Effects of Calcination Temperature on the Phase Composition, Photocatalytic Degradation, and Virucidal Activities of TiO₂ Nanoparticles

Min Gu Kim, Jeong Min Kang, Ji Eun Lee, Kang Seok Kim, Kwang Ho Kim, Min Cho,* and Seung Geol Lee*  

Cite This: ACS Omega 2021, 6, 10668−10678

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: The application of TiO₂ nanoparticles in the photocatalytic treatment of chemically or biologically contaminated water is an attractive, albeit unoptimized, method for environmental remediation. Here, TiO₂ nanoparticles with mixed brookite/rutile phases were synthesized and calcined at 300−1100 °C to investigate trends in photocatalytic performance. The crystallinity, crystallite size, and particle size of the calcined materials increased with calcination temperature, while the specific surface area declined significantly. The TiO₂ phase composition varied: at 300 °C, mixed brookite/rutile phases were observed, whereas a brookite-to-anatase phase transformation occurred above 500 °C, reaching complete conversion at 700 °C. Above 700 °C, the anatase-to-rutile phase transformation began, with pure rutile attained at 1100 °C. The optical band gaps of the calcined TiO₂ nanoparticles decreased with rising calcination temperature. The mixed anatase/rutile phase TiO₂ nanoparticles calcined at 700 °C performed best in the photocatalytic degradation of methylene blue owing to the synergistic effect of the crystallinity and phase structure. The photocatalytic virus inactivation test demonstrated excellent performance against the MS2 bacteriophage, murine norovirus, and influenza virus. Therefore, the mixed anatase/rutile phase TiO₂ nanoparticles calcined at 700 °C may be considered as potential candidates for environmental applications, such as water purification and virus inactivation.

1. INTRODUCTION

Although industrial production is critical to our world economy, the wastewaters generated during various production processes can result in serious water pollution. Other sources of fouled water can be traced to biocontaminants such as viruses and bacteria.¹,² To solve these growing threats to health and safety, the development of semiconductor-based photocatalysts that can effectively degrade organic or biological pollutants has been intensively studied in recent years.³−⁸ Among these photocatalysts, titanium dioxide (TiO₂) nanoparticles are fascinating materials with the desirable properties of chemical stability, nontoxicity, high photoreactivity, corrosion resistance, and cost-effectiveness.⁹−¹² TiO₂ naturally occurs in three distinct crystalline phases with different physical and chemical properties: brookite (orthorhombic crystal structure), anatase (tetragonal crystal structure), and rutile (tetragonal crystal structure).¹³,¹⁴ Under ambient conditions, bulk rutile is thermodynamically stable, whereas anatase and brookite are thermodynamically metastable.¹⁵ Thus, these phases can be accessed through thermally driven phase transformations, as may occur during calcination. Among the three phases, anatase and rutile are widely used for photocatalytic applications because of their facile synthesis.¹⁶ In contrast, brookite has been rarely investigated as a photocatalyst because it is not readily accessible in its pure form.¹⁷−¹⁹ However, it has been reported that the photocatalytic performance of brookite is superior to those of anatase and rutile.²⁰,²¹

Generally, the photocatalytic activity of TiO₂ is affected by its phase structure, crystallite size, specific surface area, and pore structure.²²−²⁸ Although rutile has a smaller band gap (3.0 eV) than anatase (3.2 eV), its photocatalytic activity is inferior to that of anatase because rutile exhibits a faster electron (e⁻) and hole (h⁺) recombination rate, larger grain size, and smaller specific surface area.²⁹−³² The lifetimes of electrons and holes generated upon photon absorption are
longer for anatase than rutile, enhancing the surface chemical reaction rate of the photoexcited species in anatase. Although anatase has several advantages as a photocatalyst, its performance is limited by its fast e−/h+ recombination rate.

Several researchers have shown that phasic mixtures of TiO2 exhibit substantially higher photocatalytic performance than single-phase TiO2. The different band alignments of mixed TiO2 phases can facilitate charge transfer at the interface. This enhances e−/h+ separation and reduces e−/h+ recombination.16,33–35 A well-known example is Degussa P25, a widely used commercial TiO2 photocatalyst containing 75% anatase and 25% rutile phases.36 Upon irradiation of P25 with UV light, photoexcited electrons from the anatase phase are transferred to the rutile phase, which has a lower conduction band energy, thus inhibiting the recombination of electrons and holes.37 However, the mixing ratios of the different TiO2 phases must still be explored to optimize photocatalytic performance.38–40

In this study, we investigate the effects of calcination temperature on the particle and crystallite sizes, phase transformations, and photocatalytic performance of as-prepared TiO2 nanoparticles. The samples before and after calcination were characterized using X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) specific surface area and Barrett–Joyner–Halenda (BJH) pore size analyses, field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), and UV−vis spectrophotometry. To evaluate photocatalytic performance as a function of catalyst calcination temperature, the degradation of methylene blue dye as an organic pollutant surrogate was tested with TiO2 in aqueous solution. Finally, the photocatalytic virus inactivation capabilities of the catalysts were estimated against the MS2 bacteriophage, murine norovirus, and influenza virus using a TiO2/cotton fabric system.

2. EXPERIMENTAL METHODS

2.1. Materials. Titanium tetrachloride (TiCl4, 99%), nitric acid (HNO3, 60%), and methylene blue were purchased from Junsei Chemical Co. Ltd., Japan. Sodium hydroxide pellets (NaOH, 98%) were obtained from Dae-Jung Chemicals Ltd., South Korea. Poly(ethylene glycol) (PEG) with a molecular mass of 600 was purchased from Merck, Germany. Commercially bleached cotton fabric was employed in this study. All chemicals were of analytical grade and used as received without further purification.

2.2. Synthesis Process. TiCl4 was used as a starting material to prepare TiO2 powder. A stock solution of TiOCl2 (4.0 M in Ti4+) was prepared by the careful dropwise addition of aqueous HNO3 (1.0 M) into vigorously stirred TiCl4 at 0 °C. To prepare TiO2, the stock solution was diluted with aqueous HNO3 (5.0 M) and heated at 80 °C for 15 h. After cooling to room temperature, the pH of the solution was adjusted to pH 7 by adding NaOH solution (1.0 M). The white precipitates were collected on a membrane filter and washed, first with dilute HNO3 solution (1.0 M) to eliminate titanium hydroxide and then with distilled water. After drying at 100 °C, samples were calcined at 300, 500, 700, 900, and 1100 °C (heating rate of 9 °C/min) for 2 h.

2.3. Characterization of TiO2 Photocatalysts. The phase compositions of the synthesized TiO2 nanoparticles were identified using a Philips X’pert 3 X-ray diffractometer (Eindhoven, Netherlands) with Cu Kα radiation and an accelerating voltage and current of 40 kV and 30 mA, respectively. The 2θ scanning range was 20–80° and the step size was 0.01°. The crystallite sizes of the anatase, brookite, and rutile phases were estimated using Scherrer’s equation (\( D = \frac{K\lambda}{\beta \cos \theta} \)), where \( K = 0.93, \lambda = 0.154059 \text{ nm}, \beta = \text{ full width at half-maximum (FWHM) in radians}, \) and \( \theta = \text{ the Bragg angle}. \)41 The characteristic peaks of the phases (anatase (101) peak at 2θ = 25.3°, brookite (121) peak at 2θ = 30.8°, and rutile (110) peak at 2θ = 27.5°) were used to calculate the crystallite sizes in the samples.42,43 The weight fraction of each phase was obtained using the following eq 141,43

\[
W_A = \frac{K_A A_A}{K_A A_A + A_R + K_B A_B}, \quad W_B = \frac{K_B A_B}{K_A A_A + A_R + K_B A_B},
\]

and

\[
W_R = \frac{A_R}{K_A A_A + A_R + K_B A_B}
\]

where \( W_A, W_B, \) and \( W_R \) represent the weight fractions of the anatase, brookite, and rutile phases of TiO2, respectively. \( A_A, A_B, \) and \( A_R \) are the integrated intensities of the anatase (101), brookite (121), and rutile (110) peaks of the TiO2 nanoparticles, respectively. The terms \( K_A, K_B, \) and \( K_R \) are coefficients with values of 0.886 and 2.721, respectively.41,43 Raman analysis was conducted by a Raman spectrometer (JASCO Co., NRS-5100, Tokyo, Japan) at room temperature with a solid-state laser at 532 nm with a notch filter grating of 1800 g/mm.

The BJH pore size distributions and BET surface areas were obtained from nitrogen adsorption−desorption isotherms (Quantachrome, Autosorb-iQ & Quadrasorb SI, Boynton Beach, FL). The surface morphologies of the TiO2 nanoparticles were analyzed by FESEM using a Carl Zeiss SUPRA 40VP instrument (Oberkochen, Germany). The microstructures of the TiO2 nanoparticles were observed by HR-TEM (FEI Co., TALOS F200X, Hillsboro, OR). The TiO2 nanoparticles were dispersed in ethanol and then mounted on a copper grid with formvar. The particle size of each sample was also measured by the particle size distribution histogram of HR-TEM.

2.4. Photocatalytic Degradation Tests. The photocatalytic performance of the calcined TiO2 nanoparticles was evaluated by decomposing methylene blue (MB). Calcined TiO2 nanoparticles (0.5 wt %) were added to aqueous MB solution (20 ppm, 20 mL, pH 7), and the suspension was ultrasonicated and stirred for 60 min under dark conditions. The suspension was then irradiated under UV light (8 W × 4 lamps) at room temperature. During the process of degradation, solution aliquots (2 mL) were withdrawn via a syringe at 30 min intervals up to 180 min. UV−vis spectra were collected for these samples in the 300−800 nm range, measuring the absorbance with a single-beam UV−vis spectrophotometer (Shimadzu, model UV-1280, Kyoto, Japan). The photocatalytic performance was calculated according to eq 2

\[
\text{conversion (D%) } = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\%
\]

where \( C_0 \) is the initial absorbance and \( C_t \) is the absorption at a certain irradiation time \( t \) of the MB solution (\( \lambda = 665 \text{ nm} \)). All of the analyses were conducted using a quartz cuvette as the sample holder.
2.5. Photocatalytic Virus Inactivation Test. The dip-padding method was used to coat TiO₂ nanoparticles onto the cotton fabric (area: 100 mm × 100 mm) to evaluate the photocatalytic virus inactivation performance. To remove residual impurities, the cotton fabric sample was boiled successively for 30 min with sodium carbonate solution (2.0 g/L), followed by sodium dodecylbenzene sulfonate (2.0 g/L), and then washed with distilled water and air-dried at room temperature. A PEG–TiO₂ sol was prepared by mixing TiO₂ nanoparticles (0.3 g) and PEG-600 (50 mL) in an ultrasonic mixer for 5 h. The pretreated fabric was immersed in the prepared PEG–TiO₂ sol for 1 min and then passed through a two-roller laboratory padding machine at a nip pressure of 4 bar to ensure a constant amount of TiO₂ on the fabric. After padding, the fabric was immediately dried at 100 °C for 5 min in a preheated oven and finally cured at 120 °C for 3 min.

The virus inactivation experiments were conducted in a deep Petri dish using phosphate buffer solution (20 mL, pH 7.0, 10 mM) with the target virus (MS2 bacteriophage, murine norovirus, or influenza virus) and a TiO₂/cotton fabric pad (50 mm × 100 mm). The initial populations of the virus in the disinfection experiments were controlled to about 10⁶ plaque-forming units (PFU)/mL. In the UV light experiments, illumination was provided by 3 Blacklight Blue lamps (BLB, 4 W, Philips Co.; light intensity: 1.8 × 10⁻⁶ Einstein/l s), which emitted in the 300–400 nm range.

Typically, three samples (1.0 mL) were collected over 40 min to measure the viable virus; each sampled solution was diluted to 1/10 and 1/100. Three replicate plates were used at each dilution. All disinfection experiments were repeated three times and their averaged values with statistical deviations were used for the data analysis. The same experiments were also carried out with para-chlorobenzoic acid (pCBA), a well-known OH radical probe, to investigate the role of OH radicals in virus inactivation for the TiO₂/cotton fabric system. The concentration of pCBA (initial concentration: 300 ppb) was analyzed by HPLC (Waters Co.). A reverse-phase C18 column (XTerra Rp-18, 5 μm, 150 mm × 2.1 mm) was used with a UV detector (UV–vis 151, Gilson Co.) at 230 nm.

Murine norovirus-1 strain CW1 (MNV1) was propagated in confluent monolayers using the murine macrophage cell line RAW264.7, which was cultured in HyClone Dulbecco’s modified Eagle’s medium (DMEM)/high glucose (GE Healthcare Life Sciences, Logan, UT). The culture was supplemented with 10% fetal bovine serum (FBS, Invitrogen, Carlsbad, CA) containing penicillin/streptomycin and incubated at 37 °C in a 5% CO₂ chamber. The virus was incubated for 2 days, subjected to 3 freeze–thaw cycles, and finally harvested by low-speed centrifugation at 1000g for 30 min. To concentrate the virus, the supernatant was filtered using an Amicon Ultra-15 centrifugation unit (Merck Millipore, Ireland).

The influenza A (H3N2) virus was obtained from the Korea Bank for Pathogenic Viruses (KBPV, Seoul, South Korea). The virus was propagated in Madin–Darby canine kidney (MDCK) cells (American Type Culture Collection (ATCC), Manassas, VA) and assessed by plaque titration. Cells were maintained in DMEM supplemented with 10% FBS containing 100 U/mL penicillin, 100 μg/mL streptomycin (HyClone), 0.2% bovine serum albumin (BSA, Gibco, Waltham, MA), and 25 mM HEPES (Gibco) in a humidified atmosphere containing 5% CO₂ at 37 °C.

The MS2 bacteriophage (ATCC 15597) was quantified by the soft agar overlay (double-agar layer) plaque assay method with Escherichia coli C3000 as host bacteria, cultured using 10 g/L tryptone, 1 g/L glucose, 1 g/L yeast extract, 8 g/L NaCl, and 0.8 g/L CaCl₂. The top and bottom agars for the plaque assays contained 7 and 15 g/L agar, respectively.

3. RESULTS AND DISCUSSION

3.1. Phase Structure. The XRD patterns of the TiO₂ nanoparticles before and after calcination at temperatures from 300 to 1100 °C are shown in Figure 1. The samples were designated as as-prepared, HTi-1, HTi-2, HTi-3, HTi-4, and HTi-5 according to calcination conditions (untreated, 300, 500, 700, 900, and 1100 °C, respectively). Each sample displays the main characteristic peaks of the anatase, brookite, and rutile phases at 25.3, 30.8, and 27.5 °C, respectively, as referenced from the Joint Committee on Powder Diffraction Standards (JCPDS card numbers: anatase, 21-1272; brookite, 29-1360; and rutile, 21-1276). At low calcination temperatures (<500 °C), broad XRD peaks are observed owing to the amorphous structure of the TiO₂ nanoparticles. With increasing calcination temperature (>500 °C), the XRD peaks steadily narrow and sharpen. This may be attributed to the elimination of grain boundary defects during calcination at high temperatures, which therefore increases the crystallinity of the TiO₂ nanoparticles. Further, the crystallite size of all of the samples increases with calcination temperature, as shown in Table 1. The crystallite size of each phase was calculated using Scherrer’s equation, and the weight fractions of the
Anatase, brookite, and rutile phases were estimated using eq 1. A mixture of brookite and rutile phases is observed for the as-prepared sample and HTi-1 (Figure 1a and Table 1). Since the anatase (101) diffraction peak at 25.3° overlaps the brookite (120) diffraction peak at 25.3°, Raman spectroscopy analysis is needed to check the potential presence of anatase. Identification of the composition of each phase was conducted by comparing the observed vibration modes with the literature.47−50 In Figure 1b, HTi-1 shows characteristic signals of brookite at 153 (A1g) and 247 (A1g) cm−1 and characteristic signals of rutile at 447 (Eg) and 612 (A1g) cm−1. Meanwhile, HTi-2 presents characteristic signals of brookite and rutile as well as the signals of anatase at 399 (B1g), 516 (A1g), and 639 (Eg) cm−1. Upon increasing the calcination temperature from 300 to 500 °C, the brookite phase is transformed into the anatase phase (HTi-2). At 700 °C (HTi-3), the characteristic brookite (121) peak at 30.8° disappears, indicating the complete phase transformation from brookite to anatase. With further increases in calcination temperature (to 1100 °C), the rutile phase content increases from 21 to 100%, with the higher thermal stability of the rutile phase driving the transformation at high temperatures.51 These data suggest that an increasing calcination temperature leads to higher crystallinity, a larger crystallite size, and phase transformation in the TiO2 nanoparticles.

3.2. SEM and TEM Analyses. FE-SEM and HR-TEM analyses were performed to investigate the effect of calcination temperature on the morphology and particle size of the TiO2 nanoparticles. Figure 2 shows the FE-SEM images of the calcined TiO2 nanoparticles. Clearly, the calcination temperature does not influence the morphology of the nanoparticles, which retain their irregular spherical shapes after calcination. However, the particle size increases with calcination temperature, as shown in Table 1 and Figure 2.

Figure 3 shows the morphology, d-spacing values, and selected area electron diffraction (SAED) patterns of the calcined TiO2 nanoparticles subsequent to their HR-TEM analyses. The particle and crystallite sizes of the nanoparticles

| sample no. | calcination temperature (°C) | anatase | | brookite | | rutile | |
|------------|-----------------------------|---------|--------|----------|--------|--------|
|            | size (nm) | content (%) | size (nm) | content (%) | size (nm) | content (%) |
| as-prepared | 6.35 | 81 | 4.80 | 19 |
| HTi-1 | 300 | 10.10 | 81 | 10.70 | 19 | 10.70 | 19 |
| HTi-2 | 500 | 17.01 | 39 | 13.45 | 41 | 18.17 | 20 |
| HTi-3 | 700 | 28.19 | 79 | 26.69 | 21 | 51.90 | 88 |
| HTi-4 | 900 | 46.10 | 12 | 51.90 | 88 | 77.60 | 100 |
| HTi-5 | 1100 | |

Figure 2. FE-SEM images of TiO2 nanoparticles calcined at different temperatures: (a) HTi-1, (b) HTi-2, (c) HTi-3, (d) HTi-4, and (e) HTi-5.
increase with calcination temperature. Figure 3 shows nanoparticles with both spherical and rod shapes, comprising a mixture of brookite and rutile phases. The \( d \)-spacing values between the fringes are estimated as 0.290 and 0.321 nm, which are close to the (121) lattice spacing of brookite and the (110) lattice spacing of rutile, respectively. With increasing
calcination temperature (to 500 °C, Figure 3b), a mixture of anatase (101), brookite (121), and rutile (110) phases with d-spacings of 0.352, 0.290, and 0.326 nm, respectively, is observed. Figure 3c,d shows mixtures of anatase (101) and rutile (110) phases with d-spacings of 0.351 and 0.323 nm, respectively. Figure 3e shows the single rutile (200) phase with d = 0.229 nm. The SAED patterns of the calcined TiO<sub>2</sub> nanoparticles confirm the mixtures of brookite and rutile phases, as shown in Figure 3a. After calcination at 500 °C, a triphasic mixture of anatase (101), brookite (121), and rutile (110) phases is observed. The SAED patterns shown in Figure 3c,d indicate mixtures of anatase (101) and rutile (110) phases. Finally, after calcination at 1100 °C, only the rutile (200) phase is observed, again confirming complete transformation of the anatase phase. Moreover, from the XRD results, the crystallinity increases as a result of crystallite formation of the anatase phase. Moreover, from the XRD results, the crystallinity increases as a result of crystallite formation of the anatase phase. Moreover, from the XRD results, the crystallinity increases as a result of crystallite formation of the anatase phase.

3.3. BET and BJH Analyses. Figure 4 shows the nitrogen adsorption–desorption isotherms of the calcined TiO<sub>2</sub> nanoparticles. According to the IUPAC classification, the obtained isotherms can be described as type IV<sup>55</sup> indicating the presence of well-developed mesopores associated with capillary condensation of the adsorbent. Adsorption isotherms of mesoporous TiO<sub>2</sub> nanoparticles are also described by hysteresis loops (H1–H4) that indicate the distribution and shapes of the pores within the materials.<sup>56</sup> The calcined TiO<sub>2</sub> nanoparticles present H3-type hysteresis loops, which represent isotherm curves that increase slowly and then rise sharply at high relative pressure P/P<sub>s</sub> (P: the balance pressure; P<sub>s</sub>: saturation pressure).<sup>56</sup> These results indicate that the pores are irregular with parallel, slit-like, and open-ended-tubular shapes.

Table 2 shows the surface areas and pore volumes of the TiO<sub>2</sub> nanoparticles obtained at various calcination temperatures. The surface areas of the calcined TiO<sub>2</sub> nanoparticles are 101.24, 45.68, 17.61, 5.32, and 3.25 m<sup>2</sup>/g, respectively. Thus, with increasing calcination temperature, the surface areas, and pore volumes decrease due to the crystallization of the TiO<sub>2</sub> nanoparticles.<sup>55,56</sup>

### Table 2. BET Surface Areas and Pore Volumes of TiO<sub>2</sub> (HTi) Nanoparticles Calcined at Various Temperatures

| sample no. | surface area (m<sup>2</sup>/g) | pore volume (cc/g) |
|------------|-------------------------------|-------------------|
| HTi-1      | 101.24                        | 0.268             |
| HTi-2      | 45.68                         | 0.210             |
| HTi-3      | 17.61                         | 0.132             |
| HTi-4      | 5.32                          | 0.026             |
| HTi-5      | 3.25                          | 0.015             |

3.4. Optical Analysis. The optical properties of the calcined TiO<sub>2</sub> nanoparticles were investigated before the photocatalytic performance tests because the UV–vis absorption edge is associated with the energy band of the semiconductor. The UV–vis absorption spectra of the TiO<sub>2</sub> nanoparticles in Figure 5a clearly show that the UV–vis absorption edge is shifted toward higher wavelengths with an increase in calcination temperature.

The optical band gap energies of the samples were calculated on the basis of Tauc plots. The band gap values can be determined using the following equation<sup>57,58</sup>

\[
(αhν)^n = B(hν - E_g)
\]  

where α is the absorption coefficient, hν is the photon energy, B is a constant relative to the material, E<sub>g</sub> is the energy gap, and n is a value that depends on the nature of the transition (n = 2 for a direct allowed transition, 2/3 for a direct forbidden transition, and 1/2 for an indirect allowed transition). The band gap values were calculated by extrapolating the plots of (αhν)<sup>n</sup> versus photon energy for direct (n = 2; Figure 5b) and indirect (n = 1/2; Figure 5c) transitions. The direct and indirect band gap values are depicted in Table 3. The estimated direct band gap values for the calcined TiO<sub>2</sub> nanoparticles range from 3.05 to 2.98 eV, whereas the estimated values for the indirect band gap vary from 2.99 to 2.91 eV. The band gap of rutile TiO<sub>2</sub> (HTi-5) is smaller than that of bulk rutile TiO<sub>2</sub> (3.02 eV).<sup>59</sup> For both direct and indirect transitions, the optical band gap clearly decreases with calcination temperature, and the direct band gap values are greater than the corresponding indirect band gap values. These results can be explained on the basis of particle size, which affects the optical band gap: for most semiconductors, a decrease in band gap with an increase in particle size leads to a red shift of the optical absorption edge.<sup>56,60</sup>

3.5. Photocatalytic Degradation. The photocatalytic performance of the calcined TiO<sub>2</sub> nanoparticles was evaluated in the degradation of MB under UV light irradiation. The degradation of a dye indicates that a photochemical reaction has occurred. Figure 6a,b presents the changes in MB absorption over time in the presence of HTi-3 (calcined at 700 °C) and commercial Degussa P25 as a reference, respectively. The maximum peak at 665 nm decreases sharply at high relative pressure P/P<sub>s</sub> (P: the balance pressure; P<sub>s</sub>: saturation pressure).<sup>60</sup> These results indicate that the pores are irregular with parallel, slit-like, and open-ended-tubular shapes.

Table 2 also shows the photocatalytic performance of the calcined TiO<sub>2</sub> nanoparticles and P25 in MB degradation. It is well known that the adsorption on the surface of the catalyst affects the photocatalytic performance. Therefore, the adsorption capacity under dark conditions of the sample was investigated before the sample was exposed to the light irradiation. In Figure 7a, it was observed that 7.5, 6.1, 5.8, 4.1, 2.8, 1.8, and 0.5% of MB readily adsorbed onto P25, as-prepared, HTi-1, HTi-2, HTi-3,
HTi-4, and HTi-5, respectively, during the adsorption process (in dark conditions). The lower adsorption capacity of MB on the samples calcined at higher temperatures could be ascribed to the decrease of the surface area of HTi samples (Table 2). The calcination temperature of the TiO₂ nanoparticles also has an impact on the degradation kinetics, as shown by the constants in Table 4. The first-order rate constants were calculated using ln(C₀/Cₜ) = kₜ, where k is the first-order constant, C₀ is the initial concentration, and Cₜ is the concentration of the dye after the photocatalytic reaction for time t. The order of MB degradation rate constants is HTi-3 > P25 > HTi-2 > HTi-4 > HTi-1 > as-prepared > HTi-5. Although HTi-3 (anatase/rutile = 79:21) has a similar phase composition to that of P25 (anatase/rutile = 75:25), HTi-3 shows the best photocatalytic performance, with a rate constant of 3.11 × 10⁻² min⁻¹. Generally, the photocatalytic performance of TiO₂ nanoparticles depends on many factors, including phase composition, crystallinity, crystallite size, and surface area.²²−²⁴ In our study, HTi-3 shows the best photocatalytic performance because of its high crystallinity and anatase/rutile phase composition. Further, anatase has an indirect band gap structure, while brookite and rutile have direct band gap structures. The indirect band gap structure provides longer e⁻/h⁺ lifetimes, leading to the lower recombination of e⁻/h⁺ pairs. Despite the larger surface areas in HTi-1 and HTi-2 compared to HTi-3, lower photocatalytic performance is observed, with k values of 3.68 × 10⁻² and 1.06 × 10⁻² min⁻¹, respectively. This is consistent with the study of

| sample no. | direct (αhν)² | indirect (αhν)¹/² |
|------------|---------------|-------------------|
| HTi-1      | 3.05          | 2.99              |
| HTi-2      | 3.03          | 2.98              |
| HTi-3      | 3.02          | 2.96              |
| HTi-4      | 3.01          | 2.94              |
| HTi-5      | 2.98          | 2.91              |

Figure 5. (a) UV–vis absorption spectra of TiO₂ nanoparticles calcined at different temperatures. (b) Direct and (c) indirect Tauc plots demonstrating the band gaps of TiO₂ nanoparticles calcined at different temperatures.

Figure 6. Absorption spectra changes of methylene blue under UVA light irradiation for different time periods: (a) HTi-3 (700 °C) and (b) P25.
Ozawa et al.,\textsuperscript{34} which reported that photocatalytic performance was enhanced as $W_A$ increased and $W_B$ decreased. HTi-5 delivers the lowest photocatalytic performance with $k = 1.59 \times 10^{-3}$ min$^{-1}$ because this material consists of only single-phase rutile and has the largest crystallite size (77.6 nm) and smallest surface area (3.25 m$^2$/g). Moreover, rutile has a direct band gap structure, which leads to the fast recombination of $e^-/h^+$ pairs. These results are clearly observed in Figure 7c,d, wherein both P25 and HTi-3 completely decompose MB after 180 min UV irradiation, while HTi-5 hardly degrades MB at all.

### 3.6. Photocatalytic Virus Inactivation

Since TiO$_2$ has been shown to be capable of inactivating a broad range of microorganisms, photocatalytic virus inactivation against MS2 bacteriophage, murine norovirus, and influenza virus was evaluated for the possible antimicrobial applications in public settings, such as cruise ships, nursing homes, hospitals, daycare centers, etc. Figure 8 shows photocatalytic virus inactivation profiles obtained for the HTi-3-coated cotton fabric system, which were estimated from MS2 bacteriophage, murine norovirus, and influenza virus inactivation kinetics in aqueous conditions during the 40 min BLB irradiation. In control experiments (without BLB irradiation), no inactivation of the targets is observed on the time scale of this study. As OH radicals have been shown to be major participants in microbial inactivation for TiO$_2$ systems in a previous study,\textsuperscript{61} the degradation of the well-known OH radical probe pCBA was also assayed (Figure 8 offset) under the same experimental conditions.

### Table 4. Kinetics Constants $k$ for the Degradation of Methylene Blue

| sample no. | $k$ (min$^{-1}$) |
|------------|------------------|
| P25        | $2.99 \times 10^{-2}$ |
| as-prepared| $2.97 \times 10^{-3}$ |
| HTi-1      | $3.68 \times 10^{-3}$ |
| HTi-2      | $1.06 \times 10^{-2}$ |
| HTi-3      | $3.11 \times 10^{-3}$ |
| HTi-4      | $1.02 \times 10^{-2}$ |
| HTi-5      | $1.59 \times 10^{-3}$ |

![Figure 7.](image-url) (a) Photocatalytic degradation curve and (b) corresponding degradation kinetics for degradation of methylene blue by calcined TiO$_2$ nanoparticles and P25. Images of methylene blue photodegradation by calcined TiO$_2$ nanoparticles and P25: (c) initial ($t = 0$ min) and (d) final (180 min).

![Figure 8.](image-url) Photocatalytic virus inactivation performance of calcined TiO$_2$ nanoparticles (HTi-3 with cotton fabric) with MS2 bacteriophage, murine norovirus, and influenza virus.
For the prepared fabrics, significant inactivation of the viruses is observed. The HTi3-coated cotton requires 40 min to inactivate 99.9% (3 log) of the influenza virus under BLB irradiation. From the radical probe experiment in Figure 8 (offset) and our previous assumptions\(^{11}\) (\(k_{\text{exp}} = k_{\text{OH radical}} p_{\text{CBA}} [\text{OH radical}]_0 (k_{\text{exp}} = 0.126 \text{ s}^{-1}, k_{\text{OH radical}} p_{\text{CBA}} = 5 \times 10^6 \text{ M}^{-1} \text{s}^{-1})\)), the steady-state concentration of OH radicals could be calculated as \(2.5 \times 10^{-11} \text{ M} (=4.3 \times 10^{-7} \text{ mg/L})\). Considering that the times required for 3 log inactivation of the MS2 bacteriophage, murine norovirus, and influenza virus are 36, 32, and 40 min, respectively, the required CT (disinfectant concentration × reaction time) values for 3 log inactivation of the targets can be calculated as \(1.5 \times 10^{-3}, 1.4 \times 10^{-3}, \text{and } 1.7 \times 10^{-5} \text{ mg/L}\) min, respectively. The results clearly demonstrate that the HTi3-coated cotton effectively inhibits the MS2 bacteriophage, murine norovirus, and influenza virus.

4. CONCLUSIONS

In this study, as-prepared TiO\(_2\) nanoparticles were calcined at temperatures ranging from 300 to 1100 °C to investigate the effect of calcination temperature on photocatalytic performance. The calcination temperature affected the crystallite size, crystallinity, particle size, and phase transformation in the as-prepared TiO\(_2\) nanoparticles according to XRD, SEM, and TEM analyses. The XRD patterns revealed that the calcined TiO\(_2\) nanoparticles were composed of brookite/rutile phases (300 °C calcination temperature), anatase/brookite/rutile phases (500 °C), anatase/rutile phases (700 and 900 °C), and rutile phase (1100 °C). Further, a reduction in surface area from 101.24 to 3.25 m\(^2\)/g was observed with increasing calcination temperature. The optical band gaps of the calcined TiO\(_2\) nanoparticles were determined from the UV–vis absorption spectra; the direct and indirect band gaps decreased from 3.05 to 2.98 eV and from 2.99 to 2.91 eV, respectively, with increasing calcination temperature. The mixed anatase/rutile-phase TiO\(_2\) nanoparticles calcined at 700 °C delivered the highest photocatalytic performance, superior to that of the commercial photocatalyst Degussa P25, because of the synergistic effects of crystallinity and phase structure. The photocatalytic virus inactivation tests with the MS2 bacteriophage, murine norovirus, and influenza virus also demonstrated excellent performance. Based on these results, TiO\(_2\) nanoparticles calcined at 700 °C appear to be promising candidates for environmental applications.

■ AUTHOR INFORMATION

Corresponding Authors
Min Cho — Division of Biotechnology, Advanced Institute of Environment and Bioscience, College of Environmental and Bioresource Sciences, Chonbuk National University, Iksan 54596, Republic of Korea; Email: cho317@jbnu.ac.kr
Seung Geol Lee — School of Chemical Engineering, Pusan National University, Busan 46241, Republic of Korea; Department of Organic Material and Science, Pusan National University, Busan 46241, Republic of Korea; orcid.org/0000-0001-7965-7387; Email: seunggeol.lee@pusan.ac.kr

Authors
Min Gu Kim — School of Chemical Engineering, Pusan National University, Busan 46241, Republic of Korea
Jeong Min Kang — School of Chemical Engineering, Pusan National University, Busan 46241, Republic of Korea

Ji Eun Lee — School of Chemical Engineering, Pusan National University, Busan 46241, Republic of Korea
Kang Seok Kim — Department of Organic Material and Science, Pusan National University, Busan 46241, Republic of Korea
Kwang Ho Kim — School of Materials Science and Engineering, Pusan National University, Busan 46241, Republic of Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00043

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was mainly supported by the Global Frontier Program through the Global Frontier Hybrid Interface Material (GFHIM) of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (No. 2013M3A6B1078882). This study was supported by the Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Science, ICT and Future Planning (No. 2017R1E1A1A01074266). This research was supported by the National Research Council of Science & Technology (NST) granted by the Korean Government (MSIP) (No. CRC-16-01-KRICT).

REFERENCES

(1) Reddy, P. V. L.; Kavitha, B.; Reddy, P. A. K.; Kim, K.-H. TiO\(_2\)-based photocatalytic disinfection of microbes in aqueous media: a review. Environ. Res. 2017, 154, 296–303.
(2) Binas, V.; Venieri, D.; Ktzias, D.; Kirakidis, G. Modified TiO\(_2\)-based photocatalysts for improved air and health quality. J. Materiomics 2017, 3, 3–16.
(3) Abdullah, H.; Khan, M. M. R.; Ong, H. R.; Yaacob, Z. Modified TiO\(_2\) photocatalyst for CO\(_2\) photocatalytic reduction: An overview. J. CO2 Util. 2017, 22, 15–32.
(4) Bhanvase, B.; Shende, T.; Sonawane, S. A review on graphene–TiO\(_2\) and doped graphene–TiO\(_2\) nanocomposite photocatalyst for water and wastewater treatment. Environ. Technol. Rev. 2017, 6, 1–14.
(5) Al-Mamun, M.; Kader, S.; Islam, M.; Khan, M. Photocatalytic activity improvement and application of UV-TiO\(_2\) photocatalysis in textile wastewater treatment: a review. J. Environ. Chem. Eng. 2019, 7, No. 103248.
(6) Chen, D.; Cheng, Y.; Zhou, N.; Chen, P.; Wang, Y.; Li, K.; Huo, S.; Cheng, P.; Peng, P.; Zhang, R. Photocatalytic degradation of organic pollutants using TiO\(_2\)-based photocatalysts: A review. J. Cleaner Prod. 2020, 268, No. 121725.
(7) He, X.; Wang, A.; Wu, P.; Tang, S.; Zhang, Y.; Li, L.; Ding, P. Photocatalytic degradation of microcystin-LR by modified TiO\(_2\) photocatalysts: A review. Sci. Total Environ. 2020, 743, No. 140694.
(8) Yuan, W. T.; Zhu, B. E.; Li, X. Y.; Hansen, T. W.; Ou, Y.; Fang, K.; Yang, H. S.; Zhang, Z.; Wagner, J. B.; Gao, Y.; Wang, Y. Visualizing H\(_2\)O molecules reacting at TiO\(_2\) active sites with transmission electron microscopy. Science 2020, 367, 428–430.
(9) Aruna, S. T.; Tiros, S.; Zaban, A. Nanosize rutile titania particle synthesis a hydrothermal method without mineralizers. J. Mater. Chem. 2000, 10, 2388–2391.
(10) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Environmental applications of semiconductor photocatalysis. Chem. Rev. 1995, 95, 69–96.
(11) Augugliaro, V.; Litter, M.; Palmisano, L.; Soria, J. The combination of heterogeneous photocatalysis with chemical and physical operations: A tool for improving the photoprocess performance. J. Photochem. Photobiol., C 2006, 7, 127–144.
(12) Augugliaro, V.; Bellardita, M.; Loddo, V.; Palmisano, G.; Palmisano, L.; Yurdakal, S. Overview on oxidation mechanisms of organic compounds by TiO2 in heterogeneous photocatalysis. J. Photochem. Photobiol., C 2012, 13, 224–245.

(13) Ricci, P. C.; Carbonaro, C. M.; Stagi, L.; Salis, M.; Casu, A.; Enzo, S.; Delogu, F. Anatase-to-rutile phase transition in TiO2 nanoparticles irradiated by visible light. J. Phys. Chem. C 2013, 117, 7850–7857.

(14) Hu, Y.; Tsai, H.-L.; Huang, C.-L. Effect of brokite phase on the anatase–rutile transition in titania nanoparticles. J. Eur. Ceram. Soc. 2003, 23, 691–696.

(15) Gervais, C.; Smith, M. E.; Pottier, A.; Jolivet, J. P.; Babonneau, F. Solid-state 47,49Ti NMR determination of the phase distribution of titania nanoparticles. Chem. Mater. 2001, 13, 462–467.

(16) Kandiel, T. A.; Feldhoff, A.; Robben, L.; Dillert, R.; Bahnemann, D. W. Tailored Titanium Dioxide Nanomaterials: Anatase Nanoparticles and Brookite Nanorods as Highly Active Photocatalysts. Chem. Mater. 2010, 22, 2050–2060.

(17) Beltrán, A.; Gracia, L.; Andrés, J. Density functional theory study of the brokite surfaces and phase transitions between natural titania polymorphs. J. Phys. Chem. B 2006, 110, 23417–23423.

(18) Zhang, Y.; Shi, E.; Cui, S.; Li, W.; Hu, X. Hydrothermal preparation of nanosized brookite powders. J. Am. Ceram. Soc. 2000, 83, 2634–2636.

(19) García-Ruiz, A.; Morales, A.; Bokhimi, X. Morphology of rutile and brokite nanocrystallites obtained by X-ray diffraction and Rietveld refinements. J. Alloys Compd. 2010, 495, 583–587.

(20) Li, J.-G.; Ishikagi, T.; Sun, X. Anatase, brookite, and rutile nanocrystals via redox reactions under mild hydrothermal conditions: phase-selective synthesis and physicochemical properties. J. Phys. Chem. C 2007, 111, 4969–4976.

(21) Khan, S.; Je, M.; Kim, D.; Lee, S.; Cho, S.-H.; Song, T.; Choi, H. Mapping point defects of brokite TiO2 for photocatalytic activity beyond anatase and P25. J. Phys. Chem. C 2020, 124, 10376–10384.

(22) Yu, J.; Jimmy, C. Y.; Leung, M. K.-P.; Ho, W.; Cheng, B.; Zhao, X.; Zhang, J. Effects of acidic and basic hydrolysis catalysts on the photocatalytic degradation of methylene blue under UV and visible light by brokite-rutile bi-crystalline phase of TiO2. New J. Chem. 2021, 45, 3485–3497.

(23) Yuan, W. T.; Meng, J.; Zhu, B. E.; Gao, Y.; Zhang, Z.; Sun, C. H.; Yang, Y. Unveiling the atomic structures of the minority surfaces of TiO2 nanocrystals. Chem. Mater. 2018, 30, 288–295.

(24) Yuan, W. T.; Wang, Y.; Li, H. B.; Wu, H. L.; Zhang, Z.; Solloni, A.; Sun, C. H. Real-time observation of reconstruction dynamics on TiO2(001) surface under oxygen via an environmental transmission electron microscope. Nano Lett. 2016, 16, 132–137.

(25) Zhang, Q.; Gao, L.; Guo, J. Effects of calcination on the photocatalytic properties of nanosized TiO2 powders prepared by TiCl4 hydrolysis. Appl. Catal., B 2000, 26, 207–215.

(26) Zhang, Z.; Wang, C.-C.; Zakaria, R.; Ying, J. Y. Role of particle size in nanocrystalline TiO2-based photocatalysts. J. Phys. Chem. B 1998, 102, 10871–10878.

(27) Hanaor, D. A.; Sorrell, C. Review of the anatase to rutile phase transition. J. Mater. Sci. 2011, 46, 855–874.

(28) Sclafani, A.; Herrmann, J. Comparison of the photoelectronic and photocatalytic activities of various anatase and rutile forms of titania in pure liquid organic phases and in aqueous solutions. J. Phys. Chem. A 1996, 100, 13655–13661.

(29) Musić, S.; Gotić, M.; Ivanda, M.; Popović, S.; Turković, A.; Trojko, R.; Sekulić, A.; Furić, K. Chemical and micro structural properties of TiO2 synthesized by sol–gel procedure. Mater. Sci. Eng., B 1997, 47, 33–40.

(30) Ozawa, T.; Iwasaki, M.; Tada, H.; Akita, T.; Tanaka, K.; Ito, S. Low-temperature synthesis of anatase–brokite composite nanocrystals: the junction effect on photocatalytic activity. J. Colloid Interface Sci. 2005, 281, 510–513.

(31) Qian, R.; Zong, H.; Schneider, J.; Zhou, G.; Zhao, T.; Li, Y.; Yang, J.; Bahnemann, D. W.; Pan, J. H. Charge carrier trapping, recombination and transfer during TiO2 photocatalysis: An Overview. Catal. Today 2019, 335, 78–90.

(32) Ohno, T.; Sarukawa, K.; Tokieda, K.; Matsumura, M. Morphology of a TiO2 photocatalyst (Degussa, P-25) consisting of anatase and rutile crystalline phases. J. Catal. 2001, 203, 82–86.

(33) Bickley, R. L.; Gonzalez-Carreno, T.; Lees, J. S.; Palmisano, L.; Tilley, R. J. D. A structural investigation of titanium dioxide photocatalysts. J. Solid State Chem. 1991, 92, 178–190.

(34) Anitha, B.; Kharad, M. A. Anatase–rutile phase transformation and photocatalysis in peroxide gel route prepared TiO2 nanocrystals: Role of defect states. Solid State Sci. 2020, 108, No. 106392.

(35) Secundino-Sánchez, O.; Diaz-Reyes, J.; Aguila-López, J.; Sánchez-Ramírez, J. Crystalline phase transformation of electrospraying TiO2 nanofibres carried out by high temperature annealing. J. Mol. Struct. 2019, 1194, 163–170.

(36) Liu, R.; Li, H.; Duan, L.; Shen, H.; Zhang, Q.; Zhao, X. Inflences of annealing atmosphere on phase transition temperature, optical properties and photocatalytic activities of TiO2 phase-junction microspheres. J. Alloys Compd. 2019, 789, 1015–1021.

(37) Zhang, H.; Banfield, J. F. Understanding polymorphic phase transition behavior during growth of nanocrystalline aggregates: Insights from TiO2. J. Phys. Chem. B 2000, 104, 3481–3487.

(38) Wang, W.; Gu, B.; Liang, L.; Hamilton, W.; DJ; W. Synthesis of rutile (α-TiO2) nanocrystals with controlled size and shape by low temperature hydrolysis: effects of solvent composition. J. Phys. Chem. B 2004, 108, 14789–14792.

(39) Yu, J. C.; Zhang, L.; Yu, J. Direct sonochemical preparation and characterization of highly active mesoporous TiO2 with a bicyrstalline framework. Chem. Mater. 2002, 14, 4647–4653.

(40) Park, G. W.; Cho, M.; Cates, E. L.; Lee, D.; Oh, B. T.; Vinje, J.; Kim, J. H. Fluorinated TiO2, as an ambient light-activated virucidal surface coating material for the control of human norovirus. J. Photochem. Photobiol., B 2014, 140, 315–320.

(41) Cho, M.; Chung, H. M.; Choi, W. Y.; Yoon, J. Y. Different inactivation behaviors of MS-2 phage and Escherichia coli in TiO2 photocatalytic disinfection. Appl. Environ. Microbiol. 2005, 71, 270–275.

(42) Choudhury, B.; Choudhury, A. Local structure modification and phase transformation of TiO2 nanoparticles initiated by oxygen defects, grain size, and annealing temperature. Int. Nano Lett. 2013, 3, No. 55.

(43) Tompsett, G.; Bowmaker, G.; Cooney, R.; Metson, J.; Rodgers, K.; Seakins, J. The Raman spectrum of brookite, TiO2 (PBaC, Z = 8). J. Raman Spectrosc. 1995, 26, 57–62.

(44) Swamy, V.; Muddle, B. C.; Dai, Q. Size-dependent modifications of the Raman spectrum of rutile TiO2. Appl. Phys. Lett. 2006, 89, No. 163118.

(45) Zhang, Y.-H.; Chan, C. K.; Porter, J. F.; Guo, W. Micro-Raman spectroscopic characterization of nanosized TiO2 powders prepared by vapor hydrolysis. J. Mater. Res. 1998, 13, 2602–2609.

(46) Le, V.; Zhang, L.; Fan, J. Fabrication, characterization and Raman study of TiO2 nanowire arrays prepared by anodic oxidative hydrolysis of TiCl4. Chem. Phys. Lett. 2001, 338, 231–236.

(47) Sainlinraj, S.; Ajithprasad, K. Effect of calcination temperature on non-linear absorption co-efficient of nano sized titanium dioxide
(TiO₂) synthesised by sol-gel method. Mater. Today: Proc. 2017, 4, 4372–4379.

(52) Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. On a theory of the van der Waals adsorption of gases. J. Am. Chem. Soc. 1940, 62, 1723–1732.

(53) Sing, K. Characterization of Adsorbents. In Adsorption: Science and Technology; Springer, 1989; pp 3–14.

(54) Yang, S.; Chen, G.; Lv, C.; Li, C.; Yin, N.; Yang, F.; Xue, L. Evolution of nanopore structure in lacustrine organic-rich shales during thermal maturation from hydrous pyrolysis, Minhe Basin, Northwest China. Energy Explor. Exploit. 2017, 36, 265–281.

(55) Shao, G. N.; Imran, S. M.; Jeon, S. J.; Engole, M.; Abbas, N.; Salman Haider, M.; Kang, S. J.; Kim, H. T. Sol-gel synthesis of photoactive zirconia-titania from metal salts and investigation of their photocatalytic properties in the photodegradation of methylene blue. Powder Technol. 2014, 258, 99–109.

(56) Nilchi, A.; Janitabar-Darzi, S.; Mahjoub, A. R.; Rasouligarmarodi, S. New TiO₂/SiO₂ nanocomposites-phase transformations and photocatalytic studies. Colloids Surf., A 2010, 361, 25–30.

(57) Salem, A. M.; Selim, M. S.; Salem, A. M. Structure and optical properties of chemically deposited Sb₂S₃ thin films. J. Phys. D: Appl. Phys. 2001, 34, 12–17.

(58) Singh, M. K.; Mathpal, M. C.; Agarwal, A. Optical properties of SnO₂ quantum dots synthesized by laser ablation in liquid. Chem. Phys. Lett. 2012, 536, 87–91.

(59) Hashimoto, K.; Irie, H.; Fujishima, A. TiO₂ photocatalysis: a historical overview and future prospects. Jpn. J. Appl. Phys. 2005, 44, No. 8269.

(60) Hsien, Y.-H.; Chang, C.-F.; Chen, Y.-H.; Cheng, S. Photodegradation of aromatic pollutants in water over TiO₂ supported on molecular sieves. Appl. Catal., B 2001, 31, 241–249.

(61) Cho, M.; Chung, H.; Choi, W.; Yoon, J. Linear correlation between inactivation of E-coli and OH radical concentration in TiO₂ photocatalytic disinfection. Water Res. 2004, 38, 1069–1077.