Photocatalytic activity of TiO$_2$ nanofibers prepared by liquid phase deposition

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Abstract

Using liquid phase deposition method on cellulose substrate, TiO$_2$ nanofibers were prepared with TiCl$_4$ as a precursor. TiO$_2$ nanofibers were obtained after heat treatment of the cellulose template. The remained product composed of micron-size TiO$_2$ fibers with a microstructure of nanofibers. It is shown that nanofibers are formed through the aggregation of TiO$_2$ nanoparticles. X-ray diffraction (XRD) analysis of the as prepared solution indicates formation of crystalline TiO$_2$ anatase phase. EDX analysis was employed to measure the adsorbed mass of TiO$_2$ on cellulose substrate. The effect of deposition time on the growth and morphology was investigated by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) studies demonstrate fine microstructures which are composed of 10-15 nm nanoparticles. Surface area of the TiO$_2$ fibers, measured by Brunauer, Emmett and Teller (BET) analysis, was about 104 m$^2$ g$^{-1}$. Photodegradation of Rhodamine B (Rh. B) as a standard dye shows that the prepared samples have a high photocatalytic activity due to large surface area.

Keywords: TiO$_2$ nanofibers, Liquid phase deposition, SEM, XRD, Photocatalytic activity

1. Introduction

TiO$_2$ is the most frequently used photocatalyst material. It has been used in transforming toxic organic molecules to H$_2$O, CO$_2$ and other harmless molecules [1, 2]. This property has been applied in removing bacteria and harmful organic materials from water and air, as well as in self-cleaning or self-sterilizing surfaces for places such as medical centers. Specifically, much attention has been drawn towards their photocatalytic properties because of its application in environmental purification and decomposition of toxic and organic compounds. A key requirement for improving the photocatalytic activity is to increase the specific surface area and enhance the crystallinity [3,4]. These requirements are met by crystalline nanostructured materials. These factors enhance the probability of electrons and holes reaching the surface of the photocatalyst material which are the necessary factors to make a reduction or oxidation reaction.

TiO$_2$ nanostructures have been prepared in different forms such as nanolayers [5,6], nanopowders [7], nanofibers [8-11] and nanotubes [12]. In this regard, considerable attention has been paid to nanofibrous structures as they exhibit high specific surface area for photocatalytic applications [8,11]. Several methods including the sol–gel process [13], electrodeposition [14], pulsed laser deposition [15], micelle [16,17] and hydrothermal [18,19] have been used to synthesize TiO$_2$ nanostructures. TiO$_2$ nanofibrous structures are usually synthesized by template method [20-22] which is based on the deposition of TiO$_2$ on a high surface area template. In this situation the deposited materials will follow the morphology of the template, and upon removal of the template will have a structure similar to that of the template. Liquid phase deposition and electrodeposition methods have been employed to deposit TiO$_2$ on template materials. In liquid phase deposition, either precursor molecules or nanoparticles adsorb on the surface of the template and form a deposit [14, 23].

In the present study, crystalline TiO$_2$ nanofibers have been prepared using a template method with TiCl$_4$ as a precursor. Here we report on the properties and formation mechanism of the produced nanofibers and the effect of deposition time on the photocatalytic activity of the produced nanofibers.

2. Experimental

2.1. Synthesis of TiO$_2$ nanofibers

The sol–gel process was used to synthesize aqueous TiO$_2$ suspension. One mL TiCl$_4$ (Merck, 99%) was slowly added dropwise into 10 mL EtOH (Merck, 99.8%) under vigorous stirring at room temperature. A large amount of HCl gas was exhausted and a transparent yellowish solution was formed. The as prepared solution was then heated at 80 °C for 24 hours leading to a white precipitate. About 0.1 g cotton fiber was put in the solution at different times ranging from 5 minutes to 24 hours. The impregnated fibers were dried at 100 °C for 1 hour and were then annealed at 500 °C in air for 2 hour. The obtained residue is a white fibrous substance of TiO$_2$ composition.
2.2. Characterization

Analysis of the crystalline structures was performed by XRD diffractometer (X’pert Philips) with wavelength of Cu Kα radiation in 2θ range from 10° to 80° by 0.05° sec⁻¹ steps. UV-Vis spectroscopy of the samples was taken out by a Lambda 950 spectrophotometer (Perkin Elmer) from 200 nm to 1100 nm wavelengths. TEM analysis was performed by a LEO 912 AB instrument at 200 keV accelerating energy by deposition of TiO₂ nanoparticles onto the copper grid at room temperature. SEM analysis was taken by a SEM instrument (Philips XL30) at 16 keV accelerating energy by evaporation of small drops of the dispersed nanofibers onto the Si (100) substrate at room temperature. Surface area of the nanoparticles was determined by Belsorp adsorption-desorption (BEL Japan Inc.) instrument. DI water was supplied from a Millipore water purification system (Direct-Q-3) with 18.2 MΩ-cm (0.055 µS) resistance.

Photocatalytic activity of the nanofibers was measured by photodegradation of Rh. B with the initial concentration and volume of 10⁻⁵ M and 30 mL respectively at the presence of 30 mL 0.01 wt% TiO₂ solution. First the mixed Rh. B and TiO₂ solution was stirred in dark for 30 min to equilibrate the adsorption/desorption between dye molecules and TiO₂ photocatalysts. Then it was irradiated at room temperature by a 15 W low-pressure mercury lamp, 254 nm strongest peak wavelength. The degradation rate was measured by UV–Vis spectrophotometer at the maximum absorption wavelength of Rh. B.

3. Results and discussion

3.1. XRD analysis of the products

Crystalline structure of the as prepared, dried and the remained product after heat treatment is depicted in Fig. 1. As it is clear from the XRD pattern (Fig. 1a) the as prepared sol is amorph and by heating that at 80 °C for 24 hours a white precipitation appears which is the crystalline TiO₂ in anatase phase (Fig. 1b). The obtained spectrum after heat treatment at 500 °C in air for 2 hour has the TiO₂ anatase phase peaks at 2θ = 25.3, 37.7, 47.8, 54, 62.7, 68.6, 70.3 and 75.2 degree with no impurity which is in agreement with 21-1272 standard cards from JCPDS. Heating the as prepared aqueous TiO₂ suspension leads to crystallization of TiO₂ nanoparticles in solution. The single crystalline size determined by Debye-Scherrer formula was 9 nm. Annealing the extracted powder at 500 °C in air for 2 hour did not result in any remarkable changes in the position of the peaks as is illustrated in Fig. 1c. The single crystalline size after heat treatment was 15 nm. In fact the most important advantage of heating the as prepared sol is that they transform to a crystalline sol and no more heat treatment at high temperatures is required for further crystallization. These results are in good agreement with previous reports, Hu et al [24].

3.2. Microscopic studies

Fig. 2 shows SEM images of the TiO₂-coated cellulose fibers. Fig. 2a shows the cellulose fibers immersed in as prepared solution for 5 minutes. EDX analysis demonstrates that the external surface of the fibers is coated by TiO₂. Fig. 2b shows SEM image of the TiO₂-coated cellulose fibers after heat treatment at 500 °C for 2 hours. The heat treatment of the TiO₂-coated cellulose fibers leads to the removal of organic parts of the fibers and leaves the TiO₂ fibers. The obtained result reveals shrinkage of the fibers when the cellulose is removed by heat treatment. Fig. 2c and 2d shows TiO₂ fibers obtained from the heat treatment of TiO₂-coated cellulose fibers at different magnifications. They demonstrate a fine microstructure that is in the form of nanofibers woven to form micron-size fibers.

TEM images provide more insight into the specific details of the formed nanostructures. Fig. 3a is a typical TEM image of the TiO₂ nanofibers. The nanofibers are seen to be composed of nanoparticles. The histogram of the size distribution of nanoparticles is shown in Fig. 3b. It indicates that the particles are 10 to 15 nm in size. The formed nanoparticle-based fibrous materials are expected to have a high surface area which is appropriate for photocatalytic reactions.
Using the EDX analysis, we checked the relative rate of adsorption of nanoparticles on the cellulose fibers at various deposition times. SEM images of the samples prepared at 2 and 24 hours before and after heat treatment are displayed on Fig. 4(a-d). There are no remarkable changes in size and morphology of the samples. This reveals that the 5 minutes deposition time is almost enough for TiO$_2$ nanoparticles to be coated on cellulose fibers. TiO$_2$ mass percent was measured from the absolute value of the Ti peak in EDX spectra from TiO$_2$-coated cellulose fibers (Fig. 5). We observed that the rate of deposition does not increase significantly as the deposition time increases from 5 minutes to 24 hours. Nevertheless the range of changes is about 5 percent.
3.3. Photocatalytic activity measurements

Photocatalytic activity of TiO₂ nanofibers depends on their surface area. In order to evaluate its activity we first determined the active surface area of the nanofibers. BET analysis of the sample prepared at 5 minutes deposition time gives the surface area of the nanofibers about 104 m²/g. Changes in the absorption spectrum of Rh. B under UV illumination at different irradiation times for the samples prepared at different deposition times and a Rh. B reference sample are illustrated in Figure 6. No remarkable changes in the concentration of the Rh. B solution were observed in the absence of TiO₂ nanofibers (Fig. 6a). This indicates that the main cause for decomposition of Rh. B is photoexcitation of TiO₂ nanofibers. The concentration and volume of all TiO₂ samples were chosen at 0.01 wt% and 30 mL respectively with 1:1 ratio of TiO₂ to Rh. B for all measurements. The results indicate that the concentration of Rh. B is decreasing at the presence of TiO₂ nanofibers and UV illumination, Fig. 6 (b-f).

Photocatalytic reactions on TiO₂ surface can be expressed by the Langmuir–Hinshelwood model [25]. The reaction rate after the adsorption equilibrium can be expressed as

\[-\ln \left( \frac{C}{C_0} \right) = Kt\]

Where C and C₀ are the reactant concentration at time t = t and t = 0, respectively, K and t are the apparent reaction rate constant and time, respectively. A plot of \(-\ln(C/C₀)\) versus t will yield a slope of K. The calculated reaction rate constant for the samples prepared at 5 minutes, 30 minutes, 1 hour, 2 hours and 24 hours were \(10 \times 10^{-3}\), \(12 \times 10^{-3}\), \(19 \times 10^{-3}\), \(21 \times 10^{-3}\) and \(33 \times 10^{-3}\) min⁻¹, respectively. Furthermore, compared with commercial TiO₂ photocatalyst (Degussa P25), under the same conditions, our 5 minute sample displays more photocatalytic activity (Fig. 7).
Fig. 6. Evaluating of photocatalytic activity of TiO$_2$ nanofibers by photodegradation of Rh. B. (a) Rh. B without TiO$_2$ nanofibers, (b) 5 minutes, (c) 30 minutes, (d) 1 hour, (e) 2 hours and (d) 24 hours deposition times.
Though all kinetic curves behave similarly, for the samples prepared at higher deposition times photodegradation rate is more. This can be due to more deposited TiO₂ at higher deposition times as illustrated in Figure 5.

![Fig 7. Changes of Rh. B concentration under UV illumination for the samples prepared at different deposition times.](image-url)

**4. Conclusion**

In summary, TiO₂ nanofibers were prepared by adsorption of TiO₂ nanoparticles on cellulose fibers, followed by thermal removal of the cellulose template. It was realized that formation of TiO₂ nanofibers is due to aggregation of nanoparticles adsorbed on the cellulose fibers. The crystallinity of the TiO₂ fibers was achieved by heating the as prepared solution at 80 °C for 24 hours leading to formation of crystalline anatase phase. The deposition time is not so effective in the amount of TiO₂ coated on cellulose fibers. Photocatalytic activity of TiO₂ nanofibers was investigated at the presence of Rh. B TiO₂ nanofibers prepared in this method offer a good potential for photocatalytic applications.

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**References**


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