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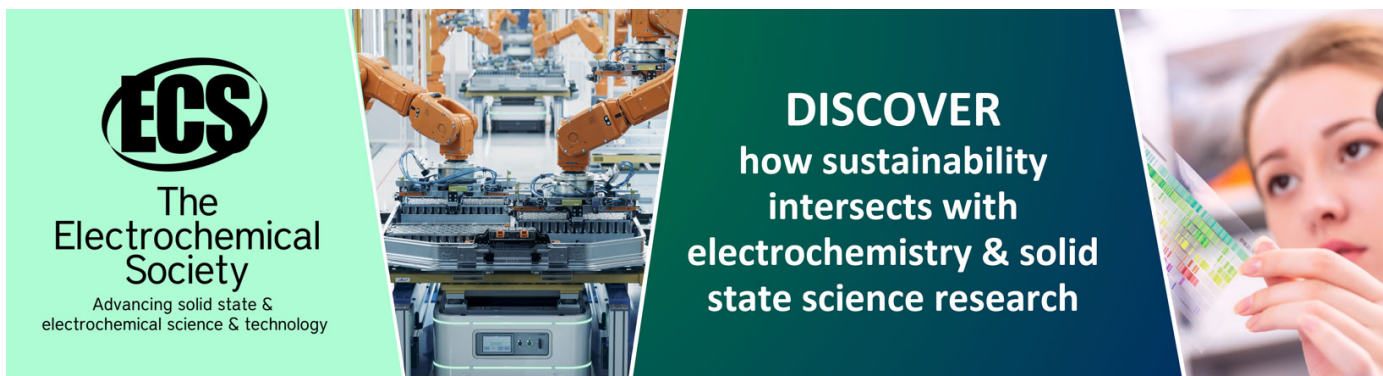
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Preparation of Reduced Graphene Oxide (RGO) Modified Titanium Dioxide Nanotube (TNTs) as Visible Light Effective Catalyst for the Conversion of CO₂ to CH₄

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Abstract. In this study, a modified visible light active photocatalyst has been prepared where titanium dioxide nanotube (TNTs) was coupled with reduced graphene oxide (RGO) through a facile synthesis process. The photoactivity of the RGO-TNTs has been evaluated by converting CO₂ to CH₄ under visible light irradiation. In order to justify the photo-effectivity of the catalysts, physical and optical characterization were performed through FESEM, EDX, UV-Vis absorption spectra and PL spectra. The morphological analysis shows homogeneous RGO distribution on the TiO₂ nanotube whereas elemental compositional analysis revealed the presence of all elements in the prepared catalyst. Visible light enhancement activity of the prepared catalyst after the incorporation of RGO was exposed by UV-Vis analysis due to its enhanced light absorption properties. Improved electron-hole separation rate was investigated for the RGO incorporated TNTs through PL analysis. The fruitful incorporation of the RGO with TNTs further affirmed by the increased photocatalytic activity by converting CO₂ to CH₄ that acquired enhanced CH₄ production (9.27%) which is 1.81 times higher than the CH₄ production rate obtained through TNTs (5.12%). Thus, this study induces a simple synthesis procedure to modify TNTs as a visible light active photocatalyst with the integration of RGO. Moreover, RGO-TNTs enhanced visible light activity were evaluated through the conversion of CO₂ to CH₄.

1. Introduction

Nanotechnology opens the diverse area in order to evaluate the numerous nanomaterials which attract different branch of science and technology. An abundance of these nanomaterials has been induced by the researchers as a catalyst for distinct applications due to its attractive catalytic properties. The catalyst used in the catalytic reaction with the input of photon energy (hν) from the solar/visible light source is a promising approach to convert the earth wastage to convenient outputs for the betterment of humankind. On the other hand, Global warming due to the extreme CO₂ emission in the atmosphere



with the burning of fossil fuels has attracted huge consideration [1]. Moreover, the depletion of fossil fuels creates energy crisis globally, utilizing photocatalytic CO₂ conversion process to valuable chemicals is a promising approach towards this dilemma [2-4].

Numerous semiconductor materials has been employed as proficient photocatalyst, like zinc oxide (ZnO), magnesium oxide (MgO), copper oxide (CuO), zirconium oxide (ZrO₂), cadmium sulphide (CdS) and Titanium dioxide (TiO₂) [5-7]. Amongst, TiO₂ has become a widely used photocatalyst for the different photocatalytic application due to its high chemical stability, non-toxicity, low cost and availability [8-10]. The photocatalytic efficiency of TiO₂ works proficiently under UV light irradiation which are only 5% of total solar spectrum [11]. Moreover, TiO₂ exhibits high recombination of photogenerated electron-hole (e⁻/h⁺) pairs during photocatalysis process [12, 13]. Hence, these characteristics of TiO₂ limits its broaden application and researchers now trying to modify its photocatalytic and charge-recombination properties towards visible light illumination (as solar spectrum comprises of 53% visible light) [11, 14]. To enhance the photocatalytic activity of TiO₂ various approaches like surface modification, composite with metals, non-metals and semiconductors have been employed whereas TiO₂ nanotube (TNTs) has long-term charge mobility and higher surface area [13, 15]. However, the photocatalytic activity of TNTs is inadequate due to its lower visible light absorption and higher e⁻/h⁺ recombination rate.

The incorporation of graphene with TiO₂ shows improved photocatalytic CO₂ conversion activity [16, 17]. Graphene, 2D allotrope of carbon, consisting of single sheet of sp² hybridized carbon atoms staged in hexagonal pattern has turn out one of the catching component for the photocatalyst synthetization [18, 19]. Graphene has remarkable properties and characteristics, including thermal and electrical conductivity, large theoretical high surface area (~2600 m² g⁻¹), and mechanical strength [20]. The photocatalytic activity of semiconductor material-graphene compounds was first uncovered by Kamat and co-workers in 2010 [21]. Afterwards, several Graphene oxide (GO)-semiconductor photocatalyst has been developed for harvesting visible light in order to convert CO₂ to hydrocarbon fuel methane (CH₄) [22, 23]. Various technique has been employed to synthesis graphene based-TiO₂ photocatalysts among them solvothermal, hydrothermal, wet impregnation are widely used [24-26]. Tan, Ong, Chai and Mohamed [20] reported enhanced photocatalytic activity of the rGO-TiO₂ photocatalyst prepared through solvothermal method. They have also narrated enhanced CH₄ production rate from the conversion of CO₂ for graphene modified TiO₂. Furthermore, the enhanced 5.6 times higher CH₄ yield for the graphene modified TNTs was attained than TNTs that were testified by Zubair and his co-workers [22]. Particularly, graphene boosts the photocatalytic CO₂ conversion process owing to its enhanced specific large surface area, optical properties, enhanced charge-carrier separation, CO₂ adsorption and high selectivity of solar products [27, 28]. Hence, these inspired to use graphene coupled with TiO₂ to convert CO₂ effectively into solar fuel with enhanced photocatalytic activity.

Recent years graphene based TiO₂ photocatalyst has been widely used in the organic pollutant degradation applications, and the photocatalytic CO₂ conversion utilizing visible light is not widely considered [29, 30]. Therefore, the objective of this study is to synthesis a visible light active RGO-TNTs photocatalyst which could retard photogenerated charge-carrier recombination of TNTs during the photocatalytic CO₂ conversion process. Besides, the charge-carrier separation efficiency of the RGO incorporated nanotubes could be explored by the enhanced CH₄ production from CO₂ conversion.

2. Experiment

2.1. Reagents and Materials

All chemicals (analytical grade reagents) were brought from Sigma-Aldrich Chemical Co. Ethylene Glycol (EG, 99.5%), Ammonium Fluoride (NH₄F, 98.0%), Sulphuric Acid (H₂SO₄, 97%), Hydrogen Peroxide (H₂O₂, 30%), Potassium Permanganate (KMnO₄, 99.39%), Phosphoric Acid (H₃PO₄, 85%), Hydrochloric acid (HCl, 37%), were used to synthesize all the catalysts. Titanium (Ti) foils (0.127

mm thickness, 99.97% purity) and Graphite powder were also brought from the Sigma-Aldrich Chemical Co. and all the reagents and materials are used as it received and stored at room temperature. Ethyl Alcohol (95%) and Acetone were used for all cleaning purpose of the metal substrates. The pure water (18 MΩ. cm at 25 °C) were used during the experiment was purified with the Nanopure® water system. A power supply (Laboratory DC Power Supply, GPS- 3030DD) was used to conduct the experiments.

2.2. Catalyst Synthesis

To synthesis of TNTs, an electrochemical anodization method was performed from our previous work with slight reformation [31]. In detail, a precise size of Ti foil (3.75cm × 1.2 cm × 0.127 mm) was cut and used as the base for TNTs. Before anodization, graphite rod (as cathode) and Ti foil (as anode) were ultrasonically cleaned with ethanol, acetone and pure water, respectively. The electrolyte containing 100 mL EG with (1.12 g NH₄F, 2 ml pure water) were prepared, and anodization were taken place at room temperature under 30 V for 4h. The sample from anode rinsed with pure water and annealed at 550 °C and again annealed for 2h at 450°C to remove the surface debris. Thus, the sample signified as TNTs.

To prepare Graphene oxide (GO) Tour's method were adopted [32]. Briefly, graphite powder oxidation was executed in oil bath and retain temperature at 50°C. 3 g of g graphite flakes was added into 360 ml of mixed acid (H₂SO₄/H₃PO₄:9/1) and stirred continuously. After that, KMnO₄ (18 g) was mixed slowly into the mixture and maintained the temperature at 50 °C. After accomplishing 24 h of continuous oxidation the suspension was cooled to room temperature and ice (400 ml) was poured into the suspension. Consequently, 3 ml H₂O₂ were added in the suspension slowly and maintained as dropwise. Then the suspension was taken for centrifuge. After that, the suspension washed for multiple times to remove left over impurities. Therefore, the product was dried at 60 °C overnight and obtained blackish sheet of GO. RGO was obtained from the thermal treatment of the GO. To obtain the RGO, certain amount of GO was heated into a preheated furnace for 5 min at 300 °C.

To make the RGO-TNTs composite, a simple immersed method applied where 3 mg of RGO were added with the 6mL of pure water and the suspension were sonicated and immersed for 3h and oven dried at 60°C for 5h. Thus, the sample signified as RGO-TNTs.

2.3. Catalyst Characterization

The physical characteristics of the prepared catalysts were examined by a Field Emission Scanning Electron Microscope (FESEM) (Brand: JEOL, Model: JSM-7800F) equipped with an EDX (energy dispersive X-ray spectroscopy) for elemental analysis. An accelerating voltage of 20 kV was implemented for taking all the images. The UV-visible-diffuse absorption spectra (UV-Vis), were measured using UV-visible spectrophotometer (UV 2600-230V, SHIMADZU). To get the PL spectra Photoluminescence (PL) spectra (EDINBURGH INSTRUMENTS, NIR 300/2) was adopted.

2.4. Photocatalytic Activity Test

The photocatalytic experiment was conducted through the fabricated gas-solid phase reactor for evaluating the photocatalytic activity of the prepared catalysts. A 500W Xenon lamp was used as visible light source. The synthesized sample were placed inside the reactor and highly purified CO₂ (99.99%) was passed through the water bubbler, and maintained the flowrate at 50 cc/min. The power of the Xenon lamp was adjusted and maintained at 300W. The product was collected and analysed by gas chromatograph-flame ionization detector (GC-FID (AGILENT, model 7890A) mounted with capillary column of dimension of 25 m × 0.32 mm (AGILENT, PoraPLOT).

3. Results and Discussion

3.1. Surface Analysis of the Prepared Catalysts

The FESEM images (Figure 1) represent the structural morphology of the prepared TNTs and RGO-TNTs. Self-organized nanotubes were full-grown with open-mouth due to the implementation of the balanced electrochemical anodization method. The nanotubes length and the inner diameter are of $\sim 1.55 \mu\text{m}$ and $\sim 60 \text{ nm}$. From Figure 1, it is clearly shown that the two-dimensional RGO sheets encircled the surface of the TNTs. It is also identified that the morphology of the TNTs persists unaffected even after the inclusion of the RGO.

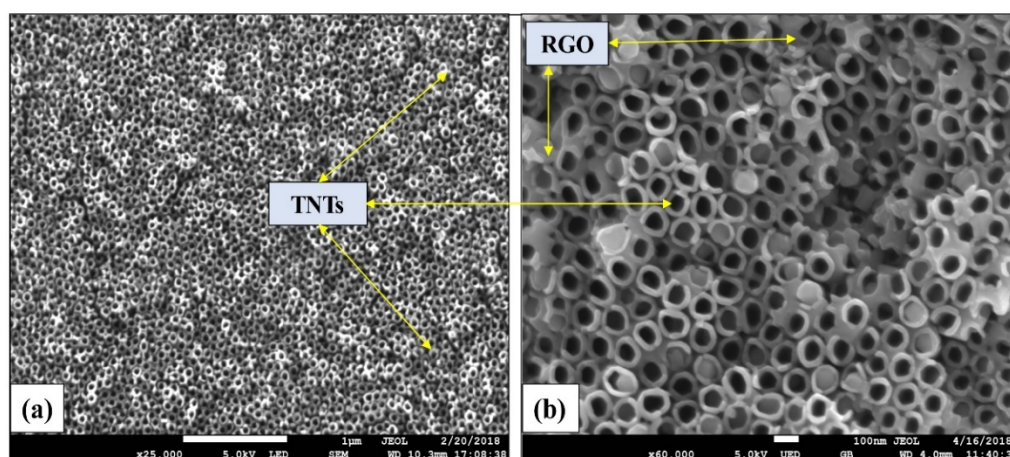


Figure 1. FESEM images of (a) TNTs and (b) RGO-TNTs.

The elemental analysis of the prepared RGO-TNTs was characterized using EDX. From Figure 2, it is observed that the Ti, O and C elements are present in the prepared RGO-TNTs nanocomposite catalyst. Furthermore, this characterization indicates the well-dispersed incorporation of RGO on the TiO_2 nanotube surface. From the elemental analysis, it is also revealed that the prepared reduced graphene oxide has no impurities which indicates the best RGO powder preparation as well as the balanced incorporation with TiO_2 .

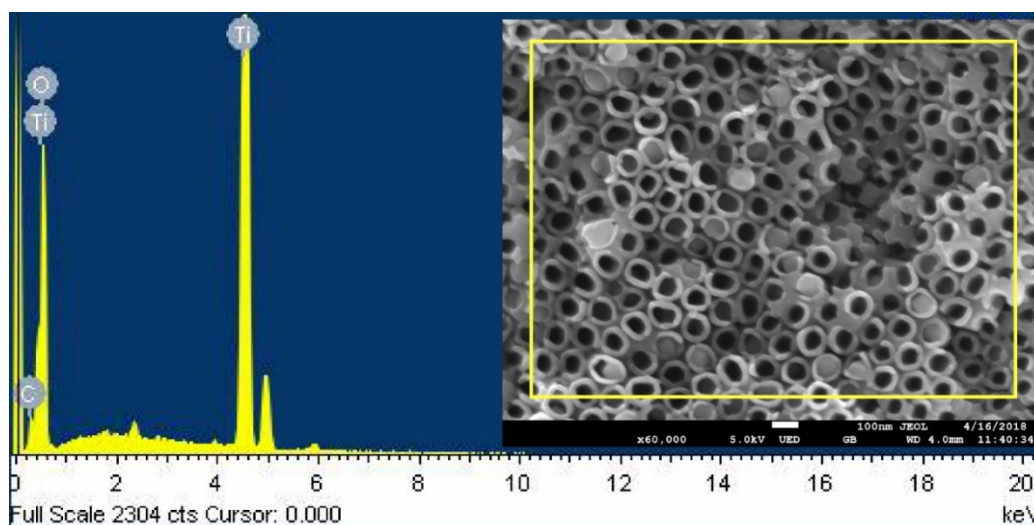


Figure 2. EDX image of RGO-TNTs.

3.2. Optical properties and PL study of the Prepared Catalysts

The UV-visible (UV-Vis) absorption spectroscopy has considered one of the strong effectual optical characterization parameters that endorse the light responsive character of the semiconductor materials. From Figure 3, it clearly emphasizes the UV-Vis absorption spectra of the TNTs and RGO-TNTs. TNTs and RGO-TNTs exhibits good absorption edge in the UV region as a result of the intrinsic band gap absorption of TiO_2 due to the electron transfer from the valence band to the conduction band ($\text{O}2\text{p} \rightarrow \text{Ti}3\text{d}$) [33]. Besides, the absorption edge in the visible region of the TNTs owing to its nanotubular shape. In addition, the RGO enhanced the visible light absorption of TNTs and a wide range (400 nm -900 nm) of absorption edge confirmed by the RGO-TNTs (Figure 3). RGO has black colour which increases the reduction of light reflection and boost up the absorption ability under visible light irradiation [28]. This phenomenon of RGO-TNTs indorsed its high photocatalytic effectivity towards visible light compared with TNTs.

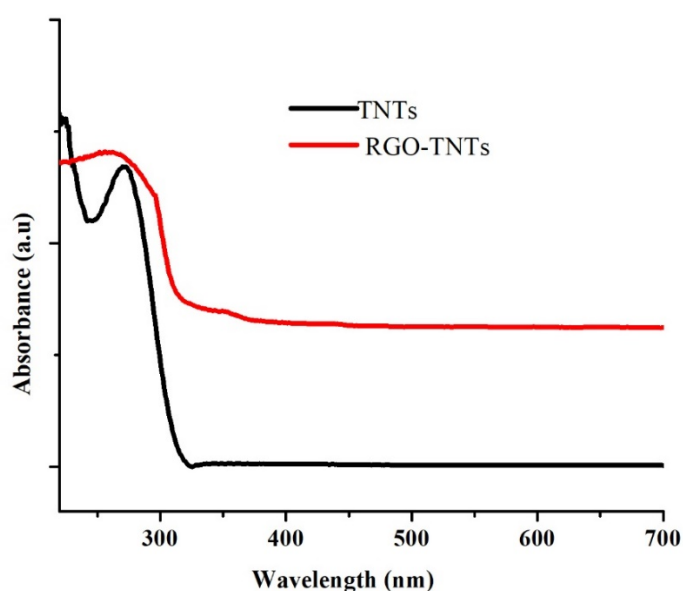


Figure 3. UV- Visible absorption spectra of TNTs and RGO-TNTs.

Photoluminescence (PL) spectra elucidate the e^-/h^+ recombination rate of the prepared catalyst in figure 4. TNTs displayed a strong emission peak at around 590 nm in the PL spectrum because of the recombination of the photoinduced e^-/h^+ pairs. Also, the intensity was drastically reduced for the RGO-TNTs. The lower intensity of the RGO-TNTs indicates the lower recombination rate of the photoinduced charge-carriers and this is because of the electron transport characteristics of RGO [34]. Hence, the lower e^-/h^+ recombination rate of the RGO-TNTs endorsed its visible light effectivity, and this hypothesis confirmed by the photocatalytic conversion of CO_2 to CH_4 using it as a photocatalyst.

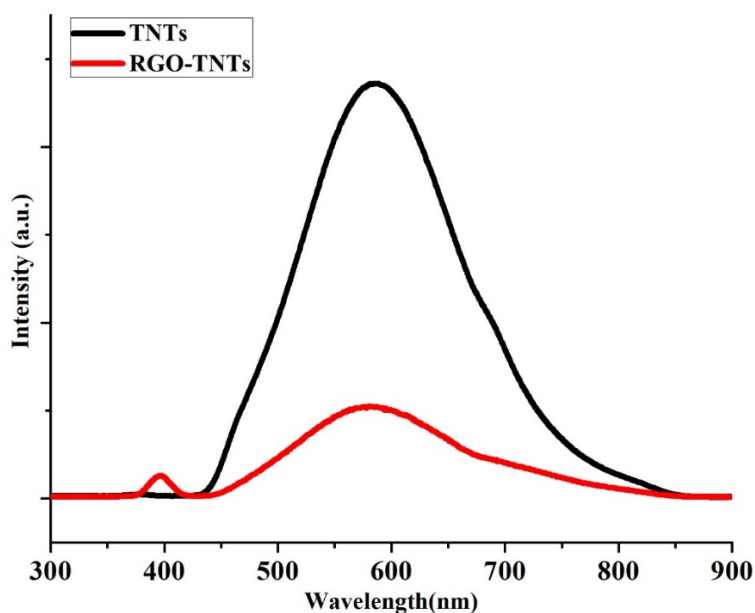


Figure 4. PL of TNTs and RGO-TNTs.

3.3. Photocatalytic conversion of CO_2 to CH_4

The photocatalytic performance of prepared catalyst TNTs and RGO-TNTs were evaluated through the reduction of CO_2 with water vapor to CH_4 using visible light. Besides, CO_2 gas was purged to the water vapor to eliminate the impurities as well. In order to confirm the CH_4 production rate of the experiment, one control experiments were conducted. This control experiment was under the conditions of, without light irradiation with the presence of photocatalyst and flow of CO_2 and water vapor. The result (Figure 5) revealed trace amount of CH_4 production, suggesting that CO_2 conversion occurred in the presence of photocatalyst, light and reactants. Thus, the total amount of CH_4 produced for TNTs and RGO-TNTs are 5.12% and 9.27%, respectively (Figure 5). The RGO-TNTs exhibits 1.81 times higher CH_4 production compared with the TNTs. The whole experiment was conducted for 120 min and the CH_4 production rate of TNTs and RGO-TNTs over time are presented in Figure 6. After 1h of continuous experiment the CH_4 amount increased gradually in comparison with the amount of CH_4 production from 30 min for both catalysts. The ascending CH_4 production rate was obtained for the prepared RGO-TNTs photocatalyst from CO_2 conversion.

The photocatalytic conversion of CO_2 to CH_4 were successfully conducted and achieved with the proper utilization of visible light and prepared photocatalysts. In addition, The incorporation of RGO in the TNTs reduce its charge recombination rate as it has two-dimensional and planar π -conjugation structure which make it electron conductive [35]. Furthermore, the RGO sheets provide a quick pathway to trap the photogenerated electrons and prolonged the recombination of charge carriers. When the light irradiates on the surface of the photocatalyst, the photogenerated e^- will move to the nearby RGO sheets, the RGO then trap the e^- and prolonged e^-/h^+ separation time. Besides, the photoinduced h^+ will oxidize H_2O and produce H^+ . In addition, RGO sheets have larger surface area that boosts CO_2 adsorption and started the complicated photocatalytic series reaction to produce CH_4 . These phenomena could be the enhanced factor of CH_4 production rate by RGO-TNTs preferably than TNTs. Additionally, the whole experiment considered repetition to ensure the photocatalytic conversion of CO_2 to CH_4 . Besides that, similar photocatalyst were used (both 30 min and 1h

experiment) to get the total amount of CH_4 in order to investigate the performance and stability of the prepared catalysts.

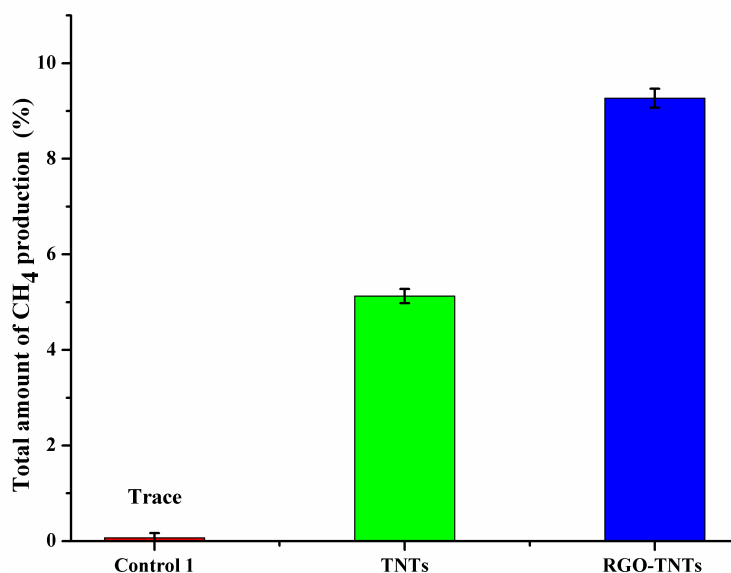


Figure 5. Total amount of CH_4 production over TNTs and RGO-TNTs. Trace amount of CH_4 under the conditional control 1 experiments.

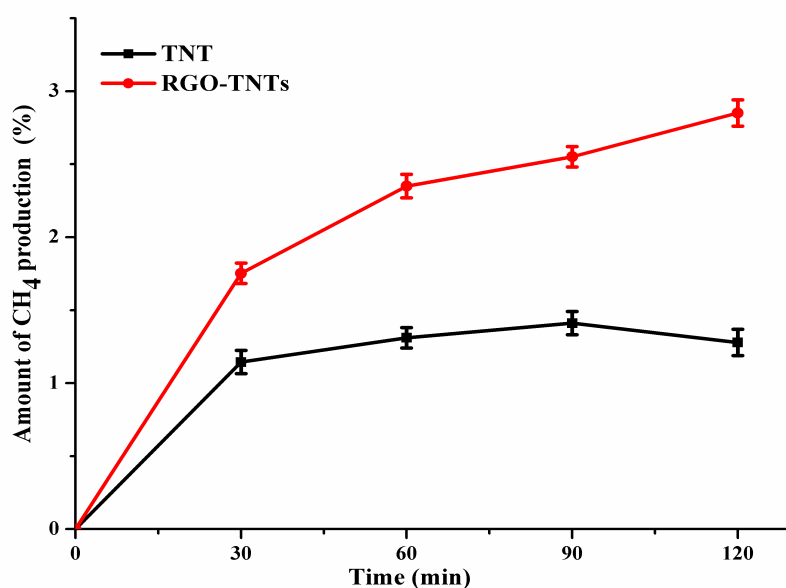


Figure 6. Amount of CH_4 production rate of the prepared photocatalyst TNTs and RGO-TNTs over time.

4. Conclusion

The visible light active RGO-TNTs was prepared by a facile synthesis mechanism and evaluated the photocatalytic activity by converting CO₂ to CH₄. Furthermore, the total amount of produced CH₄ by using RGO-TNTs photocatalyst is 9.27% which is 1.81 times higher compared with the TNTs total amount of produced CH₄ (5.12%). The integration of RGO with TNTs enhanced its visible light absorption capacity and reduced the recombination rate of the photoinduced charge carriers which confirmed by its use in the photocatalytic CO₂ conversion to CH₄ that make it as a visible light effective photocatalyst.

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