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Method of producing hydrogen and reducing CO₂

The National Centre Norway for Research and Development grants

> West Pomeranian University of Technology n Szczecin

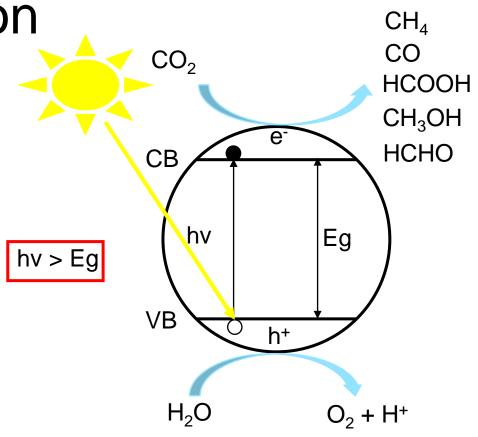
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Introduction

The increasing level of public awareness of climate change caused by excessive CO₂ emissions results in searching for solutions to capture CO₂, and then convert it into useful **products**. Currently, technologies using photocatalysts that operate under the influence of energy from solar radiation are developing dynamically. To date, many materials used for CO_2 photoreduction have been studied, including TiO_2 , ZnO and metal organic frameworks. However, often their use is associated with some difficulties. The use of our invention, which is a photocatalyst in the form of zinc and its compounds, can eliminate some of them.



The scheme of photocatalytic CO₂ reduction on photocatalyst surface

photoRed

Advantages of the invention

Homogeneous process

Zinc in the form of carbonates, hydroxides and oxides after carbon dioxide saturation is dissolved, the transparent solution is obtained, and the process takes place in the water phase. This eliminates the need for photocatalyst separation after CO_2 reduction, unlike heterogeneous photocatalysts.

Simple apparatus

Homogeneous processes do not require complicated apparatus.

Inorganic materials

Due to the fact that complex organic compounds photocatalysts are less stable than inorganic ones, they may decompose during the process and form carbon compounds. In that case the results of an experiment are not very reliable. Using inorganic photocatalyst we know for sure that reaction products such as carbon monoxide or methane are the result of CO_2 conversion only.

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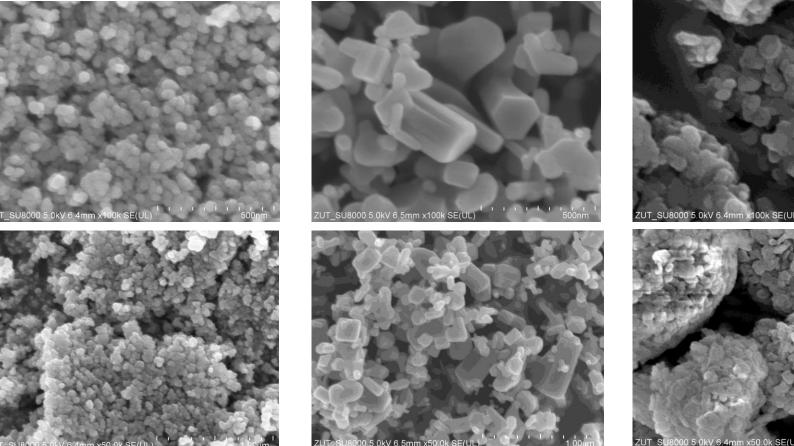
Easier reduction

The carbon dioxide molecule is thermodynamically very stable, which is associated with the fact that its reduction requires a large amount of energy, thus may leading to a low CO_2 -conversion rate. Dissolution of carbon dioxide in water leads to the formation of carbonic acid, which is in equilibrium with carbonate and bicarbonate. Therefore, the reduction process is much easier.

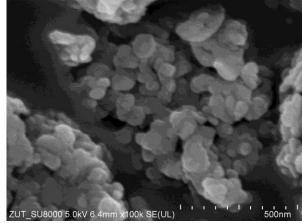
Scanning electron microscopy pictures of the tested materials

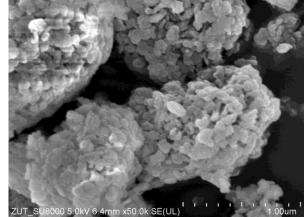
nanosized ZnO

microsized ZnO



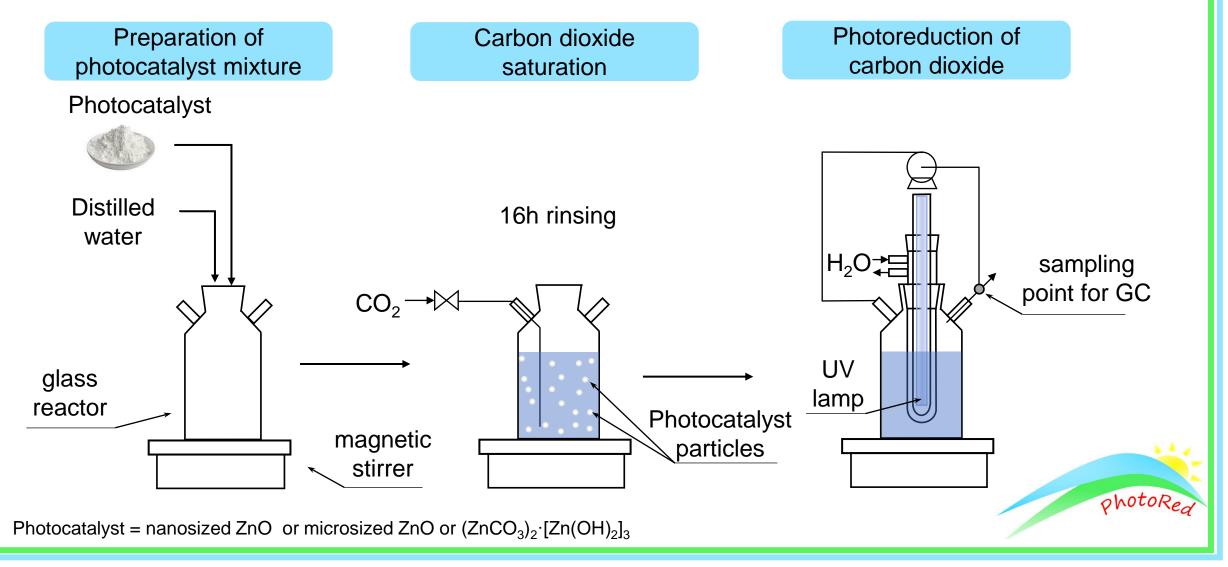
 $(ZnCO_3)_2 \cdot [Zn(OH)_2]_3$





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The scheme of the preparation process of the photocatalytic reduction of CO_2 in the liquid phase



The process of dissolving photocatalyst particles

Photocatalyst mixture



After carbon dioxide saturation



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Chemical reactions

Dissolution of carbon dioxide in water

Dissolution of ZnO particles after saturation with carbon dioxide

Photoreduction of CO₂

 $CO_{2} + H_{2}O \Leftrightarrow H_{2}CO_{3}$ $H_{2}CO_{3} \Leftrightarrow HCO_{3}^{-} + H^{+}$ $HCO_{3}^{-} \Leftrightarrow CO_{3}^{2-} + H^{+}$

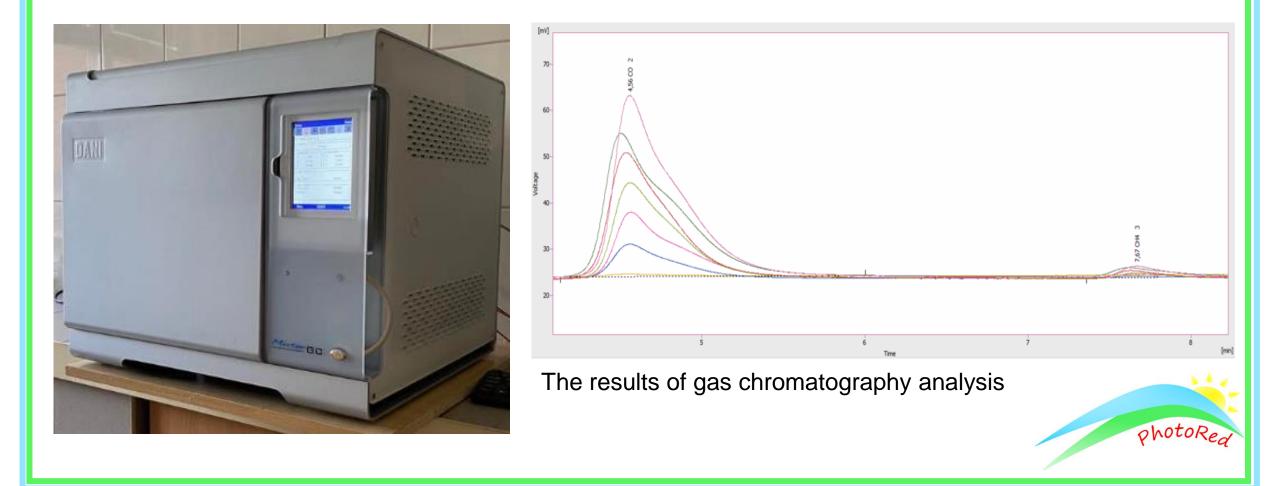
dominating reaction: $ZnO + H_2CO_3 \rightarrow ZnCO_3 + H_2O$ *side reaction:* $ZnO + 2CO_2 + H_2O \rightarrow Zn(HCO_3)_2$

 $\begin{array}{l} \mathrm{CO}_{2} + \mathrm{e}^{-} \rightarrow \mathrm{CO}_{2}^{+-} \\ \mathrm{2H}_{2}\mathrm{O} + 4\mathrm{h}^{+} \rightarrow \mathrm{O}_{2} + 4\mathrm{H}^{+} \\ \mathrm{2H}^{+} + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2} \\ \mathrm{CO}_{2} + 2\mathrm{H}^{+} + 2\mathrm{e}^{-} \rightarrow \mathrm{CO} + \mathrm{H}_{2}\mathrm{O} \\ \mathrm{CO}_{2} + 8\mathrm{H}^{+} + 8\mathrm{e}^{-} \rightarrow \mathrm{CH}_{4} + \mathrm{H}_{2}\mathrm{O} \end{array}$



Detection of products

Gas chromatography using Master GC gas chromatograph (DANI Instruments, Italy)



Contents of products in the gas phase after 6 hours of the photocatalytic process

Sample	The content in the gas phase after 6 hours of the process [µmol/g _{photocatalyst} /dm ³]		
	nanosized ZnO	44.78	14.93
microsized ZnO	3.20	10.37	0.74
$(ZnCO_3)_2 \cdot [Zn(OH)_2]_3$	10.08	9.68	0.77

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The amount of **hydrogen, carbon monoxide and methane** was measured after a 6-hour process of carbon dioxide photoreduction. The results were collected in the table above. The best results were obtained for the sample with **nanosized ZnO**.



The photo of our research team

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