



질소가 도핑된 이산화티탄 나노입자를 이용한 착색레진 미백

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Bleaching of stained resin using nitrogen doped-TiO₂ nanoparticles

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H₂O₂가 치아미백에 많이 사용되고 있다. 본 연구는 레이저 광조사 하에서 질소가 도핑된 이산화티탄 (N-doped TiO₂) 나노입자로 착색된 레진을 얼마나 미백시키는지를 평가한 것이다. 이를 위하여 시료를 줄-겔 방법으로 제조하고 광흡수도와 XRD를 평가하였다. 액상의 methylene blue와 분말입자를 함유한 젤을 이용하여 착색된 레진의 색변화를 측정하였다. 광조사를 위하여 파장이 다른 빛을 사용하였다. 그 결과 N-doped TiO₂는 보통의 TiO₂에 비하여 400 nm 이후에서 높은 흡수도를 보였고 N-doped TiO₂는 TiN 구조를 기반으로 새로운 루틸구조가 관찰되었다. 레이저가 조사되는 환경에서 methylene blue 용액과 착색된 레진은 3% H₂O₂를 함유한 N-TiO₂ 나노입자에 의해서 15% H₂O₂보다 더 큰 흡수도 감소와 색변화를 보였다.

색인단어 : 미백제, N-doped TiO₂, 흡수도, XRD, 색변화

Introduction

Due to the high expectation for clean and white teeth regardless of gender and generation, there have been many trials from Roman era using urine to recent using peroxide-based agents. Thus far, to satisfy diverse needs of the users, many tooth bleaching agents, mainly

peroxide-based, have been introduced and the resultant bleaching was mainly affected by the strength and treated time of agent regardless of products (1-3). To satisfy diverse needs of the users, many different bleaching agents are available now from OTC (over-the-counter) to specialist products.

There are many complicated causes of teeth

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Received: Aug. 26, 2019; Revised: Sep. 10, 2019; Accepted: Sep. 16, 2019.

discoloration, and they can be categorized into two factors: intrinsic and extrinsic (4-6). Of the factors, aging, pigments or metal ions in colored foods or drinks, and smoking are the prevalent sources of teeth discoloration. Generally colored compounds from these sources are adsorbed onto the tooth surface or absorbed into the subsurface and then present stain. Compounds adsorbed onto the tooth surface can be readily removed by routine tooth brushing. Abrasives in tooth paste easily detach the adsorbed compounds. However, stains by the absorbed compounds are not readily removed by tooth brushing if tooth is not fully wear out.

Bleaching (whitening) agents are the substance that makes the stained (discolored) teeth to be white. Also, they affect the color (shade) of resin composites (7, 8). Among them, peroxide-based bleaching agents (carbamide peroxide [$\text{CH}_6\text{N}_2\text{O}_3$] or hydrogen peroxide [H_2O_2]) at the concentration of 3-3.5% or over to 30-35% are the common options. Bleaching by peroxide is achieved through the formation of reactive free radicals. Stable peroxide becomes radicals by external heat or ultraviolet light (9,10). Free radicals penetrate into the tooth subsurface and decompose stains of long molecular size into short size. During the bleaching process by radicals, mineral and water loss occurs and then dehydrated tooth with shortened stains gradually looks white (11, 12).

Despite excellent bleaching capability of peroxide-based agents, it usually takes some weeks to get acceptable whitening if used with lower concentration. Higher concentration is good for reducing treatment time (less than one hour with 2-3 treatments), however, higher concentration can make sharp poking pains on teeth and some loss of minerals and water from the treated teeth (13, 14). Both in user and practitioner sides, short treatment time and less teeth damage with acceptable whiteness of teeth would be highly welcomed.

Titanium dioxide (TiO_2) induces photocatalytic reaction if interact with ultraviolet light (UV) (15-17). UV makes electrons in valence band transit to conduction band by leaving holes. Formed holes and moved electrons induce redox process and produce hydroxyl radicals. Formed radicals can effectively bleach stains in materials as oxygen-rich peroxide does. However, since UV induces carcinogenic problems, using in oral cavity is not recommended. To handle the problem, doped-titanium dioxide with gas or metal ions was suggested. According to diverse studies, doped-titanium dioxide showed high absorption of visible light and effective treatment of diverse bacteria and pollutants (15-17). The purpose of the present study was to evaluate if nitrogen (N)-doped TiO_2 nanoparticles (NPs) can bleach stains under laser irradiation as H_2O_2 does. In this study, composite resin was used as a test material prior to teeth for a preliminary test.

Materials and Methods

1. Synthesis of N-doped TiO_2 nanoparticles (NPs)

To synthesize N-doped TiO_2 NPs, commercial TiN was used. At first, 62 mg TiN was added into 30 mL of distilled water while magnetic stirring, then 6.0 mL of HCl (35%) was dropwisely added into the above solution while continuously stirring for 30 min. The final concentration of HCl is 2.0 M. The solution was then transferred to a Teflon-lined autoclave and heated for 8 h at 180°C . After cooling down to room temperature, the precipitate was collected, washed with distilled water and absolute alcohol several times, and then dried in a 80°C heat chamber for 24 h. All chemicals were analytical reagent grade, purchased from Sigma Aldrich (St. Louis, MO, USA), and used without additional purification.

2. Characterization and evaluation of NPs

Absorbance of NPs was measured using UV-VIS spectrophotometer (Jasco V-670, Jasco, Tokyo, Japan) by taking BaSO₄ as reference.

X-ray diffraction (XRD) patterns of NPs were obtained using an Ultima IV multipurpose XRD system (Rigaku, The woodland, TX, USA) at the 2θ angle between 20 and 80 degrees with a scanning speed of 0.1°/min.

For stained composite resin test, a dental composite resin (P60, 3M ESPE, St. Paul, MN, USA) of shade A3 was chosen and made a 1 mm thick disc using a metal mold. Specimens were light cured using a light-curing unit for 40 s and aged for 24 h at 37°C dry chamber. After 24 h, specimens were stored in a coffee-filled container for staining. For this, 1.6 g of coffee powder (Maxim Kanu, Dongsuh, Seoul, Korea) was mixed in 10 mL distilled water. Staining was continued for 1 week and the coffee was replaced every two days. After 1 week, carbomer gels were made by adding 1 g of carbomer 940 with 19 mL distilled water. Doped NPs was added in the gel to 1 wt% while stirring. After that, such made carbomer gel was pasted over the stained resin to 1-mm thick. Laser (405, 660 nm; LVI Technology Inc., Yongin, Korea; 50 mW/cm²) was irradiated on the pasted gel up to 3 h. Color of the stained composite resin before and after light irradiation (every 30 min) was measured using a spectrophotometer (CM3600d, Konica Minolta, Osaka, Japan) under the reflectance (%R) mode. To measure the color, the pasted gel over the resin was cleared and swiped using the wet cotton swab. The color difference was calculated as follows:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where ΔL^* , Δa^* , and Δb^* are the changes in L^* , a^* , and b^* respectively. Here, L^* represents the degree of grayness and corresponds to lightness. The parameter a^* represents the red (for + a^* value) - green (for - a^*

value) axis, whereas b^* is a parameter in the blue (for - b^* value) - yellow (for + b^* value) axis. For this study, seven different test conditions were adopted: ① gel+distilled water (DW); ② Gel + 3% H₂O₂; ③ Gel+15% H₂O₂; ④ Gel+N-TiO₂+405 nm laser; ⑤ Gel+N-TiO₂+3% H₂O₂+405 nm laser; ⑥ Gel+N-TiO₂+660 nm laser; ⑦ Gel+N-TiO₂+3% H₂O₂+660 nm laser.

4. Statistical analysis

The result of color difference was analyzed by one-way ANOVA followed by a Tukey's post-hoc test for multiple comparisons; p values <0.05 were considered significant.

Results

Figure 1 shows the tested powders for this study. TiN was used as a precursor for doping TiO₂. Unlike white TiO₂, N-TiO₂ has dark brown color similar to its precursor TiN.

Figure 2 shows the absorbance spectrum of TiN, TiO₂, N-TiO₂. Unlike TiO₂, doped N-TiO₂ showed high absorbance after 400 nm.

Figure 3 shows the XRD patterns of the tested samples. N-doped TiO₂ had well-formed crystalline nature. Over the TiN peaks, the Bragg diffraction peaks indexed as (110), (101), (111), (211), (220), (002), (311), (301), and (112) are correspond to tetragonal rutile TiO₂ (JCPDS, no. 21-1276).

Figure 4 and Table 1 show the color difference (ΔE^*) of stained resin by laser irradiation for 3 h (180 min). Initial color values (L^* , a^* , b^*) of specimen resins before stain were 60.75 ± 0.21 , -0.85 ± 0.07 , 6.87 ± 0.21 , respectively. After stain for 1 week, these values changed to 49.34 ± 0.76 , 1.63 ± 0.26 , 14.33 ± 0.55 , respectively. For bleaching test, color values of the stained resin became the initial values before treatments. During laser



Figure 1. The tested powders for this study.

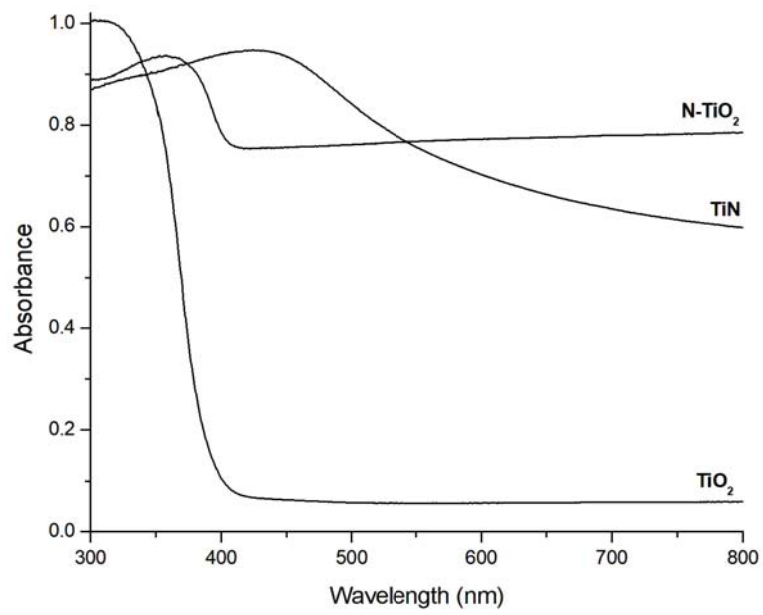


Figure 2. Absorbance spectrum of the tested powders.

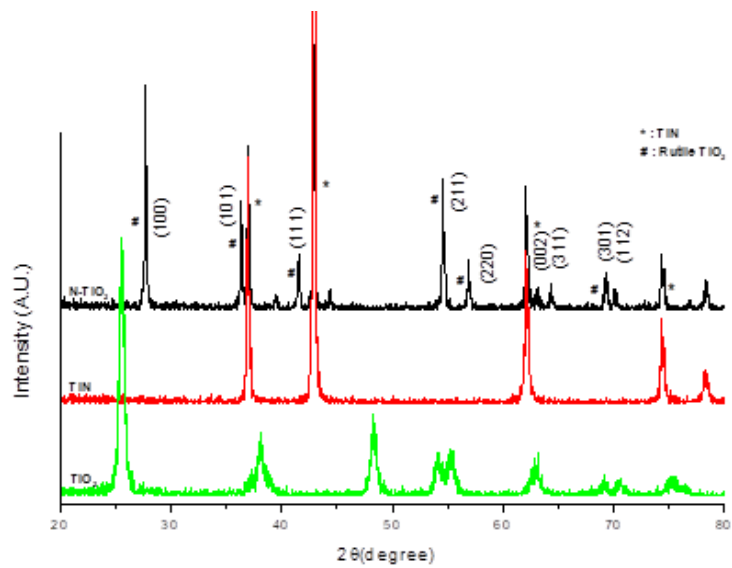


Figure 3. XRD patterns of the tested powders.

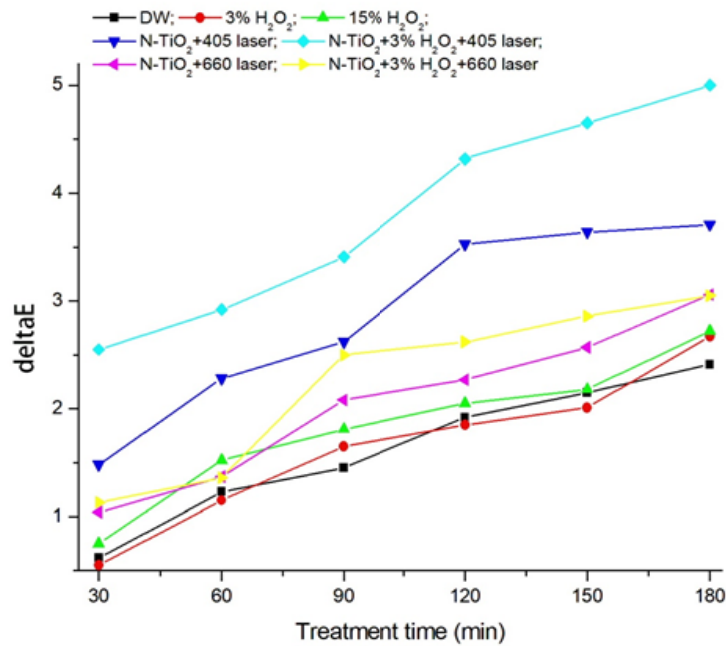


Figure 4. Color difference (ΔE^*) of the stained resins treated with different treatment conditions for 3 h.

Table 1. Different carbomer gel conditions used in the present study

Time (min)	Treatment condition						
	0 ^a	1 ^a	2 ^a	3 ^b	4 ^c	5 ^a	6 ^{ab}
30	0.62±0.10	0.55±0.11	0.75±0.15	1.48±0.31	2.55±0.40	1.04±0.19	1.13±0.20
60	1.23±0.21	1.15±0.16	1.52±0.24	2.29±0.22	2.92±0.74	1.36±0.31	1.37±0.15
90	1.45±0.13	1.65±0.23	1.81±0.16	2.62±0.33	3.41±0.50	2.08±0.13	2.50±0.41
120	1.92±0.15	1.85±0.09	2.05±0.18	3.53±0.14	4.32±0.31	2.27±0.26	2.62±0.42
150	2.15±0.20	2.01±0.19	2.18±0.11	3.64±0.12	4.70±0.37	2.57±0.16	2.86±0.23
180	2.41±0.39	2.67±0.16	2.72±0.10	3.71±0.10	5.00±0.28	3.05±0.51	3.06±0.18
p-value	$\alpha < 0.001$						

0: DW (distilled water); 1: 3% H₂O₂; 2: 15% H₂O₂; 3: N-TiO₂+405 nm laser; 4: N-TiO₂+3% H₂O₂+405 nm laser; 5: N-TiO₂+660 nm laser; 6: N-TiO₂+3% H₂O₂+660 nm laser

* Statistically significant difference is shown by superscript letters. Same letters are not significantly different ($p > 0.05$).

* On p-value, the letter α denotes color difference for different treatment condition.

irradiation, stained resins showed a linear color difference (R)0.94) regardless of incident light wavelength. Among the conditions, N-TiO₂+3% H₂O₂+405 nm laser showed the greatest (up to 5.0) and significant ($p < 0.001$) color difference (bleaching). Also, laser irradiated specimens showed higher color difference compared to that treated only with H₂O₂.

Discussion

Everybody wishes to have clean and white teeth. However, achieving and maintaining this wish is not easy owing to many daily obstacles and life styles. Tooth bleaching agents are materials that make this wish to be achieved easily and quickly with various effective

dental treatments. However, peroxide (H_2O_2)-based bleaching agents usually confront two issues depending on the concentration of H_2O_2 : long treatment time issue for low concentration agent; safety and oral damage issue for high concentration agent. Concerning teeth whitening, everybody wishes the bleaching to be achieved within short treatment time with minor soft tissue and teeth damage. The present study evaluated how N-doped TiO_2 NPs affects bleaching (whitening) if they are irradiated with visible light.

The basic mechanism that explains bleaching (whitening) of stained material is cleavage of long molecular chain that causes discoloration into short molecular chain by reactive oxygen radicals (4,6). Optically short molecular chain becomes colorless. Peroxide-based bleaching agents are the source of radicals. To break H_2O_2 for forming radicals, one of two different energies are needed: heat or light. Heat breaks molecular bond of H_2O_2 which has weak O-O bond. Heat can boost radical formations, but it simultaneously produces unpleasant feeling on teeth and can cause pulp damage if temperature rises by heat over 5°C for long time. UV light can break H_2O_2 because photon energy of UV exceeds the molecular binding energy of H_2O_2 . However, owing to high photon energy, it can generate carcinogenetic damage on tissue. Hydrogen peroxide can also be broken down via photocatalytic effect of TiO_2 with an aid of light. To initiate photocatalytic reaction from TiO_2 , at least 3.2 eV or over photon energy is required to make electrons in valence band to transit to conduction band by leaving holes in valence band. To supply this amount photon energy, UV light is required and in that case biohazard issue is inevitable.

Doping (gas or metal) ions into TiO_2 as an impurity can lower photocatalytic activation energy from UV to visible light owing to narrowed energy band gap (18-20). One advantage using visible light as a light source is that it is free from biohazard issue if it is not operated

at high power. In the present study, N- TiO_2 has much higher absorbance than TiO_2 after 400 nm (Figure 2). Compared to its precursor TiN, N- TiO_2 does not have decreasing absorbance after 400 nm and this means that any other visible light can be absorbed in N- TiO_2 NPs. For the present study, lasers of two different wavelengths have used: 405 and 660 nm with same light intensity.

Composite resins were immersed in coffee for 1 week to uniformly stain resin (21, 22). The stained resins have a coffee-adsorbed layer on their surface. To bleach the stained resins, carbomer gel which containing 1 wt% NPs without or with 3% H_2O_2 was pasted on the resin surface and then treated laser for 3 h (180 min). In the present study, as treated time increased, color difference by bleaching linearly increased. 405 and 660 nm laser treated specimens showed 1.36-1.87 and 1.12-1.15 times, respectively, higher color change (bleaching) compared to those treated only with 3 or 15% H_2O_2 after 3 h. In the laser treated specimens, addition of 3% H_2O_2 enhanced color change to 1.22-1.68 and 1.00-1.38 times, respectively, compared to those of no H_2O_2 specimens. The results here indicate that visible lasers (light) surely bleaching stain in conjunction with N-doped NPs, and in two lasers, shorter wavelength yields higher color difference (bleaching) than that by longer wavelength. Actually, from the relation E (photon energy) = $h\nu = hc/\lambda$, where h and λ are Planck's constant and wavelength of the irradiated light, respectively, light of shorter wavelength is better than that of longer wavelength owing to higher photon energy of the light of shorter wavelength.

Conclusion

Within the limitations of the present study, the following conclusions could be reached:

1. N- TiO_2 NPs showed the greatest color difference (ΔE^* : up to 5.0) if combined with 3% H_2O_2 and 405 nm

laser irradiation for 3 h. However, 15% H₂O₂ case showed only 2.7.

2. Two lasers (405 and 660 nm) achieved higher color difference compared to that by 15% H₂O₂. Between two lasers, 405 nm laser achieved higher bleaching (color difference) than that by 660 nm laser.

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Bleaching of stained resin using nitrogen doped-TiO₂ nanoparticles

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There has been increasing use of the H₂O₂-based teeth bleaching agents. The purpose of this study was to evaluate the bleaching effectiveness of the laser irradiation combined with nitrogen doped-TiO₂ nanoparticles (NPs) on the stained resin. Nitrogen (N) doped-TiO₂ NPs were prepared under sol-gel method. Light absorbance, X-ray diffraction patterns of NPs, and bleaching of methylene blue and stained resins were evaluated. For bleaching of stained resin, NPs-containing gel was used. For irradiation, light of two different wavelengths was used. Unlike TiO₂, N-TiO₂ showed high absorbance after 400 nm. N-TiO₂, which have used TiN as a precursor, showed a new rutile phase at the TiN structure. For methylene blue solution, N-TiO₂ with 3% H₂O₂ resulted in the greatest absorbance decrease after laser irradiation regardless of wavelength. For stained resin test, N-TiO₂ with 3% H₂O₂ resulted in the greatest color difference after laser irradiation, followed by group that used N-TiO₂ without 3% H₂O₂.

Key Words : Bleaching agent, N-doped TiO₂, Absorbance, XRD, Color difference
