Available online at BCREC website: https://bcrec.id

Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2) 2021, 430-439

Research Article

Electrochemical Generation of Hydrogen and Methanol using ITO Sheet Decorated with Modified-Titania as Electrode

Tariq Abbas, Muhammad Tahir*, Nor Aishah Saidina Amin

Chemical Reaction Engineering Group, School of Chemical and Energy Engineering, Universiti Teknologi Malaysia (UTM), 81310 Johor Bahru, Johor, Malaysia.

Received: 3rd March 2021; Revised: 30th April 2021; Accepted: 5th May 2021
Available online: 6th May 2021; Published regularly: June 2021

Abstract

Current issues of global warming and environmental pollution due to extensive use of fossil fuels has been reached to an alarming position. Being CO_2 as main byproduct of fossil fuel consumption and water as abundantly available on earth surface has great potential to replace fossil fuels as energy source. Herein, electrocatalytic CO_2 reduction with water for methanol and hydrogen gas (H_2) production over ITO sheet decorated with modified-Titanium nanorods (TiO_2 NR), has been investigated. The performance comparison of electrocatalytic activity of hydrothermally modified-titania with commercial TiO_2 microparticles (MP) were further investigated. Electrochemical reactor containing $KHCO_3$ aqueous solution with CO_2 as an electrolyte and modified TiO_2 nanorods (NR) as working electrodes offer an eco-friendly system to produce clean and sustainable energy system. The typical rates of product, *i.e.* methanol and H_2 generation from the ITO sheet decorated with modified TiO_2 NR layer recorded higher than those for the ITO sheet with commercial TiO_2 microparticle. At 2.0V applied potential vs Ag/AgCl as reference electrode, the modified TiO_2 NR electrocatalyst yielded methanol at a rate of 3.32 $\mu mol.cm^{-2}.L^{-1}$ and H_2 at a rate of 6 $\mu mol.cm^{-2}.L^{-1}$ which was higher than that of commercial TiO_2 MP electrocatalyst (methanol = 1.5 $\mu mol.cm^{-2}.L^{-1}$ and H_2 = 3.7 $\mu mol.cm^{-2}.L^{-1}$). The enhancement in product yields of methanol and H_2 was mainly due to the notable improvements and modification in texture of TiO_2 working electrode interface. Hence, it is concluded that the modified TiO_2 NR can be considered as a competent candidate for sustainable energy conversion applications.

Keywords: CO_2 electroreduction; water electrocatalysis; methanol; hydrogen; TiO_2 nanorods

How to Cite: T. Abbas, M. Tahir, N.A.S. Amin (2021). Electrochemical Generation of Hydrogen and Methanol using ITO Sheet Decorated with Modified-Titania as Electrode. *Bulletin of Chemical Reaction Engineering & Catalysis*, 16(2), 430-439 (doi:10.9767/bcrec.16.2.10514.430-439)

Permalink/DOI: https://doi.org/10.9767/bcrec.16.2.10514.430-439

1. Introduction

Currently, the earth's main energy sources are mostly depending on non-renewable fossil fuels such as petroleum oils, coal and natural gas [1–2]. These sources of energy are limited in nature, and their utilization and consumption process cause environmental pollution due to the emission of greenhouse gases (CO_2) and air pollution (SOx and NOx), all of these problems lead to global warming and serious climatic changes [3–4]. A cleaner production of hydrogen (H_2) has a great potential to substitute fossil fuel utilization due to its immense advantages, such as higher energy density and zero carbon

---

* Corresponding Author.
Email: mtahir@cheme.utm.my;
bttahir@yahoo.com (M. Tahir);
Tel: +60146281678

footprint up on use. Presently, most of the H_2 production is commercially done by steam reforming of natural gas, which causes CO_2 emissions [5]. Electrochemical (EC) process can be used to produce H_2 via electrocatalysis of water under low electrical bias. The CO_2 produced as byproduct of steam reforming of natural gas and utilization of other fossil fuels can also be converted back to methanol using EC process. The electrocatalytic efficiency of CO_2 reduction and direct water electrocatalysis depends on the working electrode or semiconductor used as electrocatalyst.

In recent years, numerous semiconductor materials, such as: SnO_2, InP, CdS, g-C_3N_4, Bi_2WO_6, Cu_2O, $InSe_2$, $BiVO_4$, PbO_2, rGO, CeO_2 and TiO_2 [6−12], have been investigated as electrocatalysts in EC system for CO_2 and reduction H_2 evolution reaction. However, TiO_2 has been considered as a standard benchmark for researchers after the pioneering research work conducted by Fujishima and Honda for electrocatalytic process [13,14]. High demand for TiO_2 as electrocatalyst is due to high stability in a corrosive environment, facile in preparation and structure modification, abundant availability, economical in cost and ecofriendly [15,16]. In EC applications, TiO_2 has been extensively investigated for both CO_2 reduction and water oxidation for methanol and H_2 evolution reactions [9,17,18]. Particularly, TiO_2 is considered as one of the promising electrocatalyst and semiconductor for EC processes because of its easy availability, cheap, negative flat band potential, unique electronic configuration, stable towards corrosive chemicals and ecofriendly. However, commercially available TiO_2 microparticle suffers from rapid recombination of charge, lower product selectivity, larger bandgap (~3.2 eV), and less catalytic efficiency [19]. This is due to the lower surface area and fast electrons (e^-) and holes (h^+) recombination rates which effects the efficiency of electrocatalytic activity methanol and H_2 production [20]. Both properties of TiO_2 affect the efficiency of catalytic activity in methanol and H_2 production [21].

The efficiency of TiO_2 can be improved by surface modification and changing the structure of TiO_2 crystals. TiO_2 exists in various structural phases such as brookite, rutile and anatase [22]. The anatase phase of TiO_2 is considered most efficient in electrocatalytic processes as compared to brookite and rutile phase. Moreover, the catalytic efficiency highly relies on the crystal structures of TiO_2 which exist in various forms, such as: microparticles, nanoparticles, and nanorods. High catalytic activity could be obtained with nanorods structures due to higher active sites or surface area compared to the microparticles and nanoparticles [23]. The structural morphologies can be controlled based on the synthesize method of TiO_2. The problem of charge recombination and surface area can be addressed by changing and modification of surface morphology of TiO_2 for better charge transfer and enhanced surface area [24,25]. Based on these assumptions and viewpoints, herein, we aimed to synthesize simple and uniquely modified TiO_2 nanorods electrocatalyst for efficient CO_2 reduction and direct electrocatalysis of water to produce methanol and H_2.

In this study, we synthesis the TiO_2 nanorods via hydrothermal method using sodium hydroxide as alkaline agent. The as prepared TiO_2 nanorod (NR) sample was used to fabricate electrode for electrocatalytic CO_2 reduction into methanol and H_2 production by using catalyst ink method. Commercial TiO_2 microparticles (MP) were also used in the electrode fabrication for comparison purpose. The synthesized TiO_2 NR and commercial TiO_2 MP were characterized to analyze the structural phase and surface morphology by using X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET), Field Emission Scanning Electron Microscope (FESEM), and High-resolution transmission electron microscopy (HR-TEM) techniques. Both TiO_2 NR and commercial TiO_2 MP electrodes were subjected to electrocatalytic CO_2 reduction for the electrocatalytic performance evaluation on the basis of methanol and H_2 production.

2. Materials and Methods

2.1 Materials

Titanium(IV) oxide (TiO_2), anatase (99.9%), Sodium hydroxide (NaOH) (97.0%) and Dimethylsulfoxide (DMSO) (99.5%) were analytical grade reagents and used without further purification. Indium tin oxide coated glass slide (ITO), surface resistivity 15-25 Ω/sq, Platinum (Pt) wire (purity = 99.9%), Ag/AgCl (3.5 M KCl) reference electrode and all other chemical were purchased from Sigma–Aldrich Sdn Bhd, Malaysia. Carbon dioxide (CO_2) gas (purity = 99.9%), Hydrogen (H_2) gas (purity = 99.9%) and all other gases required for gas chromatograph (GC) system were acquired from Mega Mount Industrial Gases Sdn. Bhd., Malaysia. Deionized water was used as solvent for all aqueous solutions.

2.2 Synthesis of Electrocatalyst

TiO_2 NR synthesized by using hydrothermal method, reported elsewhere [26]. In this method 1.5 g of TiO_2 (anatase) powder was added to 70 mL of NaOH (10 M) aqueous solution After stirring for 1 h, the solution was transferred to a 100 mL autoclave and heated at 200 °C for 24 h. The precipitate was centrifuged and washed with deionized water and ethanol several times until the pH value reached ~7. The wet product was kept in an oven for drying at 100 °C for 12 h. The obtained sample was crushed and calcined in a furnace at 500 °C for 5 h. The synthesized sample is denoted by TiO_2 NR afterwards.

2.3 Synthesis of Electrode

Modified TiO_2 NR electrode was fabricated on ITO slide by using catalyst ink method. For this purpose, 0.1 g of TiO_2 NR was mixed in 10 μL DMSO and sonicated for 6 h to synthesis evenly dispersed and viscus catalyst ink. After preparation of catalyst ink, the ITO slide was carefully covered with catalyst ink by drop casting method. The ITO slide covered with catalyst ink was then transferred to oven for drying at 100 °C for 6 h.

2.4 Catalyst Characterizations

The structure and degree of crystallinity were carried out using XRD technique. The XRD patterns were obtained by the D5000 Siemens instrument using Cu-kα radiation (40 kev. 40 mA). The patterns were evaluated at a scanning rate of 1.2 $°.min^{-1}$ and a scanning range of 10–90° of 2θ. The diffractometer is armed with a Ni-filtered Cu Kα radiation source (λ = 1.54056 Å). The X-ray source was operated at 40 kV and 200 mA. The phase identification of the as-prepared sample was analyzed by comparison to Joint Committee on Powder Diffraction Standards (JCPDS). The morphology of the electrodes and catalyst powder was analyzed by field emission scanning electron microscopy (FESEM) by using Hitachi SU8020. The high-resolution transmission electron microscope (HR-TEM) images of the as-prepared electrocatalyst samples was obtained from the JEOL JEM-ARM 200F HR-TEM transmission electron microscope. Electrochemical characterizations such as cyclic voltammetry (CV) was performed by using an electrochemical workstation (Keithley-2450-EC, Tektronix, USA). In a typical three-electrode system with 0.1 M $KHCO_3$ as electrolyte in a homemade EC microreactor (100 cm^3)

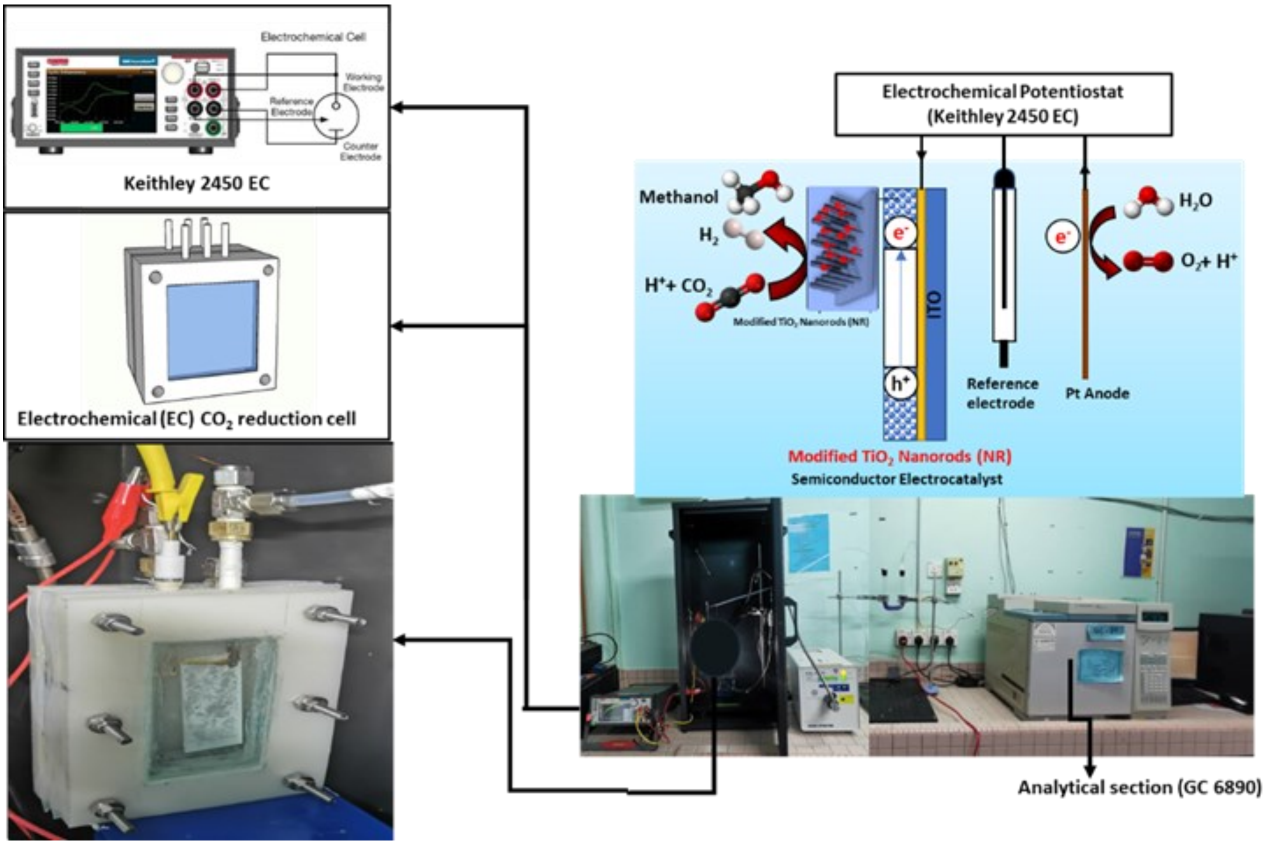


Figure 1. Electrochemical (EC) experimental setup with schematic diagram of the process.

with continuous flow/bubbling of CO_2 at 20 m/min. The prepared electrocatalyst samples, platinum plate and standard Ag/AgCl electrode were used as working, counter and reference electrode, respectively.

2.5 Experimental Setup and Reactor Configuration

The schematic of experimental setup for the homemade electrocatalytic (EC) reactor system is presented in Figure 1. The $KHCO_3$ (0.1M) as electrolyte for the EC reaction system is fed into the EC reactor cell. Then, the CO_2 is introduced into EC reactor cell by a digital mass flow controller (Alicat Scientific Mc-1Slpm-D (CO_2)) at a flow rate of 20 mL/min. The potential difference across EC reactor cell was applied by an electrochemical workstation (Keithley-2450-EC, Tektronix, USA) in a typical three-electrode system. The prepared electrocatalyst samples coated on ITO slide, platinum plate and standard Ag/AgCl electrode is used as working, counter and a reference electrode, respectively. To analyze the electrocatalysis for H_2 production and CO_2 reduction for methanol production under light irradiation, a solar simulator model number LAX-C100, Asahi Spectra was used as light source. The gas products were analyzed through an online gas chromatograph (GC) system (model No: Agilent 6890N) connected with a thermal conductivity detector (TCD) and Carbon-PLOT capillary column (0.53 mm × 30 m). The temperature of the GC system column was set at 200 °C. The liquid product was analyzed through an offline gas chromatograph (GC) system (model No: Agilent 7820N) connected with a Flame-ionization detection (FID) and a DB–WAX capillary column (0.25 mm × 30 m). The performance of the EC reactor system using different catalysts are reported and analyzed by Equations (1) and (2) product yield (μmol.cm^{-2}.L^{-1}) and Faradaic efficiency (%), respectively.

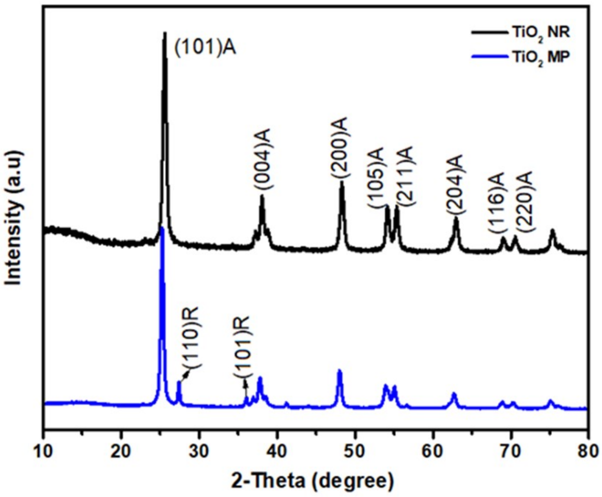


Figure 2. XRD pattern of TiO_2 nanorods (NR) and microparticle (MP) catalyst samples. *A = anatase and R = Rutile.

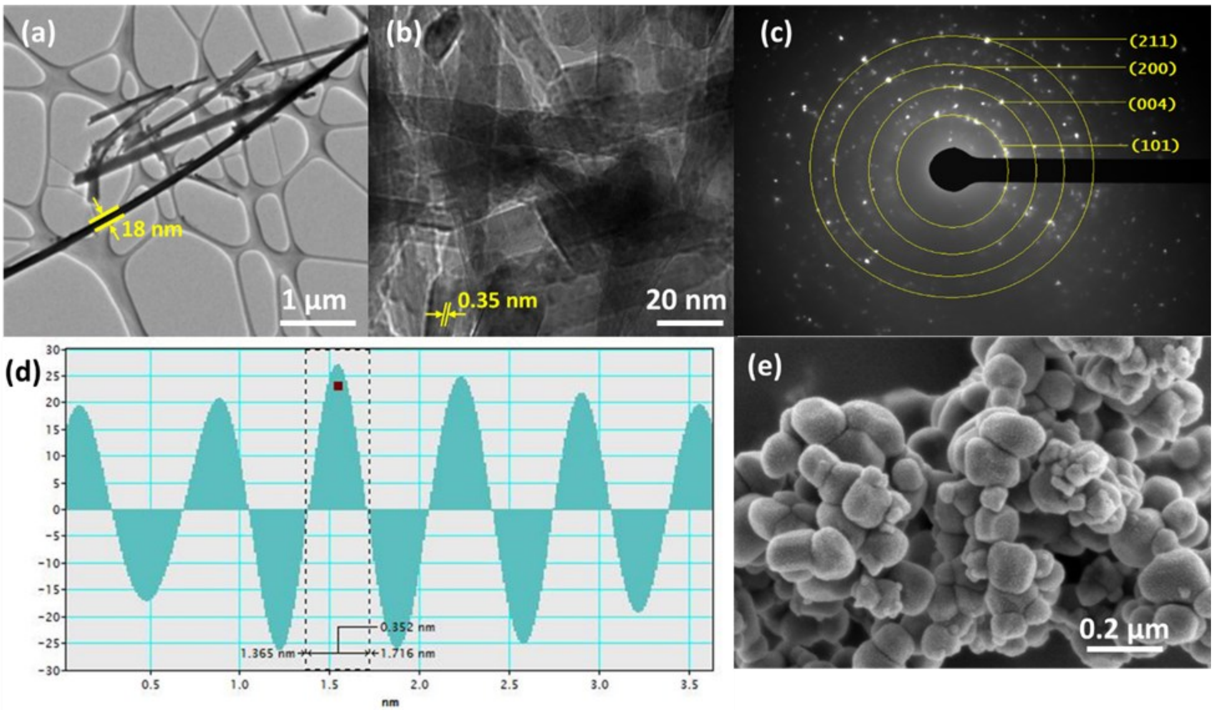


Figure 3. (a-b) HR-TEM micrographs of TiO_2 nanorods (NR), (c) SAED pattern of TiO_2 NR, (d) observed d-spacing value for TiO_2 NR and (e) FESEM of TiO_2 microparticle (MP) electrocatalyst.

$$Product\ Yield = \frac{moles\ of\ Product}{Electrode\ area\ \times Volume\ of\ reactor} \quad (1)$$

$$Faradaic\ Efficiency\ (FE) = \frac{\varepsilon \times n \times F}{Q} \times 100 \quad (2)$$

3. Results and Discussion

3.1 Characterization of Electrocatalysts

The X-ray diffraction patterns of TiO_2 NR and TiO_2 MP electrocatalyst samples, calcined at 500 °C up to 5 h are shown in Figure 2. The peaks for TiO_2 NR and MP were indicated at 2-theta (degree) 25.4°, 38.0°, 48.1°, 53.0°, 55.2° and 62.9°, which corresponds to (101), (004), (200), (105), (211) and (204) planes associated with tetragonal anatase, all in pure anatase phase. However, in TiO_2 MP diffraction patterns additional peaks at 27.4° and 36.07° can be seen, which corresponds to (110) and (101) planes associated with rutile phase [27]. Similar XRD peaks were reported by Steky *et al.* [28] for the nanostructured titania via alkaline hydrothermal treatment using ammonia solution with the presence of anatase and trace of rutile phases. It can be concluded that the TiO_2 NR structure in pure anatase phase can be acquired via hydrothermal method using NaOH as alkaline agent.

HR-TEM micrographs and FESEM of TiO_2 nanorods (NR) and TiO_2 microparticle (MP) electrocatalysts are depicted in Figure 3a-e. In Figure 3a, the HR-TEM micrographs of TiO_2 nanorods (NR) shows the formation of nanorod structures with approximately 6-8 micrometers in length and 18 nm in diameter. Figure 3b shows d-spacing of 0.35 nm which corresponds to the (101) facet of TiO_2 anatase phase. The value of d-spacing was observed by using DigitalMicrograph®, Gatan Inc. software tool, as shown in Figure 3d. From the SAED patterns as depicted in Figure 3c, the crystal interplanar spacings corresponding to diffraction rings/facets starting from inner side to outwards were (101), (112), (211), and (220). The FESEM micrograph of TiO_2 microparticle is also depicted in Figure 3e, where we can observe the TiO_2 particles are in micro-spherical form. However, HR-TEM micrographs confirms the formation of TiO_2 nanorod structure of hydrothermally synthesized electrocatalyst.

The N_2 adsorption and desorption isotherms of the calcined TiO_2 NR and TiO_2 MP are shown in Figure 4. Both microparticle and nanorods show increase in N_2 absorption above 0.9 partial pressure (P/P_0). Furthermore, N_2 adsorption-desorption isotherms revealed mesoporous structure for TiO_2 NR with hysteresis

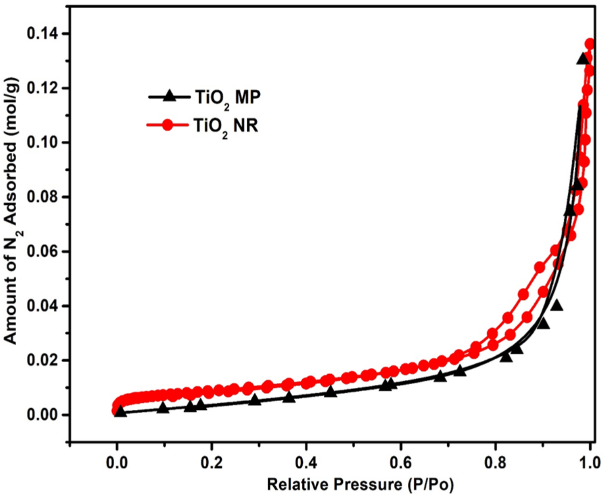


Figure 4. N_2 adsorption-desorption isotherms of TiO_2 NR and TiO_2 MP electrocatalyst.

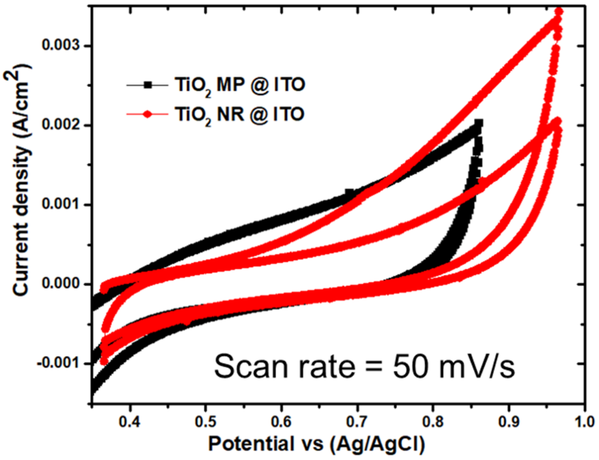


Figure 5. Cyclic voltammetry curves for various electrodes/electrocatalyst @50 mV/s and 0.3 to 1.0 V vs Ag/AgCl potential range.

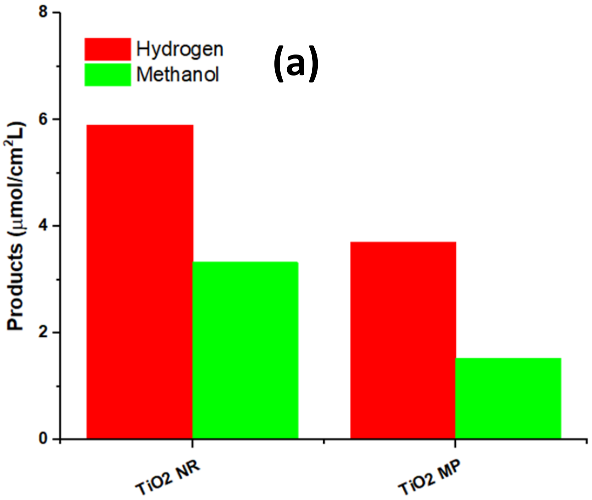
Table 1. Summary of structural properties TiO_2 NR and TiO_2 MP electrocatalyst samples.

Catalyst	BET_{SA} (m^2/g)	Pore radius (nm)	Pore volume (cm^3/g)
TiO_2 MP	25.43	9.70	0.15
TiO_2 NR	50.26	12.72	0.31

*SA = Surface Area

loop of type IV according to IUPAC. The summary of structural properties including BET surface area, pore volume and pore size/radius of TiO_2 MP and TiO NR are presented in Table 1. The BET surface area of TiO_2 MP was 25.43 m^2/g, pore volume 0.15 cm^3/g and pore radius 9.70 nm were recorded. However, BET surface area of hydrothermally modified TiO_2 NR was recorded as 50.62 m^2/g which is higher than unmodified commercial TiO_2 MP catalyst sample. Similar trends were observed in the pore volume 0.31 cm^3/g and pore radius 12.72 nm of TiO_2 NR, which were recorded higher as compared to TiO_2 MP. The significant increments in structural properties of modified TiO_2 NR was obtained through simple hydrothermal treatment and these structural properties of TiO_2 NR might enhance the electrocatalytic performance.

The measurement of cyclic voltammetry (CV) curve at 50 mV/s scan rate within a potential range ~ 0.3 to 1.0 V vs Ag/AgCl was performed for different samples and depicted in Figure 5. The CV tests shows relatively higher electrochemical surface area and current density for TiO_2 NR electrocatalyst as compared to other samples. This increment is desirable for enhanced electrocatalytic activity towards CO_2 reduction for methanol and direct water electrolysis for H_2 production. It can be observed from the cyclic voltammetry curves the current density of TiO_2 NR increases with the increase in the applied potential. It shows that with increase in the applied potential the current density increases, which results in the enhanced electrocatalytic reactions for methanol formation and H_2 production at electrode-electrolyte interface. The present cyclic voltammetry data is consistent with reported literature for electrocatalytic activity for CO_2 reduction [21].



3.2 Electrocatalytic CO_2 Reduction

To analyze the direct water electrocatalysis for H_2 production and CO_2 reduction for methanol production under 2 V of applied potential using three electrode system. An online gas chromatography (GC-TCD, Agilent 6890) equipped with Carbon plot column was used to analyze the gas products and an offline liquid GC-FID (Agilent, 7820A) equipped with DB-WAX column was used to analyze liquid products. In outlet product gas mainly H_2 was observed and in the liquid methanol was detected. Figure 6a shows the electrocatalytic activity test for different electrodes. As we can observe from the experiments that TiO_2 NR electrocatalyst showed highest catalytic activity in terms of H_2 and methanol production. The H_2 and methanol production rate for modified

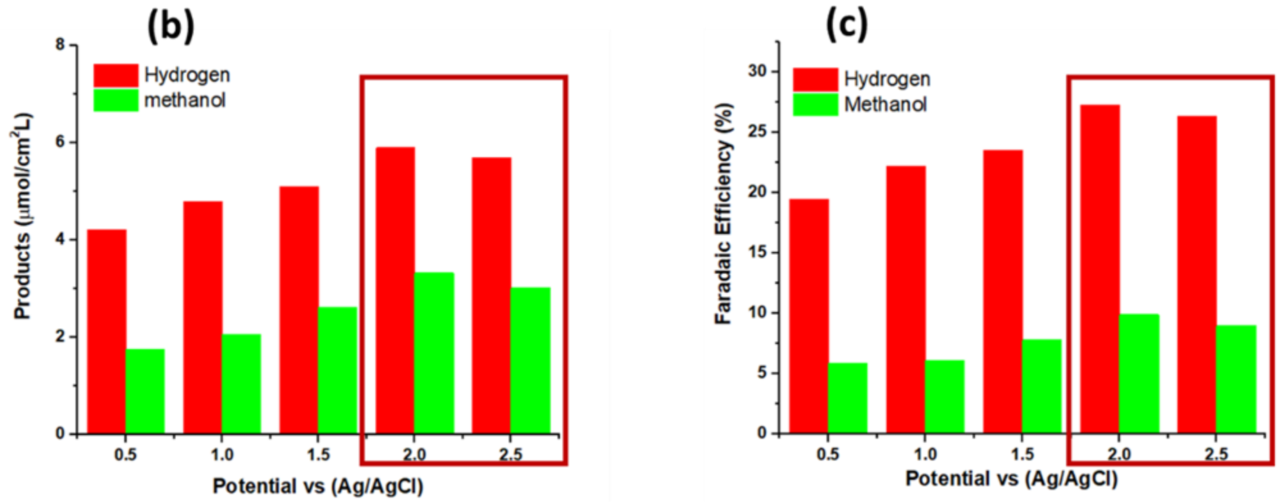


Figure 6. (a) Electrocatalytic activity test for different electrocatalysts (b-c) electrocatalytic activity of TiO_2 NR electrocatalyst under different electric potentials.

TiO_2 NR electrocatalyst at 2 V of potential vs Ag/AgCl for 1 h was recorded as ~6.0 $\mu mol.cm^{-2}.L^{-1}$ and 3.32 $\mu mol.cm^{-2}.L^{-1}$, respectively. The electrocatalytic activity of TiO_2 NR electrocatalyst was further investigated under different applied electric potentials (0.5–2.5 V), as depicted in Figure 6b and 6c. As shown in the results, product yield and faradaic efficiency for methanol and H_2 production increased gradually from 0.5 V to 2.0 V applied potentials. However, a slight decline in methanol and H_2 production rate and faradaic efficiency can be absorbed at 2.5 V applied potential. The decline in product generation and faradaic efficiency might be due to overpotential that causes excess concentration of H^+/or OH^- species around electrodes. These excess H^+/or OH^- species causes hindrance for CO_2 adsorption on catalyst surface that results in decline in production rate and faradaic efficiency. Huang *et al.* [29] also reported similar trend for product generation in electrocatalytic CO_2 reduction to methanol.

The improvement in product yields of methanol and H_2 was mainly due to the notable improvements and modification in morphology of TiO_2 electrocatalyst interface. Moreover, the improvements in catalytic activity of TiO_2 NR electrocatalyst might be due to enhanced charge separation for TiO_2 after surface modification. The cyclic voltammetry (CV) results for TiO_2 NR electrocatalyst also provide justification for the enhanced catalytic activity.

3.3 Electrocatalytic Mechanism of CO_2 Reduction

On the basis of available related literature and experiments, we propose a hypothetical reaction mechanism for electrocatalytic CO_2 reduction to methanol and H_2 over TiO_2 NR electrocatalyst. The schematics of proposed reaction mechanism is shown in Figure 7. In the first step, the oxidation of electrolyte/water containing OH^- occurs at anode side. After losing electron to anode proton/H^+ produced at anode side and due to concentration gradient, these protons/H^+ migrate towards cathode side. At cathode side, after bubbling and dissolving CO_2 through electrolyte, molecules of dissolved CO_2 start to adsorb at electrocatalyst by creating a complex $[TiO_2\ NR\text{-}CO_2]^+$ via interaction of

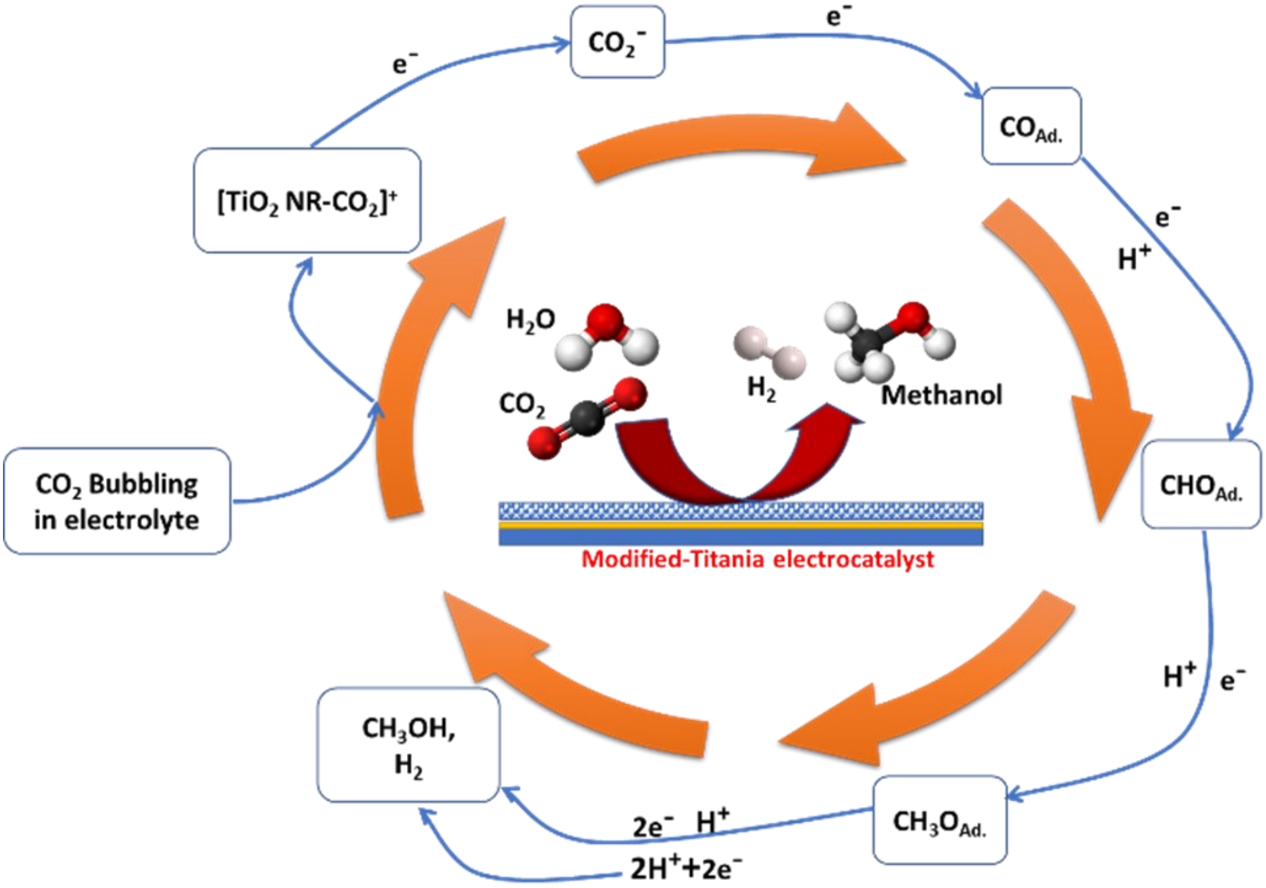


Figure 7. Schematic reaction mechanism for electrocatalytic CO_2 reduction over TiO_2 NR.

hydrogen between molecules. After adsorption of CO_2 complex on electrocatalyst, the CO_2 molecule convert into CO_2^- after reduction process. The reduced CO_2^- molecule further transfer second electron to convert into intermediate CO or adsorbed $CO/CO_{Ad.}$ After that, third transfer of electron occurs along with proton/H^+ to convert $CO_{Ad.}$ into adsorbed CHO or $CHO_{Ad.}$ intermediate. Further, electron and proton/H^+ transfer leads to conversion of $CHO_{Ad.}$ into intermediate CH_3O or adsorbed $CH_3O_{Ad.}$ intermediate. In final step, the last electron and proton/H^+ is transferred to the $CH_3O_{Ad.}$ and methanol is produced at electrocatalyst. Also, two protons/H^+ react with two electrons to produce 1 mole of hydrogen. The overall reaction is shown in Equations (3) and (4).

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E^o = -0.38\ V\ vs\ SHE\ (pH = 7) \tag{3}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^o = -0.41\ V\ vs\ SHE\ (pH = 7) \tag{4}$$

4. Conclusions

The synthesized ITO sheet decorated with TiO_2 NR electrocatalyst can efficiently boost charge separation and surface area to improve the methanol and H_2 production rates for CO_2 reduction and direct water electrocatalysis during the EC reaction. The TiO_2 NR electrocatalyst catalysts exhibit excellent EC CO_2 reduction and water electrolysis activity with methanol production value of 3.32 μmol.cm^{-2}.L^{-1} and H_2 production value of 6 μmol.cm^{-2}.L^{-1} under 2.0 V of applied electric potential. The CV experiments for TiO_2 NR electrocatalyst also confirms the justification for the improved catalytic performance. This work develops an effective and facile TiO_2 NR electrocatalyst as a competent EC working electrode for sustainable energy conversion.

Acknowledgments

The authors would like to thank Universiti Teknologi Malaysia (UTM) and Ministry of Higher Education (MoHE), Malaysia for funding this research under FRGS Grant Vot. No. 5F101.

References

[1] Zhu, J., Hu, L., Zhao, P., Lee, L.Y.S., Wong, K.Y. (2020). Recent Advances in Electrocatalytic Hydrogen Evolution using Nanoparticles. *Chemical Reviews*, 120, 851-918. DOI: 10.1021/acs.chemrev.9b00248.

[2] Tahir, B., Er, P.W., Tahir, M., Nawawi, M.G.M., Siraj, M., Alias, H., Fatehmulla, A. (2020). Tailoring metal/support interaction in 0D TiO_2 NPs/MPs embedded 2D MAX composite with boosted interfacial charge carrier separation for stimulating photocatalytic H_2 production. *Journal of Environmental Chemical Engineering*, 8(6), 104529. DOI: 10.1016/j.jece.2020.104529

[3] Zhang, W., Hu, Y., Ma, L., Zhu, G., Wang, Y., Xue, X., Chen, R., Yang, S., Jin, Z. (2018). Progress and Perspective of Electrocatalytic CO_2 Reduction for Renewable Carbonaceous Fuels and Chemicals. *Advanced Science*, 5, 1700275. DOI: 10.1002/advs.201700275.

[4] Abbas, T., Tahir, M. (2021). Tri-metallic Ni–Co modified reducible TiO_2 nanocomposite for boosting H2 production through steam reforming of phenol. *International Journal of Hydrogen Energy*, 46(13), 8932-8949. DOI: 10.1016/j.ijhydene.2020.12.209

[5] Song, R.-B., Zhu, W., Fu, J., Chen, Y., Liu, L., Zhang, J.-R., Lin, Y., Zhu, J.-J. (2020). Electrode Materials Engineering in Electrocatalytic CO_2 Reduction: Energy Input and Conversion Efficiency. *Advanced Materials*, 32, 1903796. DOI: 10.1002/adma.201903796.

[6] Yang, P., Li, W., Lian, Y., Yu, F., Dai, B., Guo, X., Liu, Z., Peng, B. (2020). A Facile Approach to Synthesize CoO-Co_3O_4/TiO_2 NAs for Reinforced Photoelectrocatalytic Water Oxidation. *Journal of Solid State Electrochemistry*, 24, 941-950. DOI: 10.1007/s10008-020-04528-y

[7] Jiang, X.X., De Hu, X., Tarek, M., Saravanan, P., Alqadhi, R., Chin, S.Y., Rahman Khan, M.M. (2020). Tailoring the Properties of g-C_3N_4 with CuO for Enhanced Photoelectrocatalytic CO_2 Reduction to Methanol. *Journal of CO_2 Utilization*, 40, 101222. DOI: 10.1016/j.jcou.2020.101222.

[8] Tahir, M., Tahir, B., Nawawi, M.G.M., Hussain, M., Muhammad, A. (2019). Cu-NPs Embedded 1D/2D CNTs/pCN Heterojunction Composite Towards Enhanced and Continuous Photocatalytic CO_2 Reduction to Fuels. *Applied Surface Science*, 485, 450-461. DOI: 10.1016/j.apsusc.2019.04.220

[9] Perini, J.A.L., Torquato, L.D.M., Irikura, K., Zanoni, M.V.B. (2019). Ag/Polydopamine-Modified Ti/TiO_2 Nanotube Arrays: A Platform for Enhanced CO_2 Photoelectroreduction to Methanol. *Journal of CO_2 Utilization*, 34, 596-605. DOI: 10.1016/j.jcou.2019.08.006.

[10] Marino, T., Figoli, A., Molino, A., Argurio, P., Molinari, R. (2019). Hydrogen and Oxygen Evolution in a Membrane Photoreactor using Suspended Nanosized Au/TiO_2 and Au/CeO_2. *ChemEngineering*, 3, 5. DOI: 10.3390/chemengineering3010005.

[11] Li, D., Wang, S., Tian, Y., Ma, H.P., Ma, C., Fu, Y., Dong, X. (2018). Preparation and Photoelectrocatalytic Performance of Ti/PbO_2 Electrodes Modified with Ti_4O_7. *ChemistrySelect*, 3, 5098-5105. DOI: 10.1002/slct.201703181.

[12] Tahir, M. (2019). La-modified TiO_2/Carbon Nanotubes Assembly Nanocomposite for Efficient Photocatalytic Hydrogen Evolution from Glycerol-Water Mixture. *International Journal of Hydrogen Energy*, 44(7), 3711-3725. DOI: 10.1016/j.ijhydene.2018.12.095

[13] Inoue, T., Fujishima, A., Konishi, S., Honda, K. (1979). Photoelectrocatalytic Reduction of Carbon Dioxide in Aqueous Suspensions of Semiconductor Powders. *Nature*, 277, 637-638. DOI: 10.1038/277637a0

[14] Fujishima, A., Honda, K. (1972). Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, 238, 37-38. DOI: 10.1038/238037a0

[15] Nasralla, N., Yeganeh, M., Astuti, Y., Piticharoenphun, S., Shahtahmasebi, N., Kompany, A., Karimipour, M., Mendis, B.G., Poolton, N.R.J., Šiller, L. (2013). Structural and Spectroscopic Study of Fe-doped TiO_2 Nanoparticles Prepared by Sol–Gel Method. *Scientia Iranica*, 20(3), 1018-1022. DOI: 10.1016/j.scient.2013.05.017

[16] Nasralla, N.H.S., Yeganeh, M., Astuti, Y., Piticharoenphun, S., and Šiller, L. (2018). Systematic Study of Electronic Properties of Fe-doped TiO_2 Nanoparticles by X-ray Photoemission Spectroscopy. *Journal of Materials Science: Materials in Electronics*, 29(20), 17956-17966. DOI: 10.1007/s10854-018-9911-5

[17] Zhu, S., Chen, X., Li, Z., Ye, X., Liu, Y., Chen, Y., Yang, L., Chen, M., Zhang, D., Li, G., Li, H. (2020). Cooperation between Inside and Outside of TiO_2: Lattice Cu^+ Accelerates Carrier Migration to the Surface of Metal Copper for Photocatalytic CO_2 Reduction. *Applied Catalysis B: Environmental*, 264, 118515. DOI: 10.1016/j.apcatb.2019.118515.

[18] Sheu, J.K., Liao, P.H., Lee, Y.C., Wang, H.K., Lee, M.L. (2020). Photoelectrochemical Generation of Hydrogen and Formic Acid using GaN Films Decorated with TiO_2/Ag Nanoparticles Composite Structure as Photoelectrodes. *The Journal of Physical Chemistry C*, 124, 9591-9598. DOI: 10.1021/acs.jpcc.0c01699.

[19] Liu, Z., Xu, K., Yu, H., Sun, Z. (2020). Synergistic Effect of Ag/MoS_2/TiO_2 Heterostructure Arrays on Enhancement of Photoelectrochemical and Photocatalytic Performance. *International Journal of Energy Research*, 1-13. DOI: 10.1002/er.6275.

[20] Baran, E., Yazici, B. (2016). Effect of Different Nano-Structured Ag Doped TiO_2-NTs Fabricated by Electrodeposition on the Electrocatalytic Hydrogen Production. *International Journal of Hydrogen Energy*, 41, 2498-2511. DOI: 10.1016/j.ijhydene.2015.12.028.

[21] Zhou, J., Li, Y., Yu, L., Li, Z., Xie, D., Zhao, Y., Yu, Y. (2020). Facile in Situ Fabrication of Cu_2O@Cu Metal-Semiconductor Heterostructured Nanorods for Efficient Visible-Light Driven CO_2 Reduction. *Chemical Engineering Journal*, 385, 123940. DOI: 10.1016/j.cej.2019.123940.

[22] Kerdnoi, P., Autthanit, C., Chitpong, N., Jongsomjit, B. (2020). Catalytic Dehydration of Ethanol over W/TiO_2 Catalysts Having Different Phases of Titania Support. *Bulletin of Chemical Reaction Engineering & Catalysis*, 15, 96-103. DOI: 10.9767/bcrec.15.1.5606.96-103.

[23] Petronella, F., Diomede, S., Fanizza, E., Mascolo, G., Sibillano, T., Agostiano, A., Curri, M.L., Comparelli, R. (2013). Photodegradation of Nalidixic Acid Assisted by TiO_2 Nanorods/Ag Nanoparticles based Catalyst. *Chemosphere*, 91(7), 941-947. DOI: 10.1016/j.chemosphere.2013.01.107

[24] Karim, K.M.R., Ong, H.R., Abdullah, H., Yousuf, A., Cheng, C.K., Khan, M.M.R. (2018). Electrochemical Study of Copper Ferrite as a Catalyst for CO_2 Photoelectrochemical Reduction. *Bulletin of Chemical Reaction Engineering & Catalysis*, 13, 236-244. DOI: 10.9767/bcrec.13.2.1317.236-244.

[25] Zarei, E., Jamali, M.R., Ahmadi, F. (2018). Highly Sensitive Electrocatalytic Determination of Formaldehyde using a Ni/Ionic Liquid Modified Carbon Nanotube Paste Electrode. *Bulletin of Chemical Reaction Engineering & Catalysis*, 13, 529-542. DOI: 10.9767/bcrec.13.3.2341.529-542.

[26] Abbas, T., Tahir, M., Saidina Amin, N.A. (2019). Enhanced Metal–Support Interaction in Ni/Co_3O_4/TiO_2 Nanorods toward Stable and Dynamic Hydrogen Production from Phenol Steam Reforming. *Industrial & Engineering Chemistry Research*, 58, 517-530. DOI: 10.1021/acs.iecr.8b03542.

[27] Lee, C.H., Rhee, S.W., Choi, H.W. (2012). Preparation of TiO_2 Nanotube/Nanoparticle Composite Particles and their Applications in Dye-Sensitized Solar Cells. *Nanoscale Research Letters*, 7(1), 48. DOI: 10.1186/1556-276X-7-48

[28] Steky, F.V., Suendo, V., Mukti, R.R., Benu, D.P., Reza, M., Adhika, D.R., Tanuwijaya, V.V., Nugraha, A.B. (2019). bcl Morphology Formation Strategy on Nanostructured Titania via Alkaline Hydrothermal Treatment. *Bulletin of Chemical Reaction Engineering & Catalysis*, 14, 513-520. DOI: 10.9767/bcrec.14.3.3853.513-520.

[29] Huang, J., Guo, X., Yue, G., Hu, Q., Wang, L. (2018). Boosting CH_3OH Production in Electrocatalytic CO_2 Reduction over Partially Oxidized 5 nm Cobalt Nanoparticles Dispersed on Single-Layer Nitrogen-Doped Graphene. *ACS Applied Materials & Interfaces*, 10(51), 44403-44414. DOI: 10.1021/acsami.8b14822

Selected and Revised Papers from International Conference on Sustainable Energy and Catalysis 2021 (ICSEC 2021) (https://engineering.utm.my/chemicalenergy/icsec2021/) (School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 16-17th February 2021) after Peer-reviewed by Scientific Committee of ICSEC 2021 and Peer-Reviewers of Bulletin of Chemical Reaction Engineering & Catalysis.
Editors (Guest) in this ICSEC 2021 section are Nor Aishah Saidina Amin, Mohd Asmadi Mohammed Yussuf, Salman Raza Naqvi, while Editor in Chief is I. Istadi.