The influences of nanoscale titanium dioxide particle size and crystal structure on light absorbance

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ABSTRACT

Nanoscale titanium dioxide is an important physical sun-block material and is widely used in sunscreen. In our test, the influences of the particle size and crystal structure on light absorbance were examined. The experiment shows that the absorbance (Abs) of nanoscale titanium dioxide in UV-ray district is much higher than it in visible light district under the same concentration (0.04 g/L). The Abs of nanoscale rutile keeps increasing, reaches the highest at 360 nm, and then starts to decrease as the wavelength becomes shorter. The nanoscale anatase has the similar light absorbance characteristic, with the highest Abs peak at 320 nm. In the UVA district, the rutile has stronger absorbance ability than the anatase, while in UVB and UVC, there is a similar absorbance between rutile and anatase. Compared with the bulk titanium dioxide, the nanoscale titanium dioxide is capable of absorbing the UV-ray more effectively and let the visible light pass through more easily. Since the anatase is of the stronger activity than rutile and thus probably harms the skin more easily, the nanoscale rutile should be the best selection used for sunscreen. However, when the particle size of rutile is too small, for example, smaller than 10 nm, its Abs tends to be much higher in UVB and UVC district, but lower in UVA and visible light district. Therefore the appropriate particle size and crystal structure should be considered when nanoscale titanium dioxide is applied for sun-block effect. The detailed test optimizations are being carried out in our lab.

Keywords: nanoscale titanium dioxide, particle size, crystal structure, light absorbance

1 INTRODUCTION

Nanoscale titanium dioxide has been widely used in cosmetic sunscreens for more than 25 years. In 2008, a survey of nanomaterials sold in EU cosmetic products amongst member companies of Colipa and national trade associations identified: One of the most frequently used materials is titanium dioxide. The test aims to examine the influences of the particle size and crystal structure of nanoscale titanium dioxide on the light absorbance. And then try to find the appropriate particle size and crystal structure for sunscreen application. Particle shape and element-doped is excluded in this text.

In this study we get six kinds of titanium dioxide samples. One is synthesized in the laboratory and four are bought in the market and one is abstracted from the sunscreen. The synthesis of nanoscale titanium dioxide in liquid phase reactions has been of great interest over the past decades [1-2]. Here we use hydrothermal methods to generate the 6~7nm nano-TiO_2 rutile samples. The four kinds of titanium dioxide are provided by Hehai Nanometer Science & Technology Co. Ltd. It is a key point to control the temperature at a low state to avoid the titanium dioxide phase changing and grain growing when abstract the titanium dioxide form the sunscreen.

2 MATERIALS AND METHODS

2.1 Material preparation

Nanoscale rutile synthesized in the laboratory: The nanoscale rutile synthesis was performed using a modified procedure as described by Cheng etc [3]. Briefly, under continuous stirring, 23 mL titanium tetrachloride slowly add into the ice water (400ml) to prepare the $TiCl_4$ suspension solution, then hydrochloric acid was used to adjust the pH <1. Next, 0.8 mol NaCl was added into the mixture and a clear solution was formed after stirring for 5~6 hours at room temperature. After heated to 90℃ and refluxed for 2h, the nanoscale TiO_2 particles were recovered from this solution. Finally, the pellet was dialyzed several times till pure enough and then was frozen-dry to get the sample Nano-R-1.

Four kinds of titanium dioxide bought in the market: They were as marked rutile (Bulk-R), nano-rutile (≤30nm, Nano-R-2), anatase (Bulk-A) and nano-anatase(≤30nm, Nano-A), respectively.

The sample abstracted from sunscreen: The sunscreen was added into the water and heated at 90℃ till the organic component was destroyed. Next, normal hexane was added to the mixture. The mixture was heated till it uniformity, then centrifugated, washed several times, and dried in an oven maintained at 60℃. The resulting powder 0912 was finally obtained.

2.2 Crystal structure and particle size measure

All nanoscale titanium dioxide powders were characterized by X-ray diffraction (XRD, D/max-2500/PC, Rigaku, Tokyo, Japan). The crystal structure can be given by the position of diffraction peak (27.4° of rutile type 110 crystal face; 25.3° of anatase type 101 crystal face). The background of the diffraction profile was determined after smoothing by Savitsky-Golay method [4]. Then separate the $K_{\alpha 1}$ and $K_{\alpha 2}$ doublet to get the full width at half maximum (FWHM) by Rachinger's algorithm [5]. At last the true FWHM can be determined without instrument broadening [6]. Then particle sizes were estimated according to the Debye-Scherrer formula:

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

Where: D is the average crystallite size, K is the Scherrer Constant (here use 0.89), λ is the wavelength of X-ray (0.154nm for Cu $K_{\alpha 1}$ radiation), β is the true FWHM, θ is the diffraction angle.

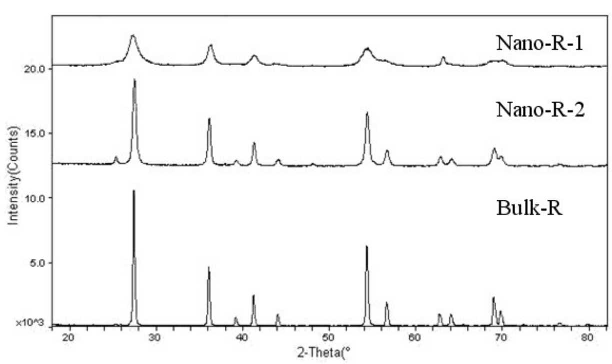
2.3 Absorbance test

All the samples are tested by spectrophotometer (U3310, Hitachi, Tokyo, Japan) at the concentration of 0.04g/L except the sample which was abstracted from sunscreens (due to sample preparation limited, the sunscreen used titanium dioxide was tested at a higher concentration). The measurement parameters are: Scan Speed: 120 nm/min; Sampling Interval: 0.20 nm; Slit Width: 1 nm; Baseline Correction: User 1; Path Length: 10.0 mm.

3 RESULTS AND DISCUSSION

3.1 The crystal structure and particle size of these samples

The crystal structure and particle size of these samples are shown as follow. All the particle size is estimated by Debye-Scherrer formula.



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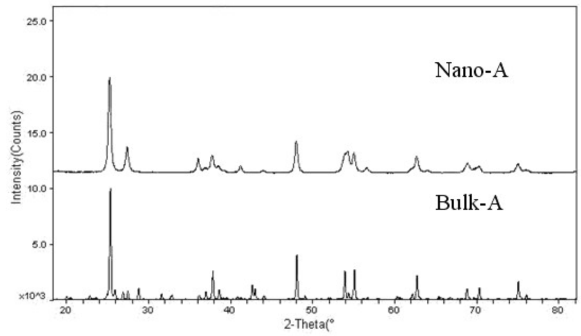

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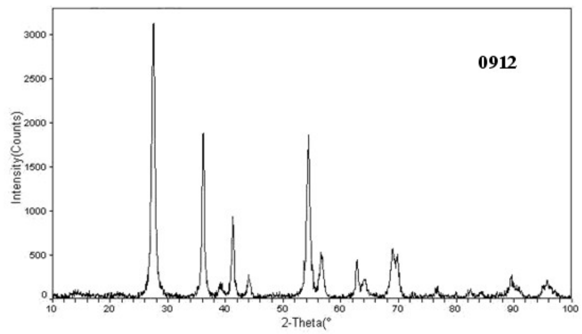

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Figure 1: The X-ray diffraction patterns of the six titanium dioxide samples

Name	Crystal structure	Particle size
Nano-R-1	Rutile	7nm
Nano-R-2	Rutile	24nm
Bulk-R	Rutile	⩾100nm
Nano-A	Anatase	22nm
Bulk-A	Anatase	⩾100nm
0912	Rutile	13nm

Table 1: The crystal structure and particle size of these samples

Fig 1.A is the X-ray diffraction pattern of the three rutile samples. Nano-R-1 is prepared in lab. Nano-R-2 and Bulk-R are bought in the market. The particle size of these samples are 7nm, 24nm and bigger than 100nm separately. Fig 1.B is the X-ray diffraction pattern of two anatase samples both are bought in the market. One is 22nm and the other is bigger than 100nm. Fig 1.C is the X-ray diffraction pattern of the titanium dioxide which abstracted from the sunscreen. It is rutile and the particle size is 13nm.

3.2 The light absorbance of different crystal structure

Fig.2 is the Abs curve of Nano-R-2, Bulk-R, Nano-A and Bulk-A. The concentration is 0.04g/L. From this figure we can conclude:

1. The Abs of the two bulk titanium dioxide is very alike. They have UV-ray absorption little than visible light absorption.

2. The Abs curve of nanoscale rutile and nanoscale anatase is also alike. They both have a higher absorption in UV-ray district higher than it in visible light district. As the wavelength become shorter the Abs of nanoscale titanium dioxide quiken up increase, the Abs of rutile reach the highest at 360nm, and then become reducing when the wavelengh get shorter. The anatase has the highest Abs at 320nm, and then become shorter too. This characteristic is very alike.

3. However, the Abs curves of the two crystal structures still have some difference. First, they have different absorbance peak point, rutile is 360nm and anatase is 320nm. Second, in the UVA (320~400nm) district the nanoscle rutile has stronger absorption ability than the nanoscale anatase, while in UVB and UVC there is a similar absorbance between rutile and anatase. Considering the long-term harm to human skin of UVA and the higher photoactivity of anatase [7], the nanoscale rutile is safer and better than nanoscale anatase for sunscreen application.

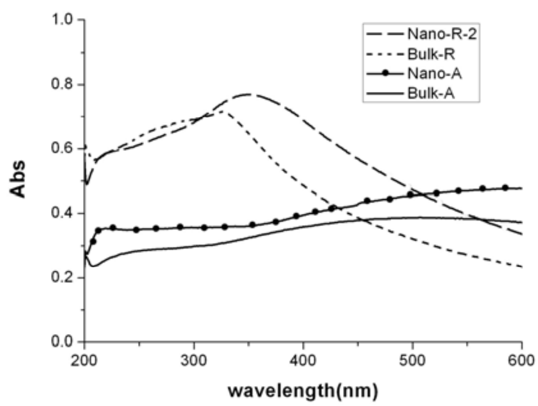

Figure 2: The Abs curve of rutile and anatase titanium dioxide samples

3.3 The light absorbance of different particle size

Fig 3 is the Abs curve of the rutile of different particle size. The concentration is 0.04g/L.

From this figure we can conclude:

1. Different particle size rutile has different light absorption ability.

2. The absorption area is blue shift as the particle size become smaller.

3. The smaller the particle is, the higher the absorbance peak is. The nanoscale rutile has a higher absorbance peak than that of bulk rutile. Compare the Abs of the Nano-R-2 and Bulk-R we can see that the tow lines are crossed at 508nm, when the wavelength longer than 508nm, the bulk has higher Abs than that of nanoscale rutile, when the wavelength shorter than 508nm, the Abs of nanoscale higher than that of bulk. Thus we can conclude that the nanoscale material has higher transimission ability in visible light district and higher absorption ability in UV-ray district than that of bulk material. The nanoscale rutile is more effective for sunscreen application.

4. However, when the particle size of rutile is too small, as shown in figure 3, the Nano-R-1 is 7 nm, it will has much higher Abs in UVB and UVC district but lower Abs in UVA district. Compare the Nano-R-1 and Nano-R-2, we can see that the Nano-R-1 has a much higher absorption peak, but the absorbance area is much narrower than Nano-R-2. These two curves crossed at 318nm, so when the wavelength is longer than 318nm, the Abs of Nano-R-1 is lower than that of Nano-R-2. Furthermore, when the wavelength is longer than 350nm, the material can absorb litter light.

It is well know that the UVA is the main UV-ray on the surface of earth, it cause the most damage to our skin. Thus, when choose sunscreen used rutile, the particle size should not be too small. The best choice is that the material has an effective absorbance area overlay UVA (320nm~400nm) and UVB (290nm~320nm).

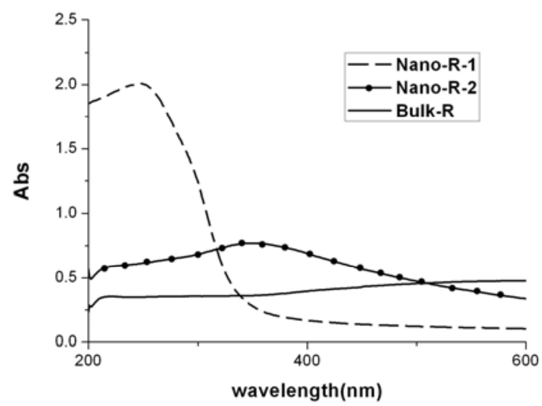

Figure 3: The Abs curve of rutile with different particle size

3.4 The light absorbance of the sunscreen used titanium dioxide

Fig 4 is the Abs of the titanium dioxide sample which is abstracted from the sunscreen, the XRD shows it is rutile with the particle size about 13nm. The concentration of the sample is higher than 0.04g/L, while the Abs curve still can be compared with the other samples' Abs curves. From fig 4 we can see:

1. The Abs of this sample in UV-ray district is higher than the Abs in visible light district.

2. The absorbance peak of this sample is 296nm, which is in the UVB range. It has an effective absorbance when the wavelength is shorter than 360nm. Compare with Nano-R-2 we can see that if the particle size is bigger, the Abs area will be wider, but at the price of lower Abs peak. Thus, when use the bigger particle size rutile, it should be add more material in the sunscreen to get a high SPF.

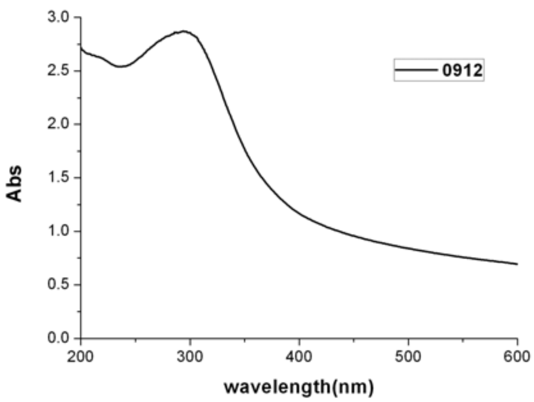

Fig 4: The Abs curve of the sunscreen used TiO_2

4 CONCLUSIONS

Six different kinds of titanium dioxide have been studied. The influences of nanoscale titanium dioxide particle size and crystal structure on light absorbance also been discussed. Considering the light absorbance ability and photoactivity, rutile is a better choice. Besides, the particle size is also very important for sunscreen used titanium dioxide. The nanoscale rutile has a stronger UV-ray absorption ability than bulk rutile and the smaller the particle is, the higher the absorbance peak it has. But as the particle size gets smaller the absorbance area is blue shift. Thus, if not considering the surface modification and element-doped, in order to get the most effective absorbance, the particle size should not be too big or too small. From our data, the particle size around 10~30 nm of rutile might be the best choice. While, different company may choose different particle size titanium dioxide to produce their special sunscreen.

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