

INSTITUTE OF LOW TEMPERATURE AND STRUCTURE RESEARCH  
POLISH ACADEMY OF SCIENCES

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Przemysław Wiewiórski, Włodzimierz Miśta, Robert Tomala, Mariusz Stefanski

Laser induced generation of hydrogen from methanol, ethanol, water and methanol vapor by using graphene target

EcoPhotonics – Wildau, Germany

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## Laser-Induced Hydrogen Generation from Methanol with Graphene Aerogel as the Target

Wieslaw Strek, Przemyslaw Wiewiórski, Włodzimierz Miśta, Taras Hanulia, and Robert Tomala\*

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Research paper

Laser induced hydrogen emission from ethanol with dispersed graphene particles

W. Strek, W. Miśta, P. Wiewiorski, R. Tomala\*

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Article

## Laser-Induced Generation of Hydrogen in Water by Using Graphene Target

Wieslaw Strek, Przemyslaw Wiewiórski, Włodzimierz Miśta, Robert Tomala and Mariusz Stefanski \*

## Laser-induced generation of hydrogen from methanol vapor

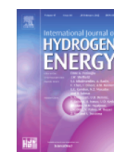
W. Strek, P. Wiewiórski, W. Miśta, R. Tomala, M. Stefanski

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Article

## Laser-Induced Hydrogen Generation from Methanol with Graphene Aerogel as the Target

Wieslaw Strek, Przemyslaw Wiewiórski, Włodzimierz Mista, Taras Hanulia, and Robert Tomala\*



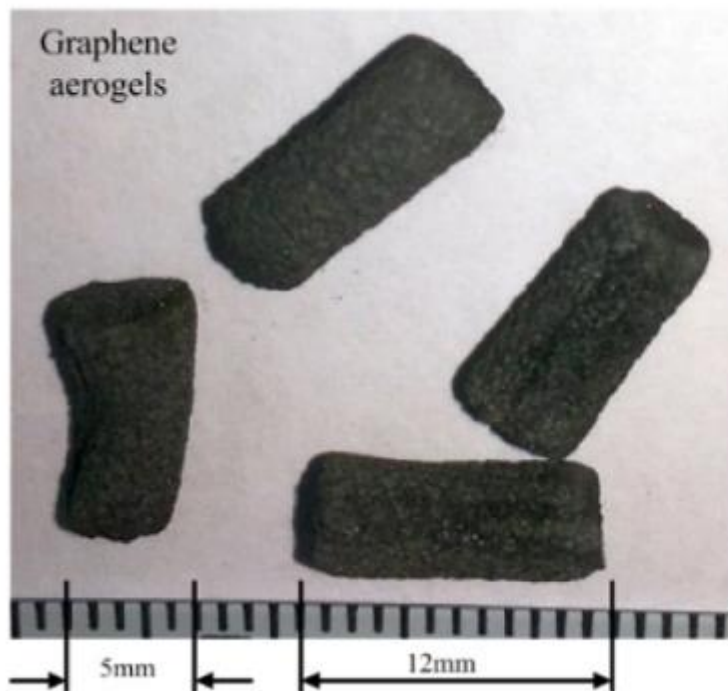
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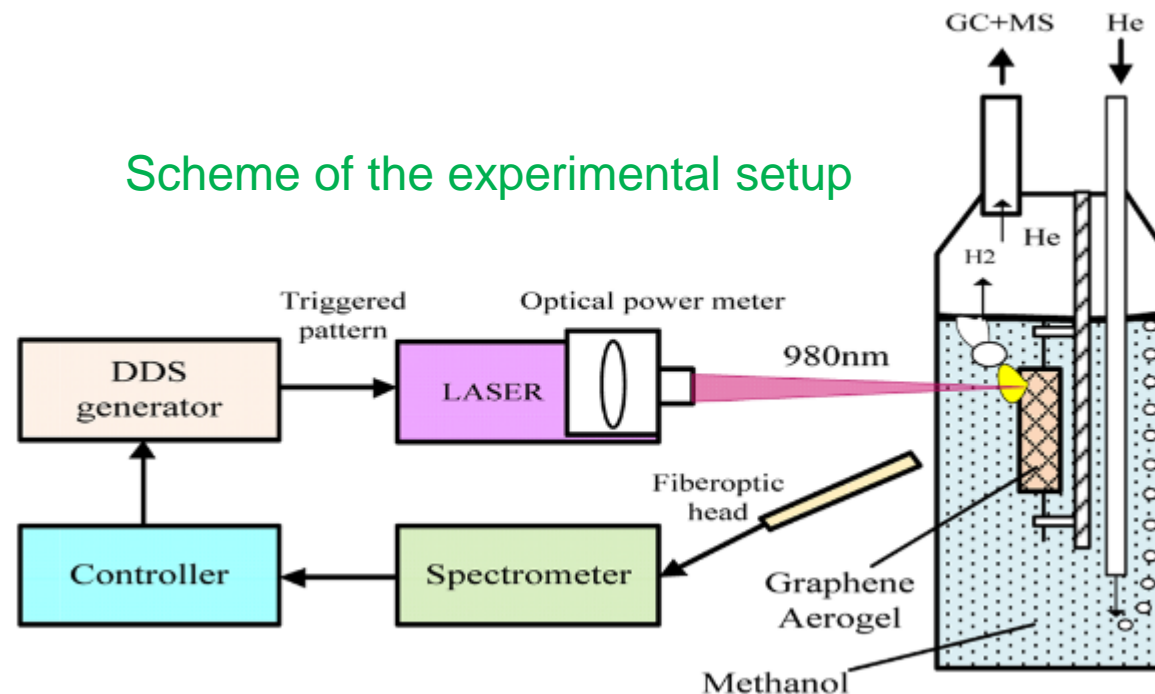
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# H<sub>2</sub> generation from **methanol** with Graphene aerogel as the target

## Graphene aerogel scaffolds



## Scheme of the experimental setup

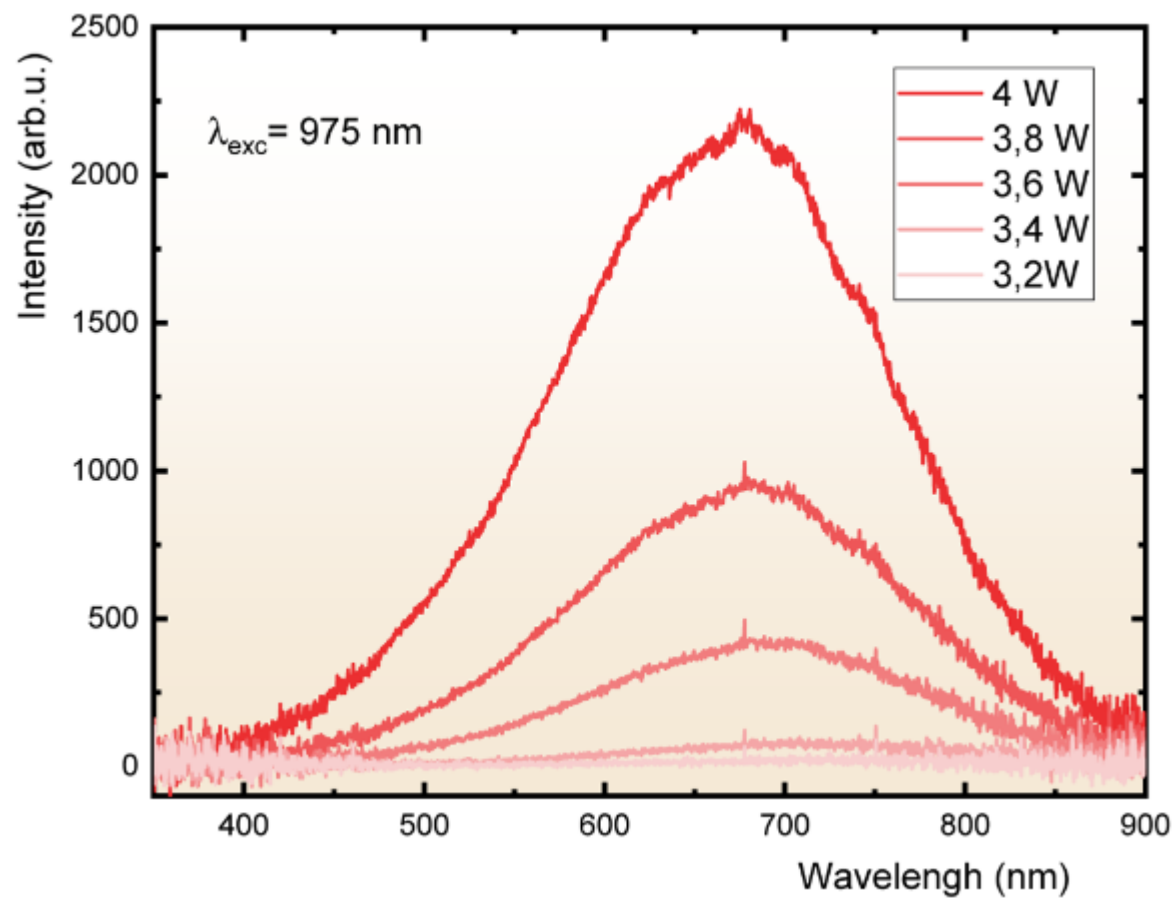
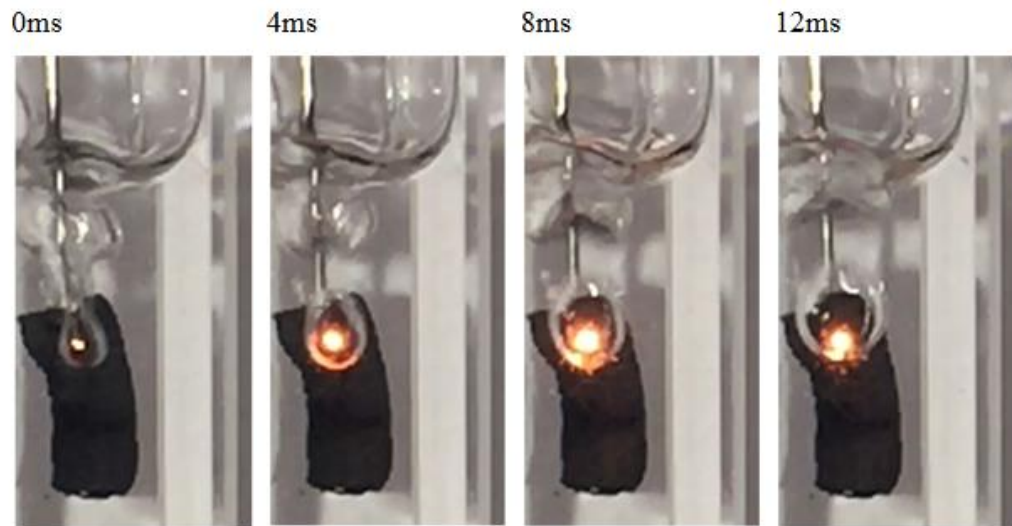


Cuvette of methanol with graphene foam scaffold after irradiation with laser diode 975 nm

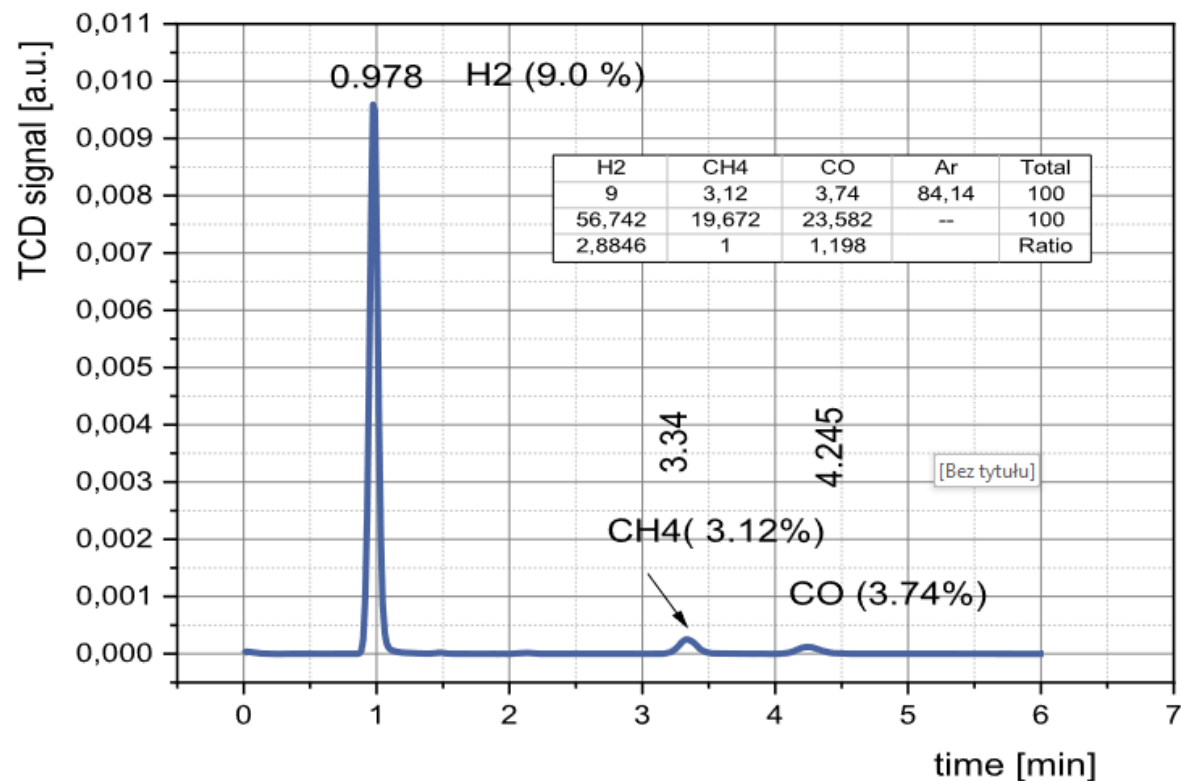
# H<sub>2</sub> generation from **methanol** with Graphene aerogel as the target



Evolution of a single bubble during continuous laser excitation of graphene aerogel in the methanol



# H<sub>2</sub> generation from **methanol** with Graphene aerogel as the target

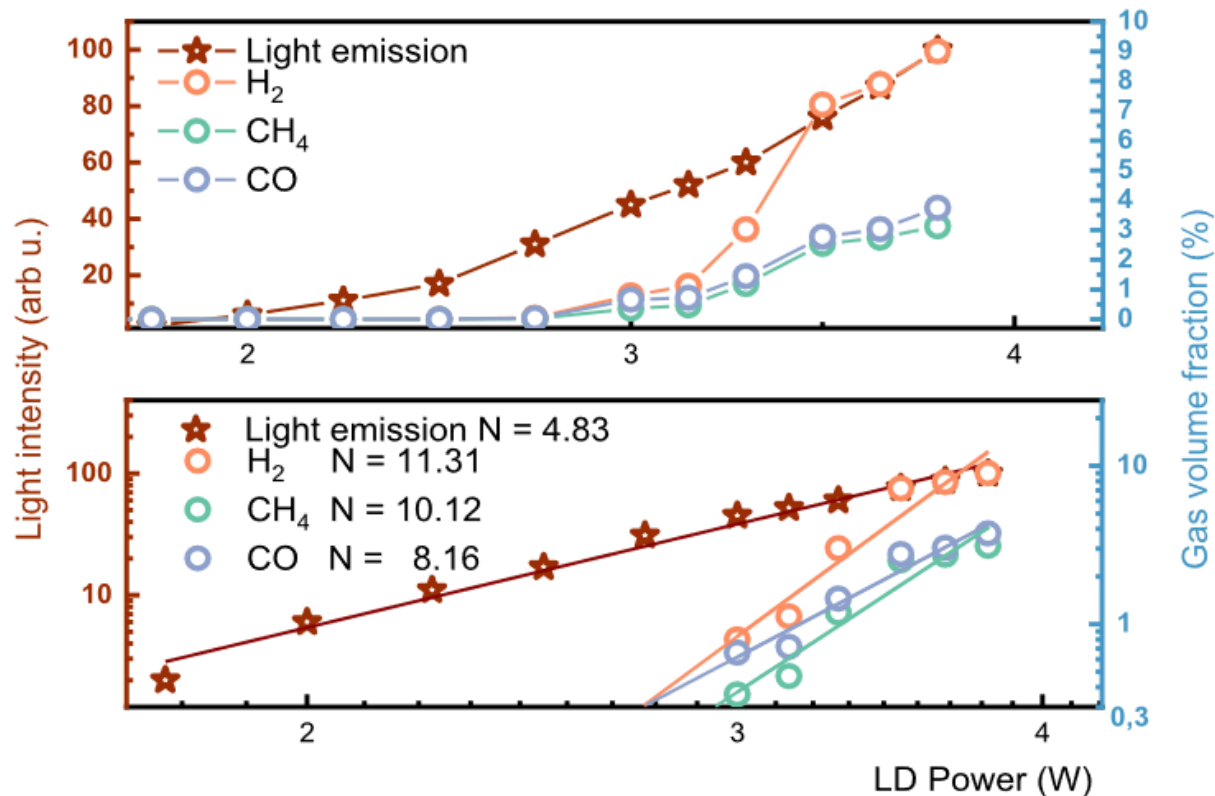


laser power $P_O$ [W]	gas products		
	hydrogen H <sub>2</sub> [%]	methane CH <sub>4</sub> [%]	carbon monoxide CO [%]
2.50	43.96	19.78	36.26
2.75	48.48	20.35	31.17
3.00	53.45	20.88	25.66
3.15	57.63	20.22	22.14
3.30	57.79	20.04	22.17
3.50	56.75	19.67	23.58
3.65	56.82	20.1	23.08
3.80	57.30	19.81	22.89

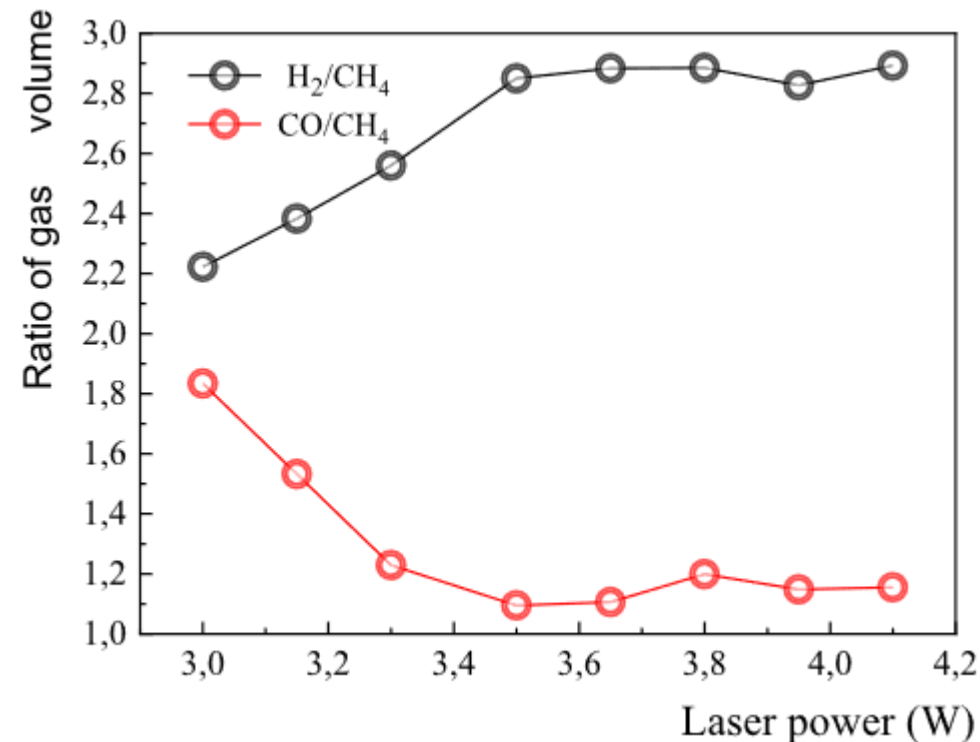
Gas products of LI dissociation of methanol by using the GA scaffold as the target (in Ar flow 5 mL/min)

# H<sub>2</sub> generation from methanol with Graphene aerogel as the target

Influence of excitation laser power on light emission and the volumes of generated gases



Comparison of LI light emission intensity and emitted gas fractions (H<sub>2</sub>, CO, and CH<sub>4</sub>) of the GA scaffold on excitation LD power in log/log scale



Influence of excitation laser power on H<sub>2</sub> and CO gas products because of photoreformation of CH<sub>3</sub>OH solution with graphene foam as the photocatalyst



# H<sub>2</sub> generation from **methanol** with Graphene aerogel as the target

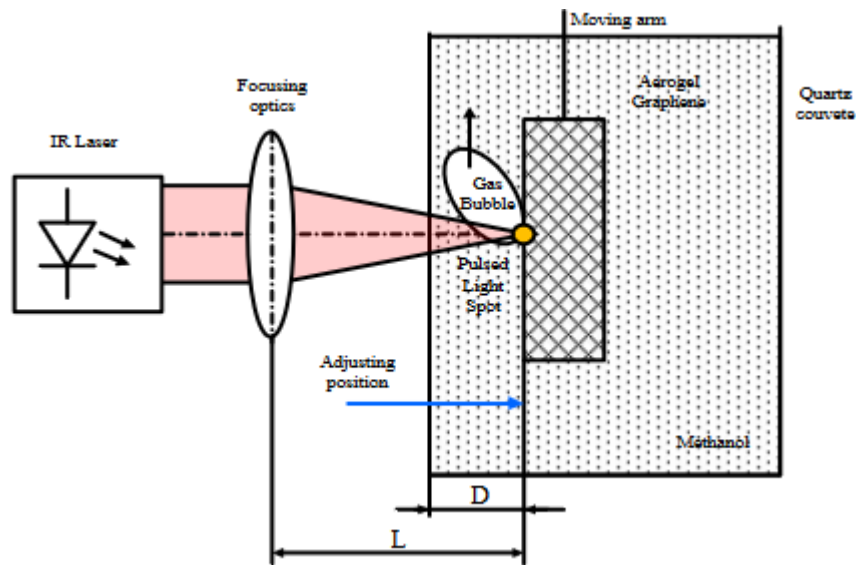
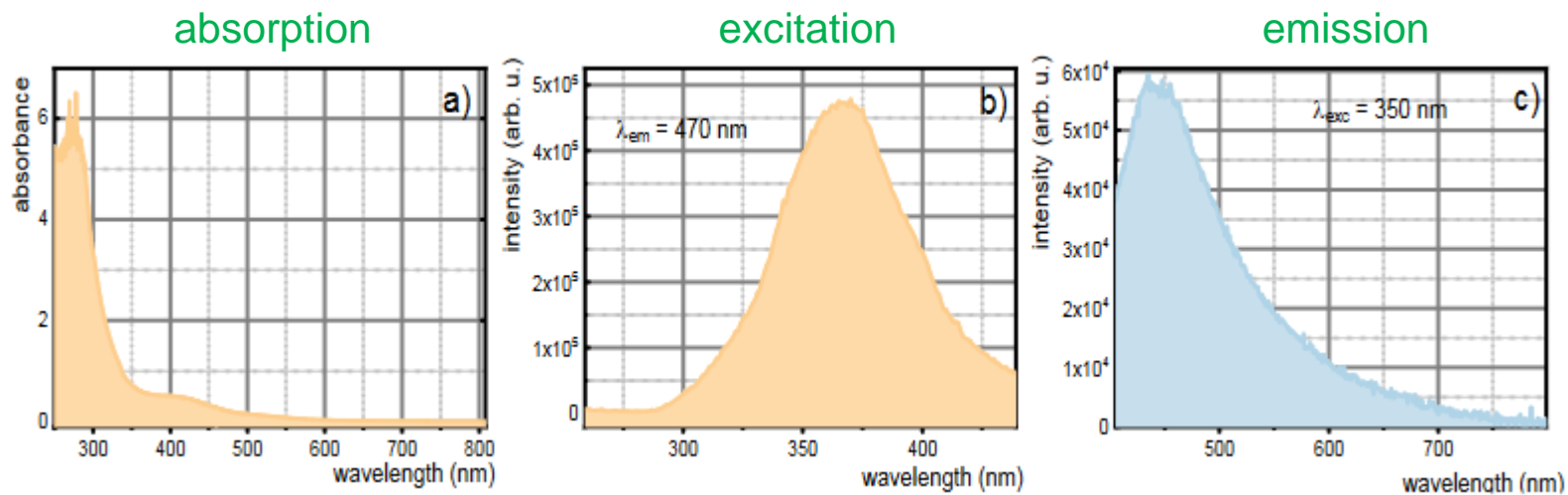


Diagram of measurement of emission spectra



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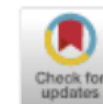


Research paper

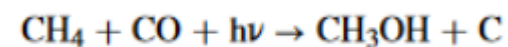
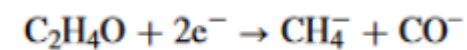
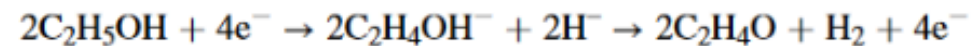
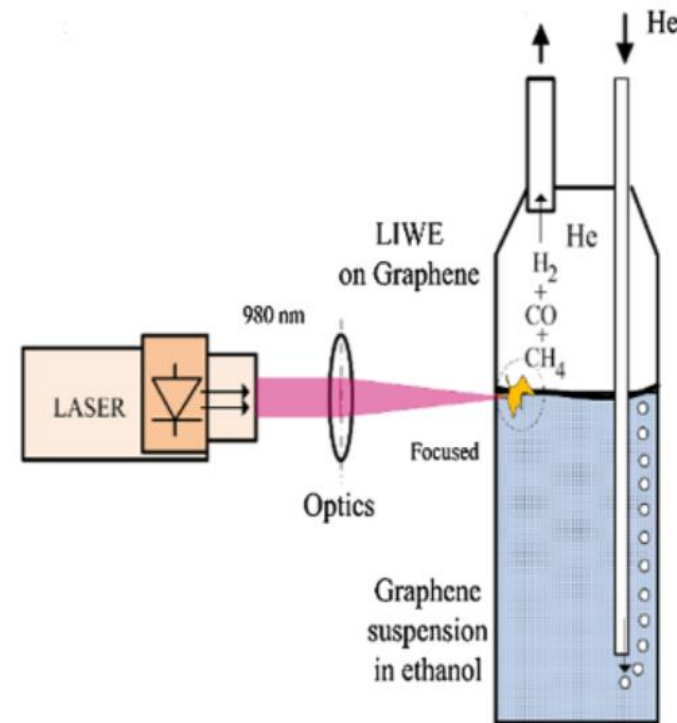
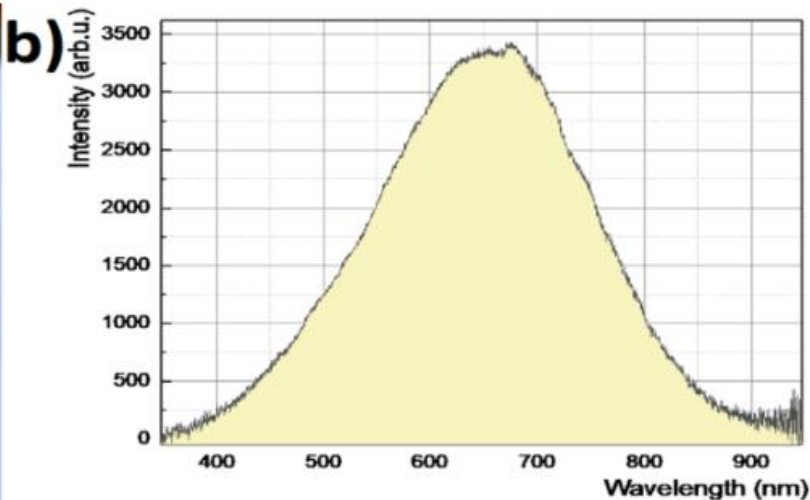
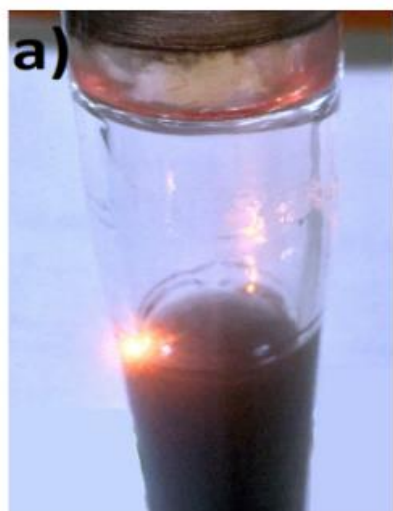
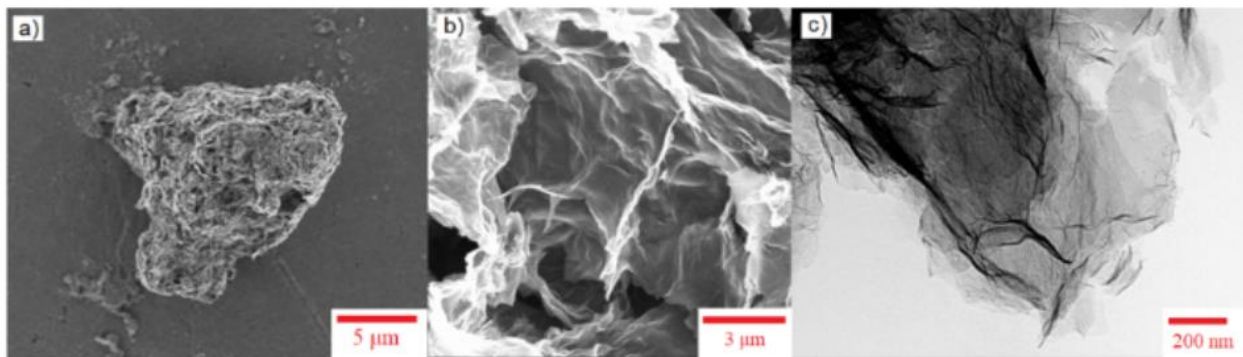
## Laser induced hydrogen emission from ethanol with dispersed graphene particles

W. Strek, W. Mista, P. Wiewiorski, R. Tomala\*

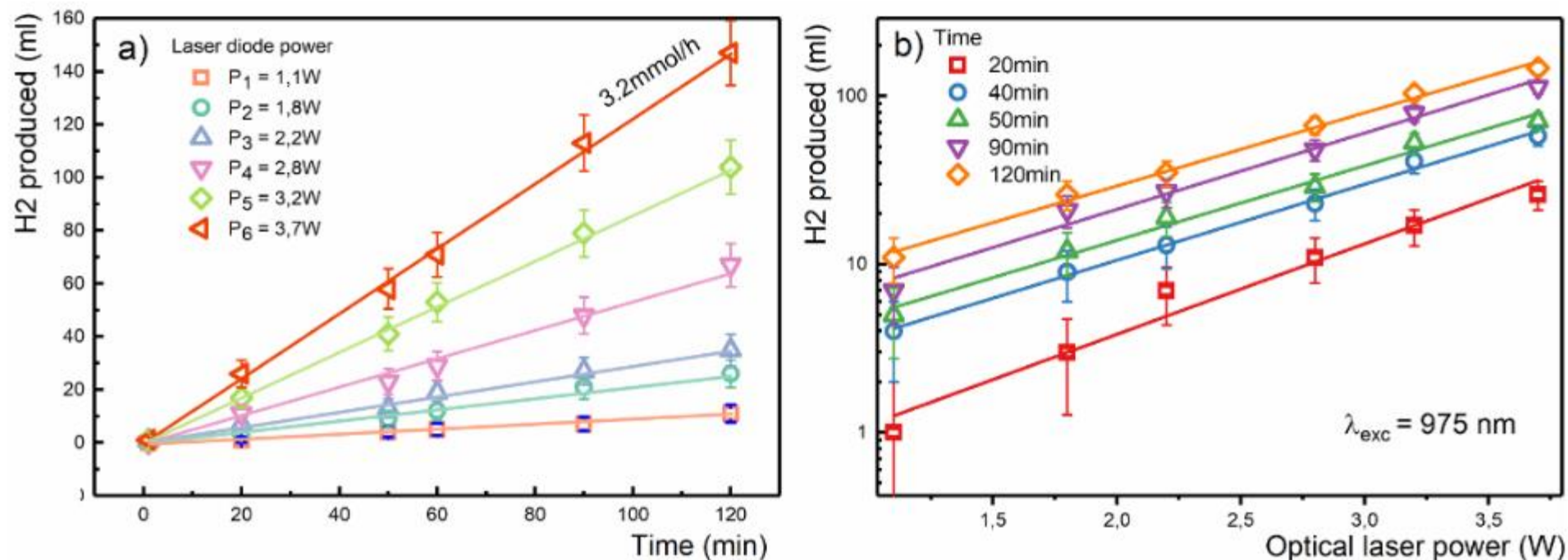
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# H<sub>2</sub> generation from ethanol with dispersed Graphene particles



# H<sub>2</sub> generation from ethanol with dispersed Graphene particles




Time evolution of generated H<sub>2</sub> volume from ethanol + GP solution irradiated with CW 975 nm laser diode for different excitation power (a). The power dependence of H<sub>2</sub> volume generated from (ethanol + GP) irradiated with CW 980 nm laser diode in different time intervals (b)



*Article*

## **Laser-Induced Generation of Hydrogen in Water by Using Graphene Target**

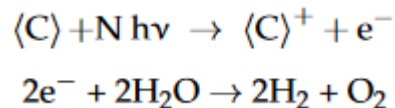
Wiesław Strek, Przemysław Wiewiórski, Włodzimierz Miśta, Robert Tomala and Mariusz Stefanski \* 

# H<sub>2</sub> generation from **water** with Graphene target

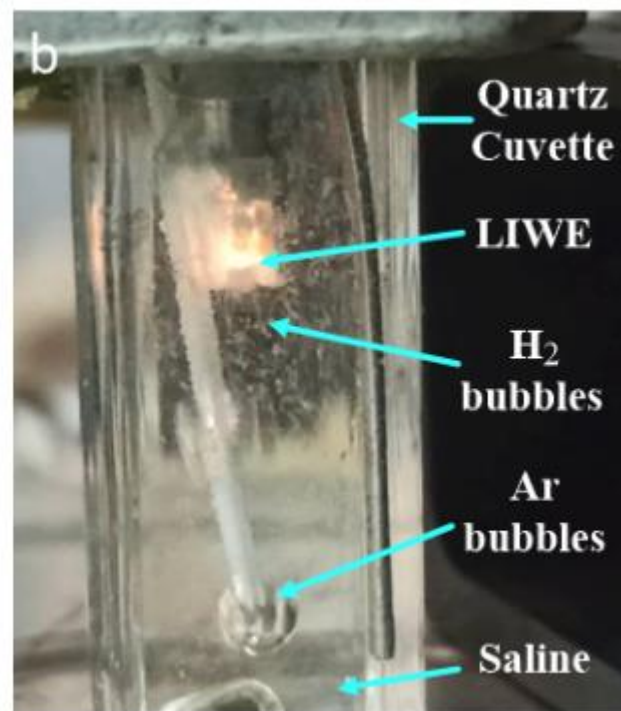
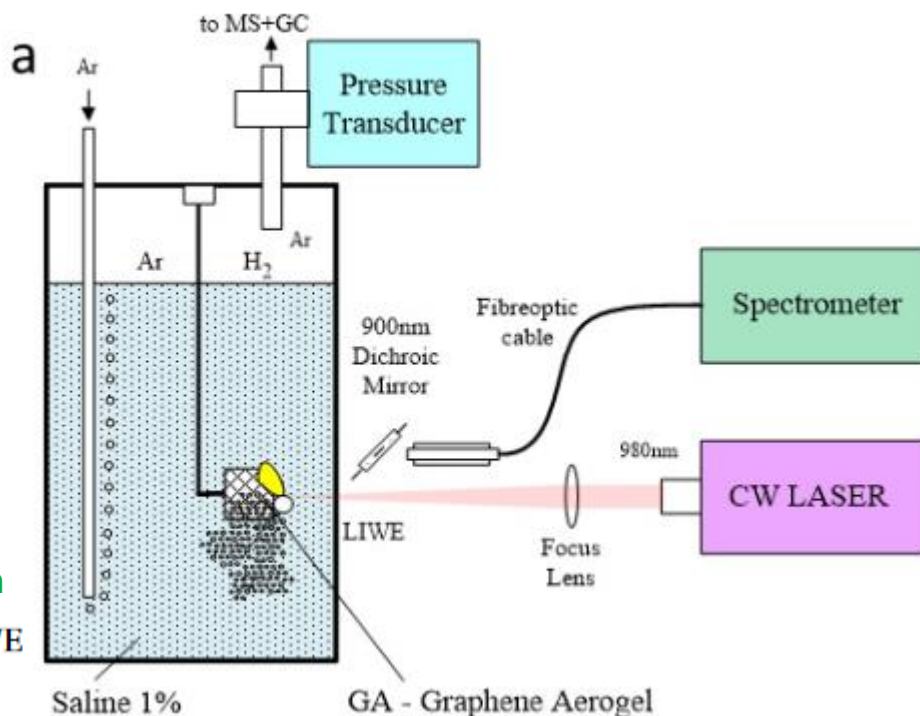
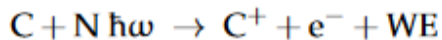
Saline: conductivity  $1.6 \cdot 10^4 \mu\text{S/cm}$   
pH=5.8

Distilled water: conductivity  $10 \mu\text{S/cm}$   
pH=7

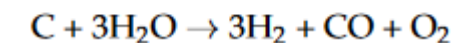
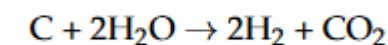
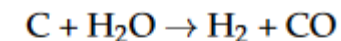
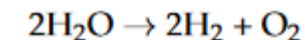
laser-induced splitting of water in the presence of graphene



multiphoton absorption

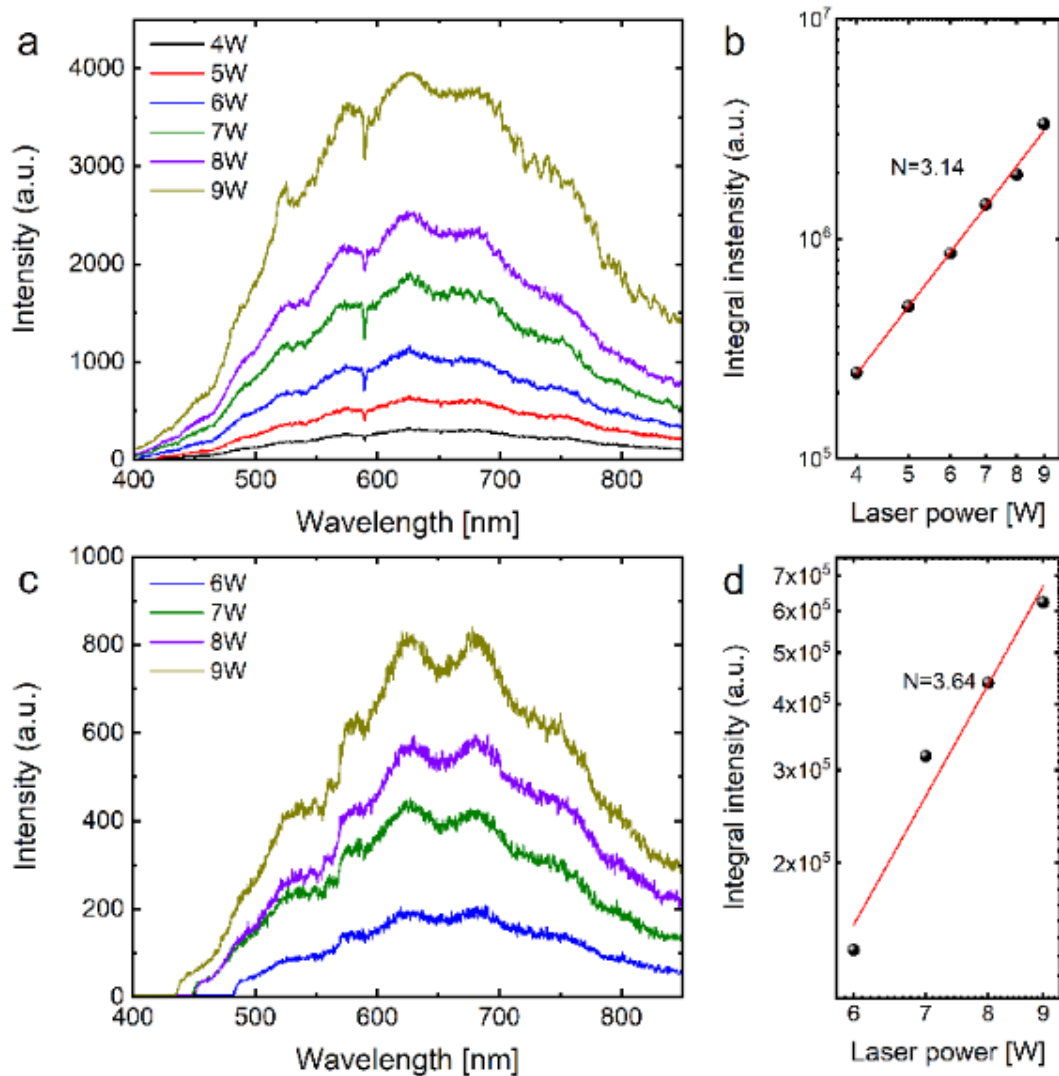


The splitting of water by electrolysis



Experimental set-up for hydrogen generation from water, using graphene as a photocatalyst (a); Photo of the cuvette of water with immersed graphene scaffold irradiated with 980 nm laser beam (b)

# H<sub>2</sub> generation from water with Graphene target



The emission spectra of laser-irradiated graphene foam with different excitation laser power in saline (a,b) and distilled water (c,d). The narrow dips observed at ~589 nm in the emission spectrum of saline water may be assigned to the Na<sup>+</sup> ions due to the dissociation of NaCl. They were not seen for distilled water.

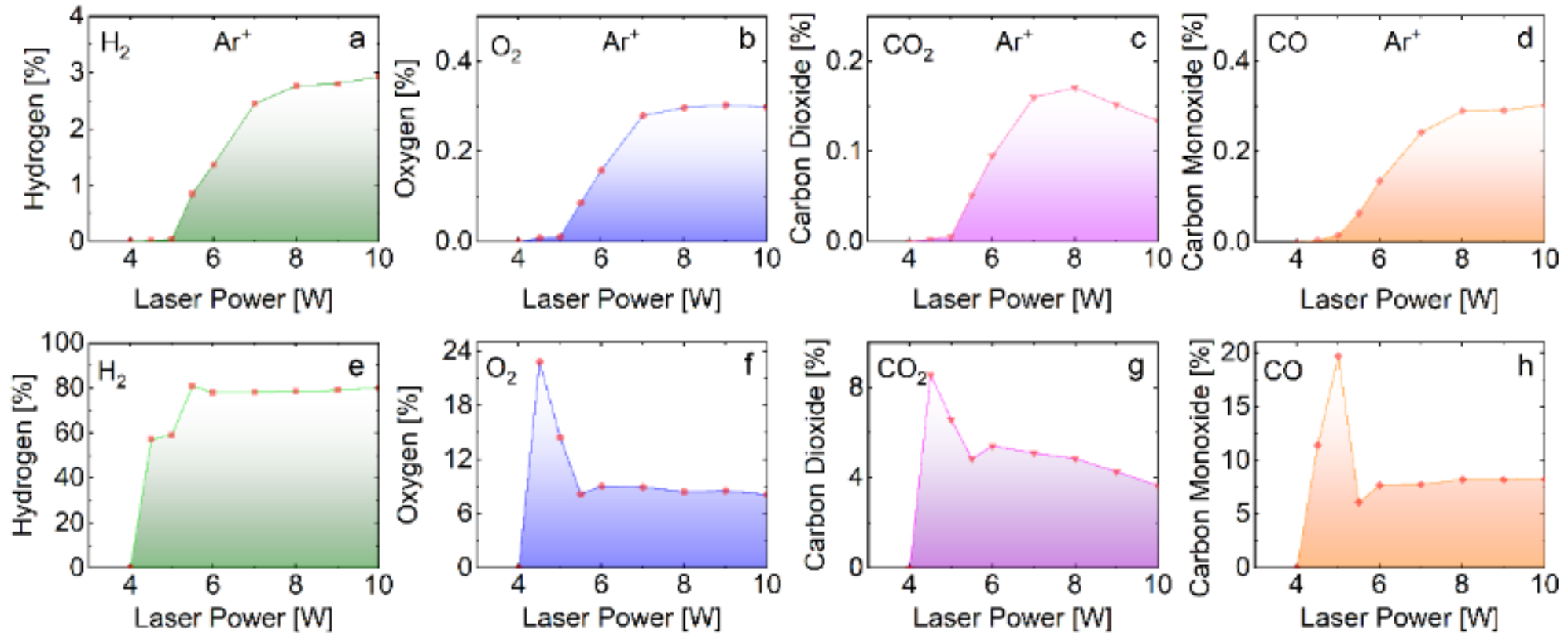
# H<sub>2</sub> generation from **water** with Graphene target

Ar 20 mL/min H <sub>2</sub> O-Distilled Water				
Laser Power [W]	Gas Products			
	H <sub>2</sub> [%]	O <sub>2</sub> [%]	CO <sub>2</sub> [%]	CO [%]
10.0	47.00	10.44	11.23	31.33
9.0	54.42	6.80	11.56	27.21
8.0	54.30	9.05	9.50	27.15
7.0	53.25	11.83	11.24	23.67
6.0	55.56	7.94	12.70	23.81

Ar 20 mL/min H <sub>2</sub> O + 1% NaCl				
Laser Power [W]	Gas Products			
	H <sub>2</sub> [%]	O <sub>2</sub> [%]	CO <sub>2</sub> [%]	CO [%]
10.0	79.95	8.13	3.66	8.27
9.0	78.99	8.52	4.27	8.21
8.0	78.48	8.43	4.85	8.23
7.0	78.21	8.93	5.10	7.75
6.0	77.81	9.07	5.42	7.70
5.5	80.91	8.17	4.84	6.08
5.0	59.21	14.47	6.58	19.74
4.5	57.14	22.86	8.57	11.43

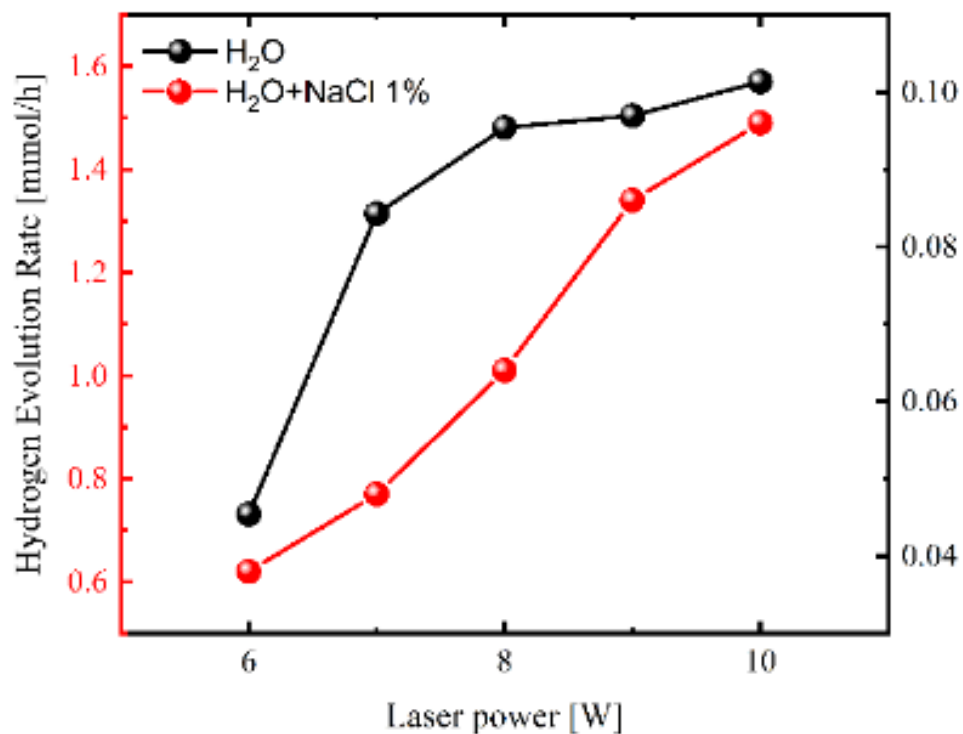


# H<sub>2</sub> generation from water with Graphene target

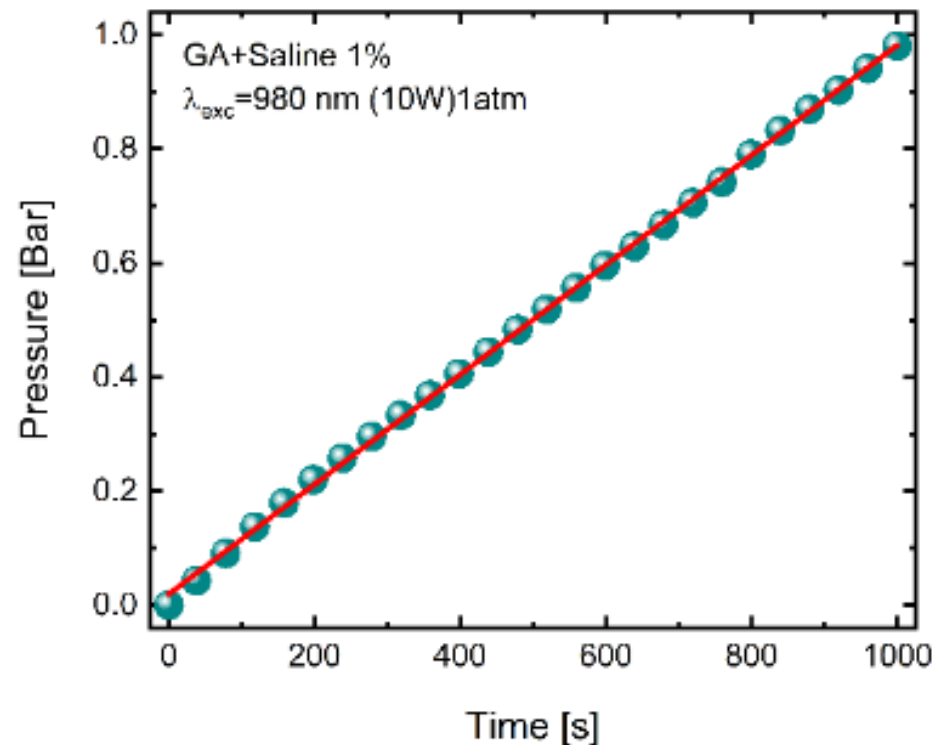


The power dependence of gas products in (a-d) and without (e-h) the presence of Ar, resulting from laser irradiation of H<sub>2</sub>O+1% NaCl

# H<sub>2</sub> generation from water with Graphene target



Hydrogen evolution rate from saline and distilled water by laser irradiation of graphene aerogel



The increase in total gas pressure during water splitting in the closed cuvette after long-time exposure

## **Laser-induced generation of hydrogen from methanol vapor**

W. Strek, P. Wiewiórski, W. Miśta, R. Tomala, M. Stefanski

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*Polish Academy of Sciences, Wrocław, Poland*

*\*corresponding author: m.stefanski@intibs.pl*

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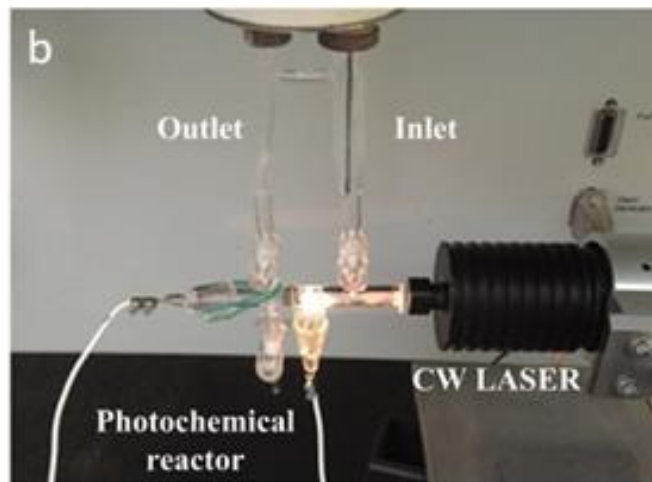
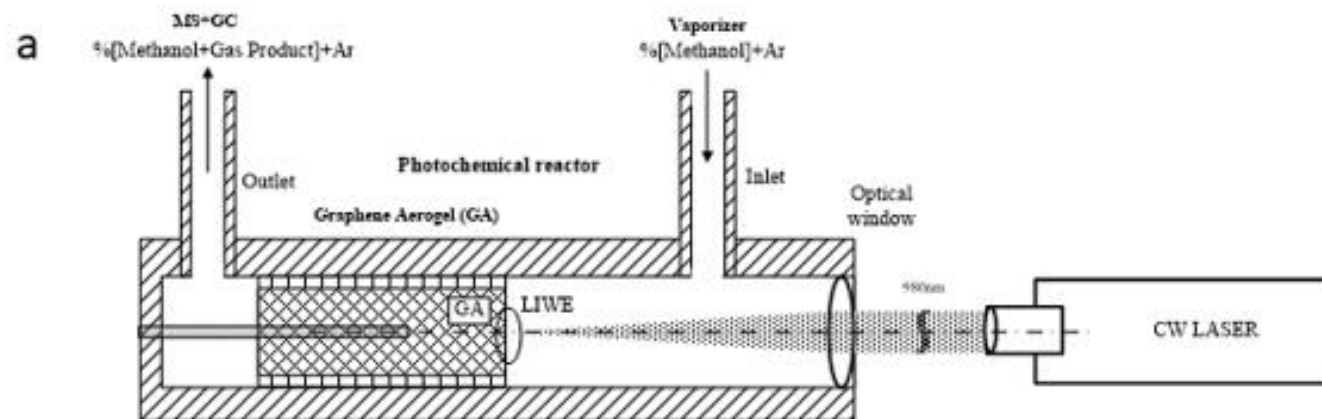


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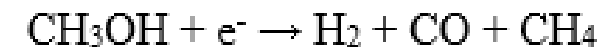
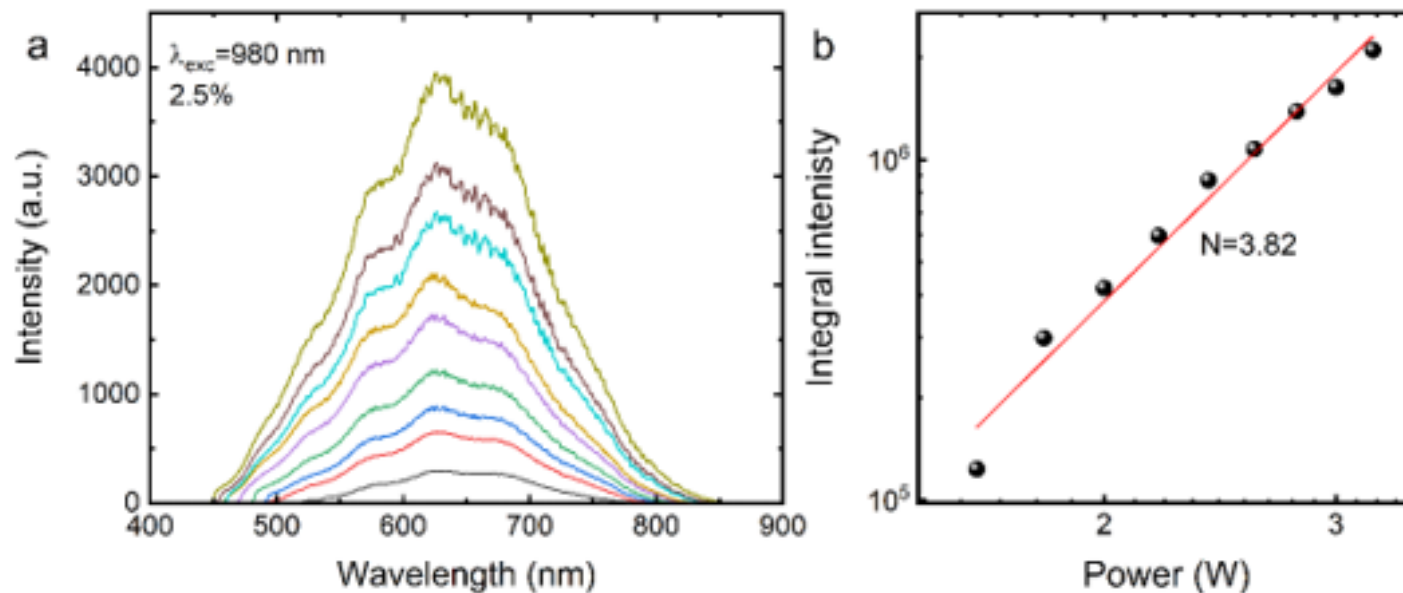
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# H<sub>2</sub> generation from **methanol vapor** with Graphene target



The experimental set-up of a laser driven photochemical reactor. LIWE means Laser Induced White Emission to hydrogen generation in methanol vapor by CW IR laser irradiation.

# H<sub>2</sub> generation from **methanol vapor** with Graphene target

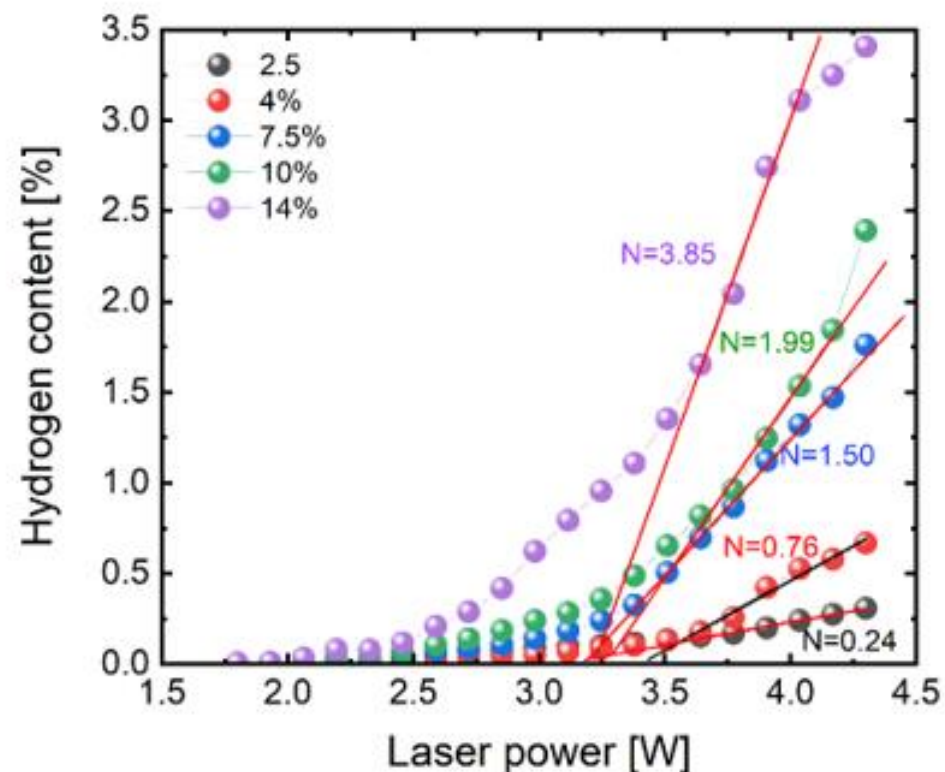


The emission spectra of graphene aerogel in methanol vapor upon irradiation with focused beam of CW 980 nm laser diode (a). The power dependence of emission intensity in log/log plot (b).

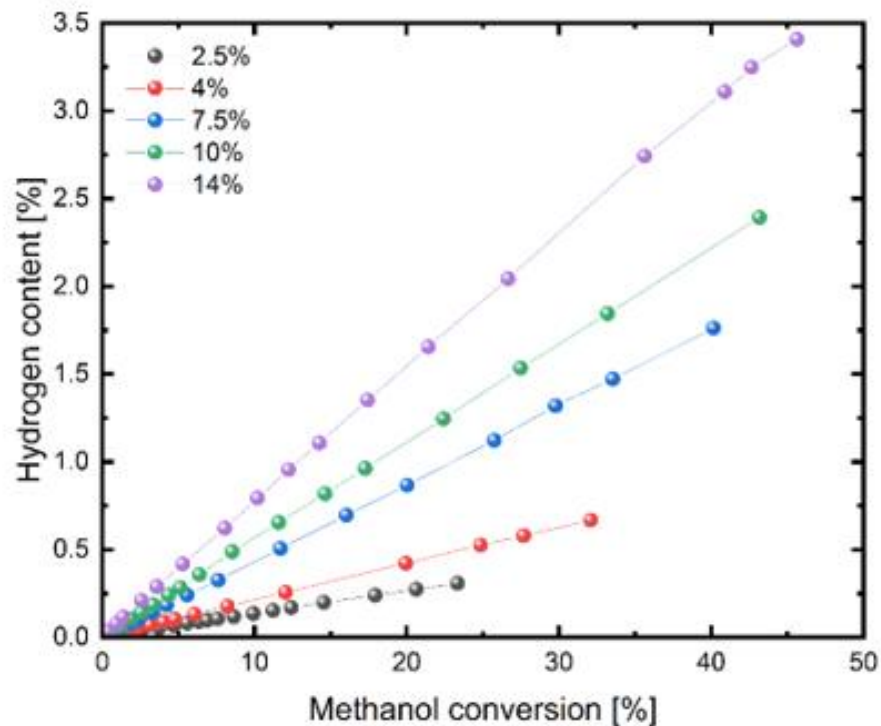
# H<sub>2</sub> generation from methanol vapor with Graphene target

Table 1. Evolution of gas products on laser irradiation of 2.5% and 14% vapor concentrations of methanol.

Laser power [W]	Ar 20ml/min, methanol [%]							
	2.5	14	2.5	14	2.5	14	2.5	14
	Gas products				Vapor			
	Hydrogen H <sub>2</sub> [%]		Carbon monoxide CO [%]		Methane CH <sub>4</sub> [%]		Methanol CH <sub>3</sub> OH [%]	
1.80	0.006	<b>0.008</b>	0.005	<b>0.007</b>	0.000	<b>0.001</b>	2.553	<b>13.750</b>
2.00	0.011	<b>0.012</b>	0.008	<b>0.008</b>	0.001	<b>0.002</b>	2.553	<b>13.744</b>
2.20	0.019	<b>0.072</b>	0.014	<b>0.059</b>	0.002	<b>0.009</b>	2.530	<b>13.626</b>
2.40	0.023	<b>0.096</b>	0.017	<b>0.059</b>	0.005	<b>0.012</b>	2.510	<b>13.599</b>
2.60	0.035	<b>0.218</b>	0.026	<b>0.135</b>	0.008	<b>0.029</b>	2.465	<b>13.385</b>
2.80	0.056	<b>0.336</b>	0.040	<b>0.209</b>	0.015	<b>0.045</b>	2.428	<b>13.176</b>
3.00	0.081	<b>0.647</b>	0.058	<b>0.430</b>	0.016	<b>0.094</b>	2.398	<b>12.595</b>
3.20	0.101	<b>0.900</b>	0.071	<b>0.565</b>	0.021	<b>0.134</b>	2.378	<b>12.167</b>
3.40	0.120	<b>1.132</b>	0.087	<b>0.735</b>	0.025	<b>0.157</b>	2.337	<b>11.742</b>
3.60	0.149	<b>1.529</b>	0.106	<b>0.995</b>	0.030	<b>0.206</b>	2.285	<b>11.035</b>
3.80	0.172	<b>2.121</b>	0.124	<b>1.393</b>	0.035	<b>0.312</b>	2.238	<b>9.940</b>
3.90	0.197	<b>2.724</b>	0.136	<b>1.771</b>	0.041	<b>0.384</b>	2.194	<b>8.888</b>
4.00	0.230	<b>3.070</b>	0.164	<b>2.060</b>	0.048	<b>0.442</b>	2.123	<b>8.194</b>
4.20	0.282	<b>3.282</b>	0.204	<b>2.189</b>	0.057	<b>0.466</b>	2.017	<b>7.829</b>
4.30	0.308	<b>3.408</b>	0.226	<b>2.389</b>	0.071	<b>0.494</b>	1.965	<b>7.475</b>



# H<sub>2</sub> generation from methanol vapor with Graphene target



The total conversion hydrogen obtained for different amounts of methanol by irradiation with laser diode

Table 2. The laser generated gas products obtained from vapor with different concentration of methanol for the highest applied laser power (4.3W).

Laser power [W]	Ar 20ml/min, methanol [%]	Gas products			Vapor	Methanol conversion [%]
		Hydrogen [%]	Carbon monoxide [%]	Methane [%]	Methanol [%]	
4.3	2.5	0.30	0.23	0.08	1.93	23
	4	0.67	0.41	0.19	2.72	32
	7.5	1.76	1.01	0.26	4.50	40
	10	2.39	1.49	0.38	5.59	43
	14	3.41	2.39	0.49	7.56	46

# Summary

- Methods of laser-induced hydrogen generation from graphene immersed in 4 different carriers (methanol, ethanol, saline, methanol vapor) are presented
- The generated volume of gases was assisted by the intense emission of white light from the irradiation spot at the graphene surface
- The H<sub>2</sub> generation process from graphene immersed in ethanol is free of O<sub>2</sub> and CO<sub>2</sub> gases emission
- This emission followed the photon driven ionization of graphene corresponding to the sp<sup>2</sup>–sp<sup>3</sup> hybridization of carbon
- The ionization process is assisted by bright white light broadband emission and the efficient ejection of hot electrons leading to the dissociation of alcohol molecules
- The percentage of generated hydrogen for salted water reached nearly 81% compared to distilled water at 47%



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**THANK YOU**