Journal of the Korean Crystal Growth and Crystal Technology
Vol. 17, No. 1 (2007) 23-29

Preparation of pitch-coated TiO_2 and their photocatalytic performance

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(Received December 22, 2006)
(Accepted January 29, 2007)

Abstract Pitch-coated anatase TiO_2 typed was prepared by CCl_4 solvent mixing method with different mixing ratios. Since the carbon layers derived from pitch on the TiO_2 particles were porous, the pitch-coated TiO_2 sample series showed a good adsorptivity and photo decomposition activity. The BET surface area for the carbon layer in the sample increases to increasing with pitch contents. The SEM results present to the characterization of porous texture on the pitch-coated TiO_2 sample and pitch distributions on the surfaces for all the materials used. From XRD data, a weak and broad carbon peak of graphene with pristine anatase peaks were observed in the X-ray diffraction patterns for the pitch-coated TiO_2. The EDX spectra show the presence of C, O and S with strong Ti peaks. Most of these samples are richer in carbon and major Ti metal than any other elements. Finally, the excellent photocatalytic activity of pitch-coated TiO_2 with slope relationship between relative concentration of MB (c/c_o) and t could be attributed to the homogeneous coated pitch on the external surface by CCl_4 solvent method.

Key words Porous carbon, BET surface area, SEM, XRD, EDX, Photocatalytic activity

1. Introduction

Titanium dioxide has been widely studied as a promising material for environment protection for the past few decades because of its prominent photocatalytic activity. Numerous studies have shown their unique performance in photo degradation of chemical toxic components in wastes, such as phenols and aromatic compounds. More recently, the combination of carbonaceous materials with photocatalysts has been of interest. We also have been interested in the carbon-titania technologies, and have found through our investigation that it is important to quantify the impact that irradiations of the carbon-coated TiO_2 have a photocatalytic activity. Carbon coating of photocatalyst anatase-type titanium dioxide was found to give many advantages such as high photosensitivity, high photocatalytic activity and high adsorptivity. And, carbon-coated TiO_2 was applied to the oxidation of different organic components in wastewater [1]. However, there are some drawbacks to the practical use of TiO_2 powder during the photocatalytic process. It is difficult to separation of powder TiO_2 from water and to suspension at high concentration as an aggregation of powder TiO_2. Early work mainly focused on coating TiO_2 on fixed supports, such as fibers, glass, stainless steal and quartz, etc. [2, 3]. It is expect that the efficiency of pollutant degaradation on carbon-coated TiO_2 is usually decreased because of the photocatalytic blocking the active site by carbon. According to former study [4], it suggested that carbon-coated TiO_2 was completely different from TiO_2-mounted carbons in the positional relation between TiO_2 and carbon. In this carbon-coated TiO_2, the contaminant molecules have to be adsorbed into the carbon layer that covers the TiO_2 particle, diffuse through the carbon layer to reach the surface of the TiO_2 photocatalyst and then be decomposed under UV irradiation.

In this work, we have prepared pitch-coated TiO_2 photocatalysts through carbon tetrachloride solvent method. The role of carbon layers are investigated through the preparation of pitch-coated anatase-type titanium dioxide photocatalysts from different pitch contents and the determination of their photocatalytic activity. The developed catalysts were characterized by BET surface area, X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX) and UV/VIS spectrophotometer.

2. Experimental

2.1. Materials

The pitch was used carbon precursor for preparation of pitch-coated TiO_2 hotocatalysts. The granular pitch was supplied from Jungwoo Chemical Co. (Korea). The

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Table 1
Nomenclatures of prepared samples with different mixing ratios of anatase to carbon precursor (pitch)

Sample	Mixing Ratios	Nomenclatures
Pitch + TiO_2	6 : 4	PT64
	5 : 5	PT55
	4 : 6	PT46
	3 : 7	PT37

TiO_2 photocatalysts was commercially available (Duk-San Pure Chemical Co., Korea), which was composed of a single phase of anatase with secondary particles of about 80~150 μm aggregated from the primary particles of about 30~50 μm. This anatase-type titanium dioxide powder had a relatively large BET surface area of about 238 m^2/g. For the melting of pitch, carbon tetrachloride (Dae-Jung Chemical Co., Korea) was used as solvent. After melting of pitch in CCl_4 solution, TiO_2 powder was mixed with pitch-CCl_4 solution. The powder mixtures with different mixing ratios of anatase to carbon precursor (pitch) were heated at 333 K for 1 h. The solvent in the mixtures was vaporized at 353 K for 6 hours. The agglomerates of pitch-TiO_2 were heated at 873 K for 1 h and then crushed at auto miller. The nomenclatures of prepared samples were listed in Table 1.

2.2. *Characterization*

For the physical parameter measurements, nitrogen isotherms were measured using an ASAP 2010 instruments (Micromeritics, U.S.A) at 77 K. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and structure of pitch-coated TiO_2 transformed through the pitch-treatment. For the elemental analysis in pitch-coated TiO_2, energy dispersive X-ray analysis (EDX) was also used. X-ray diffraction patterns were taken using an X-ray generator (Shimatz XD-D1, Japan) with Cu Kα radiation. As one of the analysis of photocatalytic activity, UV/VIS spectrophotometer (Genspec III (Hitachi), Japan) was used to characterize of catalytic efficiency of TiO_2 photocatalysts. Characterization of methylene blue ($C_{16}H_{18}N_3S$, MB) in water was determined by the following procedure. A pitch-coated TiO_2 powdered sample of 0.05 g was dispersed in an aqueous solution with a concentration of 1.0×10^{-4} mol/*l* in the dark atmosphere at room temperature. Each concentration was measured as a function of UV irradiation time from the absorbance at the range of 250~800 nm wavelength of MB measured by UV/VIS spectrophotometer.

2.3. *Photocatalytic effect*

In order to reveal the photocatalytic effect of the prepared samples, the decomposition reaction of MB in water was followed. Powdered samples of 0.05 g were dispersed in ultra sonicate for 3 min. For UV irradiation the UV lamp (20 W, 365 nm) was used at the distance of 100 mm from the solution in darkness box. By sampling 3 m*l* of solution after removal of dispersed powders through centrifuge, the concentration of MB in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 660 nm.

3. Results and Discussion

3.1. *Surface properties*

The BET surface areas measured were shown an apparent values for the powder samples composed TiO_2 and pitch. In Fig. 1, BET surface area is plotted against pitch contents of the samples prepared using different carbon mixing ratios. The BET surface area depends on the pitch contents, which was made by changing the mixing ratio of the pitch with the raw TiO_2. By using ceramic substrate, carbon coating was experimentally exposed that the carbon formed on most ceramic surface from carbon precursors was very microporous [5]. The BET surface area for pitch-coated TiO_2 prepared at 873 K give a common dependence on carbon content. It is plausible assume that thin carbon layers on TiO_2 particles derived from pitch are responsible for the BET surface area. According to the former study [6], it was found that the original pristine TiO_2 give very small sur-

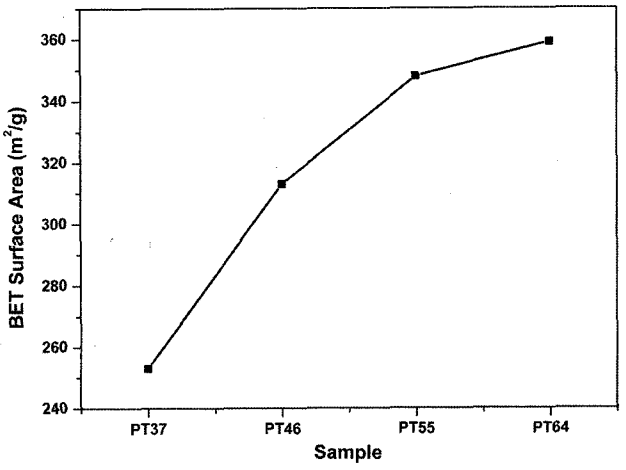

Fig. 1. BET surface area of pitch-coated titanium dioxide samples prepared with different mixing ratios.

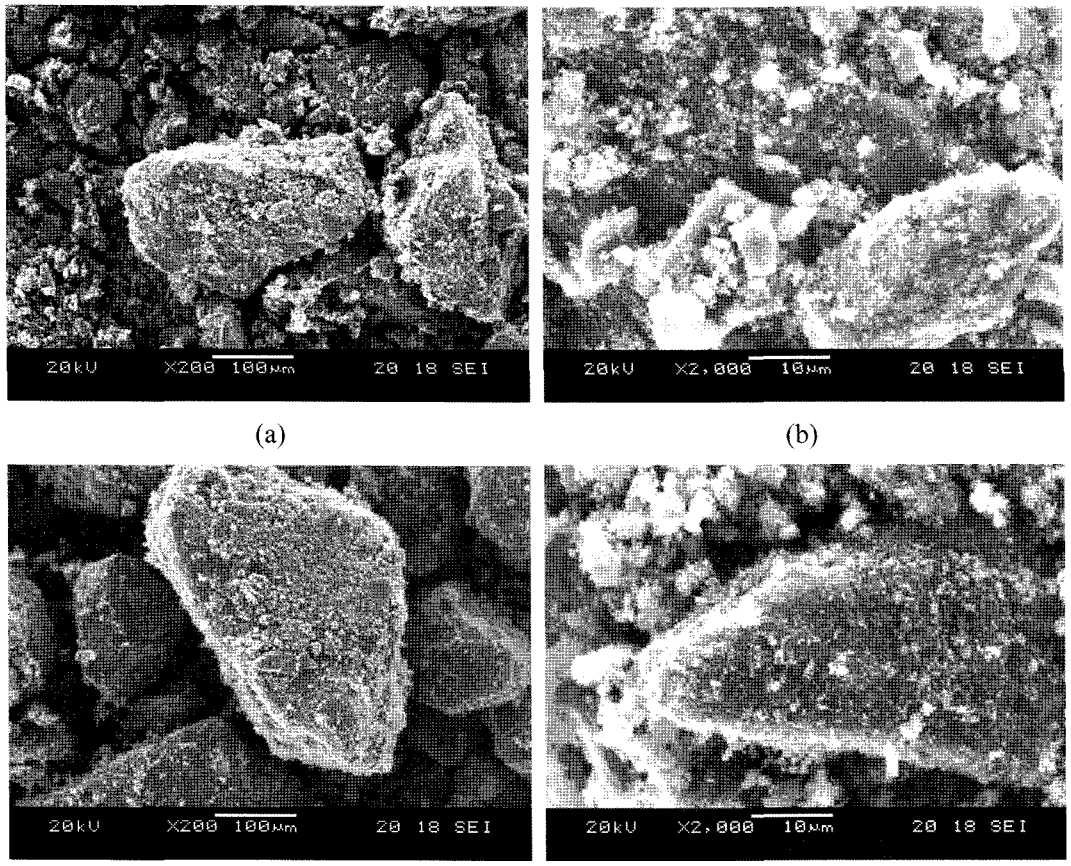

Fig. 2. SEM micrographs of pitch-coated TiO_2 prepared with different mixing ratios; (a) PT64 (× 200), (b) PT64 (× 2000), (c) PT55 (× 200), (d) PT55 (× 2000), (e) PT46 (× 200), (f) PT46 (× 2000), (g) PT37 (× 200) and (h) PT37 (× 2000).

face area (about 2 m^2/g). In our case, it was obtained that the BET surface area for the carbon layer in the sample increases to increasing with pitch contents. From this point, the present pitch-coated TiO_2 samples can be adsorbed a relatively large amount of MB in an aqueous solution.

The surface structure of the pitch-coated TiO_2 samples was investigated and the relationship between pitch deposition and pristine TiO_2, and change of their structure were investigated. Figure 2 shows SEM micrographs of pitch-coated TiO_2 sample series as a function of different mixing ratios. These figures present results from the characterization of porous texture on the pitch-coated TiO_2 sample and pitch distributions on the surfaces for all the materials used. It is shown that, when carbon derived from pitch is dispersed onto TiO_2, the surface properties are modified in some cases, this effect being developed as microporosity in pitch-coated TiO_2 sample with porosity. SEM pictures of pitch-coated TiO_2 sample provide information about the distribution of carbon on the TiO_2 surface. A homogeneous distribution of pitch with providing the large surface area can be promoting the photocatalytic efficiency for the removal of MB in aqueous solution. This point will have to be taken into account for further analysis of the removal of MB in aqueous solution because large surface strongly influences both the adsorption capacity and the photocatalytic activity for of MB in aqueous solution. Carbons derived from pitch were homogeneously covered on the partial surface of the TiO_2. Each of these analyses showed that carbons on the TiO_2 are uniformly distributed in the rounded and edges. Compare to former study [5], carbon coating on the TiO_2 was not obtained homogeneous results. In our case, however, homogeneously pitch-coated TiO_2 samples were obtained from CCl_4 solvent method as shown in Fig. 2.

3.2. Physico-chemical properties

Figure 3 showed the X-ray diffraction patterns of (a) the pristine TiO_2, (b) the pitch-coated TiO_2 prepared at 873 K. A weak and broad carbon peak of graphene with pristine anatase peaks were observed in the X-ray diffraction patterns for the pitch-coated TiO_2, as shown in

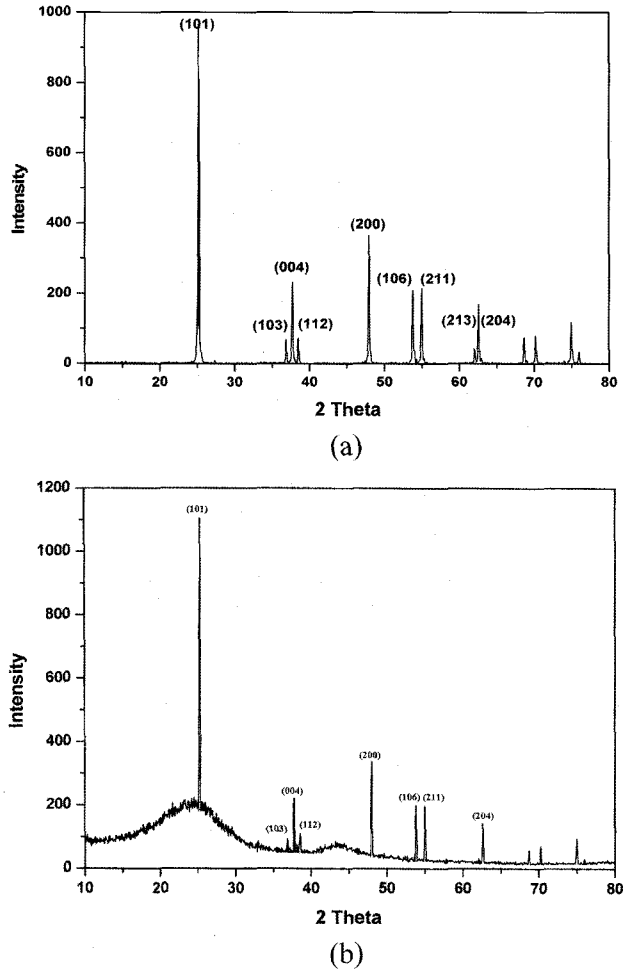

Fig. 3. XRD patterns of (a) raw TiO_2 and (b) pitch-coated TiO_2 treated at 873 K.

Fig. 3(b). These results suggested that graphene in the heat treated pitch had a very disordered structure along the c-axis, and the L_c (~0.6 nm) and L_a (~0.8 nm) values of stacked graphene layers was of quite small. High intensity and very sharp peaks of anatase crystal were observed in the XRD patterns for the pitch-coated TiO_2 annealed at 873 K and bulk sample (a).

For the elemental microanalysis of pitch-coated TiO_2 sample as a function of mixing ratios, these samples were analyzed by EDX. These EDX spectra of pitch-coated TiO_2 sample were shown in Fig. 4. These spectra show the presence of C, O and S with strong Ti peaks. Most of these samples are richer in carbon and major Ti metal than any other elements. The results of EDX elemental microanalysis of pitch-coated TiO_2 sample series were listed in Table 2. In the case of most of the samples, carbon and Ti were present as major elements in the pitch-coated TiO_2 sample. These results were observed for each sample show the spectra corresponding to almost all samples rich in C elements with an increase of the amount of pitch contents. It should be note that a decrease of the C and S (impure element derived from pitch) content with a increasing of the Ti content is observed for the over all sample series.

3.3. Photocatalytic activity

Figure 5 is represented UV/VIS spectra of MB concentration against the pitch coated TiO_2 under various time conditions. As can be seen from the figure, the absorbance maxima for the all samples slowly decrease with increase of UV irradiation time. This implies that the transparent of the MB concentration highly increase by photocatalytic effect of pitch-coated TiO_2. Figure 6 shows changes in MB concentration under UV irradiation in the aqueous solution. The changes in the relative concentration c/c_0 (where, c : measured concentration and c_0 : initial concentration) of MB in the aqueous solution with time of UV irradiation are plotted for the sample series. The relationship was shown approximately linearity, as reported on similar modified TiO_2 samples [7]. Because the pitch-coated TiO_2 samples had an adsorptivity, as above mentioned, it is considered that the decrease of MB concentration in the aqueous solution can be occurred in two physical phenomena such as adsorption by carbon and photocatalytic decomposition. According to earlier workers [8], MB molecules absorbed energy from irradiation, thereby shifting their delocalized electrons from bonding to antibonding orbital. Since MB adsorption likely occurs via π-π interactions between its delocalized electrons and the carbon's graphene layers, it is reasonable that shifts in its electron orbitals would alter adsorption. Because the photocatalytic reaction is light excited, carbon deep inside TiO_2 is not easily accessible to light because of enhanced reflection and scattering by the support and the long traveling distance. In this study, the excellent photocatalytic activity of pitch-coated TiO_2 could be attributed to the homogeneous coated pitch on the external surface by CCl_4 solvent method. Removal of MB in the solution was measured periodically over 50 min. The initial increase in the contents of TiO_2 results in a significant increase of photo active sites. For the all pitch coated TiO_2 samples prepared from different mixing ratios, slope relationship between relative concentration of MB (c/c_0) and t were observed at 1.0×10^{-4} mol/*l* of MB concentration. At slope relationship between relative concentration of MB (c/c_0) and t, it was obtained that removal effect of MB for the pitch-coated TiO_2 is better excellent than that of pristine TiO_2 for the all samples. Based

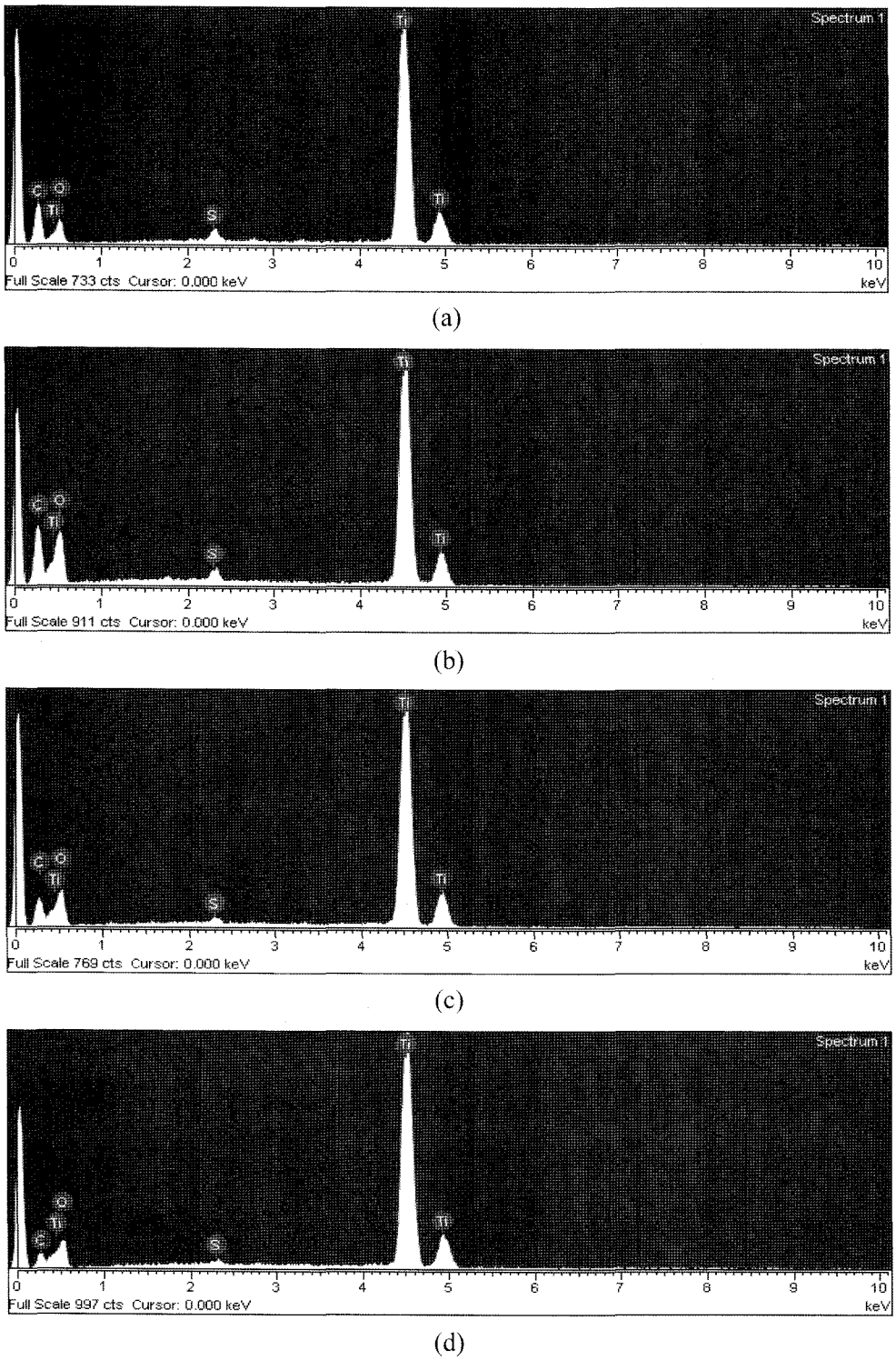

Fig. 4. EDX elemental microanalysis of prepared samples with different mixing ratios of anatase to carbon precursor; (a) PT64, (b) PT55, (c) PT46 and (d) PT37.

on these observations, we therefore can conclude that the decrease of MO concentration should be attributed to the both effects between photocatalysis of the supported TiO_2 and adsorptivity of the carbon derived from pitch.

4. Conclusion

In this study, the pitch-coated TiO_2 photocatalysts were prepared through carbon tetrachloride solvent method. The developed photocatalysts were characterized with

Table 2
EDX elemental microanalysis of prepared samples with different mixing ratios of anatase to carbon precursor (pitch)

Nomenclatures	C	O	S	Ti
PT64	21.08	28.18	1.23	49.51
PT55	20.70	31.43	0.92	46.94
PT46	13.47	37.36	0.53	48.64
PT37	8.00	36.43	0.39	55.18

surface properties, surface structure and state, crystallinity between carbon and TiO_2, elemental analysis and photocatalytic activity. The BET surface area depends on the pitch contents, which was made by changing the mixing ratios of the pitch with the raw TiO_2. The SEM results present to the characterization of porous texture on the pitch-coated TiO_2 sample and pitch distributions on the surfaces for all the materials used. From XRD data, a weak and broad carbon peak of graphene with pristine anatase peaks were observed in the X-ray diffraction patterns for the pitch-coated TiO_2. The EDX spectra show the presence of C, O and S with strong Ti

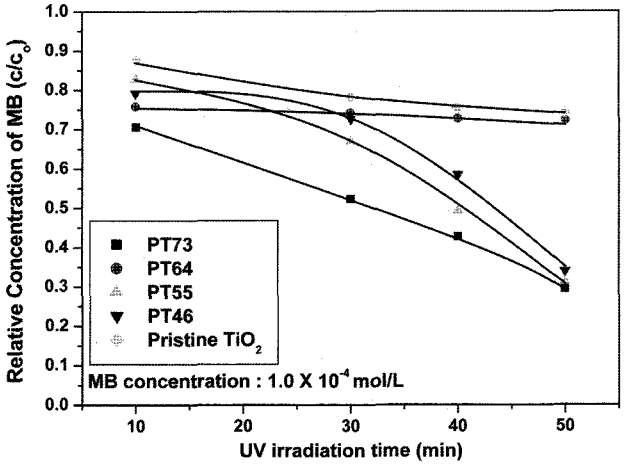

Fig. 6. Dependence of relative concentration of MB in the aqueous solution c/c_0 on time of UV irradiation for the pitch-coated TiO_2 prepared from the different mixing ratios.

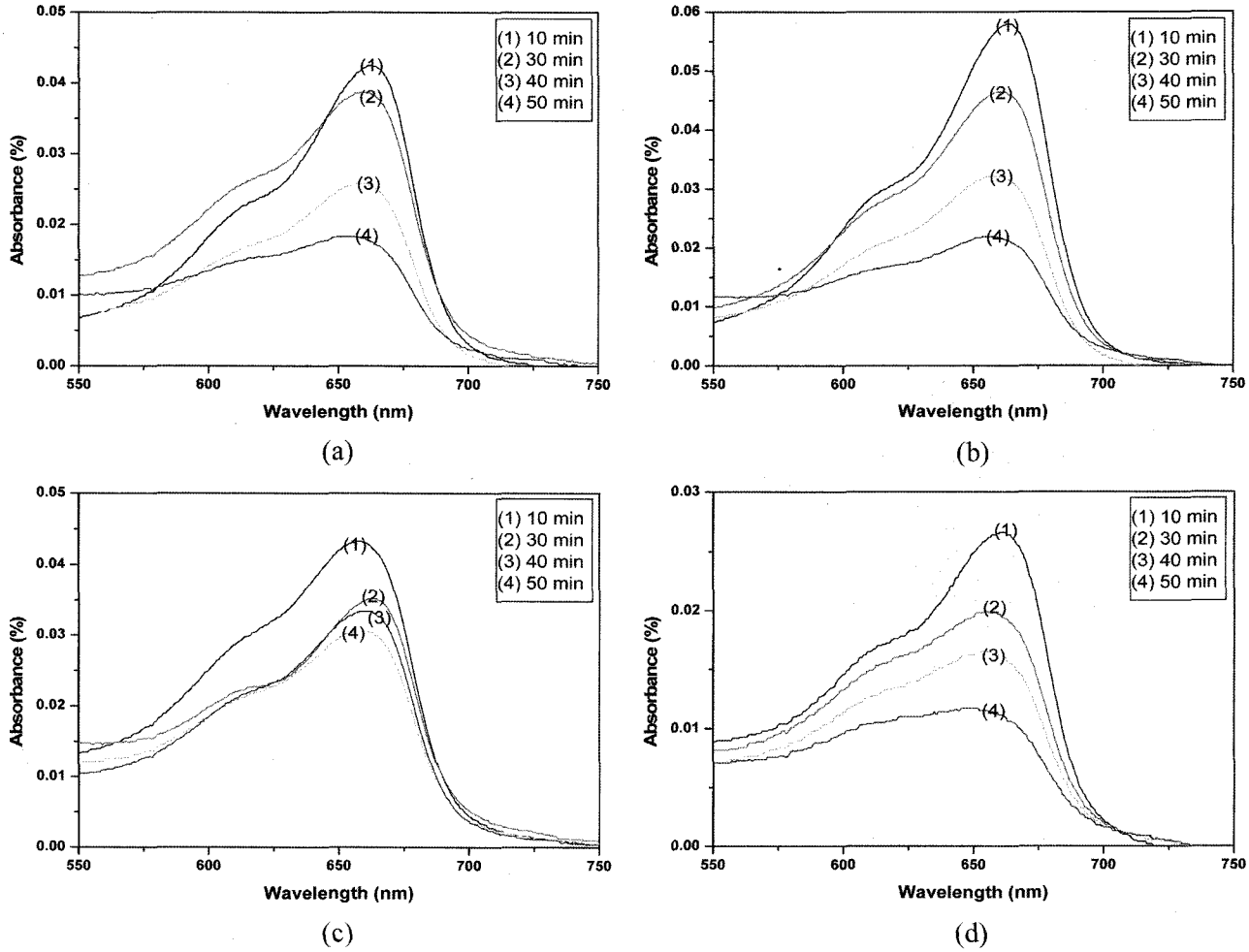

Fig. 5. UV/VIS spectra of MB concentration against the pitch coated TiO_2 under various time conditions; (a) PT64, (b) PT55, (c) PT46 and (d) PT37.

peaks. Most of these samples are richer in carbon and major Ti metal than any other elements. Finally, the excellent photocatalytic activity of pitch-coated TiO_2 with slope relationship between relative concentration of MB (c/c_o) and t could be attributed to the homogeneous coated pitch on the external surface by CCl_4 solvent method.

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