

Photocatalytic NO_x degradation performance of TiO₂-nanofiber-spray-coated foam composite according to saturated conditions

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ABSTRACT

We investigated the photocatalytic NO_x degradation performance of foam composites using various TiO₂ application methods and saturated conditions. TiO₂ powder (TP) and TiO₂ nanofiber (TF) were used. TF was fabricated using polyvinyl pyrrolidone, ethanol, acetylacetone, and titanium 4-isopropoxide via electrospinning. TF mixed with an inorganic coating material was sprayed on cementitious materials once. The NO_x degradation performance of the TF-spray-coated specimen was higher than that of specimens with TP. The NO_x removal performance of the foam composite decreased with increasing specimen water content. The TF-spray-coated foam composite with activated carbon yielded the highest NO_x removal performance.

1. Introduction

Particulate matter (PM), a main cause of air pollution, causes serious, health-related problems. Nitrogen oxides (NO_x), precursors of PM, generate PM based on their reaction with ammonia in the atmosphere [1]. The NO_x emissions from South Korea were approximately 1,190,000 tons in 2017, aggravating air pollution [2]. NO_x cause respiratory diseases, such as asthma and bronchitis, in elderly people and patients, even at low concentrations [3,4].

Many studies have been conducted to reduce NO_x in the atmosphere [5,6]. Photocatalysts activated by light energy are materials extensively used to remove NO_x from the atmosphere [7]. Among these photocatalysts, titanium dioxide (TiO₂) has been commonly used in NO_x reduction technology owing to its photoactivity, high stability, low cost, and environmental safety characteristics [7]. In addition, TiO₂ is easy to store and transport [8]. Owing to these benefits, studies on the application of TiO₂ have been conducted for NO_x reduction in various fields [9–12].

Several researchers have been studying the air-purification and self-cleaning performance of construction materials with TiO₂. Because the concrete structure is exposed to external environmental factors, the ultraviolet (UV) light required for the photocatalytic reaction of TiO₂ can

be easily received. In addition, because the concrete structure has a large surface area, a large amount of NO_x in terms of the overall area can be removed even though the photocatalytic efficiency per area is low. Dylla et al. [13] performed an experiment on NO_x reduction using concrete prepared by mixing nanostructured TiO₂ powder with cement in advance. According to their findings, the content of TiO₂ was proportional to the NO_x removal efficiency. However, the relative humidity and airflow velocity were inversely proportional to the NO_x removal efficiency. Guo et al. [14] analyzed the NO_x removal performance of the specimens mixed with nanostructured TiO₂ powder and the spray-coated specimens with nanostructured TiO₂. They found that the NO_x removal rate of the specimens coated with TiO₂ was higher than that of the TiO₂-embedded specimens. Further, they reported that the NO_x removal rate decreased when the water content in the specimen increased. Si et al. [15] investigated the NO_x removal performance by using the mortar specimens mixed with TiO₂ in three different manners. They used the specimen that was prepared by directly adding TiO₂ powder, the specimen prepared by applying TiO₂-coated aggregates to the surface, and the specimen prepared by adding TiO₂-coated aggregates. In the experimental results, the specimen prepared by applying TiO₂-coated aggregates to the surface yielded the highest NO_x reduction efficiency among the three specimens. They also reported that NO_x can

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be efficiently reduced using a smaller amount of TiO_2 . King et al. [16] investigated the effect of the specimen color on the NO_x reduction performance of TiO_2 . Specimens were prepared using white and gray cement and TiO_2 powder. These authors found (based on conducted experiments) that the NO_x reduction performance of the white cement specimen was higher than that of the gray cement specimen. They also reported that the carbonation of the specimen degrades the NO_x reduction performance.

The nanostructuring of TiO_2 considerably improves photocatalytic performance. Studies have been conducted using TiO_2 in the forms of nanoparticles, nanofibers, and nanotubes [17–21]. Various methods are available for the preparation of TiO_2 in nanoforms, including the sol–gel method, hydrothermal treatment, anodization, and electrospinning [21–24]. Electrospun TiO_2 nanofibers can be produced at a low cost, and they have been used in various fields owing to their large specific surface areas and improved semiconductor properties [18,25,26].

Nasikhudin et al. prepared PVA/ TiO_2 composite nanofibers by using the electrospinning method [27]. They investigated the removal performance of a methylene blue aqueous solution based on the photocatalytic reaction of PVA/ TiO_2 nanofiber composites in an ultraviolet (UV) light environment. They reported that the photocatalytic performance of PVA/ TiO_2 composite nanofibers was better than that of PAN-based fibers. Vild et al. investigated the photocatalytic reaction of a TiO_2 /Poly(methyl methacrylate) (PMMA) nanocomposite membrane prepared via electrospinning [28]. They evaluated the photocatalytic performance according to the TiO_2 content and found that 2 ml/L of methylene blue was purified to 100 % within 100 min when the TiO_2 content was 40 %. Xu et al. prepared an acrylonitrile/ TiO_2 /polyaniline (PAN/ TiO_2 /PANI) hybrid fiber membrane and investigated its photocatalytic regeneration properties [29]. They prepared fibers coated with PANI and TiO_2 particles that had widths of ≤ 200 nm via the electrospinning method. When they investigated the purification performance recovery characteristics of Congo Red solution by using the prepared hybrid fiber membrane, they found that the regeneration efficiency was more than 60 % even after four repeated experiments. Various studies have been conducted using TiO_2 nanofibers (TF), but studies on their application to concrete are insufficient.

In general, activated carbon (AC) has excellent adsorption performance for gaseous substances because it contains numerous micropores [30]. The addition of AC to cementitious materials leads to higher NO_x adsorption efficiency than typical cement paste owing to the large AC specific surface area [31,32]. Krou et al. [31] conducted research on the NO_x adsorption of cementitious materials mixed with AC. Experimental work showed that the specimen with AC had higher NO_x adsorption performance than the reference specimen. Horgnies et al. [32] investigated the NO_x depolluting performance of concrete mixed with activated charcoal. They found that 90 % of NO_2 was removed when the concrete specimen containing activated charcoal was exposed to air (which contained NO_2) for 20 h. UV light is required for TP/TF to photocatalyze, and solely TP/TF exposed to the surface of cementitious materials undergo photocatalysis. AC increases the micropores of the cementitious materials, thereby exposing more TP/TF to the surface of the cementitious materials. AC causes a larger amount of TP/TF to photocatalyze.

The NO_x removal efficiency of cementitious materials can be improved using nanostructured TiO_2 . However, most studies investigated the NO_x reduction performance of specimens that used TiO_2 powder (TP). The studies conducted on cementitious materials with TF are insufficient. TF can improve the NO_x reduction performance because its addition can further increase the specific surface area of cementitious materials in relation to TF alone.

This study investigated the NO_x removal performance of cementitious materials that used TP and TF. Specimens were prepared in two forms (foam composites and cement pastes) using AC, TP, and TF. TP was added to specimens during the preparation process, while TF was coated on the surfaces of specimens. The specimens were prepared based

on three saturated conditions considering the exposure conditions. The NO_x reduction performance was evaluated in accordance with the International Standardization Organization (ISO) 22197–1. The microstructures of the specimens with AC, TP, and TF were investigated by scanning electron microscopy (SEM) image analysis, and their performance was compared with the reduced NO_x performance.

2. Experimental program

2.1. Materials

In this study, ordinary Portland cement (OPC), AC, TP, and TF were used as the raw materials. Table 1 summarizes the chemical oxide composition of OPC measured with the use of an X-ray fluorescence spectrometer. The density and fineness of OPC were 3.14 g/cm^3 and $3560 \text{ cm}^2/\text{g}$, respectively.

Pitch-based AC that uses pyrolyzed fuel oil as a precursor was used [33]. Pitch-based AC was produced in a nitrogen gas environment after a three-hour carbonization and activation process at 750°C with a temperature increase rate of $5^\circ\text{C}/\text{min}$. The density of AC was 2.06 g/cm^3 [33].

The particle size distributions of OPC and AC were measured using a laser diffraction particle size analyzer. Fig. 1 shows the particle size distributions of OPC and AC. The average diameters of OPC and AC were 5.42 and $435.0 \mu\text{m}$, respectively.

For TP, the P25 product from Evonik, Germany, was used [34]. The density of TP was 4.59 g/cm^3 . Fig. 2 shows an SEM image and the X-ray diffraction (XRD) pattern of TP. Fig. 2(a) shows an SEM image of the TP, a nanosized powder that agglomerates with other powders. The TP particle size was calculated based on SEM image analysis, and the average diameter of TP was measured to be 21.96 nm. As shown in Fig. 2(b), the main crystalline minerals of TP are anatase and rutile based on the XRD analysis results. The quantitative analysis results by the Rietveld refinement method revealed that anatase and rutile represented 84.5 % and 15.5 % by weight, respectively. The bandgap energies of anatase and rutile are 3.2 and 3.0 eV, respectively, and that of P25, which is prepared by mixing anatase and rutile at a certain ratio and is mainly used as a standard photocatalyst in studies on photocatalytic oxidation, is 3.1 eV [35,36].

2.2. Fabrication of TF

In this study, nanosized TFs were prepared by employing the electrospinning process. Electrospinning is a method used to fabricate continuous fibers with micrometer to nanometer diameters by using an electric field [37]. A large bias voltage can be used to draw out a wide range of polymers and 'spin' them into a collector to produce fibers less than $1 \mu\text{m}$ in diameter. Fig. 3 shows the typical lab-scale electrospinning setup [37]. A polymer solution containing TiO_2 was prepared to fabricate nanofibers from TiO_2 . To fabricate TFs, polyvinyl pyrrolidone (PVP) polymer, ethanol (EtOH), acetylacetone (ACAC), and tetra-titanium 4-isopropoxide (TTIP) were prepared. The precursor solution to be used in the electrospinning process was prepared based on the following procedure. First, a precursor solution composed of PVP polymer (PVP: PVA = 95:5 wt ratio) 8.9 wt%, TTIP 26 wt%, and peptizing agent (0.1 M acetylacetone) was prepared. The precursor solution and water were then mixed at a ratio of 1:0.05 vol%. In addition, the metal ionic salt (NaCl) concentration in the precursor solution was set to 0.087 M to

Table 1
Chemical oxide compositions of OPC.

Label	Chemical compositions (wt.%)						
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O
OPC	61.3	21.2	4.5	2.8	2.2	1.3	0.6

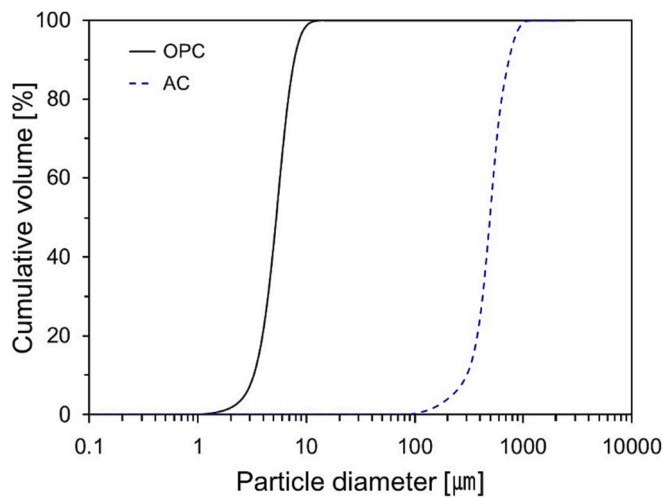


Fig. 1. Particle size distributions of OPC and AC.

increase the conductivity of the solution and control the diameter of TiO_2 fibers. Finally, the electrospinning solution was prepared by setting the molar ratio of Ti and Zn in the precursor solution to 1:1 to decrease the crystallization temperature of TiO_2 bonded particles and control the diameter of TF.

Fig. 3 shows the electrospinning machine used in this study. TF was produced by spinning the prepared precursor solution and by using the electrospinning machine. The machine consisted of a syringe and a pump for electrospinning the precursor solution, nozzles to spin TF, a collector to collect TF, and a high-voltage power supply. The precursor solution was spun at a rate of 0.1 ml/h per nozzle. The gap between the nozzles and the collector was 300 mm, and the applied voltage difference was 30 kV. The nanofiber immediately after being collected in the collector by electrospinning is in the form of TiO_2 particles contained in PVP and PVA spinning fibers. In order to secure TiO_2 crystallinity of nanofiber, the process of thermal decomposition of PVP and PVA is required. After spinning, heat treatment was performed at temperatures ranging from 400 to 450 °C for 2 h to secure the crystallinity of TiO_2 .

Fig. 4(a) shows the SEM image of the produced TF. Based on SEM image analysis, the average diameter of TF was measured to be

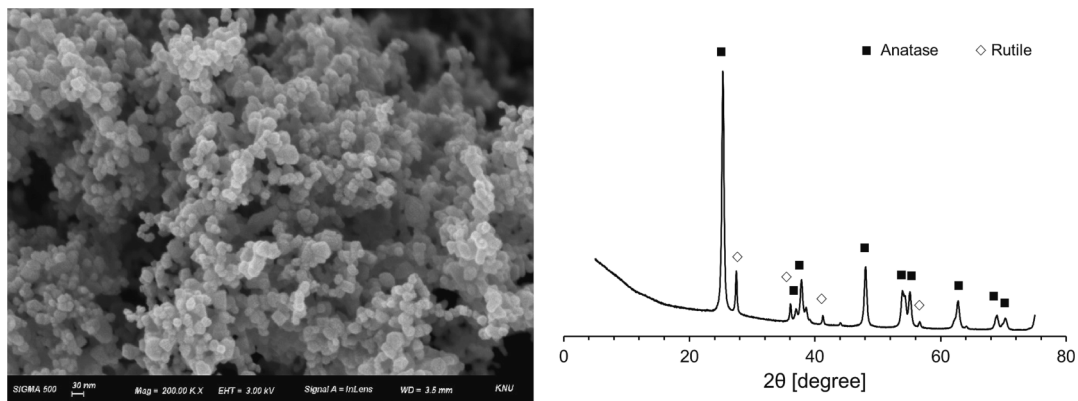


Fig. 2. SEM image and XRD pattern of TP.

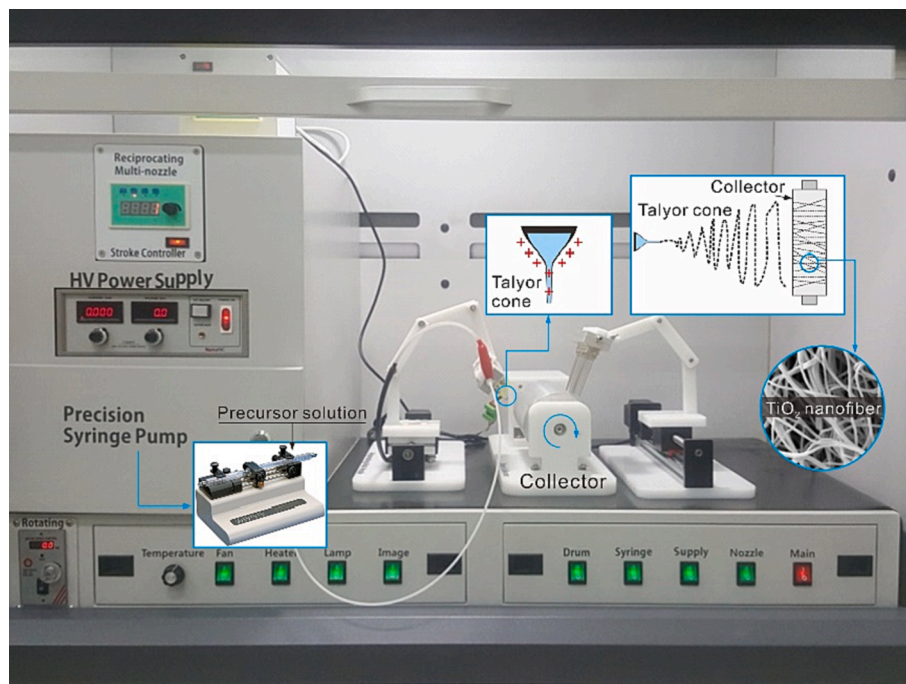


Fig. 3. Electrospinning machine.

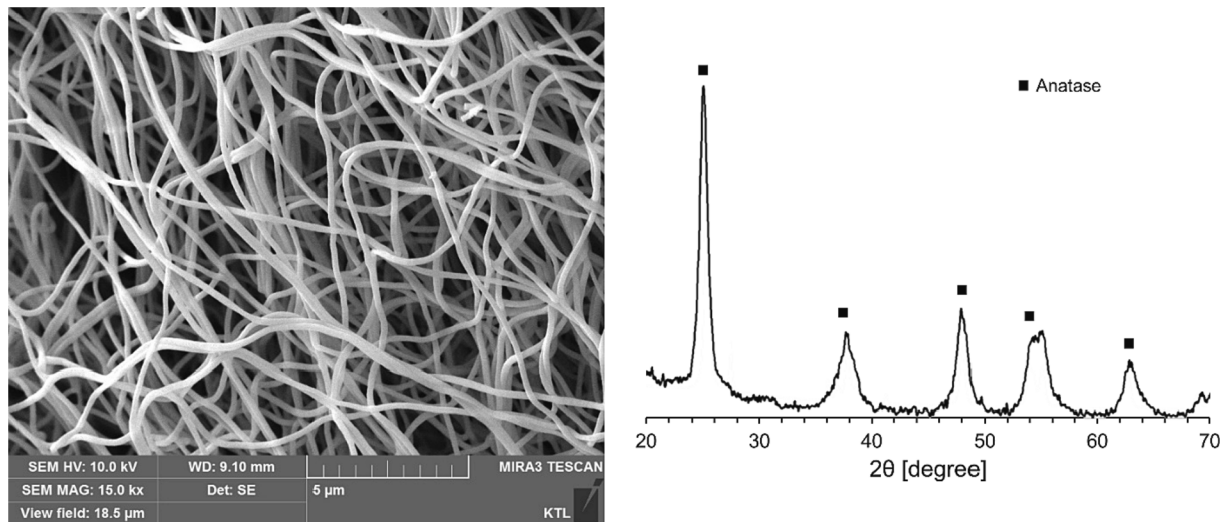


Fig. 4. SEM image and XRD pattern of TiO_2 nanofibers (TF).

approximately 200 nm. Fig. 4(b) shows the XRD pattern of TF. Only anatase peaks are observed in the analyzed results. This is different from the XRD pattern of TP, in which the peaks of anatase and rutile were observed. The efficiency of photocatalytic reaction is higher for TiO_2 in the anatase phase than for TiO_2 in the rutile phase [38]. Therefore, the NO_x decomposition performance of TF is expected to be higher than that of TP.

2.3. Mix proportions

In this study, specimens were prepared using AC, TP, and TF. They were prepared in two forms (foam composites and cement pastes). The reference specimens (FCTF and CPTF) used only OPC as a binder. Their water-to-binder (W/B) ratios and unit binders were fixed at 0.3 and 500 kg/m^3 , respectively. TP and AC were substituted by 3 and 12 %, respectively, to achieve the same binder volumes as those of the reference specimens.

To fabricate foam composites, first, a binder was added to a mixer and dry mixing was performed for approximately 1 min. Second, after adding water, the mixture was mixed for approximately 2 min to prepare a paste. Finally, a foaming composite was prepared by adding a foaming agent to the paste and mixing for approximately 2 min. The foaming agent used was an animal protein-based material, and the main component was a natural polymer peptide. The blowing agent was liquid and had a density of 1.19 g/cm^3 . For foam composites, the forming ratio was set to 63.6 %, and the slurry density was measured to be 705.3 kg/m^3 . Table 2 lists the mixture proportions of specimens. TiO_2 was applied to the specimens in two forms. The first was the addition of TP in the mixing process, and the second was the application of TF to the finished surface. The substitution rates of AC and TP for OPC were used as variables. For the specimens without TP, the surface was coated with TF.

2.4. TF coating method

To secure adhesion performance when the specimens were coated with TF, inorganic coating materials containing TF were prepared and applied to the specimen surfaces. The inorganic coating materials could be applied as a thin film to expose the TF to the outside as much as possible. In addition, binder materials were selected to prevent the photolysis of the inorganic coating materials by TF during the photolysis reaction. The inorganic coating materials contained silane as the main material, and they were prepared by applying the sol-gel process and by using the following mixture proportions of silane: EtOH (absolute): peptizing agent: dispersing agent: water = 10: 31: 58: 1.3: 0.02 by weight.

To evaluate the application characteristics of the prepared binder, the surface hardness and viscosity were investigated. The surface hardness was measured from the hardened surface after spin-coating a coating material on a glass plate and after performing curing at room temperature in accordance with the American Society of Testing and Materials (ASTM) standard D 3363 [39]. The measured film hardness on the coated surface ranged from 4 to 5H.

The viscosity of the inorganic coating materials was measured using a DV1 + viscometer (Brookfield, USA). A #61 spindle was used, and measurements were performed at 20 revolutions per minute. In the experimental results, the viscosity of the inorganic coating materials was found to range from 90 to 96 cPs. These materials yielded low-viscosity characteristics because EtOH was used as the solvent in the fabrication process.

To fix TF on the specimen surface by using the inorganic coating materials, TF was added by 3 to 5 wt% in relation to the weight of the inorganic coating materials, and dispersion treatment was performed at 750 W (20 kHz) using ultrasonic equipment. The dispersed coating materials were evenly applied to the specimen's surface, as shown in Fig. 5. Fig. 5 shows the scene of applying TF to foam composites. Surface pores are still exposed even after the application of TF. This indicates

Table 2
Mixture proportions.

Specimens	W/B (–)	Surface treatment	OPC (kg/m^3)	TP (kg/m^3)	AC (kg/m^3)	Foaming Ration (%)	Slurry density (kg/m^3)
FCTP	0.3	–	485	21.9	–	63.6	705.3
FCAC15TP			425	21.9	45.4		
CPTP			485	21.9	–		
FCTF		TF coating	500	–	–	63.6	705.3
FCAC15TF			440	–	45.4		
CPTF			500	–	–	–	–

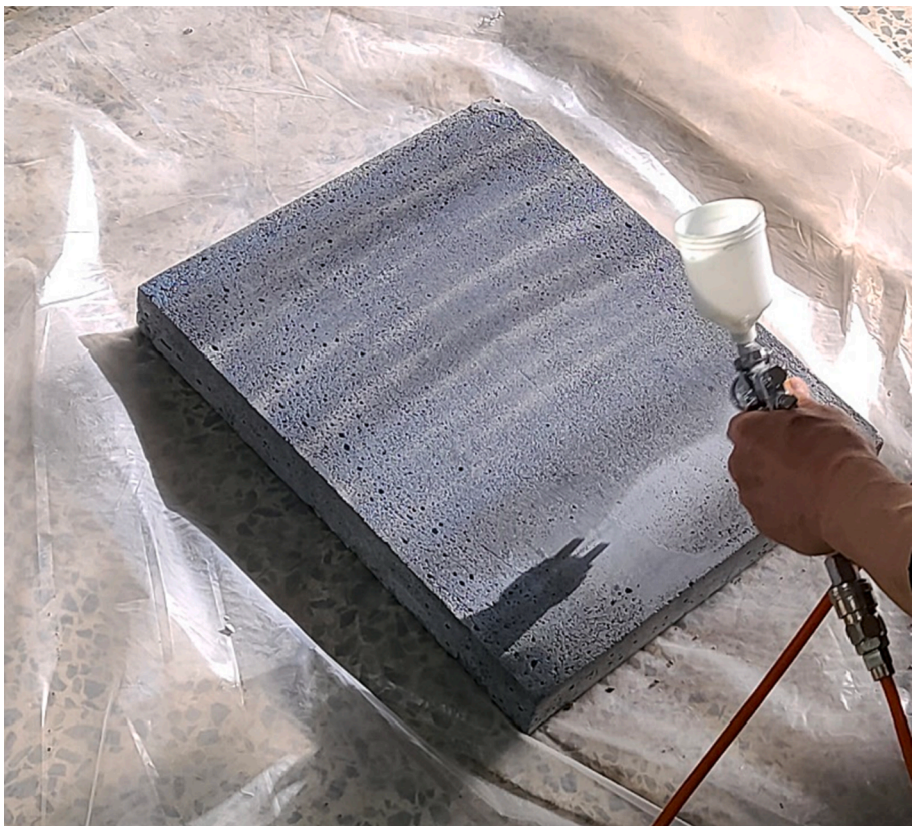


Fig. 5. TF coating of the foam composites.

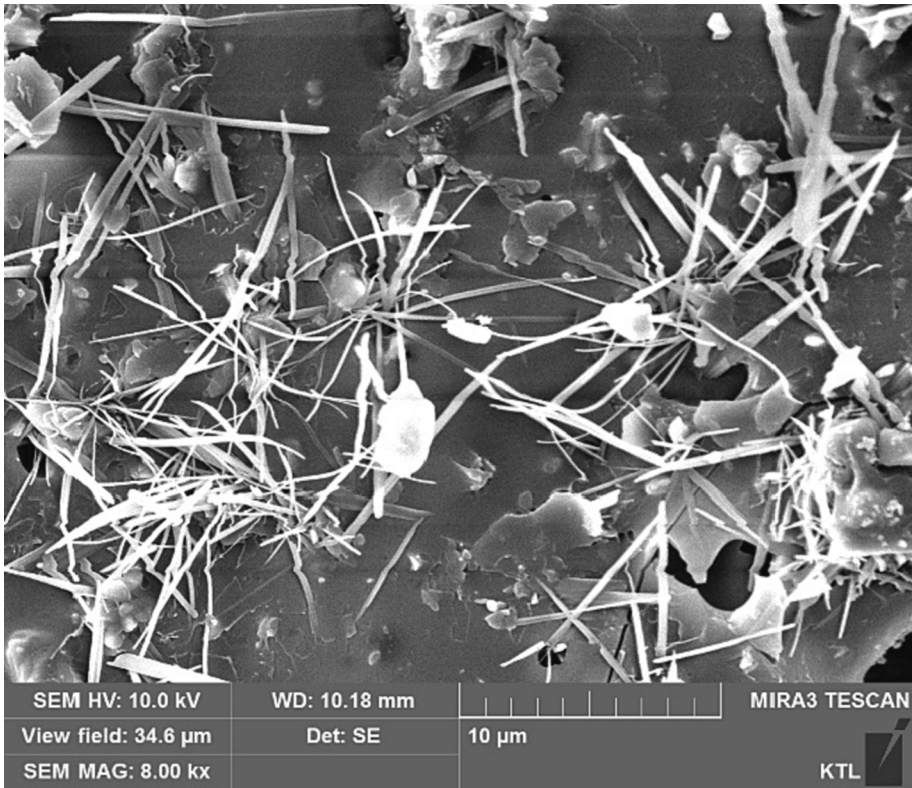


Fig. 6. SEM image of FCTF.

that the exposure areas of foam composites increase further in relation to those of cement pastes.

After the application of the coating materials, dry curing was performed for 24 h. SEM image analysis was then conducted to examine the fixed geometry of TF on the hardened surface. Fig. 6 shows the TiO₂ nanofiber SEM image of the specimen. TF is exposed on the coated surface. Given that the photocatalytic reaction of TiO₂ is caused by UV light, exposing TF on the surface is favorable for increasing the photocatalytic reaction efficiency of TiO₂. Further, it is economical because only a relatively small amount of TiO₂ is used.

2.5. Test methods

XRD was performed to analyze the mineral composition of TP. Empyrean equipment (Malvern Panalytical, United Kingdom) was used, and diffractometer scanning was performed for $2\theta = 5$ to 75° , with a step size of 0.026° and a 5 s counting time per step. Rietveld quantitative analysis was conducted using the X'Pert HighScore Plus (PANalytical) software.

To observe the morphology of AC and foam composites, SEM analysis was conducted using SIGMA500 from Carl ZEISS. Microstructural analysis was conducted by applying a platinum coating to the top surface of the specimens. The particle size distribution of AC was analyzed using a laser particle size analyzer (Horbia's LA 950).

To evaluate the NO_x reduction performance, specimens were prepared as indicated in Table 2. The specimens had a width of 50 mm, length of 200 mm, and thickness of 20 mm. The prepared specimens were cured in a chamber at $23 \pm 2^\circ\text{C}$ and a $60 \pm 10\%$ relative humidity. Fig. 7 shows the NO_x reduction performance test setup and the experimental setup. Prior to the experiment, the specimens were preprocessed in accordance with ISO-22191-1 [40]. To decompose the pollutants adsorbed on the specimens, UV light was irradiated for 16 h, and the specimens were then immersed in tap water for 30 min. The specimens were then removed and dried at 80°C .

The NO_x reduction performance test setup comprised a reaction chamber, UV lamp, gas supplier, and gas analyzer. The reaction chamber was sealed with stainless steel to minimize the absorption and leakage of NO gas. A glass plate made of borosilicate was installed in the upper part of the reaction reactor to allow the transmission of UV without loss. The UV lamp comprised three 20 W UV fluorescent tubes (the wavelength ranged from 300 to 400 nm) [41]. The distance between the UV lamp and the specimen was adjusted so that the UV intensity on the specimen surface was 10 W/m^2 . The specimen was installed inside the reaction chamber so that the mixed gas could flow over its surface.

The NO concentration in the mixed gas supplied to the reaction

chamber was fixed at 1 part per million (ppm) in accordance with the ISO 22197-1 standard. Regarding the mixed gas, NO gas (100 ppm) and the air gas composed of 21 vol% O₂ and 79 vol% of N₂ were used. To maintain the concentration of the mixed gas, the volume flows of the 100 ppm NO and air gases were adjusted to 0.03 and 3 L/min, respectively, by using a mass flow controller. The flow velocity of the mixed gas on the specimen surface corresponded to approximately 0.2 m/s. The T200 model from TELEDYNE API (detection range of 0 to 20 ppm) was used as a gas analyzer, and the NO, NO₂, and NO_x concentrations were measured in real time based on the chemiluminescent analysis method [42]. The evaluation of the NO_x reduction performance of the specimens required 4 h. An hour after the supply of the mixed gas, the UV light was turned on and irradiated for 2 h. Subsequently, the UV light was turned off for 1 h.

In this study, the effects of the water content of the specimens on the photocatalytic reaction performance of TiO₂ were investigated. To investigate the influence of the water content on the NO_x reduction performance of the specimens, experiments were performed in three conditions (oven-dry, partially saturated, and fully saturated). In the partially saturated condition, the specimens were immersed in tap water for 24 h and then dried at 40°C for 8 h. In the fully saturated condition, the specimens were immersed in tap water for 24 h, and only the surface was dried. The water content (C_w) of each specimen was calculated as follows:

$$C_w = \frac{S_i - S_d}{S_d} \times 100 \quad (1)$$

where S_d is the weight of the specimen in the oven-dry condition, and S_i is the weight of the specimen measured before the NO_x reduction experiment.

3. Results and discussion

3.1. Microstructural characteristics of AC and foam composites

Fig. 8 shows an SEM image of a pitch-based AC. As shown, AC has many cavities and fine pores on its surface. The NO gas in the atmosphere is adsorbed on the inner parts of AC as it moves from macropores to micropores through mesopores, and pores serve as adsorption sites [31,43,44]. The pitch-based AC used in this study is expected to exhibit high NO_x adsorption performance because it has many micropores.

Fig. 9 shows the optical image of the foam composite and the SEM image of TF coated on the foam composite. Fig. 9(a) shows that the foam composite is favorable for the adsorption of NO_x because it has high porosity and more open pores than normal concrete [45]. For foam

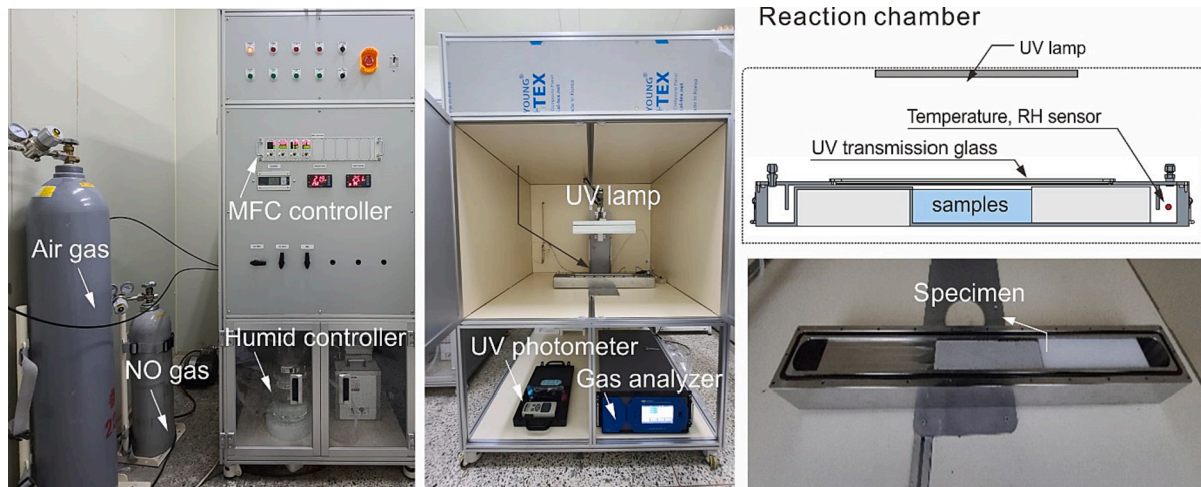


Fig. 7. Test setup of NO_x removal test.

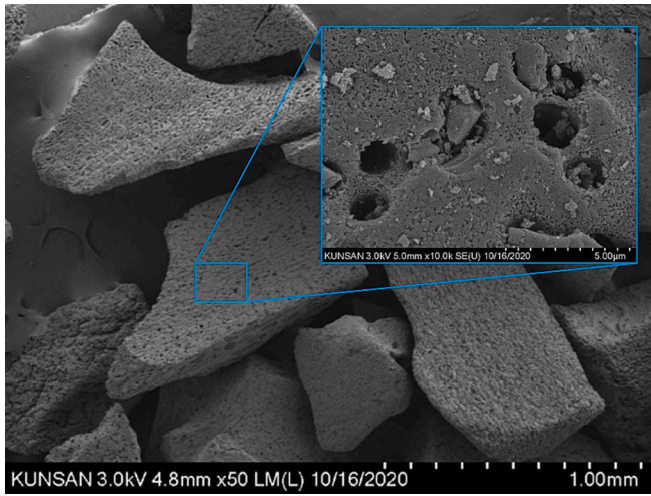


Fig. 8. SEM images of pitch-based ACs.

composites, gas may flow into the specimen through this internal pore structure [45]. In addition, TF can be coated over a larger area because foam composites have larger specific surface areas than normal concrete. Fig. 9(b) shows TF coated on foam composites. TF is distributed over a large area. Therefore, more TF is exposed to the surface of the foam composite, and the photocatalytic reaction is more active than the cement paste. Therefore, foam composites are expected to remove more NO_x when TF is applied to the same surface area. Therefore, the use of foam composites can increase the photocatalytic reaction efficiency of TF.

3.2. NO_x removal test results

In this study, the NO_x removal amount was calculated using the method suggested in the ISO-22198-1 standard [40]. In this standard, the NO_x removal mechanism is defined separately for the physical absorption of the specimen and the photocatalytic reaction of the specimen.

The amount of NO_x removed by physical absorption (η_{ads} (μmol)) was calculated using Eq. (2). Eq. (2) calculates η_{ads} (μmol) by integrating the concentration of NO_x for the section after the onset of the supply of the NO_x mixed gas and before the onset of irradiation with UV light.

$$\eta_{\text{ads}} = \left(\frac{f}{22.4} \right) \left\{ \int_{t_0}^{t_1} C_{\text{NO}_i} - C_{\text{NO}_d} dt - \int_{t_0}^{t_1} C_{\text{NO}_2} dt \right\} \quad (2)$$

where f (L/min) is the flow rate in the standard state (0 °C, 101.3 kPa). C_{NO_i} (μl/l) is the NO concentration in the mixed gas supplied to the reaction chamber. C_{NO} and C_{NO_2} (μl/l) are the NO and NO₂ concentrations measured in the mixed gas discharged from the reaction chamber, respectively, and t_0 and t_1 are the start time of the supply of the mixed gas and the time before the onset of irradiation of UV light (equal to 0 and 60 min), respectively.

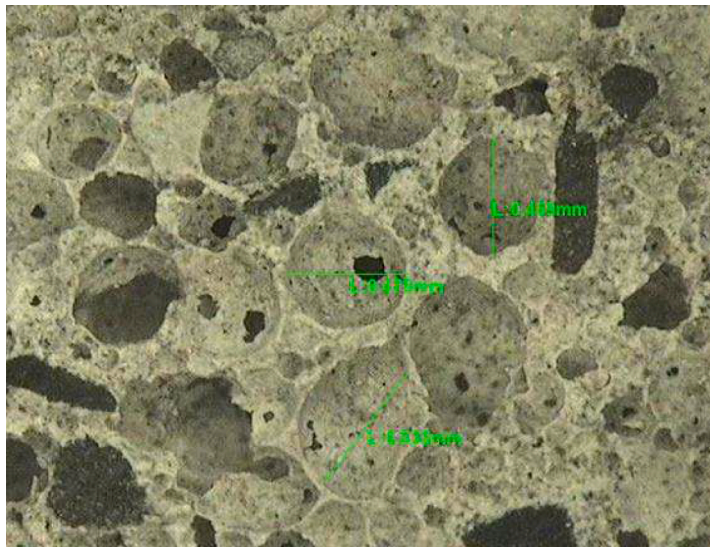
To estimate the amount of NO_x removed by the photocatalytic reaction of the specimen, the amount of NO removed by the photocatalytic reaction (η_{NO} (μmol)) and the amount of NO₂ generated by the photocatalytic reaction (η_{NO_2} (μmol)) should be calculated. η_{NO} and η_{NO_2} were calculated using Eq. (3). The total amount of NO_x removed by the specimen (η_{NO_x} (μmol)) was calculated by adding the amounts of η_{ads} and η_{NO} , and by subtracting the amount of η_{NO_2} as shown in Eq. (4).

$$\eta_{\text{NO}} = \left(\frac{f}{22.4} \right) \left\{ \int_{t_1}^{t_2} C_{\text{NO}_i} - C_{\text{NO}_d} dt \right\}, \eta_{\text{NO}_2} = \left(\frac{f}{22.4} \right) \left\{ \int_{t_1}^{t_2} C_{\text{NO}_2} dt \right\} \quad (3)$$

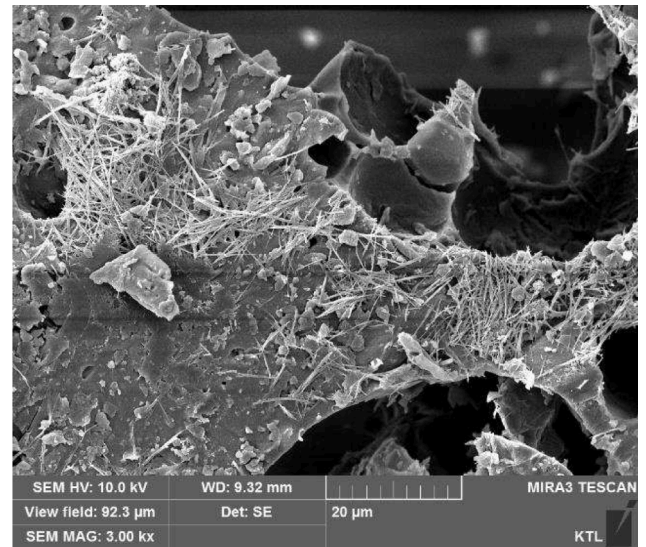
$$\eta_{\text{NO}_x} = \eta_{\text{ads}} + \eta_{\text{NO}} - \eta_{\text{NO}_2} \quad (4)$$

where t_1 and t_2 (min) are the times needed to turn on the UV light and the time to turn it off (equal to 60 and 180 min), respectively.

In this study, NO_x reduction performance was evaluated according to the water content of the foam composite. Table 3 summarizes the water content in foam composite conditions. The water content of foam composites was calculated using Eq. (1). In the table, C_{W1} , C_{W2} , and C_{W3} represent the oven-dry, partially saturated, and fully saturated conditions, respectively. In the case of the oven-dry condition, no water was found in the specimens owing to evaporation. This confirms that the experiment was performed based on the planned experimental condition (completely dry condition). Water contents in the fully saturated condition were approximately 1.9 to 2.5 times higher than those in the



(a) Foam composites



(b) TF

Fig. 9. (a) Optical image of foam composite and (b) SEM image of TF.

Table 3
Saturated condition of foam composites.

Specimens	Water content, C_w (%)	Oven-dry weight, W_d (g)	Initial weight, W_i (g)
FCTP	C_{W1} 0	112.45	112.45
	C_{W2} 16.52		131.03
	C_{W3} 34.81		151.59
FCAC15TP	C_{W1} 0	103.68	103.68
	C_{W2} 30.19		134.98
	C_{W3} 57.15		162.93
FCTF	C_{W1} 0	139.68	139.68
	C_{W2} 8.30		151.28
	C_{W3} 21.21		169.32
FCAC15TF	C_{W1} 0	118.42	118.42
	C_{W2} 16.27		137.69
	C_{W3} 32.68		157.12

partially saturated condition. This indicates that the NO_x reduction performance was evaluated, while approximately half of the pores that can be infiltrated by water were filled with water in the partially saturated condition.

The water contents of the specimens with TP were higher than those of the specimens with TF. Coating materials must be used to apply TF to specimens. Porosity decreased because the pores of the specimens were filled with the coating materials. In addition, the specimens with AC (FCAC15TP and FCAC15TF) yielded higher water content than those without AC (FCTP and FCTF). This appears to be because AC increased the porosity of the specimens.

Fig. 10 shows the NO_x reduction test results of CPTP and CPTF at 28 days. The NO_x concentration remained constant up to 60 min before the instant the UV light was turned on. CPTP yielded a lower NO_x concentration than the Blank condition. This is because NO_x is adsorbed on the microstructure of CPTP [32]. For CPTF, the NO_x concentration before 60 min was the same as the Blank condition because the adsorption of NO_x did not occur owing to surface coating. For both specimens, the NO_x concentration decreased after the UV light was turned on. In the case of CPTP, the concentration decreased to approximately 0.6 ppm and then increased to approximately 0.8 ppm. In the case of CPTF, the concentration decreased to 0.55 ppm immediately after turning on the UV light and increased to 0.7 ppm at 180 min. The NO_x removal performance of the specimen coated with TF was higher than that of the specimen mixed with TP.

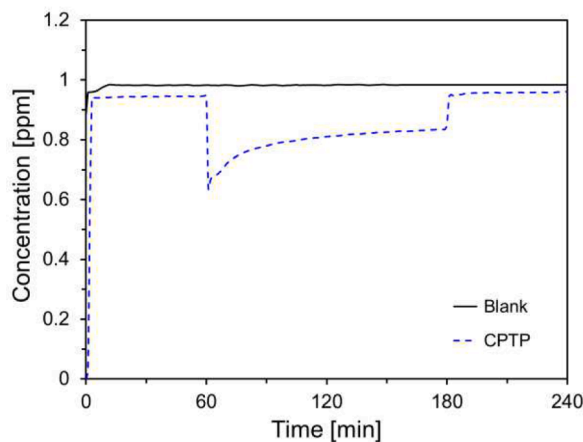
Fig. 11 shows the NO_x reduction test results of FCTP and FCTF. For FCTP and FCTF, the NO_x reduction test was conducted according to the

water content. FCTP and FCTF, which are foam composites, exhibited higher adsorption performance before 60 min than CPTP and CPTF, which are cement pastes. Regardless of the water content of the specimens, NO_x reduction was similar. This indicates that the water content of the specimens does not considerably affect the adsorption of NO_x .

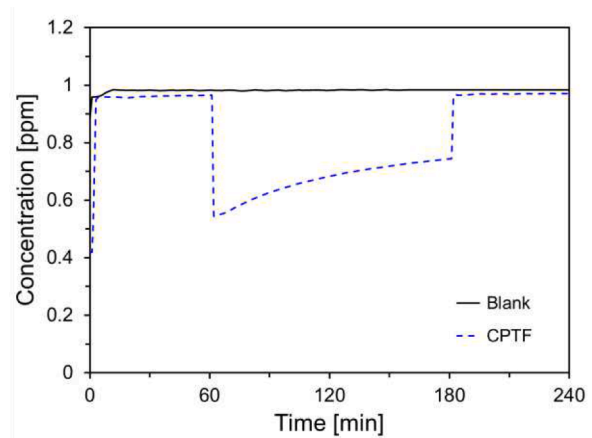
However, sixty minutes after the UV light was turned on, the NO_x concentration varied depending on the wet conditions. For FCTP, immediately after the UV light was turned on, the NO_x concentration decreased in the C_{W1} condition, but it did not in the C_{W2} condition. In the C_{W2} condition, the NO_x concentration decreased over time. In the C_{W3} condition, the NO_x concentration did not change, regardless of the onset of UV light. This indicates that the NO_x removal performance by the photocatalytic reaction of TiO_2 decreases as the water content of the specimen increases. For the removal of NO_x based on the photocatalytic reaction of TiO_2 powder, the NO_x mixed gas must be supplied to TiO_2 powder. However, when the pores of the specimen are saturated, NO_x removal by the photocatalytic reaction of TP does not occur because the mixed NO_x gas cannot reach TP. For FCTP- C_{W2} , the NO_x concentration decreased over time and became similar to that of FCTP- C_{W1} at 180 min. This appears to be because the water in the specimen was dried by the UV light, and the TP in the specimen was exposed to air.

The NO_x concentration was slightly lower for FCTF than for FCTP, with no significant difference before turning on the UV light. However, after turning on the UV light, the NO_x concentration decreased significantly in relation to FCTP. The NO_x concentration decreased to approximately 0.8 ppm for FCTP- C_{W1} and to 0.4 ppm for FCTF- C_{W1} . This indicates that the specimen coated with TF exhibits an improved NO_x reduction performance in relation to the specimen mixed with TP. Further, the NO_x removal performance of FCTF varied as a function of the water content. FCTF- C_{W2} showed no change immediately after the UV light was turned on, as with FCTP- C_{W2} , but its NO_x concentration decreased over time. The NO_x concentration reduction of FCTF- C_{W2} was larger than that of FCTP- C_{W2} . This is because the TF attached to the specimen surface was exposed when the water on the surface dried for FCTF- C_{W2} . FCTF- C_{W3} yielded the smallest NO_x concentration reduction among the three conditions. However, it showed a tendency to decrease slightly, unlike the case of FCTP- C_{W3} .

Fig. 12 shows the NO_x reduction test results of FCAC15TP and FCAC15TF. For FCAC15TP and FCAC15TF that used AC, the NO_x concentration decreased significantly in relation to that of FCTP and FCTF. In particular, for FCAC15TP which used TP, the impact of using AC was stronger than that of using FCAC15TF. Immediately after turning on the UV light, the NO_x concentration decreased to approximately 0.25 ppm

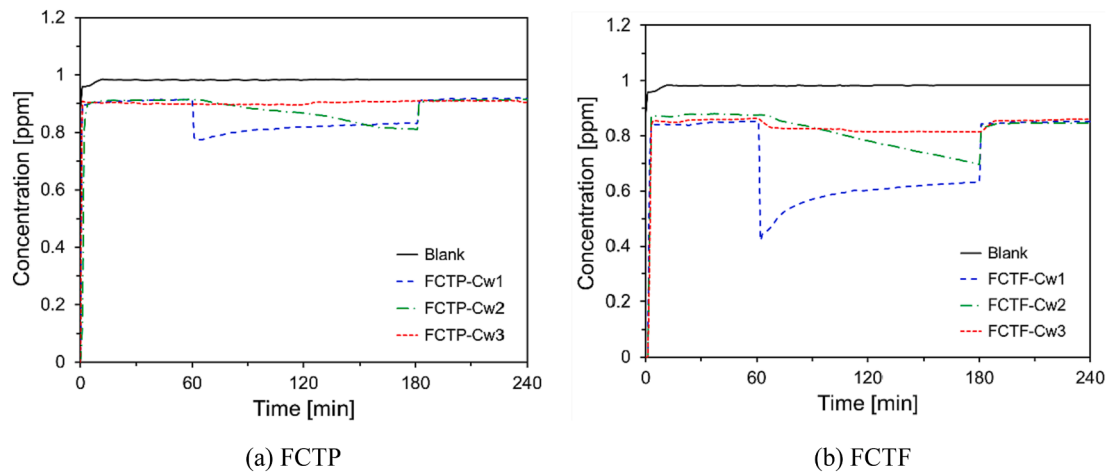
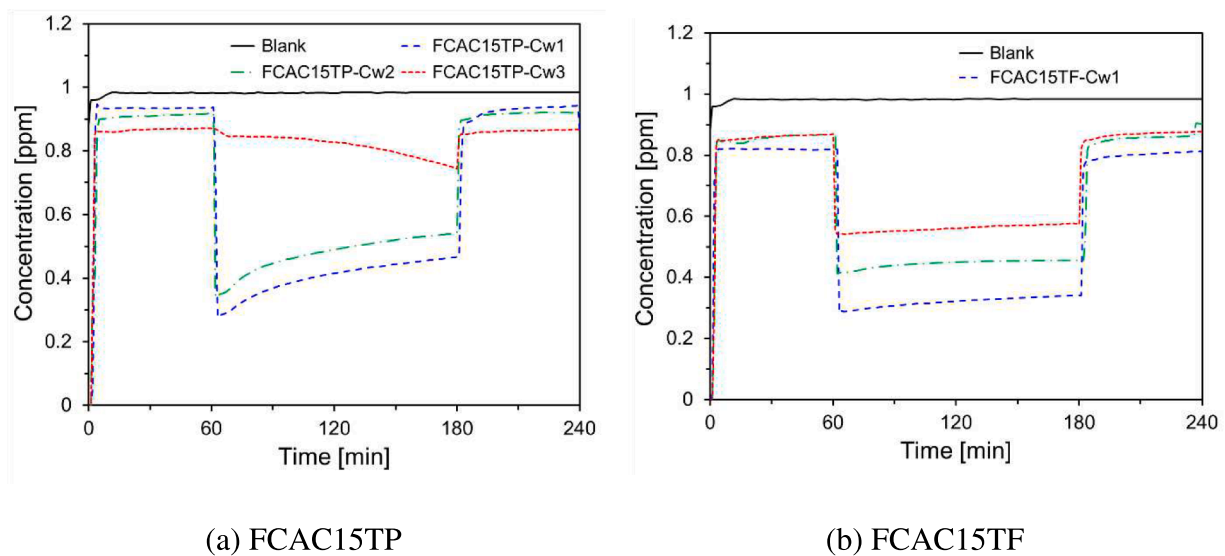


(a) CPTP



(b) CPTF

Fig. 10. NO_x reduction test results of CPTP and CPTF.

Fig. 11. NO_x reduction test results of FCTP and FCTF.Fig. 12. NO_x reduction test results of FCAC15TP and FCAC15TF.

for FCAC15TP-C_{W1} and 0.35 ppm for FCAC15TP-C_{W2}. FCTP-C_{W2} showed no change in NO_x concentration immediately after the UV light was turned on, but FCAC15TP-C_{W2} yielded a reduction in the NO_x concentration similar to the FCAC15TP-C_{W1} case. For FCAC15TP-C_{W3}, the NO_x concentration did not change immediately after turning on the UV light, but it decreased over time. This is a different result from that of FCTP-C_{W3}, which showed no change in NO_x concentration regardless of the onset of UV light. Fig. 8 shows that AC increases the reaction area of TP because it has a large specific surface area [32]. This improved the NO_x removal performance.

For FCAC15TF, the NO_x concentration also decreased owing to the use of AC. After turning on the UV light, the NO_x concentration decreased to approximately 0.25 ppm for FCAC15TF-C_{W1}, 0.4 ppm for FCAC15TF-C_{W2}, and 0.52 ppm for FCAC15TF-C_{W3}. The NO_x concentration decreased with the water content. FCAC15TF showed a reduction in NO_x concentration immediately after turning on the UV light, regardless of the wet conditions, and the NO_x concentration remained constant while the UV light was turned on.

Table 4 lists the NO_x removal amount of foam composites. η_{ads} , η_{NO} , η_{NO_2} , and η_{NO_x} were calculated using Eqs. (2)–(4). There was no correlation between the water content and η_{ads} for all specimens. The NO_x adsorption of the specimens was not affected by the water content.

Table 4

NO_x removal amount of foam composites.

Specimens	Water content, C _W (%)	NO _x removal amount (μmol)			
		η_{ads}	η_{NO}	η_{NO_2}	η_{NO_x}
FCTP	0	0.66	3.19	0.27	3.58
	16.52	0.80	2.37	0.19	2.98
	34.81	0.59	1.29	0.03	1.85
FCAC15TP	0	1.31	7.08	0.55	7.84
	30.19	1.10	3.48	0.07	4.51
	57.15	1.26	2.88	0.04	4.10
FCTF	0	0.75	10.15	0.78	10.10
	8.30	0.98	8.30	1.97	7.24
	21.21	1.09	2.90	0.27	3.70
FCAC15TF	0	1.52	11.62	0.87	12.26
	16.27	1.29	9.26	0.47	10.07
	32.68	1.27	7.18	0.17	8.21

Conversely, η_{NO} , η_{NO_2} , and η_{NO_x} exhibited decreasing tendencies as a function of the water content in all specimens. For FCTP, η_{NO_x} decreased from 3.58 to 2.98 μmol, and to 1.85 μmol according to the water condition. While there was a minor change in NO_x concentration in the case of FCTP-C_{W3} as seen in Fig. 11, the calculated η_{NO_x} was approximately

50 % of its value in the case of the C_{W1} condition.

For FCAC15TP that contained AC, η_{NO_x} was found to be equal to 7.84 μmol in the C_{W1} condition, 4.51 μmol in the C_{W2} condition, and 4.10 μmol in the C_{W3} condition. Although the water content of the C_{W3} condition was approximately twice as high as that of the C_{W2} condition, the difference in η_{NO_x} was only 10 %. Based on this, the NO_x removal performance is expected to decrease as the water content of the specimen increases, but it will be maintained constant after it reaches a certain level.

For FPTF, η_{NO_x} also decreased as the water content increased. η_{NO_x} was found to be equal to 10.10, 7.24, and 3.70 μmol in the C_{W1} , C_{W2} , and C_{W3} conditions, respectively. In the fully saturated condition, η_{NO_x} decreased to an approximate level of 35 % in relation to its value in the dry condition. The NO_x removal performance decreased further in relation to that of FCTP for which the NO_x removal performance decreased by approximately 50 % in the fully saturated condition. The η_{NO_x} value of FPTF- C_{W1} (10.10 μmol) was approximately three times higher than that of FCTP- C_{W1} (3.58 μmol). Therefore, the NO_x removal amount decreased further when it was compared in terms of the ratio between η_{NO_x} value of FPTF- C_{W1} and η_{NO_x} value of FCTP- C_{W1} . However, when the values were compared, the NO_x removal amount of FCTF- C_{W3} (3.70 μmol) was approximately twice as high as that of FCTP- C_{W3} (1.85 μmol). For FCTF, η_{NO} decreased as the water content increased, but η_{NO_2} was maximized in the C_{W2} condition.

FCAC15TF yielded the highest NO_x removal performance. The values of η_{NO_x} were found to be 12.26, 10.07, and 8.21 μmol in the C_{W1} , C_{W2} , and C_{W3} conditions, respectively. Although η_{NO_x} also decreased according to the water content, the decrements were smaller than those of other specimens. The value of η_{NO_x} in the C_{W3} condition was approximately 67 % of that in the C_{W1} condition. It was found to be higher than that of other specimens with the exception of FPTF- C_{W1} .

Construction materials, such as blocks and panels, are exposed to the atmosphere, but they mostly exist in the partially saturated conditions when it rains because some of the pores are saturated. Therefore, actual structures exist in the partially saturated conditions rather than in dry conditions. FCAC15TF, which has high NO_x removal performance in the C_{W2} condition, will be effectively used for NO_x reduction.

4. Conclusions

This study investigated the NO_x removal performance of the foam composites coated with the TF produced by the electrospinning process. The microstructures of the prepared specimens were analyzed using SEM, and the NO_x removal performance was evaluated in three saturated conditions based on the ISO 22197-1 standard. The AC was added to investigate the influence of the porosity of the foam composites, and the results were compared with the experimental results of the foam composites mixed with TP. The results can be summarized as follows:

1. A precursor solution was prepared using PVP polymer, EtOH, ACAC, and TTIP, and TF was produced based on the electrospinning process. The produced TiO_2 had a diameter of 200 nm, and anatase peaks were mainly observed.
2. Inorganic coating materials were prepared for the attachment of TFs to the surfaces of the foam composites. The coating materials and TFs were mixed, and then, they were attached to the surfaces of the foam composites. SEM image analysis confirmed that TP was evenly distributed on the foam composite surface.
3. The results of the NO_x removal evaluation test revealed that the NO_x removal performance of the foam composites coated with TF was improved in comparison to those of the foam composites mixed with TP. This is because the reaction area with the gas in the atmosphere increased owing to the large specific surface area of TFs on the specimen surfaces.
4. AC was found to improve the NO_x removal performance of TiO_2 , and FCAC15TF yielded the highest NO_x removal performance.
5. As the water content of the foam composites increased, the NO_x removal performance decreased. When AC was added, the NO_x removal performance in the saturated condition was found to be relatively high.

CRediT authorship contribution statement

Sung-Won Yoo: Writing – original draft, Formal analysis, Investigation. **Jung-Woo Lee:** Methodology. **Byoungsun Park:** Validation, Formal analysis, Conceptualization. **Young Cheol Choi:** Conceptualization, Resources, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

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.

Data availability

Data will be made available on request.

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