

ON-LINE MEASUREMENT OF PHOTOCATALYTIC ACTIVITY OF POWDERED SAMPLES

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Abstract

A method for on-line measurement of photocatalytic activity of powdered samples by UV-Vis spectrometry is demonstrated. It enables photocatalytic reaction to be monitored directly in the cuvette which also serves as photocatalytic reactor. The cuvette is placed inside a double beam UV-Vis spectrometer and photocatalytic reaction is driven by LED diode mounted on homemade cuvette holder housing. Diodes can be easily changed, enable photocatalytic reaction to be performed under light of various wavelengths which is beneficial when evaluating visible-light photocatalytic activity. Another advantage of the method presented lies in the simultaneous degradation of model dye solution and monitoring of reaction kinetics, which avoid sampling during the photocatalytic reaction. Measurement of photocatalytic activity is demonstrated on degradation reaction of Methylene blue 2B as the model dye by Zn_2TiO_4 powder under the UV ($\lambda \sim 365$ nm), and the visible light ($\lambda \sim 400$ nm) and ($\lambda \sim 425$ nm) irradiation.

Keywords: Photocatalysis, semiconductor, LED diode, photocatalytic reactor, powder material, on-line measurement

1. INTRODUCTION

Photocatalysis is a dynamic field within photochemistry with many current and potential applications. The principle of photocatalytic reaction is based on the absorption of photons with an energy equal or greater than the semiconductor's band gap, which results in a formation of an electron/hole pair that may actively participate in the redox reactions on the semiconductor surface. These processes underpin a broad range of commercial applications, such as self-cleaning glass or tiles, concrete, paints, photo-induced sterile surface, water or air purification [1]. Because of huge innovation potential, the number of papers devoted to semiconductor photocatalysis increases exponentially which in turn leads to an increased demand for unification of testing methods to make results obtained by different research groups comparable. In fact, a survey of existing literature clearly shows diversity in experimental methods used for testing of photocatalytic activity, which severely complicate the analysis of data. For example, different dyes, their concentration, volume, the amount of photocatalysts, an irradiation source, or procedure of measurement are used when the photocatalytic activity of powdered sample is determined by degradation of model pollutant. An overview of ISO standards given by Mills et al provides a comprehensive and critical insight into the testing methods related to the evaluation of photocatalytic active materials. The vast majority of these standards has been introduced only recently and there is still vivid discussion concerning their pros and cons [2, 3]. In order to make a contribution to the development of the standardized procedure for measurement and evaluation of photocatalytic activity of powdered samples, we propose the concept which enables online monitoring of photocatalytic reaction during the course of pollutant degradation. In the experimental setup presented, the cuvette placed in the spectrometer serves as the photocatalytic reactor and the rate of degradation of model dye can be measured online without the need of sampling. The photocatalytic reaction is driven by a LED diode mounted on homemade cuvette holder housing. The smart design of cuvette housing allows easy replacement of diodes, which enable the photocatalytic reaction to be performed under irradiation in a narrow interval of wavelength, covering UV and the whole visible light region. [4, 5] The performance of the proposed

experimental arrangement is demonstrated by degradation of Methyl violet 2B over Zinc titanate (Zn_2TiO_4) under the UV ($\lambda \sim 365$ nm), and the visible light ($\lambda \sim 400$ nm) and ($\lambda \sim 425$ nm) irradiation [6].

2. EXPERIMENTAL

2.1. Device construction

LED diode mounted on homemade cuvette holder housing is shown in **Figure 1**. The simple construction and portability of the cuvette holder housing make it suitable for used in a various spectrometer, which allows measurement of absorption spectra in the UV-VIS range [4].

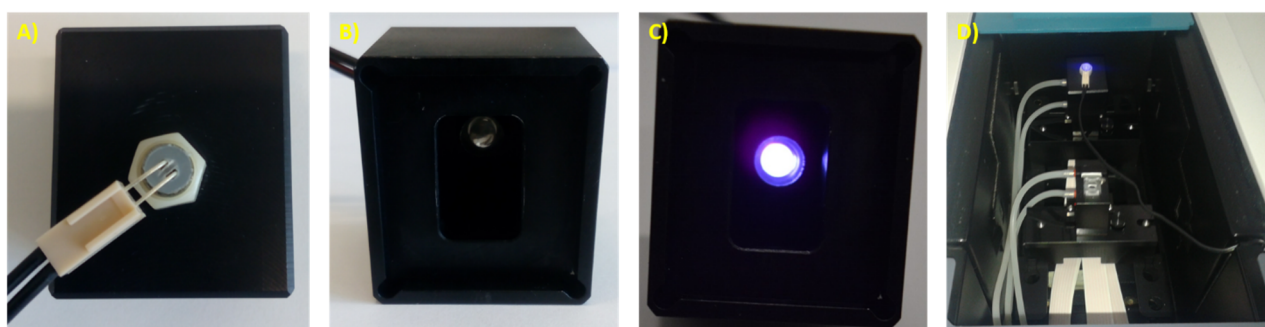


Figure 1 A), B) and C) the holder with the UV diode and D) LED diode mounted on homemade cuvette holder housing inside the chamber of the UV-Vis spectrometer Varian Cary 3

Emission maxima of commercially available diodes which can be used as irradiation source are shown in **Figure 2**. It can be seen, that both UV and the visible light region is covered.

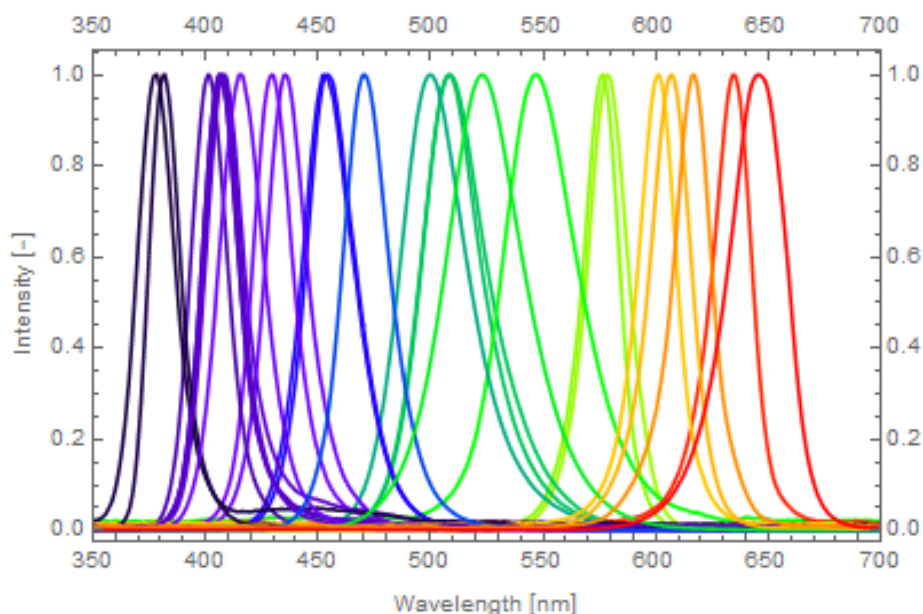


Figure 2 Emission maxima of commercially available diodes

2.2. Photocatalysts preparation

Zinc titanate (Zn_2TiO_4) was prepared by using cotton wool as a biotemplate. In the first step, 3 g of cotton wool was impregnated by 5 mL of the solution containing 1.2 mL of titanium (IV) butoxide (purity $\geq 97.0\%$, supplied by SIGMA-ALDRICH) in 30 mL of isopropylalcohol (purity $\geq 99.7\%$, supplied by mikroCHEM) and left dry in

the fume hood. Zinc cations were introduced into Ti-rich cotton wool in the second step. The solution consisted of 0.6 g of ZnO powder dissolved in 50 mL of ammonia (26% aqueous solution, supplied by mikroCHEM) and 4 mL of hydrogen dioxide (30% aqueous solution, supplied by PENTA) was applied at the same volume as Ti precursor (5 mL). Finally, dried impregnated cotton wool biotemplate was calcined at 500 °C for two hours in the muffle furnace in air atmosphere.

2.3. Assessment of photocatalytic activity

The photocatalytic activity of prepared powder was evaluated by means of degradation of Methyl Violet 2B at the concentration 3.5 mg.L⁻¹. The suspension containing 10 mg of the photocatalysts in 3 mL of dye was prepared directly in the quartz glass cuvette and placed inside the UV-VIS spectrometer Varian Cary 300. Prior the photocatalytic experiment, the suspension was left in the dark for 1 hour to reach adsorption/desorption equilibrium. After that, the LED diode was switched on and the degradation of model dye was monitored in 30 minutes intervals without the need of sampling. The temperature was held at 25 °C by Dual Cell Peltier Accessory during the course of degradation reaction. For illustration, photocatalytic activity of Zn₂TiO₄ was performed under the UV ($\lambda \sim 365$ nm) and visible light ($\lambda \sim 425$ nm) irradiation by LED (Roithner LaserTechnik, Austria) with wavelengths $\lambda \sim 365$ nm (XSL-365-5E) in the UV region, $\lambda \sim 400$ nm (VL400-5-15) and $\lambda \sim 425$ nm (VL425-5-15) in visible light region.

2.4. Sample characterization

The crystalline phase structures of prepared materials were identified by using X-ray diffractometer MiniFlex 600 (RIGAKU, Japan) equipped with Co X-ray source. Operation voltage and current were 40 kV and 15 mA, respectively. Almost all peaks in the diffractogram in **Figure 3** can be unambiguously assigned to the Zn₂TiO₄ spinel phase. The only peak that cannot be attributed to the Zn₂TiO₄ phase is the small peak at 29 °2 θ . Most likely, this is a manifestation of carbonaceous rests of the cotton wool in the prepared material.

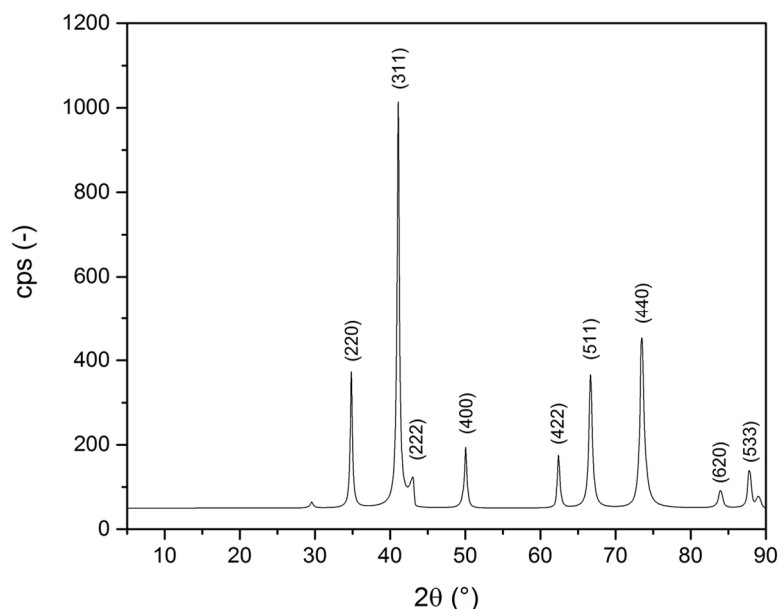


Figure 3 X-ray diffractogram of the prepared powder

The morphology of biotemplated Zn₂TiO₄ powder is shown in **Figure 4**. Low magnification image in **Figure 4a** shows that powder consists of coarse particles up to 50 microns. At closer inspection, these particles retain morphology of cotton wool fibers (**Figure 4b**). High resolution image in **Figure 4c** further reveals, that individual particles are formed by nanoparticles with the dimension of about 50 nm in diameter.

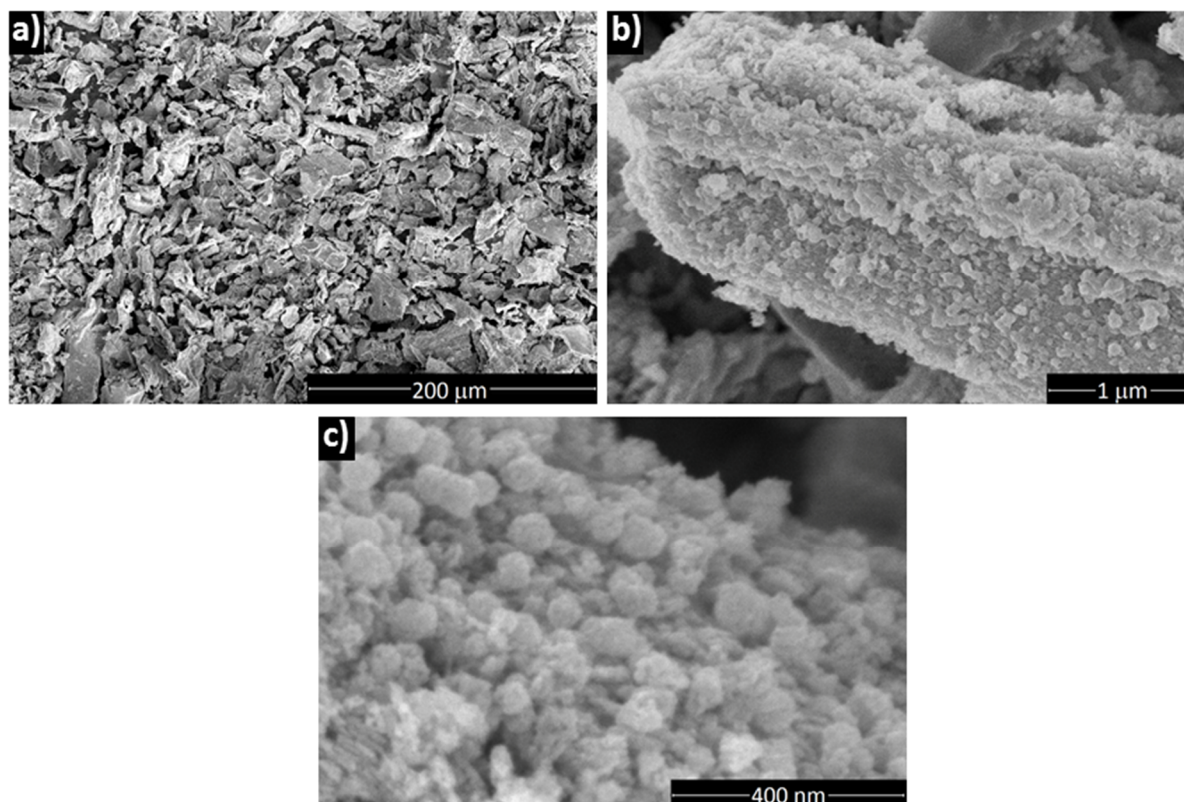


Figure 4 SEM of the prepared powder

2.5. Photocatalytic measurement

Photocatalytic activities of biotemplated Zn_2TiO_4 powder under UV and visible light irradiation are shown in **Figure 5**. The dramatic decrease of photocatalytic activity with increase of LED irradiation wavelength maxima is evident at the first sight. Degradation reaction proceed quickly under UV light irradiation (365 nm) with apparent rate constant k 0.015 min^{-1} (indicated by full black circles) and complete degradation of model pollutant was achieved after 180 min. The shift in maxima wavelength irradiation to 400 and 425 nm resulted in significant decrease of the rate constant of photocatalytic driven reaction to 0.0013 min^{-1} (indicated by a half-solid circle) and 0.0006 min^{-1} (indicated by an empty circle), respectively.

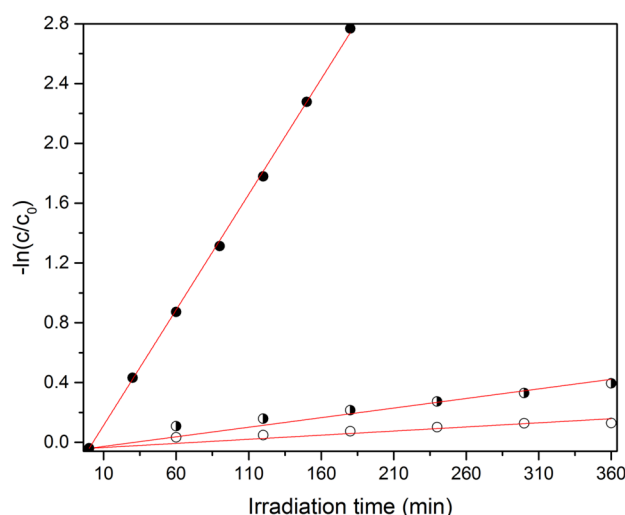


Figure 5 Evaluation of photocatalytic experiment of prepared powdered samples

CONCLUSION

A method suitable for the online measurement of the photocatalytic activity of the powdered samples in commercial spectrometers is demonstrated. Cuvette placed in UV-vis spectrometer acts simultaneously as the photocatalytic reactor and measurement cell, which functions enable on line measurement of photocatalytic reaction during the course of degradation. Therefore, no sampling during the photocatalytic reaction is necessary. Photocatalysis is driven by a LED diode mounted on a homemade cuvette holder housing. Diodes can be easily changed and the reaction can be performed under various wavelength irradiation. This is beneficial especially for evaluation of photocatalytic activity in a close vicinity of semiconductor band gap. The functionality of the method is demonstrated on the degradation of Methyl Violet 2B over Zn₂TiO₄ powder under irradiation by the diode with different maxima wavelength in the UV light region ($\lambda \sim 365$ nm) and visible light region ($\lambda \sim 400$ nm and ~ 425 nm). Further research will be focused on quantification of photon fluxes into the sample delivered by each kind of used LEDs.

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