

DEVELOPMENT OF  $\text{TiO}_2$  LOADED  $\text{CuFe}_2\text{O}_4$   
PHOTOCATALYST FOR  $\text{CO}_2$  CONVERSION INTO  
METHANOL UNDER VISIBLE LIGHT  
IRRADIATION

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**LIST OF ABBREVIATIONS**

BET	Brunauer–Emmett–Teller
CB	Conduction Band
C	Concentration
EDX	Energy dispersive X-ray spectrometer
FE-SEM	Field emission scanning electron microscopy
FWH	Full width at half-maximum
GC-FID	Agilent gas chromatography (GC); flame ionization detector (FID)
NHE	Normal Hydrogen Electrode
PL	Photoluminescence
TGA	Thermogravimetric analysis
TPES	Total Primary Energy Supply
UV	Ultra-Violet
UV-Vis	Ultra-violet visible
VB	Valence Band
VLR	Visible Light Responsive
WL	Weight loss
XRD	X-ray diffraction



**LIST OF SYMBOLS**

$E_g$	Band gap Energy
$e^-$	Electron
$h^+$	Holes
$\lambda$	Wavelength
$\Delta G^0$	Gibb's free energy
eV	Electron Volt
MPa	Mega pascal
V	Standard Potential
$\mu\text{g}$	Microgram
g	Gram
$\mu\text{m}$	Micrometer
W	Watt
M	Molarity
Nm	Nanometer
$2\theta$	Scattering angle
D	Coherent scattering length
B	Width of peak
K	Constant related to crystallite shape
$\text{\AA}$	Angstrom, m
Wt	Weight
%	Percentage

Cm	Centimeter
M	Meter
°C	Degree Celcius (Temperature)
μmol	Micro-moles
g <sub>cat</sub>	Gram catalysts
L	Litre
H	Hour
T	Treatment Time
P	Positive type junction
N	Negative type junction
B	FWHM (in radians)
ΔE	Redox potential
Θ	Diffraction angle
μg	Microgram
2θ	Scattering angle

## ABSTRACT

The production of methanol through CO<sub>2</sub> photoreduction under visible light irradiation, has gained tremendous attention in recent times due to the limited availability of fossil-fuel resources and global climate change caused by rising CO<sub>2</sub> level in the atmosphere. The present study aimed to explore visible light active photocatalyst for carbon dioxide (CO<sub>2</sub>) conversion to methanol in aqueous phase. In this context, copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>) and TiO<sub>2</sub> loaded copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub>) were synthesized following sol-gel method. The effect of different parameters, such as TiO<sub>2</sub> to CuFe<sub>2</sub>O<sub>4</sub> weight ratio, calcination temperature, light intensity, irradiation time and catalyst loading was investigated to evaluate the activity of the catalyst to produce methanol. Methanol was observed as the main product over CuFe<sub>2</sub>O<sub>4</sub>, but loading with TiO<sub>2</sub> remarkably increased the methanol yield. The maximum methanol yield was obtained on CuFe<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> calcined at 700 °C with a catalyst loading of 1 g/L. The catalyst was characterized by XRD, FE-SEM, UV-Vis, photoluminescence (PL) spectrophotometer, and EDX. The XRD results confirmed the formation of spinel type tetragonal CuFe<sub>2</sub>O<sub>4</sub> phases along with predominantly anatase phase of TiO<sub>2</sub> in the CuFe<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> hetero-structure. UV-Vis absorption spectrum suggested the formation of the hetero-junction with relatively lower band gap than that of TiO<sub>2</sub>. PL spectra analysis confirmed the slow-down of the recombination of electron-hole (e<sup>-</sup>/h<sup>+</sup>) pairs in the CuFe<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> hetero-structure. The mechanism of the photocatalysis was proposed based on the fact that the predominant species of CO<sub>2</sub> in aqueous phase were dissolved CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> at pH ~5.9. It was obvious that the CuFe<sub>2</sub>O<sub>4</sub> could harvest the electrons under visible light irradiation, which could further be injected to the conduction band of TiO<sub>2</sub> to increase the life time of the electron and facilitating the reactions of CO<sub>2</sub> to methanol. The developed catalyst showed good recycle ability up to four cycles where the loss of activity was ~25%. To increase the yield of methanol a periodic addition of catalyst into the reactor was proposed where the methanol yield could be raised significantly.

## ABSTRAK

Sejak kebelakangan ini pengeluaran metanol melalui pengurangan foto  $\text{CO}_2$  di bawah sinaran cahaya yang boleh dilihat, telah mendapat perhatian yang besar kerana sumber bahan api fosil yang terhad dan perubahan iklim seluruh dunia yang disebabkan oleh peningkatan tahap  $\text{CO}_2$  di dalam atmosfera. Kajian ini bertujuan untuk meneroka cahaya yang boleh dilihat foto-katalis yang aktif untuk penukaran karbon dioksida ( $\text{CO}_2$ ) kepada metanol. Dengan ini, ferit tembaga ( $\text{CuFe}_2\text{O}_4$ ) dan  $\text{TiO}_2$  ferit tembaga dimuatkan ( $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ ) telah disintesis mengikut kaedah “sol-gel”. Parameter yang berbeza, seperti  $\text{TiO}_2$  untuk  $\text{CuFe}_2\text{O}_4$  nisbah berat badan, suhu pengkalsinan, keamatan cahaya, masa penyinaran dan pemangkin loading telah disiasat untuk menilai aktiviti pemangkin untuk menghasilkan metanol. Methanol diperhatikan sebagai produk utama untuk  $\text{CuFe}_2\text{O}_4$  sistem, tetapi memuatkan dengan  $\text{TiO}_2$ , ia meningkat hasil metanol. Maksimum metanol diperolehi daripada  $\text{CuFe}_2\text{O}_4/\text{TiO}_2$  calcined pada  $700\text{ }^\circ\text{C}$  dengan mangkin  $1\text{ g / L}$ . Pemangkin dicirikan oleh XRD, FE-SEM, UV-Vis, photoluminescence (PL) spektrofotometer, dan EDX. Keputusan XRD mengesahkan pembentukan jenis spinel fasa  $\text{CuFe}_2\text{O}_4$  tetragonal bersama-sama dengan fasa fasa kebanyakannya anatase  $\text{TiO}_2$  di  $\text{CuFe}_2\text{O}_4/\text{TiO}_2$  hetero-struktur. UV-Vis spektrum penyerapan mencadangkan pembentukan simpang hetero dengan jurang jalur yang agak lebih rendah daripada  $\text{TiO}_2$ . PL analisis spektrum mengesahkan perlahan penggabungan semula elektron-lubang ( $e^-/h^+$ ) pasang dalam  $\text{CuFe}_2\text{O}_4 / \text{TiO}_2$  hetero-struktur. Mekanisme foto-pemangkinan telah dicadangkan berdasarkan fakta bahawa spesies utama  $\text{CO}_2$  dalam fasa akueus telah dibubarkan kepada  $\text{CO}_2$  dan  $\text{HCO}_3^-$  pada  $\text{pH} \sim 5.9$ . Ia adalah jelas bahawa  $\text{CuFe}_2\text{O}_4$  boleh menuai elektron di bawah penyinaran cahaya, dan boleh disuntik ke jalur konduksi  $\text{TiO}_2$  untuk meningkatkan masa hayat elektron dan memudahkan reaksi  $\text{CO}_2$  kepada metanol. Pemangkin dibangunkan menunjukkan kebolehan kitar semula yang baik sehingga empat kali di mana kehilangan aktiviti adalah  $\sim 25\%$ . Tambahan lagi, untuk meningkatkan hasil methanol, panambahan pemangkin dalam reaktor telah dicadangkan untuk meningkatkan hasil metanol dengan ketara.