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Synthesis and characterization of efficient TiO$_2$ mesoporous photocatalysts

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Abstract

Mesoporous TiO$_2$ powder with large surface area and high porosity was prepared via template-free method of heat-stimulated oxidizing destruction of TiC by HNO$_3$. Anatase crystalline phase of as-prepared and annealed at 200–400 °C titania was confirmed by XRD technique. Surface nitrate-nitro groups responsible for high adsorption capacity of the TiO$_2$ powders were studied by FTIR spectroscopy. The annealing temperature can be used as a factor for regulation of titania morphology and structural properties. The rise in the annealing temperature higher than the temperature of nitrate-nitro groups decomposition induces the growth of TiO$_2$ crystallites, decreasing porosity and surface area, the drop of adsorption capacity, and improving photocatalytic activity under UV irradiation.

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1. Introduction

Among various oxide semiconductors, titania is considered as the most important photocatalyst due to its biological and chemical inertness, strong oxidizing power, nontoxicity, and long-term stability against photo- and chemical corrosion [1–4]. Titania with large surface area and high porosity is often required to achieve high efficiency associated with photocatalytic applications [5]. Recently, ordered mesoporous TiO$_2$ films and powders attracted considerable interest as potential photocatalysts owing to their large surface area and narrow pore size distribution, while retaining a crystalline framework [1–10]. Moreover, the mesoporous network promotes the diffusion of reactants and products, as well as facilitates the access to reactive sites on the surface of the photocatalysts [11, 12]. Firstly, mesoporous TiO$_2$ was synthesized using alkyl phosphate as a structure-directing template and titanium isopropoxide bis-acetylacetonate as a Ti-containing precursor [13]. Since then, many efforts have been made to synthesize mesoporous TiO$_2$ films and powders with various mesostructures, pore-wall parameters, morphology, doping and crystallization degree [14–19]. The development of ordered large-pore-size mesoporous TiO$_2$ material has been mostly related with the use of surfactants or block polymers as templates. The template removal by calcination generates high-surface-area mesoporous TiO$_2$. However, thermal treatment at high temperatures may have undesirable effects such as the collapse of mesoporous framework and loss of surface area due to facile crystallization of TiO$_2$ and subsequent crystal growth [20].

The synthesis of mesoporous TiO$_2$ through template-free methods is an important issue from industrial and environmental points of view. Most of the template-free routes for the synthesis of mesoporous TiO$_2$ materials are related with the hydrolysis or oxidation reactions using nitric acid and phosphoric acid as a catalytic or oxidizing agent [21–23]. Nevertheless, the influence of inorganic acids on the process and the material structures has not been investigated systematically. This paper presents a detailed study of the fabrication of mesoporous TiO$_2$ using a mild, one-step HNO$_3$ oxidation of TiC at 70 °C, firstly reported in [23] with some modifications. In our work we used a comparatively lower concentration of HNO$_3$ to save some non-oxidized carbon species in the obtained TiO$_2$ powder. Attention was given to the characterization of structure, surface properties and photocatalytic activity of the obtained material.

2. Experimental

2.1. TiO$_2$ synthesis

1.5 g of TiC (in black powder form) was placed into a three-neck round bottom flask equipped with a stir bar, a dropping funnel filled with 18 mL of 4 M HNO$_3$ and a reflux condenser. The nitric acid was added dropwise into the flask with TiC with a rate of 2 drops per second. The synthesis was carried out on a water bath at 70 °C. After complete addition of nitric acid the reaction was allowed to run for 1 h. After that reaction time, a yellow precipitate was formed at the bottom of the flask. The precipitate was separated by filtration and washed 3 times with ethanol. Afterwards, the resulting powder was dried at 70 °C in air and then annealed at different temperatures (the heating rate was 10 °C/min$^{-1}$).

2.2. Characterization

The TiO$_2$ crystal structure was examined by X-ray diffraction on a PANalytical X’Pert PRO MRD (Multi-Purpose Research Diffractometer, Holland) with modular construction using CuKa-radiation. Recording speed was 0.4 °/min.

The surface area and porosity of the samples were measured on a Micromeritics ASAP 2020 system using nitrogen at 77 K.

The particle size and morphology were characterized by scanning electron microscopy (SEM) using a TESCAN Vega3 SB microscope operating at 20.1 kV. Samples for SEM were prepared by scattering of dispersed powder onto holder coated with solution of liquid carbon “PlanoCarbon” and the solvent was evaporated immediately under ambient conditions. No sputtering was used for prevent samples charging by electron beam.
The thermal analysis of the TiO$_2$ powders was carried out on a NETZSCH STA 449C instrument using an alumina crucible over the temperature range from 30 to 800 °C in air. The heating rate was 10° per min.

Fourier transform infrared (FTIR) spectra were collected on an AVATAR-330 (Thermo Nicolet) spectrometer supplied with a diffuse reflectance accessory in the wavenumber range from 400 to 4000 cm$^{-1}$.

Adsorption of Rhodamine on the powder was performed in 2 mL Eppendorf tubes. 10 mg of TiO$_2$ powder was dispersed in 1.5 mL of 5 mM Rhodamine B (RhB) solution. The tubes were shaken during 1 h in dark at room temperature. Then, the powder was separated by centrifugation and solution was analysed by an UV–vis spectrophotometer (Shimadzu UV-2550).

2.3. Measurement of photocatalytic activity

Photocatalytic activities of the TiO$_2$ samples were evaluated by the degradation of RhB aqueous solutions under UV irradiation. In each experiment, 80 mg of metal oxide catalyst was dispersed in 80mL of 0.02 mM RhB solution in a quartz cell at 20 °C and the dispersion was irradiated during various times. The system was mildly stirred using a magnetic stirrer. A mercury lamp (NARVA UVK-125-2) was used as the UV light source; the concentration of RhB was analyzed by an UV–vis spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction

Oxidation of black TiC powder by concentrated nitric acid gives a yellowish powder with fine-dispersed structure. X-ray diffraction patterns of the resultant material dried at 70 °C and then annealed at different temperatures are shown in Fig. 1. Only broadened peaks characteristic of anatase TiO$_2$ phase can be seen in the diffractograms, indicating that titanium carbide is completely oxidized by nitric acid resulting in the formation of fine-grained titanium dioxide [24]. The mean size of the TiO$_2$ anatase crystallites was estimated by the width of the (101) peak using Debye–Scherrer equation ($D = 0.9\lambda/k\cos\theta$, where $k$ is the full width at half-maximum (FWHM) of the peak, $\theta$ is the angle of diffraction, and $\lambda$ is the wavelength of the X-ray radiation) and is about 4 nm for dried sample and 3.9 nm and 7.4 nm for the samples annealed at 200 and 400 °C, respectively.

![Fig. 1. X-ray diffractograms of TiO$_2$ powders obtained from TiC and annealed at different temperatures.](image-url)
3.2. Scanning electron microscopy

SEM images clearly show that large well-faceted crystals of TiC were transformed to fine-porous micron-sized aggregates of titanium dioxide nanocrystallites after treatment with HNO₃ (Fig. 2).

3.3. Brunauer-Emmett-Teller (BET) analysis

The mesoporous structure of the powder prepared by oxidative destruction of titanium carbide was investigated by N₂ adsorption-desorption isotherm measurements. The isotherms of both as-prepared dried powder and the powder annealed at 200 °C can be classified as type IV according to the IUPAC recommendations [25], which is indicative of mesoporous materials. The structural properties of the TiO₂ powders dried at 70 °C and annealed at different temperatures are summarized in Table 1. The powder annealed at 200 °C has quite large BET surface area and total pore volume reaching values of 353 m² g⁻¹ and 0.300 cm³ g⁻¹, respectively. However, the surface area and pore volume of the TiO₂ powders decrease appreciably after annealing at 400 °C that indicates beginning of the mesoporous structure collapse.

| Annealing temperature (°C) | BET surface area (m² g⁻¹) | Average pore diameter (nm) | Total pore volume (cm³ g⁻¹) | Adsorption capacity of RhB (mg g⁻¹)* |
|----------------------------|---------------------------|----------------------------|-----------------------------|-------------------------------------|
| 70                         | 290                       | 3.1                        | 0.224                       | 40                                  |
| 200                        | 353                       | 3.4                        | 0.300                       | 35                                  |
| 400                        | 135                       | 5.5                        | 0.185                       | 0.5                                 |

*Adsorption of RhB from 5mM solution

3.4. FTIR spectroscopy

Structural characteristics of the TiO₂ samples were also estimated by FTIR spectroscopy. Infrared spectra of the TiO₂ powders prepared from titanium carbide and annealed at different temperatures are shown in Fig. 3.

The dominating wide band at 400±850 cm⁻¹ is attributed to vibrations in octahedrons [TiO₆]. It is a superposition of several normal ν(Ti–O) vibrations characteristic of titanium dioxide. There are also two intensive bands related to
deformation δ(\text{HO–H}) vibrations at 1629 cm\(^{-1}\) and asymmetric ν\text{as}(\text{O–H}) vibrations at 3200÷3400 cm\(^{-1}\) of water molecules. The region from 800 to 1800 cm\(^{-1}\) shows vibrations of nitro, nitrates and carboxylate groups (Fig. 3b).

Nitrate anion can be coordinated to the surface contacting the Ti as a monodentate, symmetric or asymmetric chelate bidentate, and bidentate bridging group. The symmetry of such ions differs slightly (C\(_2\)v or C\(_s\)), therefore it is difficult to distinguish them in the IR spectra. A bound nitrate group gives three normal vibrations (ν\(_3\) = 1515÷1565 cm\(^{-1}\), ν\(_1\) = 1250÷1295 cm\(^{-1}\) and ν\(_2\) = 1015÷1050 cm\(^{-1}\)), depending on the coordination of the nitrate group [26] and composite (ν\(_3\)+ν\(_4\)) vibration, which is split according to the type of nitrate group coordination in the 1645÷1710 cm\(^{-1}\) range [27]. For the as-prepared TiO\(_2\) sample, composite (ν\(_1\)+ν\(_4\)) vibration is observed from unbound nitrate group (at 1684 cm\(^{-1}\)) and from bidentate one (at 1629 and 1711 cm\(^{-1}\)). For the TiO\(_2\) sample annealed at 200°C in this region there are vibrations from unbound nitrate group (at 1680 cm\(^{-1}\)), monodentate group (at 1665 and 1680 cm\(^{-1}\)) and bidentate one (at 1644 and 1710 cm\(^{-1}\)). The lines at 1407 and 1107 cm\(^{-1}\) are the symmetric and asymmetric stretching vibrations of nitro group, respectively. All bands belonging to the nitrate and nitro groups are reduced upon annealing the samples, and after heat treatment at 400 °C the vibrations related to nitrate and nitro groups are not observed.

The broad absorption band at 2000 cm\(^{-1}\) may be due to the appearance of complexes with CO adsorbed on the TiO\(_2\) surface.

![Fig. 3. Full (a) and magnificated part (b) of FTIR spectra recorded for the TiO\(_2\) powders annealed at 70 °C, 200 °C, and 400 °C.](image.png)

3.5. Thermal analysis

According to the thermal analysis data the weight loss of the as-prepared powder occurs in three steps (Fig. 4.):

1) Up to 160 °C a weight loss of 11 % is observed belonging to removal of weakly bound water and nitric acid physically adsorbed on the surface.

2) From 160 °C to 350 °C the weight loss corresponds to 15 %. It can be associated with the decomposition of nitrate and nitro surface species, burning of carbon residues, removal of oxidized carbon species and chemically bound water. The presence of oxidized carbon species in the as-synthesized material is supported by the fact that after annealing the powder in an inert atmosphere (argon) at 400 °C its color is changed from yellowish to black.

3) Above 350 °C the decrease in weight is only 2.2 %. This weight loss accompanied by a slight exothermic effect that could be related to the elimination of tightly bound OH-groups, structural water and the most stable carbon species.
Fig. 4. TG/DTG curves for the TiO$_2$ powder obtained by oxidation of TiC with nitric acid.

3.6. Rhodamine B adsorption on the TiO$_2$ powders

The ‘dark’ adsorption capacity of the samples was estimated using a positively charged dye (RhB) (Table 1). The samples annealed at 70 °C and 200 °C adsorb 40 and 35 mg/g of RhB, respectively. Increasing the annealing temperature leads to a lowering of the adsorption capacity. The sample annealed at 400 °C almost does not adsorb RhB in neutral solution.

3.7. Rhodamine B photodegradation in TiO$_2$ slurries under UV irradiation

The synthesized TiO$_2$ samples are photocatalytically active in degradation of Rhodamine B in aqueous solutions, as depicted in Fig. 5.

Fig. 5. Photocatalytic activity of the TiO$_2$ powders annealed at different temperatures for photodegradation of RhB under UV irradiation: a) variation of the RhB concentration as a function of irradiation time and b) fitting of experimental data using first-order kinetic model.
The kinetics of Rhodamine B photodecomposition on the oxide surface can be described by the first-order equation [28]:

\[ \ln \left( \frac{C_0}{C} \right) = kt, \]  

where \( k \) is the rate constant (min\(^{-1}\)), \( C_0 \) is the initial concentration of the dye, and \( C \) is the actual concentration of the dye at irradiation time \( t \). Fig. 5b presents the linear relationship between \( \ln(C_0/C) \) and irradiation time. The rate constant \( k \) is determined from the slope of the linear \( \ln(C_0/C) \) vs \( t \) plots. The value of \( k \) gives an indication of the photocatalytic activity. The rate constant for the TiO\(_2\) sample annealed at 200 °C is 0.0066 min\(^{-1}\). Increasing the annealing temperature leads to a higher photocactivity of the TiO\(_2\) powder. The photoactivity of the sample annealed at 400 °C is close to that of commercial TiO\(_2\) photocatalyst Degussa P-25 in the UV range. The rate constants for the TiO\(_2\) sample annealed at 400 °C and for Degussa P-25 are 0.02215 min\(^{-1}\) and 0.0182 min\(^{-1}\), respectively.

3.8. Discussion about formation mechanism and properties of mesoporous TiO\(_2\)

On the basis of the experimental results obtained the mechanism of mesoporous titania formation from TiC powder during oxidation by nitric acid is proposed.

TiC powder does not react at a detectable rate with nitric acid at room temperature. The reaction begins only after thermal activation. Oxidation of titanium carbide with an intensive liberation of gases is observed at 70 °C. In a first step, titanium carbide is oxidized by nitric acid to titanium(IV) nitrate (2). However, titanium(IV) nitrate is unstable in aqueous solutions and rapidly hydrolyzes to titanium(IV) oxynitrate (3). Then, titanium(IV) oxynitrate can undergo stepwise hydrolysis up to hydrated forms of titania TiO\(_2\)\(\cdot\)xH\(_2\)O (4) or can directly oxidize titanium carbide (5). The overall process of the TiO\(_2\) formation can be illustrated by the equation (6).

\[
\begin{align*}
\text{TiC} + 12\text{HNO}_3 & \rightarrow \text{Ti(NO}_3)_2 + \text{CO}_2 + 8\text{NO}_2 + 6\text{H}_2\text{O} \quad (2) \\
\text{Ti(NO}_3)_2 + \text{H}_2\text{O} & \rightarrow \text{TiO(NO}_3)_2 + 2\text{HNO}_3 \quad (3) \\
\text{TiO(NO}_3)_2 + (x+1)\text{H}_2\text{O} & \rightarrow \text{TiO}_2\cdot x\text{H}_2\text{O} + 2\text{HNO}_3 \quad (4) \\
4\text{TiO(NO}_3)_2 + \text{TiC} & \rightarrow 5\text{TiO}_2 + 8\text{NO}_2 + \text{CO}_2 \quad (5) \\
\text{TiC} + 8\text{HNO}_3 & \rightarrow \text{TiO}_2 + 8\text{NO}_2 + \text{CO}_2 + 4\text{H}_2\text{O} \quad (6)
\end{align*}
\]

It should be noted that the mole ratio of the reagents according to equation (6) is 1:8, which is higher than used during the synthesis (1:3). Thus, carbon in titanium carbide is oxidized not completely to CO\(_2\), but also to CO, and partly oxidized carbon species can be preserved in the TiO\(_2\) powder synthesized. The presence of such species in the as-prepared material is supported by the fact that after annealing the powder in an inert atmosphere (Ar) at 400 °C, its color is changed from yellowish to black. During the synthesis, nitric acid is reduced not only to NO\(_2\), but also to N\(_2\)O\(_3\), NO, N\(_2\)O and N\(_2\). We observed the formation of a great amount of brown NO\(_2\) gas, and some amount of N\(_2\)O\(_3\) was detected. N\(_2\)O\(_3\) caused appearance of blue coloration of water in a condenser.

The XRD data show that the TiC phase is completely oxidized in the end of the synthesis (Fig. 1). The evolution of a great amount of gases during the oxidation process favours formation of the mesoporous structure of TiO\(_2\) powder, which is characterized by a large surface area (Fig. 2, Table 1). FTIR spectra demonstrate that TiO\(_2\) powders annealed at 70 and 200 °C have a great amount of nitrate and nitro groups, which are differently coordinated on the oxide surface. According to the TG data, the most intensive elimination of nitrate-nitro groups is observed between 220 and 280 °C, and the FTIR spectrum of the TiO\(_2\) sample annealed at 400 °C already indicates the absence of nitrate and nitro groups. The presence of these groups on the TiO\(_2\) surface determines a high adsorptive capacity of the powder annealed up to 200 °C to positively charged dye (RhB). The sample annealed at 400 °C almost does not adsorb RhB in neutral solutions.

Surface nitrate and nitro groups may inhibit the growth of TiO\(_2\) crystallites during heat treatment. The increase of the TiO\(_2\) crystallite size and decrease of the powder surface area are observed at temperatures higher than the temperature of nitrate-nitro group decomposition. After annealing at 400 °C the titania particle size grows twice and
the surface area is reduced by about 2.5 times. Better crystallinity and less deficiency (these factors reduce the recombination of photogenerated electron-hole pairs in the oxide) of the samples annealed at 400 °C result in their higher photoactivity, as inferred from the RhB decomposition under UV irradiation, as compared with the sample annealed at 200 °C.

4. Conclusion

Mesoporous TiO₂ powders with large surface area and high porosity were synthesized from TiC by oxidation with HNO₃ at enhanced temperature. The multistep mechanism for titanium carbide oxidation is proposed.

Great amount of nitrate and nitro groups on the surface of as-synthesized TiO₂ powder is observed by FTIR spectroscopy. These surface nitrate-nitro groups determine adsorption properties of TiO₂ and influence morphological characteristics of the samples annealed at different temperatures. The TiO₂ powder annealed at 200 °C is characterized by a crystallite size of 3.9 nm, a surface area of 353 m² g⁻¹ and an adsorption capacity towards RhB of 35 mg g⁻¹. Annealing of TiO₂ powder at temperatures higher than the temperature of nitrate-nitro groups elimination leads to growth of TiO₂ crystallites, decrease in the porosity and surface area and lowering the adsorption capacity to the positively-charged dye. At the same time, improving the photocatalytic activity of the TiO₂ powder under UV irradiation is observed. The photoactivity of the sample annealed at 400 °C is close to commercial TiO₂ photocatalyst Degussa P-25 in the UV range.

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