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ORIGINAL ARTICLE

Studies on the mechanism of printing film-coated tablets containing titanium dioxide in the film by using UV laser irradiation

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Abstract
Aim: The purpose of this article is to study a detailed mechanism of printing when film-coated tablets were irradiated by UV laser at a wavelength of 355 nm. *Methods*: Hydroxypropylmethylcellulose (HPMC) film containing titanium dioxide (TiO_2) and the film not containing TiO_2 and TiO_2 powder were lirradiated by the UV laser and estimated by the morphological observation by zoom stereo microscope, thermogravimetric analysis (TGA), total color difference (d*E*), X-ray powder diffraction (XRD), and dispersive Raman microscopy. *Results*: In the case of the film containing TiO_2, the film showed a visible change in its color from white to gray by the UV laser irradiation. By zoom stereo microscope, it was found that the entire UV laser-irradiated area was not grayed uniformly, but many black particles, whose diameter was about 2 μm, were observed on the film. When TiO_2 powder was irradiated by the UV laser, a visible change in its color from white to gray was observed similar to the case of the film containing TiO_2. There were many black particles locally in the UV laser-treated TiO_2 powder by the morphological observation, and these black particles, agglomerates of the grayed oxygen-defected TiO_2, were associated with the visible change of the TiO_2. *Conclusion*: It was found that the film-coated tablets were printed utilizing the formation of the black particles by the agglomeration of the grayed oxygen-defected TiO_2 by the UV laser irradiation.

Key words: *Color change; film-coated tablet; oxygen vacancy; printing; titanium dioxide; UV laser*

Introduction

Method and identification system to keep track of individual medicines dispensed to patients in a hospital is important to avoid severe health risks. Prior to dispensing the medicines, a verification check is performed. However, once a medicine leaves its container, it becomes impossible to check its medication content unless the container or the leaflet remains accessible[1]. If the container is emptied or lost or discarded, medicines will be unidentifiable. The problem is the lack of information on the medicine itself. Medicines come in a variety of shapes, sizes, and colors to help distinguish one from the other. However, there is a restriction in keeping good identification characteristics only with the differences in size, shape, color of tablets, or capsules so that printing directly on the medicines becomes more important as an identification method. For example, in the case of film-coated tablets, an embossing[2], an offset printing, an ink-jet printing, or a pad printing has been used for the printing. In the case of capsules, the offset printing also has been used generally.

Embossing is a method to manufacture coded film-coated tablets by coating the embossed core tablets. But the printable area is so restricted that the information for identification, for example, number and size of the letters, is not enough. Offset printing, ink-jet printing,

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and pad printing are the popular methods to print on the surface of tablets or capsules using ink. Those are easy to be affected by the surface roughness of tablets or capsules, and environmental conditions of the process room and sometimes problems such as mottled appearance, blur, or dirt of the inks were happened. In addition, generally organic solvents are used as a solvent for the inks but those are not good for health of the employee and the environment. Coding of medicine by embossing or ink printing is not sufficient yet.

Khan[3] reported about a method for marking pharmaceutical dosage units such as tablets or pills using a CO_2 laser. Yoshin[4] also reported about the development of a printing device to print on soft capsule using a CO_2 laser. When the CO_2 laser was irradiated on the soft capsule, gelatin, one of the constituents of the soft capsule shell was denatured by the heat of the CO_2 laser, and the irradiated spot became white. The printing was performed without touching the medicines and without using inks, so there were no problems such as mottled appearance, blur, or dirt because of printing. However, there were concerns whether the CO_2 laser damaged the film of the tablet or the capsule shell and whether the scorch, which was produced by heat denature of carbohydrates, was safe.

In the previous paper[5], we reported about the development and characteristics of the UV laser printing machine that printed on the film-coated tablets by UV laser at a wavelength of 355 nm. The machine makes it possible to print complicated designs or many number of letters clearly (see Figure 1) and to keep the productivity high. There was no change in the surface of the film between the marked area and the nonmarked area. When marking was performed on the enteric-coated tablet, the acid-resistant function of the tablet against 0.1 N hydrochloric acid was retained and dissolution profile was not changed. The UV laser irradiation on the film-coated tablets did not destroy the film's integrity. The marking was stable under 40°C/75% RH for 6 months or by the irradiation of 1200×10^3 lx·hour visible light by xenon lamp.

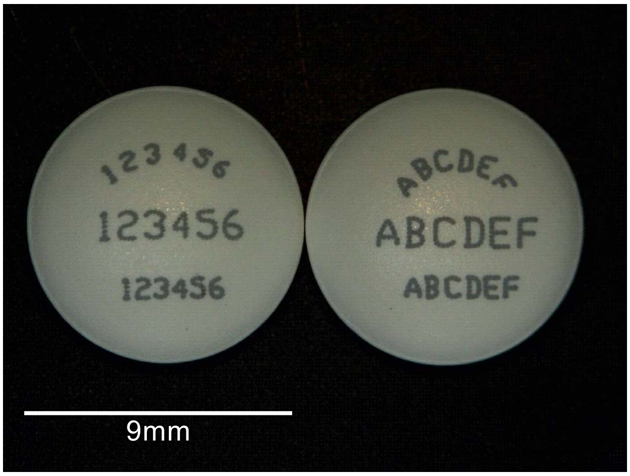


Figure 1. A photograph of tablets printed with the laser irradiation technique[5]. The diameter and the *R* of the tablets are 9 and 9 mm, respectively.

Titanium dioxide (TiO_2) is one of the popular pharmaceutical excipients as an opacifier and is often contained in the film of the film-coated tablets[6]. When TiO_2 powder is treated with high energy such as heating[7] or UV irradiation[8], oxygen ions are defected from the TiO_2 powder and the color of TiO_2 changes to gray from white. This phenomenon is known as oxygen vacancy. Recently, Lee et al.[9] reported that TiO_2 showed a visible change in its color from white to dark blue when UV laser was irradiated on it and that the color appeared permanent under ambient conditions. It was assumed that we utilized the color change of TiO_2 contained in film for our UV laser printing machine. However, the purpose of their studies was to clear the physical and photocatalytic characteristic of the UV laser-treated TiO_2, and there was no detailed information about the mechanism of the color change.

In this study, we report a detailed mechanism of printing and color change of the film when the film-coated tablets were printed by the UV laser irradiation.

Materials and methods

Materials

TiO_2 was obtained from Junsei Kagaku Co., Ltd. (Tokyo, Japan). It was of anatase type and of Japanese Pharmacopoeia grade (99.0% purity). The specific surface area determined using COULTER SA3100 (Beckman Coulter Inc., Fullerton, CA, USA) was 9.34 m^2/g so that the specific surface diameter was calculated as 0.164 μm. A rutile type of TiO_2 as an authentic sample was gifted by Toho Titanium Co., Ltd. (Kawasaki, Japan). Hydroxypropylmethylcellulose 2906 (TC-5) was purchased from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). Polyethylene glycol 8000 (PEG-8000) was from NOF Corporation (Tokyo, Japan). Talc was from Matsumurasangyo Co., Ltd. (Osaka, Japan).

Film preparation

TC-5 is one of the most popular pharmaceutical polymers for pharmaceutical film-coated tablets; in this study, the formulations in Table 1 were used for the preparation of the films. For the preparation of the film containing 4% TiO_2, a suspension consisting TC-5 (11.2 g), PEG-8000 (2.4 g), talc (5.6 g), TiO_2 (0.8 g), and purified water (180.8 g) was prepared by homogenization

Table 1. Formulation of the film with TiO_2 or without TiO_2.

	Film with TiO_2 (g)	Film without TiO_2 (g)
TC-5	11.2	11.2
PEG-8000	2.4	2.4
Talc	5.6	5.6
TiO_2	0.8	0

The materials were dissolved or suspended in purified water (180.8 g). Each of 5-g suspensions was spread with a plastic Petri dish of 11 cm diameter and the films were obtained after drying.

for 10 minutes at 5000 rpm using Polytron homogenizer (Kinemachika AG., Lucerne, Switzerland). For the film without TiO_2, TiO_2 was not added to the suspension. After removal of bubbles by stirring the suspension gently, 5 g of the suspension was deposited on a plastic Petri dish of 11 cm diameter by dropping pipette and was spread uniformly. After drying in a tray drier at 50°C, a film was obtained and was used for experiment.

UV laser irradiation

A tripled Nd : YVO4 laser (DS20H-355, Photonics Industries International, Inc., Bohemia, NY, USA), producing 20 ns pulses up to 8 W peak pulse power (pulsed by AO-Q switch to 20 kHz), was used for UV laser irradiation. The laser was set to a wavelength of 355 nm, and the diameter of the laser spot was 0.5 mm. In the case of the film, the sample was irradiated with the 3.14-W pulsed laser by scanning at a speed of 2000 mm/s parallel with 0.5 mm distance controlled by CAD system. In the case of TiO_2 powder, the powder was irradiated by the pulsed laser by scanning at a speed of 2000 mm/s parallel with 0.5 mm distance five times with agitation gently after each irradiation.

Thermogravimetric analysis

A thermogravimetric analyzer (TGA-DTA2200SA; Bruker-axs, Karlsruhe, Germany) was used. About 20 or 100 mg of the sample was introduced into a platinum pan. Samples were heated at 10°C/min scanning rate between room temperature and 1000°C under 200 mL/min O_2 gas flow.

Total color difference

The color changes of samples were examined by a spectrophotometer (VSS400; Nippon Denshoku Co. Ltd., Tokyo, Japan) using a standard white plate as a reference. This enables examination of the $L^*a^*b^*$ coordinate, which closely represents human sensitivity to color. Equal distances in this system equal perceived color differences where L^* is the lightness variable while a^* (green to red) and b^* (blue to yellow) are chromaticity coordinates. The dE is the straight-line distance between coordinates of the sample and the reference white plate and is calculated using Equation (1).

$$\mathrm{d}E=\left[(\mathrm{d}L^*)^2+(\mathrm{d}a^*)^2+(\mathrm{d}b^*)^2\right]^{\frac{1}{2}}. \tag{1}$$

X-ray powder diffraction

X-ray powder diffractometry analysis was carried out using a Discover D8 with GADDS (Bruker-axs) apparatus. Measurement conditions were described as follows: measurement mode, reflection geometry; source, sealed tube, Cu anode, 40 mA/40 kV; monochromator, flat graphite; collimator, 0.5 mm pine hole; double slits scanning range, 5–48°, divided into two flames; scanning period, 180 seconds/flame; scan step, 0.02°.

Dispersive Raman microscopy

Dispersive Raman microscopy has been performed on a Bruker SENTERRA confocal system based on an Olympus BX51 optical microscope equipped with a 532 nm diode laser (laser power: 20 mW) as source, an Andor iDUS DU420A CCD camera as detector, and a motorized XYZ stage for mapping and confocal experiments. The frequency calibration of the system was performed automatically using neon lamp. The microscopic Raman measurements were performed with a 50-fold magnification long-distance objective from Olympus. The lateral resolution is in the order of magnitude 2 μm. Data acquisition and analysis were performed using the software package OPUS6.5 (Bruker Optics, Ettingen, Germany). For each spectrum, spectral range (70–1200 cm^{-1}) was measured (Raman acquisition time per spectral region, 20 seconds; repeats per spectral region, three times; total acquisition time, 60 seconds) with a spectral resolution of 9–15 cm^{-1}.

Results and discussion

UV laser irradiation to the film containing or not containing TiO_2

In previous paper[5], we reported about the development of the UV laser printing machine that printed on the film-coated tablets by the irradiation of UV laser at 355 nm wavelength. The UV laser irradiation on the film-coated tablets did not destroy the film's integrity, and the marking was stable under 40°C/75% RH for 6 months or the

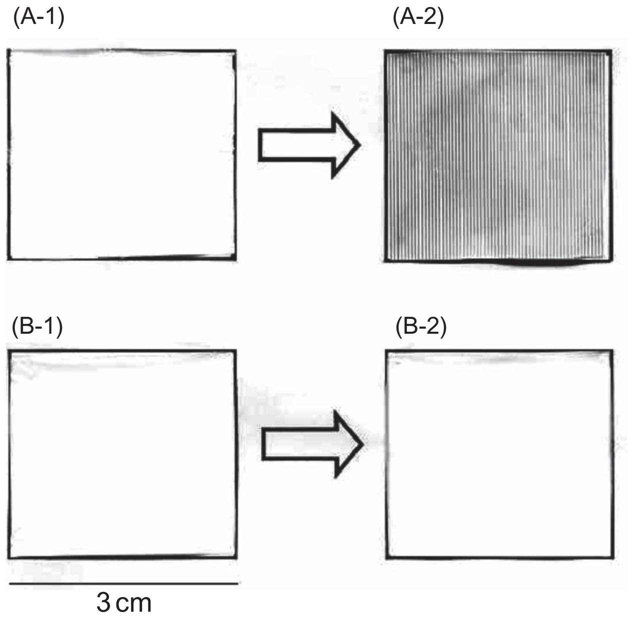


Figure 2. Photographs of color changes of the films irradiated 355 nm UV laser. (A-1) is a film containing TiO_2 before the UV laser irradiation and (A-2) is the film after the irradiation. (B-1) is a film not containing TiO_2 before the irradiation and (B-2) is the film after the irradiation.

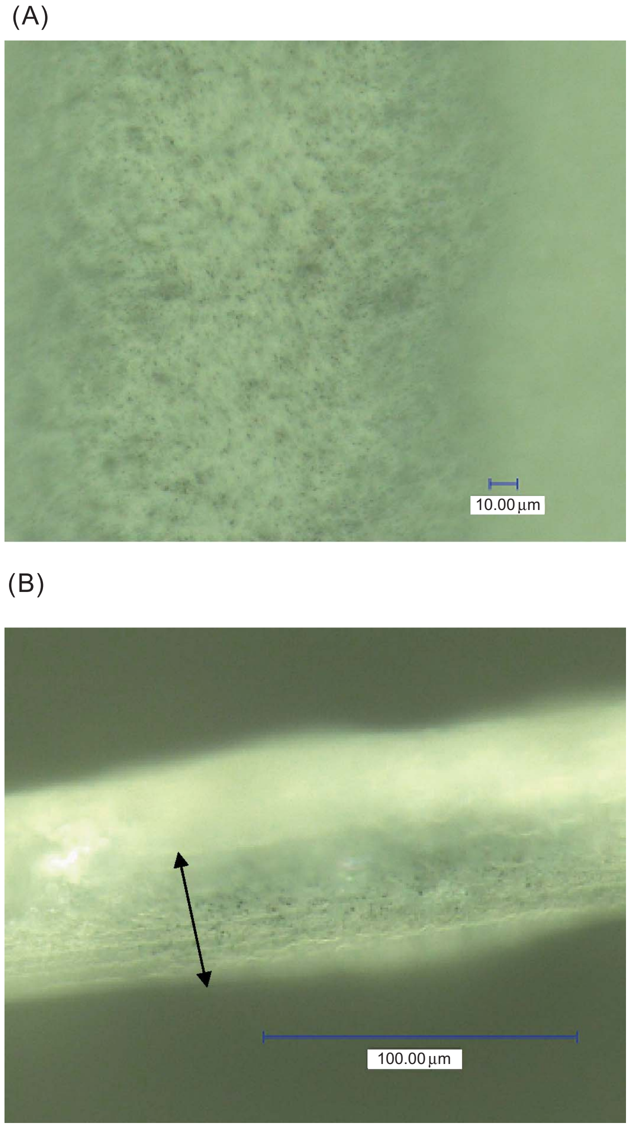


Figure 3. Photographs (×1000) of the colored part of the film by zoom stereo microscope. (A) is a photograph taken from the surface of the film and (B) is the cross section of the film. The two-headed arrow mark in (B) shows the depth where the black particles are observed.

irradiation of 1200×10^3 lx·hour visible light by xenon lamp. In this article, we report about a detailed printing mechanism. Figure 2 shows photographs of color changes of the films when those were irradiated with the UV laser at 355 nm wavelength. (A-1) is a film containing TiO_2 before the irradiation of the UV laser and (A-2) is the film after the irradiation. (B-1) is a film not containing TiO_2 before the irradiation and (B-2) is the film after the irradiation. In the case of the film containing TiO_2, the film (A-2) showed a visible change in its color from white to gray after the irradiation of the UV laser. Film-coated tablets were printed by the UV laser printing machine utilizing this color change of the film containing TiO_2 by the UV laser irradiation. On the other hand, in the case of the film not containing TiO_2, no visible change in its color was observed (B-2). This shows that TiO_2 plays an important role for printing film-coated tablets by the UV laser.

Figure 3 shows the photographs (×1000) of the colored part of the film by Zoom Stereo Microscope (VHX-900, Keyence Co., Ltd., Osaka, Japan). Panel A is a photograph taken from the surface of the film and panel B is the cross section of the film. The diameter of the laser spot was 0.1 mm, and all of the area where the UV laser was irradiated was not gray uniformly, but many black particles were observed at the colored part of the film. The diameter of the black particles was about 2 µm. The formation of the particles at the UV laser-irradiated area was associated with the printing on film-coated tablets by our UV laser printing machine. The thickness of the film prepared in this study was 74.8 ± 6.4 µm (mean ± SD, $n = 5$), and the particles were observed at the area from the surface to the 46.9 ± 3.6 µm (mean ± SD, $n = 5$) depth of the film. Such particles were not observed before the irradiation.

The dispersive Raman microscopy offers the possibility to analyze microquantities of materials without any sample preparation and without any destruction[10]. So, the characteristic of the black particle was estimated

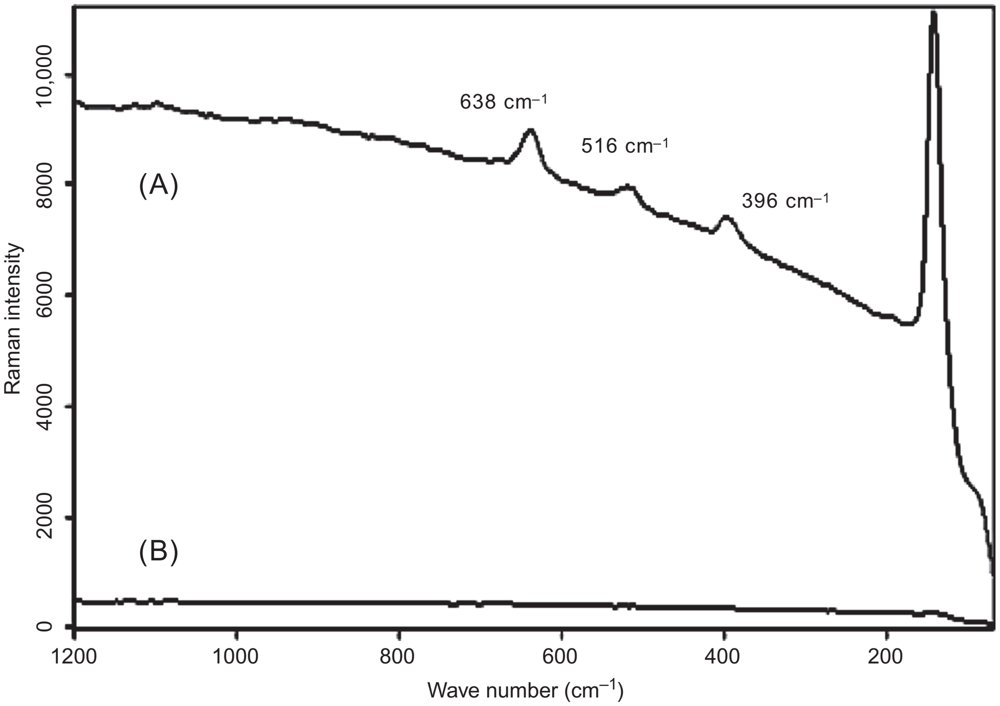


Figure 4. Raman spectra of the film (A) before the irradiation and the black particle (B) in the film after the irradiation.

by the dispersive Raman microscopy. Figure 4 is Raman spectra of the film (A) before the irradiation and the black particle (B) in the film after the irradiation. The characteristic peaks (396, 516, and 638 cm^{-1}) of anatase TiO_2 (see Figure 8) were observed in the film before the irradiation. However, in the black particle, the peaks were not observed. It is essential that Raman spectroscopy permits to analyze only molecule and structures but not isolated ions[10]. TiO_2 was a nanoparticle and was dispersed in the film uniformly, but after the UV laser irradiation, anatase TiO_2 was not observed in the black particles. The black particles formed by the UV laser irradiation were inactive to Raman spectroscopy. This shows that TiO_2 in the black particles was converted to Raman-inactive components.

UV laser irradiation to TiO_2 powder

When the films were irradiated by the UV laser, the film containing TiO_2 showed a visible change from white to gray but the film not containing TiO_2 did not, so it was expected that TiO_2 was closely associated with the printing film by the UV laser irradiation. Figure 5 is a photograph of both TiO_2 powder (A) and UV laser-irradiated TiO_2 powder (B). When TiO_2 powder was irradiated by the UV laser, a visible change in its color from white to gray was observed similar to the case of the film containing TiO_2 shown in Figure 2(A-2).

Figure 5. Photograph of TiO_2 (A) and UV-irradiated TiO_2 (B).

The UV laser-irradiated TiO_2 powder was examined by TGA and X-ray powder diffraction (XRD) spectroscopy to elucidate what physical changes occurred in the TiO_2 powder. When TiO_2 powder is treated with the high energy such as heating or UV irradiation, oxygen ions are defected from the TiO_2 powder and the color of TiO_2 powder changes to gray from white. This phenomenon is known as oxygen vacancy of TiO_2[7,8]. Recently, Lee et al.[9] reported that TiO_2 showed a visible change in its color from white to dark blue when UV laser was irradiated. They reported that when the color changed TiO_2 was heated over 600°C in air, it bound oxygen and the dark blue color of the TiO_2 disappeared. So, TGA was performed to confirm that the color change of the TiO_2 powder by the UV laser irradiation shown in Figure 5

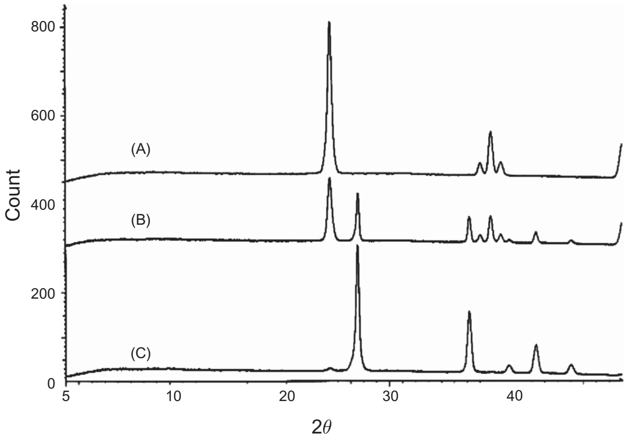
Table 2. Comparison of the color differences between TiO_2, UV laser-irradiated TiO_2, and UV laser-irradiated TiO_2 after TGA.

	L^*	a^*	b^*	dE
Standard white plate	98.15 ± 0.02	−0.15 ± 0.09	−0.03 ± 0.04	0
Anatase TiO_2	100.81 ± 0.17	−0.24 ± 0.16	1.51 ± 0.05	3.09 ± 0.15
UV laser-irradiated TiO_2	89.72 ± 1.29	−0.93 ± 0.25	−1.76 ± 0.24	8.64 ± 1.27
UV laser-irradiated TiO_2 after TGA	98.96 ± 1.34	−0.52 ± 0.09	1.63 ± 0.29	2.15 ± 0.53

Data are the mean ± SD (n = 3).

was associated with the generation of paramagnetic center, the Ti(III) sites, that is to say, the oxygen vacancy. The TGA profiles recorded from room temperature to 1000°C for the UV laser-irradiated TiO_2 powder showed no apparent weight gain of oxygen (data not shown). Table 2 shows the color differences between anatase TiO_2 powder, UV laser-irradiated TiO_2 powder, and UV laser-irradiated TiO_2 powder after the TGA. L^* is the lightness and dE is the total color difference. By the UV laser irradiation, the L^* decreased to 89.72 from 100.81 and dE increased to 8.64 from 3.09. This shows the color change from white to gray numerically. But after the TGA, the L^* and the dE returned to 98.96 and 2.15, respectively. It was confirmed that the grayed color of the TiO_2 powder disappeared and became white after the TGA. This shows that the color change of TiO_2 powder by the UV laser irradiation shown in Figure 5 was associated with the generation of Ti(III) sites, the oxygen vacancy. The extent of the generation of Ti(III) sites might be very little because the apparent oxygen weight gain was not observed by the TGA.

There are some reports about the phase conversion of TiO_2 from anatase to rutile by laser irradiation[9,11,12]. Lee et al.[9] reported that the crystal structure of TiO_2 developed a more rutile form after irradiation of pulsed laser at 355 nm using a roughly 70:30 anatase/rutile mixed TiO_2. Exarhos[11] also reported a similar phase change from anatase to rutile using anatase TiO_2 when irradiated with a 532 nm pulsed laser. Figure 6 is the XRD patterns of TiO_2 powder (A), 355 nm UV laser-irradiated TiO_2 powder (B), and authentic rutile TiO_2 powder (C). The TiO_2 used in this study was anatase and showed the typical anatase diffraction peak (2θ = 25.4). But, the laser-irradiated TiO_2 powder showed the rutile diffraction peak (2θ = 27.5) in addition to the anatase peak. This shows that phase change from anatase to rutile was caused by the UV laser irradiation and about half the amount of anatase TiO_2 was changed to rutile TiO_2. In this study, it was confirmed that when anatase TiO_2 was irradiated by the 355 nm UV laser, it became grayed by the generation of Ti(III) sites. And at the same time, it was converted to rutile TiO_2 partly by the high energy of the pulsed laser irradiation. Our results were in good agreement with previous reports[9,11,12].



2θ	Intensity (count)		
	(A)	(B)	(C)
25.4	322	163	–
27.5	–	127	304

Figure 6. XRD patterns of TiO_2 (A), UV laser-irradiated TiO_2 powder (B), and rutile TiO_2 (C).

Figure 7 is the representative photograph (×1000) of TiO_2 powder (A) or UV laser-irradiated TiO_2 powder (B) by the Zoom Stereo Microscope. As shown in Figure 5, it looked like that the UV laser-irradiated TiO_2 powder was grayed uniformly. However, when the TiO_2 powder was observed using the microscope, it was not grayed uniformly but there were many black particles locally in the UV laser-irradiated TiO_2 powder. On the other hand, there were no such black particles before irradiation. These black particles might be formed by the agglomeration of the grayed oxygen-defected TiO_2 and were associated with the visible change of the TiO_2 powder. These phenomena in concern with TiO_2 powder were similar to those with the film containing TiO_2. There are some reports that when TiO_2 was irradiated by a xenon lamp[13] or UV laser[14], color change of TiO_2 from white to blue/black was observed. But they only pointed out that the color change was associated with the formation of Ti(III) sites. Our results were also in agreement with their results. However, in this study, we found that the UV laser-irradiated TiO_2 powder was not grayed uniformly

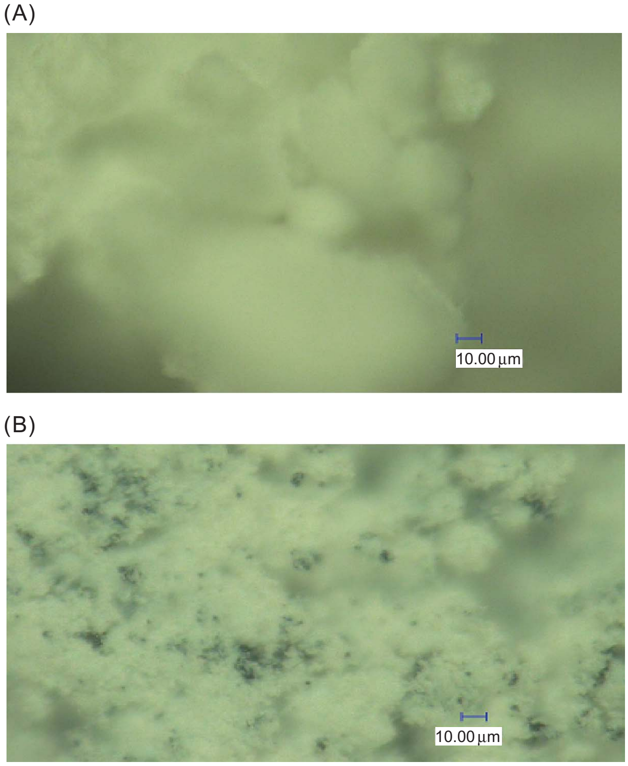


Figure 7. Representative photograph (×1000) of TiO_2 (A) and UV laser-treated TiO_2 (B) by zoom stereo microscope.

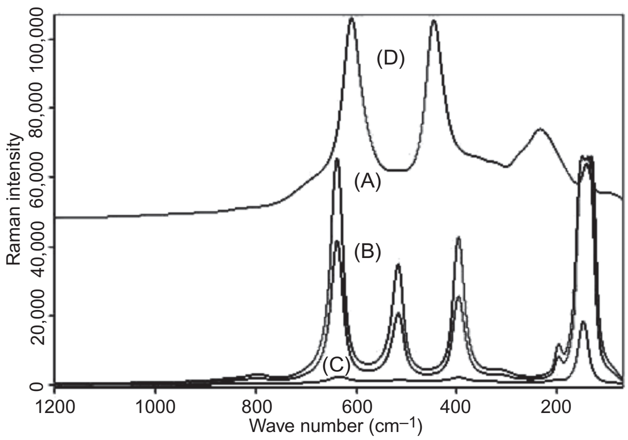


Figure 8. Raman spectra of anatase TiO_2 (A), white area (B) of the UV laser-irradiated TiO_2, and the black particles (C) shown in figure 7, and rutile TiO_2 (D).

but many black particles, which might be the agglomerates of the grayed oxygen-defected TiO_2, were formed locally in the TiO_2 powder and that those caused the color change from white to gray. There have been some reports about agglomeration or formation of nanonetwork of metal nanoparticles by pulsed laser or UV irradiation. Mafuné[15] reported that when gold nanocolloids were irradiated by UV pulse laser at 355 nm, coagulation of the gold nanoparticles was dramatically accelerated and that, in agglomeration of the gold nanoparticles, a number of nanoparticles aggregated without metallic contact between them. There were similar results reported with the gold nanoparticles using a 100-W high-pressure mercury lamp[16] and argon–ion laser at 488 nm[17]. Similar structure changes were reported with platinum nanoparticles by irradiation of UV pulse laser at 355 nm[18]. The mechanism of the black particle formation observed in this study was not clear now, but the pulsed laser with high energy might cause the size or geometry changes, for example, agglomeration, formation of nanonetwork, or fusion of nanoparticles.

XRD is a useful tool to study crystal lattice arrangement, and it was found that phase change from anatase to rutile occurred by UV laser irradiation. However, the UV laser-irradiated TiO_2 was not uniform as shown in Figure 7. We found that many black particles were formed in the grayed TiO_2 powder. The particles were so small that it was impossible to study the characteristic of the particles using XRD. So, dispersive Raman microscopy was performed to do microanalysis of the TiO_2. Figure 8 is Raman spectra of anatase TiO_2 powder (A), white area (B) of the UV laser-irradiated TiO_2 powder, and the black particles (C) shown in Figure 7. Height of each characteristic peak (396, 516, and 638 cm^{-1}) of anatase TiO_2 was about half of the anatase TiO_2 at the white area and became very small at the black particle. But, the characteristic peaks (234, 446, and 609 cm^{-1}) of rutile were not observed at the black particles. It was clear that phase change from anatase to rutile was caused by the UV laser irradiation from Figure 6, so that it was thought that the black particles formed in the UV laser-irradiated TiO_2 was rutile. Raman spectroscopy permits to analyze only molecule and structures but not isolated ions[10]. The black particles were the agglomerates of the grayed oxygen-defected TiO_2, Ti(III), so that those were not active to Raman spectroscopy. These findings about the black particles in the TiO_2 powder were in agreement with the result of the black particles in the film (Figure 4).

It was found that the film-coated tablets were printed utilizing the formation of the black particles by the agglomeration of the grayed oxygen-defected TiO_2 by the UV laser irradiation.

Conclusion

Film-coated tablets were printed by the UV laser printing machine utilizing color changes of the film containing TiO_2 by the UV laser irradiation.

In the case of the film containing TiO_2, the film showed a visible change in its color from white to gray by the UV laser irradiation. By Zoom Stereo Microscope, it was found that all of the area where the UV laser was irradiated was not grayed uniformly, but many black particles, whose diameter was about 2 μm, were observed at the colored part of the film.

When TiO_2 powder was irradiated by the UV laser, a visible change in its color from white to gray was observed similar to the case of the film containing TiO_2. The color change of TiO_2 by the UV laser irradiation was associated with the generation of Ti(III) sites, the oxygen vacancy of TiO_2. There were many black particles locally also in the UV laser-irradiated TiO_2 powder, and these black particles were associated with the visible change of the TiO_2.

It was found that the film-coated tablets were printed utilizing the formation of the black particles by the agglomeration of the grayed oxygen-defected TiO_2 by the UV laser irradiation.

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Declaration of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this paper.

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