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Synthesis and Characterisation of Silicon Dioxide Nanoparticles and Investigating Their Influence in Sunscreen Formulation

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The application of metal oxide nanoparticles benefits numerous industries. The stability and ease of manufacture of Silicon dioxide nanoparticles make them one of the most often used metal oxide nanoparticles in the cosmetic industry. In sunscreen compositions, titanium dioxide is the most often utilised additional metal oxide nanoparticle. However, various studies indicates that because titanium dioxide turns toxic when used in larger amounts and causes a white cast, which upsets customers, it should only be used in trace amounts and that concentrations should be closely monitored. Using titanium dioxide and Silicon dioxide nanoparticles together would be a better idea because the latter has a stronger temperature resistance and will increase stability further because of its uniform dispersion and water resistance. Consequently, the objective of the present study is to synthesise size-controlled Silicon nanoparticles and employ various characterization techniques to analyse their properties. The study additionally examines at the UV spectra of drugstore sunscreen that was purchased from a trusted vendor, as well as the presence and effects of titanium dioxide and Silicon in the sunscreen.
Keywords: Metal oxides nanoparticles, broad UV spectrum, sunscreen formulation, Silicon dioxide nanoparticles, Thermal stability of SiO2, vibrational analysis of SiO2.

1. Introduction

Metal oxide nanoparticles are widely utilised in various sectors due to their reduced environmental contamination. The properties of metal oxide nanoparticles are significantly altered by the process used to synthesise them. Conventional physical methods of synthesis do not produce uniform size controlled metal oxide nanoparticles. Hence researchers employ sol gel technique one of the simplest techniques to synthesise metal oxide nanoparticles. Metal oxide nanoparticles when incorporated in any sector improve the durability with no cost difference. Titanium dioxide nanoparticles are the mostly used nanoparticle in sunscreen due to their enhanced UV block. However, certain studies state that minimal amounts of titanium dioxide should be included, and that concentrations should be strictly adhered to [1]. Using SiO_2 nanoparticles in addition to titanium dioxide nanoparticles would be a preferable choice because it is more temperature resistant and would increase stability. The TGA DSC technique is used for thermal studies, and transmission electron microscopy is used to examine the morphology of the nanoparticles. Powder XRD studies were carried out to detect the phase of TiO_2 nanoparticles. Furthermore, the FTIR ATR method confirms the vibrational characteristics of SiO_2 and TiO_2. The drugstore sunscreen, which was obtained from an authorised vendor, was examined using UV-Vis technique to determine its broad UV spectrum. A broad UV spectrum would contribute to comprehensive defense against UV-A and UV-B rays. Using SEM and EDX, the presence of titanium dioxide and Silicon dioxide in the sunscreen was verified.

2. Materials and Methods

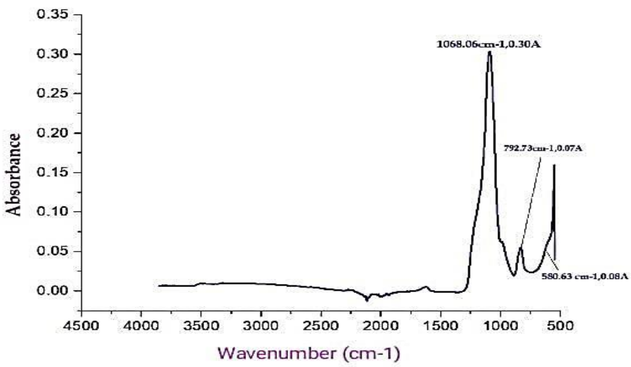
To synthesise Silicon dioxide nanoparticles, 25 ml of ethanol (C_2H_5OH) and 2.8 ml of acetic acid (CH_3COOH) are mixed at room temperature and stirred continuously for 10 minutes using a magnetic stirrer. The stirrer is heated for about ten minutes for the water molecules to vaporise and ethyl acetate ($C_2H_5COOCH_3$) sol is formed. The sol is then converted into a gel by adding a molecular precursor tetraethylorthoSiliconte (TEOS) (Si $(OC_2H_5)_4$) [2]. 12 ml of deionised water is mixed with 6 ml of TEOS solution and stirred continuously at room temperature for about three minutes. 2 ml of the precursor is added drop wise to ethyl acetate and is stirred continuously for 4 hours. The gel is then dried and calcinated at 400 °C using a high temperature hot air oven resulting in the production of fine Silicon dioxide nanoparticles (SiO_2). Synthesis of titanium dioxide nanoparticles involves ethanol as a solvent, hydrochloric acid as a catalyst, and titanium tetra iso propoxide as a precursor material [3]. Initially, 5mg Titanium tetra isopropoxide was mixed with 2 ml of HCl, 25 ml of ethanol and stirred for half an hour at room temperature. 10ml of deionized water was added to the above mixture and stirred for 2 hours at room temperature. Finally, the solution was then dried and heated at 120°C for one hour to obtain fine titanium dioxide nanoparticles.

3. Results and Discussion

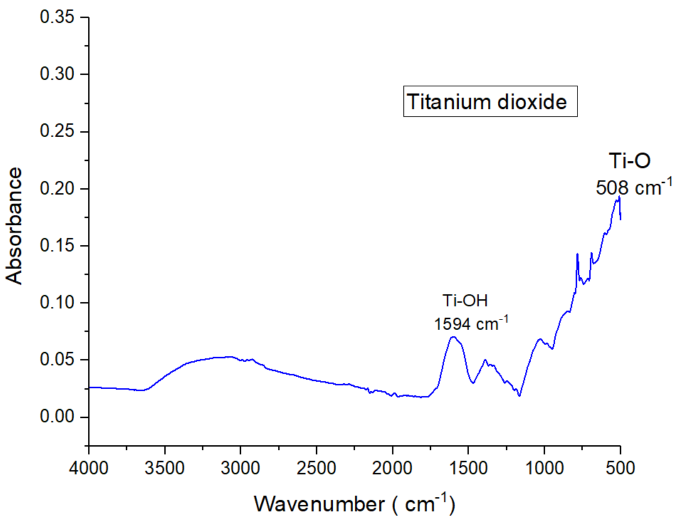
The modes of vibration of Silicon dioxide nanoparticles and titanium dioxide nanoparticles are confirmed by using FTIR ATR technique. The particles size analyser revealed the polydipsersity of index of formed Silicon dioxide nanoparticles. TEM with EDX technique calculated the average size and purity weight percentage of Silicon dioxide nanoparticles. Thermogravimetric analysis was used to study the thermal resistance of synthesised Silicon dioxide nanoparticles. Contact angle analysis was carried out to analyse the hydrophobic property of Silicon dioxide nanoparticles. Further, XRD studies were carried out to predict the phase of titanium dioxide nanoparticles.

3.1 FTIR ATR Spectral Analysis

FTIR ATR Spectral analysis is carried out using FTIR ATR spectrum 2 spectrophotometer at Sophisticated Analytical Instrumentation Facility (SAIF), SPIHER, Chennai. The analysis is carried out in the mid IR region to identify the vibrational bands present in the Silicon dioxide nanoparticles. The vibrational properties of Silicon dioxide were interpreted in Si-O-Si subunits since each silicon atom is bonded with four oxygen atoms and each oxygen atom is shared by two silicon atoms. The broad peaks at 1068 cm^{-1} and 793 cm^{-1} correspond to asymmetric and symmetric stretching modes of Si-O-Si. The peak at 547 cm^{-1} corresponds to SiO_2 bending vibration [4]. The vibrational properties of Titanium dioxide were interpreted and peaks at 1594 cm−1 and 508 cm−1 correspond to Ti-O and Ti-OH modes of vibration [5]. Hence the FTIR ATR analysis confirms the presence of Titanium dioxide nanoparticles.



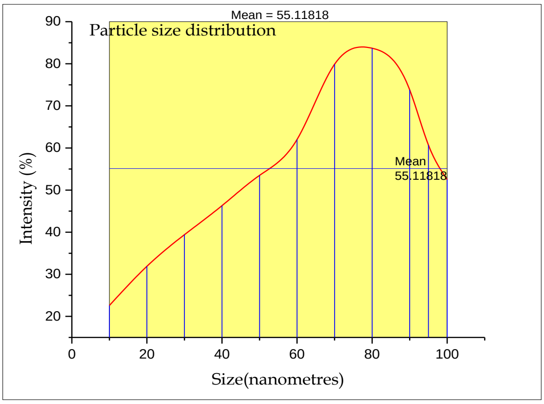
[Figure 1 FTIR ATR Spectrum of SiO_2 Nanoparticles]



[Figure 2 FTIR ATR Spectrum of TiO_2 Nanoparticles]

3.2. Particle size Analysis

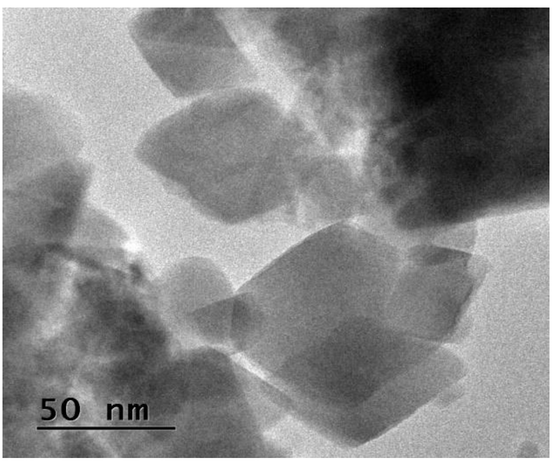
The results of the particle size analysis, which was performed at VISTAS, Chennai, using the Nanotrac Wave II instrument manufactured by Microtrac Inc., USA, to ascertain the average size of the sample, is shown in Figure 3. It is found that titanium dioxide nanoparticles have an average size of 55.1 nm. Higher particle size measurements can also be attributed to particle agglomeration. The polydispersity index (PDI), which calculates the uniform distribution of the sample, using the formula (standard deviation / particle size diameter) is found to be 0.05. The polydispersity index is mainly focused to analyse the distribution of nanoparticles in sample. Typically, a polydsipersity index less than 1 is regarded as uniform distribution [6].



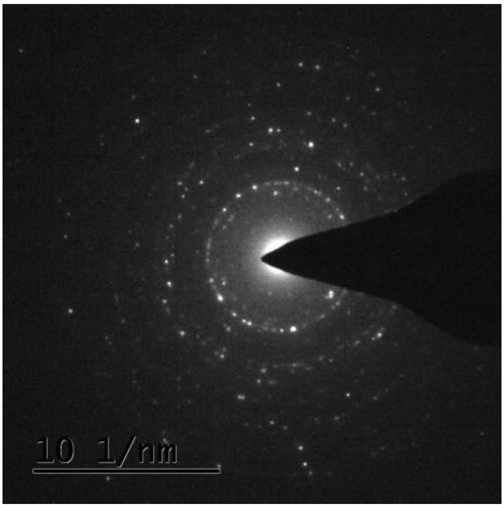
[Figure 3 Average size of Silicon dioxide Nanoparticles]

3.3. Transmission electron Microscopy with EDX analysis

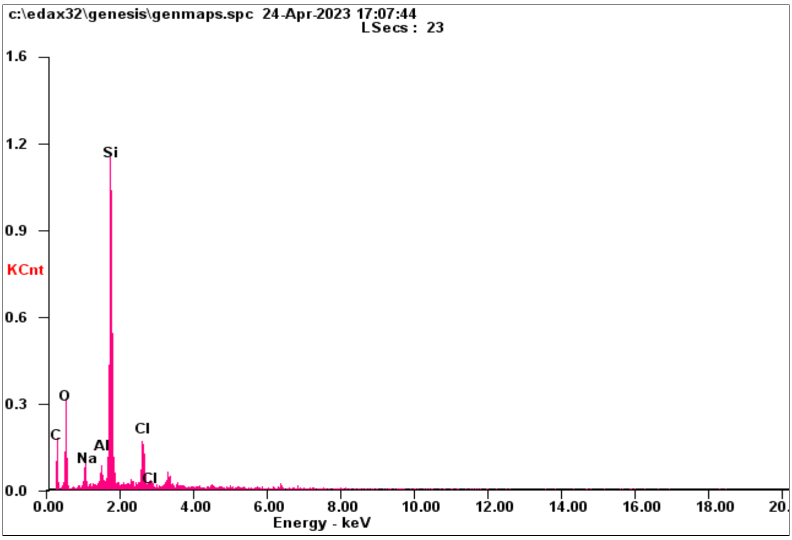
The TEM results revealed that the synthesised Silicon dioxide was in nanoparticle range and aggregation of the nanoparticles is responsible for the size variance that has been observed. The SAED pattern is provided to analyse uniform distributiom. It is discovered the purity weight percentages are determined to be 47.82% for Silicon and 29.15% for oxygen [7].



[Figure 4 TEM Image of Silicon dioxide Nanoparticles]



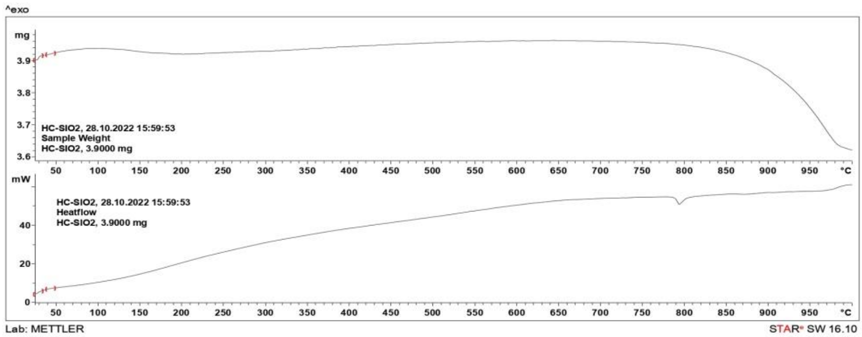
[Figure 5 SAED Image of Silicon dioxide Nanoparticles]



[Figure 6 EDX Image of Silicon dioxide Nanoparticles]

3.4 Thermo gravimetric analysis

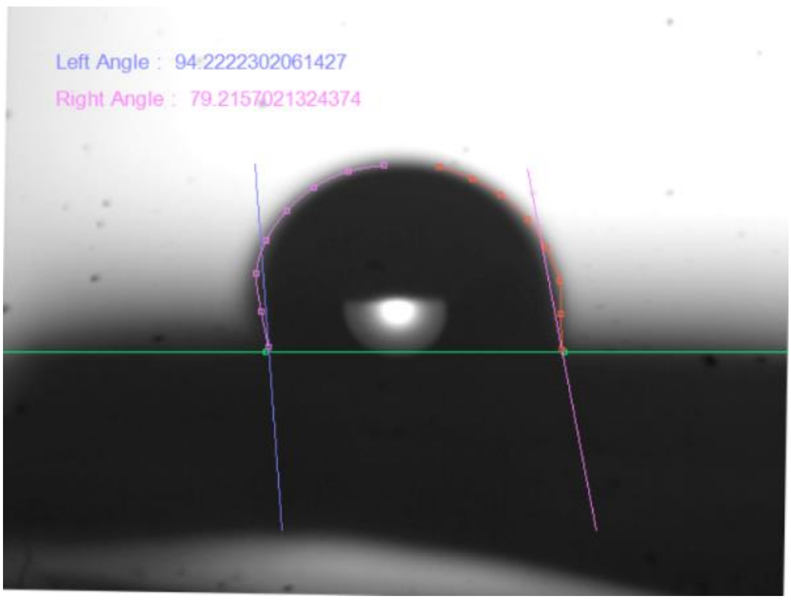
Thermo gravimetric analysis and differential scanning calorimetry is performed and from the TGA curves of Silicon dioxide nanoparticles, it is evident that no significant weight loss is observed below 800°C which indicates that higher temperature is required to breakdown the covalent bonds shared between the Silicon coupling agents to evaporate the Silicon dioxide nanoparticles. This proves that Silicon dioxide nanoparticles are highly thermal resistance and possess high melting point [8].



[Figure 7 TGA DSC of Silicon dioxide Nanoparticles]

3.5 Contact angle analysis

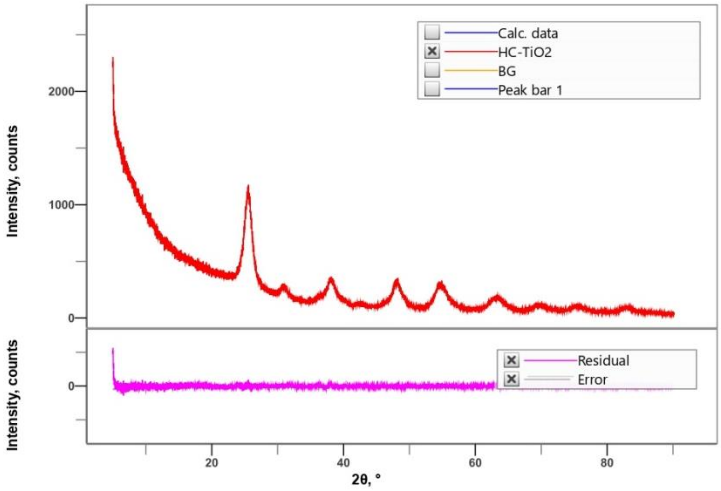
Contact angle analysis of Silicon dioxide nanoparticles were carried out and the results showcased a contact angle of 79 degrees right angle and 94 degrees left angle indicating the hydrophobic nature of Silicon dioxide nanoparticles [9]. Hydrophobic nature makes the sample to be more water resistant. Hence if hydrophobic Silicon is incorporated in sunscreen it can act sweat proof and water resistant. This is the major reason for using Silicon dioxide majorly in cosmetic industry.



[Figure 8 Contact angle of Silicon dioxide Nanoparticles]

3.6. Powder X-ray diffraction

Powder X-ray diffraction analysis is performed using Smart lab XE ray instrument at VISTAS, Chennai to measure the inner core transitions of titanium dioxide nanoparticles. Comparing the peaks obtained from the result with the JCPDS card data 21-1276, the synthesised titanium dioxide corresponds to rutile phase.



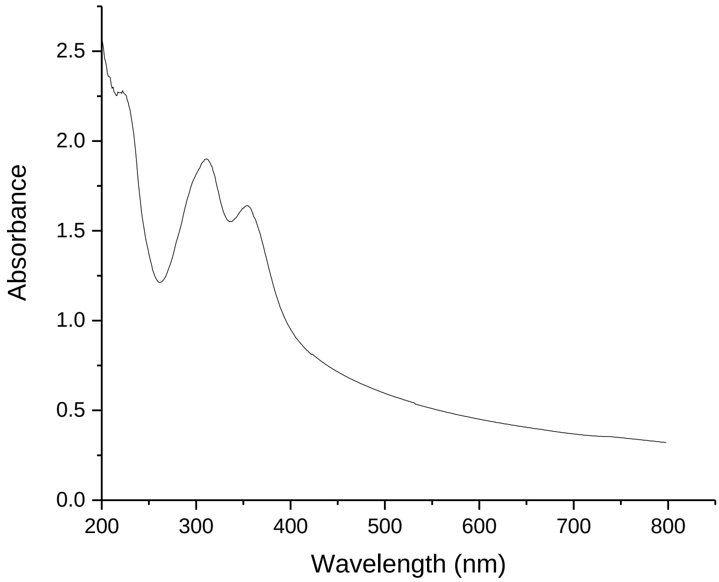
[Figure 9 Powder XRD of titanium dioxide Nanoparticles]

4. Investigation in Sunscreen formulation

A drugstore sunscreen was procured from a reliable source and analysed for the presence of Silicon dioxide and titanium dioxide nanoparticles using scanning electron microscopy and EDX technique. The sunscreen is then analysed using UV Visible spectroscopy and the results are discussed below.

4.1. Ultra violet - Visible Analysis

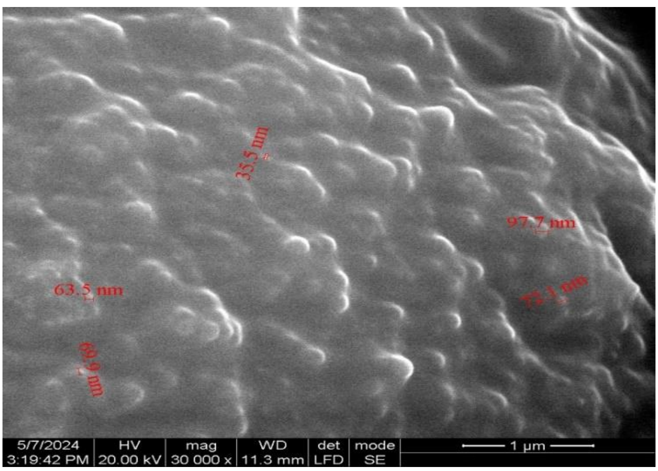
The results of the UV analysis, which was performed at VISTAS, Chennai, using to ascertain the broad UV spectrum of the sample, is shown in Figure 3. The results showcased two distinct absorbance peaks in the UV-B region (290 to 310 nm) and in the UV-A region (330 to 360 nm). Broad spectrum was observed which may be due to the uniform distribution of the components of sunscreen especially titanium dioxide nanoparticles [10]. Silicon dioxide is often reported for the uniform distribution when added with other metal oxide nanoparticles. Hence the broad uniform peaks may be due to the addition of Silicon dioxide with titanium dioxide.



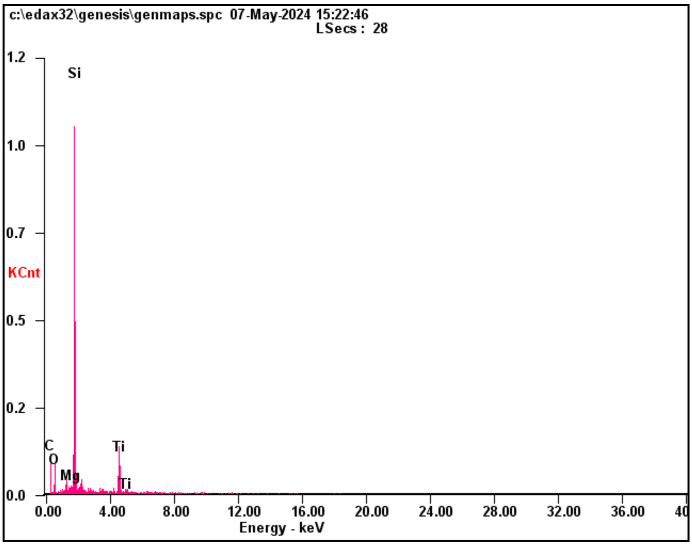
[Figure 10 UV-Visible spectrum of Sunscreen]

4.2 Scanning electron microscopy

The VEGA 3 TESCAN SEM analyzer was used at Anna University in Chennai to conduct the SEM analysis. Tiny spherical shaped nanoparticles ranging in different sizes were observed. It is discovered that the percentages of purity weight for oxygen, Silicon and titanium are 19.99%, 29.48% and 5.33%, respectively. Hence the results promise the presence of Silicon dioxide in abundance compared to the titanium dioxide particles which contributes to less toxicity and improved stability [11].



[Figure 11 SEM Image of Sunscreen]



[Figure 12 EDX Image of Sunscreen]

5. Conclusions

Nanoparticles of silicon dioxide are effectively synthesised by the sol-gel method. By using FTIR ATR characterisation technique such as the existence of Silicon dioxide nanoparticles is verified. The average particle size using particle size analyser indicated a polydispersity index of 0.05 of Silicon dioxide nanoparticles. The morphological property of Silicon dioxide and titanium dioxide are verified by transmission electron microscopy. It is concluded from TGA DSC curves that weight loss below 800°C is negligible. Contact angle analysis of Silicon dioxide nanoparticles and Powder XRD studies of titanium dioxide nanoparticles were carried out. Further the study extended its work to investigate the UV-Vis spectrum of drugstore sunscreen. The results showcased broad UV spectrum and confirmed UV block attributing to the presence of titanium and Silicon dioxide particles. Scanning electron microscopy with EDX confirms the amount if titanium and Silicon dioxide nanoparticles. The above discussion showcases that Silicon dioxide nanoparticles can act as an enhanced nanoparticle to provide stability and uniform distribution in sunscreen formulations.

References

1. Torbati TV, Javanbakht V. Fabrication of TiO2/Zn2TiO4/Ag nanocomposite for synergic effects of UV radiation protection and antibacterial activity in sunscreen. Colloids Surf B Biointerfaces. 2020 Mar;187:110652. doi: 10.1016/j.colsurfb.2019.110652. Epub 2019 Nov 17. PMID: 31785852.
2. Michael E. Coltrin, Pauline Ho, Harry K. Moffat, Richard J. Buss, Chemical kinetics in chemical vapor deposition: growth of silicon dioxide from tetraethoxysilane (TEOS), Thin Solid Films, Volume 365, Issue 2, 2000, Pages 251-263, ISSN 0040-6090,https://doi.org/10.1016/S0040-6090(99)01059-7. (https://www.sciencedirect.com/science/article/pii/S0040609099010597)

3. Lee MK, Park YC. Contact Angle Relaxation and Long-Lasting Hydrophilicity of Sputtered Anatase TiO2 Thin Films by Novel Quantitative XPS Analysis. Langmuir. 2019 Feb 12;35(6):2066-2077. doi: 10.1021/acs.langmuir.8b03258. Epub 2019 Jan 29. PMID: 30645937.Nyamukamba, P., Okoh, O., Mungondori, H., Taziwa, R., & Zinya, S. (2018). Synthetic Methods for Titanium Dioxide Nanoparticles: A Review. InTech. doi: 10.5772/intechopen.75425
4. Limon Pacheco, Jorge & Jiménez Barrios, Natalie & Déciga-Alcaraz, Alejandro & Martínez-Cuazitl, Adriana & Mata-Miranda, Monica & Vazquez-Zapien, Gustavo & Pedraza-Chaverri, José & Chirino, Yolanda & Orozco-Ibarra, Marisol. (2020). Astrocytes Are More Vulnerable than Neurons to Silicon Dioxide Nanoparticle Toxicity in Vitro. Toxics. 8. 51. 10.3390/toxics8030051.
5. Al-Amin, Mohammad & Dey, Shaikat & Rashid, Taslim & Ashaduzzaman, Md & Shamsuddin, Sayed. (2016). Solar Assisted Photocatalytic Degradation of Reactive Azo Dyes in Presence of Anatase Titanium Dioxide. 2. 14-21.
6. Yan, Y., Fu, J., Xu, L., Wang, T., & Lü, X. (2016). Controllable synthesis of sio 2 nanoparticles: effects of ammonia and tetraethyl orthoSiliconte concentration. Micro &Amp; Nano Letters, 11(12), 885-889. https://doi.org/10.1049/mnl.2016.0434
7. Baghban, Ali & Doustkhah, Esmail & Rostamnia, Sadegh & Aghbash, Khadijeh. (2016). Silicon-Supported Co3O4 Nanoparticles as a Recyclable Catalyst for Rapid Degradation of Azodye. Bulletin of Chemical Reaction Engineering & Catalysis. 11. 284. 10.9767/bcrec.11.3.568.284-291.
8. M. Almaghrabi, A. Alqurshi, S.A. Jadhav, F. Mazzacuva, A. Cilibrizzi, B. Raimi-Abraham, P.G. Royall,Evaluating thermogravimetric analysis for the measurement of drug loading in mesoporous Silicon nanoparticles (MSNs),Thermochimica Acta,Volume 730,2023,179616,ISSN 0040-6031,https://doi.org/10.1016/j.tca.2023.179616. (https://www.sciencedirect.com/science/article/pii/S0040603123001855)
9. Forny L, Saleh K, Denoyel R, Pezron I. Contact angle assessment of hydrophobic Silicon nanoparticles related to the mechanisms of dry water formation. Langmuir. 2010 Feb 16;26(4):2333-8. doi: 10.1021/la902759s. PMID: 20141200.
10. Chou J, Robinson TJ, Doan H (2017) Rapid Comparison of UVB Absorption Effectiveness of Various Sunscreens by UV-Vis Spectroscopy. J Anal Bioanal Tech 8: 355. doi: 10.4172/2155-9872.1000355
11. Dréno B, Alexis A, Chuberre B, Marinovich M. Safety of titanium dioxide nanoparticles in cosmetics. J Eur Acad Dermatol Venereol. 2019 Nov;33 Suppl 7:34-46. doi: 10.1111/jdv.15943. PMID: 31588611.