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Investigations on the photocatalytic activity of sulfur doped TiO_2

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Introduction

The intensive development of industry caused a rapid increase in environmental pollution. Water pollution due, among others, to the presence of dyes originating from industry is a global problem facing humans worldwide. One of the effective methods of wastewater treatment is heterogeneous photocatalysis which belongs to Advanced Oxidation Processes. For photocatalytic degradation of dyes semiconductors are often applied. The most commonly used photocatalyst is titanium dioxide. It is characterized by low cost, non-toxicity, chemical stability and long durability. TiO_2 has a wide band gap (3.2 eV for anatase and 3.0 for rutile) and therefore exhibits a large photocatalytic activity at the UV radiation. The light emitted by the Sun contains mainly radiation in the infrared (~52%) and visible ranges (Vis ~43%) and only ~5% is UV radiation. Therefore, for the effective exploitation of the solar energy, it is necessary to obtain a photocatalyst with a large activity at the visible light. Doping TiO_2 with small amounts of "foreign" chemical elements is the most frequently applied method to obtain a titanium catalyst active in the visible light.

Aim

The aim of research was to obtain sulfur doped TiO_2 photocatalysts that are active in the visible light area using the mechanochemical method.

Methods

3 samples were prepared by a mechanochemical synthesis (MChS) in the planetary mill. The samples contained the same initial materials TiO_2 and S (0.1, 1 and 10 % wt.). They were designated T0.1S, T1S and T10S. Part of these samples was additionally heated at 400°C for two hours (calcination stage) to obtain the next 3 samples T0.1S_C, T1S_C and T10S_C. The obtained photocatalysts were studied based on the Safranine T (ST) decomposition rate under Vis light (24 hours). The initial concentration of the dye was $C_0 = 1 * 10^{-5}$ mol /L. The concentration of ST solution was tested using a UV-Vis spectrophotometer. In order to determine the structural parameters of the obtained samples, the method of low-temperature nitrogen adsorption/desorption (77.4 K) was used. The morphology of the samples was analyzed using a scanning electron microscope (SEM).

S (0.1, 1 i 10 % wt.)

TiO_2

initial mixing ***300 rpm, 15 min***

MChS

700 rpm, 30 min

1 **T0,1S** 2 **T1S** 3 **T10S**

calcination 400°C, 2h

4 **T0,1S_C** 5 **T1S_C** 6 **T10S_C**

Tab. 1. The structural parameters of photocatalysts from the N_2 adsorption/desorption data.

Sample	S_{BET} [m²/g]	V_p [cm³/g]	R_{av} [nm]
T0.1S	7.43	0.0430	11.56
T1S	6.93	0.0396	11.44
T10S	5.41	0.0262	9.69
T0.1S_C	7.75	0.0416	10.74
T1S_C	6.58	0.0326	9.89
T10S_C	7.03	0.0320	9.11

S_{BET} – the specific surface area, V_p – the total pore volume, R_{av} – the average pore radius,

Results

Tab. 2. The degradation stage of ST under Vis light in the presence of the initial and obtained materials.

Sample	Degree of decolorization [%]	
	5h	24h
T0.1S	34.4	90.3
T1S	32.7	99.9
T10S	23.6	100
T0.1S_C	63.4	76.0
T1S_C	34.9	57.9
T10S_C	39.4	64.3
iniTiO_2	14.5	19.3

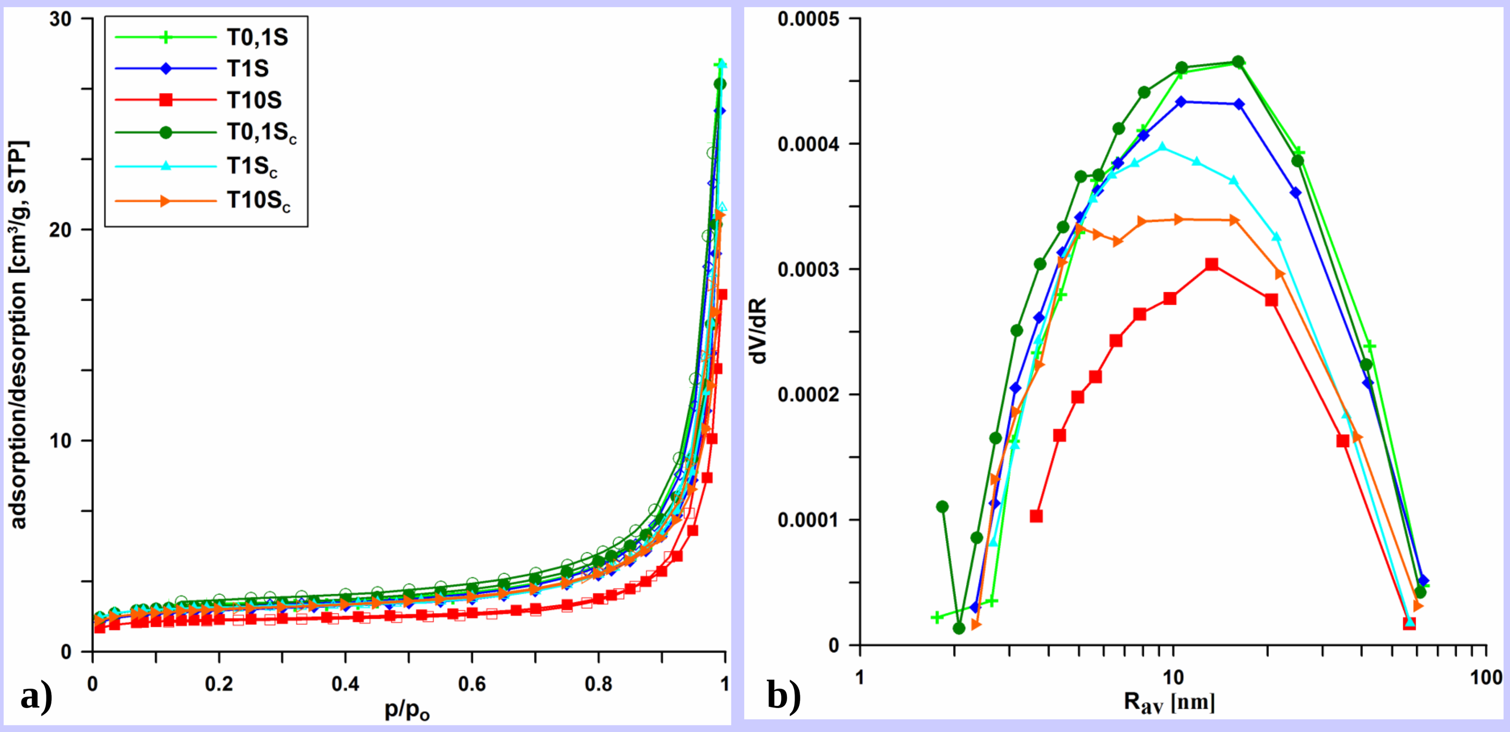

Fig. 1. The low temperature adsorption /desorption isotherms **a)** and the functions of the pore volume distribution of the obtained materials **b)**.

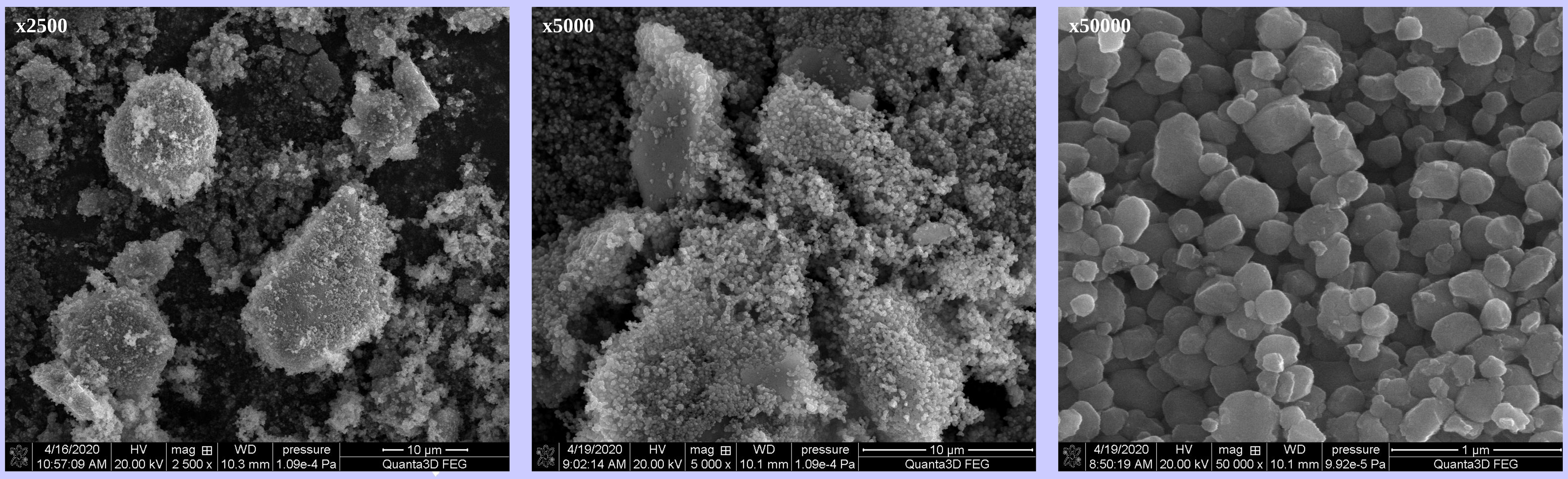

Fig. 2. The SEM images of the T10S sample.

Conclusions

- **mechanochemical synthesis enables an effective preparation of materials, including those with photocatalytic properties**
- **doping of TiO_2 with sulfur increased the photocatalytic activity of the obtained materials in the visible light region compared to the TiO_2**
- **larger content of S in the composite caused the increasing photocatalytic activity**
- **calcination stage did not improve the photocatalytic activity of the materials and did not cause significant changes in the porous structure**
- **the course of adsorption isotherms indicates that the obtained composites are mesoporous materials, in the pores of which capillary condensation is observed.**