가시광하에서 티타니아 복합체의 광촉매 특성

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Photocatalytic Properties of Titania Complex under Visible Light Irradiation

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Introduction

Generally, photocatalysis can be applied to get energy economically, synthesize the useful materials, and remove environmentally harmful materials by transforming solar energy to chemical energy. Recently, the availability of photocatalysis has largely interested in the environment of Ubiquitous. Therefore, the study for photocatalysis has progressed by many investigators in domestic [1-4].

In recent years, titania has been widely studied for its wide application in photocatalysis, solar cells and hydrogen production because of its no toxicity, stability in aqueous solution, and no photocorrosion under bandgap illumination. However, titania is a wide bandgap semiconductor (3.03 eV for rutile and 3.18eV for anatase) and can only absorb about 5% of sunlight in the ultraviolet region, which can only absorb about 5% of sunlight in the ultraviolet region, which greatly limits its practical applications. Extensive efforts have been made in the development of titanium dioxide photocatalyst that can utilize soloar or indoor light.

It has recently been demonstrated that the photocatalytic oxidation of toxic compounds, mediated by semiconducting materials, is an alternative to conventional methods for the removal of pollutants in water. Among semiconductors studied so far, nanosized TiO_2 has been known to be one of the best photocatalysts. TiO_2 is widely studied for its potential applications in catalysis, sensors and high performance photovoltaics. Composites of TiO_2 with efficient electron donor materials and dye sensitizers are widely used to increase the light harvesting capability of donor-acceptor systems. Titania is a popular photocatalyst and has three crystal phase such as anatase, brookite, and rutile. It was reported that the high temperature heat treatment with keeping anatase phase is crucial to achieve high photoactivity due to the increase of crystallinity.

The sol-gel process is very promising for the formation of metal oxides and temperature sensitive organic-inorganic hybrids, nanocomposites in which allow molecular level composition homogeneity. In the preceding parts, we have reported the fundamental aspects of the sol-gel process for the formation of anatase TiO_2 nanoparticles in the absence of acid and basis, including the solution chemistry and the specific behavior of hydroxide ions and protons, as well as the striking effect of inert electrolyte, which has a decisive influence on the formation of nanosized anatase particles in the gel-sol system.

In this study titania complex was prepared by sol-gel process with the aim of extending the light absorbtion spectrum toward the visible region. The photocatalytic activity under visible light irradiation was evaluated using methylene blue as a model organic compound. The effect of calcination temperature on the crystal phase and crystallite size was studied. The complex calcined at different temperature was characterized by X-ray diffraction (XRD). And disinfectant activity was

performed in *Escherichia coli* and *Staphylococcus aureus* and deodorization efficiency were investigated under visible light irradiation.

Experimental

Titania complex was prepared by sol-gel process and the molar ratio of titania to methanol is 10%. Tittanium (IV) isopropoxide was used as precursor of titana sol. All titania sol were dried in the dry oven at 110 ^{o}C for 24 hrs. The obtained xerogel was calcined at several temperatures ranging from 200 to 800 ^{o}C for 1 hrs. The major phase of the obtained particles was analyzed by X-ray different (Rigaku D/MAXIIC) using Cu Kα radiation over the 2θ range of 5-80°. The crystallite size of the prepared particles was determined from the broadening of the anatase main peak at 2θ=25.3° by the Schrerrer equation. The chemical structure of the prepared particles was examined using a fourier transform raman spectrophotometer (FT-Raman, Bruker, Equinox 55) operated at 140mW.

Results and Discussion

Figure 1 illustrates the XRD pattens of titania complex calcined from 200 to 500 ^{o}C. It can be seen that the diffraction peaks at corresponding angles of anatase phase become much sharper when the temperatures increase form 200 to 500 ^{o}C. The major phase of the pure TiO_2 particle is an anatase structure and a rutile peak was observed above 500 ^{o}C. The crystallite size of powders was determined from the broadening of corresponding diffraction peaks by using Scherrer's formula $D=K\lambda/\beta\cos\theta$, where λ is the wavelength on the X-ray radiation (λ=0.15418 nm), K the Scherer constant (K=0.9), θ the X-ray diffraction peak and β the full-width at half-maximum (FWHM) of (101) plane (in radians), which is corrected for the instrumental broadening prior to calculation of its real particle size broadening.

Table 1. Physical properties of nanosized powders calcined at various temperatures

Calcination temperature (^{o}C)	XRD	
	Crystal phase	Crystallite size (nm)
200	Anatase	7
300	Anatase	7
400	Anatase	8
500	Anatase/rutile	13
600	Anatase/rutile	16
700	Rutile/anatase	29
800	Rutile/anatase	34

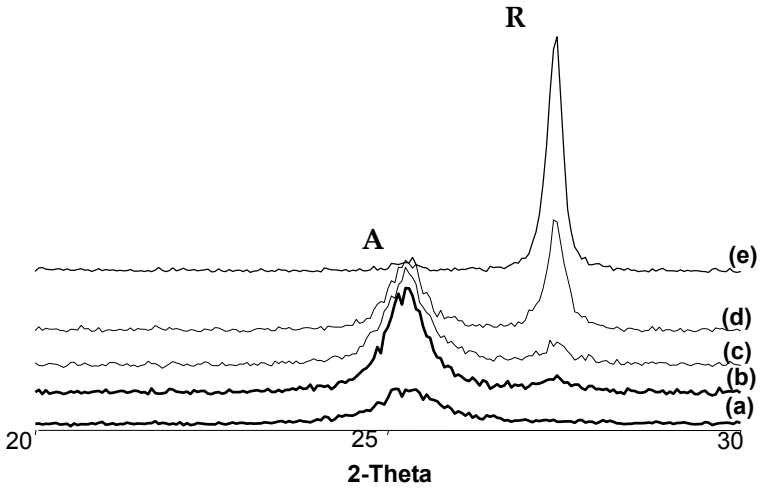


Figure 1. XRD patterns of the TiO2 nanoparticles obtained after calcination for 1 h in air at; (a) 200; (b) 300; (c) 400; (d) 500 °C . A=anatase (101) reflection; R=rutile (110) reflection.

The crystallite size of particles prepared by different calcination temperature is summarized in Table 1. One can see that the crystallite size of the anatase phase of the pure titania increased ca. 7 to 35 nm as the calcinations temperature increased from 200 to 800 ℃. This result indicates that the calcinations improve the crystallinity of the particles and the anatase phase changes into the rutile phase with an increase of calcinations temperature.

The effect of particle size on the photocatalytic activity of the titania complex for the oxidative degradation of methylene blue in distilled water under visible light irradiation was investigated. After the adsorption equibrium of methylene blue onto the catalyst was established in the dark, about 30% of the initial concentration of methylene blue is absorbed onto the titania complex. A blank experiment in the absence of irradiation but with titania complex demonstrates that no methylene blue degration occurs. It can be seen that the photocatalytic degradation of methylene blue proceeded on the titania photocatalst under visible light irradiation. After 3 hours photodegradation reaction excited by visible light, 95% methylene blue was destroyed on titania complex. The degradation of methylene blue on titania complex under visible light irradiation is attributed to the photosensitization process (not shown here).

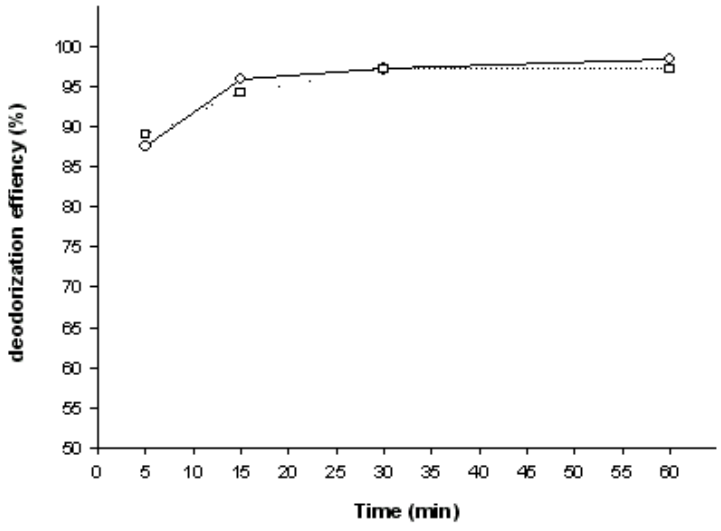
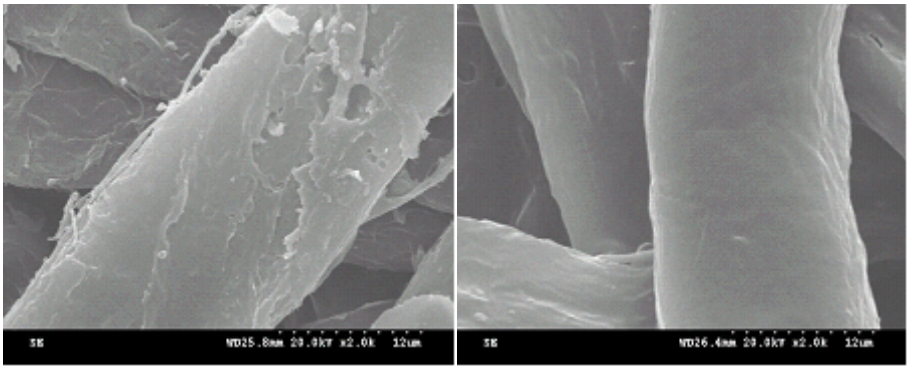


Figure 2. Photocatalytic degradation efficiency of formaldehyde (□) and ammonia (○).



(a) uncoated wall paper (b) coated wall paper

Figure 3. SEM images of uncoated wall paper (a) and coated wall paper (b).

And in case of wall-paper coated with titania sol, the deodorization efficacy was considerably increased above 98.3% and 97.8% for formaldehyde and ammonia cause indoor air pollution. Also, the disinfectant activity for Escherichia coli and Staphylococcus aureus was showed superior character above 99.9% after 24 hours.

Conclusions

From the presented results the following conclusions can be drawn:
Titania sol was prepared through titanium tetraisopropoxide alcoholysis method and particle was about 15 nm according to DLS measurement. And the powder derived from titania sol was calcinated during the temperature from 200 to 400 ^{o}C maintained pure anatase crystalization

It was found that photocatalytic compound showed effectively antibacterial activity against E. coli and S. aureus and deodorization efficencies were above 95% under visible light irridation.
Uniform transparent TiO2 thin-film could be prepared by dip coating with the titania sol. The thickness of one cycle was about 60 nm. TiO_2 coatings can maintain their hydrophilic properties indefinitely, as long as visible light is illuminated.

References

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