

SYNTHESIS OF $\text{TiO}_2\text{-SiO}_2$ FROM TETRA-N-BUTYL ORTHOTITANATE AND TETRAETHYL ORTHOSILICATE BY THE SOL-GEL METHOD APPLIED AS A COATING ON THE SURFACE OF CERAMICS

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From the last years of the twentieth century, TiO_2 materials with a photocatalytic ability have been known for their use in many applications, such as decomposing toxic organic matter, bactericides, and self-cleaning agents. However, the TiO_2 coating is usually not durable when coated on the surface of ceramics. In this study, $\text{TiO}_2\text{-SiO}_2$ was synthesised from a TiO_2 sol and an SiO_2 sol that were calcined at 500 °C and 600 °C. Analytical methods, such as Fourier Transform Infrared Spectroscopy, X-Ray diffraction analysis, and Scanning Electron Microscopy, have been applied to test the properties of the formed $\text{TiO}_2\text{-SiO}_2$. The Fourier infrared spectrum analysis showed that the samples appeared to be -OH , Ti-O-Ti , Ti-O , Si-O-Si , and Ti-O-Si . The X-Ray diffraction pattern analysis showed that the formed crystalline components of $\text{TiO}_2\text{-SiO}_2$ were rutile and anatase. The results of the morphological analysis by scanning electron microscopy showed the appearance of characteristic crystalline forms of rutile and anatase. The formation of anatase crystals shows that the $\text{TiO}_2\text{-SiO}_2$ coating can be applied as a photocatalyst material. Besides, the formed Ti-O-Si , Si-O-Si bonds also promise to improve the bonding ability of the coating to the surface of ceramics materials, helping to improve the applicability of this type of material.

INTRODUCTION.

TiO_2 is a semiconductor that has long been used in many different fields [1-4]. TiO_2 usually has three polymorphs: anatase, brookite, and rutile. However, anatase and brookite usually convert to rutile at temperatures between 800 °C and 1040 °C [5-6]. An essential property of TiO_2 that is often mentioned is its photochemical ability. Many studies have shown that the photochemical ability of TiO_2 is due to the presence of anatase in the phase composition [7-8]. Anatase is commonly known for its photocatalytic properties under ultraviolet (UV) radiation [9]. When exposed to UV light, anatase will produce free electrons that will interact with oxygen and water in the air to produce free radicals. These free radicals are also the cause of what makes TiO_2 an antibacterial. Rutile is the most stable polymorph at all temperatures due to its lower free energy than anatase and brookite. Rutile is commonly used as an additive in manufacturing refractory materials and colour glazes for ceramics. Like anatase, rutile has also a photochemical ability [10]. However, the photocatalytic property of rutile under UV exposure is not as high as that of anatase [11].

Besides the photochemical ability, the TiO_2 coating also has a super hydrophilic effect. This effect can make the surface coated with TiO_2 self-cleaning. When used as a coating for glass, TiO_2 can help glass avoid reducing visibility when affected by rainwater. A TiO_2 - coated glass retains its transparent properties for light transmission and can self-sterilise and clean thanks to its photochemical and super-wetting ability. In addition to applications on glass, TiO_2 coatings can also be suitable for other surfaces, such as metals and ceramics. For metals, this coating can be used as protection from corrosion. A TiO_2 coating can give glazed ceramic products more antibacterial properties. It can also be applied in hospitals such as sterile rooms, operating rooms, etc. From here, the great potential of TiO_2 in coating applications to improve the surface performance of many materials can be seen. However, the TiO_2 sub-layer often has poor mechanical strength and is easily peels off after a period of use. TiO_2 is often combined with other chemical compounds to improve this defect to form coatings. Depending on the type of surface to be coated, the chemical compounds used can be SiO_2 , Al_2O_3 , Fe_2O_3 , Silane, MgO , etc. SiO_2 is a chemical compound often combined with TiO_2 as a coating on glass and ceramic surfaces [12-14].

However, TiO₂ and SiO₂ are two oxides with high melting points (1877 °C for TiO₂ [15] and 1713 °C for SiO₂ [16]). Therefore, the sintering temperature required to combine TiO₂ and SiO₂ is above 1540 °C [17]. Sintering at high temperatures will consume energy and increase the production costs. Sintering at high temperatures also changes TiO₂ to a rutile polymorph, reducing its photochemical effect. Therefore, the sol-gel method is the standard method to combine TiO₂ and SiO₂. SiO₂-TiO₂ is synthesised by the sol-gel method with a low calcination temperature and still ensures the photochemical properties of TiO₂ [18, 19]. In addition, the synthesis of TiO₂-SiO₂ at low temperatures also means this material can still be applied as a coating for some materials with low melting temperatures, such as glass and metal [20, 21]. In applying the sol-gel method, M. Momeni et al. prepared TiO₂-SiO₂ at 400 °C, 500 °C, and 600 °C. TiO₂ was formed by this method, with anatase as the main mineral component. Similarly, W. Cheng et al. also fabricated TiO₂-SiO₂ at 500 °C. The results showed that TiO₂ formed in the presence of rutile and anatase minerals. The common point of the above studies shows that the wear resistance of TiO₂ increases when combined with SiO₂. However, most studies have not clarified the process of TiO₂-SiO₂ formation in each heat processing step.

In this study, the influence of the composition on the properties of TiO₂-SiO₂ synthesised by the sol-gel method was investigated. The raw materials for the synthesis of TiO₂-SiO₂ were used Tetra-n-butyl orthotitanate and Tetraethyl orthosilicate. In addition, the synthesis of TiO₂-SiO₂ through the drying and calcination stages was clarified by Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy.

EXPERIMENTAL

The raw materials used to make TiO₂-SiO₂ include Tetraethyl orthosilicate (TEOS-Si(OC₂H₅)₄), Tetra-n-butyl orthotitanate (TBT-Ti(OCH(CH₃)₂)₄), Ethanol (E-C₂H₅OH), and nitric acid (NA-HNO₃). All the ingredients are sourced from Merck. The TiO₂ sol was prepared by mixing and stirring TBT and E in a TBT/E volume ratio of 4.5/23 at 35 °C for 30 mins. The mixed solution was added to water and stirred for 30 mins. The solution/water volumetric ratio was 1/3.375. Finally, the solution was supplemented with NA and stirred for

120 mins to form a TiO₂ sol. The SiO₂ sol was constructed similarly to the TiO₂ sol with a TEOS/E volume ratio of 0.5/5.75. The TiO₂ and SiO₂ sol were mixed according to the volume ratios shown in Table 1. The mixed solutions were dried at 100 °C. After drying, the mixture was sintered at 500 °C and 600 °C. The synthesis diagram of the samples is shown in Figure 1.

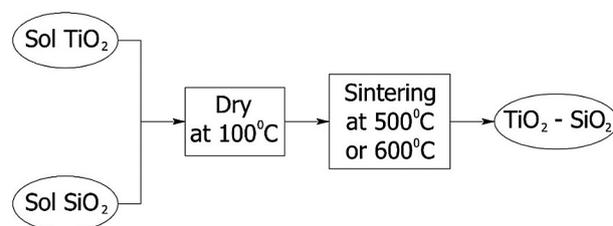


Figure 1. Synthesis diagram of the samples.

The properties and microstructure of the TiO₂-SiO₂ products were tested using Fourier Transform Infrared Spectroscopy (FTIR), mineral composition by X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM).

A Bruker-Tensor 37 FT-IR analyser was used, with an aperture of 4 mm, a frequency of 10 kHz, scan ranges from 4000-300 cm⁻¹, and a scanning step of 0.96 cm⁻¹.

A D8 Advance model XRD analyser was used. The analytical sample was put into the machine with a mass of 1g for one analysis. The voltage difference is 40 kV. The amperage is 40mA. The radiation used is Kα = 1.54184Å. The 2θ scanning angle is 20–80°. The scan step is 0.02°. Besides determining the phase composition, the XRD method is also used to calculate the number of crystals formed. The number of formed crystals was calculated according to the formula:

$$\% \text{ Crys} = \frac{S_{\text{crys}}}{\sum S_{\text{crys}}} \quad (1)$$

where % Crys is the crystal content, S_{crys} is the total area on the XRD spectrum of the crystal to be determined, ΣS_{crys} is the total crystal area over the entire XRD spectrum. The area parameters are calculated based on the Origin software.

A Hitachi S4800 SEM analyser was used. The voltage is 10 kV. The shooting mode is SE(M). The magnification is 10,000 times.

RESULTS AND DISCUSSION

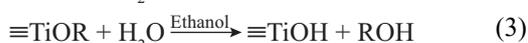
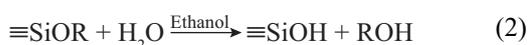
The samples were analysed by Fourier Transform Infrared Spectroscopy after heat treatment at 100, 500, and 600 °C. The vibrations of the functional groups are presented in Table 2. The results of the FT-IR spectrum in Figures 2-4 showed three main bands.

The range of vibrations was characteristic of the -OH bond. In all the samples, a vibration characteristic for the -OH functional group was seen at wavenumber

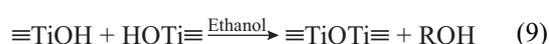
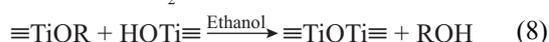
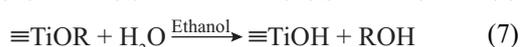
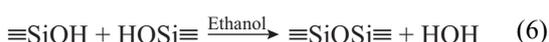
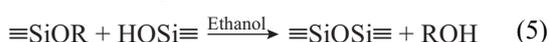
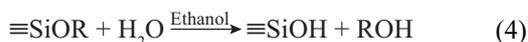
Table 1. The mixing ingredients (%).

Samples	Volume ratio (%)	
	Sol TiO ₂	Sol SiO ₂
T100	100	0
T90	90	10
T80	80	20

1636 cm⁻¹. This was the vibration of the physical water absorbed in the sample. In addition, in the samples after drying at 100 °C, the -OH functional group was also shown in the stretch vibration range from 3400 to 3200 cm⁻¹. This vibration was specific to the -OH group in the ≡Si-OH and ≡Ti-OH bonds. This result proved the formation of the TiO₂ sol and SiO₂ sol after the synthesis according to the reaction mechanism in Reactions 2 and 3. With the samples dried at a temperature of 100 °C, vibrations also appeared at positions 1396 cm⁻¹ and 1372 cm⁻¹, which were the vibrations of the -CH₃ and C-H groups. The -CH₃ groups were the remaining functional groups after synthesising the TiO₂ and SiO₂ sol. The vibrations related to the Si-OH, ≡Ti-OH, and -CH₃ bonds would gradually disappear at the heating temperatures of 500 °C and 600 °C.



The range of the vibrations were related to the Si-O-Si, Ti-O-Ti, and Ti-O bonds. At wavenumber 1059 cm⁻¹, there was a vibration characteristic for the Si-O-Si bond. The vibration at 1059 cm⁻¹ appeared only in the FT-IR spectrum of the sample using the SiO₂ sol (Figure 3 and Figure 4). Similar to Si-O-Si, Ti-O-Ti and Ti-O also appeared at the characteristic vibration at 648-625 cm⁻¹ (Figure 3-5). These results showed that the Si-O-Si, Ti-O-Ti, and Ti-O bonds were formed during sol formation according to Reactions 4-6 and 7-9. These bonds still exist in the sample at the sintering temperatures of 500 °C and 600 °C.



The range of vibration was related to the Ti-O-Si bonding group. Besides forming Si-O-Si, Ti-O-Ti, and Ti-O bonds, the FT-IR spectrum of samples using the SiO₂ sol also showed Ti-O-Si bonds at wavenumber

Table 2. Absorption frequencies of the functional groups.

Wavenumber (cm ⁻¹)	Functional groups	Ref.
3400-3200	Si-OH, Ti-OH	[22]
1636	-OH	[22]
1396	R-CH ₃	[22]
1372	C-H	[22]
1059	Si-O-Si	[23]
928	Ti-O-Si	[23]
648-625	Ti-O-Ti, Ti-O	[23]

928 cm⁻¹. These bonds existed in all the samples heat treated at 100, 500 and 600 °C (Figure 3 and Figure 4).

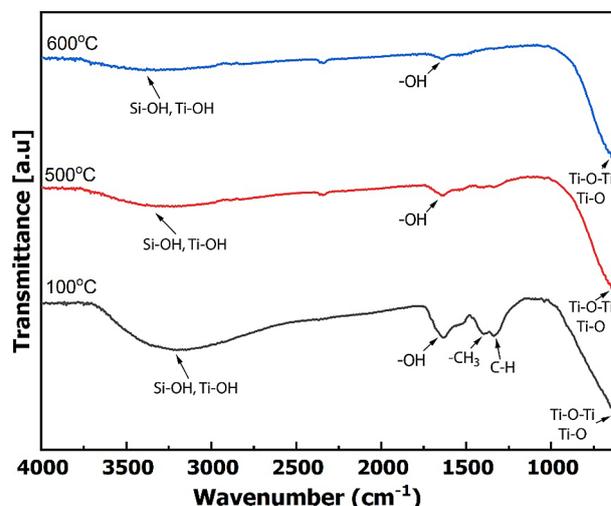


Figure 2. The transmittance spectrum of the T100 sample.

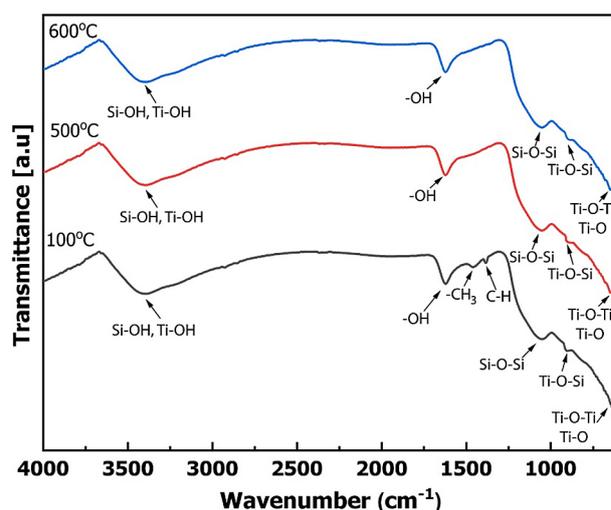


Figure 3. The transmittance spectrum of the T90 sample.

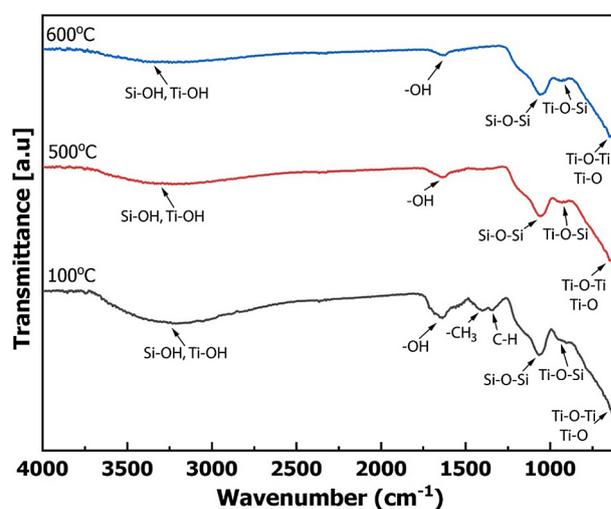
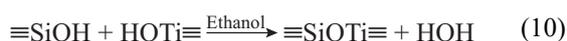


Figure 4. The transmittance spectrum of the T80 sample.

This result proved that the Ti–O–Si bond was formed right in the process of mixing the SiO₂ sol and TiO₂ sol (Reaction 10). This bond was not broken down, but remained in the samples at higher sintering temperatures. Usually, when applying a TiO₂ antibacterial layer on the surface of ceramic products, this coating is often lost after a period of use. The washout of the TiO₂ coating is because TiO₂ does not form a good bond with the ceramic bone. The Ti–O–Si bond on the FT-IR spectrum proved that the TiO₂-SiO₂ coating could adhere well to the ceramic bone and help increase the durability of the coating.



XRD patterns were used to observe the formation of crystals at different compositions and sintering temperatures. Figure 5 shows the XRD analysis results of samples T100, T90, and T80 at 500 °C and 600 °C. The results of Figure 5 show that the Ti–O–Ti, and Ti–O bonds indicated in the FT-IR spectrum were anatase and rutile crystals. The anatase crystals are characterised at diffraction sites 25.22°, 38.43°, 47.85°, 53.72°, and 62.63° [8, 24, 25]. The rutile crystals are characterised at diffraction sites 27.34°, 36.20°, 41.15°, 44.07°, and 54.86° [8, 25, 26].

TiO₂ usually has three polymorphs: anatase, brookite, and rutile. Anatase will convert to brookite at 800 °C, and brookite will convert to rutile at 1040 °C. However, anatase and brookite can also be converted to rutile under experimental conditions at approximately 600 °C [27]. Comparing the XRD patterns of the samples in Figure 5, it was found that the peaks representing the high-intensity rutile crystals did not use the TiO₂ sol (sample T100). This result showed that if the raw materials only used the TiO₂ sol, the rutile form would be dominant over anatase when the samples were sintered at 500 °C and 600 °C. In samples T90 and T80, the appearance of rutile peaks was not obvious anymore. Instead, there were peaks specific for anatase. As more

SiO₂ sol was used, the peaks characteristic for rutile became less frequent. This can be understood that the presence of SiO₂ prevents the transformation of anatase to rutile at the temperature range from 500 °C to 600 °C.

In addition, on the diffraction spectrum of samples T90 and T80, there was also a broad peak region from 23° to 28°. This diffraction region overlaps with the peak of anatase. This result proved that the Si–O–Si bond shown in the FT-IR spectrum was amorphous SiO₂. The presence of amorphous SiO₂ created the bonding ability of the TiO₂-SiO₂ coating on the ceramic bone. In addition, the amorphous SiO₂ also interfered with the conversion of TiO₂ crystals from anatase to rutile crystals. Thus, increasing the photocatalytic ability for TiO-SiO₂ coating [28].

The content of the formed anatase and rutile crystals was also calculated through Equation 1. Figure 6 was the result of calculating the content of the crystals in the samples by calculating their area on the XRD diffraction patterns.

The calculation results of the crystal composition confirmed the statements on the XRD patterns. The results showed that when increasing the sintering temperature from 500 °C to 600 °C, conversion from anatase to rutile would take place [29]. In addition, when increasing the content of the SiO₂ sol in the compound, SiO₂ would act as an inhibitor of the conversion of anatase to rutile. As a result, samples using SiO₂ had a superior anatase crystal composition compared to the rutile crystal composition. This result showed that the presence of SiO₂ helped the TiO₂ coating adhere well to the ceramic surface and increased the anatase content, which increased the photocatalytic ability of the coating. The crystal formation was also observed through scanning electron microscopy. In previous studies, the authors showed that rutile crystals have a hexagonal polyhedron [30] and anatase crystals have a spherical shape [31]. The SEM analysis results in Figure 7 show the appearance of characteristic crystalline forms of rutile and anatase crystals in all the samples. This result

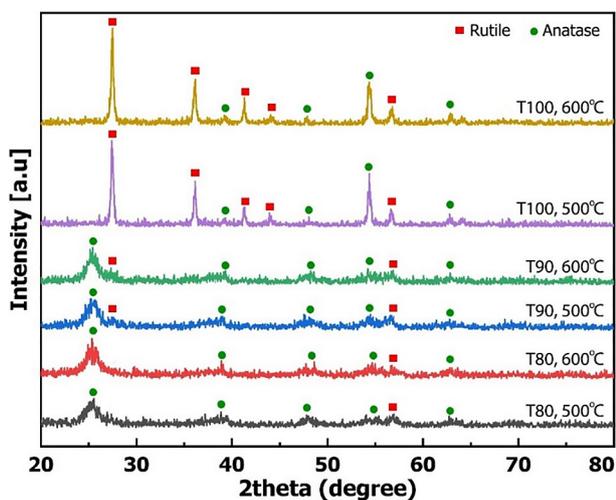


Figure 5. The XRD patterns of the samples.

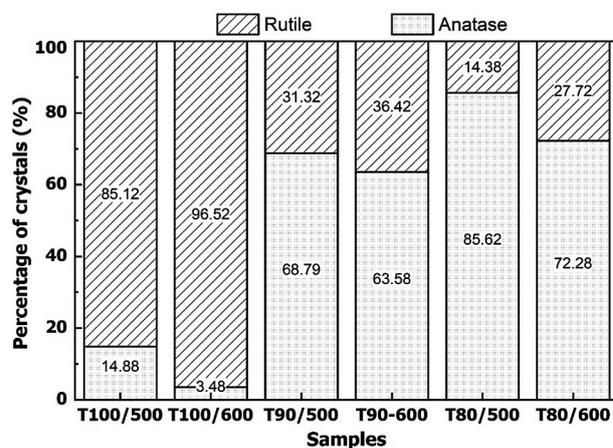


Figure 6. The crystalline composition of the samples.

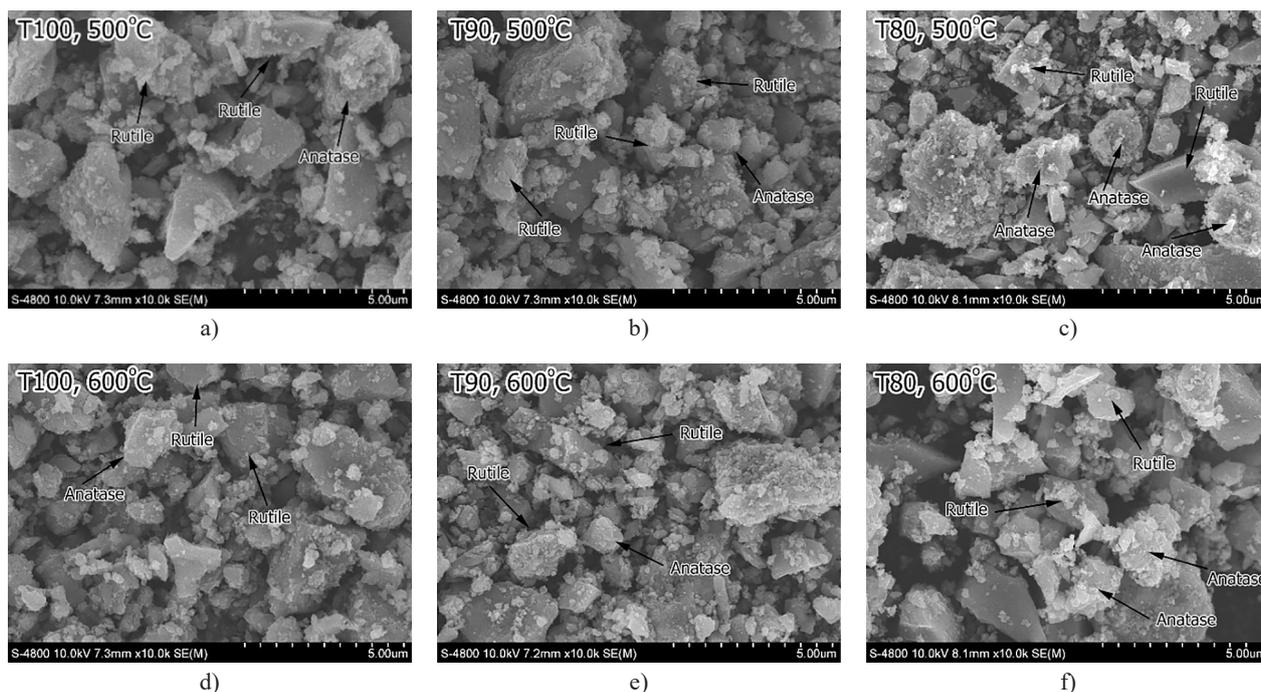


Figure 7. The SEM images of samples.

again confirmed the formation of these two crystal forms when sintering the TiO_2 sol and SiO_2 sol at 500 °C and 600 °C. Therefore, the TiO_2 - SiO_2 coating can be applied as an antibacterial coating for ceramic products.

CONCLUSION

From the results of Fourier Transform Infrared Spectroscopy, X-Ray diffraction analysis, and Scanning Electron Microscopy, it is possible to fabricate TiO_2 - SiO_2 coatings from TiO_2 and SiO_2 sols at sintering temperatures of 500 °C and 600 °C. In addition, some conclusions can be drawn as follows:

- The main bonds formed in the TiO_2 - SiO_2 coating when sintered at 500 °C and 600 °C were Ti-O-Ti, Ti-O, Si-O-Si, and Ti-O-Si.
- The main components of the coating were crystals of rutile, anatase, and amorphous SiO_2 . The amorphous SiO_2 prevented the conversion of anatase to rutile. Therefore, the anatase content in the composition TiO_2 - SiO_2 would increase when the SiO_2 sol was used as the raw material.
- The TiO_2 - SiO_2 coating with a composition containing anatase and amorphous SiO_2 can be applied as a photocatalytic coating. This coating can be used as a material capable of decomposing toxic organic matter, as well as acting as a bactericidal and self-cleaning. In addition, the presence of SiO_2 bonds also promises to increase the adhesion of the coating to the surface of the ceramic product, helping to improve the durability of the coating.

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