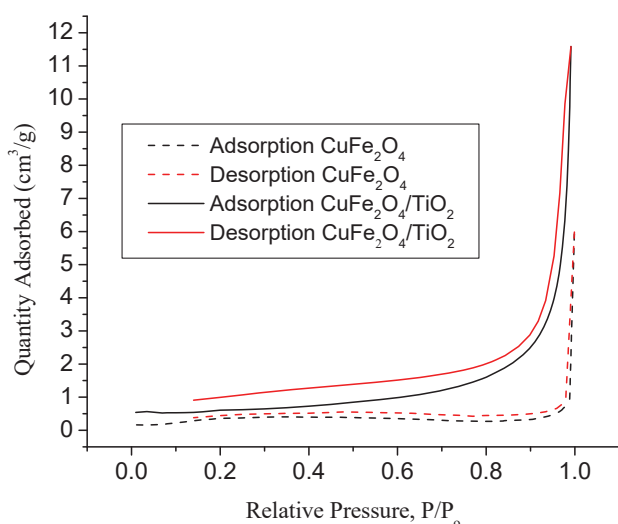
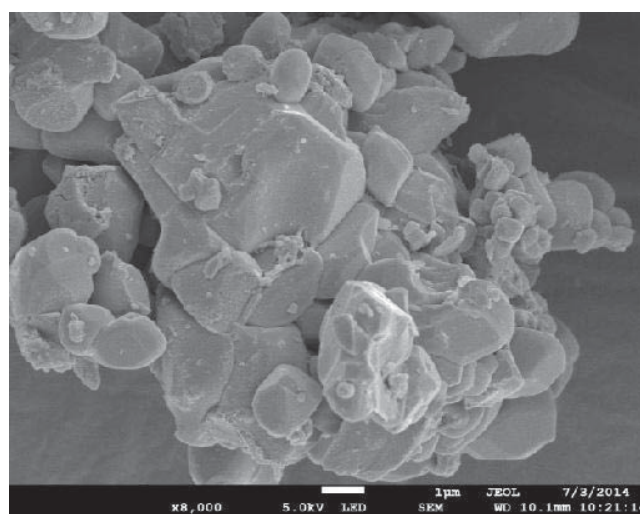


Fig. 6 N₂ adsorption-desorption isotherm of CuFe₂O₄ and CuFe₂O₄/TiO₂ photocatalyst

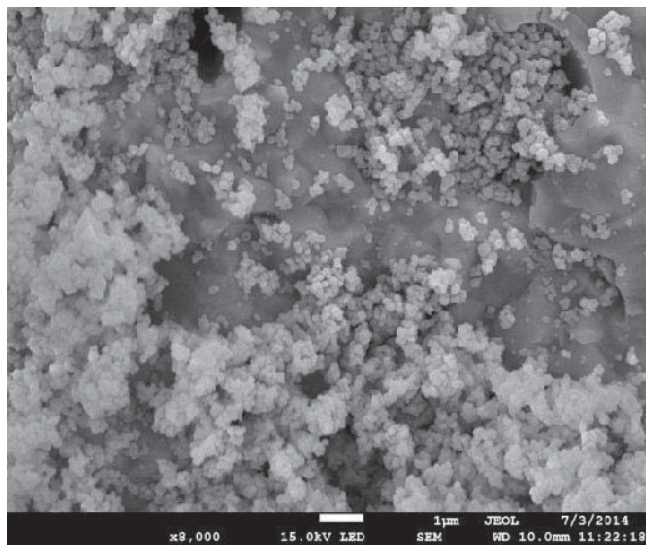
E. FE-SEM Analysis

Figs. 7 (a) and (b) portray the FE-SEM micrographs of CuFe₂O₄ and CuFe₂O₄/TiO₂ photocatalysts. The uniform shape

of the mesoporous spherical particles can be attributed to the CuFe₂O₄ crystal growth due to controlled gel formation process. EDX analysis confirmed the appearance of peaks of Cu, Fe, O, Ti in the CuFe₂O₄ and TiO₂ loaded CuFe₂O₄ sample.



(a)



(b)

Fig. 7 FE-SEM micrograph of (a) CuFe_2O_4 and (b) $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ prepared by sol-gel method

F. Photocatalytic Reduction of CO_2 : Effect of TiO_2 Loading on CuFe_2O_4

The photocatalytic reduction of CO_2 and successive formation of methanol was investigated over a period of 8 h irradiation on $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ and CuFe_2O_4 photocatalysts as shown in Fig. 8. The experimental result showed the methanol as the main product in the liquid phase. Hydrogen, CO, formaldehyde, ethane and ethylene could also be formed according to the reports in the literature [6], [9], [26], but they were undetectable in our case. Fig. 8 depicts that the highest methanol yield ($651 \mu\text{mol}/\text{g}_{\text{cat}} \text{L}$) was obtained for $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ (1:1 weight ratio) photocatalyst, compare to that of ($220 \mu\text{mol}/\text{g}_{\text{cat}}$) CuFe_2O_4 after 8 h of reaction. A slight decline of the catalyst activity after 6h of reaction, both catalysts indicated the unavailability of the active sites or the deactivation of the catalyst. The yield of methanol with $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ for the photocatalytic reduction of CO_2 under visible light was significantly higher than the results presented in literature [6].

G. Photocatalytic Reduction of CO_2 : Effect of Catalyst Loading for CO_2 Reduction

To study the effect of catalyst loading on methanol yield, the catalyst loading was varied from 0.5 to 2 g/L. The results are presented in Fig. 9. From the figure, the methanol yield was increased with the increase in catalyst loading. The highest yield of methanol for $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ photocatalyst was $695 \mu\text{mol}/\text{g}_{\text{cat}}\text{L}$ at 2 g/L catalyst loading after 6 h irradiation. In comparison with the 1 g/L catalyst loading the methanol yield was increased only 6.8% by doubling the catalyst amount into the solution. According to the figure, in case of increasing the catalyst loading from 0.5 g/L to 1 g/L, methanol production was drastically raised to around 70% but further increasing of catalyst loading yield was not significant might be due to the exhaustion of the active sites. The result is consistent with the literature finding where 1 g/L showed the

optimum methanol yield [7], [22], [30].

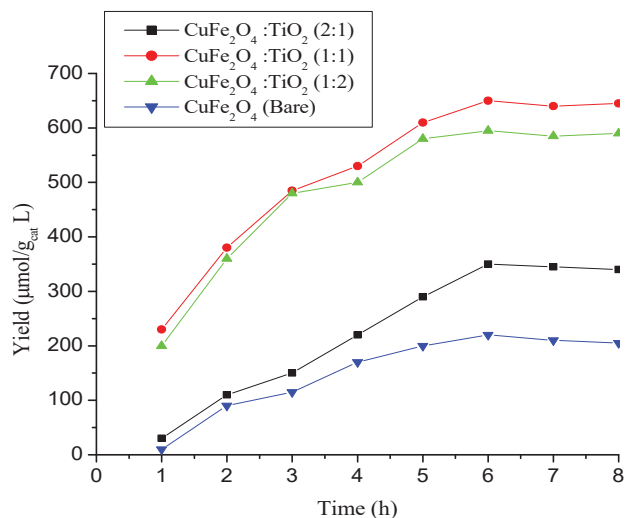


Fig. 8 Effect of $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ ratio for photocatalytic reduction of CO_2 to methanol under visible light irradiation for 8 h

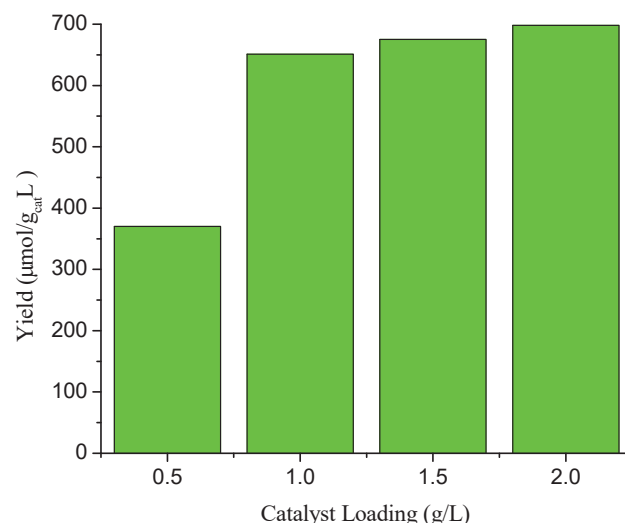


Fig. 9 Effect of catalyst loading for CO_2 conversion at 6 h irradiation (Light intensity = $240 \text{ W}/\text{m}^2$)

H. Photocatalytic Reduction of CO_2 : Effect of Light Intensity for CO_2 Reduction

The effect of visible light intensity on photocatalytic CO_2 reduction process is presented in Fig. 10. Fig. 10 illustrates the direct effect of the light intensity on photocatalytic reduction of CO_2 into methanol for 8 h irradiation period. After increasing the light intensity methanol yield was significantly increased about 14% (at 8 h irradiation). The light intensity of $249 \text{ W}\cdot\text{m}^{-2}$ was chosen as optimum, as further increase in light intensity could not increase the methanol yield.

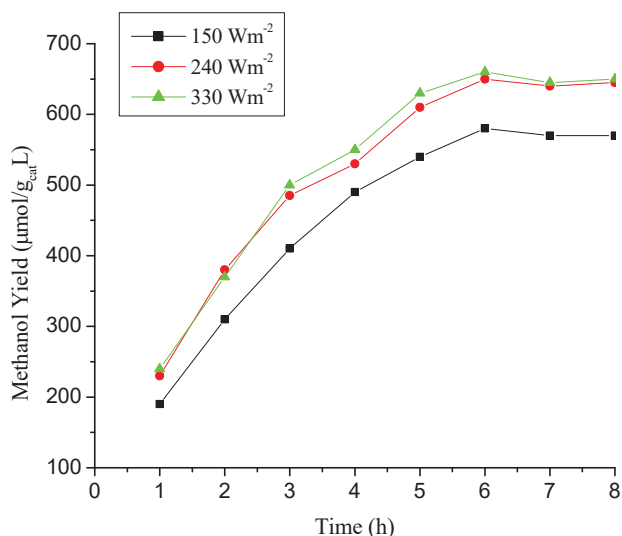


Fig. 10 Effect of light intensity on CO₂ conversion to methanol under visible light irradiation for 8 h (catalyst loading = 1 gL⁻¹)

I. Recycling of Catalyst for CO₂ Reduction

The catalyst recycling for four different cycles was performed and presented at Fig. 11. After each run, the whole reaction mixture was centrifuged, before reuse in the second reaction cycle; the recovered catalyst was dried over night at 100 °C and subsequently used for new cycle under the optimum operating conditions. It was observed that the catalyst activity gradually decreased during 8 h irradiation (Fig. 11) and the activity was decreased about 25.6% after four cycles of operation compare to the first cycle. The UV-visible and PL data suggested the loss of active phase in the recycled catalysts might be the reason for the reduction of the activity.

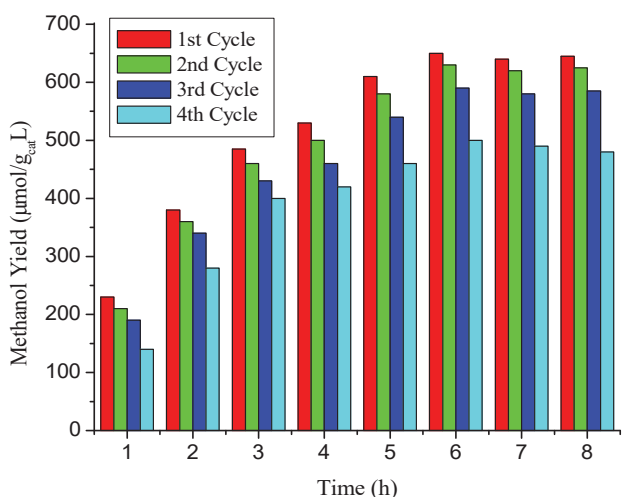


Fig. 11 Effect of catalyst recycles on methanol production over CuFe₂O₄/TiO₂ (each cycle duration = 8 h; Light intensity = 240 Wm⁻²; room temperature)

J. Mechanism of Methanol Formation

The mechanism of methanol formation over prepared CuFe₂O₄ and CuFe₂O₄/TiO₂ photocatalysts are shown in Fig.

11. At pH ~ 5.9, CO₂ may exist as dissolved CO₂ and HCO₃⁻, but the predominant species at low pH are the dissolved CO₂ and HCO₃⁻ [31].

As shown in Fig. 12, the reduction potential of the possible reactions of these species of CO₂ falls in between the VB and CB of both CuFe₂O₄ and CuFe₂O₄/TiO₂ suggesting that the reaction can occur on both photocatalysts [9], [32]. Comparing the band gap, CuFe₂O₄ (1.24 eV) is more visible light active than the TiO₂ (3.1 eV). According to the standard reaction potential (E⁰_{ox} = -0.39 V), the of methanol formation alone on CuFe₂O₄ is low due to the large difference between the potential of the CB (-1.03 V) of CuFe₂O₄ and the redox couple (-0.38 V). Under visible light, excited e⁻ could move from VB to CB of CuFe₂O₄ whereas CB (-1.03 V) edge of CuFe₂O₄ is higher than that of the TiO₂ CB (-0.97 V), the excited e⁻ can easily transferred to the CB of TiO₂ in CuFe₂O₄/TiO₂ hetero-structure where the CO₂ reduction can take place. The hetero-structure should increase the e⁻ life time by suppressing the e⁻/h⁺ recombination. The reduction of the e⁻/h⁺ recombination rate in the hetero-structure was evident from Fig. 5. Therefore, CuFe₂O₄/TiO₂ hetero-structure can promote the charge pair separation and prolong the recombination of e⁻/h⁺ pairs resulting in higher CO₂ reduction efficiency.

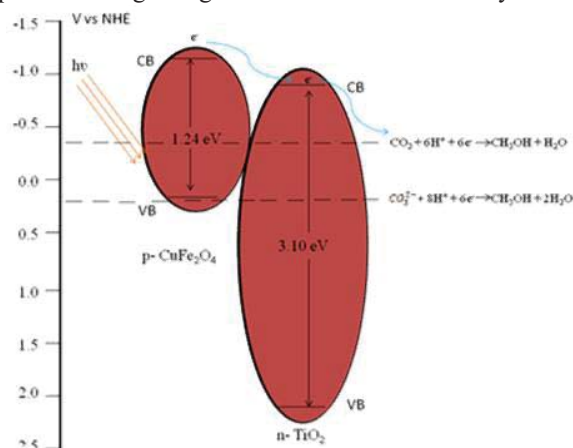


Fig. 12 The mechanism of CO₂ reduction to methanol over prepared CuFe₂O₄ and CuFe₂O₄/TiO₂ photocatalysts

IV. CONCLUSIONS

In summary, significant enhancement of the photocatalytic reduction of CO₂ under visible light irradiation was observed when TiO₂ was deposited on CuFe₂O₄. The catalyst composition and the reaction parameters were studied for methanol production and optimum TiO₂/CuFe₂O₄ ratio, catalysts loading and light intensity were found as 1/1, 1 gL⁻¹ and 240 Wm⁻² respectively. The XRD patterns of CuFe₂O₄ and CuFe₂O₄/TiO₂ confirmed their tetragonal structure, and crystallite sizes of ~59 nm (CuFe₂O₄) and ~108 nm (TiO₂), respectively. The modification of CuFe₂O₄ with TiO₂, enhanced its photocatalytic activity by shifting the band-gap of commercial TiO₂ (3.1 eV) into a new band-gap of CuFe₂O₄/TiO₂ (2.61 eV) photocatalyst, enabling the generation of photo electron under visible light. CuFe₂O₄/TiO₂ showed lower e⁻/h⁺ recombination compared to CuFe₂O₄. The

maximum yield of methanol over CuFe_2O_4 and $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ photocatalysts under visible light irradiation were 220 and 651 $\mu\text{mol/g}_{\text{cat}} \text{L}$, respectively.

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REFERENCES

- [1] A. Kezzim, N. Nasrallah, A. Abdi, M. Trari, "Visible light induced hydrogen on the novel hetero-system $\text{CuFe}_2\text{O}_4/\text{TiO}_2$," *Energy Conversion and Management*, vol. 52, no. 8-9, 2011, pp. 2800-2806.
- [2] Y. Izumi, "Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond," *Coordination Chemistry Reviews*, vol. 257, no. 1, 2013, pp. 171-186.
- [3] S. C. Roy, O. K. Varghese, M. Paulose, C. A. Grimes, "Toward solar fuels: photocatalytic conversion of carbon dioxide to hydrocarbons," *ACS Nano*, vol. 4, no. 3, 2010, pp. 1259-1278.
- [4] Q. Zhang, C. F. Lin, B. Y. Chen, T. Ouyang, C. T. Chang, "Deciphering Visible Light Photoreductive Conversion of CO_2 to Formic Acid and Methanol Using Waste Prepared Material," *Environ Sci Technol*, vol. 49, no. 4, 2015, pp. 2405-2417.
- [5] J. Mao, T. Peng, X. Zhang, K. Li, L. Zan, "Selective methanol production from photocatalytic reduction of CO_2 on BiVO_4 under visible light irradiation," *Catalysis Communications*, vol. 28, no. 2012, pp. 38-41.
- [6] K. Kočí, K. Matějů, L. Obalová, S. Krejčíková, Z. Lacný, D. Plachá, L. Čapek, A. Hospodková, O. Šolcová, "Effect of silver doping on the TiO_2 for photocatalytic reduction of CO_2 ," *Applied Catalysis B: Environmental*, vol. 96, no. 3-4, 2010, pp. 239-244.
- [7] M. Tahir, N. S. Amin, "Advances in visible light responsive titanium oxide-based photocatalysts for CO_2 conversion to hydrocarbon fuels," *Energy Conversion and Management*, vol. 76, no. 2013, pp. 194-214.
- [8] H. Yang, J. Yan, Z. Lu, X. Cheng, Y. Tang, "Photocatalytic activity evaluation of tetragonal CuFe_2O_4 nanoparticles for the H_2 evolution under visible light irradiation," *Journal of Alloys and Compounds*, vol. 476, no. 1-2, 2009, pp. 715-719.
- [9] X. Li, J. Chen, H. Li, J. Li, Y. Xu, Y. Liu, J. Zhou, "Photoreduction of CO_2 to methanol over $\text{Bi}_2\text{S}_3/\text{CdS}$ photocatalyst under visible light irradiation," *Journal of Natural Gas Chemistry*, vol. 20, no. 4, 2011, pp. 413-417.
- [10] A. Di Paola, M. Bellardita, L. Palmisano, "Brookite, the Least Known TiO_2 Photocatalyst," *Catalysts*, vol. 3, no. 1, 2013, pp. 36-73.
- [11] A. Di Paola, E. García-López, G. Marci, L. Palmisano, "A survey of photocatalytic materials for environmental remediation," *J Hazard Mater*, vol. 211, no. 2012, pp. 3-29.
- [12] W. Hou, W. H. Hung, P. Pavaskar, A. Goepfert, M. Aykol, S. B. Cronin, "Photocatalytic Conversion of CO_2 to Hydrocarbon Fuels via Plasmon-Enhanced Absorption and Metallic Interband Transitions," *ACS Catalysis*, vol. 1, no. 8, 2011, pp. 929-936.
- [13] W.-N. Wang, J. Soulis, Y. J. Yang, P. Biswas, "Comparison of CO_2 photoreduction systems: A review," *Aerosol and Air Quality Research*, vol. 14, no. 2, 2014, pp. 533-549.
- [14] M. L. P. Dalida, K. M. S. Amer, C.-C. Su, M.-C. Lu, "Photocatalytic degradation of acetaminophen in modified TiO_2 under visible irradiation," *Environmental Science and Pollution Research*, vol. 21, no. 2, 2014, pp. 1208-1216.
- [15] H. Fan, H. Li, B. Liu, Y. Lu, T. Xie, D. Wang, "Photoinduced charge transfer properties and photocatalytic activity in $\text{Bi}_2\text{O}_3/\text{BaTiO}_3$ composite photocatalyst," *ACS Appl Mater Interfaces*, vol. 4, no. 9, 2012, pp. 4853-4857.
- [16] D. Monllor-Satoca, R. Gomez, W. Choi, "Concentration-dependent photoredox conversion of As(III)/As(V) on illuminated titanium dioxide electrodes," *Environ Sci Technol*, vol. 46, no. 10, 2012, pp. 5519-5527.
- [17] P. Roy, A. P. Periasamy, C. T. Liang, H. T. Chang, "Synthesis of graphene- ZnO -Au nanocomposites for efficient photocatalytic reduction of nitrobenzene," *Environ Sci Technol*, vol. 47, no. 12, 2013, pp. 6688-6695.
- [18] M. R. Uddin, M. R. Khan, M. W. Rahman, A. Yousuf, C. K. Cheng, "Photocatalytic reduction of CO_2 into methanol over $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ under visible light irradiation," *Reaction Kinetics, Mechanisms and Catalysis*, vol. 116, no. 2, 2015, pp. 589-604.
- [19] J. Yan, H. Yang, Y. Tang, Z. Lu, S. Zheng, M. Yao, Y. Han, "Synthesis and photocatalytic activity of $\text{CuYFe}_{2-y}\text{O}_4\text{-CuCo}_2\text{O}_4$ nanocomposites for H_2 evolution under visible light irradiation," *Renewable Energy*, vol. 34, no. 11, 2009, pp. 2399-2403.
- [20] O. Lemine, "Microstructural characterisation of nanoparticles using, XRD line profiles analysis, FE-SEM and FT-IR," *Superlattices and Microstructures*, vol. 45, no. 6, 2009, pp. 576-582.
- [21] L. Huang, F. Peng, H. Wang, H. Yu, Z. Li, "Preparation and characterization of $\text{Cu}_2\text{O}/\text{TiO}_2$ nano-nano heterostructure photocatalysts," *Catalysis Communications*, vol. 10, no. 14, 2009, pp. 1839-1843.
- [22] X. Li, H. Liu, D. Luo, J. Li, Y. Huang, H. Li, Y. Fang, Y. Xu, L. Zhu, "Adsorption of CO_2 on heterostructure $\text{CdS}(\text{Bi}_2\text{S}_3)/\text{TiO}_2$ nanotube photocatalysts and their photocatalytic activities in the reduction of CO_2 to methanol under visible light irradiation," *Chemical Engineering Journal*, vol. 180, no. 2012, pp. 151-158.
- [23] M. Hussain, N. Russo, G. Saracco, "Photocatalytic abatement of VOCs by novel optimized TiO_2 nanoparticles," *Chemical Engineering Journal*, vol. 166, no. 1, 2011, pp. 138-149.
- [24] J. T. Carneiro, T. J. Savenije, J. A. Moulijn, G. Mul, "How phase composition influences optoelectronic and photocatalytic properties of TiO_2 ," *The Journal of Physical Chemistry C*, vol. 115, no. 5, 2011, pp. 2211-2217.
- [25] M. Tahir, N. S. Amin, "Indium-doped TiO_2 nanoparticles for photocatalytic CO_2 reduction with H_2O vapors to CH_4 ," *Applied Catalysis B: Environmental*, vol. 162, no. 2015, pp. 98-109.
- [26] N. Ahmed, M. Morikawa, Y. Izumi, "Photocatalytic conversion of carbon dioxide into methanol using optimized layered double hydroxide catalysts," *Catalysis Today*, vol. 185, no. 1, 2012, pp. 263-269.
- [27] D.-H. Chen, X.-R. He, "Synthesis of nickel ferrite nanoparticles by sol-gel method," *Materials Research Bulletin*, vol. 36, no. 7, 2001, pp. 1369-1377.
- [28] C. G. Reddy, S. Manorama, V. Rao, "Preparation and characterization of ferrites as gas sensor materials," *Journal of materials science letters*, vol. 19, no. 9, 2000, pp. 775-778.
- [29] I. Sandu, L. Presmanes, P. Alphonse, P. Tailhades, "Nanostructured cobalt manganese ferrite thin films for gas sensor application," *Thin Solid Films*, vol. 495, no. 1, 2006, pp. 130-133.
- [30] L. L. Ma, H. Z. Sun, Y. G. Zhang, Y. L. Lin, J. L. Li, E. K. Wang, Y. Yu, M. Tan, J. B. Wang, "Preparation, characterization and photocatalytic properties of CdS nanoparticles dotted on the surface of carbon nanotubes," *Nanotechnology*, vol. 19, no. 11, 2008, pp. 115709.
- [31] S. K. Lower, Carbonate equilibria in natural waters, in: Simon Fraser University, 1999.
- [32] L. Liu, "Understanding the Reaction Mechanism of Photocatalytic Reduction of CO_2 with H_2O on TiO_2 -Based Photocatalysts: A Review," *Aerosol and Air Quality Research*, vol. no. 2014, pp.