



A silica aerogel synthesized from olivine and its application as a photocatalytic support

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HIGHLIGHTS

- Silica aerogel is synthesized from olivine via ambient pressure drying.
- Heat treatment of silica aerogel at 500 °C increase the pore size and pore volume significantly.
- The crystal size of anatase formed on the aerogel substrate is around 12 nm.
- The photocatalytic efficiency of silica aerogel-TiO₂ composite is higher than that of pure P25.

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ABSTRACT

This study investigates the performance of a silica aerogel-based air purifying coating to functionalize building materials. The air-purifying function comes from an increased photocatalytic activity when the photocatalyst is supported on a silica network with a large specific surface area like silica aerogels. In this study, silica aerogel was first synthesized with a low energy-consumption method from olivine via ambient pressure drying and was applied as a support to load photocatalytic anatase crystals. The silica aerogel production includes sol-gel synthesis, ion-exchange, surface modification and ambient pressure drying. The produced silica aerogel obtained a high specific surface area (694 m²/g) and pore volume (2.99 cm³/g), with a uniform pore size distribution and mesoporous structure. Titania was loaded onto the prepared silica aerogel through a precipitation method. The resulting samples were characterized by measuring the conversion efficiency to oxidize nitric oxide under UV-light irradiation, nitrogen physisorption and FTIR. The silica aerogel coating with titania crystals had a photocatalytic activity of 99.6%, showing it to be a promising photocatalyst in the built environment.

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1. Introduction

Air pollution in large urban cities is becoming a big threat to human health, especially for the harmful gases such as nitrogen oxides (NO_x). The reduction of the concentration of these pollutants with the use of photocatalytic coatings on roads and buildings has been paid much attention [1–4]. Generally, semiconductors like Titanium oxide (TiO₂) can have this effective photocatalytic function and can be applied for air purification. Recently it has been shown that the titania with the combination of a silica substrate obtained higher photocatalytic efficiency and cost-effectiveness [5–7]. However, the silica applied is normally random porous silica that can limit the performance of titania since they cannot spread evenly on the silica substrate.

Silica aerogel is an ultra-light inorganic material that contains above 90% porosity filled with air. Silica aerogels contain an ultra-low density (0.03–0.2 g/cm³), high specific surface area (500–900 m²/g) and ultra-high porosity (90–99%). Due to these properties of aerogels, many researchers have synthesized different kinds of silica aerogels and applied them as thermal insulation [8–11], catalytic supports [12,13] and absorbent of pollutants [14,15]. However, the industrial silica aerogels are mostly produced from organic silica sources like tetrathoxysilane (TEOS) and methyltrimethoxysilane (MTMS), through supercritical drying [16]. These processes are energy intensive and obtain a high carbon footprint [17]. Therefore, it is not suitable for commercialized silica aerogel to apply as a silica substrate. Hence, a sustainable and low energy consumption method to produce silica aerogel would be a more desirable way to produce silica aerogel and used as a green and cost-effective support for catalysts.

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In the last few years, researchers developed several methods to produce silica aerogel from alternative silica sources, like kaolin [18] and fly ash [19]. However, all these methods include a calcination process that can increase the carbon footprint and energy consumption. Recently a novel nano-silica was produced from olivine at low temperatures (50–90 °C) [20,21]. Olivine silica is produced by the dissolution of olivine in acid and shows advantages in terms of lower CO₂ footprint, energy consumption and costs [22]. In this research, olivine silica is prepared at 50 °C and obtains a silica purity higher than 99% with SSA_{BET} between 100 and 400 m²/g, indicating a fast reaction with sodium hydroxide solution and a pure water glass formation. Thus, olivine silica has great potential to be a sustainable silica source in the production of silica aerogel while the total energy consumption is lower. In terms of drying procedure, ambient pressure drying was applied in this study due to the lower pressure and temperature that used compared to supercritical drying [16]. This drying method includes a surface modification process that transforms the surface –OH group on silica gel surface to –CH₃ group with TMCS and heptane as an agent. Therefore, with a ‘spring back’ effect the silica gel can re-expand the volume under ambient pressure drying and lower the density and increase the porosity of the final silica aerogel.

Thanks to the large pore volume and porosity of silica aerogel, it is promising to apply silica aerogel as a support to load a catalyst like photocatalytic titania. Several researchers have investigated the possibility of applying TiO₂-SiO₂ composite for a better catalytic efficiency during the last decade. Zhang et al. [23] have synthesized a TiO₂-SiO₂ aerogel nanocomposite absorbent using sol-gel method and investigated the photocatalytic degradation on automobile exhaust. It was shown to be effective due to the high surface area and big average pore size. Wang et al. [24] have investigated the photocatalytic activity of TiO₂ supported SiO₂-Al₂O₃ aerogels from fly ash. It was shown that the composite had higher photocatalytic activity for dibutyl phthalate degradation than that of pure TiO₂. Liu et al. [25] studied WxTiO₂ nanoparticles on silica aerogel with a high absorptivity and photocatalytic activity. The nanocomposite was highly efficient in removing RhB from water and could be recycled many times. Zu et al. [26] have invented a chemical liquid deposition method to prepare a silica-titania composite aerogel as a photocatalyst. It was demonstrated the small particle size, high SSA, and enhanced crystallinity after heat treatment at 600 °C contributed to the excellent photocatalytic property of the silica-titania composite aerogel. Cheng et al. [27] have prepared SiO₂-TiO₂ composite aerogel via ambient pressure drying and tested the photocatalytic performance. The photocatalytic performance was evaluated by degradation of methylene blue and showed promising results. Therefore, silica aerogel is an emerging candidate for photocatalytic support for many nano-sized catalysts.

However, most of the studies mentioned above rarely include thermal treatment of the silica aerogel that can increase the pore size and pore volume significantly. In this study, it is found that with a thermal treatment at 500 °C, the pore size increased significantly and pore volume nearly doubled. As previous research suggested, the crystal size of well-prepared anatase (ranging from 10 to 14 nm) can be smaller than the majority of the pore sizes in the thermally treated silica aerogel (15–20 nm) [6]. Therefore, it is possible to apply the aerogel as a catalyst support to make a great spread of the titania on and inside the aerogel for a high photocatalytic activity. Therefore, in this research, silica aerogel was first synthesized from olivine via ambient pressure drying. The modified silica aerogel is thermal treated at 500 °C for 3 h. Then the modified silica aerogel was applied as a photocatalytic support to load titania and the photocatalytic efficiency of the silica aerogel-TiO₂ coating was measured. Furthermore Fourier-transform infrared spectroscopy (FTIR) and nitrogen physisorption were used to

analyze the microstructure of the resulting silica aerogel-TiO₂ composite coating.

2. Methodology

2.1. Materials

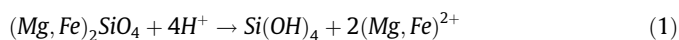
Olivine used in this research was from Norway supplied by Eurogrip (GL70). Table 1 lists the oxides composition of GL70 measured by X-ray fluorescence (XRF). The loss on ignition and the olivine content are also shown in Table 1.

Sodium hydroxide pellets (NaOH, VWR), Ethanol absolute (CH₃CH₂OH, 100%, VWR), n-Heptane (C₇H₁₆, Analytic grade, Biosolve), Ammonia solution (NH₃·H₂O, 5 N, Sigma-Aldrich), Trimethylchlorosilane (C₃H₉SiCl, >99%, Sigma-Aldrich) and Amberlyst 15 hydrogen form (Strongly acidic cation exchange resin, Sigma-Aldrich) were used to prepare silica aerogel from olivine GL-70. Olivine silica was prepared according to our previous research [28] and its chemical composition is shown in Table 1. Titanium (IV) isopropoxide 97% (Sigma-Aldrich) was used as the precursor to produce the titania monomer. Commercial titania P25 was used as a reference to compare the performance of titania-aerogel composite sample.

2.2. Methods

2.2.1. Preparation of silica aerogel from olivine

Silica was first prepared by the dissolution of olivine in sulfuric acid. The reaction of the silica extraction was proceeded as follows:



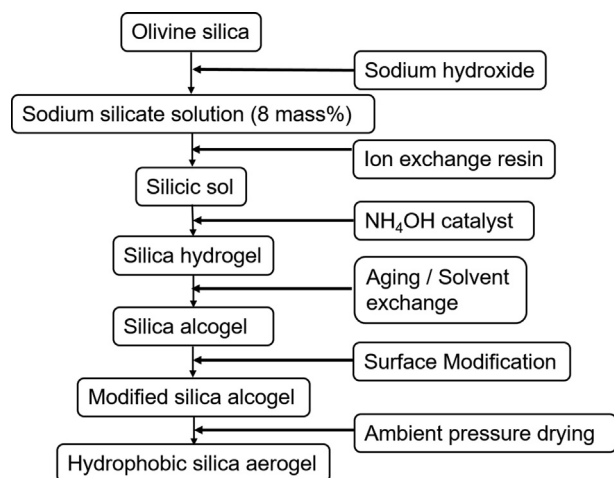
The extraction of silica from olivine was carried out at 50 °C with an exothermal process [22]. Therefore, the silica can be produced at a lower temperature, with lower energy consumption compared to other silica production processes. Water glass was formed from the reaction of sodium hydroxide and the olivine silica.

The primary procedures for the preparation of silica aerogel via ambient pressure drying include ion-exchange, network strengthening, solvent exchange and surface modification. For the ion-exchange, the as-prepared water glass from olivine silica was passed through Amberlyst 15 resin to obtain the silicic acid with a pH around 2.0–3.0. Then the pH of the silicic acid was adjusted to 4.5–6.0 by adding 0.5 M ammonium hydroxide to form the silica hydrogel. Aging times of 36 and 48 h were chosen to strengthen the network of the silica hydrogel. For the solvent exchange, ethanol and n-heptane with low surface tension were used to lower the surface tension of the pore liquid of silica hydrogel. The surface tension can be reduced through stepwise solvent exchange and hence prevent capillary pressure from damaging the network of silica aerogel during ambient pressure drying. Ethanol and n-heptane were used to exchange water in hydrogel pores and each solvent was exchanged for two days. For the surface modification, the hydroxyl groups of the aerogel can be replaced by non-polar silyl groups through the use of trimethylchlorosilane (TMCS) and n-heptane as solvent. When drying a hydrophobic gel, the skeleton of the silica network is barely influenced by the surface tension of water, thus avoiding the collapse of the pores of the aerogel. Furthermore, the ‘spring back’ effect further lowers the density of the silica aerogel due to inert –CH₃ groups attaching on the surface of the gel. During the full evaporation of the pore liquid, the silica aerogel was bounce back and increased the volume of the aerogel. The schematic process of the projected silica aerogel production is presented in Fig. 1.

Table 1

Composition of GL-70 from Norway and olivine silica.

Composition	MgO	Fe ₂ O ₃	SiO ₂	Cr ₂ O ₃	Al ₂ O ₃	NiO	MnO	CaO	LOI ^a	Olivine
GL-70	49.3	7.32	41.4	0.31	0.46	0.32	0.09	0.15	0.59	88.9
Olivine silica	0.03	0.02	99.8	b	b	b	b	0.03	b	b

^aLoss on ignition.^bNot detected.**Fig. 1.** Schematic process of silica aerogel production from olivine silica.

2.2.2. Preparation of titania-silica aerogel composite

The silica aerogel was first calcined at 500 °C for 4 h to remove the —CH₃ groups on the surface of silica. Subsequently, 1 g of silica aerogel was weighed and then milled with a mortar. Then silica aerogel was dispersed in a 500 mL ethanol absolute solution and the pH was adjusted to 3–4 by adding small amounts of sulfuric acid in order to have a slower hydrolysis reaction and opposite charge between the silica and formed titania. The molar ratio of titania and silica aerogel was kept at 1:1, which was determined according to our previous study [6]. Afterwards, 4.16 g TP (Titanium isopropoxide) was added into the solution quickly to avoid any contact with moist air. Then water was slowly added during 12 h by using a syringe pump (Instrument model Harvard Apparatus Pump 11 Elite) until the water content of the dispersion medium reached 2.5 vol%. After the synthesis of the composite, the resulting sample was filtered and washed 2 times with 100 mL ethanol and 4 times with 100 mL distilled water. Lastly, the sample was dried overnight at 105 °C and then calcined at 300 °C for 3 h. The illustration of the titania doped silica aerogel process is shown in Fig. 2.

2.2.3. Characterization methods

The as-prepared silica aerogel-TiO₂ composite was coated on a glass plate with the size of 100 * 200 * 1 mm. In specific, 1 g of silica aerogel-TiO₂ composite powder was dispersed in 30 mL distilled water. Afterwards, the suspension was coated on the glass plate and dried at room temperature overnight.

Finally, the coated glass plate was used for the photocatalytic test. The resulting photocatalytic properties of silica aerogel-titania composites were evaluated by testing their photocatalytic conversion of NO under UV-light using the ISO 22197-1 standard for comparative purpose. The setup for these measurements is shown in Fig. 3.

Chemical bonds in the silica aerogel were detected by Fourier-transform infrared spectroscopy (FTIR), which was performed with a Varian 3100 instrument with the wavenumbers ranging from

4000 to 400 cm⁻¹ at a resolution of 2 cm⁻¹. Nitrogen physisorption was performed with a Tristar II equipment at 77 K using liquid nitrogen to determine the specific surface area using the BET theory and pore size distribution using the BJH theory.

The size of the anatase crystals can be calculated with the Scherrer equation:

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where L is the crystal size (m), K is the particle shape factor (0.89 was used), λ wavelength of the used X-ray, β width of a peak at half the maximum intensity in radians and θ corresponding peak angle. An approximation on the average size of the measured crystal structure can be calculated using this equation because the width of the XRD peaks depends on this value if the material consists of nano-sized crystals.

3. Results and discussion

3.1. Properties of olivine silica aerogel

The density and porosity of the prepared silica aerogel is shown in Table 2. All the silica aerogel obtained a porosity beyond 93.6% and density below 0.134 g/cm³. It can be observed that 48 h aging slightly increased the particle density of the silica aerogel. The reason behind this is that a longer aging time means a higher degree of poly-condensation between colloidal particles and hence a denser silica gel microstructure. The strength of the silica network increased, and could more easily resist the pressure caused by evaporation of the solvent, but with the sacrifice of an increase in density and decrease in porosity. Also, excessive aging reduces the permeability of the silica gel and make it difficult for the solvent exchange process to work properly. Therefore, a suitable aging time of 36 h is suggested in this study.

The pH of the silicic acid can also influence the density of the produced silica aerogel by changing the hydrolysis and condensation rates of the silicic sol. When the pH of the silicic sol is 4.5, the silica monomer concentration increases too fast and forms silicate nuclei rather than cross linking silica networks, leading to an increase in density. It is observed that a pH of 5.5 can balance the hydrolysis rate and condensation rates, which means condensation immediately follows hydrolysis of silicate and a uniform nanoporous structure can be formed. The silicate monomer concentration is low and favours to grow and form cross-linking silica particles. Therefore, the strength of the gel would increase and less shrinkage happened, leading to a lower density and higher porosity of silica aerogel.

The specific surface area and pore size distribution of the silica aerogel (pH 5.5, A36) is shown in Fig. 4. It can be seen from Fig. 4(a) that the isotherm of the aerogel shows a typical type IV isotherm with an obvious hysteresis. The hysteresis is caused by the narrow pore size distribution with most of the pores being around 8 nm as shown in Fig. 4(b). The specific surface area and pore volume of the aerogel is 694 m²/g and 2.99 cm³/g, respectively. After calcination at 500 °C for 4 h, the SSA of silica aerogel rises to 920 m²/g and pore

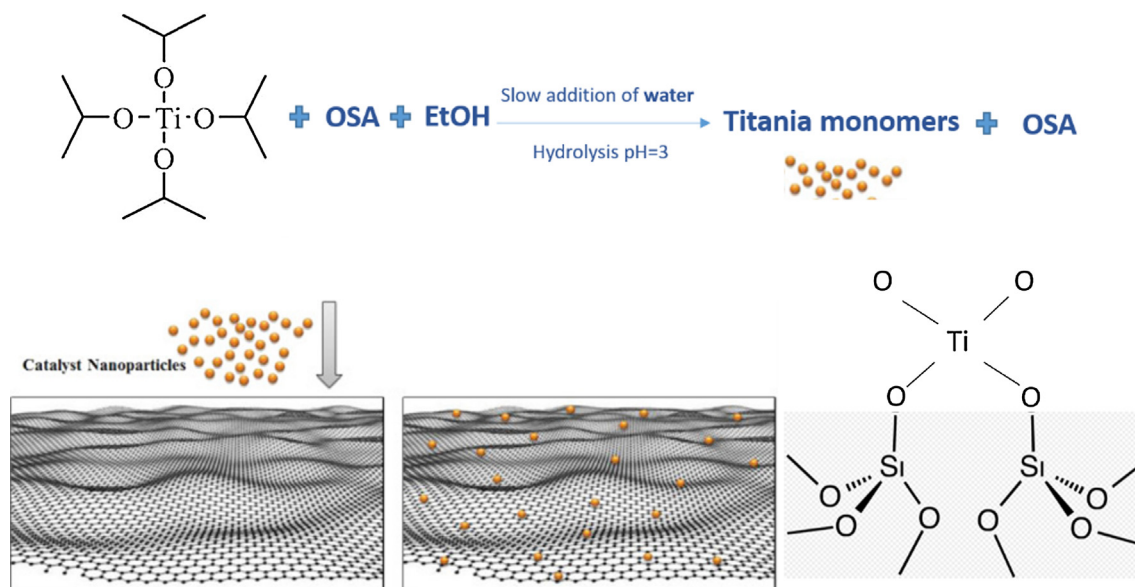


Fig 2. Illustration of the reaction process of titania doped olivine silica aerogel (OSA).

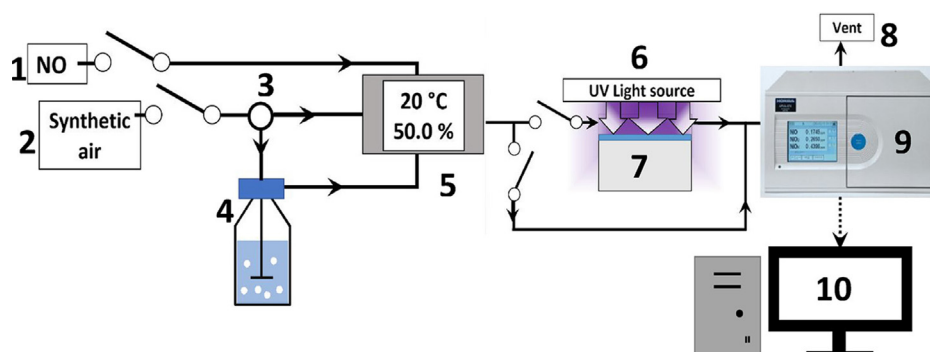


Fig 3. Schematic view of the PCO measurement setup: 1) NO gas source, 2) synthetic air source, 3) valve, 4) bottle containing water, 5) humidity and temperature sensor, 6) light source, 7) reactor, 8) air vent, 9) NO_x detector and 10) computer to control inflow of gasses and data collection (Permission from [6]).

Table 2
Particle density and porosity of olivine silica aerogel.

Density (g/cm ³)/porosity (%)	pH 4.5	pH 5.0	pH 5.5	pH 6.0
A36	0.134/93.6	0.124/94.1	0.0972/95.4	0.110/94.8
A48	0.138/93.8	0.128/94.3	0.105/95.0	0.125/94.0

volume to 5.30 cm³/g. The reason behind this result is that the calcination process makes the aerogel expand its pore size and coarsens the backbone of silica particles. The silica aerogel after heating to 500 °C has a larger pore size, which is around 18 nm, indicating a different pore structure and silica network. Also, the amount of absorbed nitrogen increases at a high relatively pressure, indicating a higher SSA and bigger pore size as well. A few researchers have also investigated the effect of pyrolysis on silica aerogel microstructure. He et al. [29] demonstrate the surface area reduced after thermal treatment at 500 °C, but with an increase in pore size of silica aerogel. Mariia Gordienko et al. simulated the structure of Si-F-R before and after pyrolysis, and determined that the particles within the aerogel would expand after heat treatment [30]. These properties are suitable for silica aerogel function as a catalytic support with the aim of a better spread of titania both around and inside the pores of silica aerogel.

3.2. Microstructure of titania-silica aerogel composite

The physisorption isotherm and pore size distribution before and after incorporation of titania are shown in Fig. 5. The hysteresis loop of the silica aerogel-titania composite is quite small compared to the pure silica aerogel, indicating a smaller pore size of the composite samples, as shown in Fig. 5(b). The pore size shrank to 10 nm and pore size distribution is broader than the sole silica aerogel. Moreover, the pore volume decreased significantly, which reduced from 4.99 cm³/g to 1.77 cm³/g. The thermally treated silica aerogel also contained a moderate amount of pores larger than 20 nm. However, these meso and macropores of modified silica aerogel disappeared after the titania doping. Therefore, it can be inferred from the nitrogen physisorption results that titania crystals are inside the pores of silica aerogel which makes the pore volume decrease significantly.

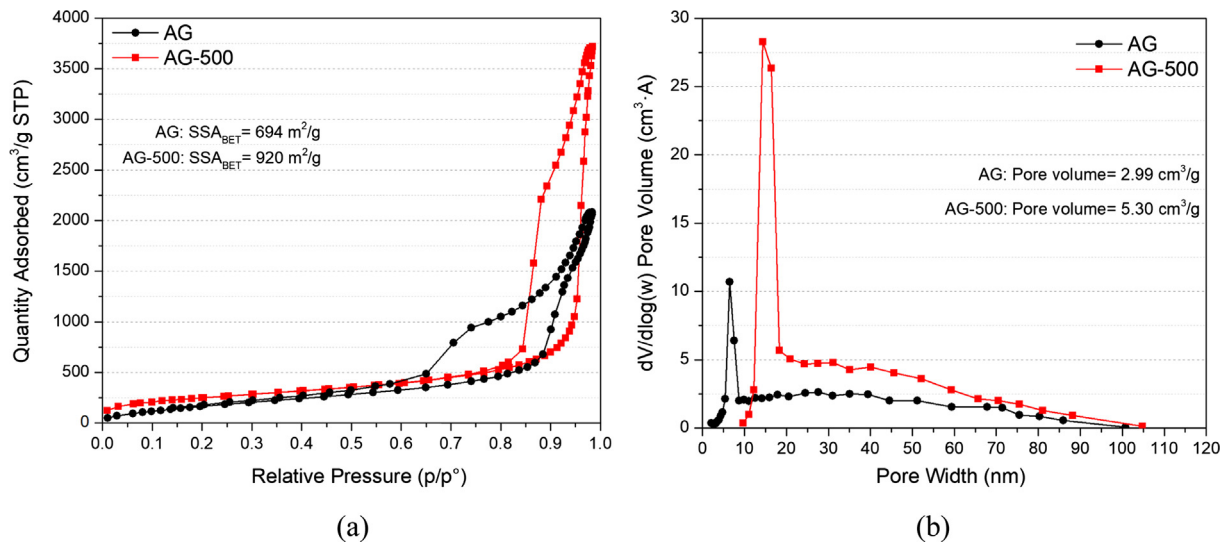


Fig 4. Physorption isotherm (a) and pore size distribution (b) of olivine silica aerogel before and after 500 °C calcination using BET and BJH methods.

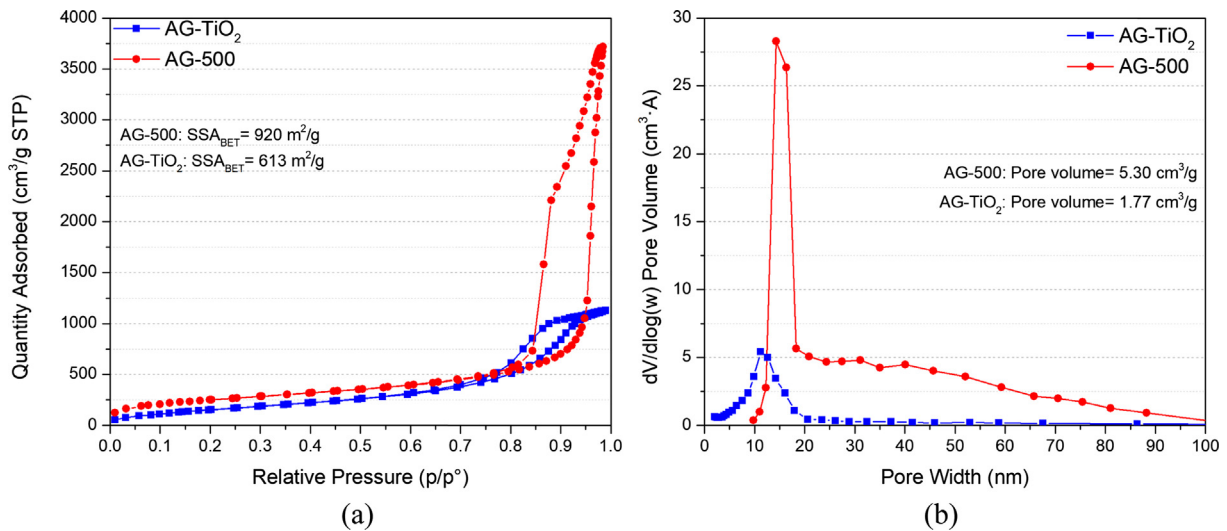


Fig 5. Physorption isotherm (a) and pore size distribution (b) of thermally modified silica aerogel before and after incorporation of titania.

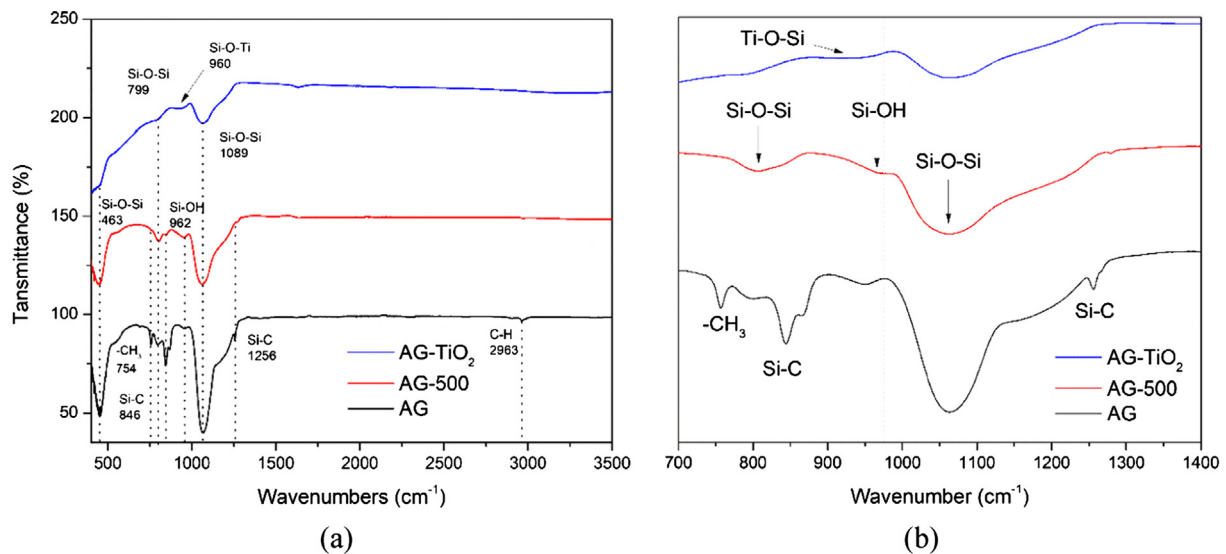


Fig 6. FTIR spectra of silica aerogel and silica-titania composite (a) 400–4000 cm^{-1} (b) 700–1400 cm^{-1} .

As can be observed in Fig. 5(a), the surface area of the silica aerogel-titania composite is very large, reaching $613 \text{ m}^2/\text{g}$. This high specific surface area is due to the substrate of silica aerogel, which can increase the absorptivity of pollutants and increase the activity of photocatalysts. Pure P25 has a surface area around $50 \text{ m}^2/\text{g}$. Therefore, the much higher surface area of silica aerogel-titania composite is an important factor that influence the degradation efficiency of NO and NO_x .

The FTIR spectra (Fig. 6) shows the $-\text{CH}_3$ groups are grafted on the surface of the original silica aerogel. After 500°C heat treatment, the $-\text{CH}_3$ groups disappear and $-\text{OH}$ groups are visible, which may be due to the moisture in the atmosphere forming the silanol bond. With the incorporation of titania, the Si-O-Ti bond is visible at 960 cm^{-1} , indicating a good chemical combination between silica aerogel and titania. The reason behind this is that the pH around 3–4 of the reacting solution leads to opposite charge between the silica aerogel and formed titania. Moreover, the pH value is lowered to 3–4 for the sake of a slower hydrolysis reaction of TP. According to a model proposed from [14], the ratio between the Ti-O-Si bond and Si-O-Si bond is around 0.059, indicating a moderate bonding between these two materials.

XRD was performed to observe the anatase crystals formed inside and around the silica aerogel as shown in Fig. 7. The calculated crystal size of the prepared anatase is around 12 nm. This size is below the average pore size of olivine silica aerogel (18 nm), which means the anatase crystals can be loaded into the mesopores of silica aerogel and chemically bonded to the silica network according to FTIR analysis. The broad peak around 29 degree is the indication of amorphous silica aerogel substrate.

3.3. PCO efficiency of the titania-silica composite

The degradation efficiency of the NO and NO_x gases by oxidation of silica aerogel- TiO_2 composite and reference sample P25 is shown in Fig. 8 and Table 3. The degradation of NO with P25 is 99.2%, which is almost the same as that of the coating using silica aerogel- TiO_2 composite (99.6%). However, the degradation of NO_x (which is the combination of NO and the intermediate NO_2) is higher with the silica aerogel composite. The overall conversion on the composite of NO_x is 93.6%, while only 57.8% for the reference P25. The higher conversion of NO and NO_x is due to the titania forming inside and around the silica aerogel, which fills the pores and as a result, some of the titania being spread evenly. This is confirmed by the nitrogen adsorption and FTIR test in the previous

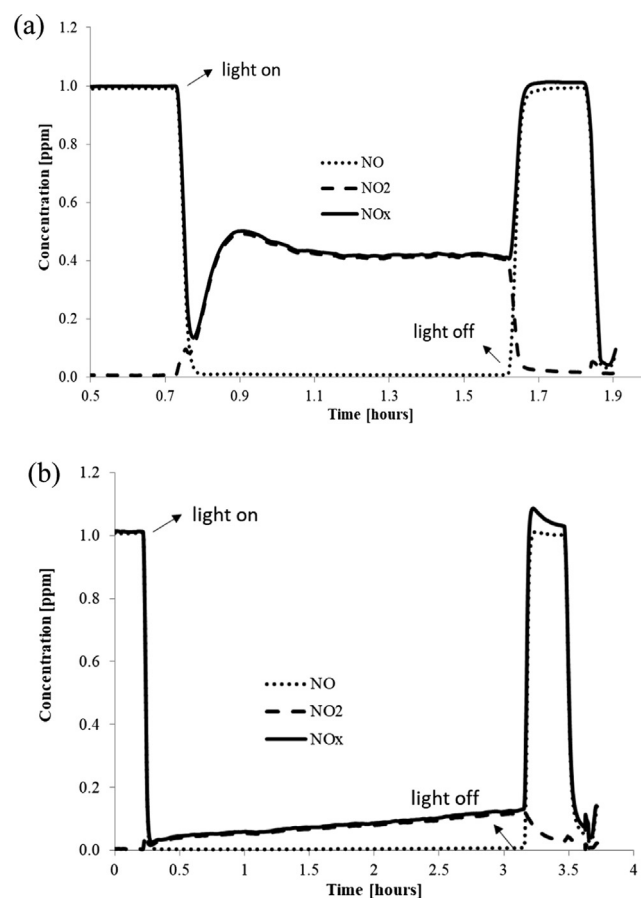


Fig. 8. Concentration of NO, NO_2 and NO_x in time, showing degradation due to conversion by titania. (a) Reference P25 (b) silica aerogel- TiO_2 composite.

Table 3

Degradation efficiency of NO and NO_x by P25 and silica aerogel- TiO_2 composite.

Group	Degradation of NO (%)	Degradation of NO_x (%)	Concentration of titania (g/m^2)
Pure titania P25	99.2	57.8	25
Aerogel- TiO_2	99.6	93.6	25

section. As the intermediate product NO_2 is significantly more dangerous than even NO, the silica aerogel- TiO_2 composite is a promising photocatalyst and can be applied on the surface of construction materials to improve the air quality.

4. Conclusions

This research shows that coating silica aerogel particles with titania can result in promising photocatalysts for air purifying. First, silica aerogel was successfully synthesized from olivine silica via ambient pressure drying. Next, the thermally treated silica aerogel was used as the photocatalytic support to improve the photocatalytic performance of titania. Finally, the new photocatalyst has been evaluated on its NO_x removal abating qualities. According to the results of this research, the following conclusions can be drawn:

- The pH of the silicic sol controls the hydrolysis and condensation speed of silicate. The optimal conditions for the preparation of high-porosity and low-density silica aerogel is pH 5.5 with an aging time of 36 h in this research.

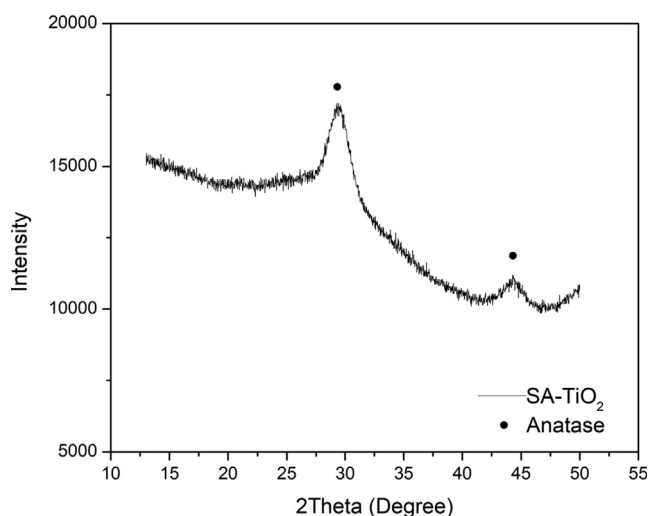


Fig. 7. XRD pattern of silica aerogel- TiO_2 composite.

- The specific surface area and pore volume of silica aerogel increases from 694 m²/g and 2.99 cm³/g to 920 m²/g and 5.3 cm³/g after heat treatment at 500 °C for 4 h. The reason of this phenomena may due to the coarsening of the silica aerogel 3D network and also the spring back effect caused by —CH₃ groups.
- Titania was loaded into the mesopores of silica aerogel by using a precipitation method. The specific surface area and pore size both decreased significantly after the titania doping. The crystal size of the prepared anatase in silica aerogel is around 12 nm, which is below the average pore size of the modified silica aerogel.
- The prepared silica aerogel-titania coating shows a higher conversion efficiency (99.6% for NO and 99.3% for NO_x) than the reference sample P25 (99.2% for NO and 57.8% for NO_x). Therefore, it is a promising alternative to the current photocatalysts for air purifying in built environment.

CRedit authorship contribution statement

Y.X. Chen: Conceptualization, Investigation, Methodology, Writing - original draft. **Y. Hendrix:** Conceptualization, Methodology, Writing - review & editing. **K. Schollbach:** Supervision, Writing - review & editing. **H.J.H. Brouwers:** Supervision, Project administration.

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.

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