Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.25373

184 (2020) 225–231
April

On the electrocatalytic reduction of CO_2 using Cu-nanoparticles decorating Au electrode

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Received 4 September 2019; Accepted 19 December 2019

ABSTRACT

CO_2 is electrocatalytically reduced in aqueous solutions ($NaHCO_3$ and Na_2SO_4) at polycrystalline gold (Au) both bare and modified with copper nanoparticles (nano-Cu) (nano-Cu/Au). Copper nanoparticles were deposited by the cycling of potential in the range (–0.2–0.7 V) for various potential cycles. The effect of the electrolyte, as well as the nano-Cu loading on the electroreduction of CO_2, has been investigated. Nano-Cu/Au electrode has been voltammetrically and morphologically characterized. It has been found that the type of electrolyte, that is, $NaHCO_3$ and Na_2SO_4, is critical in the electrochemical reduction of CO_2; for instance, the CO_2 reduction is obscured by hydrogen evolution in $NaHCO_3$ solutions (pH 9.2) at both electrodes, that is, bare Au and nano-Cu/Au electrodes, the well-defined redox peak is obtained at both electrodes in Na_2SO_4 solution (pH 7), even though the pH of Na_2SO_4 is smaller. The extent of catalysis is based on the copper loading at the nano-Cu/Au electrode as well.

Keywords: CO_2 electroreduction; Electrocatalysis; Copper nanoparticles; pH

1. Introduction

CO_2 is the main source of climate change. It is kinetically and thermodynamically stable, easily formed as a result of oxidation of organic molecules during combustion and respiration [1]. Research on the electroreduction of CO_2 is increasing aiming at its level reduction in the atmosphere, being used in large-scale energy storage and the development of CO_2 sensors [2–4]. The first aim is wishful and the second seems not promising, and thus research focuses on the last goal. Nowadays great efforts are devoted to both the efficient capture and sequestration of this pollutant or its conversion to a value-added product such as the conversion to chemical fuel. This may help in utilizing CO_2 in closed systems and synthesis of organic compounds on the basis of CO_2 [5–7].

Several ways have been reported for the reduction of CO_2 to environmentally neutral compounds [8–11]. However, those ways are tedious, time-consuming, non-selective and non-efficient. Electrochemical methods are a promising way as it can be easily controlled and optimized in addition to cost-effectiveness. On the other hand nanoscience and the based-on field nanotechnology are now in the heart of leading research both from theoretical and technological points

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of view. Nanostructured materials have several advantages compared with their counterparts as a result of the unique and superior properties including large surface to size ratio [12,13]. Several nanostructured materials have been reported to present high electrocatalytic activity towards many electrochemical reactions, even though their bulk counterparts are inert towards those reactions [14–19]. As for example, they have been used for unsaturated alcohols and aldehydes catalytic hydrogenation, oxidation of glucose, oxygen reduction and CO oxidation at low temperature [15,18,20,21]. Irrespective of the huge reports regarding the applications of nanoscience in the electrocatalysis of many reactions, reports regarding the electroreduction of CO_2, greenhouse gas, are few, albeit of equal importance to other electrochemical reactions. Those reports deal with the CO_2 electroreduction in different media at different bulk electrodes, bare and modified with organic and/or metals Yet, all these suffer the large over potential needed for the electroreduction of CO_2 and consequently the non-selectivity and the low current efficiency [5,8,22–28].

The present research concerns with a decoration of copper nanoparticles onto a polycrystalline gold electrode (nano-Cu/Au) for the electrocatalytic reduction of CO_2 at relatively low potential. Not only the size but also the morphology and the surface topography of the nanoparticles can be controlled [29,30]. This is a crucial point in catalysis as many shape-selective reactions are reported in the literature [31,32], in which the final product is markedly dependent on the morphology of the used catalyst. The effect of the loading of nanoparticles as well as the type of on the electroreduction of carbon dioxide has been studied.

2. Experimental section

2.1. Chemicals

Solutions were prepared using deionized water, and all the chemicals were of analytical grade. All chemicals were used as received. $CuSO_4$ (Aldrich) of the appropriate concentration (0.1 mM) was prepared in 0.05 M H_2SO_4.

2.2. Electrodes

The polycrystalline gold (poly-Au) electrode of diameter 1.6 mm was pre-treated as usual by fine alumina powder and subsequent sonication in water. Then, it is electrochemically pre-treated until the cyclic voltammetry (CV) characteristic for a clean Au electrode is obtained [33,34].

2.3. Fabrication of modified electrode

Gold electrode modified with nano-Cu (nano-Cu/Au) was prepared using CV; from 0.1 M phosphate buffer solution (pH 7) containing 1 mM $CuSO_4$ by applying various potential cycles in the potential range (–0.2 and 0.7 V) vs. Ag/AgCl/KCl (sat.) with a scan rate of 0.05 V s^{-1}.

2.4. Measurements

CV measurements were performed using a PGSTAT30 potentiostat/galvanostat in a conventional three-electrode cell in which the working electrode and the counter electrode (a platinum spiral wire) are separated by a porous glass. An Ag/AgCl (NaCl sat.) electrode was used as the reference electrode. Electrolyte solutions were, if necessary, deaerated by bubbling N_2.

Atomic force microscopy (AFM) images of the modified electrode were acquired with a VN-H1V8 VN Viewer (KEYENCE Nanomicroscope, Japan). Energy-dispersive X-ray spectroscopy (EDS) analysis of the modified electrode was carried out using a JSM-T220 scanning electron microscope (JEOL Optical Laboratory, Japan) at an acceleration voltage of 20 kV and a working distance of 4–5 mm.

3. Results and discussion

3.1. Morphological characterization

Fig. 1 shows AFM images of the nano-Cu/Au electrode. A relatively sparse deposition of nano-Cu of ca. 100–300 nm is shown. Fig. 2 shows the EDS spectra of the nano-Cu/Au electrode. The peak of copper is feasible at the energy around 0.75 eV [35] along with the peak corresponding to the underlying gold substrate at around 2.2 eV.

3.2. Electrochemical characterization

Fig. 3 shows CVs at (a) bare Au, (b) nano-Cu/Au electrodes in 0.1 M $NaHCO_3$ solution. The CV, in the studied potential range, of bare Au electrode is featureless, only the background current is obtained. In curve b, which is obtained at nano-Cu/Au electrode, two differences are noticed, as compared with bare Au electrode (curve a); the first is the redox couple obtained in the potential range (0.1–0.2 V) which corresponds to Cu^{2+}/Cu^{+} [36–38] couple. The correspondence of this redox couple still is not clarified; some authors reported it belongs to the Cu^{2+}/Cu^{+} redox couple. Others reported that it belongs to the Cu^{2+}/Cu couple [40,41]. The second feature is the significant increase in the current at potential larger than –0.8 V, that is, in the vicinity of hydrogen evolution, as a result of the enhancement of hydrogen evolution as a competing reaction [42]. Probably,

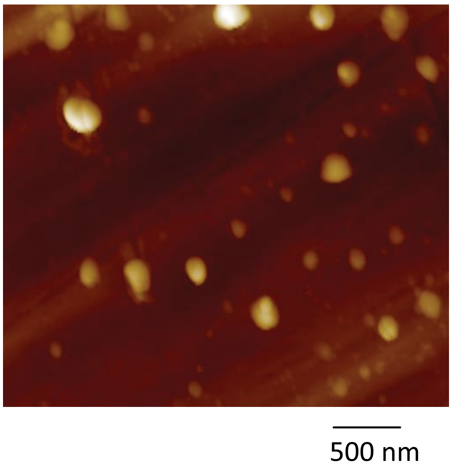

Fig. 1. AFM images obtained at the nano-Cu/Au electrode. Nano-Cu/Au was prepared by electrodeposition using 4 potential cycles, as mentioned in the experimental section.

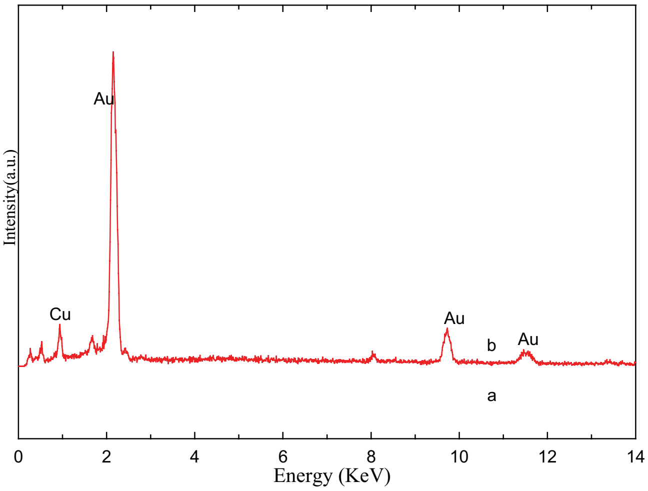

Fig. 2. EDS spectra for the nano-Cu/Au electrode.

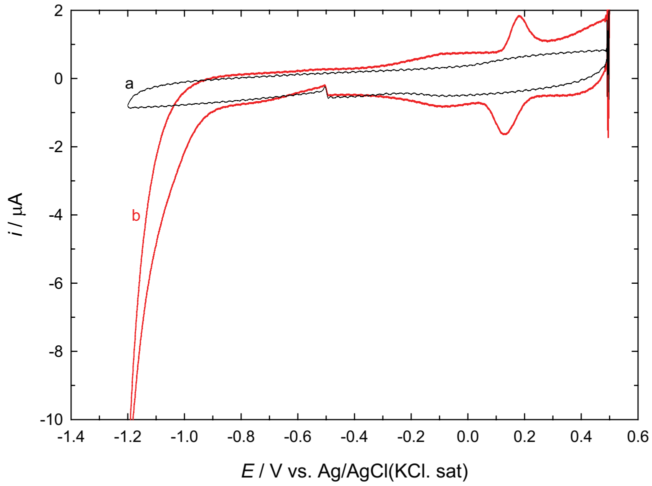

Fig. 3. CVs obtained at (a) bare Au, (b) nano-Cu/Au electrodes in N_2-saturated 0.1 M $NaHCO_3$. Nano-Cu/Au was prepared by electrodeposition using 2 potential cycles, as mentioned in the experimental section.

this is attributed to the difference in the exchange current density of the hydrogen evolution at copper and gold electrodes. The exchange current density of hydrogen evolution is larger at copper compared with gold [42]. These two features ensure the deposition of copper onto the underlying gold electrode, consistently with the reported AFM and EDS shown above.

3.3. Effect of electrolyte

Fig. 4 shows CVs obtained at bare gold electrode in (a,b) N_2- and (c, d) CO_2-saturated (a,c) 0.1 M $NaHCO_3$ and (b,d) 0.1 M Na_2SO_4 solutions. The potential was scanned cathodically starting from –0.5 V to –1.2 V, then reversed to 0.5 V, and finally to the starting potential (–0.5 V). In curves, a and b the expected behavior of bare gold electrode is obtained. The onset potential of hydrogen evolution started at potential around –0.8 V. In curves, c and d obtained in the presenceof CO_2, the current in the potential range of hydrogen evolution is significantly increased, and probably, the increase accord with the concentration of CO_2. This increase cannot be accounted by the decrease in the pH due to the bubbling of CO_2 as the pH values were checked before and after bubbling and the decrease was found to be slight. Thus it is clear that bare gold is active for CO_2 reduction under the present conditions. The increase in the current in the vicinity of the hydrogen evolution is coupled with the emerging of a new anodic peak, at around 0.1 V, which its current increases with increasing CO_2 (data are not shown). Probably this anodic peak is an oxidation of the reduction product produced in the cathodic scan. These results are inconsistent with that reported at copper nanoparticles synthesized by hydrothermal flow method and modified onto glassy carbon electrode [43]. Interestingly, in the present case where copper nanoparticles are prepared by simple electrochemical methods, the well-defined reduction peak of CO_2 is clearly revealed at ca. –0.8 V (see curve d) indicating the prominent role of the supporting electrolyte. Also, the anodic peak is revealed in this case, but at a larger positive potential and with larger peak current. It has been reported that the electroreduction of CO_2 is inherently dependent on the supporting electrolyte [44,45], and its constituents. Most reported studies have focused on the reduction of CO_2 in neutral solutions, as used in the present study, to avoid the interference of hydrogen evolution. Also selecting a supporting electrolyte with suitable cation is crucially important. For instance, while CO_2 reduction is favorable in Na^+ containing solutions, H_2 evolution prevails CO_2 reduction in, for example, Li^+ electrolytes. Also, the anionic part of the electrolyte significantly affects the reduction product; while, for example, methane is favored as a reduction product in the case of HCO_3^- solutions, alcohols are preferable in the case of using sulfate solutions [46]. Recall Fig. 4, it is clearly shown the voltammetric behavior critically depends on the anionic part of the supporting electrolyte.

It is noteworthy to mention that regarding the pH, it is an important parameter in the electrochemical reduction of CO_2 since hydrogen ions are required for CO_2 reduction [47].

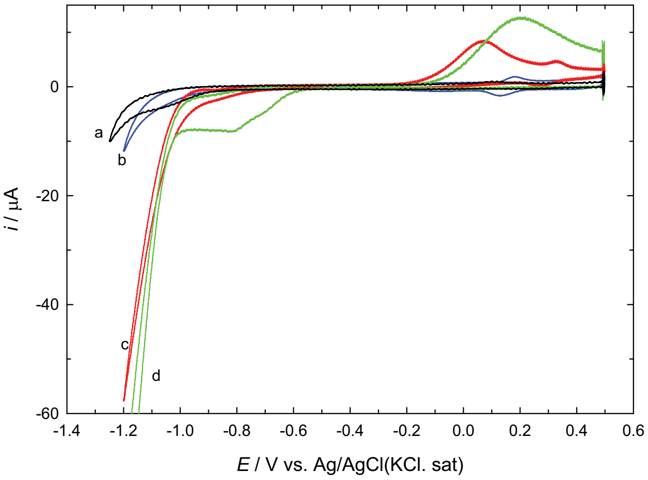

Fig. 4. CVs obtained at bare gold electrode in (a,b) N_2- and CO_2-saturated, (c) $NaHCO_3$, and (d) Na_2SO_4 solutions.

However, CO_2 reduction is usually carried out at pH close to a neutral one. Thus, in the present case, relatively high pH is selected to avoid the high interference from the hydrogen evolution. In this case, the source of a proton is water according to, for example, the following reaction;

$$CO_2 + 2H_2O + 2e^- = CO + 2OH^- \quad E^o = -1.37\ \text{V} \tag{1}$$

3.4. Effect of modification of gold by nano-Cu

Fig. 5 shows CVs obtained at (a,b) bare gold and (c,d) nano-Cu/Au electrodes in (a,c) N_2- and (b,d) CO_2-saturated 0.1 M Na_2SO_4 solutions. The potential was scanned in the same manner as in Fig. 4. In curves, a and c the expected behavior of bare gold electrode and nano-Cu/Au electrodes are revealed. In the presence of CO_2, the reduction potential peak of CO_2 at nano-Cu/Au electrode (curve c) is enhanced, that is, positively shifted by ca 150 mV compared with that obtained at the bare gold electrode (curve b) along with a slight increase in the peak current and this shift for the reduction peak is coupled also by a similar positive shift in the corresponding anodic peak. It has been reported that modification of glassy carbon electrode by copper electrocatalyst to enhance the electroreduction of CO_2. However, the electrocatalysis was revealed as an increase in the vicinity of the hydrogen evolution [2]. Similarly, an increase in the electrochemical response in the presence of CO_2 was obtained at the alkynyl-substituted rhenium complex modified onto a Pt-plate electrode [48]. Regarding the combined effect of using gold and copper and based on the presented results in the present manuscript, one can clearly conclude that the deposition of copper nanoparticles onto an underlying gold substrate is reflected on the enhancing of the kinetics of the electroreduction of CO_2 as reflected on realizing the reduction peak at lower negative potentials. Also, the current response to the reduction of CO_2 is increased. It has been reported that while CO is the main product for the reduction of CO_2 at gold electrode as a result of the weak adsorption properties of CO on gold, CH_4 is the main product obtained at copper electrode due to that the adsorption of CO onto Cu is of intermediate strength [49,50].

3.5. Effect of loading of nano-Cu

The effect of the loading of copper was studied in $NaHCO_3$ (Fig. 6) and Na_2SO_4 (Fig. 7). The loading of copper was determined indirectly via calculating the surface coverage of the underlying substrate from the voltammetric behavior obtained at bare and nano-Cu/Au electrodes in N_2-saturated 0.5 M H_2SO_4 solutions (data are not shown). Surface coverage was estimated from the decrease in the reduction peak of gold oxide upon the deposition of copper and values were found to equal 0.24 and 0.28 for nano-Cu/Au electrode prepared by two and four cycles, respectively, details are mentioned elsewhere [51]. Fig. 6 shows the CVs obtained at Cu nanoparticles modified gold electrode in (upper panel) N_2-saturated and (lower panel) CO_2-saturated $NaHCO_3$ solution. As clearly shown increasing the loading of copper increases the hydrogen evolution. At Cu modified gold electrode (curves a) the increase in the current in the vicinity of the hydrogen evolution increases significantly upon bubbling CO_2. However when the loading of Cu increases the hydrogen evolution significantly increases (curves b,c, and d, upper panel). The current in the presence of CO_2 (curves b,c, and d, lower panel) is almost constant

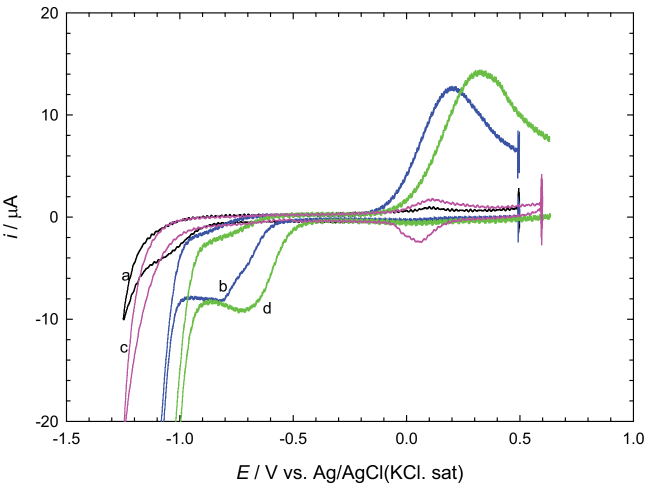

Fig. 5. CVs obtained at bare (a,b) Au and nano-Cu/Au (c,d,e) electrodes in the absence (a,c) and presence (b and d) of CO_2-saturated 0.1 M Na_2SO_4 solutions. Nano-Cu/Au electrodes were prepared by 4 potential cycles.

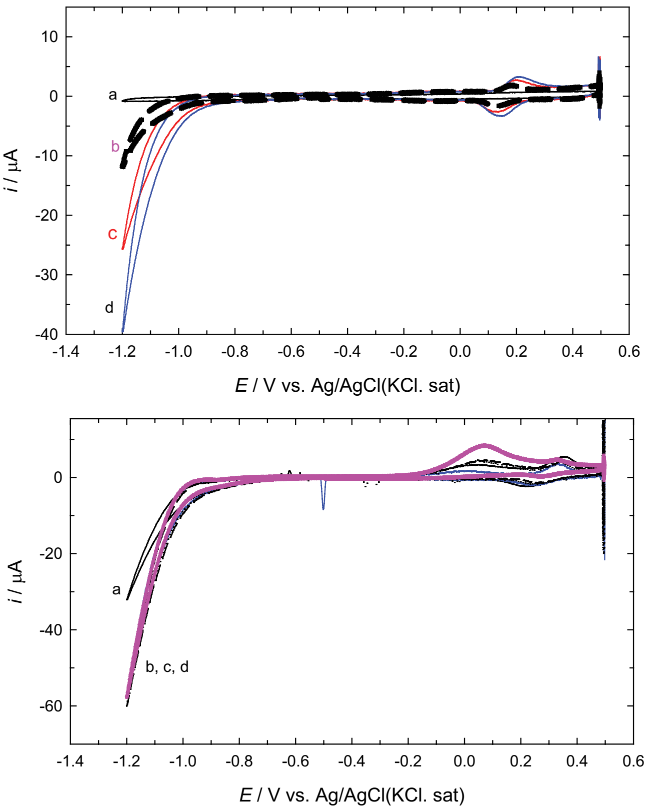

Fig. 6. CVs obtained at Cu nanoparticles modified gold electrode in (upper panel) N_2-saturated and (lower panel) CO_2 saturated $NaHCO_3$ solution. Nano-Cu/Au electrodes were prepared by (a) 0, (b) 2, (c) 4, and (d) 6 potential cycles.

due to that hydrogen evolution precludes the CO_2 electroreduction. This again proves the dependency of the CO_2 reduction on the electrolyte type.

Fig. 7 depicts CVs at bare Au (a,b) and nano-Cu/Au (c,d, and e) electrodes in the absence (a,c) and presence (b, d, and e) of CO_2- saturated 0.1 M Na_2SO_4 solutions. Comparing curves a and c one can see the significant increases in the hydrogen evolution at potentials more negative than –1.1 V. At bare Au (curve c) in the presence of CO_2 a clear reduction peak is obtained at around –0.87 V, probably corresponds to the reduction of CO_2. At Cu modified Au electrodes (curves c and d) the reduction peak is positively shifted, and this shift increases upon increasing Cu loading. The reduction peak is coupled with a new anodic peak at ca. 0.2 V corresponds to the oxidation of the product formed in the cathodic scan. The correspondence of this peak was confirmed by changing the direction of potential scan as seen in Fig. 8 in which the effect of direction of potential scan on voltammograms is shown. The starting potential in both cases is –0.5 V. In curve a, the potential was first scanned in the cathodic direction, and in curve, b was scanned first in the anodic direction. As clearly shown in curve a, the reduction peak obtained at –0.87 is coupled with one oxidation peak at around 0.2 V for the product formed in the cathodic going scan. On the contrary, when the scanning was started to the anodic direction, there was no anodic peak except the one, at ca. 0.3 V, which corresponds to Cu^{2+}/Cu^{+} couple. It has become clear that

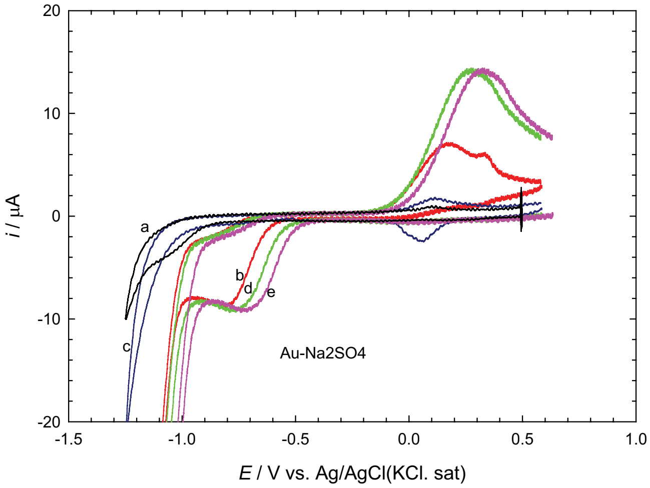

Fig. 7. CVs obtained at bare (a,b) Au and nano-Cu/Au (c,d,e) electrodes in the absence (a,c) and presence (b,d,e) of CO_2-saturated 0.1 M Na_2SO_4 solutions. Nano-Cu/Au electrodes were prepared by (b) 2 and (d) 4 potential cycles.

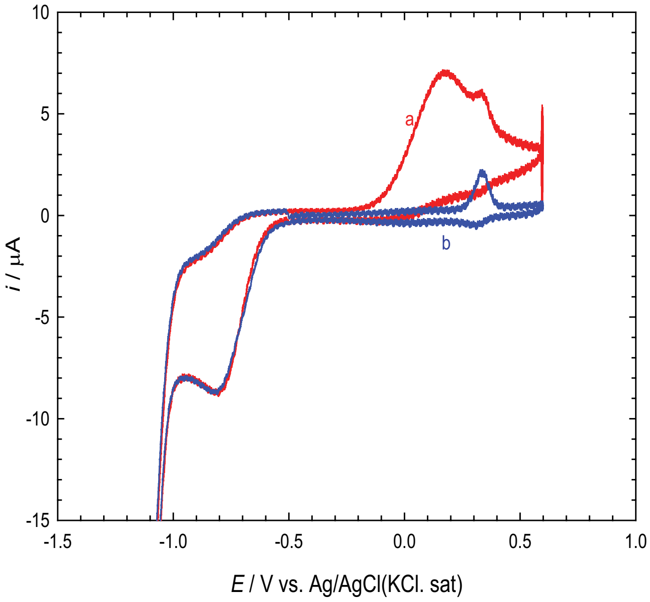

Fig. 8. CVs obtained at the nano-Cu/Au electrode in CO_2-saturated 0.1 M Na_2SO_4 solutions. Starting potential-0.5 V. In curves a and b the potential was scanned to the negative and positive directions, respectively.

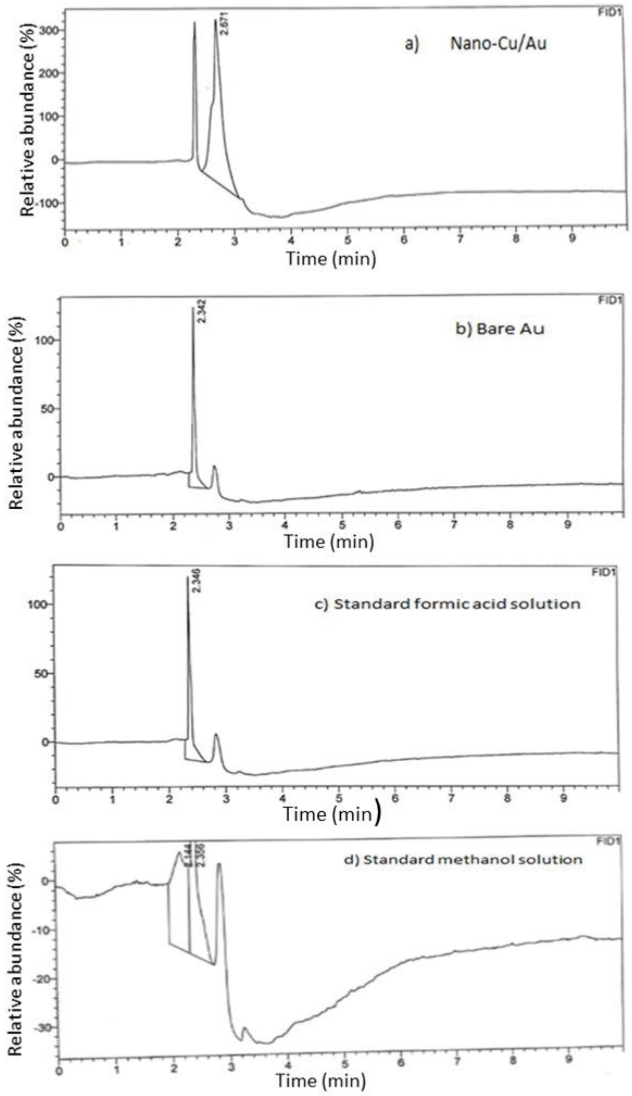

Fig. 9. Gas chromatograms for the reduction products obtained by applying a potential of – 0.9 V at (a) nano-Cu/Au and (b) bare Au electrodes for 1 h. Chromatograms c and d are for standard formic acid and methanol solutions, respectively.

the well-defined redox peak for CO_2 is realized, for the first time at gold and nano-Cu/Au electrodes and the nanoparticle loading and the supporting electrolyte play a prominent role in the reduction.

For inspection of the oxidation products a potential of –0.9 V is applied at nano-Cu/Au and bare Au electrodes for 1 h and the resulting electrolyzed solutions were analyzed using gas chromatography and results are shown. The analysis for the solution obtained by the electrolysis at bare Au electrode (curve b) is characterized by one sharp peak at 2.4 min. Probably, it corresponds to formic acid as compared with the chromatogram obtained for the standard formic acid solution (curve c). Gas chromatogram for the solution obtained by the electrolysis at the nano-Cu/Au electrode (curve a) shows a new peak at 2.8 in addition to the one obtained at 2.4 min. The former one corresponds to the methanol as compared with the chromatogram obtained for the standard methanol solution (curve d). Further investigation for the complete distribution of the resulting electrolyzed solution under the present conditions in addition to the full spectrum of experimental conditions is underway.

4. Conclusions

The electroreduction of carbon dioxide at bare Au and nano-Cu/Au electrodes has been studied in $NaHCO_3$ and Na_2SO_4 solutions. It has been found that the copper nanoparticles loading and the type of electrolyte significantly affect the reduction behavior of CO_2; in Na_2SO_4 solution, CO_2 is reduced at lower potential at the modified electrode compared with the bare Au electrode, The enhancement is based on the loading extent at the modified electrode, In $NaHCO_3$ solution, the reduction peak for CO_2 is not revealed at both electrodes as it is obscured by hydrogen evolution.

Acknowledgment

The author's thanks Umm Al-Qura University for giving permission to conduct the analysis and for access to analytical equipment and Jouf University, too.

References

[1] A. Gennaro, A.A. Isse, M.-G. Severin, E. Vianello, I. Bhugun, J.-M. Saveant, Mechanism of the electrochemical reduction of carbon dioxide at inert electrodes in media of low proton availability, J. Chem. Soc., Faraday Trans., 92 (1996) 3963–3968.

[2] V.S. Bagotzky, N.V. Oetrova, Electrochemical reduction of carbon dioxide, Russ. J. Electrochem., 31 (1995) 409–412.

[3] C. Costentin, M. Robert, J.M. Saveant, Catalysis of the electrochemical reduction of carbon dioxide, Chem. Soc. Rev., 42 (2013) 2423–2436.

[4] C.F.C. Lim, D.A. Harrington, A.T. Marshall, Altering the selectivity of galvanostatic CO2 reduction on Cu cathodes by periodic cyclic voltammetry and potentiostatic steps, Electrochim. Acta, 222 (2016) 133–140.

[5] Y. Song, R. Peng, D.K. Hensley, P.V. Bonnesen, L. Liang, Z. Wu, H.M. Meyer III, M. Chi, C. Ma, B.G. Sumpter. A.J. Rondinone, High-selectivity electrochemical conversion of CO_2 to ethanol using a copper nanoparticle/n-doped graphene electrode, Chemistry Select, 1 (2016) 6055–6061.

[6] S. Kaneco, K. Iiba, H. Katsumata, T. Suzuki, K. Ohta, Electrochemical reduction of high-pressure carbon dioxide at a Cu electrode in cold methanol with CsOH supporting salt, Chem. Eng. J., 128 (2007) 47–50.

[7] Q. Zhu, X. Sun, D. Yang, J. Ma, X. Kang, L. Zheng, J. Zhang, Z. Wu, B. Han, Carbon dioxide electroreduction to C2 products over copper-cuprous oxide derived from electrosynthesized copper complex, Nat. Commun., 10 (2019) 3851.

[8] M. Jitaru, D.A. Lowy, M. Toma, B.C. Toma, L. Oniciu, Electrochemical reduction of carbon dioxide on flat metallic cathodes, J. Appl. Electrochem., 27 (1997) 875–889.

[9] R.P.S. Chaplin, A.A. Wragg, Effects of process conditions and electrode material on reaction pathways for carbon dioxide electroreduction with particular reference to formate formation, J. Appl. Electrochem., 33 (2003) 1107–1123.

[10] K. Subramanian, K. Asokan, D. Jeevarathinam, M. Chandrasekaran, Electrochemical membrane reactor for the reduction of carbon dioxide to formate, J. Appl. Electrochem., 37 (2007) 255–260.

[11] M. Gattrell, N. Gupta, A. Co, A review of the aqueous electrochemical reduction of CO_2 to hydrocarbons at copper, J. Electroanal. Chem., 594 (2006) 1–19.

[12] J.A. Darr, J. Zhang, N.M. Makwana, X. Weng, Continuous hydrothermal synthesis of inorganic nanoparticles: applications and future directions, Chem. Rev., 117 (2017) 11125–11238.

[13] P. Ball, G. Li, Science at the atomic scale, Nature, 355 (1992) 27–28.

[14] M.I. Awad, B.A. AL Jahdaly, M.A. Kassem, O.A. Hazazi, Nickel oxide nanoparticles modified gold electrode for fractional determination of dopamine and ascorbic acid, J. Anal. Chem., 73 (2018) 1172–1178.

[15] M. Lucas, C. Mohr, U. Rodemerck, A. Bruckner, J. Radnik, H. Hofmeister, P. Claus, Supported gold nanoparticles: in-depth catalyst characterization and application in hydrogenation and oxidation reactions, Catal. Today, 72 (2002) 63–78.

[16] S.H. Joo, K. Kwon, D.J. You, C. Pak, H. Chang, J.M. Kim, Preparation of high loading Pt nanoparticles on ordered mesoporous carbon with a controlled Pt size and its effects on oxygen reduction and methanol oxidation reactions, Electrochim. Acta, 54 (2009) 5746–5753.

[17] I. Roche, E. Chaine, M. Chatenet, J. Vondrak, Carbon-supported manganese oxide nanoparticles as electrocatalysts for the oxygen reduction reaction (ORR) in alkaline medium: physical characterizations and ORR mechanism, J. Phys. Chem. C, 111 (2007) 1434–1443.

[18] M.L. Calegar, F.H. Lima, E.A. Ticianelli, Oxygen reduction reaction on nanosized manganese oxide particles dispersed on carbon in alkaline solutions, J. Power Sources, 158 (2006) 735–739.

[19] W. Yao, J. Yang, J. Wang, Y. Nuli, Chemical deposition of platinum nanoparticles on iridium oxide for oxygen electrode of unitized regenerative fuel cell, Electrochem. Commun., 9 (2007) 1029–1034.

[20] G.C. Bond, Gold: a relative new catalyst, Catal. Today, 72 (2002) 5–9.

[21] M. Haruta, Size- and support-dependency in the catalysis of gold, Catal. Today, 36 (1997) 153–166.

[22] A.S. Danial, M.M. Saleh, S.A. Salih, M.I. Awad, On the synthesis of nickel oxide nanoparticles by sol–gel technique and its electrocatalytic oxidation of glucose, J. Power Sources, 293 (2015) 101–108.

[23] M. Haruta, M. Date, Advances in the catalysis of Au nanoparticles, Appl. Catal., A, 222 (2001) 427–437.

[24] K. Hara, A. Kudo, T. Sakata, Electrochemical CO_2 reduction on a glassy carbon electrode under high pressure, J. Electroanal. Chem., 421 (1997) 1–4.

[25] R. Ortiz, O.P. Marquez, J. Marquez, C. Gutiérrez, FTIR spectroscopy study of the electrochemical reduction of CO_2 on various metal electrodes in methanol, J. Electroanal. Chem., 390 (1995) 99–107.

[26] H. Li, C. Oloman, Development of a continuous reactor for the electro-reduction of carbon dioxide to formate – part 1: process variables, J. Appl. Electrochem., 36 (2006) 1105–1115.

[27] E. Portenkirchner, J. Gasiorowski, K. Oppelt, S. Schlager, C. Schwarzinger, H. Neugebauer, G. Knçr, N.S. Sariciftci,

Electrocatalytic reduction of carbon dioxide to carbon monoxide by a polymerized film of an alkynyl-substituted rhenium(I) complex, ChemCatChem, 5 (2013) 1790–1796.

[28] S. Kaneco, N.-H. Hiei, Y. Xing, H. Katsumata, H. Ohnishi, T. Suzuki, K. Ohta, Electrochemical conversion of carbon dioxide to methane in aqueous $NaHCO_3$ solution at less than 273 K, Electrochim. Acta, 48 (2002) 51–55.

[29] S. Kaneco, K. Iiba, H. Katsumata, T. Suzuki, K. Ohta, Electrochemical reduction of high-pressure CO_2 at a Cu electrode in cold methanol, Electrochim. Acta, 51 (2006) 4880–4885.

[30] S. Kaneco, K. Iiba, H. Katsumata, T. Suzuki, K. Ohta, Effect of sodium cation on the electrochemical reduction of CO_2 at a copper electrode in methanol, J. Solid State Electrochem., 11 (2007) 490–495.

[31] B. Innocent, D. Liaigre, D. Pasquier, F. Ropital, J.M. Léger, K. Kokoh, Electro-reduction of carbon dioxide to formate on a lead electrode in an aqueous medium, J. Appl. Electrochem., 39 (2009) 227–232.

[32] Y. Tomita, S. Teruya, O. Koga, Y. Hori, Electrochemical reduction of carbon dioxide at a platinum electrode in acetonitrile-water mixtures, J. Electrochem. Soc., 147 (2000) 4164–4167.

[33] V.M. Barragan, A. Heinzel, Estimation of the membrane methanol diffusion coefficient from open circuit voltage measurements in a direct methanol fuel cell, J. Power Sources, 104 (2002) 66–72.

[34] C. Paliteiro, N. Martins, Electroreduction of oxygen on a (100)-like polycrystalline gold surface in an alkaline solution containing Pb(II), Electrochim. Acta, 44 (1998) 1359–1368.

[35] S. Strbac, R. Adzic, The influence of pH on reaction pathways for O_2 reduction on the Au(100) face, Electrochim. Acta, 41 (1996) 2903–2908.

[36] C.J. Chang, Y. Deng, C. Shi, C.K. Chang, F.C. Anson, D.G. Nocera, Electrocatalytic four-electron reduction of oxygen to water by a highly flexible cofacial cobalt bisporphyrin, Chem. Commun., 15 (2000) 1355–1356.

[37] P. Salaun, B. Planer-Friedrich, C.M.G. van den Berg, Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode, Anal. Chim. Acta, 585 (2007) 312–322.

[38] A. Hamelin, Cyclic voltammetry at gold single-crystal surfaces. Part 1. Behavior at low-index faces, J. Electroanal. Chem., 407 (1996) 1–11.

[39] M.I. Awad, T. Ohsaka, An electrocatalytic oxygen reduction by copper nanoparticles-modified Au(100)-rich polycrystalline gold electrode in 0.5 M KOH, J. Power Sources, 226 (2013) 306–312.

[40] E. Chow, E.L.S. Wong, T. Böcking, Q.T. Nguyen, D.B. Hibbert, J.J. Gooding, Analytical performance and characterization of MPA-Gly-Gly-His modified sensors, Sens. Actuators, B, 111 (2005) 540–548.

[41] I. Kereković, Electrochemical evaluation of binding copper and copper histidine complex on histidine modified gold electrode, Int. J. Electrochem. Sci., 9 (2014) 5596–5606.

[42] D. Pletcher, The cathodic reduction of carbon dioxide—what can it realistically achieve? a mini-review, Electrochem. Commun. 61 (2015) 97–101.

[43] X. Zhu, K. Gupta, M. Bersani, J.A. Darr, P.R. Shearing, D.J.L. Brett, Electrochemical reduction of carbon dioxide on copper-based nanocatalysts using the rotating ring-disc electrode, Electrochim. Acta, 283 (2018) 1037–1044.

[44] R. Kortlever, K.H. Tan, Y. Kwon, M.T.M. Koper, Electrochemical carbon dioxide and bicarbonate reduction on copper in weakly alkaline media, J. Solid State Electrochem., 17 (2013) 1843–1849.

[45] A. Schizodimou, G. Kyriacou, Acceleration of the reduction of carbon dioxide in the presence of multivalent cations, Electrochim. Acta, 78 (2012) 171–176.

[46] Y. Hori, A. Murata, R. Takahashi, Formation of hydrocarbons in the electrochemical reduction of carbon dioxide at a copper electrode in aqueous solution, J. Chem. Soc. Faraday Trans., 21 (1990) 2309–2326.

[47] A.S. Varela, M. Kroschel, T. Reier, P. Strasser, Controlling the selectivity of CO_2 electroreduction on copper: the effect of the electrolyte concentration and the importance of the local pH, Catal. Today, 260 (2016) 8–13.

[48] R.S. Kumar, S.S. Kumar, M.A. Kulandainathan, Highly selective electrochemical reduction of carbon dioxide using Cu based metal-organic framework as an electrocatalyst, Electrochem. Commun., 25 (2012) 70–73.

[49] Z.W. Seh, J. Kibsgaard, C.F. Dickens, I. Chorkendorff, J.K. Nørskov, T.F. Jaramillo, Combining theory and experiment in electrocatalysis: insights into materials design, Science, 355 (2017) 1–12.

[50] C. Shi, H.A. Hansen, A.C. Lausche, J.K. Nørskov, Trends in electrochemical CO_2 reduction activity for open and close-packed metal surfaces, Phys. Chem. Chem. Phys., 16 (2014) 4720–4727.

[51] M.A. Kassem, O. Hazazi, T. Ohsaka, M.I. Awad, Electroanalysis of pyridoxine at copper nanoparticles modified polycrystalline gold electrode, Electroanalysis 2015, 28 (2016) 539–545.