Photocatalytic reduction of CO\(_2\) to hydrocarbons by using photodeposited Pt nanoparticles on carbon-doped titania

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1. Introduction

One main environmental challenge in our time is to avoid or reduce the impacts of global warming. In recent years, consumption of fossil fuels generated greenhouse gases (GHG) especially carbon dioxide (CO\(_2\)), regarded as the main cause of the worldwide global warming [1]. It is vital to reduce the accumulation of CO\(_2\) in the atmosphere. Therefore, researchers make special efforts to convert CO\(_2\) into more useful compounds. Photocatalytic reduction of CO\(_2\) with H\(_2\)O is considered as a promising method to simultaneously reduce the level of CO\(_2\) emission and produce renewable and sustainable fuels [1,2]. However, the development of efficient photocatalysts for CO\(_2\) conversion still remains in the developing phase [3]. In the photocatalytic reduction of CO\(_2\) three main reactions (a–c) have been proposed and validated. The main products are methane (CH\(_4\)) and carbon monoxide (CO) [4]. H\(_2\) is a product from photocatalytic water splitting which is usually competing with CO\(_2\) reduction:

\[
\begin{align*}
\text{CO}_2 + 8\text{H}^+ + 8e^- &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \text{(a)} \\
\text{CO}_2 + 2\text{H}^+ + 2e^- &\rightarrow \text{CO} + \text{H}_2\text{O} \quad \text{(b)}
\end{align*}
\]

2. H\(_2\)O $\rightarrow$ 2H\(_2\) + O\(_2\) \quad \text{(c)}

Titania (TiO\(_2\)), as the most explored semiconductor, has been highly investigated for photocatalytic applications due to its outstanding chemical and thermal stability. However, titania has two main drawbacks: low photocatalytic activity and limited utilization of solar energy, resulting from the fast recombination rate of photoinduced electron-hole pairs and high band gap energy. Therefore it is required to improve the electron-hole separation efficiency and light utilization ability of titania [5,6]. Several methods have been used to improve the photocatalytic efficiency of TiO\(_2\) materials by developing the structural modification of titania with metal [7–9] or metal-free strategies [10–13]. Among them, surface modification of titania is widely applied for inhibiting the recombination of photogenerated electron-hole pairs on TiO\(_2\) [14–17]. Different metal nanoparticles including Pt, Au, Ag, and Pd have been loaded on TiO\(_2\) and proved to be effective for enhancing its photocatalytic activity and in fact, Pt indicates as the most effective co-catalyst to utilize the photogenerated electrons for the CO\(_2\) reduction to methane [18–21]. Pt is the most studied co-catalyst which is widely employed in various systems including TiO\(_2\), titinates and...
carbon nitrides [22]. An optimal loading of the co-catalyst at which the highest photocatalytic activity is achieved is always searched for [23]. In addition, different parameters such as loading, elemental composition, particle size, dispersion, structure, morphology can influence the CO2 reduction. Furthermore, the size of Pt nanoparticles is also playing a critical role in the photocatalytic reduction of CO2 as shown by Dong et al. [34]. In principle doping with non-metals creates heteroatomic surface structure and modify the physic-chemical properties and activity of TiO2. Generally, dopant metals act as a sink and trap the electron generated by the semiconductor under excited state [4].

The highest photocatalytic activity is achieved is always searched for [23]. In addition, different parameters such as loading, elemental composition, particle size, dispersion, structure, morphology can influence the CO2 reduction. Furthermore, the size of Pt nanoparticles is also playing a critical role in the photocatalytic reduction of CO2 as shown by Dong et al. [34]. In principle doping with non-metals creates heteroatomic surface structure and modify the physic-chemical properties and activity of TiO2. Generally, dopant metals act as a sink and trap the electron generated by the semiconductor under excited state [4].

In this research, Pt nanoparticles supported by photodeposition on carbon-doped titania (Pt/C-TiO2, 0.5–3.0 wt.% Pt) was used as the photocatalyst and investigated towards the photocatalytic reduction of CO2. C-TiO2 was used as the source of titania because of its higher photocatalytic activity in comparison to pure titania [25–27]. The aim of this work is focused on the effect of Pt on the physicochemical properties of C-TiO2 and its photocatalytic activity towards the photocatalytic reduction of CO2.

2. Experimental

2.1. Co-photocatalyst preparation

The desired amount of H2PtCl6·6H2O solution (8 wt.% in H2O) to obtain catalyst loadings of 0.5–3.0 wt% was dissolved under stirring into 180 ml of distilled water. The solution was bubbled with N2 gas for 15 min to remove the dissolved oxygen. Thereafter, 2 g of C-TiO2 powder was added under vigorous stirring. The suspension was irradiated with a 300 W Xenon lamp (L.O.T. Oriel Quantum Design) equipped with a cut-off filter (λ > 395 nm), for 2 h. After 2 h, 20 ml methanol was subsequently added to the suspension and irradiation was continued for further 2 h. The suspension was then centrifugated (Biofuge stratus, Heraeus, 8500 rpm, 15 min) to collect the catalyst, which was washed with distilled water and acetone, and finally dried at 80 °C for 24 h under a reduced pressure of about 80 mbar.

2.2. Characterization

The crystalline phases of synthesized photocatalyst powders were examined by XRD. The XRD patterns were obtained on a Bruker D8 Advance using Cu Kα radiation in the range between 10 and 80° with a step size of 0.034°. The average crystallite size was estimated by the Scherrer equation. The Brunauer–Emmett–Teller (BET) surface area, pore volume and pore size of the powder specimen were calculated from the nitrogen adsorption–desorption isotherms at 77 K, using the Micromeritics-Gemini chemisorption system. The Pt loading was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Inc., USA). To dissolve the platinum, a microwave method (Discover SP–D, CEM, USA) was used. Calibration of the setup was done with a standard platinum solution (concentration of 1000 mg L–1, Sigma-Aldrich). The diffuse reflectance UV/Vis absorption spectra were measured using a UV–vis spectrophotometer equipped with an integrating sphere (LAMBDA 650 UV/Vis with 150 mm integrating sphere, Perkin Elmer, USA). Indirect band-gap energies were determined by plotting the Kubelka–Munk transformation of the original diffuse reflectance spectra vs. photon energy (Tauc’s plot): $F(R) = (1-R_\infty)^2/2R_\infty$, where $R_\infty$ is the measured reflectance ($R_\infty = R_{\text{sample}}/R_{\text{standard}}$).

Morphology of as-prepared photocatalysts was obtained by transmission electron microscopy (TEM) (TECNAI G220, FEI company, USA) operated at 200 kV, with LaB6 electron emitter and scanning electron microscopy (SEM) (Hitachi SEM type SU8030 microscope operated at an acceleration voltage of 10 kV and a probe current of 15 pA).

Photoelectrochemical measurements were carried out using a photovoltaic electric spectrometer coupled with potentiostat and 150 W Xe lamp (Instytut Fotonowy, Poland). The photocurrent responses were recorded using a three-electrode setup. A platinum wire and saturated Ag/AgCl were used as the counter and reference electrodes, respectively. The working electrode was prepared by depositing the photocatalyst powder onto an indium-tin oxide (ITO) foil and 0.1 M KNO3 solution was used as an electrolyte. The photocurrent spectra were recorded within the range of 280–470 nm with the step of 10 nm in the potential range of -0.2 to 1.0 V, step 0.1 V. Before the measurement, the cell with electrolyte was purged by argon to ensure an oxygen free environment. The argon purge was also kept constant during the whole measurement.

2.3. Photocatalytic reaction test

The photocatalytic reduction of CO2 proceeded in a homemade batch stainless-steel reactor (volume 357 ml) with a quartz window. As the light source, an 8 W Hg UV lamp (peak intensity at 254 nm wavelength; Ultra-Violet Products Inc.) was used, which was placed on top of the quartz window of the reactor (Fig. 1).

The reactor was filled with 0.1 g of the investigated photocatalyst and 100 ml of a 0.2 M NaOH solution. Before the start of the photocatalytic reaction, the reactor was tightly closed and purged with CO2. The pressure sensor (Greisinger, GMDS 3.5 BAE) was placed at the top of the reactor to control the experiment.

The gaseous samples were analyzed every two hours for a total reaction time of 14 h. The samples were taken with a gastight syringe (Hamilton Co., Reno, USA) and analyzed in a gas chromatograph (Shimadzu Tracer GC-2010Plus) equipped with a carrier discharge detector (BID) for its composition. Each experiment was repeated in order to ensure the reproducibility of the experimental data. The blank tests were also performed.
3. Results and discussion

3.1. Physico-chemical structure of co-photocatalyst

The XRD patterns of C-TiO₂ and Pt/C-TiO₂ photocatalysts are shown in Fig. 2. The crystalline phase of TiO₂ and Pt/TiO₂ are composed of anatase (JCPDS No. 21-1272) as indicated by the peaks emerging with (101), (004), (200), (211), (204), (220), and (215). In detail, C-TiO₂ contains anatase crystalline structure which by loading Pt nanoparticles remains accordingly. This result is in agreement with the literature [6, 17]. No peaks for Pt compounds were detected for catalysts with loadings of 0.5 till 1.5 wt.% Pt (Fig. 2), however as it is shown in Fig. 2, by loading 3.0 wt.% Pt, there is a small shoulder around 40° which is Pt (01-087-0647). We assume that in case of low Pt loading due to almost similar ionic radii of Ti⁴⁺ and Pt⁴⁺, Pt ions are replacing some Ti ions in the crystal lattice points [28, 29]. It is also possible that small dispersed Pt, maybe as a single atom species, is present on TiO₂ surface similar to the literature [8, 30].

In detail, the crystallite size, BET surface area, Pt loading, and band gap energy of investigate d photocatalysts are listed in Table 1.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Crystallite size (nm)</th>
<th>Surface area (S_{BET}) (m² g⁻¹)</th>
<th>Pt content from ICP-OES (wt.%)</th>
<th>Indirect band-gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-TiO₂</td>
<td>7.67</td>
<td>232</td>
<td>0</td>
<td>3.26</td>
</tr>
<tr>
<td>0.5 wt.% Pt/C-TiO₂</td>
<td>8.14</td>
<td>233</td>
<td>0.46</td>
<td>3.26</td>
</tr>
<tr>
<td>1.0 wt.% Pt/C-TiO₂</td>
<td>8.32</td>
<td>238</td>
<td>0.88</td>
<td>3.27</td>
</tr>
<tr>
<td>1.5 wt.% Pt/C-TiO₂</td>
<td>9.31</td>
<td>226</td>
<td>1.35</td>
<td>3.27</td>
</tr>
<tr>
<td>3.0 wt.% Pt/C-TiO₂</td>
<td>9.40</td>
<td>215</td>
<td>2.62</td>
<td>3.25</td>
</tr>
</tbody>
</table>

The specific surface area of photocatalysts varied from 215 m²/g to 238 m²/g. C-TiO₂ exhibited a specific surface area of 232 m²/g while the specific surface area increases to 238 m²/g with increasing amount of Pt to 1.0 wt.%. The specific surface area then decreases to 215 m²/g for 3.0 wt.% Pt loading. This behavior could be caused by the growth in particle size and may be caused by the deposition of Pt NPs within the pores of C-TiO₂ on the surface [6, 31].

The corresponding values of band-gap energies were determined by using the Tauc plot. The band-gap energy of all catalysts is about 3.3 eV. As expected, no significant changes are observed upon deposition of Pt [30].

The actual amount of Pt was measured by ICP –OES. As it can be seen, the Pt amount by photodeposition is very close to the nominal amount for 0.5–3.0 wt%. A loading efficiency of about 90% was obtained by photodeposition as a result of the higher BET surface area of the catalysts [8]. In contrast, lower BET surface usually results in lower loadings at similar conditions [32].

The morphology and structure of TiO₂ and 1.0 wt.% Pt/TiO₂ are shown in Fig. 3 (TEM images) and Fig. 4 (SEM images) which clearly show the different morphology and structure of C-TiO₂ and Pt/C-TiO₂ photocatalysts. It is essential to mention that the 1.0 wt.% Pt/TiO₂ photocatalyst was chosen as it shows the highest activity for photocatalytic CO₂ reduction.

From Fig. 3, the lattice fringes of C-TiO₂ nanoparticles are clear and confirm the crystal form of anatase for C-TiO₂. No Pt nanoparticles can be seen in the TEM images which can be due to the integration of ultrafine Pt nanoparticles inside the titania structure which is in accordance with the N₂ sorption results and XRD results (Fig. 2 and Table 1).

As shown in Fig. 4, the morphology of C-TiO₂ did not change by loading Pt nanoparticles, as it was expected. In contrast to TEM, where no Pt particles were found, some bigger Pt nanoparticles (agglomerates) on the surface of C-TiO₂ can be detected (white points which are marked with a red circle) because in SEM a bigger fraction of the sample is imaged. It is also obvious that Pt nanoparticles are not homogenously dispersed on the titania powders indeed part of the Pt nanoparticles are present on the surface and part are integrated inside the titania structure.

To get a better insight into the utilization of photons during irradiation, C-TiO₂ and Pt/C-TiO₂ catalysts were investigated by photoelectrochemical measurements that confirmed the generation of charge carriers after irradiation. Fig. 5 shows the dependence of generated photocurrent on wavelength and it is obvious that the number of charge carriers after irradiation. Fig. 5 shows the dependence of generated photocurrent on wavelength and it is obvious that the number of charge carriers increased. Lower loadings of platinum slightly increase the generation of charge carriers compared to pure C-TiO₂ which means that loading low amount of Pt inhibits the recombination rate of photogenerated electron-hole pairs (in case of 0.5 wt.% Pt/C-TiO₂ and 1.0 wt.% Pt/C-TiO₂) (Fig. 5).

3.2. Photocatalytic reduction of CO₂

After characterization of the catalysts, their photocatalytic activity towards the photocatalytic reduction of CO₂ was studied. Figs. 6 and 7 show the yields of products as a function of irradiation obtained for a time interval from 0 to 14 h. The main product is methane, however, carbon monoxide is also detected in the lower amount. Hydrogen is also formed as a product coming from the photocatalytic splitting of water. The product yields (μmol/μgcat.) were detected in this order: a) hydrogen (H₂), b) methane (CH₄) and c) carbon monoxide (CO).

As it is shown, for pure C-TiO₂, generation of H₂, methane, and CO occurred only after an irradiation time of 8 h. In the presence of Pt as co-catalyst, the reaction is significantly accelerated. In detail, by increasing the amount of Pt from 0.46 wt.% (0.5 wt.% Pt/C-TiO₂) to 0.88 wt.% (1.0 wt.% Pt/C-TiO₂), the yields of CH₄, CO and H₂ increase while the production rate of CH₄ intensively increases (Figs. 6 and 7).
This behavior could be due to the enhances the enrichment of electron density on the catalysts surface or on the other hand, as it is written in Table 1, loading of 0.88 wt.% Pt (1.0 wt.% Pt/C-TiO₂) causes increasing the crystallite size and the specific surface area to 8.32 nm and 238 m² g⁻¹, respectively. By increasing more Pt loading to 1.35 wt.% (1.5 wt.% Pt/C-TiO₂) the rate of CH₄ production decreases while the rate of CO and H₂ slightly decrease (Figs. 6 and 7). A similar trend is observed by loading 2.26 wt.% Pt (3.0 wt.% Pt/C-TiO₂), as by adding more amount Pt the rate of all reaction products decrease (Figs. 5 and 6). These results are in agreement with our previous work [8] and the results observed by Xie [33].

The highest yields of all products were achieved in the presence of 1 wt. % Pt/C-TiO₂. Among the Pt/C-TiO₂ samples, the order of yield of CH₄ production as the desired product is 1.0 wt.% < 1.5 wt.% < 0.5 wt.
% < 3 wt.%. The amount of CH4 is always higher than the amount of CO and Pt can work as an electron trap to provide more electrons for the CO2 reduction which is useful for CH4 production [6,17,34]. As it is shown in Fig. 6, the amount of CO and H2 are decreasing by time while the formation of methane increases with irradiation time in the presence of Pt/C-TiO2 photocatalysts.

In general, photocatalytic reduction of gaseous CO2 depends on two factors: the capability of the photocatalyst to adsorb CO2 and the efficiency of the transfer of the excited electrons. Thus the surface characteristics of the photocatalyst, such as surface charge and surface area, are very important parameters influencing the photocatalytic CO2 reduction activity [16]. C-TiO2 photocatalysts were used as titania source because M. Janus [35] investigated the adsorption of CO2 on bare TiO2 (anatase structure obtained from POLICE) and C, N-TiO2 which was calcined for 1 h at different temperatures (T = 100 to 600 °C). The results show that the C, N-TiO2 shows higher CO2 absorption in comparison to bare and commercial TiO2 (for example Degussa P-25). Also, a higher surface area is beneficial for CO2 adsorption and the 1.0 wt.% Pt/C-TiO2 photocatalyst can supply more adsorption site for CO2 molecules so that the concentration of localized CO2 on the TiO2 surface is higher and the photocatalytic reduction of CO2 is accelerated [14,36]. It is important to mention that high surface area photocatalysts with high porosity show higher photocatalytic activity [37–39]. In addition, the Zeta potential of C-TiO2 is more negative [40] compared to commercial P25 [41], which also is beneficial for CO2 adsorption. To provide more electrons for CO2 reduction, catalysts with a higher photocurrent response might be beneficial because of better utilization of the photons. As shown in Fig. 5, the photocurrent densities of 0.5 wt.% Pt/C-TiO2 and 1.0 wt.% Pt/C-TiO2 are higher than C-TiO2 showing that their efficiency for electron-hole pair separation is higher.

It is worth to mention that the photocatalytic reduction of CO2 is a very complex reaction with very low yields and the development of efficient photocatalysts for CO2 conversion under solar irradiation still remains in the developing phase. In fact, photocatalytic reduction of CO2 is always with the parallel water decomposition reaction which competing with CO2 reduction. The redox potentials for CO2 reduction is close to that of H2O to H2 and activation of H2O is generally being much easier than CO2, it makes it so that the photocatalysts tends to reduce H2O to H2. Therefore, a suitable catalyst and reaction condition (such as irradiation source, CO2 concentration, amount of H2O, reactor geometry, light position and ...) can considered as major challenges in photocatalytic CO2 reduction. In addition, the economically and environment-friendly reduction of CO2 to value added chemicals is highly desired which is possible if renewable energy such as solar energy is used as an energy source.

4. Conclusion

Pt/C-TiO2 photocatalysts with different Pt amount (0.5–3.0 wt.%)

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**Fig. 5.** The dependence of photocurrent on wavelength. Measured at 1 V external potential.

**Fig. 6.** Time dependence of yields of H2, CO and CH4 after 14 h of irradiation in the presence of investigated photocatalysts (amount of photocatalyst = 0.1 g).
C-TiO2. CH4, CO, and H2 were detected as the main reaction products. The photocatalytic activity of C-TiO2 increases by loading Pt, whereby

were synthesized by the photodeposition method and tested towards the photocatalytic reduction of CO2. The crystallite size of C-TiO2 increases by Pt loading while the surface area decreases. The actual separation is optimized.

Yields of products (umol/gcat.)

Fig. 7. Comparisons of proportion of reaction products (after 14 h of irradiation).

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References

were synthesized by the photodeposition method and tested towards the photocatalytic reduction of CO2. The crystallite size of C-TiO2 increases by Pt loading while the surface area decreases. The actual amount of Pt was measured by ICP-OES and is only slightly lower than the nominal value, which can be attributed to the higher surface area of C-TiO2. CH4, CO, and H2 were detected as the main reaction products. The photocatalytic activity of C-TiO2 increases by loading Pt, whereby the amount of Pt is crucial for the performance of the photocatalyst. The highest yields for all products were achieved for an actual Pt loading of 0.88 wt.%, where utilization of photo-induced electrons via charge separation is optimized.


