Available online at www.sciencedirect.com
ScienceDirect
Materials Chemistry and Physics 105 (2007) 38–46
MATERIALS CHEMISTRY AND PHYSICS
www.elsevier.com/locate/matchemphys

Preparation, characterization and photocatalytic activity of optically transparent titanium dioxide particles

Václav Štengl [a,*], Snejana Bakardjieva [a], Nataliya Murafa [a], Jan Šubrt [a], Hana Měšťánková [b], Jaromír Jirkovský [b]

[a] *Institute of Inorganic Chemistry AS CR v.v.i., 250 68 Řež, Czech Republic*
[b] *J. Heyrovský Institute of Physical Chemistry AS CR, Dolejškova 3, Prague 8, Czech Republic*

Received 29 September 2005; received in revised form 28 February 2007; accepted 8 April 2007

Abstract

The transparent particles of titanium dioxide (anatase or brookite modification) was prepared by hydrolysis of aqueous solution of titanium(III) chloride in the presence of polyethyleneglycol. The prepared samples were characterized by measurement of particle size distribution and selected area electron diffraction (SAED), morphology and microstructure were obtained by HRTEM. The crystallinity of the samples and its photocatalytic activity increased with the time of ageing in the aqueous solutions up to 60 days. Photocatalytic activity of prepared samples of titanium dioxide was determined by degradation of aqueous solution of Orange II dye under UV radiation, in comparison to Degussa P25 photocatalyst.

Keywords: Optically transparent particles; Polyethyleneglycol; Titanium(III) chloride; Anatase; Brookite; Q-TiO_2

1. Introduction

There are three types of crystal structures in natural titanium oxide: rutile type, anatase type and brookite type (see Fig. 1). All three of these types are expressed using the same chemical formula (TiO_2); however, their crystal structures are different. Titanium oxide absorbs light having an energy level higher than that of the band gap, and causes electrons to jump to the conduction band to create positive holes in the valence band. Despite the fact that the band gap value is 3.0 eV for the rutile type and 3.2 eV for the anatase type, they both absorb only ultraviolet rays. However, the rutile type can absorb the rays that are slightly closer to visible-light rays.

As the rutile type can absorb light of a wider range, it seems logical to assume that the rutile type is more suitable for use as a photocatalyst. However, in reality, the anatase type exhibits higher photocatalytic activity. One of the reasons for this is the difference in the energy structure between the two types. In both types, the position of the valence band is deep, and the resulting positive holes show sufficient oxidative power. However, the conduction band is positioned near the oxidation–reduction potential of the hydrogen, indicating that both types are relatively weak in terms of reducing power. It is known that the conduction band in the anatase type is closer to the negative position than in the rutile type; therefore, the reducing power of the anatase type is stronger than that of the rutile type. Due to the difference in the position of the conduction band, the anatase type exhibits higher overall photocatalytic activity than the rutile type. The absorption of ultraviolet rays shorter than this wavelength promotes reactions. These ultraviolet rays are near-ultraviolet rays contained in the sunlight reaching the earth and emitted by room lights, and they have a very limited range of weak light throughout the spectrums of sunlight and room lights.

The development of a visible-light photocatalyst may be considered as a solution, but no substance superior to titanium oxide as a material for photocatalysts has yet been discovered. One major reason for this is that a semiconductor with a smaller band gap than that of titanium oxide results in autolysis if it receives light in the presence of water. In titanium oxide, the absorption of ultraviolet rays with a wavelength of 388 nm or shorter promotes reactions; however, it is known that 254-nm rays having a greater energy level, which are used in germicidal lamps, are absorbed by the DNA of living organisms and form pyrimidine dimers, thereby damaging the DNA.

* Corresponding author. Tel.: +420 2 6617 3534; fax: +420 2 2094 0157.
E-mail address: stengl@iic.cas.cz (V. Štengl).

0254-0584/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2007.04.037

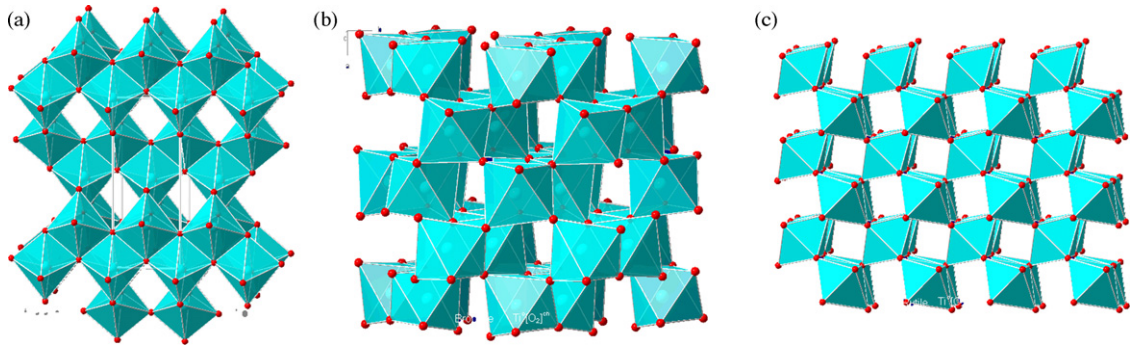

Fig. 1. Crystal structures of titanium oxide: (a) anatase, (b) brookite and (c) rutile.

Titanium oxide photocatalyst does not require ultraviolet rays that have an energy level as high as 254 nm and are hazardous to humans. It also allows reactions to be initiated by the near-ultraviolet rays with relatively long wavelengths contained in sunlight and emitted by fluorescent lamps.

Extremely small particles of titanium dioxide exhibited a quantum size effect [1]. Their physico-chemical properties depended on the particle dimension. Comparing to macroscopic TiO_2 powder materials, these particles showed a blue shift [2] in their absorption spectra due to broadening of the band gap. Their aqueous dispersion do not practically scatter light. The synthesis of transparent colloidal solutions of extremely small titanium dioxide particles in water or ethanol by hydrolysis of $TiCl_4$ [3] or nanometer size Q-TiO_2 particles [4] prepared by the sol–gel method are presented. In work [5] detailed kinetic study of the photocatalytic degradation of diuron in aqueous colloidal solutions of the Q-TiO_2 particles prepared by hydrolysis of $TiCl_4$ is reported.

In this paper preparation, characterization and photocatalytic activity of transparent particles (aqueous colloidal solutions of Q-TiO_2 particles) prepared by hydrolysis of $TiCl_3$ solution in the presence polyethyleneglycol (PEG) is described.

2. Experimental

2.1. Chemicals and raw materials

Polyethyleneglycol (mol. mass 200–35,000, p.a.) and titanium, evaporation slug 99.99% was supplied by Fluka (Munich, Germany). Ten grams of metal titanium was diluted in 70 ml hydrochloric acid in electrical heating nest in round-bottom flask with reflux cooler to purple solution of titanium(III) chloride. The prepared solution of titanium(III) was filled to total volume 100 ml with hydrochloric acid.

2.2. Synthesis of transparent titanium dioxide particles

Ten milliliters of violet solution of titanium(III) chloride was added to the solution of 50 g polyethyleneglycol (PEG) of 800 ml ethanol a 3200 ml distilled water in the 5 l baker (see Table 1). The reaction mixture was heated at temperature 70 °C under stirring. After decolorize of the reaction mixture the heating and stirring was terminated. The formation of transparent particles was determined by ground of Tyndall effect [6] by means of red laser. Ageing process of transparent particles was realized at 35 °C by aqueous thermostate.

2.3. Characterization methods

The particle size distribution was determined by laser scattering using the ZEN 1600 equipment (Malvern Co., USA). The sample was measured in a square glass cuvette with round aperture (PCS8501).

Transmission electron microscopy was carried out on two instruments Philips EM 201 at 80 kV and on a JEOL JEM 3010 at 300 kV (LaB_6 cathode). Copper grid coated with a holey carbon support film was used to prepare samples for TEM observation. The copper grid was dipped into solution with transparent particles.

Kinetics of the photocatalytic degradation as well as mineralization of 25 ml 0.25 mM Orange II dye [7] and 200 ml solutions with transparent particles of titanium oxide (200 mg l^{-1}) were measured. Quartz water-jacketed laboratory photoreactor, magnetically stirred and continuously irradiated with one "black light" lamp ($\lambda = 365$ nm, $I_0 = 5.3 \times 10^{-5}$ einstein dm^{-3} s^{-1}), was used. The laboratory irradiation experiments were performed in a self-constructed photoreactor. It consists of two coaxial quartz tubes placed in the middle of a steel cylinder with an aluminum foil covering its inner wall. Inner quartz tube (diameter 24 mm, length 300 mm) was filled with the investigated suspension (70 ml) and magnetically stirred. Cooling water was circulating between the

Table 1
Reaction conditions and particle size distribution of titanium dioxide particles

Sample	Molecular weight of PEG	ED	Average particle size (nm)	Particle distribution					
				(nm)	(%)	(nm)	(%)	(nm)	(%)
PEG200	200	Anatase	36.4	–	–	44.5	94.7	4,590	1.2
PEG300	300	Anatase	39.2	–	–	42.7	86.7	1,094	13.3
PEG600	600	Anatase	43.9	–	–	50.8	96.1	4,485	3.8
PEG1000	1,000	Anatase	61.7	34.2	51.1	360.6	47.9	5,428	1.1
PEG2000	2,000	Brookite	41.2	39.1	75.7	348.3	34.5	–	–
PEG4000	4,000	Anatase	76.4	15.5	3.5	99.1	95.4	4,809	1.1
PEG10000	10,000	Brookite	83.6	80.6	77.2	529.6	12.5	4,653	10.3
PEG20000	20,000	Brookite	65.6	–	–	90.3	100	–	–
PEG35000	35,000	Brookite	74.5	–	–	85.4	92.8	4,322	7.2