

Photothermal Reduction of Carbon Dioxide Using Magnetite Photocatalyst [†]

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Abstract: One promising approach to achieving sustainable energy while simultaneously addressing various environmental issues is to utilize solar-driven transformation of the greenhouse gas CO₂ into valuable chemical fuels. The main obstacle in achieving this goal has consistently been the identification of cost-effective, stable, and non-toxic photoactive materials that can efficiently convert CO₂ into chemical fuels. Photothermal catalysis offers a viable solution to address the challenges related to sunlight absorption and low quantum efficiency often encountered in conventional photocatalysts. In this study, we used a magnetite catalyst for the photothermal reduction of CO₂. Various characterization techniques, including PXRD, TEM, and XPS, were employed to confirm the catalyst phase, crystallinity, particle size, and the electronic structure of the magnetite catalyst. The results of the photothermal conversion of carbon dioxide revealed that carbon monoxide was the only product, with a selectivity of 100%. Furthermore, the Fe₃O₄ catalyst produced significantly higher CO under high-intensity illumination (2076 μmolgc^{−1}h^{−1}) than in the dark (820 μmolgc^{−1}h^{−1}) under the same temperature of 315 °C. The activation energy obtained for the tests conducted under high-intensity illumination was lower than that obtained in the dark. The use of photothermal catalysts such as Fe₃O₄ to drive useful chemical reactions such as CO₂ conversion to useful products contributes to advancing the field of sustainable energy and marks a significant stride toward realizing real solutions for mitigating climate change.

Keywords: photothermal catalysis; magnetite; solar energy; carbon dioxide reduction; heterogeneous catalysis



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1. Introduction

The rising concentration of atmospheric carbon dioxide (CO₂) is a major driver of global climate change, highlighting the urgent need for innovative CO₂ reduction strategies. Anthropogenic activities, particularly the burning of fossil fuels for energy, have led to unprecedented levels of CO₂ in the atmosphere, resulting in severe environmental consequences such as global warming, ocean acidification, and disrupted weather patterns [1]. To combat these challenges, researchers are exploring a variety of methods to capture and convert CO₂ into useful products, thereby reducing its atmospheric concentration and mitigating its harmful effects [2,3]. One of the most promising approaches is the heterogeneous chemical conversion of CO₂ using photoactive catalysts that harness sunlight to drive beneficial chemical transformations. Specifically, the reverse water gas shift (RWGS)

reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) is an important industrial process. Using H_2 from a sustainable source, CO_2 can be converted into CO, a crucial chemical feedstock and fuel for the synthesis of higher-chain hydrocarbons. However, this reaction is typically catalyzed by expensive rare earth metals, which limits its long-term sustainability. Additionally, due to the endothermic nature of the RWGS reaction, cost-effective catalysts developed for this reaction often require high temperatures of over 600 °C to obtain a meaningful CO yield, necessitating substantial energy input to drive the process [4]. The challenge, therefore, is to find exceptionally cost-effective, stable, and environmentally benign photoactive nanomaterials capable of efficiently driving these heterogeneous chemical reactions [5]. An ideal photocatalyst should efficiently harness the abundant solar energy radiated by the sun. Photothermal catalysts present a promising avenue due to their potential for high efficiency and utilization of a broad spectrum of solar energy. These catalysts combine the advantages of photocatalysis and thermal catalysis, harnessing sunlight to drive chemical reactions at elevated temperatures, thereby enhancing reaction rates and product yields. Moreover, photothermal catalysts eliminate the need for solar concentrators to achieve the high temperatures required for purely thermochemical catalysts. In this context, magnetite (Fe_3O_4) has garnered attention as a potent catalyst for photothermal processes, owing to its unique magnetic properties, thermal stability, and ability to absorb a broad spectrum of light [6]. Magnetite, a naturally occurring iron oxide, exhibits several characteristics that make it an ideal candidate for photothermal CO_2 reduction. Its magnetic nature facilitates easy separation and recycling, while its strong light absorption properties enable efficient solar energy conversion. Furthermore, magnetite's thermal stability ensures that it can withstand the high temperatures required for effective photothermal catalysis. These attributes collectively contribute to its potential in enhancing the efficiency and sustainability of CO_2 reduction processes.

CO_2 reduction by Fe_3O_4 catalysts has been investigated over the years [7]. When employed as a photothermal catalyst, Fe_3O_4 is often supported on carbon nanotubes or other carbonaceous materials. For example, Chew et al. delved into the realm of CO_2 hydrogenation by employing iron nanoparticles anchored on oxygen-functionalized carbon nanotubes, yielding a diverse array of hydrocarbons [8]. Similarly, Minett et al. engineered arrays of iron nanoparticle-carbon nanotube arrays grown on monolithic structures to effectuate CO_2 conversion into various hydrocarbons [9]. They ascribed the efficacy of this process to the presence of magnetite and iron carbide, which facilitate both CO_2 hydrogenation and Fischer–Tropsch synthesis. O'Byrne et al. pursued a similar objective, focusing on the conversion of CO_2 and CO to hydrocarbons through the utilization of bridged Fe nanoparticles tethered onto carbon nanotubes, achieving remarkable conversion rates [10]. Tu et al. devised a novel approach by enveloping Fe_3O_4 nanocrystals within carbon shells, enabling the reduction of CO_2 to multiple hydrocarbons [11]. Gupta et al., on the other hand, investigated the influence of the composition of a nanostructured iron-based carbon-coated core–shell nanocatalyst on the hydrogenation of CO_2 [12]. Throughout these investigations, carbon emerges as a pivotal support or encapsulant for the Fe_3O_4 catalyst, harnessing its large surface area, superior heat transfer properties, and robust thermal stability. Moreover, under elevated temperatures, the carbon coating undergoes transformation into Fe_5C_2 , a catalytically active species profoundly adept at CO_2 hydrogenation [12]. In a recent breakthrough, Song et al. conducted an in-depth analysis of photothermal CO_2 conversion to CO using an unsupported commercial magnetite catalyst [13]. Their study unveiled the pivotal role of Fe_3O_4 in driving CO_2 reduction through photothermal effects while meticulously delineating the contributions of both thermal and non-thermal mechanisms to the conversion process. In a more recent study, Ali et al. examined the structural changes and evolution of the active state of an iron-based catalyst using a range of in situ characterization techniques [14]. Their findings revealed that the activated catalyst predominantly comprised Fe_3O_4 and metallic iron. Notably, they demonstrated that the Fe_3O_4 -based catalyst displayed remarkable activity in converting CO_2 to CO under

solar-simulated light without the need for external heating, across various reactor setups including batch, flow, and light-emitting diode reactors.

In this study, we provide insights into the synthesis, characterization, and application of magnetite as a photothermal catalyst, highlighting its potential in advancing CO₂ reduction technologies. The findings presented herein aim to contribute to the growing body of research focused on sustainable energy and environmental preservation. This manuscript explores the role of magnetite in facilitating the photothermal reduction of CO₂. We investigate the catalytic performance of magnetite under various conditions, aiming to understand the photothermal efficiency of the catalyst. By leveraging magnetite's properties, we seek to enhance the efficiency of CO₂ conversion into valuable hydrocarbons, thus contributing to the broader goal of developing sustainable energy solutions and mitigating the impact of greenhouse gases on our environment.

2. Experimental

Although Fe₃O₄ is a commercially available catalyst, we aimed to synthesize our own version to achieve the desired morphology and nanoparticle size, optimizing its performance for the reverse water gas shift reaction. By tailoring the synthesis process, we sought to enhance the catalytic properties, ultimately improving the efficiency and effectiveness of the reaction. This approach allowed us to fine-tune the structural characteristics of Fe₃O₄, ensuring better control over its catalytic behaviour and achieving superior results compared to commercially available options.

2.1. Materials

Ferrous ammonium sulfate [FeSO₄(NH₄)₂SO₄·6H₂O] (99.997%), hydrogen peroxide (H₂O₂) (30% (*w/w*) in water) and sodium hydroxide (NaOH) (98%) were all procured from Sigma Aldrich. The high purity of these reagents ensured the reliability and reproducibility of the synthesis process for the Fe₃O₄ catalyst. Ferrous ammonium sulfate served as the iron source, while hydrogen peroxide acted as the oxidizing agent, and sodium hydroxide was used to facilitate the precipitation reaction. These chemicals were used without further purification, maintaining consistency across all experimental procedures.

2.2. Catalyst Synthesis

The Fe₃O₄ catalyst was synthesized through the rapid oxidation of Fe²⁺ with H₂O₂. Specifically, a solution of FeSO₄(NH₄)₂SO₄·6H₂O was mixed with a 2 M NaOH solution, resulting in the formation of a green precipitate. Immediately, 5 mL of 30% H₂O₂ was added, causing the precipitate to turn reddish-brown within a few seconds. The resulting products were washed and dried in an oven at 40 °C. Subsequently, the catalyst was reduced inside a tube furnace at 300 °C for 2 h while under a flow of 10% H₂/Ar at a rate of 80 mL/min resulting in a black Fe₃O₄ catalyst. The Fe₃O₄ catalyst was deposited onto a 1 cm × 1 cm borosilicate filter paper for the photocatalytic measurement experiments.

2.3. Catalyst Characterizations

The powder X-ray diffraction (PXRD) pattern was recorded using a Bruker D2 Phaser instrument with Cu-K_α radiation at 30 kV. High-resolution environmental transmission electron microscopy (HRTEM) was employed to further examine the crystallinity of the Fe₃O₄ catalyst, utilizing a Hitachi H-3300 TEM operating at a voltage of 300 kV to image the samples. X-ray photoelectron spectroscopy (XPS) measurements were conducted to investigate the surface and electronic structure of the samples. The XPS analysis was performed in an ultrahigh vacuum chamber with a base pressure of 10^{−9} mTorr, using a Thermo Scientific K-Alpha XPS spectrometer with an Al K_α X-ray source operating at 15 kV and 27 A, providing X-ray energy of 1486.7 eV. The spectra were acquired with an analyzer pass energy of 50 eV and energy spacing of 0.1 eV. All data analysis was conducted using Thermo Scientific AdvantageTM V6 software.

2.4. Photocatalytic Measurements

A custom-built batch reactor was used for the gas-phase photoreduction of CO_2 . Before starting the photocatalytic measurements, the reactor was purged with hydrogen (H_2) for twenty minutes. After purging, the reactor was filled with CO_2 and H_2 at a 4:1 H_2 : CO_2 ratio. The lamp was switched on once the reactor valves were closed. Pressure inside the reactor was monitored using an Omega PX309 pressure transducer. Each experimental run lasted for 30 min. Product gases were analyzed using a flame ionization detector (FID) and a thermal conductivity detector (TCD) integrated into an SRI-8610 Gas Chromatograph (GC), equipped with a 3' Mole Sieve 13a and a 6' Haysep D column. The spectral output was measured using a StellarNet Inc. spectrophotometer, and the incident irradiation power was measured using a Spectra-Physics power meter (model 407A). The test samples measured $1\text{ cm} \times 1\text{ cm}$.

3. Results and Discussion

3.1. Characterizations

Numerous characterization techniques, including PXRD, TEM and XPS, were used to study the Fe_3O_4 catalyst. Powder X-ray diffraction reveals that the only phase present is the magnetite phase, as shown in Figure 1. The X-ray diffractograms display distinct magnetite signatures, with peaks observed at angles of 18.1° , 30.0° , 35.2° , 36.9° , 42.9° , 53.3° , 56.9° , and 62.2° . These peaks correspond to the crystallographic planes (111), (220), (311), (222), (400), (422), (511), and (440), respectively [15].

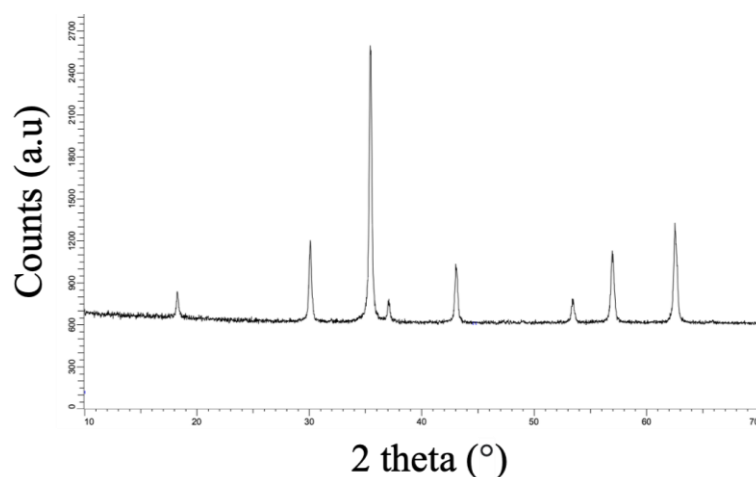


Figure 1. PXRD of magnetite catalyst, indicating that Fe_3O_4 is the only phase present.

High-resolution TEM was also employed to investigate the internal structure of the catalyst. The detailed microstructural analysis revealed various magnetite planes, as depicted in Figure 2. The Fe_3O_4 nanoparticles had a particle size of 20–50 nm. The selected area electron diffraction (SAED) pattern shown in the inset of Figure 2b further corroborates these findings, displaying several rings of the lattice fringes. Specifically, the diffraction planes identified include (311), (222), (422), (533), and (951) with corresponding lattice d-spacings of 0.253 nm, 0.242 nm, 0.171 nm, 0.124 nm, and 0.081 nm, respectively. This analysis confirms the presence of well-defined crystallographic planes within the magnetite structure, providing insights into the material's crystalline properties.

In addition, we have used XPS to analyze the oxidation states of the elements present at the surface of the catalyst. This was achieved by analyzing the Fe2p and O1s peak of the Fe_3O_4 catalyst. As shown in Figure 3a, the Fe2p spectrum displays a shoulder peak around 709 eV, which uniquely identifies Fe_3O_4 among iron oxides. This shoulder peak distinctly signifies the presence of Fe^{2+} in Fe_3O_4 [16]. Additionally, a notable feature of Fe_3O_4 is the absence or reduced intensity of the Fe2p_{3/2} satellite peak, usually found at around 719 eV in the spectra of other iron oxides [16].

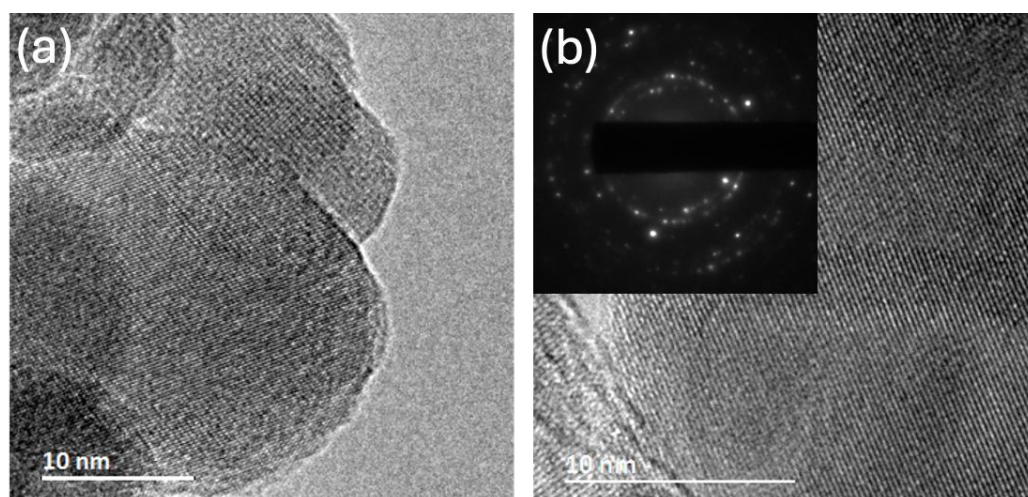


Figure 2. (a) TEM image of the Fe_3O_4 catalyst, (b) higher magnification TEM image along with SAED showing the different diffraction planes of the Fe_3O_4 catalyst.

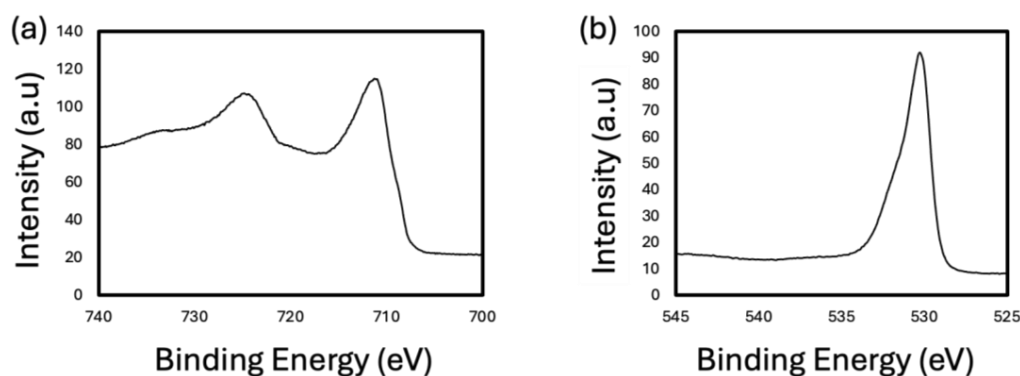


Figure 3. XPS spectra of Fe_3O_4 catalyst showing the (a) $\text{Fe}2p$ spectrum and (b) $\text{O}1s$ spectrum.

In the $\text{O}1s$ spectrum, the main peak corresponding to Fe-O-Fe lattice oxygen in the Fe_3O_4 structure is observed around 530 eV, while the shoulder peak associated with oxygen vacancies and surface hydroxyl groups appears around 532 eV, as shown in Figure 3b. This pattern is consistent with the characteristics of Fe_3O_4 reported in the literature.

3.2. Catalyst Performance

The photocatalytic activity of the Fe_3O_4 towards CO_2 reduction was evaluated in a custom-built batch reactor (see Figure 4a). This was achieved by measuring the rate of production of gaseous products in the product stream. During the photocatalytic measurements, the reactor was charged with CO_2 and H_2 at a 4:1 ratio. The lamp was switched on once the reactor valves were closed. The temperature profile during the test, monitored as shown in Figure 4b, indicated that the temperature rose rapidly upon illumination, remained fairly constant throughout the test, and dropped once the high-intensity lamp was turned off. Under illumination with a 15 kWm^{-2} Xe Arc lamp and without any external heating, the sample temperature reached an average of 315°C . Consequently, two tests were performed: one under high-intensity illumination of 15 kWm^{-2} without external heating, and the other with resistive heating at 315°C (matching the catalyst temperature under illumination without external heating). Each test lasted approximately 30 min. The results, shown in Figure 4c, revealed that carbon monoxide was the only product with a selectivity of 100%. The CO production rate in the dark at 315°C was $820 \mu\text{molcat}^{-1}\text{h}^{-1}$, while under high-intensity illumination, the CO production rate was $2076 \mu\text{molcat}^{-1}\text{h}^{-1}$, representing almost a threefold increase. To confirm that the CO produced in our reactor originated from

the reactant CO_2 and not from any other carbon sources, we used C-13 labelled CO_2 as the reactant gas for all our tests. Since naturally occurring carbon predominantly consists of the C-12 isotope, using C-13 labelled CO_2 ensures traceability. The products collected from the reactor confirmed the formation of ^{13}CO . Figure 4d presents the GC-MS spectra, displaying the 29 amu mass fragment for Fe_3O_4 samples, which verifies the production of ^{13}CO . The enhanced CO production rate under high-intensity illumination compared to resistive heating at the same temperature of 315 °C indicates an efficient photothermal effect. The Fe_3O_4 catalyst, black in colour, exhibits a broadband absorption spectrum spanning the UV-Visible to infrared regions of the solar spectrum. The heat generated when the catalyst absorbs incident light accelerates the endothermic RWGS reaction, with thermal energy playing a crucial role in boosting the reaction rate.

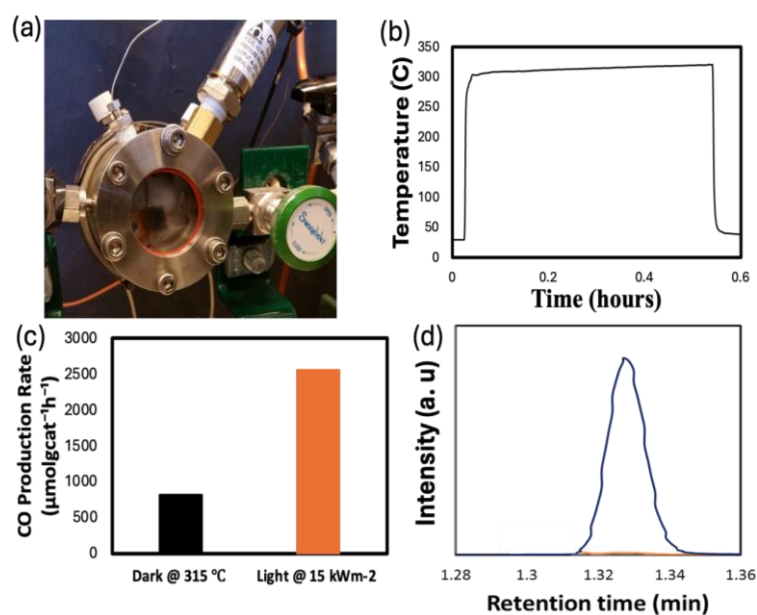


Figure 4. (a) Custom-built batch reactor used for the photocatalytic measurements, (b) Temperature profile of the catalyst in the batch reactor during high-intensity illumination, indicating the average temperature of the catalyst at 315 °C, (c) CO production rate in the dark at 315 °C and under high-intensity illumination, (d) GC-MS spectrum at 29 amu obtained during the photocatalytic measurements of the Fe_3O_4 catalyst.

To gain further insights into the photothermal properties of the Fe_3O_4 catalyst, we investigated its activity at various temperatures (210 °C, 225 °C, 240 °C, 255 °C, 270 °C, 285 °C, 300 °C, and 315 °C) using resistive heating, as shown by the orange dots in Figure 5a.

Additionally, we adjusted the intensity of the Xenon Arc lamp to achieve the same temperatures for comparison, indicated by the blue dots in Figure 5a. The results demonstrate that the CO production rate was higher under high-intensity illumination compared to resistive heating for the same corresponding temperature. For instance, at 300 °C, the CO production rate was 1568 $\mu\text{molcat}^{-1}\text{h}^{-1}$ under high-intensity illumination, compared to 376 $\mu\text{molcat}^{-1}\text{h}^{-1}$ under resistive heating. This difference in CO production rates might be due to higher local temperatures under high-intensity illumination than those recorded by the thermocouple. It is known that photothermal catalysts can heat up significantly under intense illumination, or other photo-enhanced processes, such as photochemical reactions, may accelerate the reverse water gas shift reaction favourably. The data from Figure 5a were used to create a pseudo-Arrhenius plot, shown in Figure 5b. An activation energy of 99.64 kJ/mol was recorded for the sample heated with high-intensity illumination, compared to 111.03 kJ/mol for the sample heated using resistive heating. The lower activation energy in the high-intensity illuminated sample also explains the enhanced reverse water gas shift reaction rate. This is because the greater the light intensity impinging on the

catalyst surface, the more reactant molecules will acquire the necessary activation energy to react, thereby accelerating the reverse water gas shift reaction. This increase in light intensity boosts the number of photons interacting with the catalyst's surface, enhancing its photo-activation, and facilitating a higher rate of reaction. As a result, the overall efficiency of the reverse water gas shift process is significantly improved, leading to faster conversion rates and potentially CO yields.

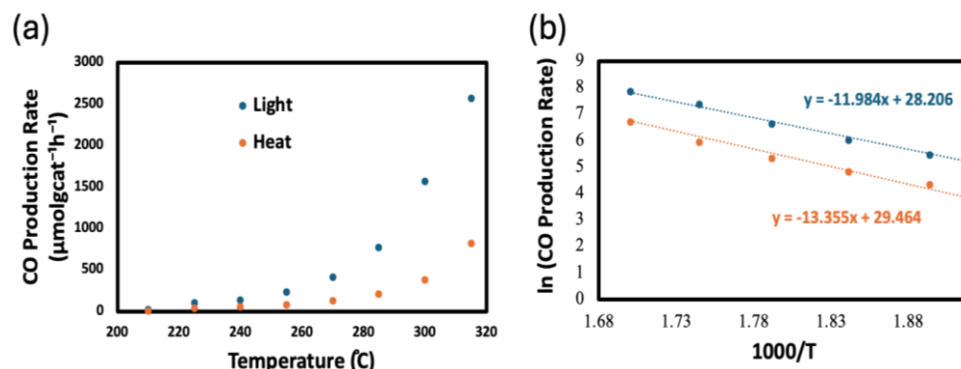


Figure 5. (a) CO production rates as a function of temperature for the Fe_3O_4 catalyst in the dark (orange) and under high-intensity illumination (blue), (b) Arrhenius plot corresponding to the measurements presented in (Figure 5a) used to obtain the activation energies in the dark and under high-intensity illumination.

4. Conclusions

In summary, we have synthesized Fe_3O_4 catalyst and applied it for the photothermal reduction of CO_2 . Characterization tools, including PXRD and TEM, confirmed that Fe_3O_4 was the only phase present and provided details on the particle sizes and crystallinity of the catalyst. XPS analysis further confirmed the presence of Fe_3O_4 by identifying characteristic peaks in the Fe2p and O1s spectra. The catalyst's activity was assessed at various temperatures using resistive heating and high-intensity illumination. The results demonstrated higher CO production rates under illumination for the same temperatures, attributed to higher local temperatures and potential photo-enhanced processes. Additionally, the activation energy was lower for the illuminated sample (99.64 kJ/mol) compared to the resistively heated sample (111.03 kJ/mol), indicating enhanced reaction rates under illumination. Photothermal catalysts like Fe_3O_4 present a promising avenue for converting gaseous CO_2 into chemicals and fuels, as they effectively utilize the entire solar spectrum, unlike purely photochemical catalysts constrained by their semiconductor bandgap.

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