METHOD FOR COMPARING CATALYST REACTIVITY AND EFFICIENCY BY MEASURING CHANGES IN THE ILLUMINATION INTENSITY OF H_2 BUBBLES DURING WATER ELECTROLYSIS

Jaroslav HÖLZEL[1,2], Karel KLOUDA[1,2], Jiří TILHON[1]

[1] *Research Institute for Labour and Social Affairs, v. v. i., Jeruzalémská 1283/9, 110 00 Prague, Czech Republic, EU, jaroslav.holzel@rilsa.cz, karel.klouda@rilsa.cz, jiri.tilhon@rilsa.cz*

[2] *VSB – Technical University of Ostrava, FBI, Lumírova 13, 700 30 Ostrava, Czech Republic, EU*

https://doi.org/10.37904/nanocon.2025.5198

Abstract

This study provides a description of a simplified, accelerated and economically advantageous method for determining the catalytic activity of carbon compounds based on graphene oxide (GO) and graphitic carbon nitride g-C_3N_4 during the electrolysis of water. The method proposed in this study for determining the catalytic activity of carbon compounds based on graphene oxide and graphitic carbon nitride is based on measuring the amount of H_2 bubbles formed by the process of the dissociation of water on a cathode. A swarm of rising bubbles indicated the effectiveness of the catalysts. The principle of the proposed method for determining catalytic activity is based on measuring changes in the intensity of light illuminating the cathode. Such changes are influenced by the amount of bubbles formed. The experiments confirmed that the nanostructures employed enhanced reactivity and provided support for the photocatalytic reactions involved in the production of hydrogen.

Keywords: Light intensity, electrolysis, GO, g-C_3N_4, H_2 bubbles

INTRODUCTION

The method proposed in this study for determining the catalytic activity of carbon compounds based on graphene oxide and graphitic carbon nitride is based on measuring the amount of H_2 bubbles formed by the process of the dissociation of water on a cathode. The size of the bubble swarm formed is directly correlated with the photocatalytic efficiency. The principle of the proposed method for determining catalytic activity comprises the measurement of changes in the intensity of the light that illuminates the cathode. Such changes are influenced by the amount of bubbles formed.

1. PHOTOCATALYTIC EXPERIMENTS

1.1. Aims of the experiment

Since researchers discovered that TiO_2 acts as a photoanode and splits water into hydrogen and oxygen when exposed to light [1], many photocatalytic materials have been explored [2], [3], [4]. Graphitic carbon nitride (g-C_3N_4) has gained attention due to its easy mass preparation and environmental friendliness [5], [6].

The aims of the photocatalytic experiments can be summarised as follows:

a) Preparation of the nanomaterials – graphene oxide (GO, GO-MEN), reduced graphene oxide (rGO) and graphitic carbon nitride (g-C_3N_4) and the testing of their efficiency with concern to photocatalytic processes
b) Determination and testing of a simple approach for the measurement of the efficiency of photocatalysts

The principle of the experimental measurement of the amount of H_2 bubbles produced via the process of the dissociation of water on the cathode (negative electrode) is based on measuring changes in the intensity of the light, which is measured in lux (lx). The cathode is illuminated by a light source, which is detected by a sensor placed behind the cathode directly opposite the light source (**Figure 1**). The scheme of the electrolyser assembly for the measurement of the H_2 bubbles.

The bubbles swarm formed impacts the intensity of the light, which is recorded over time. Increases in the amount of H_2 bubbles that develop on the cathode are reflected in proportional decreases in the intensity of the light on the sensor, which can be recorded over time and presented in graph form and evaluated, for example, using an Excel spreadsheet.

The experiments involved the use of the g-C_3N_4 photocatalyst in combination with the following nanomaterials: GO (graphene oxide prepared at the VIPSV, Prague), GO-MEN (graphene oxide prepared at Mendel University, Brno) and rGO (reduced graphene oxide, VIPSV, Prague).

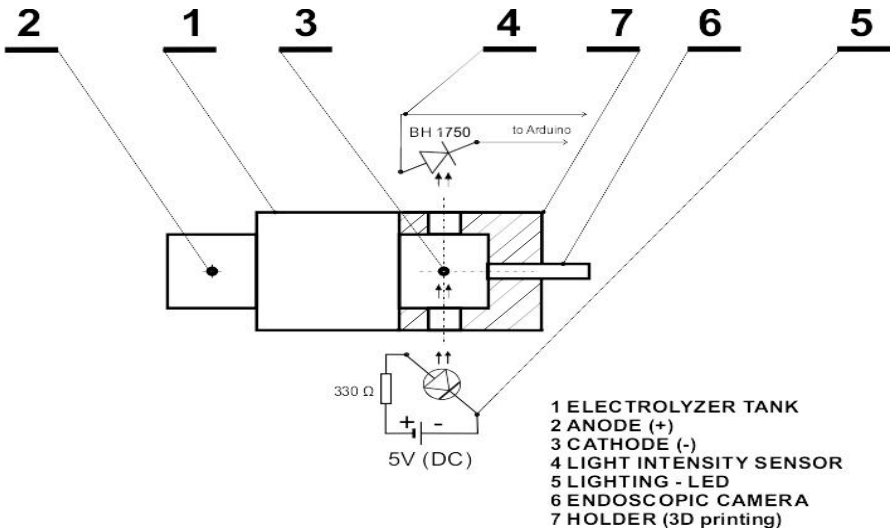

Figure 1 The scheme of the electrolyser assembly for the measurement of the H_2 bubbles

1.2. Preparation of the nanomaterials for the photocatalyst experiments

- Graphene oxide (GO) – prepared via the chemical oxidation of natural graphite (sulphuric acid, potassium permanganate, sodium nitrate) [8,10]
- Graphene oxide (GO-MEN) – provided for the experiments by the staff of Mendel University, Brno [9]
- Reduced graphene oxide (rGO) – prepared via the reduction of graphene oxide (GO) applying ascorbic acid at a temperature of 60 °C – 70 °C [2]
- Preparation of graphitic carbon nitride (g-C_3N_4) – prepared via the polycondensation of melamine in an electric oven at a temperature of 511 °C [7]

2. EXPERIMENTAL PART

The conducting of the experiments firstly required the determination of the variable and fixed conditions. The fixed conditions did not change during the measurement process and comprised:

- Illumination – green LED diode, wavelength 550 nm, voltage U=3 – 3.2 V, current I=20 mA
- Cathode voltage – 30 V DC, stabilized source

One of the crucial conditions for the successful conducting of the experiment comprised maintaining the sufficient transmission of light through the electrolyte. This requirement is of even greater importance when

using suspension particles, which must be allowed to settle for a certain time. In the case of the experiments performed herein, the sedimentation time was 10 to 90 minutes depending on the size of the suspension component. Three measurements were taken during this interval, followed by the calculation of the average values. Table 1 shows the values from the individual measurements. As can be seen from the graphic presentation of the measurement of the 10% methanol electrolyte (**Figure 2**), the measurement immediately following the preparation of the electrolyte suspension with the catalysts failed to provide relevant results.

2.1. Description of the measuring device

A common laboratory electrolyser with titanium electrodes commonly used for school experiments was used for experimentation purposes. The holder for the light source and the sensor was produced for the cathode container on a 3D printer at the RILSA. As can be seen from the diagram of the electrolyser assembly (**Figure 1**), the light source, cathode and BH1750 sensor were positioned on the same axis. An endoscopic camera was subsequently fitted to the light source and sensor holder for the optical inspection of the cathode. The BH1750 light intensity sensor had a measurement range of 1 to 65 535 lux (lx) and operated at a voltage of 3.3 V or 5 V and was connected via a Data Logger Shield (recording of the data on an SD card) to an Arduino Uno single-board computer. A special program loop was created for the Arduino computer for the measurement and recording of the intensity of the light. The values of the changes in the light intensity were saved automatically on the SD card, from which the data was then transferred to an Excel spreadsheet, which was used for the evaluation of the measured data obtained.

2.2. Measurements

Aimed at obtaining the basic information on the reactivity of the catalyst as quickly as possible, the measurement time interval was set at 4 to 6 minutes, and the selected time period was divided into 3 parts. The first part was passive, i.e. without the application of current to the electrodes, and lasted for 60–120 (s); the second part was active, with the application of a DC current of 30 V, which lasted for 120–180 (s); and the third part was again in the passive state, without the application of current, and lasted for 60–120 (s). The average values of the illumination intensity (lx) from the passive periods were then compared with the average values from the active period. Higher differences (Δ lx) indicated the ability of the catalyst to produce enhanced amounts of H_2. Three measurement campaigns were performed for each catalyst. The suspension particles of the catalysts were stirred manually in the electrolyte using a glass rod, mechanically shaken in a closed glass cylinder and then poured into the electrolyser container, with the exclusion of sonification or an inert atmosphere in the electrolyser.

2.2.1. Electrolyte without a catalyst

The development of bubbles was preferentially tested only for the 10% methanol electrolyte (**Figure 3**). The average values served as the standard for comparing the efficiencies of the catalysts.

The first minute was measured without the application of electric current, followed by 2 minutes of electrolysis and then 1 minute without electric current. The temperature of the electrolyte was 23 °C. The first measurement campaign was conducted 90 minutes following the mixing of the methanol and water. The measurement results are shown in the evaluation (**Table 1**). The average value of the decrease in the intensity of illumination in this case was Δ (lx) = 1,197 lx.

2.2.2. Electrolyte with the C_3N_4 and GO (graphene oxide) photocatalyst

Subsequently, the C_3N_4 (0.1 g) + GO (0.1 g) photocatalyst was added to the electrolyte and the resulting suspension was mixed via shaking. The temperature of the electrolyte was 23 °C. The measurements were taken 10 minutes following sedimentation as follows: 1 minute without current, 3 minutes of electrolysis and 1 minute without current (**Figure 4**). The average value of the decrease in the intensity of illumination was Δ (lx) = 1,529 lx.

2.2.3. Electrolyte with the C_3N_4 and GO-MEN photocatalyst

The electrolyte was prepared via the mixing of 10% methanol with the C_3N_4 (0.1g) + GO-MEN (0.1g) photocatalyst. The resulting suspension was then mixed via shaking. The temperature of the electrolyte was 23 °C. The measurements were taken 60 minutes following sedimentation: 1 minute without current, 2 minutes of electrolysis and 1 minute without current (**Figure 5**). The average value of the decrease in the intensity of illumination was Δ (lx) = 1,548 lx.

2.2.4. Electrolyte with the C_3N_4 photocatalyst

The electrolyte was prepared via the mixing of 10% methanol and the C_3N_4 (0.1g) photocatalyst. The temperature of the electrolyte was 23 °C. The measurements were taken 10 minutes following sedimentation: 30 seconds without current, 90 seconds of electrolysis and 30 seconds without current (**Figure 6**). The average value of the decrease in the intensity of illumination was Δ (lx) = 817 lx.

2.2.5. Electrolyte with the C_3N_4 and rGO (reduced graphene oxide) photocatalyst

For the final experiment, the electrolyte was prepared via mixing 10% methanol with the C_3N_4 (0.1g) + rGO (0.1g) photocatalyst. The resulting suspension was then mixed via shaking. The temperature of the electrolyte was 23 °C. The measurements were taken 60 minutes following sedimentation: 40 seconds without current, 100 seconds of electrolysis and 60 seconds without current (**Figure 7**). The average value of the decrease in the intensity of illumination was Δ (lx) = 1,254 lx.

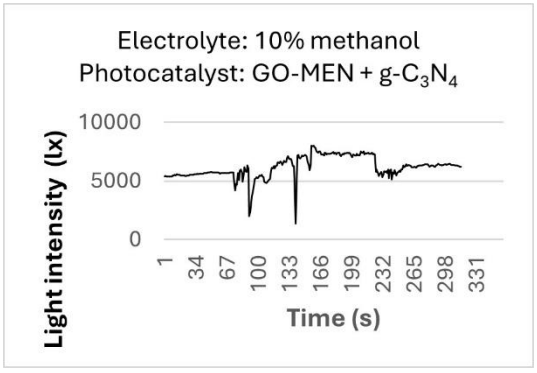

Figure 2 Measurement immediately following the mixing of the electrolyte with the catalysts

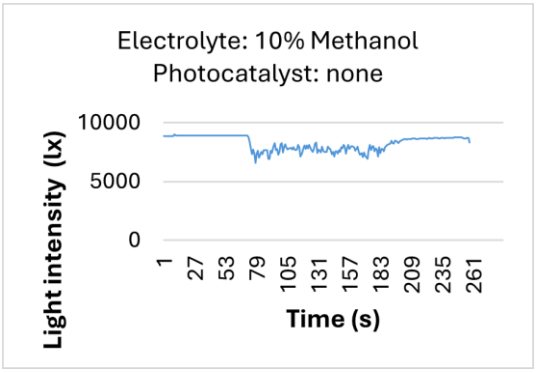

Figure 3 Evolution of the H_2 bubbles without a catalyst

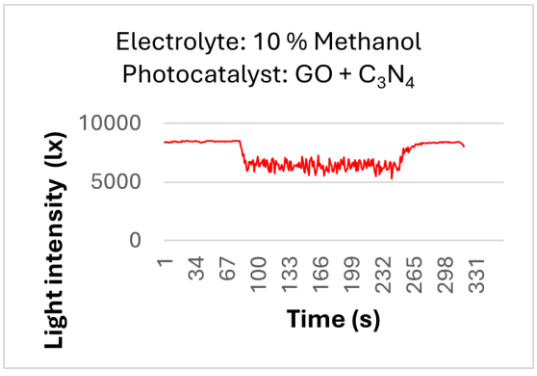

Figure 4 Evolution of the H_2 bubbles with GO + g-C_3N_4

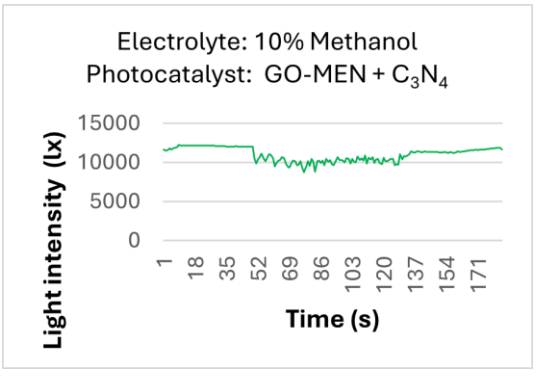

Figure 5 Evolution of the H_2 bubbles with GO-MEN + g-C_3N_4

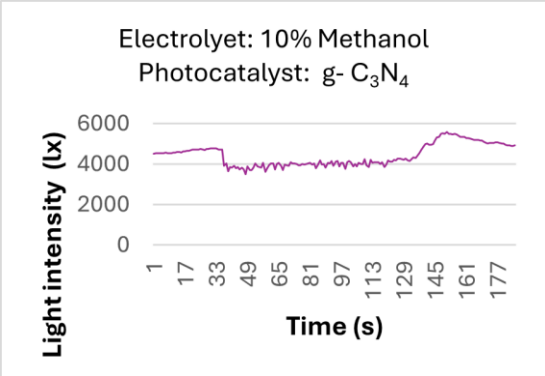

Figure 6 Evolution of the H_2 bubbles with g-C_3N_4

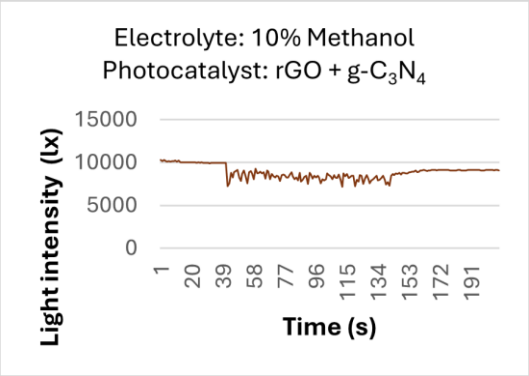

Figure 7 Evolution of the H_2 bubbles with rGO + g-C_3N_4

2.3. Evaluation of the measurement results

Table 1 presents the light intensity values obtained before and after the formation of H_2 bubbles in the electrolyte without the addition of a catalyst. Three separate measurements were performed for each electrolyte, taking into account the sedimentation time. The average values of the decrease in the light intensity **(Table 1)** were calculated from the individual measurement values, and thus the amount of bubbles that formed. The assumption that higher amounts of bubbles are reflected in lower degrees of light intensity was confirmed. The calculation of the average values was performed in Excel.

Since sedimentation was observed to stabilize between approximately 10 and 90 minutes, the average value of the Δ lux was calculated from the individual measurements. This served as a comparative standard for determining the reactivity (efficiency) of the experimental photocatalysts. The individual results are listed in the final column of the table.

The efficiency coefficients comprised multiples of the standard value. The higher the coefficient, the greater the efficiency (reactivity) of the respective photocatalyst.

Table 1 The measurement results

Reactivity of the photocatalysts					
Measurement	1	2	3	Calculation	
Catalyst	Δ (lx) [a]	Δ (lx)	Δ (lx)	Average Δ (lx) from 3 measurements [b]	Average reactivity [c]
No catalyst (standard)	1,263	1,170	1,158 [d]3	1,197	1.00
0.1g GO + 0.1g g-C_3N_4	1,958 [d]4	1,411	1,218	1,529	1.28
1 ml GO-MEN + 0.1g C_3N_4	1,222	1,524	1,898 [d]5	1,548	1.29
0.1 g g-C_3N_4	822 [d]6	871	758	817	0.68
0.1 g rGO + 0.1g g-C_3N_4	973	1,749 [d]7	1,039	1,254	1.05
Electrolyte: 100 ml 10% methanol. Volume in the electrolyser 50 ml. Green LED illumination 550 nm					

Note:

a) **Δ (lx):** difference between the average light intensity value without bubbles (without electric current) and the value with bubbles (electric current switched on). The average measurement values were calculated from an Excel graph

b) **Average Δ (lx)**: average of the illumination intensities from the experimental average measurement values

c) **Average reactivity** (catalyst): ratio between the average value of the Δ (lx) of the catalysts and the standard

d) **Graph:** after the letter "d" is the number of the figure - graph

CONCLUSION

The H_2 bubble measurement method applying the reactivity rate of various photocatalysts described in this study produced measurable results. We suggest that this pilot method should be further tested and refined prior to its use for the rapid assessment of the effectiveness of experimental (photo)catalysts. The method can also be used for the measurement of the sedimentation rates of suspended particles.

The experiments confirmed that the nanostructures employed enhanced reactivity and provided support for the photocatalytic reactions involved in the production of hydrogen. Unfortunately, elevated amounts of particles prevent the passage of light, whereupon the bubble measurement method reaches its upper limit, and it is no longer possible to take empirical measurements (**Figure 2**).

The most significant catalytic impacts with concern to the applied method were exerted by the GO-MEN (graphene oxide from Mendel University) + g-C_3N_4 suspension (**Table 1**). Similar results were obtained for the catalyst containing GO + g-C_3N_4. The combination rGO + g-C_3N_4 evinced a somewhat lower level of efficiency.

ACKNOWLEDGEMENTS

This study was supported financially via institutional support for the long-term conceptual development of research organizations for the period 2023–2027 and forms part of the "The mechanical and thermal disruption of electrochemical processes in modern batteries and capacitors: Analysis of impacts on occupational safety and health protection" research area (No. 931602) addressed by the Research Institute for Labour and Social Affairs, v. v. i. in the period 2025-2028.

REFERENCES

[1] FUJISHIMA, A., HONDA, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 1972, vol. 238, pp. 37-38

[2] WU, X., GAO, D., WANG, P., YU, H., YU, J. NH_4Cl-induced low-temperature formation of nitrogen-rich g-C_3N_4 nanosheets with improved photocatalytic hydrogen evolution. *Carbon*, 2019, vol. 153, pp. 757-766.

[3] WU, X., WANG, X., WANG, F., YU, H. Soluble g-C_3N_4 nanosheets: Facile synthesis and application in photocatalytic hydrogen evolution, Appl. *Catal. B: Environ. Times*. 2019, vol. 247, pp. 70-77.

[4] XING, W., TU, W., HAN, Z., HU, Y., MENG, Q., CHEN, G. Template-induced high-crystalline g-C_3N_4 nanosheets for enhanced photocatalytic H_2 evolution. *ACS Energy Lett.* 2018, vol. 3, pp. 514-519.

[5] JIANG, K., ZHU, L., WANG, Z., LIU, K., LI, H, HU, J., PAN, H. FU, J., ZHANG, N, QIU, X., LIU, M. Plasma-treatment induced H_2O dissociation for the enhancement of photocatalytic CO_2 reduction to CH_4 over graphitic carbon nitride. *Appl. Surf. Sci.*. 2020, vol. 508, Article 145173.

[6] FU, J., JIANG, K., QIU, X., YU, J., LIU, M. Product selectivity of photocatalytic CO_2 reduction reactions. *Mater. Today*. 2020, vol. 32, pp. 222-243.

[7] CHEN, L., MAIGBAY, M.A., Lim. Synthesis and Modification Strategies of g-C_3N_4 Nano Sheets for Photocatalytic Applications. *Advanced Powder Materials.* 2024, vol. 3, 100150.

[8] ROUPCOVÁ, P. *Monitoring of the ecotoxicity of the carbon-based nanoparticles*. Dissertation Thesis, VSB – Technical University of Ostrava, Faculty of Safety Engineering, 2018.

[9] BYTEŠNÍKOVÁ, Z.; BIRGUSOVÁ, E.; PEKÁRKOVÁ, J., ŠVEC, P., RICHTERA, L. A novel method for modification of poly (lactic acid) filament by graphene oxide for 3D print. In *Proceedings 15th International Conference on Nanomaterials - Research & Application*. Brno: Tanger Ltd, 2023, pp. 298–302. ISBN 978-80-88365-15-0. ISSN 2694-930X. Available from: https://doi.org/10.37904/nanocon.2023.4799.

[10] ROUPCOVA, P., KLOUDA, K., ZAZIMAL, F., FILIPI, B., VRABLOVA, M., REPECKA, L., KUBATOVA, H., BARABASOVA, M., DOSTAL, M., DEBNAROVA, S., MORAVEC, Z., GEMENIER, P., HOMOLA, T. Graphene Oxide-Based Sorbents: Characterization and Efficiency in Pharmaceutical Adsorption and Biological Activity. *Applied Biochemistry and Biotechnology*. 2024. ABAB-D-25-01413 (preprint). Available from: https://dx.doi.org/10.2139/ssrn.5073711