Microwave-assisted synthesis and photocatalytic properties of sulphur and platinum modified TiO$_2$ nanofibers

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Abstract. In the present work formation of active TiO$_2$ nanofibers in microwave synthesis and their modification with platinum were studied. Mixture of anatase and rutile nanopowder and 10M KOH solution were used as raw materials. Microwave assisted synthesis method permitted to obtain TiO$_2$ nanofibers with a diameter of 10nm and a specific surface area up to 40.2 m$^2$/g. In order to modify TiO$_2$ nanofibers with platinum it was stirred in H$_2$PtCl$_6$ solution and illuminated with UV irradiation or reduced with sodium borohydride. To modify titania with sulphur and prepare co-doped nanofibers platinum doped samples were extra treated in hydrogen sulphide atmosphere. 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 TiO$_2$ nanofibers. The doped TiO$_2$ nanofibers were appropriate for degradation of harmful organic compounds.

1. Introduction

The synthesis of nanofibers has become one of the most important research subjects in nanotechnology and various nanotubular materials have been produced during the last decades. TiO$_2$ is one of the most widely used photocatalyst for photocatalytic decomposition of organic compounds, splitting water and for dye sensitized solar cells because of its high photocatalytic activity, excellent chemical stability, relatively low price, and low toxicity [1-2]. However, because of its wide band gap energy of ~3.2eV, it is only active in ultraviolet irradiation. As a consequence, significant efforts have been made to develop modified forms of TiO$_2$ that are active under visible light irradiation [3].

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]. It is established that photocatalytic activity of TiO$_2$ nanoparticles can be increased by doping with nitrogen, sulfur [5, 6], with such metal oxide as WO$_3$ [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. However, it is difficult to compare their effectiveness for photocatalysis, because the conditions of preparation methods differ. The aim of the present work is to determine the characteristics of TiO$_2$ nanofibers doped with Pt and co-doped with platinum and sulfur, in dependence on doping agent content and to compare their photocatalytic activity.
2. Experimental

2.1. TiO$_2$ nanofiber preparation

The TiO$_2$ samples were prepared by a microwave method similar to hydrothermal method but in shorter reaction time. For this purpose, a certain amount of mixture of TiO$_2$ anatase and rutile nanopowder (Sigma–Aldrich, ≥99.7%, <25nm particle size) was dissolved in 700mL of 10M KOH at room temperature. This aqueous solution was poured into a microwave vessel made from teflon. The microwave treatment was performed at 230°C for 40min by using Anton Paar Masterwave BTR microwave system. Solution was stirred with speed 700rpm during the reaction time. The as-obtained solution was then cooled until room temperature and left to precipitate TiO$_2$ particles. After this procedure KOH solution was decanted from the vessel and the obtained TiO$_2$ 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 1M HCl was added to TiO$_2$ suspension to reduce pH to 7.0. The obtained solution was filtered by using a 1.0µm cellulose nitrate membrane filter. Particles were washed on the filter several times with deionised water and 96% ethanol. The powder was submitted to drying at 110°C for 24h. After drying TiO$_2$ nanofiber powder was stirred in 1M HCl solution for 24h to remove titanates. This procedure also allowed decreasing the absorption process of MB on TiO$_2$ nanofibers surface.

2.2. TiO$_2$ nanofiber modification with platinum and sulphur

Two methods were used to modify TiO$_2$ nanofibers with platinum nanoparticles:

A) H$_2$PtCl$_6$.6H$_2$O was dissolved in 100mL of deionised water and stirred for 5min. TiO$_2$ nanofiber powder was added to the obtained solution and stirred for 30min. To modify TiO$_2$ nanofibers with platinum UV light source (FEK-56, 120W mercury high pressure UV lamp) was used. The solution was transferred into a quartz beaker and stirred under UV irradiation for 40min. The distance from the light source to the beaker was 11cm. Under UV irradiation PtCl$_6^{2-}$ anions were reduced and TiO$_2$ nanofibers were doped with platinum.

B) TiO$_2$ and H$_2$PtCl$_6$.6H$_2$O were dissolved in 60mL ethyl alcohol. Sodium borohydride was added and the suspension was stirred for 1h while PtCl$_6^{2-}$ anions were reduced and TiO$_2$ nanofibers were doped with platinum.

After the modifications all suspensions were filtered by using 1µm cellulose nitrate membrane filter. The obtained powders were submitted to drying at 110°C for 24h. After the drying process TiO$_2$ photocatalyst nanofibers were calcinated at 500°C for 2h to obtain anatase.

Co-doped with platinum and sulfur the TiO$_2$ nanofibers were prepared by platinum doped sample extra treatment at 380°C in H$_2$S flow for 2h. For H$_2$S gas synthesis the reaction between FeS and HCl in Kipp's apparatus was used.

2.3. Determination of photocatalysts activity

Photocatalytic properties of the obtained TiO$_2$ nanofibers were tested using the degradation of MB solution under UV and visible light irradiation. FEK-56, a 120W mercury high pressure UV lamp was used as the UV light source, and Philips Tornado 23W halogen lamp as the visible light source. The degradation process of the MB solution was controlled using the Janwey 6300 spectrophotometer. The absorption of the MB solution was measured at wave length of 662nm.0.0500g TiO$_2$ nanofiber powder was used for the degradation of 100mL MB( 7.2mg/L). The samples were centrifuged before the measurements for 5min with a rotation speed of 10 000rpm.
3. Results and discussion

Characterizations of physical properties 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 was obtained by using BET method and HROM 3 gas analyzer. Results of the specific surface area measurements and dopant content are shown in Table 1.

Table 1. Comparison of specific surface area and dopant content in various TiO$_2$ samples

| Sample | Specific surface area $m^2/g$ | Platinum content % | Sulfur content % |
|--------|-------------------------------|-------------------|-----------------|
| Pure TiO$_2$ nanopowder (anatase and rutile mixture) (commercial) | 45.0 | - | - |
| Pure TiO$_2$ nanofibers | 40.2 | - | - |
| C: TiO$_2$ nanofibers $+$ Pt (Borohydride reduction) after calcination in air at 500$^\circ$C for 2h | 29.8 | 1.06 | - |
| D: TiO$_2$ nanofibers $+$ Pt (Borohydride reduction) after calcination in air at 500$^\circ$C for 2h | 28.2 | 0.44 | - |
| G: TiO$_2$ nanofibers $+$ Pt (UV reduction) after calcination in air at 500$^\circ$C for 2h | 25.7 | 6.15 | - |
| H: TiO$_2$ nanofibers $+$ Pt (UV reduction) after calcination in air at 500$^\circ$C for 2h | 26.4 | 1.86 | - |
| L: TiO$_2$ nanofibers $+$ Pt (Borohydride reduction) after calcination in H$_2$S flow at 380$^\circ$C for 2h | 31.1 | 1.39 | 10.84 |

In these experiments nanofibers with a specific surface area up to 40.2$m^2/g$ were prepared and tested. Doped with Pt, TiO$_2$ nanofibers had a specific surface area 25.7 to 29.8$m^2/g$ depending on Pt content. Co-doped with platinum and sulfur, TiO$_2$ nanofibers had a specific surface area 31.1$m^2/g$.

The chemical analysis was done by using an X-ray fluorescent spectrometer Bruker Pioneer S4. It was obtained that doped samples contain platinum from 0.44% to 6.15% and sulfur from 1.15% to 10.84%. SEM results show that samples were with nanofiber structure, and individual nanowires had a diameter of 10nm and length up to 15µm. Nanofibers were coated with nanosize Pt particles (Fig. 1).

The phase composition was determined by using an X-ray diffraction analysis with a D8 Advance, Bruker AXS system. Samples C, D, G and H were calcinated at 500$^\circ$C for 2h to crystallize amorphous TiO$_2$ before the XRD analysis. XRD patterns of the prepared samples showed anatase and rutile maxima and Pt maxima for sample G with high content of Pt. No other shifts of the diffraction maxima were observed.
Results of MB degradation under UV (Fig.3) and visible light (Fig. 4) show that all prepared samples are active photo catalysts. Under UV irradiation up to 90% of MB was degraded in the 45min experiment and up to 50% under visible light in the 180min experiment. Sample L containing 1.39% Pt and 10.84% sulfur shows the highest activity under UV and also under visible light irradiation. Samples modified with platinum by the UV irradiation for H\textsubscript{2}PtCl\textsubscript{6} reduction were with higher activity with respect to those that were prepared by using sodium borohydride as reducing agent.

Figure 1. SEM micrograph of platinum modified TiO\textsubscript{2} nanofibers.

Figure 2. Results of the XRD analysis: A-anatase, Pt-platinum, R-rutile

Figure 3. Degradation of MB solution under UV irradiation

Figure 4. Degradation of MB solution under visible light irradiation

4. Conclusions

TiO\textsubscript{2} nanofibers were successfully fabricated through a simple microwave treatment of TiO\textsubscript{2} anatase and anatase/rutile mixture nanopowders. The obtained pure nanofibers, doped with platinum and co-doped with platinum and sulfur have specific surface area of up to 40.2m\textsuperscript{2}/g. Individual TiO\textsubscript{2} nanowires had a diameter of 10nm. Platinum and sulfur doping can effectively enhance the photoelectrocatalytic activity of TiO\textsubscript{2} under UV and visible light irradiation. The highest photocatalytic activity of doped TiO\textsubscript{2} nanofibers were shown by sample L containing 1.39% Pt and 10.84% sulfur. Modification with platinum and sulfur allows increase photocatalytic activity of TiO\textsubscript{2} nanofibers up to 40% under UV irradiation and up to 50% under visible light irradiation. Samples
modified by using UV light source for PtCl$_2^-$ anions reduction had a higher specific surface area and photocatalytic activity than samples modified using sodium borohydride as reducing agent.

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