The impact of anode materials on the performance of electrochemical CO₂ reduction to carbon monoxide

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Abstract

Electrochemical carbon dioxide reduction reaction (CO₂RR) has been investigated for decades. CO₂RR to value-added products is an indispensable option to address climate change and energy storage needs. We believed that CO₂RR performance can be influenced by the anode materials employed for the oxidation half-reaction. Although H₂O oxidation near-neutral solution does not being received greater attention, there is also an idea that it plays an important role not only in completing CO₂ reduction cycle, but also to significantly influence the cathode during reduction. Therefore, the present study aimed to investigate the impact of three different anode materials (platinum, glassy carbon, and hematite) on the activity and selectivity of the gold cathode in an electrochemical CO₂ reduction reaction. Linear sweep voltammetry and electrochemical impedance spectroscopy have been used to study electrocatalytic properties. In the meantime, x-ray diffraction is used to investigate the crystal planes of the as-prepared electrodes, while the work function and morphology of Au films were measured by atomic force microscope. Similar activity and selectivity to CO formation were observed when platinum and hematite were used as counter electrodes, while the least CO formation was recorded on the glassy carbon counter electrode.

Graphic abstract

The protons (H⁺) obtained from the oxidation of H₂O onto these three different anodic materials (platinum, glassy carbon, hematite) are moving faster through the bulk of the solution to the working electrode. Consequently, the reaction occurred on the working electrode can be influenced by the number of protons coming from the anode.

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1 Introduction

The advancement of feasible and sustainable energy is an unavoidable issue for researchers due to the harmful effect of fossil fuels on the environment. The ignition of fossil fuels for energy use emits huge amount of pollutant gases, like carbon dioxides [1–3]. It has been a great deal of attention in the scientific community to find clean and sustainable energy source in order to circumvent the climate change [4, 5]. Carbon dioxide (CO₂) is the major greenhouse gas that largely contributes to global warming. Various strategies have been developed to reduce the accumulated CO₂ in the atmosphere [6–9]. And hence, the desire to advance the CO₂ utilization technologies such as electrochemical CO₂ reduction (CO₂R) at ambient temperatures and pressures; which has a strong passion towards saving the world from the existing global warming [10, 11] is becoming accustomed. This approach has been a promptly intensifying field of research after the work of Hori et al. on gold [12] and copper [13, 14] electrodes. CO₂ can be converted into a wide range of chemicals and fuels including C₁ products like CO, and multi-carbon products such as hydrocarbons and oxygenates [15, 16]. Interestingly, CO₂ can directly be converted into syngas in a systematic approach [17, 18].

However, most of the scientific communities widely focused on the performance of the working electrode during the electrocatalytic reduction of CO₂, while the counter electrodes can significantly influence the cathode. Interestingly, Sun and coworkers have suggested using suitable anode materials for the oxidation half

reaction during the CO₂RR, which enables to boost the reaction rates at low overpotentials. The authors further notified that the consideration of synthesizing highly active and stable electrocatalysts should be given to both anode and cathode processes to improve the CO₂ reduction performance [19, 20]. So far, the oxygen evolution near-neutral solution has not received a greater attention in the research community, which is still in its infancy. Therefore, we believed that it plays an important role not only in completing CO₂ reduction cycle, but also to considerably impact the cathode performance. Currently, the electrochemical CO₂ reduction experiments are measured based on three-electrode configurations that employed platinum as counter electrode. Because platinum (Pt) is a renowned catalytically active material that has got an immense attention for a practical application in various fields of heterogeneous catalysis. In electrochemistry, it is a crucial catalyst that is used as a foil or in the form of nanoparticles to facilitate the hydrogen evolution and oxygen reduction [4, 21]. Its cost and slow electro/chemical dissolution, however, significantly hinder its practical use for an extended period of time. Previous reports on H₂ evolution revealed that the use of Pt as a counter electrode showed a significant impact on the experimental results owing to the electrochemical deposition of dissolved Pt in the process [22–24]. Similarly, in the electrochemical CO₂ reduction, the Pt counter electrode has been found as a cathode contaminant by electrochemical deposition of dissolved Pt which leads a strong carbon monoxide (CO) adsorption on the catalyst surface, facilitating catalyst corrosion [25, 26]. As a result, the research community needs

to investigate other potential materials to replace the Pt counter electrode.

In this study, we have demonstrated electroreduction of CO₂ to CO using three different counter electrodes based on the three-electrode configuration. Platinum foil (Pt), glassy carbon (GC), and hematite nanorods (α -Fe₂O₃) were the three different counter electrodes used for the electrochemical CO₂ reduction. The E-beam deposited 150 nm Au film on fluorine-doped tin oxide (FTO) substrate was used as working electrode. Under the same nominal applied bias, the system based on Pt and Fe₂O₃ counter electrodes exhibited similar performance (activity and selectivity to CO formation). Yet, the system based on glassy carbon counter electrode showed the lowest CO₂ reduction performance to CO.

2 Experimental section

2.1 Anode and cathode preparation

The working electrode of Au film (150 nm thick) was deposited by E-Beam (Ohmiker-50B) on fluorine doped tin oxide (FTO) substrate. The substrate was cleaned ultrasonically in acetone, ethanol, and Milli-Q water for 15 min each, respectively, and dried by nitrogen stream. About 10 nm Chromium (Cr) was deposited at a 0.5 angstrom/sec deposition rate and a pressure of 1×10^{-6} Torr for adhesion purposes. A 150 nm Au film was then deposited on top of the as-deposited Cr at a pressure of 1×10^{-6} Torr and 1.5 angstrom/sec deposition rate.

The hematite (α -Fe₂O₃) nanorod was synthesized by hydrothermal method. Prior to synthesis, a piece of fluorine-doped tin oxide (FTO) substrate was cleaned ultrasonically in acetone, ethanol, and distilled water, respectively and allowed to dry by nitrogen stream. The typical experiment is made by dissolving 0.15 M FeCl₃ and 0.15 M urea in aqueous solution. The precursor solution (25 mL) was added to a Teflon-lined stainless steel autoclave which contains ultrasonically cleaned piece of FTO substrate upside down. After thermal treatment at 100 °C for 6 h a yellowish color β -FeOH film was grown on the FTO substrate. It was then rinsed with distilled water several times to remove the residual salts followed by annealing at 600 °C for 3 h in air atmosphere. Finally, the yellowish colored β -FeOH film has converted into an orange red hematite (α -Fe₂O₃) nanorod like structure.

2.2 Characterization of the electrodes

The crystal structure of the as-synthesized Fe₂O₃ and as-deposited Au film were measured by D8 focus X-ray

diffractometer with Cu K α irradiation (0.154184 nm) at a 2 θ range of 30 to 85° and a scan rate of 0.1°/s, while the morphology of the as-synthesized Fe₂O₃ was measured by scanning electron microscopy (SEM). Moreover, morphology, surface roughness, work function, and particle size of the as-deposited Au film were determined via Atomic force microscopy (BRUKER). The work function was calculated using Eq. 1. Lambda 750 UV/visible/NIR spectrophotometer was employed to measure the Optical absorption of Fe₂O₃ in the range of 300–800 nm wavelengths.

$$spd = \frac{(\Phi_{tip} - \Phi_{Au})}{-e} \quad (1)$$

where spd- Surface potential difference obtained from the AFM images using NanoScope Analysis software, Φ_{tip} —work function of the tip, Φ_{Au} —work function of gold (5.1 eV).

2.3 Electrocatalytic properties

The electrochemical properties of the as-synthesized Fe₂O₃ and Au electrodes were studied using the electrochemical work station (ZAHNER IM6) in three-electrode configuration, Au film as working electrode, Ag/AgCl/(sat. KCl) as reference electrode, and three different materials (platinum foil, glassy carbon, and Fe₂O₃) as counter electrodes, and the potential is reported against the reversible hydrogen electrode (RHE), using the formula, $ERHE(V) = E_{Ag/AgCl}(V) + (0.059 V \times pH) + 0.197 V$, where $E_{Ag/AgCl}$ is the applied potential vs. Ag/AgCl, otherwise stated. The Linear Sweep Voltammetry (LSV) curves of the electrodes were measured between 0 to −1.0 V in CO₂ ($\geq 99.999\%$) saturated 0.1 M KHCO₃ electrolyte at a scan rate of 50 mV·s^{−1}. The electrochemical impedance spectrometer (EIS) of Au film was measured in the frequency range of 10 mHz to 10 kHz and amplitude of 10 mV using three different counter electrodes.

2.4 Electrocatalytic CO₂ reduction

The electrocatalytic CO₂ reduction was measured using an airtight O-ring glass reactor connected with a pressure controlled glass assembly system. To remove the dissolved gases, the 0.1 M KHCO₃ electrolyte was vacuumed three times. To attain saturation, the electrolyte was purged by CO₂ for 30 min. The electroreduction of CO₂ was measured at two different potentials (−0.4, and −0.6 V vs RHE) using three different counter electrode based on three electrode configurations in CO₂ saturated 0.1 M KHCO₃ (pH 6.8). A gas chromatography mass spectrometer (SHIMADZU, GCMS-DP2020) equipped with a barrier discharge

Fig. 1 **a** Atomic force microscopy (AFM) images of 150 nm Au film, **b** X-Ray Diffraction (XRD) analysis of the as-deposited Au film

ionization detector (BID-2010 plus) was used to quantify the gaseous products (i.e., H₂ and CO) at one hour. The carrier gas employed was ultrahigh purity helium (He; 99.999%).

3 Results and discussion

3.1 Characterization of the electrodes

Figure 1a indicates the atomic force microscopy (AFM) image of the 150 nm Au film. The work function and surface roughness of the Au film were determined from the topographic AFM image. The respective surface roughness and work function of the Au film were 3.33 ± 0.09 and 5.03 ± 0.03 eV, where the obtained work function is in good agreement with previous works [27, 28]. The crystal structure of the Au film was examined by X-ray diffraction (XRD) (Fig. 1b). The peaks corresponding to (111), (200), (220), (311), and (222) were observed at a respective 2θ values of 38.2°, 44.4°, 64.6°, 77.6°, and 81.9° on the Au film (PDF # 65–2870).

On the other hand, the Pt and glassy carbon (GC) counter electrodes were used as received, while hematite (α -Fe₂O₃) was synthesized hydrothermally and used as an alternative anode material for oxidation half-reaction because of its outstanding stability in alkaline and near neutral solution [29–32]. Figure 2a indicates the scanning electron microscopy (SEM) image of hydrothermally synthesized Fe₂O₃ structure. A preferential (110) and (104) facets of Fe₂O₃ were observed as analyzed by X-ray diffraction (Fig. 2b) (PDF#: 01–085-0599). The absorbance spectrum of Fe₂O₃ is shown in Fig. 2c with band gap

energy of 2.0 eV as presented in the Tauc plot (Fig. 2d), which is in the same agreement with previous reports [33].

3.2 Electrocatalytic measurements

The measurement was made using linear sweep voltammetry (LSV) which comprised Au film as working, three different materials (Pt, GC, and α -Fe₂O₃) as counter, and Ag/AgCl as reference electrodes in CO₂ saturated 0.1 M KHCO₃ electrolyte solution (Fig. 3a). The systems are abbreviated as Au/Pt, Au/GC, and Au/Fe₂O₃ for simplicity, where Au is the working electrode and Pt, GC, and Fe₂O₃ are the platinum, glassy carbon and hematite counter electrodes, and Ag/AgCl is the reference electrode which was the same in all the three systems. The onset potential (the potential required to draw a current density of -0.1 mAcm⁻²) in the Au/Pt system was shifted positively by about 120 and 68 mV than the systems in Au/GC and Au/Fe₂O₃, respectively. Moreover, in terms of the increased current density, there is a clear catalytic activity enhancement in the Au/Pt system than the other two (Fig. 3a blue line). On the other hand, the current density obtained in the Au/GC system is the lowest (Fig. 3a black line) with a moderate catalytic activity in the Au/Fe₂O₃ system that shows similar catalytic performance as that of Pt at lower negative potentials (Fig. 3a red line). In this study, the observed disparities in the onset potential and current density arise from the different capability of H₂O oxidation onto the three different counter electrodes. Because H₂O oxidation takes place onto the anode electrode, while the reduction reaction occurs onto the working electrode. Therefore, the H₂O oxidation onto the counter electrode is the key factor for the perceived catalytic activity. The number of protons that travel from the anode to the negatively

Fig. 2 Characterizations of hydrothermally synthesized Fe_2O_3 : **a** Scanning electron microscopy (SEM) image, **b** X-Ray Diffraction (XRD) analysis, **c** UV-vis absorption spectrum, **d** Tauc plot for the as-synthesized Fe_2O_3

charged working electrode through the bulk of the solution depends strongly on the degree of H_2O oxidation. In other words, enhancing the performance and dropping oxygen evolution reaction overpotentials enables reducing the overall CO_2 reduction energy requirement [19, 20]. Therefore the two half-reactions i.e. the oxidation-half reaction and the reduction-half reaction should perform in well-balanced circumstances. However, the current density being higher in the Au/Pt system attributed that H_2O oxidation is superior in Pt counter electrode and hence large number of protons can be reached onto the working electrode for the reduction reaction. The current density is actually the contribution of both the electroreduction of CO_2 to CO and the competing H_2 evolution. The shoulder observed at about -0.10 V (close to 0.0 V) in all the three systems refer to the formation of hydrogen, while

the second shoulder appeared at about -0.40 V in the Au/Pt and Au/ Fe_2O_3 systems (Fig. 3a inset) indicate the formation of carbonaceous species. The absence of the shoulder at -0.4 V in the Au/GC system indicates that the formation of carbonaceous species in this system is not favorable as that of the other two systems possibly due to the lower number of protons reached onto the working electrode from the counter electrode. This causes the formation of COO^- intermediate instead of COOH or CO.

Similarly, a smaller semicircle was achieved in the Au/Pt system than that of the Au/GC system with a comparable diameter in the Au/ Fe_2O_3 system at -0.6 V as shown in the Nyquist plot measured by the electrochemical impedance spectroscopy (EIS) (Fig. 3b), the equivalent circuit is displayed in the inset of Fig. 3b. The respective charge transfer resistances (RCT) of the Au/Pt, Au/ Fe_2O_3 , and Au/

Fig. 3 The influence of different counter electrodes on the electroreduction of CO₂ to CO using Au film (150 nm) as a cathode; **a** LSV curves measured in CO₂-saturated 0.1 M KHCO₃ electrolyte at

50 mV s⁻¹ scan rate, and **b** EIS spectra at -0.6 V vs RHE, green lines are fitted spectra and the inset is the equivalent electric circuit

Fig. 4 V-t curves measured using different counter electrodes at; **a** -0.4 V, and **b** -0.6 V versus RHE

GC systems are 69.86, 76.94, and 140.30 Ω. These reflect the improvement of charge transfer process on the electrode–electrolyte interface in the Au/Pt system followed by Au/Fe₂O₃ system. The highest charge transfer resistance observed in the Au/GC system is due to the lower H₂O oxidation occurred on the GC counter electrode which ultimately has a negative impact on the performance of the working electrode. As mentioned above, the lower number of protons reached onto the working electrode discourage the formation of COOH or CO intermediates. These intermediates help the ease desorption of CO₂ reduction products to occur. The scarcity of enough protons onto the working electrode leads to the formation of the sluggish COO⁻ intermediate that resulted in lower carbonaceous products and H₂ evolution. Therefore, the

enhanced catalytic activities and decreasing charge transfer resistance on the Au/Pt and Au/Fe₂O₃ systems arise from the greater H₂O oxidation occurred on the Pt and Fe₂O₃ counter electrodes.

3.3 Electrocatalytic CO₂ reduction

Figure 4a and 4b demonstrate the current density versus time measured during electroreduction of CO₂ at two different applied potentials (-0.4 and -0.6 V) using the three different systems. The current density in the Au/GC system rises gradually in the first ~20 min at -0.4 V, and then it starts to decline marginally after around 20-min electrolysis time (Fig. 4a red line). In this system, the product yield is very low. The current is mainly limited by the

Fig. 5 Parameters of electrochemical CO₂ reduction to CO and H₂: formation rates at; **a** –0.4 V, **b** –0.6 V, Faradaic selectivities at; **c** –0.4 V, **d** –0.6 V, and partial current densities at; **e** –0.4 V, **f** –0.6 V

interfacial dynamics, rather than the mass transport. The polarization equilibrium is ultimately established and the current density remains almost unchanged. However, in the other two systems (Au/Pt and Au/Fe₂O₃) the current density start to decline even in the beginning of the electrolysis at the same applied potential (Fig. 4a blue and

black lines). The current density start to decline in the beginning of the electrolysis time in all the three systems (Fig. 4b) at –0.6 V and in the Au/Pt and Au/Fe₂O₃ systems at the lower cathodic potential (–0.4 V), which indicates that the polarization equilibrium has reached faster. Likewise, the current density in these systems is mainly due

to the electroreduction of CO₂ to CO and the competitive H₂ evolution. The gradual decline in the current density observed in these systems as electrolysis time passes can be due to the active site coverage by the carbonaceous species of adsorbed COOH intermediate and adsorbed CO intermediate on the working electrode that can hinder the desorption of CO and block the competitive H₂ evolution, which eventually deactivate the Au electrode. In addition, the cathodic deposition of cation impurities on the catalyst surface from the electrolyte may contribute to this decay too [34, 35].

Figure 5 shows the formation rate ($\mu\text{mol cm}^{-2} \text{ h}^{-1}$), Faradaic selectivity, and partial current density (mA cm^{-2}) of CO and H₂ in the three different systems. The formation rate of CO and H₂ is higher in the Au/Pt and Au/Fe₂O₃ systems than that of the Au/GC system. The CO and H₂ production rates in Au/Pt system are about 2.7 and 6-order of magnitude higher relative to Au/GC system at -0.4 V , respectively. While in the Au/Fe₂O₃ system, the formation rates have increased by about 3 and 5-times for CO and H₂ over the Au/GC system at the same bias, respectively (Fig. 5a). However, the formation rate of CO at -0.6 V in Au/Pt system increased by about 60-times compared with the Au/GC system, while that of H₂ is raised by almost 2-times, which showed a decline relative to the formation rate observed at the lower cathodic bias. Similarly, the production rate of CO in Au/Fe₂O₃ system increased by approximately 55-fold compared with the Au/GC system and the H₂ formation rate is almost the same as that of the Au/GC system (Fig. 5b). The comparable H₂ evolution observed in the Au/GC with the other two systems does not show a similar performance of H₂O oxidation onto the counter electrodes. Therefore, the Au/GC has been identified as the least active system for the CO formation at both potentials examined. On the other hand, a comparable CO formation activity was recorded in the Au/Pt and Au/Fe₂O₃ systems with a slightly higher formation rate of H₂ in the Au/Pt system. These results indicate that the electrochemical CO₂ reduction performance is highly influenced by the counter electrodes. The H₂O oxidation onto the counter electrode and the reduction reaction onto the working electrode should be balanced by using an appropriate anode and cathode materials. Therefore, based on the performances observed in this study, the Pt counter electrode can be replaced by the Fe₂O₃ dark anode to avoid contemplated electro/chemical dissolution of Pt.

On the other hand, the CO selectivity obtained in the Au/GC system is about 16%, whereas the respective CO selectivity achieved in the Au/Pt and Au/Fe₂O₃ systems are nearly 8% and 11% at -0.4 V . The selectivity towards CO formation at this cathodic potential is 2-orders of magnitude higher in the Au/GC system than the Au/Pt. Because the H₂O oxidation is much higher when Pt is used as a

counter electrode than the glassy carbon. The protons (H⁺) produced onto the anode from the oxidation of H₂O are transporting faster through the bulk of the solution to the negatively charged cathode [36]. The number of protons reached onto the negatively charged cathode may be higher in the Au/Pt system, while desorption of the carbonaceous products such as CO is sluggish at this lower cathodic potential. Therefore, the protons can be protonated easily and evolve as H₂ gas and the selectivity towards H₂ evolution reached to approximately 92%. At a relatively higher cathodic bias of -0.6 V , however, the selectivity observed towards CO formation in the Au/GC system is the lowest (nearly 9%), the remaining 91% selectivity goes towards H₂ evolution. The Au/Pt system showed about 77% selectivity towards CO production. The best CO selectivity (about 83%) was recorded in the Au/Fe₂O₃ system, which exhibited approximately 9-times higher in selectivity over the Au/GC system. As shown in Fig. 5e&f, the partial current densities of each system have been calculated and the results are according to the formation rates. Because both parameters provide information related to the activities of the systems. Therefore, the least activity has been recorded in the Au/GC system on both potentials employed, which is in accord with the formation rate.

3.4 Mechanistic insights

As discussed above, the highest catalytic activity towards CO and H₂ evolution was achieved in the Au/Pt system. Whereas, the selectivity towards CO formation was found to be higher in the Au/Fe₂O₃ system, particularly at the

Scheme 1 Schematic illustration of the combined systems for the working, counter, and the reference electrodes with an electrochemical cell, and a bias from the potentiostat

higher cathodic potential. At the higher cathodic potential, the Au/Fe₂O₃ system exhibited a greater activity towards CO formation than the other two systems. However, the least activity towards both CO and H₂ formation was obtained in the Au/GC system compared with the Au/Pt and Au/Fe₂O₃ systems at the potentials under investigation. In Au/GC system, the activity and selectivity was higher towards H₂ evolution. For high CO selectivity, the catalyst needs to balance the adsorption of reactants and desorption of CO, and in the meantime inhibiting the competing H₂ evolution. The activity of a given catalyst during the chemical reaction, on the other hand, depends on how fast the desorption rate of products from its surface. A catalyst with a greater activity towards CO articulates a higher rate of CO formation, but a catalyst with lower CO formation activity denotes the sluggish removal of this product from the catalyst surface. Although the catalyst used as a working electrode is the same in all the three systems, the counter electrodes were different and hence the oxidation of H₂O on these systems performs differently. The protons (H⁺) obtained from the oxidation of H₂O onto the three different anodic materials are moving faster through the bulk of the solution to the working electrode [36]. Consequently, the reaction occurred on the working electrode can be influenced by the number of protons coming from the anode. As depicted in Scheme 1, the number of protons traveled from the counter electrode to the negatively charged cathode directly involves in a chemical reaction with the adsorbed CO₂ and electrons from the external circuit. When large numbers of protons have reached on the working electrode the competing H₂ evolution can be dominant. That was the case observed for the Au/Pt system.

4 Conclusions

In summary, we have used three different systems for electrochemical CO₂ reduction which are abbreviated as Au/Pt, Au/GC, and Au/Fe₂O₃ to assess the influence of counter electrodes on the performance of the working electrode. The impact of these counter electrodes have been evaluated in terms of the CO and H₂ formation activities and selectivities. The lowest yield of CO and H₂ were obtained in the Au/GC system regardless of the applied bias. Similarly, the lowest CO formation activity and selectivity were recorded on this system at −0.6 V. Comparable yields were observed in the Au/Pt and Au/Fe₂O₃ systems. The activity and selectivity towards CO formation were slightly higher in the Au/Fe₂O₃ system than the Au/Pt system at the lower cathodic bias (−0.4 V). On the other hand, a greater selectivity of 83% and a slightly higher activity towards CO formation was achieved in the Au/Fe₂O₃ and Au/Pt systems

at −0.6 V, respectively. The activities for CO formation recorded in the Au/Fe₂O₃ and Au/Pt systems were about 55 and 60-orders of magnitudes higher relative to the Au/GC system. In general, the Au/Fe₂O₃ system exhibited better selectivities than the Au/Pt system at both applied potentials, and a greater CO formation activity at −0.4 V with comparable CO production activity at −0.6 V. The selectivities and activities towards H₂ evolution, however, were higher in the Au/Pt system than the Au/Fe₂O₃. Therefore, the Fe₂O₃ dark anode (the most stable, inexpensive, and widely available semiconductor) can substitute the Pt counter electrode.

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Declarations

Conflicts of interest The authors declare that they have no competing interests.

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