



# PHYSICAL CHEMISTRY 2016

*13<sup>th</sup> International Conference on  
Fundamental and Applied Aspects of  
Physical Chemistry*

*Proceedings  
Volume I*

**BELGRADE**  
**September 26 - 30, 2016**

**ISBN 978-86-82475-34-7**

**Title:** Physical Chemistry 2016 (Proceedings)

**Editors:** Željko Čupić and Slobodan Anić

**Published by:** Society of Physical Chemists of Serbia, Studentski trg 12-16, 11158, Belgrade, Serbia.

**Publisher:** Society of Physical Chemists of Serbia

**For Publisher:** S. Anić, President of Society of Physical Chemists of Serbia

**Printed by:** "Jovan", Printing and Publishing Company; 200 Copies.

**Number of pages:** 6+502; Format B5; printing finished in September 2016

Text and Layout: "Jovan"

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*200 - Copy printing*



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*13<sup>th</sup> International Conference on  
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*Organized by*

*The Society of Physical Chemists of  
Serbia*

*in co-operation with*

*Institute of Catalysis Bulgarian Academy of Sciences*

*and*

*Boreskov Institute of Catalysis Siberian Branch of  
Russian Academy of Sciences*

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## ONE-STEP HYDROTHERMAL SYNTHESIS OF PHOTOCATALYTICALLY ACTIVE TiO<sub>2</sub>/CARBON COMPOSITE

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### ABSTRACT

TiO<sub>2</sub>/carbon composite (TiO<sub>2</sub>/HTC), synthesized by hydrothermal carbonization, was characterized by thermogravimetric analysis, nitrogen adsorption-desorption isotherms and X-ray diffraction. The possibility of using TiO<sub>2</sub>/HTC as photocatalysts for UV and visible light assisted degradation of methylene blue in aqueous solution was examined. It was found that carbon presence in TiO<sub>2</sub>/HTC leads to the higher porosity and increase in the share of photocatalytically active anatase phase. Compared to the hydrothermally synthesized TiO<sub>2</sub>, TiO<sub>2</sub>/HTC showed the superior photocatalytic activity under UV irradiation. In addition, TiO<sub>2</sub>/HTC show high recycling ability with degradation ratio of methylene blue higher than 81 % after five cycles. Also, TiO<sub>2</sub>/HTC is expected to be a promising candidate for photocatalytic processes using visible light.

### INTRODUCTION

Photocatalytic processes, in the presence of different photocatalysts, have proven to be efficient methods for removal of organic pollutants (drugs, pesticides and organic dyes). Titanium dioxide (TiO<sub>2</sub>) is one of the most effective and the most commonly used photocatalysts. Also, highly reactive photocatalysts can be obtained by combining titanium dioxide with different carbon materials, as a catalysts carrier [1]. In this work photocatalytic activity of hydrothermally synthesized TiO<sub>2</sub>/carbon composite was examined in the process of photocatalytic degradation of methylene blue (MB) under UV and visible irradiation, and compared to photocatalytic activity of hydrothermally synthesized TiO<sub>2</sub>. The possibility of reusing TiO<sub>2</sub>/carbon composite was examined through the determination of photocatalytic activity after each of five cycles.

## EXPERIMENTAL

Hydrothermal synthesis of TiO<sub>2</sub>/carbon composite (TiO<sub>2</sub>/HTC) was carried out using titanium isopropoxide and glucose solution to achieve Ti/C molar ratio of 0.30. TiO<sub>2</sub> – hydrothermal (TiO<sub>2</sub> – hyd) was obtained by similar procedure, using water instead of glucose solution.

The thermogravimetric (TG) analysis was performed from room temperature to 800 °C in O<sub>2</sub> atmosphere using SDT Q600 instrument (TA Instruments). Nitrogen adsorption–desorption isotherms were determined using a Micromeritics ASAP 2020 instrument. From obtained data, specific surface area (S<sub>BET</sub>), pore size distribution and volume of the mesopores (V<sub>meso</sub>) was calculated. XRD spectra were recorded in the range of 2θ of 20° – 60° with a scan speed 1° C/min<sup>1</sup> using a Philips PW1710 diffractometer with CuKα radiation. Anatase and rutile phase content were determined [2], and grain sizes were calculated by Debye–Scherrer equation.

Photocatalytic experiments were performed at room temperature with 1 g/dm<sup>3</sup> of TiO<sub>2</sub>/HTC and the initial concentration of MB was 10 mg/dm<sup>3</sup>. The suspension was magnetically stirred in the dark for 60 min to establish the adsorption/desorption equilibrium, and then exposed to the either UV or visible irradiation. The TiO<sub>2</sub>/HTC reuse was examined through the five cycles. Concentration of MB was measured using visible spectrophotometer (Specol, Carl-Zeiss, Jena), by measuring absorbance at 675 nm.

## RESULTS AND DISCUSSION

Thermogravimetric analysis showed that TiO<sub>2</sub>/HTC contained 11.02 wt.% of carbon. Textural properties TiO<sub>2</sub> – hydrothermal and TiO<sub>2</sub>/HTC, summarized in Table 1, show that carbon present in TiO<sub>2</sub>/HTC leads to the decrease of average pore diameter and V<sub>meso</sub> and to the increase in S<sub>BET</sub> and V<sub>micro</sub>. XRD patterns (Fig. 1) of TiO<sub>2</sub> – hydrothermal and TiO<sub>2</sub>/HTC show characteristic peaks for the anatase (101) (2θ = 25.6°) and rutile (110) (2θ = 27.7°) phase.

**Table 1.** Textural properties of examined samples

Sample	S <sub>BET</sub> , m <sup>2</sup> /g	V <sub>meso</sub> , cm <sup>3</sup> /g	D <sub>av</sub> <sup>*</sup> , nm
TiO <sub>2</sub> -hyd	49.63	0.2375	17.22
TiO <sub>2</sub> /HTC	174.08	0.1995	3.78

D<sub>av</sub><sup>\*</sup> - Average pore diameter

It can be observed that presence of carbon in TiO<sub>2</sub>/HTC induces increase of peak intensity of the anatase phase, while peak intensity of the rutile phase decreases. The observed increase of anatase phase is confirmed by the results presented in

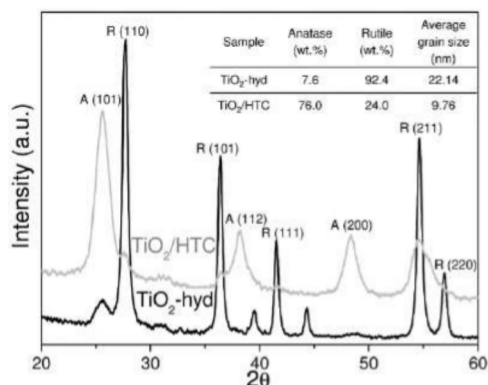
Fig. 1. The average grain size decrease with carbon presence can be the consequence of inhibitory effect of amorphous carbon on grain growth of TiO<sub>2</sub>. Grain size decrease, accompanied with increase in BET surface area,

is in very good agreement with the values of average pore diameters, indicating that pores measured are most likely interparticle spaces.

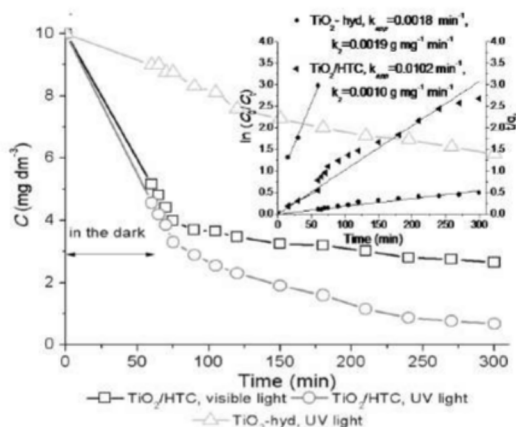
The process of removing MB in the presence of  $\text{TiO}_2/\text{HTC}$  (shown in Fig. 2) takes place in two phases. The first phase involves the removal of MB by adsorption in the dark, while the second phase represents photocatalytic degradation of MB under UV or visible irradiation. As it can be observed (Fig. 2),  $\text{TiO}_2/\text{HTC}$  showed superior photocatalytic activity in the overall process of MB removal.

Carbon species present in  $\text{TiO}_2/\text{HTC}$  can provide more active sites and adsorb more reactive species due to large surface area and pore volume, which causes the enhanced photocatalytic activity. Additionally, high photocatalytic activity of  $\text{TiO}_2/\text{HTC}$  can be explained by the presence of photocatalytically active anatase phase and the ratio of anatase and rutile phase (Fig. 1) which is nearly identical with the one in photocatalytically active Degussa P25.

Obtained results (Fig. 2) showed that UV irradiation induces a higher decrease of MB concentration than the visible light. Nevertheless, concentration of MB was decreased for about 70 % in the presence of  $\text{TiO}_2/\text{HTC}$  and visible irradiation. The regeneration and recycling of  $\text{TiO}_2$  photocatalysts is one of key steps in practical applications of this heterogeneous photocatalysis in water purification. Therefore, an examination of the photocatalytic activity of the recycled  $\text{TiO}_2/\text{HTC}$  was carried out under UV light irradiation. The results are presented in Fig. 3.



**Figure 1.** XRD patterns of obtained samples



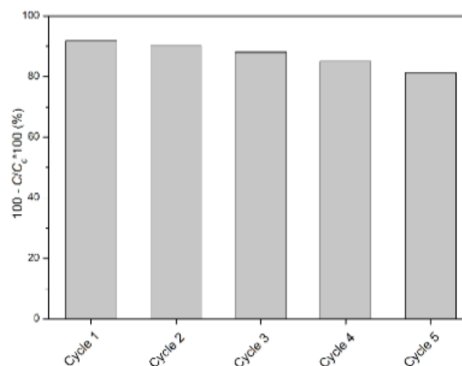
**Figure 2.** MB removal in the presence of  $\text{TiO}_2/\text{HTC}$  under the UV and visible light with embedded kinetics graph

The degradation rate in first cycle was 91.9 %, while after five cycles degradation rate was decreased to 81.2 %.

### CONCLUSION

Photocatalytically active  $\text{TiO}_2/\text{carbon}$  composite was obtained by hydrothermal carbonization, using titanium isopropoxide and glucose as a titanium and carbon precursors, respectively. It was found that photocatalytic activity increases with addition of glucose precursor solution, due to the increase in the share of photocatalytically active anatase phase in obtained  $\text{TiO}_2/\text{carbon}$  composite. Also,

carbon presence in  $\text{TiO}_2/\text{HTC}$  leads to the higher surface area, which synergistically improved the photocatalytic activity by enhancing the adsorption of the organic pollutants. Consequently,  $\text{TiO}_2/\text{HTC}$  showed the superior photocatalytic activity toward methylene blue, under UV irradiation and satisfactory photocatalytic activity under the visible light. In addition,  $\text{TiO}_2/\text{HTC}$  could be used for multiple degradation cycles with slight decrease in photocatalytic activity, as well as a promising candidate for photocatalytic processes using visible light.



**Figure 3.** Recycle of the  $\text{TiO}_2/\text{HTC}_4$  composite for the degradation of MB (initial concentration of MB  $10 \text{ mg dm}^{-3}$ , 50 ml)

### Acknowledgement

This work was supported by Ministry of Education, Science and Technological Development Republic of Serbia through the project No 172007 and No 45006.

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544(082)  
66.017/.018(082)  
502/504(082)  
663/664:658.56(082)  
615.31:547(082)

INTERNATIONAL Conference on Fundamental and Applied Aspects of Physical Chemistry (13 ; 2016 ; Beograd)

Physical Chemistry 2016 : proceedings. Vol. 2 / 13th International Conference on Fundamental and Applied Aspects of Physical Chemistry, Belgrade, 26-30 September 2016 ; [editors Željko Čupić and Slobodan Anić]. - Belgrade : Society of Physical Chemists of Serbia, 2016 (Belgrade : Jovan). - IV, 507-930 str. : ilustr. ; 24 cm

Tiraž 200. - Bibliografija uz svaki rad.

ISBN 978-86-82475-33-0

1. Society of Physical Chemists of Serbia (Beograd)

а) Физичка хемија - Зборници б) Наука о материјалима - Зборници с) Животна средина - Заштита - Зборници д) Животне намирнице - Контрола квалитета - Зборници е) Фармацеутска хемија - Зборници  
COBISS.SR-ID 225802508

08.09.2016

