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Visible-Photocatalytic Performance of TiO₂ Particles Simply Achieved by Surface Nitridation and Application for Self-Cleaning Glass Fabricated by Electrophoretic Deposition (EPD) Process

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Corresponding Author:	chenning ZHANG, Ph.D National Institute for Materials Science Tsukuba, Ibaraki JAPAN
First Author:	chenning ZHANG, Ph.D
Order of Authors:	chenning ZHANG, Ph.D Tetsuo Uchikoshi Takaya Akashi
Abstract:	Originally, surface-nitridated TiO ₂ particles were prepared by urea decomposition under hydrothermal treatment. After the surface nitridation, the absorption onset was extended to the visible region due to narrowed band gap of ~3.10 eV comparable to that of ~3.28 eV for pristine TiO ₂ . Due to narrowed band gap, the surface-nitridated TiO ₂ distinguishably had the visible photocatalytic ability under 440 nm. The visible-photocatalytic nitridated TiO ₂ particles was successfully fabricated as dense coatings with controllable transparency by electrophoretic deposition (EPD) process.
Suggested Reviewers:	chika Takai-Yamashita Associate Professor, Gifu University c_takai@gifu-u.ac.jp Kento Ishii Assistant Professor, Nagoya Institute of Technology ishii.kento@nitech.ac.jp Yuji Masubuchi Associate Professor, Hokkaido University yuji-mas@eng.hokudai.ac.jp



NATIONAL INSTITUTE FOR MATERIALS SCIENCE

Materials Processing Unit

1-2-1, Sengen, TSUKUBA, IBARAKI, 305-0047, JAPAN

Dear Editor,

We would like to submit the enclosed manuscript entitled “**Visible-Photocatalytic Performance of TiO₂ Particles Simply Achieved by Surface Nitridation and Application for Self-Cleaning Glass Fabricated by Electrophoretic Deposition (EPD) Process**” to *Materials Letters*. This manuscript includes 4 figures and about 1945 words.

In this work, surface-nitridated TiO₂ particles were prepared by urea decomposition under hydrothermal treatment. After the surface nitridation, the absorption onset of nitridated TiO₂ was extended to the visible region due to narrowed band gap of ~3.10 eV comparable to that of ~3.28 eV for pristine TiO₂. The surface-nitridated TiO₂ distinguishably had the visible photocatalytic ability under 440 nm, by comparing with that of untreated TiO₂. The visible-photocatalytic nitridated TiO₂ particles was successfully used to fabricate dense coatings with controllable transparency by electrophoretic deposition (EPD) process, which is expected to be potentially used as self-cleaning glass with enhanced photocatalytic efficiency in UV-visible wavelength region.

On behalf of my co-authors, I certify that this work is an original research that has neither been published previously nor is under any considerations for publication in another journal at the time of submission by any of the authors, in whole or in part.

We deeply appreciate your consideration for our manuscript. We look forward to receiving the comments from reviewers.

Best regards.

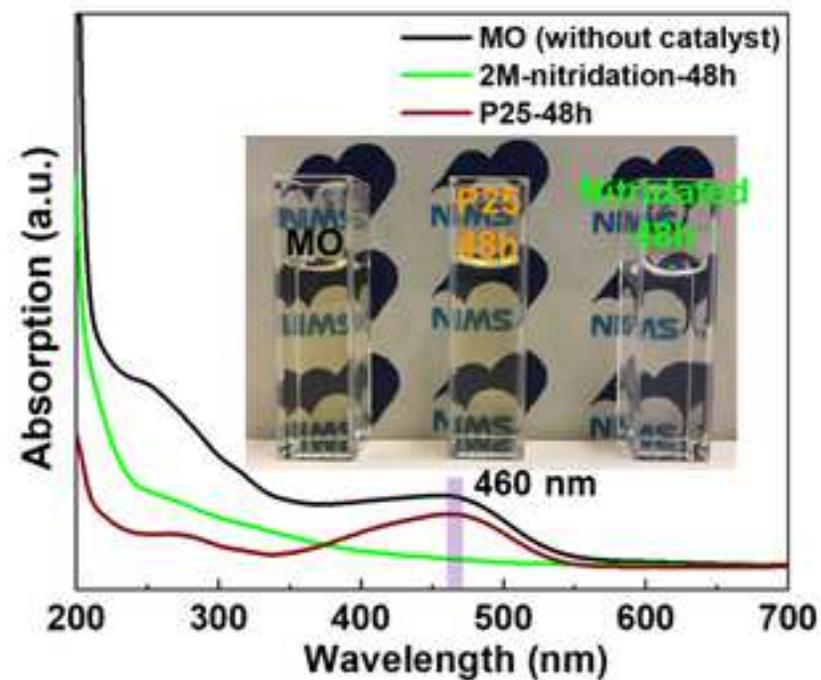
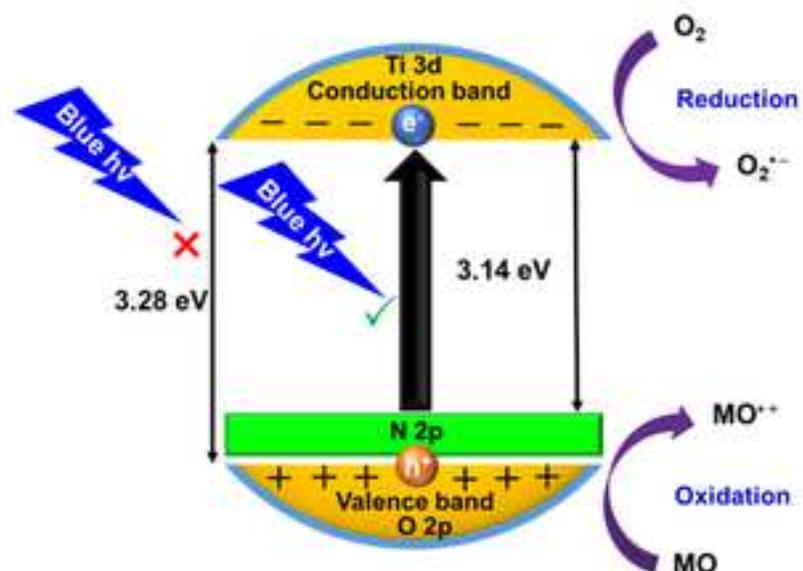
Yours sincerely.

Dr. Chenning ZHANG

Research Center for Electronic and Optical Materials

National Institute for Materials Science (NIMS), Japan

E-mail: zhang.chenning@nims.go.jp



After surface nitridation upon TiO₂ particles, the band gap became narrowed from ~3.28 to ~3.10 eV, resulting to extend the absorption onset to visible region of blue light and therefore causing visible photocatalytic ability under 440 nm illumination.

Highlights

- Surface-nitridated TiO₂ particles were originally prepared by hydrothermal treatment
- After nitridation, band gap of TiO₂ became narrowed responsible for visible light
- Surface-nitridated TiO₂ had a visible photocatalytic ability under 440 nm
- Nitridated TiO₂ particles is expected to be used as self-cleaning glass by EPD

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Visible-Photocatalytic Performance of TiO₂ Particles Simply Achieved by Surface Nitridation and Application for Self-Cleaning Glass Fabricated by Electrophoretic Deposition (EPD) Process

Chenning Zhang,^{a, b, *} Tetsuo Uchikoshi,^{a, *} Takaya Akashi,^b

^a Research Center for Electronic and Optical Materials, National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan

^b Department of Chemical Science and Technology, Hosei University, Koganei, Tokyo 184-8584, Japan

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*** Corresponding author:**

Dr. Chenning ZHANG

E-mail: zhang.chenning@nims.go.jp

Prof. Dr. Tetsuo UCHIKOSHI

E-mail: UCHIKOSHI.Tetsuo@nims.go.jp

Abstract

Originally, surface-nitridated TiO₂ particles were prepared by urea decomposition under hydrothermal treatment. After the surface nitridation, the absorption onset was extended to the visible region due to narrowed band gap of ~3.10 eV comparable to that of ~3.28 eV for pristine TiO₂. Due to narrowed band gap, the surface-nitridated TiO₂ distinguishably had the visible photocatalytic ability under 440 nm. The visible-photocatalytic nitridated TiO₂ particles was successfully fabricated as dense coatings with controllable transparency by electrophoretic deposition (EPD) process.

1. Introduction

Nano-sized particle of P25 TiO₂ (commercial AEROXIDE® P25 TiO₂ powder, anatase≈80 wt.% and rutile≈20 wt.%) is one of the promising photocatalysts because of its relatively high levels of activity in many photocatalytic reaction systems [1]. Despite this, P25 TiO₂ has poor efficiency in the visible region of the solar spectrum due to its wide band gap of ~3.2 eV, which makes it typically requires exposure of ultraviolet (UV) light for photocatalytic reactions, therefore seriously limiting the photocatalytic application of P25 TiO₂.

It has been reported that the band gap of the synthesized TiO₂ was successfully narrowed by doping N into the lattice of TiO₂, which effectively increased its photocatalytic activity induced by visible light [2]. However, the doping N into the lattice of TiO₂ needs high synthesis temperature, special equipment, and complicated process, therefore, it is necessary to conceive a facial strategy for narrowing the band gap of TiO₂. It has been known that urea starts to decompose and produce ammonium as nitrogen by hydrolysis reaction when temperature is more than ~130 °C [3], and hydrothermal treatment provides a condition of high pressure for reaction [4].

In this work, it is the first time to successfully modify particles of commercial P25 TiO₂ by surface nitridation with using urea decomposition under hydrothermal treatment. The mechanism of nitridation was systemically investigated and the effect of nitridation on visible-photocatalytic performance was clearly elucidated in detail. The visible-photocatalytic coatings were effectively fabricated by EPD process as an application of the surface-nitridated P25 TiO₂.

2. Experimental

Commercial AEROXIDE® P25 TiO₂ powder (Nippon Aerosil, Ltd., Tokyo, Japan) was dispersed in 50 mL of distilled water with dissolving urea (Co(NH₂)₂, Kanto Chemical Co., Inc. Tokyo, Japan) under continuous ultrasonic dispersion. The prepared P25 TiO₂ suspension was put into a Teflon-lined autoclave under hydrothermal treatment at 180 °C for 24 h for achieving particle surface nitridation. The decomposition of urea occurred above ~130°C temperature and the decomposed product of NH₄⁺ ions in the water as nitrogen source were adsorbed around the surface of the P25 TiO₂ particles, then making the surface nitridation under the condition of high pressure during the process of hydrothermal treatment. After the hydrothermal treatment, the product was washed by distill water for four times and dried at 60 °C for 24h, finally followed by powder collection.

Photocatalytic performance was evaluated by bleaching 20 μM of methyl orange (MO) (C₁₄H₁₄N₃NaO₃S, reagent grade, Wako Pure Chemical Industries, Ltd, Osaka, Japan) solution mixing with the pristine and surface-nitridated P25 TiO₂ powders inside a temperature-controlled chamber (SH-222, Espec Corp., Osaka, Japan) used as a dark box at a constant temperature of 25°C. The blue light was generated by a 300 W Xe light source (MAX-303, Asahi Spectra Co., Ltd., Tokyo, Japan) equipped with optical filters.

Phase identification was performed by X-ray diffraction (XRD) on X-ray diffractometer (model RINT 2200, Rigaku Corp., Tokyo, Japan). Observations for particle morphology and coating microstructure were performed by field-emission scanning electron microscopy (FE-SEM) (model S-4800, Hitachi, Ltd., Tokyo, Japan). Element mapping was detected by energy dispersive X-ray (EDX) spectrometer (model EDAX Apollo XL, EDAX Inc., Mahwah, NJ, USA). Ultraviolet-visible (UV-vis) spectra was made on Jasco V-570 spectrophotometer (Jasco Corp., Hachioji, Tokyo, Japan) after baseline calibration. The thickness of the coating fabricated by the EPD process was measured by constant pressure thickness gauge (PG-20J, Teclock Co., Ltd. Nagano, Japan).

3. Results and discussion

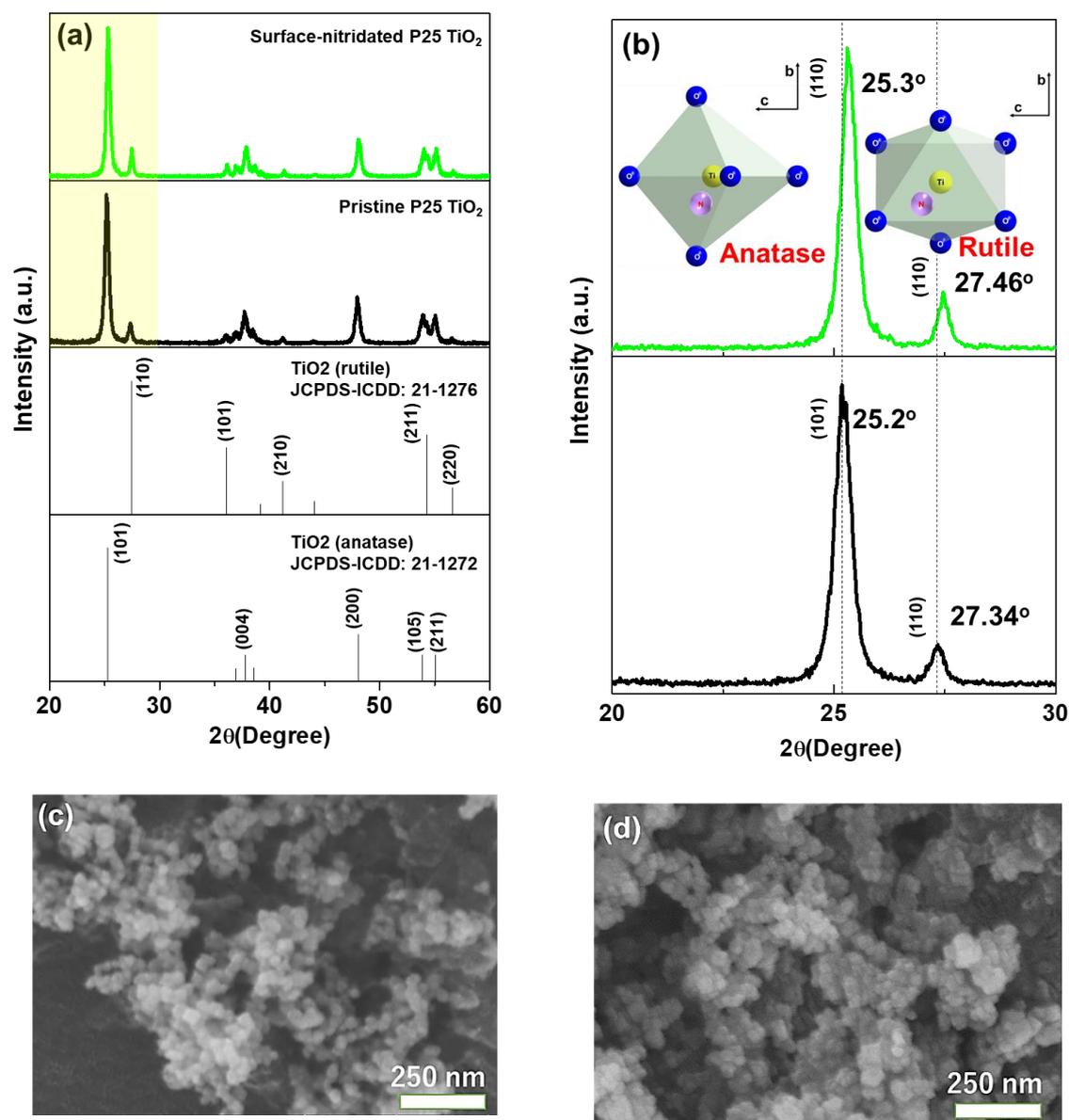
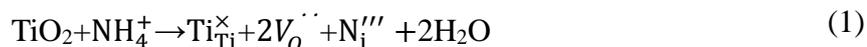


Fig. 1 XRD patterns of (a) P25 TiO₂ powders before and after surface nitridation, (b) local region in 2Theta range of 20–30°, and micrographs of morphologies of (c) pristine and (d)

1 surface-nitridated P25 TiO₂ particles, respectively. The insets in (b) are interstitial N doping in
 2 the lattices of anatase-and rutile-TiO₂, respectively.
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 5 The influence of the surface nitridation on phase composition was investigated in the XRD
 6 patterns of the TiO₂ P25 powders before and after surface nitridation, as exhibited in Fig. 1a.
 7 By identification, the phase composition of P25 TiO₂ is mixture of anatase and rutile, in which
 8 the anatase fraction was estimated as ~82.5 wt.% from the integrated intensity of the anatase
 9 (101) diffraction peak, according to the equation [5]. After the surface nitridation, no any
 10 obvious change was found on the anatase fraction of ~82.7 wt.%, indicating that the phase
 11 composition of P25 TiO₂ was almost invariable after the surface nitridation at 180°C in this
 12 work. Fig. 1b shows the XRD patterns of pristine and surface-nitridated P25 TiO₂ powders in a
 13 local region of 20–30°. By comparing with the XRD patterns of the P25 TiO₂ powders before
 14 and after surface nitridation, the diffraction peak of anatase (101) and rutile (110) was found to
 15 be slightly shifted towards high angle by 0.1° and 0.14°, respectively. Moreover, after the
 16 surface nitridation, the axes of *a* and *c*, and unit cell volume of *v* all became small
 17 (*a*=3.78982→3.78125 Å, *c*=9.51346→9.49348 Å, and *v*=136.64→135.74 Å³), therefore
 18 reasonably deducing that N ions did not substitute for O ions in the lattice of TiO₂ after the
 19 surface nitridation, instead, came into the interstitial site of lattice, as a result, causing oxygen
 20 defects in the lattice, as below:
 21



23 where $\text{Ti}_{\text{Ti}}^{\times}$ denotes the Ti ion at Ti site, $V_{\text{O}}^{\cdot\cdot}$ is oxygen defect, and $\text{N}_i^{\prime\prime\prime}$ is N at interstitial site,
 24 and symbols of \cdot , \times , and \prime are the Kröger-Vink notations for net charge +1, the zero net charge,
 25 and net charge -1, respectively [6], as shown in the insets of interstitial N doping in the lattices
 26 of anatase-and rutile-TiO₂ in Fig. 1b. Similar reports concerning lattice shrinkage caused by the
 27 formation of oxygen defects are also found in other literatures [7]. Figures 1c and 1d
 28 demonstrate the morphology micrographs of the pristine and surface-nitridated P25 TiO₂
 29 particles, respectively. It is comparably distinguished that no any obvious changes in particle
 30 morphology (particle size≈~25 nm) after hydrothermal treatment. Thus, it is more accurate to
 31 confirm the contribution from the surface nitridation on photocatalytic property.
 32

33 UV-vis spectra of the P25 TiO₂ powders before and after the surface nitridation and
 34 calculated band-gap energies of these samples are shown in Figs. 2a and 2b, respectively.
 35 Comparably, the absorption onset of the P25 TiO₂ powder extended to visible region after the
 36 surface nitridation. The band-gap energies (E_g) of the pristine and surface nitridated P25 TiO₂
 37 powders were calculated following the equations [8]. Before the surface nitridation, the
 38 calculated band-gap energy of P25 TiO₂ is ~3.28 eV, however, after the nitridation, that became
 39 narrowed to ~3.14 eV. The narrowed E_g provides an evidence that the nitridation was
 40 effectively performed after the hydrothermal treatment in this work.
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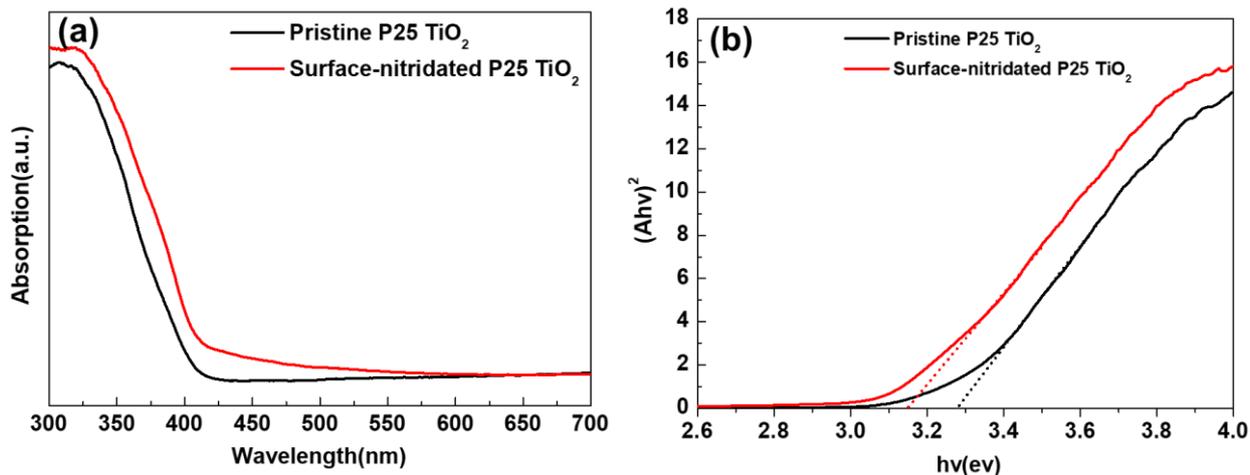


Fig. 2 (a) UV-vis spectra of the pristine and surface-nitridated P25 TiO₂ powders and (b) their calculated band-gap energies.

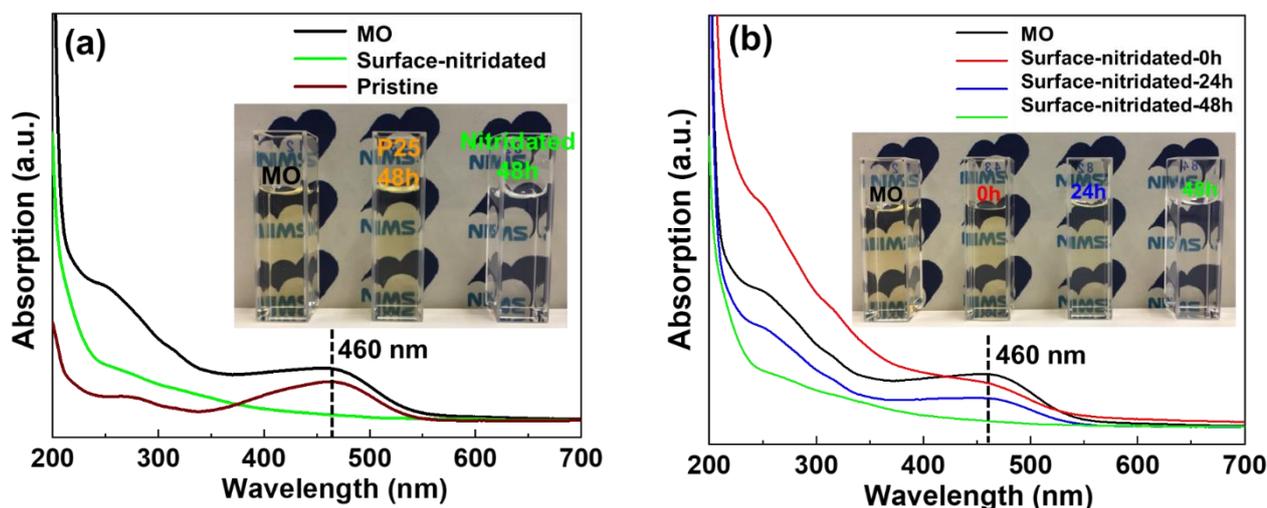


Fig. 3 UV-vis spectra of the MO solutions after photocatalytic reaction (a) with mixing the P25 TiO₂ powders before and after the surface nitridation under 440 nm irradiation for 48 h and (b) with mixing the surface nitridated powders under 440 nm irradiation for 0–48 h. The insets in (a) and (b) are the photographs of MO solutions after the photocatalytic reaction. The absorption spectra of the MO solution without any catalyst are used as reference herein.

As seen in Fig. 3a, after the irradiation, the intensity of absorption peak at ~460 nm became slightly decreased for the pristine P25 TiO₂, but became seriously weakened for the surface-nitridated one, suggesting that the photocatalytic performance under 440 nm irradiation was significantly improved after the surface nitridation, due to the narrowed band gap from ~3.28 eV to ~3.14 eV responsible for extending the absorption region to 440 nm. The quite difference in the color of bleached MO solution is shown in the inset of Fig. 3a. The reason for visible-photocatalytic property after the surface nitridation upon P25 TiO₂ is explained as that when N

incorporated into the lattice of anatase-and rutile-TiO₂ as intensital doping after the surface nitridation upon P25 TiO₂, the N 2*p* band above O 2*p* valence band formed a new mid-gap energy state and eventually narrowed the band gap of TiO₂ P25 and shifted the optical absorption to visible light region. For the MO solution with mixing the surface nitridated P25 TiO₂ powders, the intensity of absorption peak at ~460 nm became weak with 440 nm irradiation time from 0 h to 48 h, as shown in Fig. 3b. In particularly, after 48 h irradiation, the absorption peak became almost flat, suggesting the almost MO molecules were decomposed by the photocatalytic reaction, which is clearly demonstrated by the color variation of MO solutions in the inset of Fig. 3b. According to the (L–H) model [9], when initial concentration is very diluted (20 μM in this experiment), reaction-rate constant was calculated as ~5.60×10⁻⁶ s⁻¹ for the surface nitridated P25 TiO₂ powders under 440 nm irradiation.

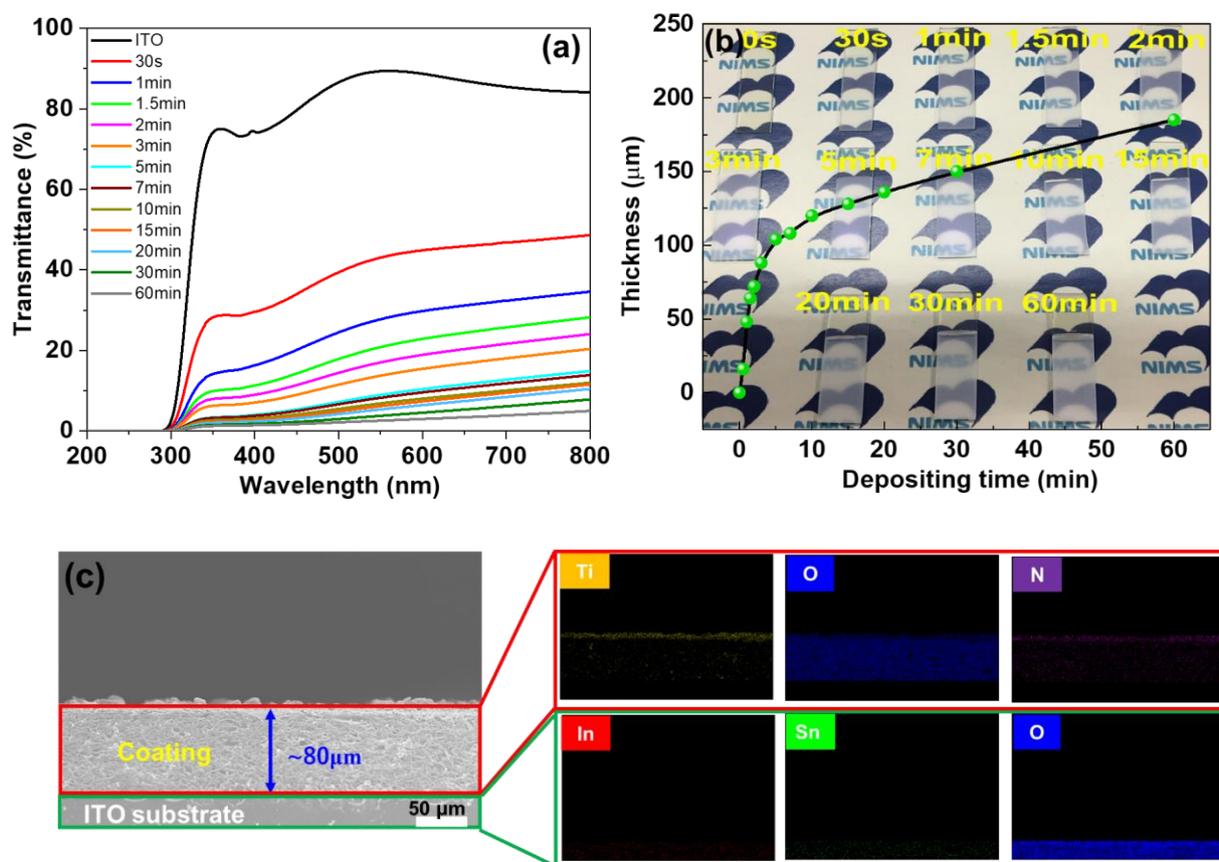


Fig. 4 (a) UV-vis spectra of transmittance for the coatings of surface nitridated P25 TiO₂ powders deposited by the EPD process at various depositing time of 0s–60min, (b) thickness of the coating as a function of depositing time and their appearances, and (c) FE-SEM image of cross-section for the coating fabricated by the EPD process under 10 V at 3 min depositing time with its EDX element mapping.

Fig. 4 exhibits (a) the transmittance in UV-vis spectra for the coatings of surface nitridated

1 P25 TiO₂ deposited onto the surface of ITO glass by the EPD process at various depositing time
2 of 0s–60min, (b) the relationship between coating thickness and depositing time, and (c) cross-
3 section of the deposited coating with its EDX element mapping. The variation in the
4 transmittances of coatings fabricated by the EPD process as a function of depositing time is
5 obvious and the fabricated coating (thickness as ~80 μm) is dense with component elements.
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9 **4. Conclusions**

10 Commercial P25 TiO₂ particles were surface-nitridated by urea decomposition under
11 hydrothermal treatment. After the surface nitridation, the absorption onset was extended to the
12 visible region. The narrowed band gap played a role in photocatalytic performance under visible
13 irradiation. Visible-photocatalytic coatings with controllable transparency were successfully
14 fabricated by EPD process.
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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: