Synthesis and Investigation of Visible-Light-Activated Rutile Phase Modified TiO2

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Nitrogen-containing dye-sensitizers loading on TiO2 has decreased the electron excitation energy and therefore has improved the photocatalytic performance by increasing the sensitivity under visible light irradiation. The addition of metal cations such as platinum on TiO2 *via* the intermediation role for moving the conduction band electron to electron acceptors and increasing the pair electron-holes long-life has increased the photocatalytic reaction rate and has improved the photocatalytic activity. In this study, at first titanium isopropoxide precursore has been used by the sol-gel method for TiO2 synthesizing. Then, the effect of calcination temperatures in forming of the nanosize photocatalyst was studied. In addition, their phases were studied with XRD test and analyzed their specific surface area using the BET test. Finally, the ability of the absorption of visible light by all of samples was investigated by means of diffuse reflectance spectra and has been compared with commercial TiO2-P25 (consist of 80 % anataze phase and 20 % rutile phase).

Key Words: Photocatalyst, TiO2, Visible light, Dye sensitization, Platinization, Anatase, Rutile.

INTRODUCTION

Titanum dioxide (TiO2) is a semiconductor that has been extensively investigated and applied to a wide spectrum of chemical disciplines. Instances arise in selective oxidation and reduction and use in photo-degradation of organic and inorganic compounds such as environmental pollutions. However, because of its large band gap energy (3.0-3.2 eV), the absorption spectra of nanocrystalline titanium dioxide are within the ultraviolet region where only 4 % of the solar radiation is effective, which limits practical application of natural solar light[1,2]. Visible light applications usually require semi-conductors with band gaps lower or equal to 3.0 eV, such as rutile TiO2 (reported with a band gap of 3.0 eV or a band edge at 413 nm)[3], thus ruling out to use of the conventional 3.2 eV band gap anatase phase. Rutile is usually reported to be less active than anataseas a photocatalyst[1,4]. Pure rutile phase is generally obtained by high-temperature treatment of anatase, leading to a low surface area and low porosity material with large sintered TiO2 particles. Different rutile synthesis methods including *e.g.* mist plasma evaporation, pulse magnetron sputtering and RF thermal plasma have been recently reported for powder and film growth[5-11]. The synthesis of large amounts of small diameter rutile particles with tunable porosity to allow a good accessibility of pollutants to the adsorption sites and a high surface area for dispersing metallic nanoparticles. Various methods were developed to extend the absorption spectra of TiO2 to visible spectra region such as dye photosensitization[12-14], in which a dye adsorbed on TiO2 surface gets excited by absorbing visible light and an intercomponent electron transfer is realized between dye molecules and TiO2 has proved to be an inexpensive and efficient method to extend the absorption spectra of TiO2 into visible region. In the present work cobalt(II) phthalocyanine-tetrasulfonate (Co PcTs) have chosen as dye-photosensitizer. Further the addition of VIII group metals on TiO2 has been frequently employed to improve the activity of photocatalysts[15-21]. The presence of noble metal deposits on TiO2 is known to increase the photocatalytic reaction rate through the Schottky-barrier electron trapping and consequent longer electron-hole pair lifetimes. In many studies, platinum was the most active in enhancing photocatalytic activities of TiO2 where the electron trapping into the platinum phase typically occurred whitin $1 \mu s$[22]. Since the back electron transfer to oxidized dye also proceeded in the time scale of about $1 \mu s$[23], the electron trapping process on platinum could compete with the back electron transfer. Therefore, the other way for the improvement of photocatalytic activity at visible light region ($\lambda > 400$ nm) is modification of TiO2 with deposition of platinum. In order to clarify the role of base TiO2 in a platinum-modified TiO2 photocatalyst, we synthesized a rutile TiO2 sample and

performed deposition of platinum on this sample and other time on TiO₂ (DegussaP25). Ultimately platinum-modified TiO₂-P25 was dye sensitized and compared with platinum-modified rutiles were dye sensitized with cobalt(II) phthalo-cyanine-tetrasulfonate in visible light region.

EXPERIMENTAL

Rutile synthesis: The high surface area rutile synthesis consisted of a sol-gel procedure in which the titanium isopropoxide (TIP, Fluka, purum) was first hydrolyzed under vigorous stirring by the addition of a 2 mol L⁻¹ aqueous solution of hydrochloric acid (with a ratio of 14 mL of titanium isopropoxide per 23.5 mL of HCl solution). After 48 h of aging at room temperature of the hydrosol, poly(ethyleneglycol) (PEG-4000, 50 mg/mL of sol) used as porogen was introduced under stirring and the resulting mixture was dried at room and further at 110 ºC for 24 h, before calcination in air at 350, 400 and 450 ºC for 6 h (heating rate of 2 ºC/min).

Preparation of Pt/TiO₂ photocatalyst: The platinum deposition (1 wt. %) was performed on to the TiO₂ (rutile and P25) with using an aqueous solution of H_2PtCl_6 (0.005 M) with 26 mL per 2.5 g of TiO₂. An equimolar reagent (Merck, NaBH₄, 0.07 g in 10 mL distilled water) solution was dropped for platinum reduction. The resultant slurry, which was grayish in colour, was filtered and washed with distilled water. The precipitated catalyst was dried overnight in an oven at 80 ºC.

Loading of cobalt(II) phthalocyanine-tetrasulfonate (CoPcTs) on TiO₂: CoPcTs was loaded onto TiO₂ by stirring the TiO₂ powder (0.5 g) in dye solution (1 mM in 100 mL distilled water) at room temperature for 12 h in the dark. After filterating and washing, the sample was dried and kept in the dark.

RESULTS AND DISCUSSION

The synthesis of low-temperature rutile was performed by using a sol-gel method for which a longer aging duration of the titania sol during the synthesis favours the rutile phase *versus* anatase and consisting of dissolving and recrystallizing an oxide in its mother liquor in order to obtain a more stable crystalline phase compared to anatase[24]. Appearance of rutile beside the anatase phase in the hydrosol occurred after few hours of aging, whereas a 48 h aging that rutile phase was growing and after calcinations to remove the poly(ethyleneglycol) porogen, rutile (83 %) was observed by XRD. The role of poly(ethyleneglycol) was increasing the specific surface area and porosity volumes[25]. We calculated from XRD pattern that increasing calcination temperature leading to increasing rutile *versus* anataze (Fig. 1).

It is observed that the sample with 350 ºC calcinations temperature was not crystalline form and it was amorphous (Fig. 2). Also observed in BET results that specific surface area from 50 m² g⁻¹ for TiO₂ (P25) increased to 65 m² g⁻¹ for synthesized rutile with 450 ºC calcination temperature but the problem was growing up the particle size that resulted decreasing the adsorption. Increasing calcinations temperature from 350 to 450 ºC leading to growing up the particle size from 15.36 to 29.43 nm.
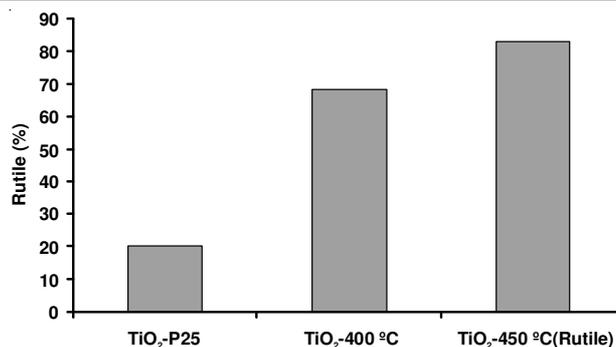

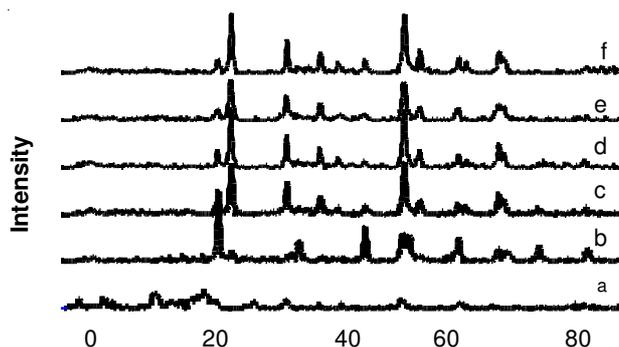Fig. 1. Effect of calcinations temperature in % rutile phase

Fig. 2. XRD patterns that: (a) synthesized TiO₂ with calcinations temp. = 350º C; (b) Pt/TiO₂-P25; (c) Pt/rutile; (d) N/Pt/rutile; (e) synthesized TiO₂ with calcinations temp. = 400 ºC; (f) synthesized TiO₂ with calcinations temp. = 450 ºC; (this sample called rutile in this paper)

Platinum loading on rutile (were not changed the XRD pattern and rutile *versus* anatase) improved the particle size to 22 nm. Deposition of CoPcTs on Pt/rutile increased the particle size to 23.8 nm. The effect of the platinum loading on TiO₂ (P25) also decreased the particle size to 20.58 nm (Table-1 and Fig. 2).

TABLE-1
OBSERVATION OF XRD AND BET TESTS

Sample	Size (nm)	Specific surf-ace area (m² g⁻¹)	Rutile (%)
Synthesized TiO₂ with calcination temp. = 400 ºC	15.4	-	68.3
Synthesized TiO₂ with calcination temp.= 450 ºC (we called rutile)	23.4	65	83
Pt/rutile	22	-	-
N/Pt/rutile	23.8	-	-
Pt/TiO₂-P25	20.6	50	20
TiO₂-P25	21	-	-

The comparison of the activities of the synthesized photocatalysts in visible light region performed with diffuse reflectance spectra test. The absorption of TiO₂ was in UV region but the absorption of synthesized rutile was a little in visible light region. The case of Pt/rutile was similar to the Pt/TiO₂-P25 and maximum of absorption occurred at 700 nm in visible region but in Pt/rutile the absorption was more than Pt/TiO₂-P25. Observation of the dye sensitization maximum of absorption was for the dye/Pt/TiO₂ instead of dye/Pt/rutile because of Pt/TiO₂ nanoparticle size was smaller than Pt/rutile and resulted better dispersion for Pt/TiO₂ nanosize particle and better deposition of dye sensitizer on basis (Fig. 3).
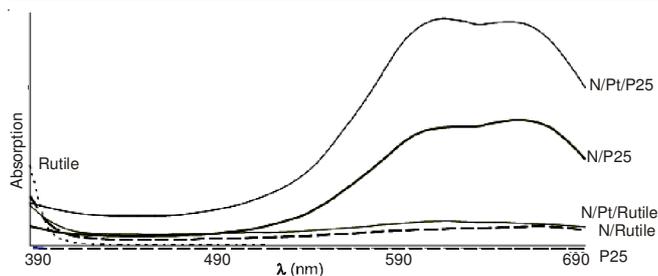
Fig. 3. Comparison of DRS of TiO_2, Rutile, TiO_2 loaded with Pt(Pt/TiO_2) and Rutile loaded with Pt(Pt/rutile) that modified them with CoPcTS dye

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