Pt-modified nitrogen doped reduced graphene oxide: a powerful electrocatalyst for direct CO₂ reduction to methanol

Ali A. Ensafi*, Hossein A. Alinajafi, B. Rezaei

Department of Chemistry, Isfahan University of Technology, Isfahan 84156–83111, Iran

Abstract

Reduction of CO₂ to useful chemicals such as carbon monoxide, oxalic acid, and methanol has recently attracted considerable attention because of its decisive roles in the climate change and energy cycle. Here, Pt@nitrogen doped reduced graphene oxide (Pt@rNGO) is introduced as a new catalyst effective in the direct production of methanol from the reduction of CO₂ at various potentials and pH levels. The electrolytic reduction of CO₂ in a CO₂ saturated solution at a Pt@rNGO modified glassy carbon electrode is achieved under the optimum conditions of an applied potential of –0.30 V (vs. Ag/AgCl) and a pH equal to 2.0. The methanol thus produced is monitored by ¹³C-NMR. The Faradic efficiency of the methanol production is found to be 41%. Results reveal that, compared to its counterparts used in previous studies, Pt@rNGO as a heterogeneous electrocatalyst requires a lower applied reduction potential and serves as a direct pathway for the conversion of carbon dioxide to methanol.

Keywords: Carbon dioxide reduction, Pt@nitrogen doped reduced graphene oxide, Direct methanol production, Electrocatalyst.

* Corresponding Author: Phone: (98) 31–33913269. Fax: (98) 31–33912350. E-mail: Ensafi@cc.iut.ac.ir; aaensafi@gmail.com; ensafi@yahoo.com.

1. Introduction

A sustainably safe environment can be guaranteed if a balance is stricken between CO₂ production and its atmospheric emission. However, intensified energy-consuming activities such as industrial processes and fuel combustion have led to increased carbon dioxide emissions into the atmosphere and, consequently, to enhanced environmental pollution and green house effects [1]. Accordingly, conversion of CO₂ to useful materials is of paramount importance so that most states have been encouraged to invest heavily in studies to address the problem of air pollution in order to finding remedies for abating the associated environmental hazards [2]. Fossil fuel combustion constitutes the primary global source of energy production. An excessive amount of CO₂ is produced in this process and released into the atmosphere, which has led to the global climate change presently threatening life on earth. One solution that has received much attention in current research is CO₂ reduction into products that can be used as alternatives to fossil fuels. A variety of photochemical, electrophotocatalytic, and electrochemical methods have been proposed for CO₂ reduction [3–5]. However, a growing interest has been recently shown to electrochemical methods on grounds of their following advantages [1]. In this method, CO₂ reduction is controlled by the electrode potential, temperature, and electrolyte [2] while the supporting electrolyte can be fully recovered [3] and renewable energy sources can be deployed to provide the required electricity for the process [6–8]. The primary products of electrochemical reduction of CO₂ are carbon monoxide, formic acid, oxalic acid, formaldehyde, methanol, methane, ethylene, and ethanol, among others [2]. However, the best CO₂ reduction product is methanol because it can be used not only as fuel in internal combustion engines and fuel cells but also as input to the production of light olefins [19]. The electrocatalysts used for the electrochemical reduction of CO₂ include a wide variety of compounds such as those containing transitional metals (e.g., titanium, molybdenum, chromium, tungsten, iron, cobalt, nickel, tin, manganese,

and the Pt group) [2,9–11] as well as alkaline and alkaline earth metals [12]; multiwall carbon nanotubes [13]; aromatic amine [14,15]; radical anion [16]; ionic liquid [17]; and gold nanoparticles [18].

The present study was designed and implemented to use the Pt-modified nitrogen doped reduced graphene oxide (Pt@rNGO, Scheme 1) as the electrode for the reduction of CO₂ to methanol. The electrode has a relatively low toxicity, compared to pyridine formerly used in CO₂ reduction. Besides, Pt@rNGO can be employed as a heterogeneous catalyst; thus, not only is less catalyst required but it does not need to be separated from the product either.

For the purposes of this study, optimal electrolysis conditions were determined by investigating the electrolyte pH, electrolysis potential, and other related parameters. Finally, a Faradic efficiency of 41% (given by $([\text{MeOH}] \times 6e^-)/I_{\text{t}}$, where I_{t} is the integrated bulk electrolysis current) was achieved for methanol production under the optimum conditions thus obtained.

“Here Scheme 1”

2. Experimental

2.1. Reagents

Double distilled water were used in all experiments. KMnO₄, K₂S₂O₈, KNO₃, P₂O₅, HCl, graphite and NaOH were purchased from Merck. All other chemicals (analytical grade) were purchased from Sigma-Aldrich.

2.2. Apparatus

An electrochemical instrument, Autolab, Model PGSTAT 30 potentiostat/galvanostat (Eco-Chemie, The Netherlands) controlled by a microcomputer, was used for electrochemical measurements. GPSE and FARA-4.9.007 software were used for collection of the data and background correction, respectively. EIS data were collected using

ZView®2.3 software. A three-electrode cell, containing a platinum wire as an auxiliary electrode, an Ag/AgCl (KCl saturated) as a reference electrode and the modified glassy carbon working electrode, were used. Scanning electron microscopy (SEM) images were prepared using SEM Philips (Model XL30), and transmission electron microscope (TEM, Model Philips/FEI CM200) was used to get the TEM images. For surface analysis of the nanocomposites, a D8-Advance Bruker X-ray diffraction instrument (XRD) and X-ray photoelectron spectroscopy (XPS) were carried out in ultra-high vacuum (UHV) set-up equipped with a concentric hemispherical analyzer and VG Microtech twin anode XR3E2 X-ray. A JASCO FT-IR (680 plus) spectrophotometer was applied to record the IR spectra of the nanocompounds. ^{13}C -NMR, Model 400 MHz (Avance III 400 Bruker instrument), was used to detect the products.

2.3. Synthesis of rNGO

Initially, graphene oxide was synthesized by modified Hummers method [20]. rNGO was synthesized by hydrothermal method. For this purpose: 70 mL of ammonium hydroxide solution (30%) was added to 0.070 g of GO, stirring them for 1 h at 40 °C and sonicated for 30 min. Then, the mixture was autoclave for hydrothermal reaction at 220 °C for 24 h. This hydrothermal step was also reduced the nitrogen doped graphene oxide (NGO) to nitrogen doped reduced graphene oxide (rNGO). The final product was centrifugation to collect the nanocomposites. Then, the nanocomposites were washed with water and dried at room temperature [21].

2.4. Modified electrode fabrication

Prior to modifying the glassy carbon electrode (GCE), a GCE was polished in 0.3 μm of alumina slurry for 3 min and sonicated in an ethanol/water bath. This was followed by

dispersing 2.0 mg of rNGO in 1.0 mL of water before sonication until a homogenized suspension was obtained. Then, 10 μL of the suspension was dropped on the surface of GCE and the solvent was allowed to evaporate at room temperature (rNGO/GCE). After the rNGO/GCE had been dried, Pt was electrodeposited at the surface of rNGO/GCE (Pt@rNGO/GCE) by cycling the electrode potential from -0.30 to $+1.30$ V at a scan rate of 100 mV s^{-1} in 0.5 mol L^{-1} of H_2SO_4 containing 0.050 mmol L^{-1} of K_2PtCl_6 . The number of cycles for the electrodeposition of Pt on the surface of the electrode was optimized. From the results, 35 cycles was selected as the optimum cycle number for the reduction of CO_2 to methanol.

3. Results and discussion

3.1. Characterization of graphene oxide

SEM, EDS, FT-IR, and Raman spectroscopy were used to verify the synthesized GO. The SEM image of GO (Fig. 1A) confirms the synthesis of GO in very thin layers of less than 50 nm. EDS technique (Fig. 1B) was used to verify the elements in the GO structure and to ensure the absence of impurities during the synthesis of GO. The presence of carbon and oxygen peaks and the absence of peaks of other elements were as the evidence for the purity of the GO structure. FT-IR spectrum of GO (Fig. 1C) provided several absorbance peaks corresponding to the stretching of O–H (3400 cm^{-1}), C=O (1741 cm^{-1}) of carboxyl and carbonyl, C=C (1618 cm^{-1}), C–O–C, and C–O (1100 cm^{-1}) [22]. The Raman spectrum of the GO layers (Fig. 1D) contained D and G bands as well as a 2D band at 1340, 1590, and 2670 cm^{-1} , respectively. The Raman spectrum of the graphite powder did not reveal any D bands present. The presence of D bands confirms the successful synthesis of the graphene oxide. Comparison of the 2D peak of the synthesized GO in the Raman spectrum obtained in the

present study and those reported elsewhere indicated that the number of synthesized GO sheets in the present experiment ranged between 5 and 10 [23]. **“Here Fig. 1”**

3.2. Characterization of rNGO

XPS technique was used to prove the synthesis of rNGO (Fig. 2). The XPS pattern indicates the presence of carbon (C1s = 285.3 eV), nitrogen (N1s = 401.4 eV), and oxygen (O1s = 533.6 eV). The successful synthesis of rNGO is verified by the presence of the nitrogen peak. The deconvoluted high-resolution N1s in the XPS spectra of rNGO (Fig. 2B) clearly indicates the following four types of nitrogen configurations present on the rNGO: pyridinic-N (399.91 eV), pyrrolic-N (402.8 eV), graphitic-N (402.9 eV), and N-oxide (405.0 eV). Figs. 3A and 3B present the SEM image and EDS of the rNGO, respectively. The presence of carbon, oxygen, and nitrogen peaks and the absence peaks of other elements in the EDS confirms the purity of the rNGO structure.

Fig. 3C shows the SEM image of rNGO after Pt (Pt@rNGO) had been electrodeposited. Platinum particles with diameters below 100 nm are observed in the SEM image, confirming that the Pt nanoparticles were decorated on the surface of rNGO.

“Here Figs. 2 & 3”

3.3. Determination of surface pK of nitrogen doped reduces graphene oxide

Electrochemical impedance spectroscopy was conducted in the presence of an electrochemical redox probe, $\text{Fe}(\text{CN})_6^{3-}$, to study the effect of pH on the charge transfer resistance (R_{ct}) in the terminal acid or base groups. A surface pK_a can be investigated from the variation of R_{ct} as a function of solution pH [24]. $\text{Fe}(\text{CN})_6^{3-}$ was used as an electrochemical redox probe to study the effect of pH on R_{ct} at the Pt@rNGO modified glassy electrode. Fig. 4A shows the results of electrochemical impedance spectroscopy of the modified glassy carbon electrode in solutions with varying pH levels. Clearly, R_{ct} increased

with increasing the solution pH. Pyridine in the structure of rNGO at pH 2.0 (optimum pH) accepts a proton to form pyridinium ion (-PyH^+) (Scheme 2A). This means that the nitrogen groups in the structure of rNGO are protonated at low pH levels and that the electrode surface, therefore, has a positive charge. Thus, an electrostatic attraction is expected to occur between the surface of the electrode and Fe(CN)_6^{3-} ions (in the solution), thereby decreasing R_{ct} . The attractive force between the electrode surface and Fe(CN)_6^{3-} ions (as a probe in the solution) decreases with increasing pH, indicating that the nitrogen groups in the structure of rNGO are gradually deprotonated at higher pH values and R_{ct} is, thereby, increased. The surface pK_a value was obtained from the midpoint of the impedimetric-pH titration curve; it is at this point that 50% of the nitrogen groups in the structure of rNGO is protonated. According to the impedimetric-pH titration curve (Fig. 4B), the calculated pK_a was 8.5. A simple Randle's circuit is shown in the inset of Fig. 4A.

“Here Fig. 4”

3.4. Optimum conditions for the electrochemical reduction of CO_2

The efficiency of the electrochemical CO_2 reduction is affected by the applied reduction potential and electrolyte pH [25]. For the purposes of this study, solution pH was adjusted in the range of 2.0 to 6.0 using 0.1 mol L^{-1} KNO_3 with HNO_3 and KOH 1.0 mol L^{-1}) and its effects on the efficiency of CO_2 reduction was investigated using an applied potential of -0.20 and a scan rate of 50 mV s^{-1} . It was observed that the optimum pH level for the reduction of CO_2 to methanol was 2.0. Thus, a pH equal to 2.0 was selected as the optimum level for the next steps (Fig. 5A). The influence of the applied potential on the reduction of carbon dioxide to methanol was investigated using a potential range of 0.00 to -0.50 V (vs. Ag/AgCl) to find enhanced reduction with increasing applied potential from 0.00 to -300 mV before it declined from -350 to -500 mV. This is because hydrogen gas was released at the electrode surface at a potential range between -350 and -500 mV. The gas released at the

electrode surface caused the rNGO to detach from the glassy carbon electrode surface. Therefore, an applied potential of -300 mV was selected as the optimum value (Fig. 5B). The anodic peak observed around 0.50 V in Figs. 5A and 5B is attributed to the oxidation of methanol produced at the surface of Pt@rNGO/GCE in the electrolysis stage. In addition to these two parameters, the amount of electrodeposited platinum was also be optimized. To obtain the optimum conditions, a saturated carbon dioxide electrolyte was electrolyzed at Pt@rNGO/GCE and the cyclic voltammogram of the electrode under the optimum conditions was recorded. To optimize the amount of Pt at the electrode surface, Pt-nanoparticles were electrodeposited on the surface of rNGO/GCE in a solution of 0.05 mol L^{-1} potassium hexachloro platinate (K_2PtCl_6) using cyclic voltammetry. The amount of platinum was controlled by the numbers of the cycles in the cyclic voltammetry experiments during the electrodeposition (Fig. 5C). Therefore, the optimum number of cycles was obtained to be 35 for the electrodeposition of Pt at a scan rate of 100 mV s^{-1} . The optimum amount of platinum deposited was found to be $5.9 \times 10^{-8} \text{ mol cm}^{-2}$, as determined from the following equation:

$$\Gamma = Q/nFA$$

where, Γ is the surface excess, Q is the charge under the voltammetric peak for the Pt in Fig. 5C, n is some electrons, A is the area of the electrode, and F is the Faraday constant.

The concentration of CO_2 in a CO_2 saturated solution was estimated by titration with sodium hydroxide. The reaction of sodium hydroxide with carbon dioxide (as carbonic acid) occurs in two steps; first, formation of bicarbonate from carbonic acid followed by transformation to carbonate. Since the conversion of carbon dioxide to bicarbonate will be complete at pH 8.3, phenolphthalein was used as a color indicator for the titration and CO_2 concentration was determined to be $0.0150 \pm 0.0007 \text{ mol L}^{-1}$. The number of electrons required for the reduction of CO_2 to methanol was calculated to be 6.0 and the diffusion coefficient of carbon dioxide (as H_2CO_3) was calculated to be $5.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

“Here Fig. 5”

3.5. Proposed mechanism for the electrocatalytic reduction of CO₂ to methanol

Nitrogen-containing heterocycles, such as pyridinium, have been used as catalysts in the catalytic reduction of CO₂ [2]. As shown in Schematic 1, there are pyridine groups on the nitrogen doped reduced graphene oxide structure. The calculated pK_a for the rNGO was 8.5, as already explained in Sec. 3.3. So, pyridine in the structure of rNGO at pH 2.0 (optimum pH) should accept a proton to form pyridinium ion (-PyH⁺) (Scheme 2A). Hydrogen atoms are then formed to be adsorbed on the surface of the Pt electrodeposited at the surface of rNGO/GCE (Scheme 2B). In the presence of CO₂, hydrogen atoms adsorbed on the Pt are susceptible to electrophilic attack by CO₂, such that COOH forms on the surface of the electrode and its interaction with PyH⁺ leads to the formation of PyH⁺...COOH. Finally, the reduction of PyH⁺...COOH on the surface of the electrode leads to the production of methanol (Schemes 2C and 2D) [14,26].

“Here Scheme 2”

3.6. Diffusion coefficient of carbonic acid (as carbon dioxide)

At low pH values, CO₂ is converted to carbonic acid and H₂CO₃ is, therefore, the dominant species which represents the amount of dissolved CO₂ in the solution. The diffusion coefficient (D) of H₂CO₃ was estimated using the Cottrell Equation below based on the chronoamperogram results:

$$I_d = nFAD^{0.5}C^*/(\pi t)^{0.5}$$

where, n is number of electrons, A is the area of the electrode, F is the Faraday constant, and C is the bulk concentration of carbon dioxide (as H₂CO₃). The concentration of CO₂ by titration was determined to be $0.015 \pm (7.1 \times 10^{-4})$ mol L⁻¹. Also, the number of electrons required for the reduction of CO₂ to methanol was found to be 6.0. Thus, the estimated value of the diffusion coefficient of H₂CO₃ was 5.7×10^{-7} cm² s⁻¹ (Fig. 6). **“Here Fig. 6”**

3.7. Analysis of the products

The products of CO₂ reduction were analyzed using ¹³C-NMR spectroscopy and cyclic voltammetry in the electrolysis solution. Electrolysis was performed in a CO₂ saturated solution at pH 2.0 and at −0.30 V (vs. Ag/AgCl) at the surface of Pt@rNGO/GCE. The ¹³C-NMR showed two peaks at 48 and 123 ppm corresponding to methanol and CO₂ in the electrolysis solution, respectively (Fig. 7). **“Here Fig. 7”**

The formation of products at electrode surfaces was monitored using the voltammetric method. Figs. 8a and 8b show the cyclic voltammograms of rNGO/GCE and Pt@rNGO/GCE, respectively, in a free CO₂ solution at pH 2.0. Fig. 8c presents the voltammogram of Pt@rNGO/GCE after electrolysis of CO₂ saturated solution for 30 min under optimum conditions while Fig. 8d shows that of Pt@rNGO/GCE in the presence of 0.1 mmol L^{−1} methanol. As shown in Fig. 8d, methanol oxidation peak at the surface of Pt@rNGO/GCE appeared at around +0.50 V. In Fig. 6c, which corresponds to the electrolysis of a carbon dioxide saturated solution, an oxidation peak appeared at a potential of around 0.50 V. Comparison of the voltammograms in Fig. 8 verifies that methanol is the main product of CO₂ reduction at the Pt@rNGO/GCE electrode. The concentration of methanol thus produced was determined to be 3.3 mmol L^{−1} in a 20 mL solution, and the Faradic efficiency of methanol formation was 41%. Faradaic efficiency is given by $([\text{MeOH}] \times 6e^-) / (It)$, where $I \times t$ is the integrated bulk electrolysis current. (Fig. 9).

“Here Figs. 8&9”

4. Conclusion

A glassy carbon electrode was modified with Pt@rNGO to study the electrochemical reduction of CO₂ at Pt@rNGO/GCE. The optimum conditions for CO₂ reduction including pH and reduction potential were determined to be −0.30 V and 2.0, respectively. The product of the electro-reduction of CO₂ was detected by ¹³C-NMR. The result of the NMR spectra

showed that the only product of the electrochemical reduction of CO₂ at the Pt@rNGO/GCE was methanol. The concentration of the methanol thus produced was 3.3 mmol L⁻¹ in a 20 mL solution, and a Faradic efficiency of methanol formation of 41% was achieved under the optimized reduction potential and pH of -0.30 V and 2.0, respectively.

Acknowledgements

The authors wish to thank the Iran National Science Foundation and National Elites Foundation, for their support.

References

- [1] G.R. Dey, K. Kishore, Photo/electrochemistry and photobiology in the environment, in: S. Kaneco (Ed.), Energy and Fuel, Research Signpost, Kerala 2005, p. 357.
- [2] K.J.P. Schouten, E. Pérez Gallent, M.T.M. Koper, The influence of pH on the reduction of CO and CO₂ to hydrocarbons on copper electrodes, J. Electroanal. Chem. 716 (2014) 53–57
- [3] M. Gattrell, N. Gupta, A. Co, A review of the aqueous electrochemical reduction of CO₂ to hydrocarbons at copper, J. Electroanal. Chem. 594 (2006) 1–19.
- [4] J. Yuan, P. Wang, C. Hao, G. Yu, Photoelectrochemical reduction of carbon dioxide at CuInS₂/graphene hybrid thin film electrode, Electrochim. Acta 193 (2016) 1-6.
- [5] B.M. Setterfield-Price, R.A.W. Dryfe, The influence of electrolyte identity upon the electro-reduction of CO₂, J. Electroanal. Chem. 730 (2014) 48–58.
- [6] J.H. Baricuatro, C.B. Ehlers, K.D. Cummins, M.P. Soriaga, J.L. Stickney, Y.G. Kim, Structure and composition of Cu(hkl) surfaces exposed to O₂ and emersed from alkaline solutions: Prelude to UHV-EC studies of CO₂ reduction at well-defined copper catalysts, J. Electroanal. Chem. 716 (2014) 101–105
- [7] Y. Li, G. Ruan, A.S. Jalilov, Y.R. Tarkunde, H. Fei, J.M. Tour, Biochar as a renewable source for high-performance CO₂ sorbent, Carbon 107 (2016) 344-351.
- [8] A.B. Fuertes, M. Sevilla, High-surface area carbons from renewable sources with a bimodal micro-mesoporosity for high-performance ionic liquid-based supercapacitors, Carbon 94 (2015) 41-52.
- [9] O. Scialdone, A. Galia, G. Lo Nero, F. Proietto, S. Sabatino, B. Schiavo, Electrochemical reduction of carbon dioxide to formic acid at a tin cathode in divided and undivided cells: effect of carbon dioxide pressure and other operating parameters, Electrochim. Acta 199 (2016) 332-341.

- [10] J. Hawecker, J.M. Lehn, R. Ziessel, Electrocatalytic reduction of carbon dioxide mediated by $\text{Re}(\text{bipy})(\text{Co})_3\text{Cl}$ (bipy = 2,2'-bipyridine), *J. Chem. Soc. Chem. Commun.* 28 (1984) 328-330.
- [11] M. Tezuka, T. Yajima, A. Tsuchiya, Y. Matsumoto, Y. Uchida, M. Hidai, Electroreduction of carbon dioxide catalyzed by iron-sulfur cluster compounds $[\text{Fe}_4\text{S}_4(\text{SR})_4]^2$, *J. Am. Chem. Soc.* 104 (1982) 6834-6836.
- [12] G.Z. Kyriacou, A.K. Anagnostopoulos, Influence CO_2 partial pressure and the supporting electrolyte cation on the product distribution in CO_2 electroreduction, *J. Appl. Electrochem.* 23 (1993) 483-486.
- [13] A. Schizodimou, G. Kyriacou¹, Acceleration of the reduction of carbon dioxide in the presence of multivalent cations, *Electrochim. Acta* 78 (2012) 171-176.
- [14] E.B. Cole, P.S. Lakkaraju, D.M. Rampulla, A.J. Morris, E. Abelev, A.B. Bocarsly, Using a one-electron shuttle for the multielectron reduction of CO_2 to methanol: kinetic, mechanistic, and structural insights, *J. Am. Chem. Soc.* 132 (2010) 11539-11551.
- [15] C C.H. Lim, A.M. Holder, C.B. Musgrave, Mechanism of homogeneous reduction of CO_2 by pyridine: proton relay in aqueous solvent and aromatic stabilization, *J. Am. Chem. Soc.* 135 (2013) 142-154.
- [16] A. Gennaro, A.A. Isse, J.M. Saveant, M.G. Severin, E. Vianello, Homogeneous electron transfer catalysis of the electrochemical reduction of carbon dioxide. Do aromatic anion radicals react in an outer-sphere manner? *J. Am. Chem. Soc.* 118 (1996) 7190-796.
- [17] L.L. Snuffin, L.W. Whaley, L. Yu, Catalytic electrochemical reduction of CO_2 in ionic liquid EMIMBF₃Cl, *J. Electrochem. Soc.* 158 (2011) F155–F158.
- [18] V. Lates, A. Falch, A. Jordaan, R. Peach, R.J. Kriek, An electrochemical study of carbon dioxide electroreduction on gold-based nanoparticle catalysts, *Electrochim. Acta* 128 (2014) 75-84.

- [19] S. Du, Y. Lu, R. Steinberger-Wilckens, PtPd nanowire arrays supported on reduced graphene oxide as advanced electrocatalysts for methanol oxidation, *Carbon* 79 (2014) 346-353.
- [20] Y. Xu, H. Bai, G. Lu, C. Li, G. Sh, Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets, *J. Am. Chem. Soc.* 130 (2008) 5856-5857.
- [21] Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, Co_3O_4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction, *Nature Materials* 10 (2013) 780-786.
- [22] Z. Liu, X.Y. Ling, X. Su, J.Y. Lee, Carbon-supported Pt and Pt Ru nanoparticles as catalysts for a direct methanol fuel cell, *J. Phys. Chem. B* 108 (2004) 8234-8240.
- [23] O. Akhavan, Bacteriorhodopsin as a superior substitute for hydrazine in chemical reduction of single-layer graphene oxide sheets, *Carbon* 81 (2015) 158-166.
- [24] K. Kim, J. Kwak, Faradaic impedance titration of pure 3-mercaptopropionic acid and ethanethiol mixed monolayers on gold, *J. Electroanal. Chem.* 512 (2001) 83-91.
- [25] J. Zhao, C.R. Cabrera, Z. Xia, Z. Chen, Single-sided fluorine-functionalized graphene: A metal-free electrocatalyst with high efficiency for oxygen reduction reaction, *Carbon* 104 (2016) 56-63.
- [26] J.A. Keitha, E.A. Carter, Theoretical insights into pyridinium-based photoelectrocatalytic reduction of CO_2 , *J. Am. Chem. Soc.* 134 (2012) 7580-7583.

Legend for the schemes and figures

Scheme 1. Chemical structure of rNGO.

Scheme 2. The proposed mechanism for the electrochemical reduction of CO₂.

Fig. 1. (A): SEM image, (B): EDX microanalysis spectrum, (C): FT-IR spectrum, and (D): Raman spectrum of graphene oxide.

Fig. 2. A): XPS data, and (B) High-resolution XPS spectra of N1s for rNGO.

Fig. 3. A): SEM image of rNGO; B): EDS of rNGO; C): SEM image of Pt@rNGO/GCE.

Fig. 4. A) Complex plane plots obtained for Pt@rNGO/GCE in the presence of 0.5 mmol L⁻¹ Fe(CN)₆³⁻ containing 0.1 mol L⁻¹ KNO₃ at different pH range from 4.0 to 12.0; The inset: a simple Randle's circuit (conditions: DC potential, +0.25 V; AC amplitude, 10 mV; frequency range, 10 kHz to 0.1 Hz). (B) Faradaic impedance titration curve for Pt@rNGO/GCE.

Fig. 5. A): Effect of solution pH (2.0 to 6.0, containing 0.1 mol L⁻¹ KNO₃) on the current efficiency of the reduction of CO₂ at applied potential of -0.20. (scan rate of 50 mV s⁻¹) B): Effect of the applied potential on the current efficiency of the reduction of CO₂ at pH 2.0; C): Influence of the numbers of the cycles in cyclic voltammetry during the controlled electrodeposition of Pt at the optimum conditions.

Fig. 6: Diffusion coefficient (D) of H₂CO₃.

Fig. 7: ¹³C-NMR of the product solution, after electrolysis of CO₂ saturated solution (containing 0.1 mol L⁻¹ KNO₃ at pH 2.0) for ~3 h at -0.30 V vs. Ag/AgCl on the surface of Pt@rNGO/GC electrode. The products peaks are observed for methanol and unreacted CO₂ at 48 ppm and 123 ppm, respectively.

Fig. 8. Cyclic voltammogram of (a) rNGO/GCE in a free CO₂ solution at pH 2.0, (b) Pt@rNGO/GCE in a free CO₂ solution at pH 2.0, (c) Pt@rNGO/GCE after 30 min electrolysis of a saturated CO₂ solution, and (d) Pt@rNGO/GCE in the electrolyte solution containing 0.1 mmol L⁻¹ methanol. Conditions: 0.1 mol L⁻¹ KNO₃ at pH 2.0 and at a constant potential of -0.20 V (vs. Ag/AgCl) with a scan rate 100 mV s⁻¹.

Fig. 9: A calibration curve (using cyclic voltammetry technique) was used to determine the concentration of the produced methanol.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Pyridinic-N
 Pyrrolic-N
 Graphitic-N
 Oxide-N