EFFECTS OF ATMOSPHERIC PRESSURE AIR PLASMA ON PHOTOCATALYTIC ACTIVITY OF TiO_2 NANOFIBERS

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TiO_2 based materials are used in various applications, such as self-cleaning surfaces, energy storage and conversion devices, solar cells or air and water purification systems. For purification purposes, it is important to find ways to enhance photocatalytic activity of the semiconductor. In this work, we focused on increasing activity of electrospun TiO_2 nanofibers with atmospheric pressure air plasma generated by Diffuse coplanar surface barrier discharge (DCSBD).

1. Introduction

In recent years, photocatalysts are widely studied, mostly for their use in energy production and storage[1], and in purification systems[2]. TiO_2 is arguably the most promising photocatalysts for several reasons: it is durable, biologically and chemically inert, non-toxic, easy to produce, transparent to visible light and strong oxidizing abilities.

The most important requirement for the photocatalyst to decompose organic compounds is that the redox potential of H_2O/*OH lies within the band gap of this semiconductor. Upon absorption of UV light corresponding to TiO_2 band gap (varying for different crystal phases), electron-hole pairs separate in the material. After the separation, the charge carriers then diffuse into the material, where most of them recombine, and the energy is converted to either photons or phonons. Only those, that reach the surface of the material can drive the redox reactions. Using 1D structures such as fibers or tubes increases active reaction surface and limits diffusion in other two dimensions, which leads to improved photocatalytic effectivity.

In the past, several studies have shown enhancing effects of plasma on photocatalytic activity of titanium dioxide. Kong et al. used argon plasma etching to introduce surface defects to the nanosheets, remove organic contaminants and create porous structure. Oxygen vacancies and Ti^{3+} defects were also formed on the surface, which lead to narrowing of the band gap, broadening the light absorption spectrum.[3]

In our work, nanofibers were used because of several advantages they have as a photocatalyst – big surface area to volume ratio, limited diffusion, and contrary to nanoparticles, can form a self-standing structure. The goal was to examine the possibility of improving photocatalytic activity of TiO_2 nanofibers using low-temperature atmospheric pressure air plasma treatment.

2. Materials and methods

For our experiments, we used TTIP/PVP (tetraisopropoxide/polyvinylpyrrolidone) (80:20 ratio) nanofiber mats prepared by electrospinning using Nanospider™.

In the first step, as-spun fibers were exposed to DCSBD plasma generated in air at atmospheric pressure, using 15 kHz high voltage power source operating at 400 W for 30 minutes. After the plasma treatment, the nanofiber mat was calcinated at 500°C for 2 hours with rapid heating rate 22.5°C/min.

Photocatalytic activity was measured by the rate of decomposition of methylene blue in 10mg/l solution under the UV light. Quantitative values were obtained by absorption measurement at λ=664nm.

We compared the photocatalytic activity of plasma treated and thermally calcinated fibers with fibers calcinated under the same conditions without plasma treatment and for reference, we also measured absorbance of methylene blue solution without photocatalyst sample.

The WDX analysis of the treated samples was performed to compare changes in chemical composition. Under normal circumstances, nanofibers are relatively thin (under 1 μm) to be examined by WDX with interaction volume reaching several μm into the material. For this reason, the samples were homogenized using laboratory mortar and pestle, creating nanopowder. Another reason for this was natural microscopic non-homogeneity of as-spun fibers. After homogenisation, high pressure was applied to create small solid tablets. By this, the issues with non-homogeneity and small interaction volume were resolved, the ability to analyse the changes on the surface of the fibers was lost in the process, which might be important for the purification application as well. For this, another diagnostic method will need to be used.

3. Results and discussion

WDX analysis (**Error! Reference source not found.**) showed the lower content of carbon residue and proportional higher ratio of titanium in plasma treated TiO_2 fibers compared to nontreated. In previous research it was found, that DCSBD plasma during plasma assisted calcination can help decomposition of organic part of TTIP/PVP before thermal treatment and the final product after sintering contains less carbon compounds.[4] Additionally, plasma treatment primarily affects the surface of fibers. Measurements of the homogenized samples provide information about chemical composition of volume of material.

	C (at%)	O (at%)	N (at%)	Ti (at%)
Nontreated	10.67 ± 0.13	69.11 ± 0.57	8.91 ± 0.46	11.31 ± 0.37
Plasma treated	10.01 ± 0.12	68.84 ± 0.57	9.05 ± 0.46	12.10 ± 0.38

Table 1 Stoichiometric ratios of homogenized non-treated and plasma treated TiO_2 nanofibers measured by WDS

In our experiments, we observed improvement in photocatalytic activity of plasma treated TiO_2 nanofibers represented by increased rate of photocatalytic methylene blue decomposition under UV irradiation.

The effect of plasma pre-treatment on photocatalytic activity of prepared TiO_2 fibers measured by decomposition of MB solution under UV irradiation showed more effective MB removal when sample was treated by plasma before sintering. The plasma pre-treatment caused significantly higher rate of MB decomposition. After 3 minutes, the absorbance of MB solution with plasma pre-treatment sample was comparable with non-treated sample, however, after 6, 12 and 18 minutes of UV irradiation, the absorbance of MB solution was by 2.6, 10.3 and 15.1 % (respectively) lower compared to untreated sample.

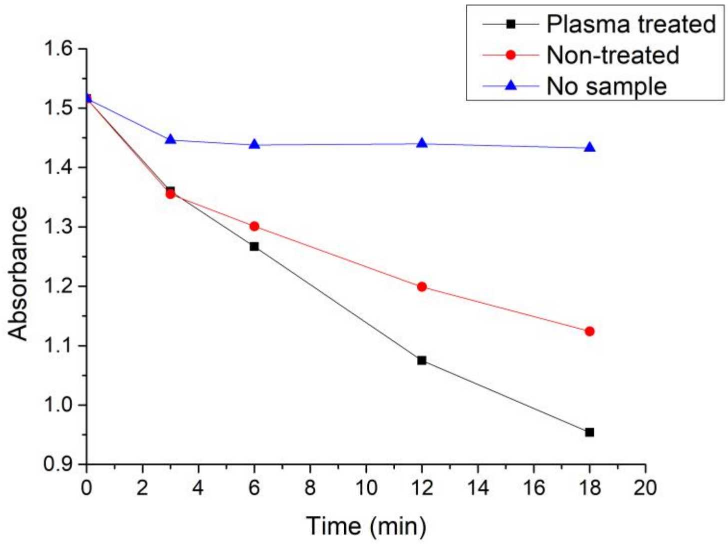

Figure 1: Absorbance of methylene blue solution at λ=664nm vs. irradiation time

4. Conclusion

In this work, the influence of plasma pre-treatment in preparation of TiO_2 fibers by the plasma assisted calcination was studied in term of effect on properties, which are important for application of mentioned material. TiO_2 is known for its photocatalytic activity and we found out, that the pre-treatment of initial TTIP/PVP fibers not only reduce the organic part of these hybrid fibers proved by previous research, but DCSBD plasma treatment also causes better photocatalytic activity of this material by significantly higher rate of methylene blue solution decomposition with presence of samples treated by plasma compared to untreated sample. This effect indicated higher decomposition of organics and is very prospective in application for water and air purification, where TiO_2 is one of the most studied material.

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5. References

[1] D.P. Opra, S. V. Gnedenkov, and S.L. Sinebryukhov, *J. Power Sources*, **442**, 227225 (2019).
[2] S. Riaz and S.J. Park, *J. Ind. Eng. Chem.*, **84**, 23–41 (2020).
[3] X. Kong, Y. Xu, Z. Cui, Z. Li, Y. Liang, Z. Gao, S. Zhu, and X. Yang, *Appl. Catal. B Environ.*, **230**, 11–17 (2018).
[4] V. Medvecká, D. Kováčik, A. Zahoranová, and M. Černák, *Appl. Surf. Sci.*, **428**, 609–615 (2018).