THE EFFECT OF CALCINATION ON THE STRUCTURE OF INORGANIC TiO_2 NANOFIBERS

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Abstract

Nanofibers are defined as fibres with sub-micron diameter. Due to their thickness they offer extremely large specific surface area. The most frequently mentioned ceramic material with nanofiber morphology is a titanium dioxide. The possibility of industrial use of TiO_2 nanofibers is conditioned by a highly efficient continuous production technology. This is allowed by a modified Nanospider™ device. Titanium tetrabutoxide is used as the spinning solution. After spinning process, the nanofibrous layer consists from a mixture of organic and inorganic material, that's why a subsequent calcination is necessary. During the calcination any organic components will be incinerated and pure titanium dioxide fibres with a crystalline structure are obtained. In the present work a high resolution scanning electron microscope and X-Ray diffraction were used for the assessment of the structure and phase composition of resulting TiO_2 nanofibers.

Keywords: calcination, nanofibers, photocatalysis, structure, titanium dioxide.

1. INTRODUCTION

In the recent years a considerable attention is devoted to nanostructured materials. When the dimensions fall under 100 nm some extraordinary properties can be observed. In the case of nanofibrous materials the most pronounced property is their extremely high surface area hyperbolically increasing with decreasing fibre diameter [1, 2]. Electrospinning method was considered as the most effective way of nanofiber production This method uses electric forces to form nano-sized fibres from a solution or melt [3-5]. For the production of inorganic TiO_2 nanofibrous layers was used modified Nanospider™ device, where a rotary brush was used as a collector. Produced inorganic nanofibers were taken from the brush through a combination of a comb and pneumatic extraction which provides a continuous process for nanofibers production [6-9].

1.1. Titanium dioxide

Titanium dioxide (TiO_2) may have the crystal structure of anatase or rutile depending on the arrangement of titanium and oxygen atoms in the crystal lattice. Recently, a considerable attention is devoted to anatase for its interesting features, especially for its photocatalytic activity and photocatalytic superhydrophobicity. Naturally, the properties of TiO_2 depend also on its particle size. If particles of TiO_2 are large, they serve as an excellent white pigment by scattering visible light, while when they are small enough, TiO_2 is transparent to visible light, but absorbs UV radiation. The effect of calcination temperature on the phase composition of TiO_2 nanoparticles was previously published in [10]. The phase transformation temperature from anatase to rutile was found between 500 and 600 °C. The accompanying undesirable effect of high temperature treatment was TiO_2 particles growth leading to a decrease of specific surface area.

1.2. Photocatalysis

When photocatalytic surface of TiO_2 is illuminated with energy equal to or larger than the bandgap energy, it excites the electrons from the valence band to the conduction band. It results to the formation of an electron-hole pair. The electron in the conduction band reduces the oxygen adsorbed to photocatalyst, whereas the positive hole in the valence band oxidizes either pollutants directly or water to produce ·OH radical able to undergo secondary reactions. The ability to decompose organic and microbial matter is the reason why TiO_2-based materials can be applied to the treatment of water and air, for self-cleaning and antibacterial layers. It can produce electricity in nanoparticle form. Applications include light-emitting diodes, liquid crystal displays and electrodes for plasma displays. Under exposure to UV light, it becomes increasingly hydrophilic and can be used for anti-fogging coatings and self-cleaning windows. It also has disinfecting properties making it suitable for applications such as medical devices, food preparation surfaces, air conditioning filters and sanitary ware surfaces [11-14].

2. EXPERIMENTAL METHODS

The nanofibers were spinned from tetrabutoxide spinning solution using modified Nanospider™ device [7-9]. Spinned material has been subsequently calcined at temperatures in a range from 100 to 1000 °C. The main purpose of calcination was to achieve the anatase structure and to remove organic component. The effect of calcination on the phase composition was evaluated on the basis of high temperature powder XRD measurement. The structure of nanofibers calcined at 600 °C for 120 min was studied using high resolution SEM; for the image analysis was used SW NIS Elements.

3. RESULTS AND DISCUSSION

The effect of calcination temperature (from 100 to 1000°C) on the phase composition was evaluated on the base of high temperature XRD powder diffraction. From the **Fig. 1** it is obvious, that spinned non-calcined material is mostly amorphous. At 500 °C appears a peak corresponding to anatase phase. This peak grows with the temperature up to 800 °C, where anatase phase completely transforms to rutile. From this experiment a temperature of 600 °C was selected for the heat treatment because higher temperature enables to minimize the necessary calcination time and thus to achieve higher production effectivity. On the other hand, finer anatase grains should by produced at lower calcination temperatures and anatase → rutile phase transformation will not occur.

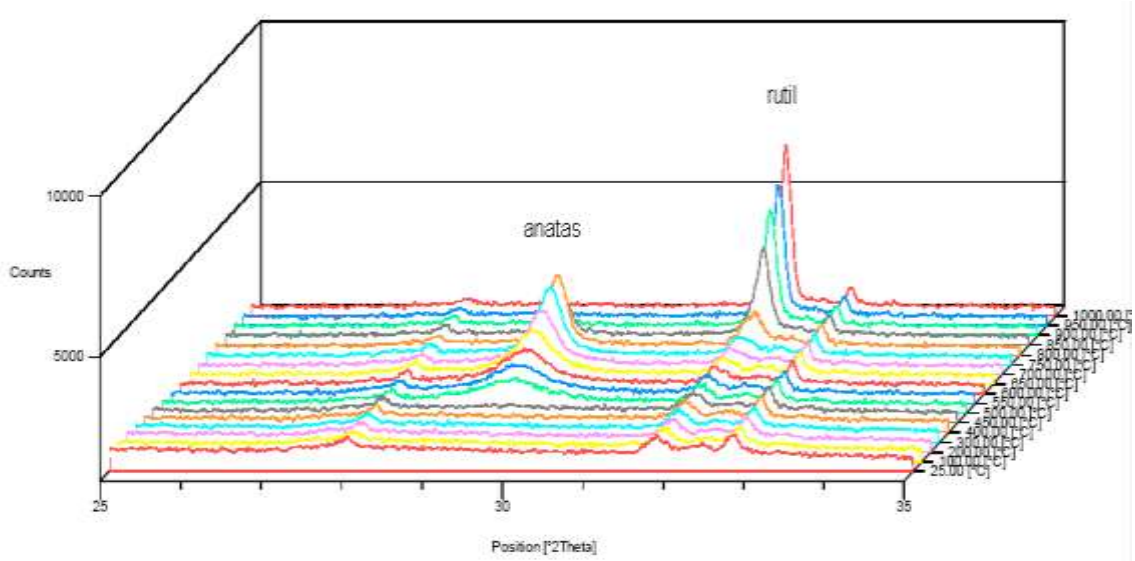

Fig. 1 XRD curves shoving the effect of temperature on the crystal structure of TiO_2 nanofibers. At low temperatures the spinned fibres are almost amorphous. Anatase appears in the structure at 500 °C and its amount increases up to 700 °C. Above 700 °C the anatase transforms to rutile phase.

The structure of the spinned material is shown in **Fig. 2**. The fibres surface is smooth; their average diameter is approx. 300±70 nm. In **Fig. 3** there are TiO_2 nanofibers after the calcination at 600 °C. Their fragmentation indicates significant increase in their brittleness caused by evaporation of the organic phase. Thermal decomposition/evaporation of carbon-based compounds and crystallisation of anatase result to formation of rough-surface fibres and reduction of the diameter to approximately 190 nm. Their porosity and fine nano-crystalline structure can lead to considerable increase of the specific surface area [15]. We can assume that this roughness increases the photocatalytic efficiency compared to the smooth fibers.

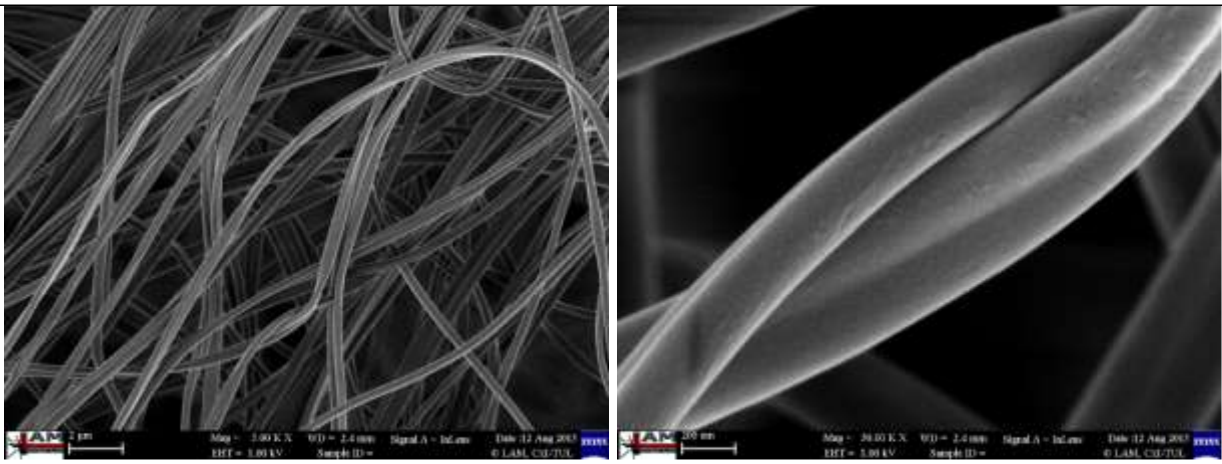

Fig. 2 SEM images of the smooth fibres after the electrospinning process.

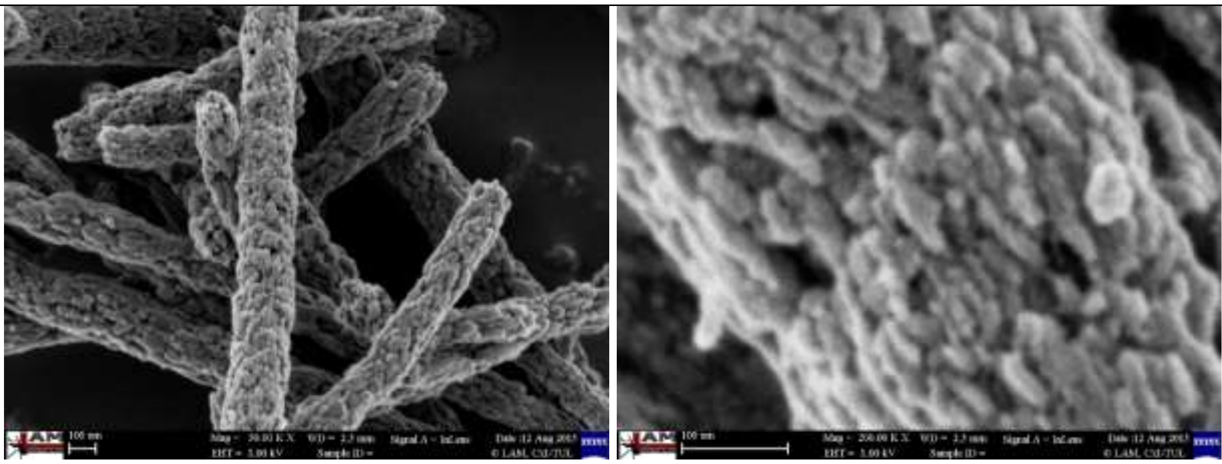

Fig. 3 TiO_2 fibres after the calcination at 600 °C. The porous surface and nanocrystal structure are clearly visible in the detailed image. The size of anatase crystals is in a range of tens of nm.

4. CONCLUSION

Modification of Nanospider™ enables a continuous production of inorganic TiO_2 nanofibers. Subsequent calcination is necessary to remove organic compound and to achieve anatase crystaline structure. The optimal calcination temperature and time were determined on the basis of XDR measurement. As the optimum was found heating at 600 °C for 2 hours. The resulting TiO_2 nanofibers are rough-surface, porous and brittle due to removing of organic phase. Their average diameter is approximately 185±29 nm. They mostly consist of nanocrystalline anatase phase; the crystals size is about 20±4 nm. Further work will be focused on the study of calcination time and temperature on specific surface area and on its photocatalytic activity.

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