Dual-functional paired photoelectrocatalytic system for the photocathodic reduction of CO₂ to fuels and the anodic oxidation of furfural to value-added chemicals

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Abstract

Photoelectrochemical cell (PEC) conversion of CO₂ into fuels is a highly effective strategy for reducing CO₂ in the atmosphere. In a typical PEC, CO₂ reduction at the cathode is accompanied by water oxidation at the anode to produce O₂, which is not of significant value. Herein, we report the first work on the design of a paired PEC electrolyzer cell for the reduction of CO₂ to CH₃OH and the oxidation of furfural to 2-furoic acid (2-FA) and 5-hydroxyfuroic acid (5-HFA). The paired PEC electrolyzer is constructed with Au/α-Fe₂O₃/RGO as the photocathode and Ru/RGO-modified Pt as the anode. The photocathode-driven half-cell PEC CO₂ conversion test shows a high CH₃OH yield of 43 μmol L⁻¹ cm⁻² at 21.5% quantum efficiency with a Faradaic efficiency of 91% at -0.6 V under 450 nm simulated light irradiation. In a paired PEC electrolyzer, the CH₃OH yield reached a twofold enhancement over that of half-cell PEC conversion along with electro-oxidation of furfural to high yields of 2-FA and 5-HFA at 82% FF conversion efficiency. The electro-oxidation of furfural is a 2e⁻/H⁺ and 4e⁻/H⁺ process, which leads to instant PEC CO₂ conversion into CH₃OH at the photocathode. A paired electrolyzer possible mechanism is discussed. This research highlights the great prospects of techno-economic processes for producing valuable products at both electrodes.

Keywords: Photoelectrocatalytic CO₂ reduction; Photocathode; Methanol; Electro-oxidation of furfural; Sustainable liquid fuel production
1. Introduction

Photoelectrochemical cells (PECs) are the most significant approach to the reduction of CO₂ to high-value chemicals to alleviate climate change and the energy crisis and advance a low-carbon economy.¹,² With the input of solar energy, PEC CO₂ reduction to CH₃OH, formate, ethanol, methane, and CO has been widely recognized as a promising approach to CO₂ mitigation.³,⁴ In typical PECs, CO₂ reductive products are formed by photoelectrocatalytic reduction reactions at the surfaces of semiconducting photocathodes. The PECs, which connect a metallic anode for water oxidation (2H₂O → O₂ + 4H⁺) to produce O₂ along with protons (H⁺), and a p-type photocathode could produce sufficient photogenerated electrons over a wide range of solar light wavelengths; thus, the produced H⁺ and e⁻ can effectively participate in the reduction of CO₂ at the cathode surface.⁵ Usually, various nanostructured p-type semiconductors and their composites, including Cu NP/f-RGO/CF,⁶ CuFe₂O₄@PANI,⁷ Au NP-modified glass carbon electrodes,⁸ porphyrin-modified cobalt sulfide,⁹ CuBi₂O₄/TiO₂-NTs,¹⁰ Pt-modified TiO₂ nanotubes,¹¹ CuO/g-C₃N₄,¹² GO–CuFe₂O₄,¹³ Ag/Cu₂O/CuO electrodes,¹⁴ S-TiO₂@GS,¹⁵ CuBi₂O₄/TiO₂-NTs,¹⁰ worm-like FeS₂/TiO₂ nanotubes,¹⁶ Cu@porphyrin-COFs nanorods,¹⁷ TiO₂NT@PDA electrodes,¹⁸ Pd-Cu cathodes,¹⁹ ZnO:rGO-Cu:Cu₂O,²⁰ Cu/Cu₂O-Cu(BDC-NH₂),²¹ and FTO/Cu/Bi₂Se₃-Se/Cu2O electrodes²², were successfully used as the photocathode or photoanode for PEC CO₂ reduction for fuel production.

However, the production of O₂ via water oxidation in the anodic chamber is not economically favored because of its low market value. Recent works have demonstrated that the anodic reaction would have potentially favorable kinetics for the conversion of bio-oil compounds into value-added chemicals to enhance the utility and efficiency of PECs.²³ Current state-of-the-art paired electrolysis cells are configured for the simultaneous oxidation and reduction of 5-(hydroxymethyl) furfural (HMF) over Ag/C catalysts. A paired electrochemical cell was successfully used for the simultaneous conversion of HMF to 2,5-bis(hydroxymethyl)furan (BHMF) and 2,5-furandicarboxylic acid (FDCA) with a combined electron efficiency of 187% at a controlled cathodic potential of -1.3 V.²⁴ NiBₓ is used as a common electrocatalyst for paired electrodes and can enhance the 99% product selectivity during the hydrogenation of p-nitrophenol to p-aminophenol and the simultaneous electro-oxidation of HMF to FDCA.²⁵ A bifunctional electrocatalyst of Ni₂P/Ni/NF acts as the electrocatalyst for the cathode and anode for the integrated electrocatalysis of H₂ evolution and FF oxidation to 2-furoic acid (2-FA) with 100%
Faradaic efficiency (FE). Furthermore, an H-type two-electrode catalysis system assembled with Ni2P/CFC as the anode and Cu3P/CFC as the cathode simultaneously produces 2-FA with FEs of 90.0–98.0% and furfuryl alcohol (FAL) with FEs of 92.0–98.0%. However, these processes required a higher anodic potential (0.8 to 1.4 V) for the oxidation reactions and a higher cathodic potential (-0.8 to -1.4 V) for the reduction of bio-oil compounds. The higher anodic and cathodic potentials lead to undesirable reactions of H2 and O2 evolution via water decomposition, thus resulting in decreases in the electrochemical biomass conversion and Faradaic efficiency (FE). For this issue, such a paired electrolysis system may be extended to concurrent photoelectrochemical reduction of CO2 and oxidation of bio-oil compounds at lower negative potentials of -0.3 to -0.8 V. To date, no studies have been reported for the simultaneous photoelectrocatalytic reduction of CO2 to a highly selective product of CH3OH and the electro-oxidation of bio-oil compounds at a lower negative bias under solar light irradiation. During the paired electrolysis reactions, photogenerated electrons and holes are produced at the surfaces of the photocathode under solar light irradiation, while the bio-oil compounds are efficiently oxidized along with many protons (H+), which could potentially be involved in the reduction of CO2 at cathode surfaces. In this techno-economic process, CO2 is the main cathodic reactant for the selective production of CH3OH, while the selection of a suitable bio-oil compound is necessary for the anodic oxidation reaction, which can supply many protons to PEC CO2 reduction. Recently, a few studies have reported the direct electro-oxidation of furfural to produce 2-FA and 5-HFA along with much H+ and e− discharge over the surfaces of anodes. This investigation clearly shows that the reduction rate of CO2 can be effectively enhanced when furfural is an oxidation agent in paired electrolysis PEC systems. Therefore, the benefits of developing paired PEC systems are twofold: reduction of CO2 to CH3OH and oxidation of furfural to the valuable chemical platforms of 2-FA and 5-HFA at an ambient temperature and pressure to minimize the O2/H2 evolution reactions. However, tuning the product selectivity, enhancing the reduction rate, and increasing solar energy use by suitable photo- and electrocatalysts are the major challenges for this paired electrolyzer system. Ideal nanostructured p-type semiconductors, which can efficiently reduce CO2 to fuels with low energy consumption, play a vital role in addressing the aforementioned issues. The p-type semiconductor α-Fe2O3 is known as a visible light-driven and cost-effective photocathode for the generation of H2 by water splitting because of its smaller band gap of ~2.1 eV. Research results showed that the incorporation of metallic Au nanoparticles and
RGO incorporated with α-Fe2O3 can potentially enhance the photocurrent because of the plasmonic effect of Au under visible light and the higher electrical conductivity of the π-conjugated structure of RGO.\textsuperscript{33,34}

This work aimed at designing a paired PEC for the simultaneous reduction of CO₂ to fuels and electro-oxidation of FF to value-added chemicals. Plasmonic Au- and RGO-incorporated α-Fe₂O₃ nanorods (Au/α-Fe₂O₃/RGO) were used as photocathodes for the effective reduction of CO₂ to highly selective CH₃OH, while the Ru/RGO-modified Pt electrode was used as an anode for the oxidation of furfural to the value-added chemicals 2-FA and 5-HFA, respectively. The yield of the reductive cathodic product of CH₃OH was tuned by varying the concentration of anodic reactant furfural at a lower cathodic potential of -0.6 V under simulated solar light irradiation. The reductive and oxidative mechanisms of paired PECs were clearly depicted based on the experimental results. The feasibility, target desired products, efficiency, and advantages of the paired PEC system were discussed with the help of other literature in the field.

2. Experimental Methods

2.1 Materials

Graphite flakes (~105 μm flakes), furfural (99%), 5-hydroxy-2(5H)-furanone, 2(5H)-furanone, 2-propanol, furoic acid (98%), potassium hydroxide (KOH), ferrous chloride tetrahydrate (FeCl₂·4H₂O), ethanol, methanol, 5% and 20% w/w Nafion solutions in aliphatic alcohols, potassium permanganate (KMnO₄), gold(III) chloride, sodium hydroxide (NaOH), and hexadecyltrimethylammonium bromide (CTAB) were purchased from Sigma Aldrich without further purification. Moreover, GO was prepared via a modified Hummer’s method.

2.2 Synthesis of Au/α-Fe₂O₃/RGO nanocomposites

In a typical process, 0.5 M CTAB was dissolved in 30 mL Milli-Q water and magnetically stirred for 30 min at room temperature. Further, 0.2 M FeCl₂·4H₂O and 0.1 M NaOH were dissolved in a CTAB micelle solution. Afterwards, the Fe(OH)₂-CTAB micelle suspension was mixed with 30 mL of GO solution (2 mg/mL), and the reaction temperature was kept at 70 °C for 30 min to form an Fe(OH)₂-CTAB/GO suspension. Moreover, 50 mM gold(III) chloride was dissolved in 10 mL of deionized water. A 5 mL aliquot of lemon juice was used as a green reducing agent to reduce the Au³⁺ ions into metallic Au⁰. Furthermore, the metallic Au⁰ solution was slowly added to the Fe(OH)₂-CTAB/GO suspension, and the complete mixture was transferred into a 100 mL Teflon-
lined stainless steel autoclave. The hydrothermal treatment was performed at 180 °C for 12 h. After completion of the reaction, the residue was separated and washed with deionized water several times and then with ethanol. Finally, the obtained precipitate was dried overnight using a vacuum oven at 100 °C to obtain a Au/α-Fe₂O₃/RGO nanocatalyst. The same experimental procedure was followed for the preparation of Au/α-Fe₂O₃ without the addition of GO solution using a hydrothermal process. Additionally, a hydrothermal method was used for the synthesis of Ru/RGO at 180 °C for 12 h, and the synthesis procedure is presented in the supplementary information.

2.3 Characterizations

The sample morphology, elemental composition and crystallinity were collected from HR-TEM (Titan TEM 300 kV) with the FFT pattern and SEM (JEOL JSM-7610F FEG-SEM) with EDS. XRD patterns of the catalysts were collected using PANalytical Empyrean at 40 kV and 40 mA with Cu Kα radiation. Raman measurements were performed by a Witec Alpha 300 Raman spectrometer (laser wavelength: 532 nm). FT-IR analysis of the catalyst was performed using a Bruker Vertex 80v FT-IR spectrometer (wavenumber range of 450 to 4500 cm⁻¹). An ESCALab MKII XPS was used to analyze the chemical states and composition of the catalyst. The surface area of the catalyst was estimated via a Quantachrome Autosorb 06 surface area analyzer at –196 °C under N₂. Prior to the adsorption measurement experiments, the catalyst was degassed at 250 °C for 4 h. PL spectra of the various catalysts were obtained using a PerkinElmer LS55 luminescence spectrophotometer, and a UV 2600 spectrometer (Shimadzu) was used to acquire the UV-vis spectra of the catalysts.

2.4 Photoelectrochemical analysis of the catalysts

The photoelectrochemical analysis of the various catalysts was performed in an H-cell using a three-electrode configuration in which the Ru-RGO-modified Pt electrode (1×1 cm²) was used as the anode, the Au/α-Fe₂O₃/RGO nanocatalyst-modified ITO was used as the photocathode (1×1 cm²), and Ag/AgCl was used as the reference electrode. The photocathode and anode electrodes were prepared via a simple drop-cast technique. Briefly, 5% and 20% w/w Nafion solutions in aliphatic alcohols and 100 mg of the catalyst were sonicated for 4 h to obtain the catalyst ink. Furthermore, the ink was uniformly drop-cast on the ITO substrate and subsequently dried at 60 °C in a vacuum oven for 4 h to obtain photocathodes. The Ru-RGO-modified Pt anode was prepared using the same method as above. The amount of active catalyst was estimated from the
difference between before and after coating the catalyst over the electrode substrate. A VMP-300 (BioLogic Instruments, US) was used to analyze the electrochemical characterization of the electrodes. Initially, chronoamperometry and electrochemical impedance techniques were used to record the photoelectrochemical activity of the catalysts. Linear sweep voltammetry (LSV) and EIS spectra were obtained in 0.1 M KOH aqueous electrolyte solution at a scan rate of 50 mV s\(^{-1}\) with and without illumination of simulated visible light. A xenon lamp (wavelength of 340 to 450 nm) was used as the light source for the photoelectrochemical studies. Additionally, the CO\(_2\) reactant gas was supplied to the cathode chamber to determine the catalytic performances of the as-prepared catalyst under visible light.

### 2.4 Photoelectrochemical conversion of CO\(_2\)

The photoelectrocatalytic CO\(_2\) reduction was performed in a homemade H-type reactor, and all the experiments were conducted in 0.1 M KOH electrolyte solution at an applied potential of \(-0.6\) V with a cutoff filter of 450 nm. The working, counter, and reference electrodes were Au/\(\alpha\)-Fe\(_2\)O\(_3\)/RGO/ITO, Ru-RGO modified Pt, and Ag/AgCl, respectively. The cathodic and anodic chambers were separated using a proton exchange membrane (Nafion N-117). Before conducting each experiment, N\(_2\) was purged through the cathode side, and a 5 sccm flow rate of high-purity CO\(_2\) gas (99.99\%) was bubbled through the catholyte solution. The CO\(_2\) photoreduction products were analyzed using an Agilent gas chromatography mass spectrometry (GC/MS) system (Agilent 7890B GC & amp; 5977A MSD) equipped with flame ionization detection (GC-FID). A Tedlar bag was used to collect the gaseous products throughout the reaction and then analyzed using a gas chromatograph (Agilent 7890B, USA) equipped with a thermal conductivity detector. Further, additional experiments were conducted at various applied potentials (-0.4 to -1.0 V) in 0.1 M KOH electrolyte solution with a cutoff filter of 400 nm. The incident photon-to-current conversion efficiency (IPCE), Faradaic efficiency (FE), and quantum efficiency (QE) were estimated using equations (1), (2), and (3):

\[
\text{IPCE} (%) = \frac{123.7 \times J}{\lambda (\text{nm}) \times I (\text{mW/cm}^2)} \times 100 \quad (1)
\]

\[
\text{QE} (%) = \frac{\text{moles of electrons passed to form products}}{\text{moles of incident photons}} \quad (2)
\]

\[
\text{FE} (%) = 2F \times \frac{n_i}{(I \times t)} \quad (3)
\]
where \( j \) is the current density (mA cm\(^{-2}\)), \( \lambda \) is the wavelength of the light, \( F \) is Faraday’s constant (96,485 C mol\(^{-1}\)), \( n_i \) is the number of moles of products, \( I \) is the photocurrent (A), and \( t \) is the time (s).

### 2.4 Simultaneous photoelectrochemical conversion of CO\(_2\) and electrocatalytic oxidation of furfural

The simultaneous photoelectron reduction of CO\(_2\) and electrocatalytic oxidation of furfural were conducted in a homemade H-type cell that was combined with a Fe\(_2\)O\(_3\)/RGO/ITO photocathode, Ru-RGO-modified Pt anode, and Ag/AgCl reference electrode, as previously described. Prior to the experiments, N\(_2\) was purged through the catholyte and anolyte for 10 min under stirring. An aliquot of 0.1 M KOH was used as the electrolyte for both chambers. High-purity CO\(_2\) gas (99.99%) was bubbled through the catholyte solution, and 10 mmol of furfural was added to the anolyte. The electrochemical cell was operated by controlling the cathode potential of -0.6 V with simulated solar light (wavelength of 400 nm). After the reaction, the liquid products from the catholyte and anolyte were collected separately and analyzed via a GC/MS (Agilent 7890B GC & amp; 5977A MSD) equipped with flame ionization detection (GC-FID). Eqns. (1), (2), and (3) were used to estimate the incident photon-to-current conversion efficiency (IPCE), Faradaic efficiency (FE), and quantum efficiency (QE) of photoelectrocatalytic CO\(_2\) reduction. The furfural conversion (X, %), product yield (Y, %), and selectivity (S, %) were estimated based on Eqns. (4), (5), and (6).

\[
\text{FF conversion} (\%) = \frac{I_{FF} - F_{FF}}{I_{FF}} \times 100 \quad (4)
\]

\[
\text{Yield} (\%) = \frac{m_{FF}}{I_{FF}} \times 100 \quad (5)
\]

\[
\text{FFA selectivity} (\%) = \frac{m_{FFA}}{I_{FF} - F_{FF}} \times 100 \quad (6)
\]

where \( I_{FF} \) is the initial FF concentration in M, \( F_{FF} \) is the final FF concentration in M, and \( m_{FFA} \) is the final number of moles of obtained products.

### 2. Results and Discussion

#### 3.1 Structural, optical and morphological analysis

XRD spectroscopy was used to determine the phase purity and crystalline structure of the Au/\( \alpha \)-Fe\(_2\)O\(_3\) and Au/\( \alpha \)-Fe\(_2\)O\(_3\)/RGO electrocatalysts, as shown in Figure 1a. In the XRD pattern of the...
Au/α-Fe₂O₃ electrocatalyst, the diffraction peaks at 2θ = 23.97°, 32.78°, 35.56°, 40.71°, 49.17°, 53.77°, 62.29°, 63.92°, and 72.96° represent the crystal planes of (012), (104), (110), (113), (024), (116), (213), (300), and (021), respectively, of pure phase hematite with a rhombohedral crystal assembly (hematite, JCPDS No. 24-0072) with lattice parameters of a = 0.29 nm and c = 0.57 nm. In addition, a noticeable diffraction peak at 2θ = 37.63° was observed for the (111) crystal plane of the cubic phase of metallic Au NPs. Debye-Scherer’s equation is used to estimate the crystallite sizes of the α-Fe₂O₃ nanorods and metallic Au NPs in the Au/α-Fe₂O₃ sample as 168 and 7 nm, respectively. Furthermore, the XRD pattern of the Au/α-Fe₂O₃/RGO ternary electrocatalysts showed peaks similar to those of Au/α-Fe₂O₃, while an additional weak graphitic peak appeared at 26.5° associated with the (002) plane of RGO in the Au/α-Fe₂O₃/RGO nanocatalyst. The average crystallite sizes were calculated to be 37 and 6 nm, corresponding to α-Fe₂O₃ and Au crystalline phases in the Au/α-Fe₂O₃/RGO ternary electrocatalyst. The XRD study adds to the evidence that the Au ions were completely reduced by lemon juice as a green reducing agent and homogeneously disseminated on the surfaces of α-Fe₂O₃/RGO under the hydrothermal technique, resulting in the formation of smaller crystallite sizes of the Au NPs on the surfaces of α-Fe₂O₃/RGO sheets. The crystallite size of α-Fe₂O₃ was found to decrease in the presence of RGO in the ternary Au/α-Fe₂O₃/RGO sample, indicating that RGO could effectively control the nucleation growth of α-Fe₂O₃ nanorods in the presence of SDS micelles. Additionally, rod-like CTAB micelles played a vital role in promoting the c-axis growth of α-Fe₂O₃, resulting in the formation of rod-like α-Fe₂O₃ nanostructures under hydrothermal reaction conditions. Recent research results clearly show that rod-like α-Fe₂O₃ can provide a larger surface area, which can potentially enhance the available photoelectrocatalytic sites for the effective reduction of CO₂ to fuels. Furthermore, Raman spectroscopic analysis was performed to investigate the ordered and disordered crystal structures of the as-developed Au/α-Fe₂O₃ and Au/α-Fe₂O₃/RGO nanocatalysts through molecular vibration studies. The Raman spectrum of Au/α-Fe₂O₃ in Figure 2b exhibits peaks at 221, 291, 401, 607, and 1300 cm⁻¹, which are in accordance with the existing literature. The peaks at 221 and 401 cm⁻¹ are associated with the A₁g modes, while the E₉ modes of α-Fe₂O₃ are related to the peaks at 291 and 607 cm⁻¹. Remarkably, the peak at 607 cm⁻¹ is associated with the phase purity of disordered α-Fe₂O₃ without any impurities, such as the hematite matrix. Additionally, the Raman spectrum of Au/α-Fe₂O₃/RGO confirms the presence of defects and cavities by presenting the characteristic D band peaks at 1354 cm⁻¹, as shown in Figure 2b. The appearance of the broad peak at 1589 cm⁻¹
(G band) signifies the degeneration of the phonon mode (E\textsubscript{2g} symmetry) at the Brillouin zone center and relates to the well-organized graphitic nature. Additionally, the smaller intensity Raman active modes of A\textsubscript{1g} and E\textsubscript{g} correspond to the hematite phase in the ternary electrocatalyst. The D and G energy bands were ascribed to the vibrations of sp\textsuperscript{3} (C–C) and sp\textsuperscript{2} (C=C) carbon atoms of disordered graphite in the ternary nanocatalysts. In addition, the degree of structural disorder in Au/α-Fe\textsubscript{2}O\textsubscript{3}/RGO was predicted by calculating the intensity ratio (I\textsubscript{D}/I\textsubscript{G}). The relatively low structural defects (I\textsubscript{D}/I\textsubscript{G} = 0.852) ensure the superior electrical conductivity of the synthesized electrocatalyst, and hence it could be a promising material for photocatalytic and electrochemical applications, such as photoelectrocatalytic CO\textsubscript{2} reduction.

Figure 1 (a) X-ray diffraction analysis, (b) Raman spectrum, (c) FT-IR analysis of Au/α-Fe\textsubscript{2}O\textsubscript{3} and Au/α-Fe\textsubscript{2}O\textsubscript{3}/RGO nanocatalysts, (d) diffuse reflectance spectrum, (e) Tauc plot of (αhν)\textsuperscript{2} versus photon energy (hν), and (f) PL analysis of α-Fe\textsubscript{2}O\textsubscript{3} and Au/α-Fe\textsubscript{2}O\textsubscript{3} and Au/α-Fe\textsubscript{2}O\textsubscript{3}/RGO nanocatalysts.

The chemical structure and functional groups on the Au/α-Fe\textsubscript{2}O\textsubscript{3} and Au/α-Fe\textsubscript{2}O\textsubscript{3}/RGO nanocatalysts were identified using the FT-IR spectra of the samples, as shown in Figure 1c. The FT-IR spectrum of the Au/α-Fe\textsubscript{2}O\textsubscript{3} nanocatalyst exhibits two intense peaks at 572 cm\textsuperscript{-1} and 3406 cm\textsuperscript{-1} attributed to the heavy metal vibrations of Au–Fe–O and a stretching vibration of water
molecules, respectively. Similarly, the FT-IR spectrum of the Au/α-Fe₂O₃/RGO ternary nanocatalyst displayed six characteristic peaks at 562, 1634, 1710, 2847-2916 and 3431 cm⁻¹ corresponding to the Au-Fe-O vibration in Au/α-Fe₂O₃, the stretching vibration of C=O, the stretching of C=O in COOH groups, the C-H stretch of the methylene groups and a stretching vibration of water molecules, respectively. Furthermore, the intense peaks at 1710, 2847-2916 and 3431 cm⁻¹ confirm the availability of the various remaining oxygen-based functional groups on the surface of RGO, and hence these groups are the active sites for the functionalization and incorporation/impregnation of Au and α-Fe₂O₃ nanorods. Noticeably, for the composite material (Au/α-Fe₂O₃/RGO), the intensity of C=O stretching decreased to 562 cm⁻¹, while the skeletal vibrations of C=C were identified at higher intensity. These results confirm the incorporation of Au/α-Fe₂O₃ nanoparticles on the surface of RGO nanosheets preferentially through oxygen-containing functional groups (COOH).

The UV-visible absorption spectra and PL spectra of α-Fe₂O₃, Au/α-Fe₂O₃, and Au/α-Fe₂O₃/RGO were observed to explore the optical properties of the nanocatalysts and are depicted in Figure 1d-f. The UV-visible spectra of the α-Fe₂O₃, Au/α-Fe₂O₃, and Au/α-Fe₂O₃/RGO nanocatalysts are presented in Figure 1d. All the photocatalysts exhibited wider absorbance spectra in the wavelength range of 400 to 700 nm, which exposed their efficient visible light harvesting capability. Compared with α-Fe₂O₃, Au/α-Fe₂O₃ exhibits more intensive absorption in the visible region because of the surface plasmon resonance of metallic Au NPs. The results suggest that the Au/α-Fe₂O₃ catalyst possesses better visible light absorption characteristics than those of pure α-Fe₂O₃ nanorods. Interestingly, the absorption spectrum of the Au/α-Fe₂O₃/RGO nanocatalyst is slightly shifted to shorter wavelengths because of the size reduction effect of the α-Fe₂O₃ nanorods in the ternary nanocatalysts, thus changing the light absorption wavelength from lower energy to higher energy in the visible region. These results clearly show that the Au/α-Fe₂O₃/RGO nanocatalyst is a promising potential photocatalyst for harvesting solar light. The optical band gap (E_g) of pure hematite and its associated nanocomposites can be calculated from the absorption spectroscopy data as shown using the following equation:

\[(\alpha h\nu)^2 = A (h\nu - E_g)\]

where ‘α’ represents the absorption coefficient, and ‘A’ and ‘hν’ are a constant and the energy of light, respectively. The relationship between (αhν)^2 and photoenergy (hν), known as the Tauc plot,
is illustrated in Figure 2e. The linear intercepts of the Tauc plots with the energy axis demonstrate the energy gaps of the developed materials. Briefly, pristine $\alpha$-Fe$_2$O$_3$ exhibited a photon energy ($E_g$) of 2.15 eV, while the Au/$\alpha$-Fe$_2$O$_3$ and Au/$\alpha$-Fe$_2$O$_3$/RGO nanocatalysts exhibited $E_g$ values of 2.26 and 2.39 eV, respectively, as displayed in Figure 2e. The increase in band energy is due to the smaller diameter of $\alpha$-Fe$_2$O$_3$ in the composite nanomaterials, which is consistent with the XRD analysis of the nanocatalysts. The wider bandgap of the Au/$\alpha$-Fe$_2$O$_3$/RGO nanocatalyst is beneficial for visible light absorption in the lower wavelengths of the visible region, resulting in enhanced photogenerated electrons and prevention of the recombination effect of the e$^-$/h$^+$ pairs. Additionally, photoluminescence (PL) spectral analysis is used to investigate the recombination processes of the photoinduced e$^-$/h$^+$ pairs in the nanocomposites. The migration/transfer of photoexcited e$^-$ and h$^+$ between the valence band (VB) and the conduction band (CB) is responsible for exciting the compound and yielding emission at a specific wavelength. The PL spectra of the pure $\alpha$-Fe$_2$O$_3$ nanocatalyst and the Au/$\alpha$-Fe$_2$O$_3$ and Au/$\alpha$-Fe$_2$O$_3$/RGO nanocatalysts are shown in Figure 1f. All the photocatalysts exhibited intense PL emission peaks from 640 to 680 nm. The high intensity of the PL spectrum of pristine $\alpha$-Fe$_2$O$_3$ is due to the electronic transitions that originate from the recombination of photoinduced e$^-$/h$^+$ pairs within $\alpha$-Fe$_2$O$_3$ nanoparticles, and this luminescence can be visually perceived even at room temperature. Importantly, a slight decline in PL intensity was observed by incorporating Au onto $\alpha$-Fe$_2$O$_3$ because of the strong electron-transfer ability of the metallic Au NPs, which decreased further in the Au/$\alpha$-Fe$_2$O$_3$/RGO ternary nanocatalyst because of the higher electrical transport property of the $\pi$-conjugated structure of RGO. The decrease in the PL emission intensity indicates e$^-$/h$^+$ pair separation by considerably influencing the radiative alignment of photogenerated charge carriers, which is highly desirable for photochemical reduction of CO$_2$ to fuels.
X-ray photoelectron spectroscopy (XPS) is a powerful tool for analyzing the interaction and charge transfer mechanism of nanoparticles in composite materials. For instance, the impregnation of Au/α-Fe₂O₃ onto the surface of RGO is confirmed by conducting XPS analysis of photochemically synthesized ternary nanocatalysts. The complete survey spectrum of Au/α-Fe₂O₃/RGO comprises four dominant peaks at 85, 284.35, 530 and 711 eV attributed to Au 4f, C 1s, O 1s and Fe 2p, respectively, as demonstrated by Figure 2a. The XPS survey spectrum of the nanocomposite indicates the presence of Au and α-Fe₂O₃ on the surface of RGO nanosheets. Figure 2b shows the deconvoluted Au 4f XPS spectrum, which is deconvoluted to Au 4f₇/₂ and Au 4f₅/₂ at binding energies of 82.1 and 85.8 eV, respectively. The presence of this intense metallic Au peak suggests that the Au³⁺ ions were completely formed by lemon juice as a green reducing agent and were successfully incorporated on the surfaces of α-Fe₂O₃/RGO. To investigate the carbon states in the ternary nanocatalyst, the C 1s core levels are also deconvoluted and shown to consist of four intense peaks attributed to the carbon-oxygen binding arrangements, as depicted in Figure 2c.

Specifically, the peaks centered at binding energies of 284.0 eV and 288.1 eV represent the
nonoxygenated aromatic sp² carbon ring (C=C) of RGO, while the remaining two peaks are due to the oxygenated functional groups C=O (286.1 eV) and O-C=O (288.9 eV) of the ternary nanocomposite. Moreover, the deconvolution of the O 1s spectrum in Figure 2d displays four distinct peaks at 528.6, 529.9, 531.6 and 533.2 eV corresponding to Fe-O, C-O-Fe, C=O, and C-O, respectively. Additionally, the oxidation state of Fe in Au/α-Fe₂O₃/RGO was examined and is indicated by Figure 2e, which shows two wider peaks at 710.1 eV and 724.2 eV due to the spin orbital coupling of Fe 2p into Fe 2p₃/₂ and Fe 2p₁/₂, corresponding to Fe²⁺ and Fe³⁺, respectively.³⁸ A low intensity curve in the Fe 2p XPS spectrum associated with the shoulder satellite peak was also detected, indicating that very small amounts of impurities (γ-Fe₂O₃ or FeO in the nanocomposites) are present on the surfaces of α-Fe₂O₃. The XPS spectra revealed that Au/α-Fe₂O₃/RGO is a mixed valence hetero-nanostructured material with superior physicochemical characteristics and is a promising material for catalytic applications. Furthermore, the surface area and porous features of the synthesized nanocatalyst were examined via N₂ adsorption-desorption isotherms. The Au/α-Fe₂O₃/RGO sample exhibited a distinctive type IV IUPAC isotherm with an H₃ hysteresis loop for the P/P₀ range of 0.1 to 1.0. Furthermore, the as-produced ternary nanocomposite exhibited a BET specific surface area of 180 m² g⁻¹ with pore sizes ranging between 2 and 10 nm, as measured using the BJH adsorption pore size distribution technique, as shown by the inset of Figure 2f. The gold-incorporated hematite matrix on the surface of the RGO nanosheets exhibited a unique mesoporous nature and hence is more favorable for catalytic activities, fast ion/electron transfer mechanisms and electrolyte penetration, which may enrich the photoelectrocatalytic applications for CO₂ reduction.
Figure 3 (a) TEM image of Au/α-Fe$_2$O$_3$/RGO nanocatalysts, (b) HR-TEM image of Au/α-Fe$_2$O$_3$/RGO nanocatalysts with an inset of RGO layered structures, (c) HR-TEM image with lattice firings of individual α-Fe$_2$O$_3$ nanorods, (d) FFT pattern of α-Fe$_2$O$_3$ nanorods, (e) HR-TEM image with lattice firings of individual Au NPs, (f) FFT pattern of Au NPs, and (g) formation mechanism of Au/α-Fe$_2$O$_3$/RGO nanocatalysts with assisted rod-like CTAB micelles via the hydrothermal method at 180 °C for 12 h.

Furthermore, the morphology and crystalline structure of the Au/α-Fe$_2$O$_3$ and Au/α-Fe$_2$O$_3$/RGO nanocatalysts were examined using FE-SEM and HR-TEM with fast Fourier transform (FFT), and the elemental composition of the samples was confirmed by EDS analysis. The FE-SEM images with different magnifications in Figure S1a-c show that smaller sizes of metallic Au NPs were grown on regularly shaped α-Fe$_2$O$_3$ nanorods. The high-resolution FE-SEM image in Figure 1c indicates that the obtained α-Fe$_2$O$_3$ nanorods were 168 nm in length and 34 nm in diameter and
the Au NPs were 7 nm, consistent with crystallite sizes evaluated from Scherrer’s formula. Figure S2a, b shows FE-SEM images with different resolution micrographs of Au/α-Fe2O3/RGO nanocatalysts, which further emphasizes the decoration of metallic Au NPs and α-Fe2O3 nanorods on the surfaces of RGO nanosheets. This result reveals that the smaller Au NPs and α-Fe2O3 nanorods were uniformly dispersed on the transparent RGO with few micron-sized agglomeration-free 2D nanosheets. The EDS analysis in Figure S2c shows that the Au/α-Fe2O3/RGO nanocatalysts consist of carbon (C), oxygen (O), Au, and Fe, and no other impurities were observed in the as-synthesized sample. TEM and HR-TEM were used to obtain clear images of the Au/α-Fe2O3/RGO nanocatalysts, as depicted in Figure 3a, b. Six-nm spherical-like Au NPs and regularly shaped, highly crystalline α-Fe2O3 nanorods 120 nm in length with diameters ranging from 15-20 nm were uniformly dispersed on the RGO nanosheets. The inset in Figure 3b clearly shows that RGO consists of few-layered transparent nanosheets under an electron beam in the presence of dual crystalline particles, including Au and α-Fe2O3. The HR-TEM image in Figure 3c displays the lattice fringes of α-Fe2O3 nanorods with a d-spacing of 0.3178 nm, which can be indexed to the (110) plane of the rhombohedral α-Fe2O3 structure, consistent with the FFT pattern of individual α-Fe2O3 nanorods, as displayed in Figure 3d. The clear lattice fringes of individual Au NPs show a d-spacing of 0.2137 nm, corresponding to the (111) plane of the cubic Au crystalline structure, as shown in Figure 3e. Furthermore, the FFT pattern in Figure 3f confirms the polycrystalline nature of the Au NPs that are present in the Au/α-Fe2O3/RGO nanocatalysts. In particular, CTAB was effectively used as a structure directing agent for the preparation of highly c-axis oriented α-Fe2O3 nanorods in the ternary nanocomposites, whose formation mechanism is schematically depicted in Figure 3g. Initially, a 0.1 M critical micelle concentration leads to the formation of rod-like CTAB micelles that are effectively adsorbed by Fe2+ ions via electrostatic interactions. When the pH increased to 10.0, nanorod-like goethite (α-FeOOH) was obtained at 70 °C, and the goethite nanorods were homogeneously dispersed on the surfaces of GO nanosheets. The epoxy, hydroxyl and carboxylic oxygenated groups on GO acted as anchoring sites for the electrostatic adsorption of goethite nanorods, resulting in enhanced agglomeration of free individual nanorods present on the GO surfaces. Meanwhile, Au3+ ions were effectively reduced to metallic Au clusters by lemon juice, which acted as a green reducing agent, and then the nanosized Au colloidal clusters dispersed onto goethite/GO surfaces under magnetic stirring for the required time. The resulting goethite and Au colloidal clusters simultaneously underwent
hydrothermal recrystallization on the GO surfaces. During nucleation growth, Au\textsuperscript{0} clusters self-assembled into metallic Au nanoparticles, and goethite phases were converted into hematite (\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}), while GO could thermally reduce into RGO, resulting in the formation of Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}/RGO ternary nanocomposites.\textsuperscript{50} The HR-TEM image in Figure 3b clearly indicated that the Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}/RGO ternary nanocomposite consisting of 7 nm sized Au NPs and regularly shaped, highly crystalline \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanorods 120 nm in length and 15-20 nm in diameter were uniformly dispersed on the surfaces of RGO nanosheets. Compared with the spherical-like \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanoparticles, the smaller diameter \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanorods in the ternary nanocomposite possess a larger surface area and can potentially harvest sunlight into photogenerated electrons toward photoelectrochemical reduction of CO\textsubscript{2} into fuels.

### 3.3 Photoelectrochemical activity

The photoelectrochemical performances of the as-fabricated photocathodes of Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} and Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}/RGO were successively evaluated in 0.1 M KOH electrolyte as depicted in Figures 4a and 4b. Initially, LSV was performed for Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}- and Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}/RGO-based electrodes at a scan rate of 50 mV s\textsuperscript{-1} in 0.1 M KOH under N\textsubscript{2}-saturated conditions. The LSV curve of Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} exhibited a noticeable cathodic current (~4.9 mA/cm\textsuperscript{2}), which may be related to the water-proton reduction reaction. The LSV curve of Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}/RGO in Figure 4a shows a substantial enhancement of the cathodic current density (~11.2 mA/cm\textsuperscript{2}) at the same potential, which correlates to the higher electrical conductivity of RGO, which facilitates charge carrier transport between electrocatalysts and the external circuit. Evidently, the Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}/RGO electrode is favored over the HER. These results indicated that the addition of RGO to the Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} catalyst can remarkably improve the electrochemical properties. Under light illumination, Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}/RGO exhibits a larger current density of ~23 mA cm\textsuperscript{-2} with a lower onset potential than that of LSV measured in the absence of light. This enhancement in the photocurrent density of Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}/RGO can be explained in terms of the presence of semiconductor/metal junctions in these hybrids. In the case of the Au/\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}/RGO photocathode, metallic Au NPs can act as good electron sinks to capture photogenerated electrons from semiconducting \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}, thus effectively reducing the rate of electron-hole recombination.\textsuperscript{8} Additionally, metallic Au NPs have excellent light absorption ability due to the SPR effect, which is beneficial for enhancing charge separation via the formation of a Schottky barrier at the junction of metallic Au NPs and semiconducting \(\alpha\)-
Fe₂O₃ NRs.⁸ As a result, α-Fe₂O₃ NRs effectively generate photoelectrons under light illumination, which are further captured by metallic Au NPs, whereas RGO sheets function as excellent electron acceptors and transporters, resulting in an increase in the lifetime of the photogenerated electrons.⁶ Furthermore, the photogenerated electrons are effectively involved in the reduction of CO₂ to alcohols over the Au/α-Fe₂O₃/RGO photocathode. This synergetic effect was further confirmed with LSV measurements over the Au/α-Fe₂O₃/RGO photocathode in the presence of CO₂ under light illumination. The cathodic current density is greatly increased up to ~31.5 mA cm⁻² over that of the Au/α-Fe₂O₃/RGO photocathode with a lower negative overpotential in the presence of CO₂ under light-on conditions. The enhancement of the cathodic current density confirms that CO₂ participates in the reduction process. These investigations revealed that the Au/α-Fe₂O₃/RGO photocathode is a potential candidate for the photoelectroreduction of CO₂ to alcohols.

Furthermore, the kinetics of electron-transfer processes on the Au/α-Fe₂O₃ and Au/α-Fe₂O₃/RGO electrodes were determined via EIS measurements in 0.1 M KOH solution in the absence of light and CO₂. The Nyquist plots of Au/α-Fe₂O₃ and Au/α-Fe₂O₃/RGO are shown in Figure 4b and fitted with the Randles equivalent circuit.⁶,¹⁴ The Au/α-Fe₂O₃/RGO electrode showed a charge transfer resistance Rₘ of ~167 Ω, which is lower than that of Au/α-Fe₂O₃ (~230 Ω), indicating higher Faradaic reaction rates and lower ohmic resistance on the Au/α-Fe₂O₃/RGO electrode surface.⁵¹ The reduced impedance confirmed that the 2D RGO in the nanohybrids provided abundant electron transfer pathways, which further facilitated electron transfer. Under light illumination, the Rₘ value of Au/α-Fe₂O₃/RGO is estimated to be ~82 Ω, which is 2.5-fold smaller than that of Au/α-Fe₂O₃/RGO under dark conditions. This lower Rₘ value primarily arises because of the generation of photoelectrons over the surfaces of the photoelectrode under solar light irradiation. Specifically, the photogenerated electrons from α-Fe₂O₃ NRs can be transferred to Au NPs and then migrate to the surfaces of RGO, which can prevent recombination of the charge carriers, resulting in a decrease in Rₘ under solar light irradiation. In addition, Au/α-Fe₂O₃/RGO exhibits a much smaller semicircle in the presence of CO₂ under solar light irradiation. The lower Rₘ value of ~65 Ω for Au/α-Fe₂O₃/RGO can be attributed to CO₂ participating in the photoelectrochemical reduction process.
Figure 4 (a) Linear sweep voltammetry (LSV) curves, (b) EIS of Au/α-Fe₂O₃, Au/α-Fe₂O₃/RGO, Au/α-Fe₂O₃/RGO LON, and Au/α-Fe₂O₃/RGO LON with CO₂ electrodes. Reaction conditions: 0.1 M KOH aqueous electrolyte solution, Ru/RGO-modified Pt counter electrode, Ag/AgCl reference electrode with a scan rate of 50 mV s⁻¹ and a light source of 450 nm. (c) Yields of CH₃OH and CO (μmol/L, cm²) over various catalysts of α-Fe₂O₃, Au/α-Fe₂O₃, Au/α-Fe₂O₃/RGO, and Au/α-Fe₂O₃/RGO LON. Reaction conditions: Ru/RGO-modified Pt anode, Au/α-Fe₂O₃/RGO/ITO photocathode, Ag/AgCl reference electrode, CO₂-saturated 0.1 KOH aqueous solution, 120 min of optimized reaction time, 450 nm light source, and a potential of -0.6 V vs. SCE. (d) Different applied potentials vs. yields of CH₃OH and CO (μmol/L, cm²) over the Au/α-Fe₂O₃/RGO/ITO photocathode, Ru/RGO-modified Pt anode, Ag/AgCl reference electrode, CO₂-saturated 0.1 KOH aqueous solution, 120 min of optimized reaction time, and a 450 nm light source. (e) Proposed CO₂ reduction mechanism over the Au/α-Fe₂O₃/RGO photocathode.

3.4 Photoelectrochemical reduction of CO₂

To evaluate the photoelectrocatalytic reduction performance of the Au/α-Fe₂O₃/RGO photocathode, studies comparing the use of α-Fe₂O₃ and Au/α-Fe₂O₃ as photocathodes and Ru/RGO-modified Pt as the anode were performed. Photoelectrocatalytic CO₂ reduction over different photocathodes was conducted at -0.6 V in 0.1 M KOH electrolyte solution under simulated solar irradiation. Figure 4c shows the product generation yields of the EC and PEC cells.
using α-Fe2O3, Au/α-Fe2O3, Au/α-Fe2O3/RGO, and Au/α-Fe2O3/RGO in the presence of a light-based electrode configuration. A substantial quantity of methanol (CH3OH) was observed as a major product of CO2 reduction for all the photocathodes, while a low yield of CO was observed in the gas products. As shown in Figure 4c, the EC cell configuration of the α-Fe2O3 cathode and Ru/RGO-modified Pt anode exhibits a 9 μmol/(L cm²) yield of CH3OH and a 2 μmol/(L cm²) yield of CO with negligible amounts of other products. The Au/α-Fe2O3 cathode showed a 17 μmol/(L cm²) yield of CH3OH with a 3 μmol/(L cm²) CO yield owing to the greater availability of Au metallic sites, which potentially enhanced the electrocatalytic reduction of CO2. Furthermore, the Au/α-Fe2O3/RGO cathode exhibits an improved performance with a 26 μmol/(L cm²) CH3OH yield and a 4 μmol/(L cm²) CO yield under dark reaction conditions. As expected, the presence of RGO possessing a larger surface area and the improved electron transferability of the nanocomposites resulted in enhanced electrochemical reduction of CO2.11,13 On the other hand, the PEC activity of the Au/α-Fe2O3/RGO photocathode for the reduction of CO2 under simulated solar light was conducted under identical experimental conditions, as shown in Figure 4c. The PEC results showed that the overall CH3OH and CO yields were increased substantially because of photogenerated electrons from the photocathode at a potential of -0.6 V in 0.1 M KOH electrolyte solution. Notably, the Au/α-Fe2O3/RGO photocathode in the PEC cell exhibited a 43 μmol/(L cm²) larger yield of CH3OH and a 3 μmol/(L cm²) yield of CO than those of the Au/α-Fe2O3/RGO cathode in the EC cell and the Au/α-Fe2O3/RGO cathode in the PC cell (Figure S4). This higher photoelectrocatalytic efficiency of the PEC cell can be attributed to the EC and PC synergetic activity by the Au/α-Fe2O3/RGO photocathode. Additionally, Eqn. (2) and Eqn. (3) were used to estimate the quantum efficiency (QE, %) and the Faradaic efficiency (FE, %) of the PEC CO2 reduction to CH3OH. The QE and FE efficiencies of 21.5% and 91%, respectively, were estimated for CH3OH formation in the PEC cell using the Au/α-Fe2O3/RGO photocathode.

Furthermore, the influence of the cell potential on the PEC CO2 reduction and product yields over the Au/α-Fe2O3/RGO photocathode was investigated by applying cell potentials of -0.4, -0.6, -0.8 and -1.0 V, and the results are displayed in Figure 4d. The applied cell potential is observed to have a substantial effect on the formation of CH3OH and other side products: As the applied cell potential increases from -0.4 to -0.6 V, the CH3OH yield increases from 26 to 43 μmol/(L cm²), while the CO yield increases from 2 to 3 μmol/(L cm²), suggesting that the cell potential promotes PEC CO2 reduction over the Au/α-Fe2O3/RGO photocathode. A further increase in the applied cell
potential, i.e., from -0.6 and -0.8 V, causes a decrease in the yield of CH$_3$OH from 43 to 28 μmol/(L cm$^2$), while the yield of CO increases from 3 to 21 μmol/(L cm$^2$), along with the production of formic acid (3 μmol/(L cm$^2$)). On the other hand, a higher applied cell potential of -1.0 V leads to a decrease in the yield of CH$_3$OH (13 μmol/(L cm$^2$)) because of the competition of H$_2$ evolution, while the yields of the other products, including those of CO, FA, and H$_2$, increase up to 10, 19, and 5 μmol/(L cm$^2$), respectively. Therefore, the maximum CH$_3$OH yield (68%) is obtained at a cell potential of -0.6 V in 0.1 M KOH electrolyte over the Au/α-Fe$_2$O$_3$/RGO photocathode under simulated solar light irradiation.

Based on this study and previous work described elsewhere, a conversion mechanism for the photoelectrocatalytic reduction of CO$_2$ to CH$_3$OH is schematically depicted in Figure 4e.\textsuperscript{7–13,16} In this mechanism. Several basic steps are involved in the PEC reduction of CO$_2$ to CH$_3$OH over the Au/α-Fe$_2$O$_3$/RGO photocathode and Ru/RGO-modified Pt anode at -0.6 V in 0.1 KOH electrolyte solution. In the first step, low bandgap α-Fe$_2$O$_3$ nanorods adsorbed photon energy from the irradiated light source and then generated photoelectrons and holes under a negative cell voltage of -0.6 V. In the second step, the generated photoelectrons migrated to the conduction band of the α-Fe$_2$O$_3$ nanorods and were easily transferred to metallic surfaces of Au NPs.\textsuperscript{8} The large specific surface area of RGO offered abundant photoelectron transfer pathways toward the reduction of CO$_2$, and RGO offered a larger adsorption site for the adsorption of CO$_2$ molecules. By this time, photogenerated holes (h$^+$) reacted with water (H$_2$O) molecules at the anode surface, which efficiently produced protons (H$^+$).\textsuperscript{12} The complete anodic and photocathodic reactions are expressed in Eqns. (1), (2), and (3) as follows:

\[
\text{Cathode: } \alpha\text{Fe}_2\text{O}_3 + h\nu \rightarrow \alpha\text{Fe}_2\text{O}_3(h_{vb}^+ + e_{cb}^-) \quad (1)
\]

\[
\text{Cathode: } \alpha\text{Fe}_2\text{O}_3(h_{vb}^+ + e_{cb}^-) + \text{Au} + \text{RGO} \rightarrow \alpha\text{Fe}_2\text{O}_3 + \text{Au} + \text{RGO}(e_{cb}^-) \quad (2)
\]

\[
\text{Anode: } 4h^+ + 2H_2O \rightarrow O_2 + 4H^+ \quad (3)
\]

In the third step, the H$^+$ ions generated at the anodic chamber passed through the proton exchange membrane (Nafion N-117) to the cathodic chamber where they potentially took part in the CO$_2$ reduction reaction.\textsuperscript{11} Finally, the CO$_2$ molecules were reduced at the cathodic chamber in the presence of protons (H$^+$) and photogenerated electrons to form CH$_3$OH, CO, and FA, as demonstrated in Eqns. (4), (5), and (6) as follows:

\[
\text{(4)}
\]

\[
\text{(5)}
\]

\[
\text{(6)}
\]
\[
\text{Cathode: } 6H^+ + 6e^- + CO_2 \rightarrow CH_3OH + H_2O \quad (4)
\]
\[
\text{Cathode: } 2H^+ + 2e^- + CO_2 \rightarrow CO + H_2O \quad (5)
\]
\[
\text{Cathode: } 2H^+ + 2e^- + CO_2 \rightarrow HCOOH \quad (6)
\]
Hence, the superior activities of PEC CO₂ reduction using Au/α-Fe₂O₃/RGO as the photocathode and Ru/RGO-modified Pt as the anode can be ascribed to the following points. First, the α-Fe₂O₃ nanorods had more photoelectrocatalytic active sites, which potentially enhanced the photogenerated electron-holes under solar light irradiation. Second, the photogenerated electrons migrated to the metallic Au sites and then transferred to the RGO surfaces, which suppressed the \(e^-/h^+\) recombination rate. In particular, metallic sites of Au NPs can act as good electron sinks to harvest photoelectrons from the conduction band of α-Fe₂O₃ nanorods, and a higher electrical conductivity of RGO acts as an abundant photoelectron adsorbent that can effectively separate photoelectrons and photoholes.¹³ Third, photogenerated holes react with water to produce protons at the surfaces of the Ru/RGO-modified Pt electrode, which can effectively participate in the reduction of CO₂ molecules at the surfaces of the Au/α-Fe₂O₃/RGO cathode. Thus, it can be concluded that the developed PEC possessed a higher efficiency for the reduction of CO₂ to fuels under mild reaction conditions.

3.5 Photoelectrochemical reduction of CO₂ and electrochemical oxidation of furfural

This outstanding photoelectrocatalytic performance of the PEC, a new techno-economic process, was developed for the simultaneous reduction of CO₂ and oxidation of furfural for practical implementation. In this study, the anionic electro-oxidation of furfural replaced OER to produce value-added chemicals rather than generating O₂ gas of low economic value in the anodic chamber. The paired photoelectrochemical CO₂ reduction reaction and electrochemical FF oxidation reaction was conducted at a controlled cathodic potential of -0.6 V in 0.1 M KOH electrolyte solution in the presence of solar light irradiation using an H-type electrochemical cell. A 10 mmol sample of FF was dissolved in 0.1 M KOH solution in the anode compartment; thus, the oxidation of FF bypassed the OER reaction and generated more protons (H⁺) at the anode surfaces of the Ru/RGO-modified Pt electrode. This result means that many H⁺ ions are effectively involved in the photoelectrocatalytic reduction of CO₂ to the targeted product of CH₃OH over the Au/α-Fe₂O₃/RGO cathode at a controlled negative potential of -0.6 V in 0.1 M KOH electrolyte solution. These outstanding paired electrolysis results are depicted in Figure 5a. In the cathodic reaction,
CO₂ was successfully photoelectrochemically converted to a 51 μmol/(L cm²) yield of CH₃OH and a 2 μmol/(L cm²) yield of CO over the Au/α-Fe₂O₃/RGO cathode at -0.6 V in 0.1 M KOH under solar light irradiation. The quantum energy (QE) and Faradaic efficiency (FE) of CH₃OH are estimated to be 27 and 93%, respectively, which are greater than those of half-cell electrolysis reactions. In the anodic reaction, the main liquid products were 2-furoic acid (2-FA) and 5-hydroxyfuoric acid (5-HFA), along with insignificant amounts of maleic acid (MA) and 2(5H)-furanone. The Ru/RGO-modified Pt electrode exhibited superior electrocatalytic oxidation of FF with a conversion efficiency of 78% and product yields of 59% 2-FA and 19% 5-HFA, as displayed in Figure 5a. Particularly, the RGO in the Ru/RGO-modified Pt electrode provided not only a dispersion platform for the Ru-Pd NPRs but also anchoring sites for the adsorption of FF, which brought the FF molecule near the catalyst sites, thereby promoting the electro-oxidation of FF to the selective production of 2-FA and 5-HFA. Zeta potential analysis was used to determine the FF molecule adsorption properties of the RGO and Ru/RGO nanocomposites. The obtained zeta potential values of -45, -32, and -25 mV correspond to pure FF, RGO, and an FF mixed RGO suspension, respectively, under sonication for 10 min. Notably, the lower zeta potential value of the FF mixed RGO suspension clearly demonstrated that the FF molecules can effectively be adsorbed on the surfaces of RGO nanosheets. An additional electro-oxidation experiment was conducted using Ru/RGO/carbon paper and pure Pt sheets as different anodes for the oxidation of FF under identical experimental conditions, as depicted in Figure S5. Compared with that of the Ru/RGO modified Pt electrode, electro-oxidation of FF over the Pt anode showed a lower FF conversion efficiency of 32% with 27% 2-FA, 3% 5-HFA, and 2% others. This work opens an avenue for producing tunable yields of anodic and cathodic products using various concentrations of FF, as depicted in Figure 5b. In particular, many H⁺ ions are produced during the electro-oxidation of FF at different concentrations, which is beneficial for the reduction of more CO₂ molecules under the optimized experimental conditions of a -0.6 V applied potential in 0.1 M KOH electrolyte in the presence of solar light irradiation.³⁰ The anodic and cathodic products can be tuned by varying the FF concentration from 5 to 35 mmol. In an anodic reaction, as the FF concentration increases from 5 to 25 mmol, the FF conversion efficiency increases from 60 to 82%, and the 2-FA yield increases from 42 to 63%, while the 5-HFA yield increases from 18 to 19%. These results indicate that an increase in FF concentration stimulates the oxidation of FF molecules over Ru/RGO-modified Pt because of the higher number of catalytic active sites of the
electrodes. Interestingly, the cathodic product of CH₃OH yield increases from 52 to 63 μmol/(L cm²), and the CO yield increases from 2 to 4 μmol/(L cm²) with increasing FF amount from 5 to 30 mmol in the anodic chamber. However, the maximum Faradaic efficiency of the formation of CH₃OH reached 95% at a 30 mmol FF amount with a quantum efficiency of 27%. Therefore, the paired electrolysis PEC cell potentially enhanced the reduction of CO₂ to CH₃OH and oxidation of FF to 2-FA and 5-HFA under identical experimental conditions.

Figure 5 (a) Simultaneous reduction of CO₂ over the Au/α-Fe₂O₃/RGO/ITO photocathode and oxidation of FF to 2-FA and 5-HFA over the Ru/RGO/Pt anode. Reaction conditions: FF amount of 10 mmol, 0.1 KOH aqueous solution, 120 min of optimized reaction time, 450 nm light source, and an applied potential of -0.6 V vs. SCE. (b) Effect of FF amount vs. conversion and yields of 2-FA and 5-HFA from the anode chamber and the effect of FF amount vs. the yields of CH₃OH and CO from the cathode chamber. Reaction conditions: FF amount from 5 to 35 mmol, 0.1 M KOH aqueous solution, 120 min of optimized reaction time, 450 nm light source, and an applied potential of -0.6 V vs. SCE. (c) Proposed mechanisms for the simultaneous reduction of CO₂ and oxidation of FF via a paired electrode system using an H-cell
It is known that the amount of protons (H+) and e− formed was certain at a higher FF conversion, which potentially enhanced the protoelectrocatalytic reduction of CO2 over the Au/α-Fe2O3/RGO cathode.26,27,30,52 This is one of the first demonstrations of techno-economic processes for the simultaneous reduction of CO2 and oxidation of furfural into valuable chemicals. With the aforementioned results in hand, a possible photoelectrolysis reaction mechanism is schematically depicted in Figure 5(c). The paired electrolyzer consists of anode and photocathode production/separation parts. This simultaneous electrolyzer reaction is considered a cascade production process in which anode products of protons and electrons are supplied as photocathode reactants to reduce CO2 to methanol, while cathode products of h+ ions react with water molecules to produce OH− ions, which are supplied as anode reactants to oxidize FF to 2-FA. The paired electrolyzer cell was constructed with Au/α-Fe2O3/RGO as the photocathode and Ru/RGO-modified Pt as the anode. The intertwined anionic and cationic membranes were used to separate both electrolyte chambers. In this reaction, the potential of the photocathode was controlled at -0.6 V to maximize the CH3OH yield over Au/α-Fe2O3/RGO in the presence of solar light irradiation, while FF conversion at the Ru/RGO-modified Pt effectively served as the electro-oxidation reaction, as its potential was not controlled. In the cathode production part, photoelectrons (e−) and holes (h+) were generated when Au/α-Fe2O3/RGO was under solar light irradiation. The photogenerated electrons were transferred to metallic Au sites and then trapped by the π-conjugated structure of RGO, where RGO could act as CO2 reduction sites. In the anode production part, photogenerated holes react with water to produce OH− and then react with FF to produce 2-FA and 5-HFA along with H+ + e− discharge over Ru/RGO-modified Pt.26,27,30,52 Because the electro-oxidation of FF to 2-FA and 5-HFA is a 2e− and 4e− process, respectively, it leads to instant oxidation of FF over the surfaces of the anode under a controlled cathodic potential of -0.6 V.11,26 Furthermore, the discharged e− is passed to the cathode by a potentiostat, while the H+ ions migrate through the cationic exchange membrane to reach the cathodic chamber for the photoelectrocatalytic reduction of CO2.12 The paired PEC reaction for the electro-oxidation of FF to 2-FA and 5-HFA over Ru/RGO-modified Pt and the photoelectrocatalytic reduction of CO2 to the selective production of CH3OH on Au/α-Fe2O3/RGO can be represented as follows:

Anode: Furfural + H2O → 2 − Furpic acid + 2 H+/ 2e− (1)

Anode: Furfural + 2H2O → 5 − Hydroxy furpic acid + 4 H+/ 2e− (2)
\[ \text{Cathode: } \text{Au}/\alpha - \text{Fe}_2\text{O}_3/\text{RGO} + h\nu + \text{CO}_2 \xrightarrow{H^+ + e^-} \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (3) \]

Notably, a larger amount of FF (30 mmol) could be effectively converted over the anode under oxidative electrochemical conditions, thus leading to a higher yield of 2-FA and 5-HFA along with much H\(^+\) and e\(^−\).26 This abundance of produced H\(^+\) and e\(^−\) is potentially involved in the photoelectroreduction of CO\(_2\) to CH\(_3\)OH over the Au/\(\alpha\)-Fe\(_2\)O\(_3\)/RGO photocathode. This result indicated that the oxidation of FF promotes the reduction of CO\(_2\) to selective production of CH\(_3\)OH, which further improved with increasing FF concentration under paired electrolyzer reaction conditions. In comparison to the half-cell PEC system, the paired electrolyzer PEC system is a techno-economic process for the simultaneous reduction of CO\(_2\) to fuels and oxidation of FF to value-added chemicals.

4. Conclusion

In summary, a paired photoelectrochemical (PEC) cell was successfully constructed using Au/\(\alpha\)-Fe\(_2\)O\(_3\)/RGO as the photocathode and Ru/RGO-modified Pt as the anode for the simultaneous reduction of CO\(_2\) to alcohols and oxidation of FF to value-added chemicals. A simple hydrothermal method was used for the synthesis of Au/\(\alpha\)-Fe\(_2\)O\(_3\)/RGO ternary nanocomposites at 180 °C for 12 h with the assistance of nanorod-like CTAB micelles as structure directing agents for the formation of \(\alpha\)-Fe\(_2\)O\(_3\) NRs. The as-prepared \(\alpha\)-Fe\(_2\)O\(_3\), Au/\(\alpha\)-Fe\(_2\)O\(_3\), and Au/\(\alpha\)-Fe\(_2\)O\(_3\)/RGO nanocatalysts were well characterized via XRD, Raman, FT-IR, XPS, FE-SEM, HR-TEM, and UV–vis and PL spectral techniques. HR-TEM images demonstrated that the Au/\(\alpha\)-Fe\(_2\)O\(_3\)/RGO ternary nanocomposite consists of 7 nm sized Au NPs, and \(\alpha\)-Fe\(_2\)O\(_3\) NRs, with lengths and diameters under 15 to 20 nm and 120 nm, respectively, were uniformly dispersed on the RGO surfaces. The optical properties of Au/\(\alpha\)-Fe\(_2\)O\(_3\)/RGO are explored on the basis of tailoring the bandgap (E\(_g\)) via the size effect of \(\alpha\)-Fe\(_2\)O\(_3\), the plasmonic effect of Au and chemical interaction between \(\alpha\)-Fe\(_2\)O\(_3\) NRs, Au and RGO nanosheets. The higher band gap of Au/\(\alpha\)-Fe\(_2\)O\(_3\)/RGO (2.39 eV) has a high absorption intensity in the higher energies of the visible region, thus enhancing the photogenerated electrons and preventing the recombination effect of the e\(^−/\)h\(^+\) pairs. The specific surface area and pore size distribution of the Au/\(\alpha\)-Fe\(_2\)O\(_3\)/RGO nanocatalyst are estimated to be 180 m\(^2\) g\(^−1\) and 2 to 10 nm, respectively. A formation mechanism of Au/\(\alpha\)-Fe\(_2\)O\(_3\)/RGO is depicted based on the experimental results. The fabricated Au/\(\alpha\)-Fe\(_2\)O\(_3\)/RGO photocathode showed a greater photocurrent response of \(~31.5\) mA cm\(^−2\) at a lower negative overpotential of -0.6 V in 0.1 M KOH electrolyte in the presence.
of CO₂ under light-on conditions. In EIS studies, Au/α-Fe₂O₃/RGO exhibits a much smaller semicircle and lower Rₘ value of ≈65 Ω in the presence of CO₂ under solar light irradiation, which can be attributed to CO₂ participating in the photoelectrochemical reduction process. In PEC CO₂ conversion, the Au/α-Fe₂O₃/RGO photocathode exhibited a maximum yield of CH₃OH (43 μmol/(L cm²)) with Qₑ and FE efficiencies of 21.5% and 91%, respectively, at -0.6 V in 0.1 M KOH electrolyte under solar light irradiation. A PEC conversion mechanism of CO₂ to CH₃OH has been schematically explained well. The design of a paired PEC electrolyzer for simultaneous CO₂ reduction and furfural oxidation is the key objective of the present study. A paired PEC electrolyzer was fabricated with Au/α-Fe₂O₃/RGO as the photocathode and Ru/RGO-modified Pt as the anode for the simultaneous cathodic reduction of CO₂ to CH₃OH and anodic oxidation of furfural to 2-FA and 5-HFA. PEC CO₂ reduction and furfural oxidation in the paired PEC electrolyzer achieved a higher yield of CH₃OH (63 μmol/(L cm²)) and 82% FF conversion with a 63% 2-FA yield and 19% 5-HFA yield under varying anolyte concentrations. These research findings indicated that the fabricated paired PEC electrolyzer is a technoeconomic process compared with a half-cell electrolyzer for PEC CO₂ conversion to CH₃OH and anodic oxidation of FF to value-added chemicals.

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Figure S1(a-c). FE-SEM images with different magnifications of Au/$\alpha$-Fe$_2$O$_3$ nanocatalysts
Figure S2(a and b). FE-SEM images with different magnifications and (c) EDS spectrum of Au/α-Fe$_2$O$_3$/RGO nanocatalysts.
A simple hydrothermal method was used for the synthesis of Ru/RGO nanocomposite at 180 °C for 12 h. In a typical synthesis process, 0.5 M of RuCl$_3$.xH$_2$O was added to 50 mL of GO solution (concentration - 2mg/mL) under magnetic stirring for 20 min. Then, 10 mL of NaBH$_4$ solution (100 mM) was slowly added to the above solution and the complete solution was transferred into 100 mL Teflon-lined stainless steel autoclave. The autoclave was heated at 180 °C for 12 h. After the reaction, the solid precipitate was separated and washed with deionized water several times and followed by ethanol. The final product was dried overnight in a vacuum oven at 70 °C. The obtained Ru/RGO nanocomposite was characterized with XRD, Raman, HR-TEM with EDS and the results are displayed in Figure S3(a-f). The XRD pattern of Ru/RGO nanocomposite in Figure S3(a) exhibits the diffraction peaks at 43.7, 58.1, and 69.4° corresponds to the (101), (102), and (110) planes of face centered cubic (fcc) Ru(0) crystal. The RGO peaks are disappeared due to higher crystallinity of Ru suppressed the planes of RGO. However, Raman analysis clearly exhibits the dual phases of Ru and RGO in the composite sample as displayed in Figure S3(b). The two strong peaks at 1343 and 1586 cm$^{-1}$ corresponding to the D-band that arises from a breathing mode of K-point phonons of A$_{1g}$ symmetry and G-band that arises from
the first scattering of E_{2g} phonon of sp\textsuperscript{2} carbon atoms in the RGO, respectively. The I_D/I_G ratio was calculated to be 1.03 which confirms the successful loading of Ru NPs on the surfaces of RGO nanosheets. Additional peaks at 494 and 612 cm\textsuperscript{-1} corresponding to the Ru–O and RuO\textsubscript{2}, respectively. Furthermore, the crystalline structure, morphological features, and elemental compositions of the Ru/RGO nanocomposites were systematically studied through HR-TEM, SAED and EDS analysis. The HR-TEM image in Figure S3(c) depicts the formation of Ru NPs on the surfaces of few-layered RGO nanosheets. Furthermore, HR-TEM image in Figure S3d clearly shows the formation of spherical-like Ru NPs with an average sizes of 5 nm. The crystalline structure and phases of Ru/RGO nanocomposite was further determined via the SAED pattern depicted in Figure S3(e). The pattern exhibits the diffraction peak of (002) assigned to the graphitic structure of RGO and the crystal planes of (101), (102), and (110) corresponding to the polycrystalline structure of fcc Ru, respectively. Figure S3(f) shows the EDS analysis of Ru/RGO nanocomposite which consist of C, O, and Ru without any other impurities.

![Graph showing products yield over EC, PC, and PEC](image)

**Figure S4.** Yields of CH\textsubscript{3}OH and CO (µ mol/ L, cm\textsuperscript{2}) over EC (absence of light), PC (absence of voltage, -0.6 V) and PEC cell.
Figure S5. PEC anodic products (FF conversion efficiency, 2-FA yield, and 5-HFA yield) over Ru/RGO/Pt, Ru/RGO/carbon paper, and Pt sheets. Reaction conditions; FF concentration - 10 mmol, 0.1 KOH aqueous solution, 120 min of optimized reaction time, light source of 450 nm, and applied potential of -0.6 V vs. SCE