

Microwave Assisted Synthesis, Modification with Platinum and Photocatalytical Properties of TiO₂ Nanofibers

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In the present work formation of active TiO₂ nanoparticles in microwave synthesis and their modification with platinum were studied. Anatase nanopowder and 10 M KOH solution were used as raw materials. Microwave assisted synthesis method permitted to obtain TiO₂ nanofibres and nanowires with a diameter of 10 nm and a specific surface area in the range of 70–150 m²/g. In order to modify TiO₂ nanofibers with platinum it was stirred in H₂PtCl₆ solution under UV irradiation. Photocatalytic activity was determined by degradation of the methylene blue (MB) solution under UV and visible light irradiation. The obtained samples showed higher photocatalytic activity with respect to pure TiO₂ nanofibers. The doped TiO₂ nanofibers were appropriate for degradation of harmful organic compounds as well as for hydrogen production by water splitting.

Keywords: titania nanofibers, nanowires, anatase, platinum, photocatalysis.

1. INTRODUCTION

The synthesis of nanotubes has become one of the most important research subjects in nanotechnology and various nanotubular materials have been produced during the last decades [1]. Titania nanotubes, nanowires and nanofibers due to large specific surface area and relatively simple and cost-effective preparation methods are a promising material for photocatalytic decomposition of organic compounds, splitting water and for dye sensitized solar cells [2, 3]. Many efforts have dedicated to the modification of TiO₂ nanoparticles in their morphology and phase structures through various methods, such as the hydrothermal synthesis method, sol–gel, anodization and template method. The microwave-assisted hydrothermal method has unique advantages of uniform and rapid heating in comparison with the conventional one. In addition, this method can significantly reduce the reaction time, leading to the fast crystallization and simplification of the preparation procedure [4]. However titania due to wide band-gap (3.2 eV) exhibits high photocatalytic activity under ultraviolet illumination. Only 5 % from sunlight is UV radiation but about 45 % is visible light. A large number of investigations aimed at increase TiO₂ photocatalytic activity under visible light have been carried out over last years. It is established that photocatalytic activity of TiO₂ nanoparticles and nanotubes can be increased by doping with nitrogen, sulfur [5, 6]. The improved photocatalytic activity of TiO₂ nanoparticles and mesoporous films has been achieved by doping with such metal oxide as WO₃ [7]. One more promising dopant is platinum [8–10]. The short reaction times provided by microwave synthesis make it ideal for rapid reaction

scouting and optimization of reaction conditions [11]. Although, it is difficult to compare their effectivity for photocatalysis, because conditions of preparation methods differ. The aim of the present work is to determine characteristics of TiO₂ nanofibers and nanowires doped with Pt, in dependence on doping agent content and to compare their photocatalytic activity.

2. EXPERIMENTAL DETAILS

2.1. Microwave synthesis of TiO₂ nanofibers and nanowires

The TiO₂ samples were prepared by a microwave method similar to hydrothermal method but in shorter reaction time. For this purpose, a certain amount of TiO₂ anatase nanopowder (Sigma–Aldrich, ≥ 99.7 %, < 25 nm particle size) was dissolved in 700 mL of 10M KOH at room temperature. This aqueous solution was poured in to microwave vessel made from teflon. The microwave treatment was performed at 230 °C for 40 min by using Anton Paar Masterwave BTR microwave system. Solution was stirred with speed 700 rpm during the reaction time. The as obtained solution was then cooled to room temperature and left to precipitate TiO₂ particles. After this procedure, KOH solution was decanted from vessel and obtained TiO₂ suspension was diluted with large amount of deionised water to decrease concentration of KOH. Washing and decanting procedures were repeated several times. Finally a certain amount 1 M HCl was added to TiO₂ suspension to reduce pH to 7.0. Obtained solution was filtered by using 1.0 μm cellulose nitrate membrane filter. Particles were washed on filter several times with deionised water and 96 % ethanol. The powder was submitted to drying at 110 °C for 24 h. After drying TiO₂ nanofiber powder was stirred in 1 M HCl solution for 24 h to remove titanates. This procedure also allowed to

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decrease absorption process of MB on TiO₂ nanofibers surface.

2.2. TiO₂ nanofiber and nanowire modification with platinum

0.0300 g H₂PtCl₆·6H₂O were dissolved in 100 mL deionised water and stirred for 5 min. 1.00 g or 0.20 g TiO₂ nanowire powder were added to obtained solution and stirred for 30 min. To modify TiO₂ nanofibers with platinum, UV lightsource (FEK-56, 120 W mercury high pressure UV lamp) was used. Solution was transferred into quartz beaker and stirred under UV irradiation for 40 min. The distance from light source to beaker was 11 m. Under UV irradiation PtCl₆²⁻ anions were reduced and TiO₂ nanofibers and nanowires were doped with platinum.

After modification suspension was filtered by using 1 μm cellulose nitrate membrane filter and was washed with deionised water for several times. The obtained powder was submitted to drying at 110 °C for 24 h. After drying process TiO₂ photocatalyst nanopowder were calcinated at 500 °C for 2 h to obtain anatase.

2.3. Photocatalytic properties

Photocatalytic properties of the obtained TiO₂ nanopowder were tested by using degradation of MB solution under UV and visible light irradiation. FEK-56, 120 W mercury high pressure UV lamp was used as UV light source and Philips Torndoo 23 W halogen lamp as visible light source. 100 mL MB solution (7,2 mg/L) were poured in quartz beaker and stirred in the dark for 30 min to control absorption process on TiO₂ surface. Degradation process of MB solution was controled by using spectrophotometer Janwey 6300. Absorption of MB solution was measured at wave lenght of 662 nm. As reference with 100 % transmission deionized water was used.

During the experiments every minute suspension samples (2 ml) were taken out and centrifuged to remove nanopowder particles before absorption was measured.

3. RESULTS AND DISCUSSION

3.1. Characterization of physical properties

Characterization of physical properties such as morphology, crystallization, chemical content, surface areas were done by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), BET surface area analysis methods, respectively.

Specific surface area were obtained by using BET method and HROM 3 gas analyzer. Results of specific surface area measurements are shown in Table 1. As prepared TiO₂ nanofibers and nanowires were with extremly large specific surface (122.6 – 158.5 m²/g). Thermal treatment decreased specific surface area down to 125 m²/g and down to 85 m²/g after 24 h stirring process at 1 M HCl.

Doped with Pt TiO₂ nanofibers and nanowires were with specific surface area in the range of 70 – 53 m²/g depending on Pt content.

The chemical analysis was done by using X-ray fluorescent spectrometer Bruker Pioneer S4. It was

obtained that samples doped with platinum contains 6.27 % and 1.22 % Pt.

Table 1. Comparison of specific surface area of various TiO₂ samples

Sample	Specific surface area, m ² /g
Pure TiO ₂ nanopowder (comercial)	98.2
Pure TiO ₂ nanofibers and nanowires	158.5
TiO ₂ nanofibers and nanowires after calcination at 500 °C for 2 h	125.1
TiO ₂ nanofibers and nanowires after 24 h stirring in 1M HCl and calcination at 500 °C for 2 h	85.5
Pure TiO ₂ + 1.22 % Pt nanofibers	122.6
TiO ₂ + 1.22 % Pt nanofibers calcinated at 500 °C for 2 h	70.3
TiO ₂ + 6.27 % Pt nanotubes calcinated at 500 °C for 2 h	53.5

The phase composition was determined by using X-ray diffraction analysis with D8 Advance, Bruker AXS system. All samples were calcinated in 500 °C for 2 h to crystallise amorphous TiO₂ before XRD analysis. XRD patterns of prepared samples showed anatase peaks and small amount TiO₂ with monocline base centred structure indicating that TiO₂ nanofibers and nanowires were still a bit X-ray amorphous. All XRD patterns of the calcinated samples were similar and beside intensive peaks exhibited also weak peak of amorphous phase (Fig. 1). Influence of Pt as dopant on phase composition were well shown in diffraction spectra of sample doped with 6.27 % Pt. Diffraction spectrum of sample doped with 1.22 % Pt was without Pt peaks. It could be explained with detection limit of system. No other shifts of the diffraction peaks were observed.

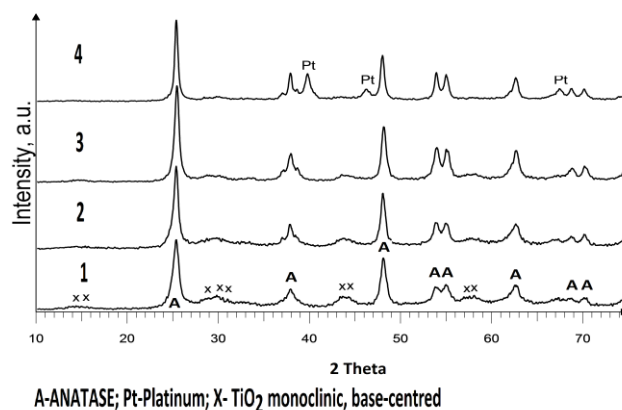
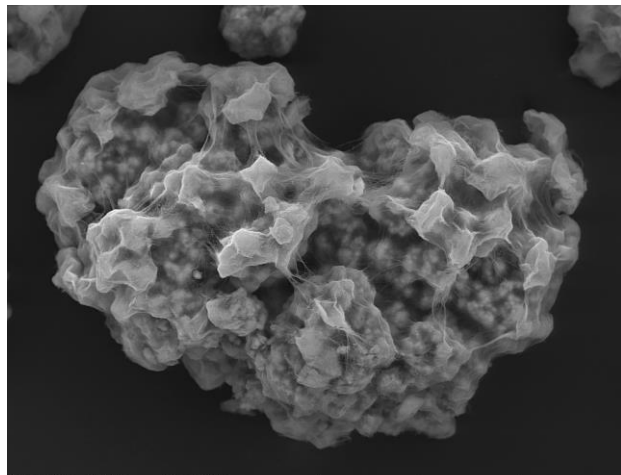


Fig. 1. XRD patterns of the calcinated TiO₂ nanofiber samples: pure TiO₂ nanofibers and nanowires (1); TiO₂ nanofibers and nanowires after stirring 24 h in 1M HCl (2); TiO₂ nanofibers and nanowires doped with 1.22 % platinum (3) and TiO₂ nanofibers and nanowires doped with 6.27 % platinum

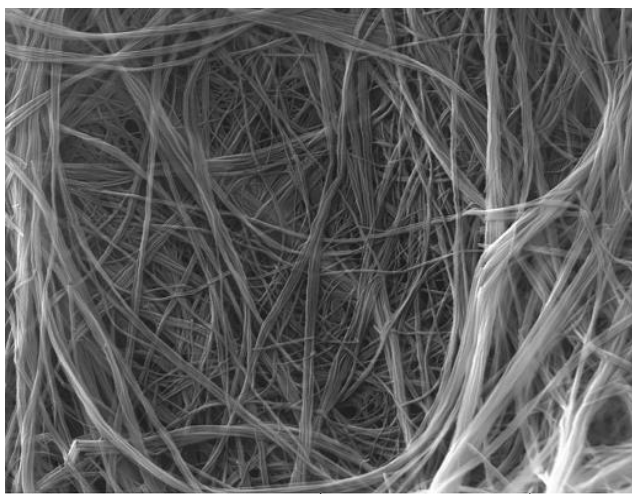
Morphological characterization of prepared TiO₂ samples were carried out by scanning electron microscope FE SEM MiraLMU, Tescan. SEM images are shown in Fig. 2. It is well shown that TiO₂ nanofiber agglomerates containing from large amount of individual nanowires where obtained in the microwave synthesis process. Homogeneous individual nanowires were with diameters from 10nm and with length more than 15 μm.



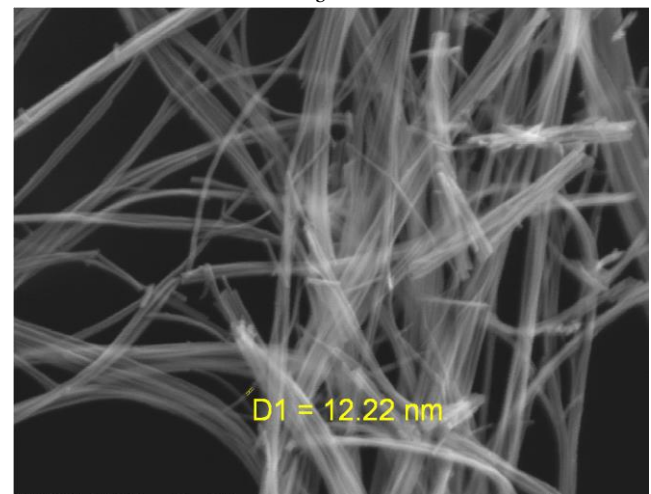
a



b



c



d

Fig. 2. SEM images of Pt-doped TiO₂ nanofibers and nanowires under various magnification levels: a – 1000x; b – 5000x; c – 50 000x; d - 100 000x

Photocatalytic activity was measured in UV and VIS light irradiation. As pure TiO₂ nanofibers and nanowires after microwave assisted synthesis were with extremely high specific surface area, there was a problem with high absorption of MB on TiO₂ photocatalysts surface. It was noticed that already in stirring process in dark up to 95 % of MB was absorbed on catalysts surface and nanopowder was blue while solution transparent. To fix this problem samples were stirred in 1 M HCl for 24 h. After this procedure no absorption on catalysts surface while stirring in the dark were obtained and nanopowder was still white or light brown (for TiO₂ sample containing 6.22 % Pt) after MB degradation measurements. The pure TiO₂ nanofibers and nanowires degraded about 58 % of MB during 20 min under UV radiation. Prepared Pt- doped TiO₂ photocatalysts had with up to 30 % higher activity with respect to pure TiO₂ nanofiber and nanowire powder. It was degraded up to 87 % MB after 20 min under UV irradiation (Fig. 3). Sample with only 1.22 % Pt content had about 7 % greater activity than sample containing 6.27 % Pt in UV irradiation. Under visible light irradiation the activity of prepared photocatalysts was much lower

(Fig. 4). Only about 11.5 % MB were degraded in 270 min experiment with sample containing 1.22 % Pt and about 6.5 % in experiment with sample containing 6.27 % Pt.

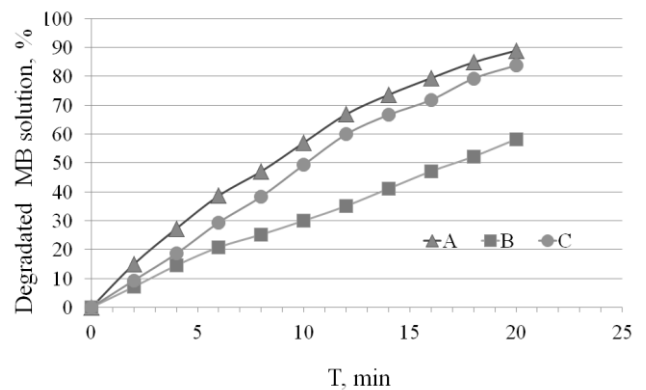


Fig. 3. Degradation of MB solution under UV irradiation: pure TiO₂ nanofibers and nanowires (B); TiO₂–1.22 % Pt nanofibers and nanowires (A) and TiO₂–6.27 % Pt nanofibers and nanowires (C)

Activity of pure TiO₂ nanofiber and nanowire photocatalysts in visible light was close to zero. Also after measurements under visible light photocatalysts were white or light brown (for TiO₂ sample containing 6.27 % Pt). The reason of this difference could be explained by insufficient activity of the photocatalysts and by different radiation intensity.

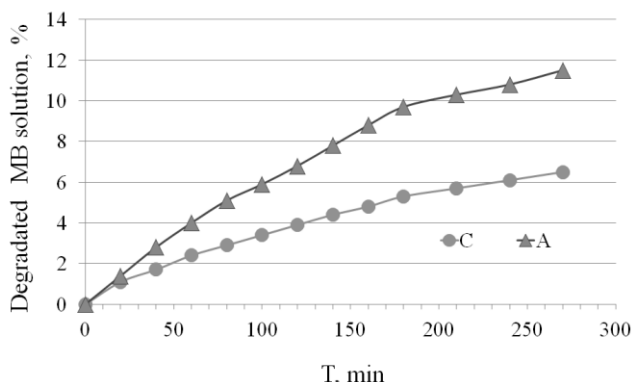


Fig. 4. Degradation of MB solution under visible light irradiation: TiO₂ – 1.22 % Pt nanofibers and nanowires (A) and TiO₂ – 6.27 % Pt nanofibers and nanowires (C)

Comparing results with literature it was notice that Pt doped nanofibers are with 20 to 30 % higher photocatalytic activity in UV irradiation than Pt doped TiO₂ nanotubes Literature data for photocatalytic activity of Pt doped TiO₂ nanotubes under visible light irradiation should be examined critically because it is shown that the activity for pure TiO₂ nanotubes under visible light is already 12 % while it is well known that pure TiO₂ is active only under UV irradiation [9].

4. CONCLUSIONS

Platinum doped TiO₂ nanofibers and nanowires were successfully fabricated through a simple microwave treatment of the TiO₂ anatase nanopowder. Obtained pure nanofibers and nanowires have specific surface area up to 158 m²/g and up to 122 m²/g when doped with Pt. Individual anatase nanowires were with diameter from 10 nm and length up to 15 μm. Platinum doping can effectively enhance the photoelectrocatalytic activity of TiO₂ under UV and visible-light irradiation. The highest photocatalytic activity of Pt-doped TiO₂ nanofibers and nanowires were shown by sample containing 1.22 % Pt. Modification with platinum allows increase photocatalytic activity of TiO₂ nanofibers and nanowires up to 30 % under UV irradiation and up to 11.5 % under visible light irradiation.

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