

# Photocatalytic Degradation of $\beta$ -carotene with $\text{TiO}_2$ and Transition Metal Ions Doped $\text{TiO}_2$ under Visible Light Irradiation

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**Abstract**  $\beta$ -carotene, one of the carotenoids, was photodegraded under visible light irradiation by using pure  $\text{TiO}_2$  and M- $\text{TiO}_2$  (M= metal; Ag, Fe, Ru). The photocatalysts were prepared by a sol-gel method and incipient wetness impregnation method, and investigated by means of X-ray diffraction and scanning electron microscopy for characterization. The effects of photocatalyst and oxygen content were investigated, which was based on the absorbance at 450 nm of photodegradation of  $\beta$ -carotene as the main index. The study of photocatalytic activity indicated that Ag-doped  $\text{TiO}_2$  showed higher photocatalytic activity than other photocatalysts. And also a quick decrease of  $\beta$ -carotene in the presence of oxygen was observed.  $\beta$ -cyclocitral, 5,6-epoxy- $\beta$ -ionone and dihydroactinidiolide, the main photocatalytic degradation products of  $\beta$ -carotene were confirmed by gas chromatograph-mass spectrometer (GC-MS) analysis. All these degradation products can be used for fragrance and flavoring agents, such as cigarette flavoring ingredients.

**Keywords**  $\beta$ -carotene, M- $\text{TiO}_2$ , Photocatalytic Degradation, Sol-gel Method, GC-MS Analysis, Cigarette Flavoring

## 1. Introduction

Carotenoids are organic pigments which contain two classes, Xanthophylls and carotene. The main difference between them is whether they contain oxygen or not. All carotenoid are tetraterpenoids, which are formed with 8 isoprene molecules and contain 40 carbon atoms[1].  $\beta$ -carotene, one of the carotenoids, and its degradation products are often found in tobacco, fruit and plant[2-4], which can be synthesized from vitamin A[5], also it can be cut via the cross metathesis to retinoids[6].  $\beta$ -carotene is

sensitive to light, temperature and oxygen, and its degradation products have been mentioned by many former researches. Many authors have mentioned about the thermal degradation of  $\beta$ -carotene in aqueous or oil system[7-9]. Kanasawud and his colleague studied the mechanism of how degradation products formed by heat treatment[10]. Isoe early reported that the degradation of  $\beta$ -carotene in aqueous system depended on oxygen and illumination intensity, and the photo oxygenation products mainly contained dihydroactinidiolide (DHA) [11]. These are very useful spices. Robert Aman and his colleagues reported the effect on the degradation and isomerization between the lutein and  $\beta$ -carotene under thermal treatment and light exposure, and also they made a comparison of stabilities between pure carotenoids and chloroplast-bound carotenoids for the first time[12].

Taking the environmental protection and energy into consideration, light is a kind of clean energy[13]. In order to use the visible light for the photodegradation of  $\beta$ -carotene, it is important to screen the photocatalyst. In many fields,  $\text{TiO}_2$  has been used as photocatalyst because of its stability, cleanness and catalysis efficiency. It has been extensively studied in the degradation of organic pollutants under UV irradiation (<387nm). While one obstacle of this material is the band gap, only 5% (UV light) can be absorbed by  $\text{TiO}_2$ , so the improvement of the photocatalytic efficiency of  $\text{TiO}_2$  is to shift its optical response from UV range to the visible range[14]. For this purpose, in the last decades, the metal ions doped  $\text{TiO}_2$  has been widely studied. Many organic substances can be degraded by using the Fe- $\text{TiO}_2$  catalysts, like 2,4-dichlorophenol[15], maleic acid[16] and gas-phase ethanol[17]. In the meantime, the effect of photocatalytic activity of  $\text{TiO}_2$  can be also efficiently improved by the dopant of silver[18,19]. Due to the fact that textile industries produce a large amount of dye pollutants, most of them are azo dyes which contain conjugated double bond[20], Ag- $\text{TiO}_2$  can be used in photocatalytic degradation of them,

like Direct Red 23[21], Crystal Violet, Methyl Red dye[22-24], etc. To our knowledge, the photocatalytic degradation of  $\beta$ -carotene over transition metal doped TiO<sub>2</sub> under visible light irradiation has been hardly reported.

The purpose of our work was to study the photodegradation of  $\beta$ -carotene over transition metal (Ag<sup>+</sup>, Fe<sup>3+</sup>, Ru<sup>2+</sup>) doped TiO<sub>2</sub> under visible light irradiation and obtain the flavor substances employed as the cigarette flavoring ingredients. In this paper, the transition metal doped TiO<sub>2</sub> selected as catalysts were prepared by sol-gel method and incipient wetness impregnation method. While compared with pure TiO<sub>2</sub> and P25, the results indicated that the Ag-doped TiO<sub>2</sub> demonstrated high photocatalytic activity in the system of  $\beta$ -carotene degradation.

## 2. Experimental

### 2.1. Photocatalysts Preparation

#### 2.1.1. Sol-gel Method

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. The synthesis was done by the hydrolysis of titanium (IV) tetrabutoxide (TNTB) as a precursor in mixed solution of glacial acetic acid as chelating agent and anhydrous ethanol. 17.0 mL TNTB and 4.8 mL glacial acetic acid were dissolved in 34 mL anhydrous ethanol, and stirred for 30 min. 1 mL distilled water and 10 mL anhydrous ethanol were added dropwise to let the hydrolysis process take place. After an hour, the pale yellow, stable, well-distributed, transparent TiO<sub>2</sub> gel was obtained, and aged for 2 days. The TiO<sub>2</sub> gel was dried at 373 K for 32 h and then ground. The dried powder was calcined at 773 K for 2 h to obtain pure sol-gel TiO<sub>2</sub> powder in muffle furnace.

TiO<sub>2</sub> doped with Ag, Fe and Ru series catalysts were synthesized by sol-gel method. Transition metal ions were doped into TiO<sub>2</sub> with the doping content of 4 mol% by adding AgNO<sub>3</sub>, FeCl<sub>3</sub> and Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O in the distilled water prior to hydrolysis of TNTB, respectively.

#### 2.1.2. Incipient Wetness Impregnation Method

1 g Nano TiO<sub>2</sub> (P25 anatase) was dispersed in 25 mL distilled water. Doping was performed by impregnation of TiO<sub>2</sub> with aqueous solution of AgNO<sub>3</sub>, FeCl<sub>3</sub> at room temperature. The mixture was stirred for 12 h. Then, water was evaporated by heating at 343 K. At last, the photo catalysts were calcined at 573 K for 4 h. Metallic solution concentration was the one required to obtain 4 mol% of doping content [25].

### 2.2. Equipment

X-ray diffraction (XRD) analysis of M- TiO<sub>2</sub> series samples were performed via using a diffractometer (Bruker

Focus D8) with CuK $\alpha$  irradiation ( $\lambda = 1.541 \text{ \AA}$ ), of which  $2\theta$  range was 10-70°. The size and surface morphology of TiO<sub>2</sub> particles were observed by Scanning Electron Microscope (SEM, Hitachi S-4800). 23 W white fluorescent lamp (Philips Tornado 23 W E27) was used as the visible source. The UV-Vis spectrophotometer (Agilent 8453) was used to obtain the absorption spectrum of  $\beta$ -carotene, and followed the track of the degradation. Gas Chromatography –Mass Spectrometer (Agilent 6890GC/ 5973N) was carried out to the separation and analysis of  $\beta$ -carotene. The degradation products were separated by using DB-5MS (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m) column (Agilent). The pressure of carrier gas, helium gas, was 10 psi. The temperature of injection port was 533 K and the carrier gas flow was 1 mL min<sup>-1</sup>; the Gas Chromatography operated at 323 K, then programmed to 473 K at 5 K min<sup>-1</sup>, and held 4 min; then programmed to 533 K at 25 K min<sup>-1</sup>, and held 4 min. The sample volume was 1  $\mu$ L, the split ratio was 10:1 and the solvent delay was 5 min. The source temperature was 423 K and the ionization energy was 70 eV. The degradation products were identified by automatic search in Nist98 library and quantified by peak area normalization method.

### 2.3. Experimental Conditions

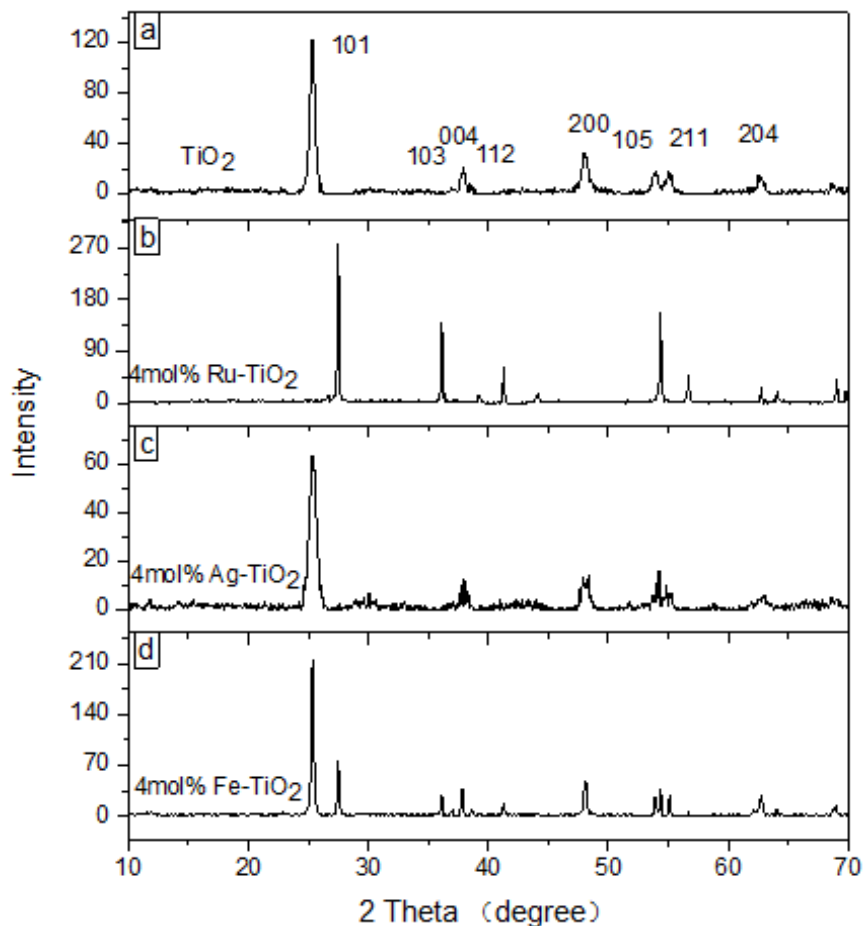
10 mg  $\beta$ -carotene and 0.15 g Nano TiO<sub>2</sub> was suspended by sonication in 50 mL of solvents in 150 mL light reaction tube for 10 min to make the  $\beta$ -carotene completely dissolved in solvent. Then under the condition of a certain temperature (298 K), the photocatalytic degradation started by magnetic stirring under visible light irradiation until the  $\beta$ -carotene suspension turned into a transparent solution. (In some experiments, the suspensions were saturated with nitrogen or with oxygen before sealing the light reaction tube.) After the reaction completed, the suspensions were centrifuged for 10 min to get supernatant fluid. The liquid were filtered for GC-MS detection, and then the analysis results of degraded product composition were obtained.

## 3. Results and Discussion

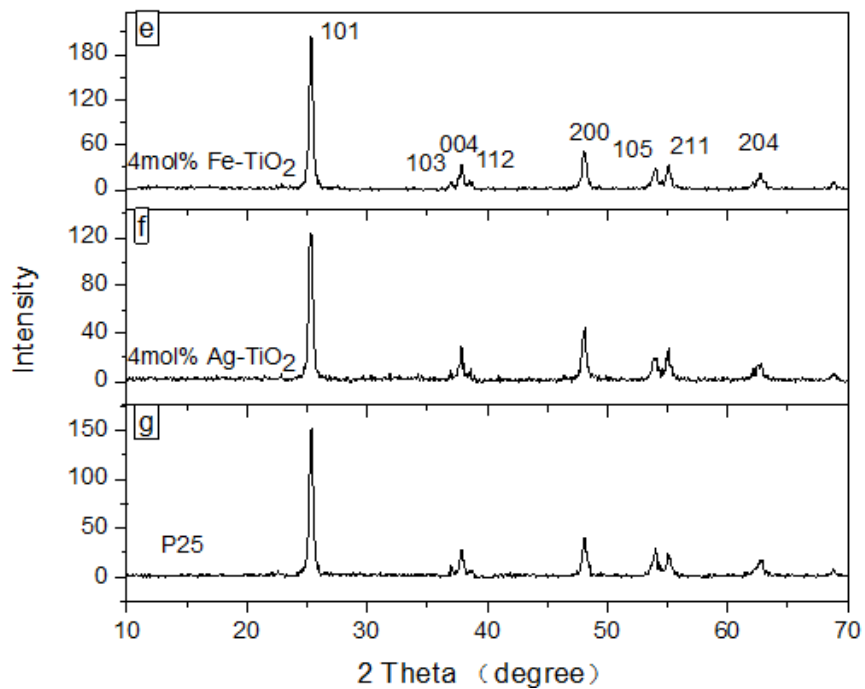
### 3.1. Characterization of Morphology and Structure of TiO<sub>2</sub> Particle

Figure 1 show that by using the sol-gel method, metal ions doped catalysts were compared to pure TiO<sub>2</sub> (calcined at 773 K). At 773 K, As to Ag doped TiO<sub>2</sub>, the analysis of XRD showed mainly anatase phases, while TiO<sub>2</sub> with 4mol% Fe were the mixture of rutile and anatase phases. Because of the low concentration, Ru<sup>2+</sup>, Ag<sup>+</sup> and Fe<sup>3+</sup> were not high enough to allow its detection in the catalysts.

Also XRD analysis had been obtained from the P25 and P25 with 4mol% doped M (Ag, Fe) (Fig. 2). However, the presence of iron or silver was also not detected.



**Figure 1.** XRD patterns of the  $\text{TiO}_2$  powders by using the sol-gel method (calcined at 773 K) (A) pure  $\text{TiO}_2$  and 4 mol% metal ions doped  $\text{TiO}_2$  (B) Ru-doped  $\text{TiO}_2$ , (C) Ag-doped  $\text{TiO}_2$ , (D) Fe-doped  $\text{TiO}_2$



**Figure 2.** XRD patterns of the  $\text{TiO}_2$  powders by using the wetness impregnation method (calcined at 773 K) 4 mol% metal ions doped P25 (E) Fe-doped P25, (F) Ag-doped P25 and (G) P25

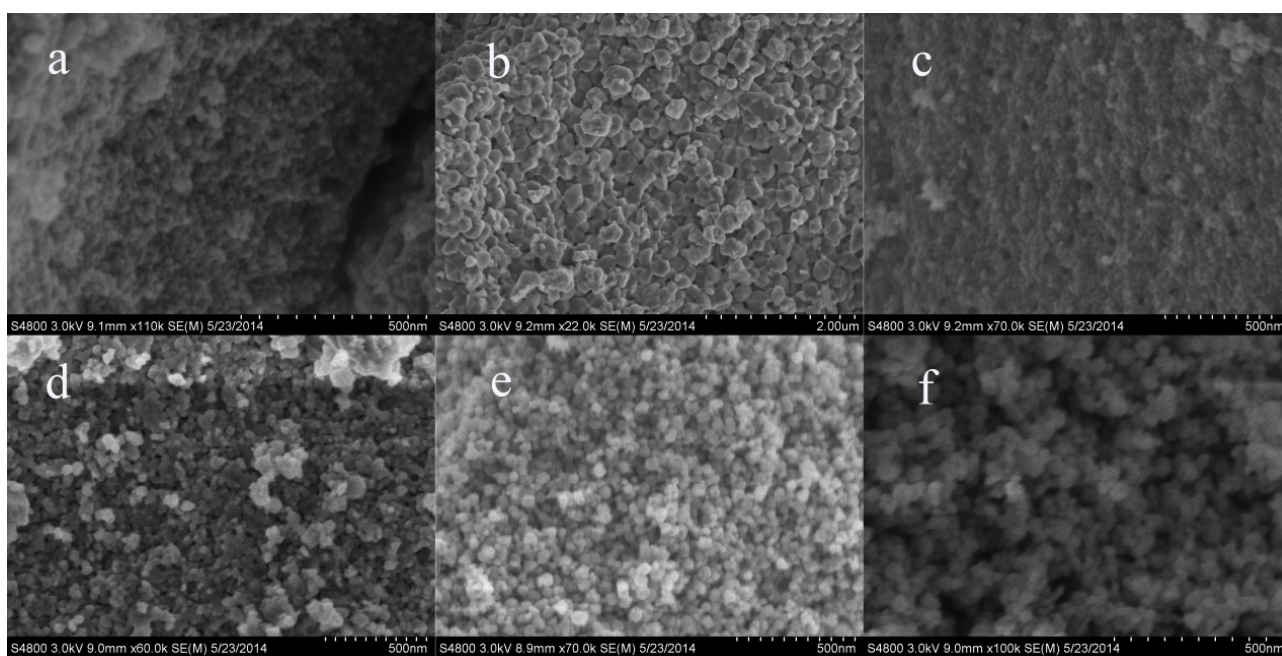
The crystallite sizes of pure  $\text{TiO}_2$  and doped  $\text{TiO}_2$  were estimated from the peak FWHM (full width half maximum) by using the Scherrer equation and shown in Table 1.

**Table 1.** Physical properties of 4mol% M- $\text{TiO}_2$  series samples, pure  $\text{TiO}_2$  and P25

Samples	Phase	Crystallite size /nm
$\text{TiO}_2$	anatase	16.7
4mol% Ru- $\text{TiO}_2$	rutile	106.6
4mol% Ag- $\text{TiO}_2$	anatase	11.6
4mol% Fe- $\text{TiO}_2$	anatase, rutile	44.7
4mol% Fe-P25	anatase	36.0
4mol% Ag-P25	anatase	24.1
P25	anatase	28.8

It was found that the crystallite size was in the range of 11.6-44.7 nm, except Ru- $\text{TiO}_2$ . The sizes were 16.7, 106.6, 11.6, 44.7, 36.0, 24.1, 28.8 nm, respectively. Among them, the size of Ru- $\text{TiO}_2$  was larger than average. It indicated that the same dopant of Ru led to the increase of the crystallite size. Meanwhile, the phase of Ru- $\text{TiO}_2$  was mainly rutile. Statistics indicated that the dopant of Ag promoted the decrease of crystallite size, while the dopant of Fe promoted a little bit increasing of the size.

Figure 3 shows the SEM image of surface morphology of  $\text{TiO}_2$  and metal-doped particles through hydrolytic process and calcination at 773 K. From SEM images, the nanoparticles sizes were approximately 50 nm, except Ru-doped  $\text{TiO}_2$  particles.



**Figure 3.** Observation of surface morphology of  $\text{TiO}_2$  particles by SEM (calced at 773 K) (A) pure  $\text{TiO}_2$  powder; (B) Ru-doped  $\text{TiO}_2$ ; (C) Ag-doped  $\text{TiO}_2$ ; (D) Fe-doped  $\text{TiO}_2$ ; (E) Fe-doped P25; (F) Ag-doped P25

### 3.2. Standard Curve of $\beta$ -carotene in Hexane

5 mg  $\beta$ -carotene were dissolved in hexane, and then diluted with hexane to 100 mL in the volumetric flask, so the 50 mg/L standard solution was got. Then a set of 5 concentrations of  $\beta$ -carotene (1, 2, 3, 4, 5 mg/L) in 100 mL volumetric flask was obtained. By measuring the absorbance of standard solution in the wavelength of 450 nm, and the linear regressive equation was established:  $Y = 0.04177 + 0.06801X$ ,  $R^2 = 0.99571$ .

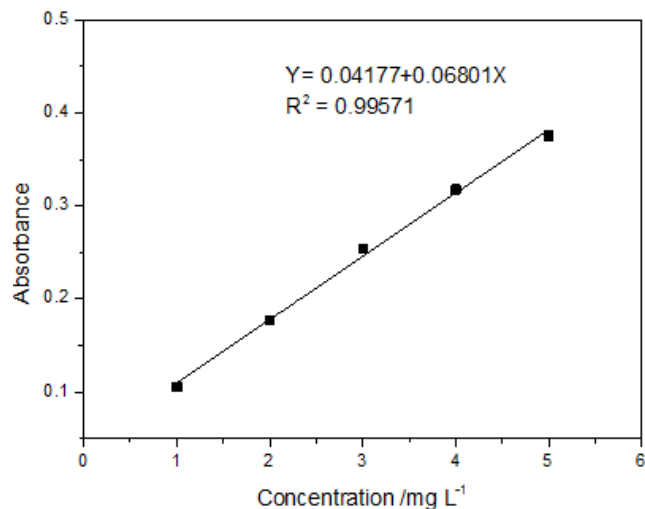


Figure 4. Standard curve of  $\beta$ -carotene in hexane

### 3.3. Photocatalytic Activity

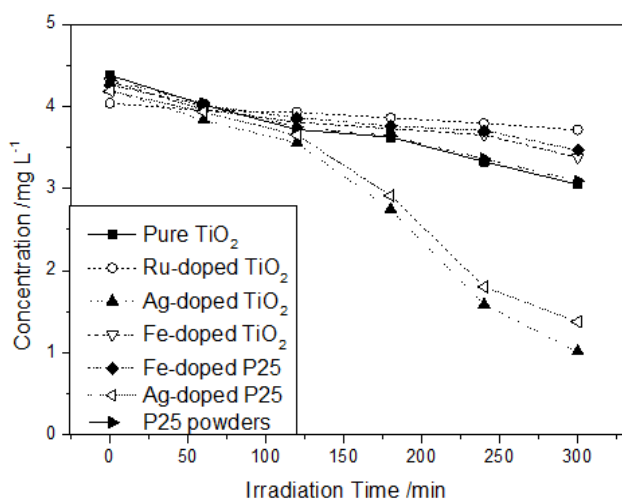


Figure 5. Comparison of the photocatalytic degradation of  $\beta$ -carotene in the presence of pure  $\text{TiO}_2$ , Ru-doped  $\text{TiO}_2$ , Ag-doped  $\text{TiO}_2$ , Fe-doped  $\text{TiO}_2$ , Fe-doped P25, Ag-doped P25 and P25 powders under visible light irradiation.

Figure 5 shows the decrease of concentration of  $\beta$ -carotene in the air under visible light irradiation (wavelengths  $> 400$  nm). 0.25 mL reaction liquid was diluted to 10 mL, and then UV-Vis Spectrophotometer was used to follow the track of the reaction. No obvious changes of concentration of  $\beta$ -carotene with Fe-doped  $\text{TiO}_2$  and Fe-doped P25 were found in 300 min. The Ag-doped  $\text{TiO}_2$  and Ag-doped P25 show a higher photocatalytic activity than other photocatalysts. Meanwhile, Ag-doped  $\text{TiO}_2$  was a little better than Ag-doped P25, as it achieved a decrease of approximately 76% of the concentration of  $\beta$ -carotene. In the presence of P25 and pure  $\text{TiO}_2$ , the concentration of  $\beta$ -carotene decreased 30% and 28% in 300 min. However, Ru-doped  $\text{TiO}_2$  showed very lower photocatalytic activity in 300 min.

The degradation of  $\beta$ -carotene in the presence of air, oxygen and nitrogen was followed at room temperature with Ag-doped  $\text{TiO}_2$  under visible light irradiation. The method of dilution was same as above. Obviously, in the presence of nitrogen atmosphere, there was almost no change of concentration. It indicated that photodegradation of  $\beta$ -carotene in the nitrogen atmosphere was very slow. Shown in Figure 6 is observed a quick decrease of  $\beta$ -carotene in the oxygen atmosphere. With achieving a decrease of approximately 86% of the concentration, it has the highest level in the photocatalytic degradation of  $\beta$ -carotene.

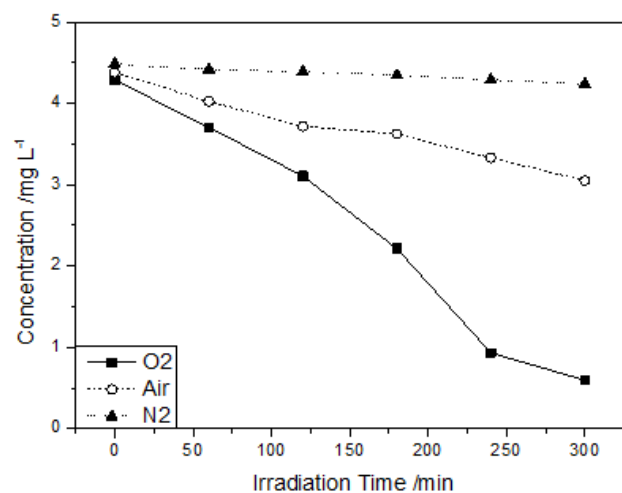
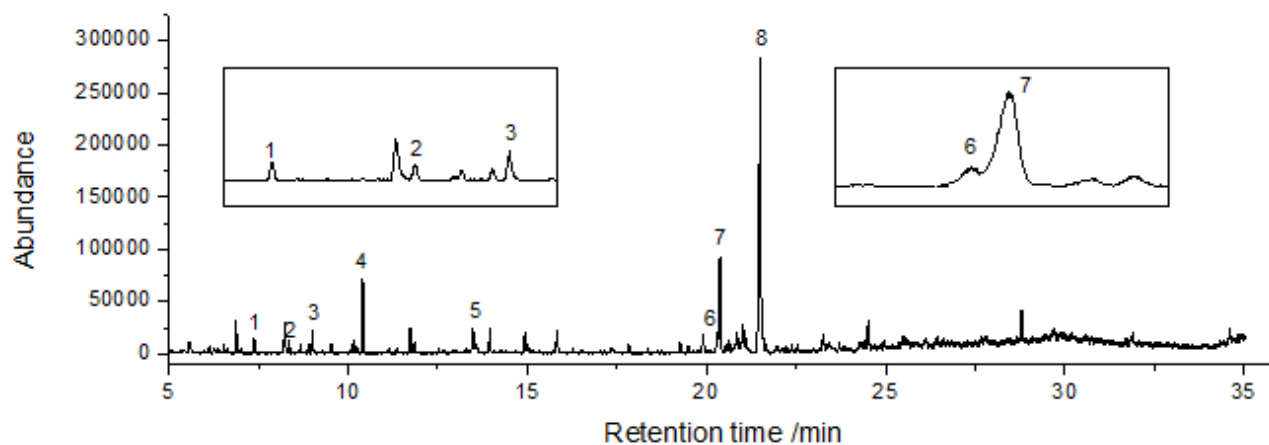


Figure 6. Comparison of the photocatalytic degradation of  $\beta$ -carotene in the presence of oxygen, air and nitrogen with Ag-doped  $\text{TiO}_2$

### 3.4. Identification of Compounds

Figure 7 shows the gas chromatograms of the photocatalytic degradation products from  $\beta$ -carotene. Since the photodegradation experiment was carried out at room temperature (298 K), eight of the compounds were identified. The structures and retention time were shown below.



**Figure 7.** The photocatalytic degradation products of  $\beta$ -carotene in the presence of oxygen by GC-MS detection (the gas chromatography operated at 323 K, then programmed to 473 K at 5 K  $\text{min}^{-1}$ , and held 4 min; then programmed to 533 K at 25 K  $\text{min}^{-1}$ , and held 4 min).

The compounds isolated under visible light are given in Table 2. Most of them have been identified in the other system before, like the thermal degradation of  $\beta$ -carotene in the solution [10]. The major photocatalytic degradation products contain esters, ketones, alcohols and aldehydes. Among these degradation products, 3,5,5-trimethyl-2-cyclohexen-1-one (isophorone), 2,6,6-trimethyl-1-cyclohexene-1-carboxaldehyde ( $\beta$ -cyclocitral),  $\beta$ -ionone, 5,6-epoxy- $\beta$ -ionone and dihydroactinidiolide are all spice materials. In the detection of the components, isophorone has an aroma of mint or camphor, which can increase the flavor of cigarette.  $\beta$ -cyclocitral is fruity.  $\beta$ -ionone, which is the main source of rose fragrance, and is also an important spice. Adding  $\beta$ -ionone into the tobacco can increase the unique aroma of the cigarette. Dihydroactinidiolide' addition can also achieve the same effect.

**Table 2.** Photocatalytic degradation products of  $\beta$ -carotene in the presence of oxygen at room temperature

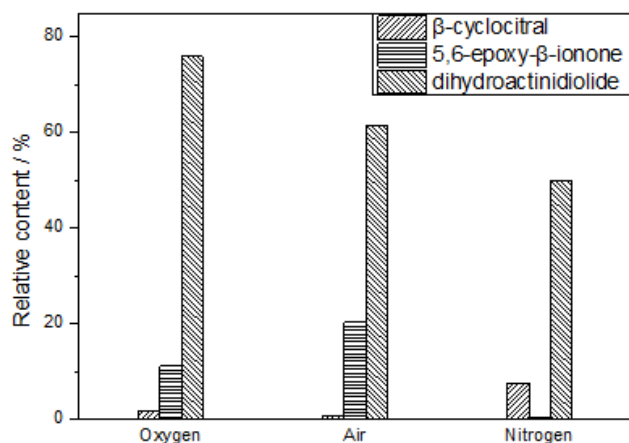
Peak (FIG.8.)	Degradation products	Retention time	Chemical formula	Molecular formula	Molecular weight
1	2-methyl-2-hepten-4-one	7.382		$\text{C}_8\text{H}_{14}\text{O}$	126
2	2,2,6-trimethylcyclohexanone	8.358		$\text{C}_9\text{H}_{16}\text{O}$	140
3	3,5,5-trimethyl-2-cyclohexen-1-one	9.001		$\text{C}_9\text{H}_{14}\text{O}$	138
4	2,6-dimethylcyclohexanol	10.409		$\text{C}_8\text{H}_{16}\text{O}$	128
5	2,6,6-trimethyl-1-cyclohexene-1-carboxaldehyde	13.468		$\text{C}_{10}\text{H}_{16}\text{O}$	152
6	$\beta$ -ionone	20.286		$\text{C}_{13}\text{H}_{20}\text{O}$	192
7	5,6-epoxy- $\beta$ -ionone	20.375		$\text{C}_{13}\text{H}_{20}\text{O}_2$	208
8	dihydroactinidiolide	21.497		$\text{C}_{11}\text{H}_{16}\text{O}_2$	180



### 3.5. The GC-MS Analysis of the Photocatalytic Degradation Products

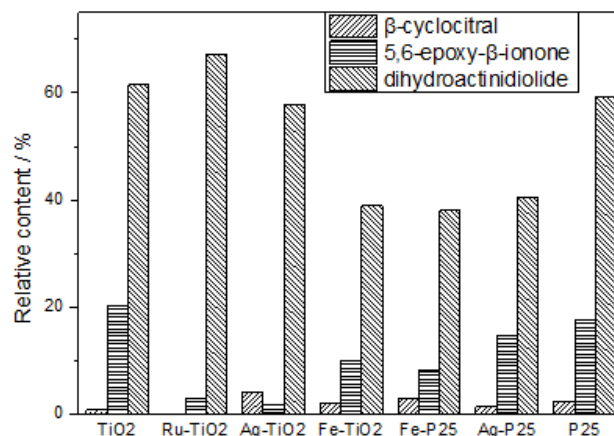
According to the compositional analysis of degradation products, and comparison of the content of degradation products percentage,  $\beta$ -cyclocitral, 5,6-epoxy- $\beta$ -ionone and dihydroactinidiolide were the major products and selected to carry out a comparative analysis. These three kinds of substances were also the important sources of aroma.

Figure 8 shows that in the different gas atmosphere, oxygen, air, nitrogen, respectively, with other conditions unchanged (room temperature, Ag-doped  $\text{TiO}_2$  as photocatalyst), oxygen content was changed to analyze how it influenced the degradation products of  $\beta$ -carotene. In the presence of pure oxygen, more dihydroactinidiolide was obtained. While 5,6-epoxy- $\beta$ -ionone was obtained more than other two situations in the air atmosphere, correspondingly, the content of DHA was less. In nitrogenous atmosphere, not only was the degradation of  $\beta$ -carotene slow, but also it was not easy to generate 5,6-epoxy- $\beta$ -ionone, the content was very low, but the  $\beta$ -cyclocitral was higher.



**Figure 8.** The influence of oxygen content on the degradation products of  $\beta$ -carotene

Figure 9 show that different photocatalysts influence the degradation products of  $\beta$ -carotene (in the presence of air). When Ru-doped  $\text{TiO}_2$  was a photocatalyst in the degradation reaction, DHA were obtained more than others, while  $\beta$ -cyclocitral was hard to be detected. Meanwhile, the participant of Ru-doped  $\text{TiO}_2$  degraded  $\beta$ -carotene very slowly, so for this degradation, maybe Ru-doped  $\text{TiO}_2$  was not a good photocatalyst. Compared with other photocatalysts, 5, 6-epoxy- $\beta$ -ionone was obtained more when the pure  $\text{TiO}_2$  took part in the degradation.



**Figure 9.** The influence of different photocatalysts on the degradation products of  $\beta$ -carotene

## 4. Conclusions

Photocatalytic activity studies on  $\beta$ -carotene degradation with pure  $\text{TiO}_2$  and metal ions doped  $\text{TiO}_2$  had shown that Ag- $\text{TiO}_2$  showed a better catalytic ability than others, and in the presence of oxygen atmosphere, a quick decrease of  $\beta$ -carotene was observed.

From the analysis of GC-MS, eight important degradation products were identified. In the oxygen atmosphere, it was easy to produce DHA, while the content of 5, 6-epoxy- $\beta$ -ionone was very low in the presence of nitrogen. When Ag-doped  $\text{TiO}_2$  was a photocatalyst in this degradation reaction, it was easy to form  $\beta$ -cyclocitral. While compared with other photocatalysts, 5, 6-epoxy- $\beta$ -ionone was obtained more when the pure  $\text{TiO}_2$  took part in the degradation.

## Acknowledgements

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