

Determination of the amorphous phase in titania and its influence on photocatalytic properties

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Abstract. In the present work, we compare the photocatalytic activity of titania samples normalized to the sample weight and specific surface area (SSA), and show a correlation between the PCA of titania catalysts with similar phase compositions and amorphous phase contents. Catalysts with a significant amorphous content were annealed and processed by partial dissolution in acid and included in the analysis. PCA was measured by methyl orange (MO) photodegradation in an aqueous catalyst suspension under high-pressure Hg bulb illumination and the pH was controlled using phosphate buffer (pH 6.9). The weight percentage of the amorphous phase was determined using reference intensity ratios (RIR) for X-ray diffraction patterns of the titania samples measured with crystalline silicon additives. The reproducibility of the proposed method was demonstrated by measuring the amorphous content in mixtures of the sample and XRD-amorphous titania. The obtained results show that the PCA of the titania samples decreases with the weight percentage of the amorphous phase.

Introduction

Due to its photochemical properties, titania are extensively studied in many practical applications, such as water photolysis, solar cell, etc. [1]. The following characteristics of titanium dioxide are usually considered key factors that affect high photocatalytic activity (PCA): high surface area, surface hydroxyls, crystallinity, and optimal particle size. High surface area is believed to have more active site for photocatalytic reaction, on the other hand, high surface is usually associated with low crystallinity and a high concentration of defects, and these may lead to low photocatalytic activity [2] [3]. The amorphous phase means high concentration of structural defects, which has no photocatalytic activity. Thus, comparing the PCA of different samples, we must determine the amorphous phase content [4] [5]. But analyzing the amorphous phase is limited for the complicated atomic structure. The aim of this essay was to develop a method for quantitative analysis of the amorphous phase content in TiO₂ and to determine the impact of amorphous phase on PCA.

Experimental

Mesoporous titania was synthesized with a solvothermal method [6]. 2g Pluronic P123 (molar weight 5800g/mol, Aldrich 435465) was dissolved into 60 ml HCl solution (pH=2, Aldrich 38282), then added 17 mmol tetrabutyl titanate (TBT) in the solution. The solution was kept in a 80°C oven 24h. The result product was washed with deionized water and ethanol three times and dried in an oven. The resultant powders were calcined at 360°C tube furnace for 12 hours and produce the final mesoporous TiO₂. Commercial titania samples, P25 and Hombikat UV100 were used without modification.

Results and discussion

The sample microstructure was characterized using scanning electron microscopy (SEM, Zeiss Leo Supra 50VP) and transmission electron microscopy (TEM, Zeiss Libra 200). Figure 1a shows scanning electron microscopy (SEM) images of the prepared calcined mesoporous TiO₂ using Zeiss

Leo Supra 50VP. The samples possessed very smooth surfaces with a diameter of 1200nm. In TEM images, there are micropore surrounded around the surface, and the diameter is about 4nm.

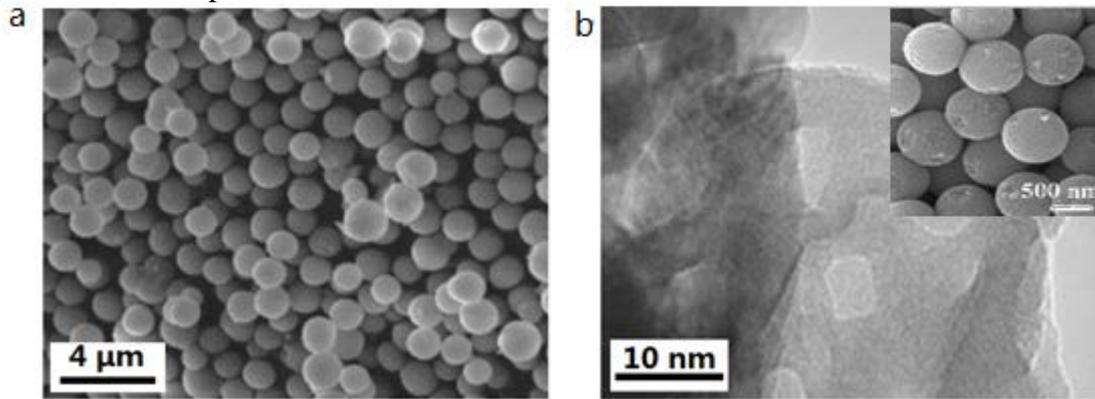


Fig.1. a. SEM, b. TEM image of the mesoporous TiO₂ after calcination at 350°C

The corresponding X-Ray Diffraction (XRD) pattern of the prepared precursor materials and the calcined mesoporous TiO₂ was shown in Fig. 2, which was measured with Rigaku D/MAX 2500 XRD diffractometer. From the XRD data, the mesoporous titania consist of anatase with a small amount of brookite. The normalized integral intensities of anatase and brookite are 108±18 and 6±1 respectively. Calculated the crystalline part of mesoporous TiO₂ is composed of 87±2% anatase and 13±2% brookite, according to the reference intensity ratios (RIRs) from Table 1. The prepared precursor materials without calcined powder shows no diffraction peaks and only a weak, broad hump, which means that the precursor materials without calcined powder is XRD-amorphous TiO₂. The crystalline part of commercial P25 consist of rutile-anatase mixture and the UV100 is pure anatase. From the integral intensities obtained by profile fitting with respects to the RIRs, the crystalline part of P25 is 86±2% anatase and 14%±2 rutile, which agrees well with reference [7].

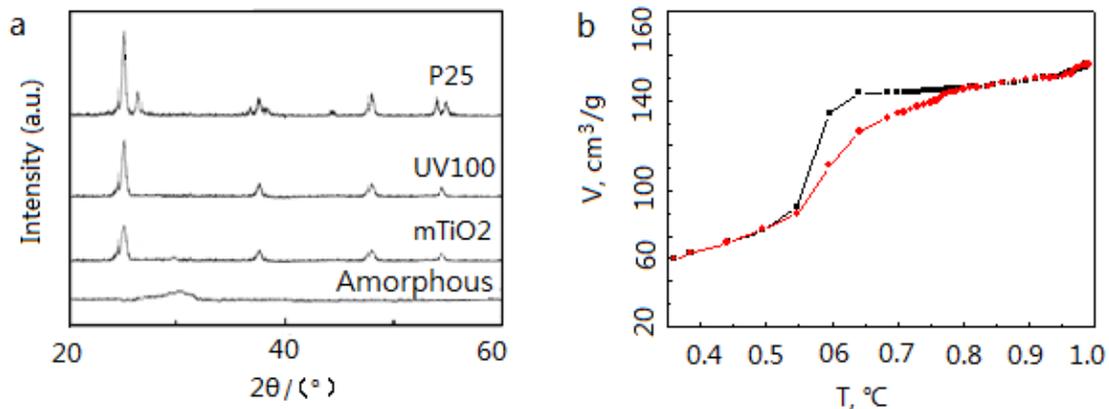


Fig. 2. a. XRD patterns of precursor material material (amorphous) and the calcined at 350°C mesoporous TiO₂, b. Nitrogen sorption isotherms of the calcined mesoporous TiO₂

It is necessary to measure samples' specific surface area (SSA) to determine their PCA. The nitrogen sorption isotherms for multipoint Brunauer–Emmett–Teller (BET) analysis and Barrett–Joyner–Halenda (BJH) calculations were obtained at 77 K using a Quantachrome Nova 2400e instrument, as shown in fig. 2 b. Before measurements, the samples were evacuated for 6h at 200°C. It was shown that the mesoporous titania has a SSA about 160 m²/g, and the pore size distribution with a maximum pore radius of 4 nm, which was in consistence with TEM.

Table 1. ICDD card numbers.

phase	RIR	ICDD Card
Silicon	4.7 ± 0.2	27-1402, 75-0589
Anatase	4.8 ± 0.5	71-1169, 78-2486, 84-1286
Brookite	1.6 ± 0.3	76-1934
Rutile	3.4 ± 0.2	21-1276, 72-1148, 73-1232

We added different weights of amorphous TiO₂ with standard material, silicon powder, and

measured the XRD data, as shown in fig. 3 a. The le Bail method of profile analysis was used for integral intensity measurements for the XRD patterns. And the composition of the crystalline component of amorphous phase $\omega_{XRD}(A_i)$ was calculated.

$$X_i = \frac{I(A_i)}{RIR_i} \quad \omega_{XRD}(A_i) = \frac{X_{A_i}}{\sum_j X_j} \cdot 100\% \quad (1)$$

In the formula, $I(A_i)$ is averaging the strong peak of each phase, $\langle hkl \rangle$, intensities and normalizing to the theoretical intensities. $\omega_{XRD}(A_i)$, corresponds to the percentage of the A_i phase in the crystalline portion of the mixture.

To determine the amorphous weight of the sample, we calculated with formula 3. m_{Sample} is the real weight of the sample, m_{St} is crystalline standard amount, $\omega_{real}(St)$ is corresponds to real weight percentage of the crystalline phase.

$$\omega_{Am} = 100\% \cdot m_{Am} / m_{total} \quad (2)$$

$$\omega_{real}(St) = \frac{m_{St}}{m_{St} + m_{Sample}} \cdot 100\% \quad (3)$$

$$\omega_{Am} = 100\% \frac{m_{Am}}{m_{Sample}} = 1 + m_{St} / m_{Sample} \cdot (1 - 1 / \omega_{XRD}(St)) \quad (4)$$

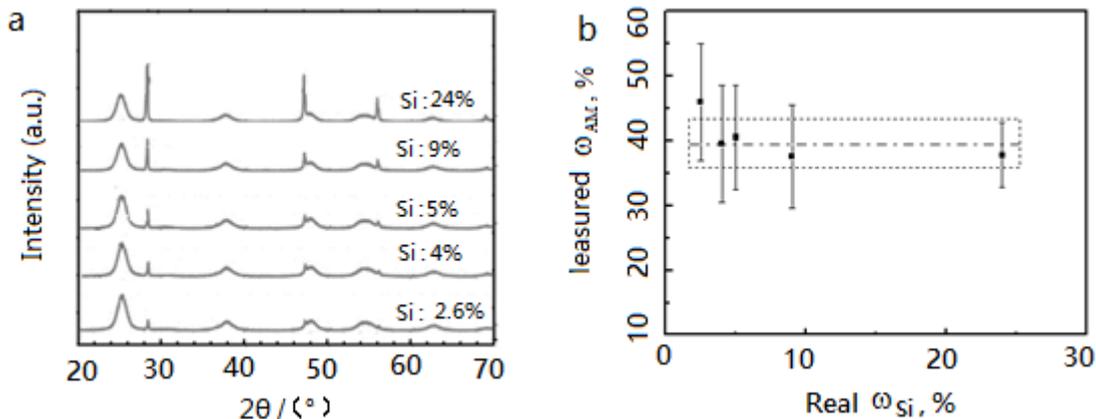


Fig. 3. a. XRD patterns of Si and mTiO₂ sample mixture. b. Calculated ω_{Am} vs Si amount, mean value with deviation labeled with a straight line.

To reduce these errors and confirm the results, we measure every sample a few times with the addition of different amounts of the amorphous sample and crystalline standard. For this, we prepared five mixtures of each sample and the silicon standard powder, with Si weight percentages ranging from 2.6% to 50%. Then the measured XRD patterns and was fitted using le Bail method to measure the intensities of the peaks for anatase and silicon. And based this, we the mean integral intensity of silicon for each mixture and calculated ω_{Am} . Then we plotted the calculated ω_{Am} against ω_{Si} , as shown in fig.3b. We can observe that all the data and check the slope coefficient, and they are within the error range. We average all of the ω_{Am} and calculate the standard deviation. From the fig. 3b, we can be sure of the consistency of this method. Data from other samples obtained by this method are shown in table 2.

Table 2 Crystalline phase composition, SSA, measured amount of amorphous phase and PCA.

Sample	R: A: B	SSA, m ² /g	PCA _m , %	ω _{Am} , %
Amorphous TiO ₂	-:-:-	250	0	100
P25	14:86:±2	40	100	14±1
UV100	-:100:-	330	15	32±2
UV100ac	-:100:-	280	75	32±2
UV100@400	-:100:-	170	45	25±2
UV100@500	-:100:-	130	42	20±2
mTiO ₂	-:87:13±3	160	5	30±1
mTiO ₂ ac	-:87:13±3	160	33	24±2
mTiO ₂ @400	-:87:13±5	110	60	23±2
mTiO ₂ @500	-:90:10±5	60	85	19±2

R: A: B – rutile: anatase: brookite weight ratio in crystalline portion

mTiO₂ is mesoporous TiO₂ calcined at 350°C, mTiO₂ac is removed amorphous titania with nitric acid, mTiO₂@400 and mTiO₂@500 are after annealed at 400°C and 500°C mesoporous TiO₂.

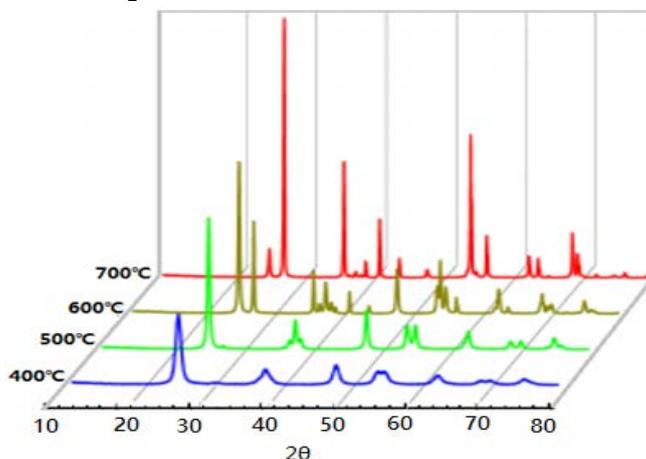


Fig. 4. XRD patterns of mesoporous TiO₂ calcined with different temperature.

To remove the amorphous portion of TiO₂, we can anneal the samples at temperatures higher than 400°C. But during annealing, crystallization might be with phase transition and agglomeration of TiO₂ particles with the decrease in SSA, which may significantly affect the PCA of the samples. So we performed fast annealing, the sample was placed in a hot oven for 15 min. The rutile phase is observed in the samples obtained by fast heating to 600°C, as shown in fig.4. Due to the impact of the phase composition on the PCA, we used only the samples annealed at 400°C and 500°C.

Different titania phases with different dissolution rates in acids. So, based on the fast dissolution of amorphous titania in acid, we can selectively remove amorphous titania from samples by exposure to diluted nitric acid for a short time. A portion of the TiO₂ sample was added to 1M HNO₃ and stirred for 3h, then washed with distilled water and dried at 60°C in an oven. The PCA of all samples were measured in the buffer solution (pH 6.9), therefore, a small amount of residual acid should not change the measured PCA. Both annealing and acid method decrease the amorphous titania amount, and significantly increase the PCA of the samples, as shown in table 2.

The PCA was measured through the decoloration of methyl orange (MO) in aqueous buffer solutions under high-pressure Hg bulb (5W) illumination. All measurements were performed at a temperature of 40°C. 3mg of sample was used in each measurement, and the TiO₂ concentration is 0.2mg/L in the reaction mixture. The MO concentration in the mixture was 47 mg/L. It is well known that the order of this reaction is pseudo-first in the case of both direct and indirect oxidation [8-11], therefore, decoloration rates were calculated by the linear approximation of the relative concentration of MO against time in a semi-log scale. To compare the measured rates of decoloration with the results of other groups, we defined the relative PCA of our samples by relating their MO decoloration rates of the samples (r_s) to that of P25 (r_{P25} = -0.035 1/(h mg))

measured under the same conditions:

$$PCA_m(S) = \frac{r_S/m_S}{r_{P25}/m_{P25}} \cdot 100\% \quad (5)$$

$$PCA_{SA}(S) = PCA_m(S) \cdot \frac{SSA_{P25}}{SSA_S} \cdot 100\% \quad (6)$$

Where $PCA_m(S)$ is the PCA of the sample, normalized to the sample weight. $PCA_{SA}(S)$ is normalized to the surface area. The PCA vs. $PCA_m(S)$ and PCA vs. $PCA_{SA}(S)$ for all crystallized samples was all plotted in fig.5.

In fig.5, it was demonstrated that all titania samples annealed at 400°C and 500°C or after acidification, the amorphous phase percentage were decreased, which leads to the PCA increased. In fig. 5.c, in curve UV100 sample, one can see that even small changes in amorphous content and SSA may result in strong increases of the PCA. This effect is probably due to changes in the spatial distribution of the amorphous phase [12]. Therefore, the influence of the amorphous phase spatial distribution on PCA should be investigated in the future.

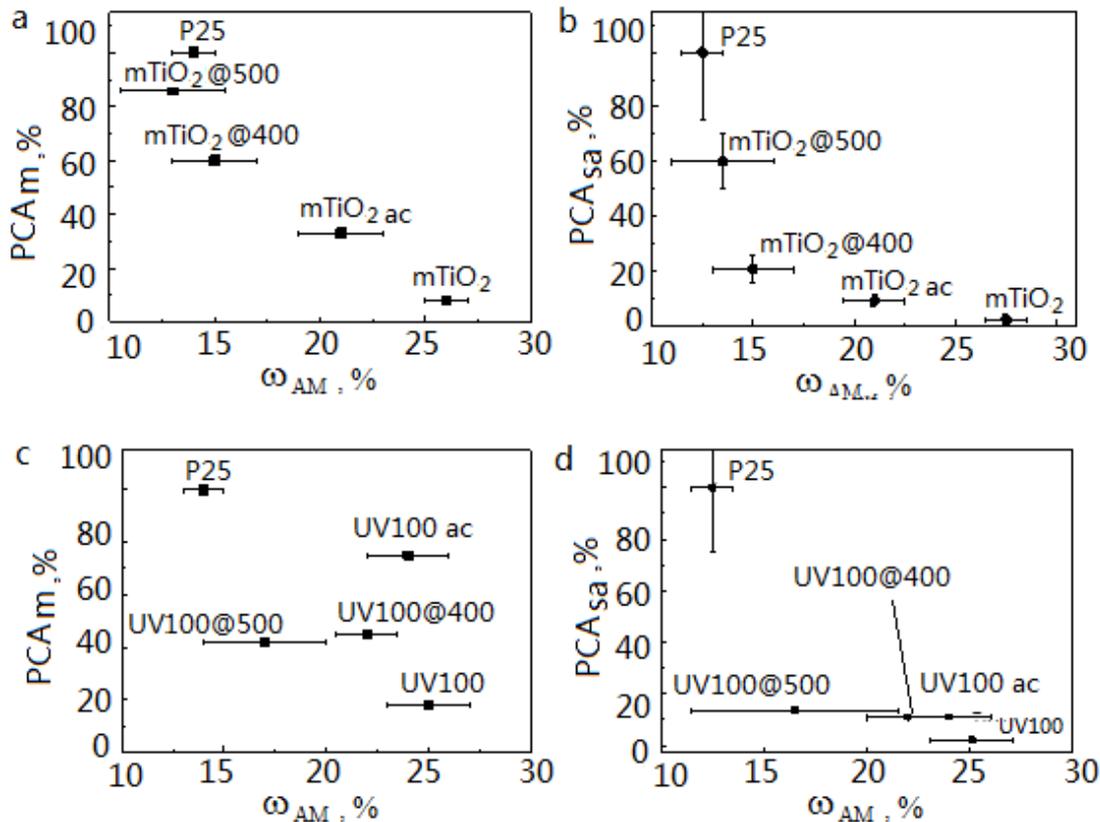


Fig. 5. a. Dependence of photocatalytic activity, normalized on the sample weight vs. amorphous titania amount, b. Dependence of photocatalytic activity, normalized on the sample surface area vs. amorphous titania amount of mesoporous TiO₂ c. Dependence of photocatalytic activity, normalized on the sample weight vs. amorphous titania amount, d. Dependence of photocatalytic activity, normalized on the sample surface area vs. amorphous titania amount of mesoporous UV100.

Conclusions

In this work, we demonstrate that the presence of the amorphous TiO₂ phase can directly affect the PCA. As measured, the samples containing a higher amount of the amorphous phase show a lower PCA. The proposed method for the quantitative analysis of the XRD-amorphous phase allows one to measure the weight percent of the amorphous titanium fraction with high accuracy.

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