Phase Transition of SiO₂ Nanoparticles Prepared from Natural Sand: The Calcination Temperature Effect

Munasir¹,²,³, Zainul Arifin Imam Supardi¹,², Mashadi¹, Zumrotun Nisa¹, Diah Hari Kusumawati¹,², Nugrahani Primary Putri¹,², Ahmad Taufiq³, Sunaryono³, Nurul Hidayat³, Darminto⁴

¹Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Surabaya (Unesa), Kampus Ketintang, Jl. Ketintang, Surabaya, 60231, Indonesia
²Research Center of Advanced Materials, Faculty of Mathematics and Natural Sciences, Universitas Negeri Surabaya (Unesa), Kampus Ketintang, Jl. Ketintang, Surabaya 60231.
³Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 64145, Indonesia
⁴Department of Physics, Faculty of Mathematics and Natural Sciences, Institut Teknologi Sepuluh Nopember Surabaya (ITS), Kampus ITS Sukolilo, Surabaya 60111, Indonesia

*Corresponding author’s email: munasir.physics@unesa.ac.id

Abstract. In this paper, we systematically report the synthesis of nano silica powder from natural silica sand by a continuous process. Extraction of sodium silicate from silica sand was through a hydrothermal process, then sodium silicate was ready to be used as a precursor in the form of silicate slurry by coprecipitation process. The silicate slurry of SiO₂·XH₂O was then dried in a furnace at 150 °C for 4 hours until obtaining a pure white SiO₂ powder. At a calcination temperature of 900 °C, the sample was then tested by XRD to analyze the transformation of the crystal phase of SiO₂ nanoparticles. Identification of functional group absorption was undertaken by FTIR test, and the particle grain microstructure was analyzed by SEM. At calcination temperature of 900 °C, the SiO₂ silica nanoparticles experienced a change of phase from amorphous to crystal or amorphous-cristobalite phase; a shift in stiffness for positions of functional group absorption of Si–O stretching or LO functional groups, Si–O stretching or TO, Si–O–Si bending and Si–O–Si rocking and OH-functional groups occurred; the growth of particle grains happened with a spherical and oval trend, with a larger size. SiO₂ nanoparticles were successfully synthesized by a continuous method and 900 °C calcination temperature had a significant effect on structural phase changes, the formation of siloxane functional groups, silanol, and grain growth on SiO₂ nanoparticles.

Keywords: Silica, nanoparticle, natural sand, calcination, amorphous, cristobalite.
1. Introduction
Quartz sand in nature contains many oxide elements such as SiO₂, Fe₂O₃, Al₂O₃, TiO₂, CaO, MgO and K₂O [1-3]. Silica has crystalline polymorphs namely quartz, cristobalite and tridymite, stishovite, and coesite [4-6] structures. Amorphous silica can be synthesized from natural materials (minerals), such as quartz sand [1], siliceous sands [3], and Douiret sands [7]. The synthesis method which can be used is by a dry method or known as an alkali-fusion process, reacting with an alkaline compound in the furnace; KOH with temperature of 350 °C [8], NaOH with temperature of 500 °C [1], and Na₂CO₃ with temperature of 1100 °C [7]. It can also be done by wet or hydrothermal or chemical processes [9] such as the sol-gel process [10], coprecipitation, etc. [11].

Silica is widely used in various applications such as a mixture of concrete [12,13], tire industry, rubber nanocomposite [14], wall-paint emulsion [15], improved lotions and cosmetics, increased ingredient cosmetic efficacy [16], packaging and anti-bacterial [17,18]. Modification of hydrophobic and hydrophilic properties of nano silica also provides many applications in technology, such as superhydrophobic textiles and ultra-violet yarns [19,20], and super-hydrophobic semi-transparent thin films [21,22]. Nano silica can also be applied as a base material for Ion-Lithium batteries: electrode [23], electrolyte [24,25] and the separator and the like [26].

In nature, the stable silica structure is a quartz phase, so that in macro and micro sizes the silica particles have a crystal structure phase while the nanometer-size silica particles are generally amorphous structured [11]. In various processes of extraction and synthesis of nano silica from the natural (organic or inorganic) material, an amorphous structure is obtained [11,27,28]. Recently, nano-silica synthesized from quartz sand using the coprecipitation method obtained nano silica that encapsulated SiO₂-cristobalite and tridymite [11], the amorphous-crystal phase. Nano silica that was processed from organic rice husk through the process of combustion at 900 °C, could also attain tridymite and cristobalite nano silica powder [29].

From the previous research reports, the transformation mechanism of the crystal phase of SiO₂ was influenced by the temperature and pressure. In the crystal phase of SiO₂, the things that possibly happen are α-quartz (trigonal), β-quartz (hexagonal), α-tridymite (orthorhombic), β-tridymite (hexagonal), α-cristobalite (tetragonal), and β-cristobalite (cubic). The phase transformation of α-quartz ↔ β-quartz occurred at 573 °C; β-quartz↔β-tridymite occurred at 870 °C; α-tridymite ↔β-tridymite occurred at 117 °C; β-tridymite ↔β-cristobalite occurred at 1470 °C, and β-cristobalite → liquid silica occurred at temperature ≥1710 °C [30,31,32]. The next is how to explain the mechanism of transformation of silica nanoparticles that commonly have an amorphous structure to be crystalline structure. Generally, the raw materials of silica sand have a crystal structure of α-quartz. After the hydrothermal process in the autoclave at the pressure above 1 atmosphere and temperature of ~350-1100 °C, the silicate sodium was produced; generally, amorphous silica or amorphous-crystal was created through coprecipitation process [11]. After that is how the silica nanoparticle properties and the process of phase transformation continue to the crystal.

This research concerned on natural sand purifying process and producing silica powder in nanometer using hydrothermal and coprecipitation methods. The effect of calcination temperature on the silica nanoparticles (amorphous) samples and the phase transformation of amorphous-crystalline were analyzed using X-ray Diffraction (XRD) and the functional groups were analyzed using FTIR spectroscopy wave absorption, and the particle form and the growth of particle grain were analyzed by SEM test.

2. Materials and Methods
The raw materials in this study were as follows: Natural silica sand, HCl 37%, NaOH 99%, and de-mineralized water. The synthesis employed a continuous method (hydrothermal-coprecipitation). The first step was the formation of silicate sodium precursor through hydrothermal. It was then mixed with NaOH 5 M solution and stirred wisely for 2 hours. The second stage was the coprecipitation process; the sodium silicate solution was dried at ambient condition for 24 hours and followed by stirring and
adding HCl (2 M) to reach a neutral pH (8 - 7). The solution was looked muddy and formed a white gel. The precipitated gel was then filtrated and cleaned by de-mineralized water for several times. The precipitated Si(OH)₄ was dried in the oven with the temperature of 200 °C for 2 hours. The silica gel (SiO₂) was finally characterized by means of X-ray diffraction (XRD) to identify p structure and crystal phase. The analysis of functional groups in SiO₂ (Silanol, siloxane) used Fourier Transform Infra-Red (FTIR) test. The morphology of the particles (the form of particles) and the formation of the particles were observed using Scanning Electron Microscope (SEM).

3. Results and Discussion

3.1. XRD Analysis

The data of diffraction pattern of SiO₂ powder that had been synthesized using continuous method (coprecipitation-hydrothermal) for the hydrothermal time of 10 hours (Figure 1 (a)) showed the single peak at the position of (2θ) 21.6°. The diffraction pattern indicated that this silica powder was in an amorphous condition (Shinohara et al., 2004). If the calcination was done to the samples (silica powder) of the synthesis results at the temperature of 900 °C in the furnace for 10 hours, it would result in the diffraction pattern with the position of angle hump of (2θ) 22.01°. The diffraction pattern of XRD began to show the formation of tridymite crystal phase (Figure 1 (b)). Lastly, the samples calcinated at the temperature of 1000 °C (Figure 12(c)) showed the phase transformation of amorphous SiO₂ to polycrystal phase signed by the formation of some peaks on the crystal structures. The dominant crystal phases were Quartz, Tridymite, and Cristobalite. The XRD pattern showed one characteristic of Quartz phase forming the peak at 26.68° in accordance with Quartz (database 96-900-5018), the tridymite phase at 21.53° and 35.71° (database 96-901-3493), and the cristobalite phase formed the peak at (2θ) 22.05°, 28.49°, 31.43°, and 35.99° (database 96-900-8111) [30]. The analysis results showed multi-spaces with the majority of cristobalite phase (77.4%), a little bit tridymite phase (14.2%), and quartz phase (8.4%). If we see the transition process, the samples transformed from the Quartz phase to cristobalite phase and from cristobalite to tridymite. This case is a little bit different from the phase diagram of silica showing that the phase transformation from tridymite phase to cristobalite phase occurred at 1470 °C with the low pressure (below 20 kbar). The gel silica with the calcination at the temperature of 900 °C will form β-cristobalite form signed at (111), (110) and (120) and it will be more obviously formed at the temperature of 1400 °C [32]. The phase change from α-quartz to β-quartz or the other way around, from β-quartz to β-cristobalite was extremely influenced by the various temperatures [32].

The phase transformation process was different from the previous results for the raw material of SiO₂ crystal quartz (material from nature) with the particle size of micrometer as explained by Marthe Erdal Kjelstadli: quartz → tridymite (870 °C); tridymite → cristobalite (1470 °C) and cristobalite → liquid silica (1710 °C) [33]. This result strengthens the previous finding of Arianit A. Reka, et al. stating that the phase transformations were β-quartz ↔ β-tridymite at 870 °C, β-tridymite ↔ β-cristobalite at 1470 °C, and β-cristobalite → vitreous glass at 1705 °C [34].
3.2. **FTIR Analysis**

FTIR characterization aims to know the pattern of wave absorption in the samples. The pattern of infrared wave absorption of SiO sample for the condition before and after the calcination at 900 °C is shown in Figure 3 (a-b). The analysis results and matching of the pattern of infrared absorption in the functional groups of the sample as displayed in Figure 3, at the wavelength of 465-475 cm\(^{-1}\), 800-870 cm\(^{-1}\), and 3000-4000 cm\(^{-1}\) showed the absorption pattern of the Si-O functional group, –OH group of SiO, and O-H group. Such absorptions were in accordance with the characteristics of the absorption pattern of silica obtained from reference [34,35].

The absorption pattern of the Si-O-Si group (siloxane) as the synthesis result was located at the wavelength of 1098 cm\(^{-1}\). Such result corresponded to the reference having the range of 1050-1115 cm\(^{-1}\). The pattern of O-H-Si group (siloxane) had the absorption at the wavelength of 1639 cm\(^{-1}\) [11, 30, 37]. The absorption pattern of Si-O-Si (siloxane) group as the synthesis result took place at the wavelength of 1095 cm\(^{-1}\). Such result was in line with the reference having the range of 1050-1115 cm\(^{-1}\) [29, 35, 37]. The pattern of O-H (water molecule) functional group had the absorption at the wavelength of 1639 cm\(^{-1}\) [11, 29, 35, 37].

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**Figure 1.** XRD pattern of the samples without (a) and with calcination at (b) 900 °C and (c) 1100 °C

**Figure 2.** IR Spectroscopy of SiO\(_2\) without (a) and with calcination at 900 °C
The absorption change of O-H functional group was shorter. This indicated that the water (OH) content was more eliminated while the Si-O-Si functional group was still dominant (the vibration was better), and for Si-O group was also getting dominant. This showed that the crystal characteristic of SiO₂ was also better (the crystal phase was formed). The results of FTIR characterization clearly showed the phenomena of the loss of the absorption pattern on O-H (water molecule) group as the calcination temperature used was getting higher [11,37,38]. Figure 2 respectively shows the absorption pattern of silica without calcination, and the absorption pattern (with calcination at 900 °C) indicating the decrease in the absorption pattern of O-H (water molecule) functional group. Besides, the phenomenon of shifting to the right (the wavelength was getting higher). The absorption position of silica functional group: Si-O-Si rocking, Si-O-Si banding, Si-O stretching transversal optic (TO) and Si-O stretching longitudinal optic (LO) [21, 22, 39].

Table 1. Corresponding the functional groups of the results of FTIR with reference

| Wavelength (cm⁻¹) | Functional Group | Wavelength literature (cm⁻¹) | Reference |
|------------------|------------------|-----------------------------|-----------|
| experimental data (a) | (b) | | |
| 469 | 470 | Group vibration Si-O | 465 - 475 | [11, 29, 37] |
| 800 | 800 | OH group vibration of Si-O | 800 - 870 | [11, 19, 29, 40] |
| 1098 | 1095 | Si-O-Si group asymmetry vibration | 1050 - 1115 | [11, 19, 37, 40] |
| 1639 | 1639 | O-H (water molecule) group vibration | 1639 | [11, 37, 38] |
| 3463 | 3456 | O-H group vibration | 3000 - 4000 | [17, 28, 38, 40, 41] |

3.3. SEM Analysis

In this research, the morphology of silica as the synthesis result using hydrothermal-coprecipitation methods without calcination, with calcination at 900 °C (SEM data) is displayed in Figure 3. It is shown that the particle size was smaller and spherical which tended to be oval; the grain border was clear; the estimation showed the particle size of ~ 72.85 nm (≤ 100 nm). The sample with the calcination temperature of 900 °C for 10 hours had shown the growth of its particles so that it formed the bigger size (Figure 3 (b)) so that the particle size was getting bigger with the more dense particle structure, the getting fewer grain borders indicated by the space between particles which disappeared. The particle size resulted was greater; the growth of the particle size caused the grain border between particles disappeared. When the calcination temperature was getting higher (started at 900 °C), the agglomeration process happened to form the bigger particles. The particles looked like a ball and crystal box as shown in Figure 3 (c).
Figure 3. Micrograph SEM of SiO$_2$ nanoparticles: (a) without calcination, (b) after calcination at 900 °C for 10 hours, and (c) the form of sample particles (b) in the position of taking the different picture with the magnification: like-spherical and crystal box.

4. Conclusion
Finally, it can be obviously stated that the continuous method has been successfully applied to produce silica (SiO$_2$) powder nano-crystalline with submicron particle size. The silica from natural sand can be separated from its contaminant and the particle size of the silica can be reduced to the nanoscale. The final product was in the form of SiO$_2$ nanoparticles powder with the amorphous phase with the size of ~72.85 nm. At 900 °C calcination temperature for 10 hours, the phase transformation happened from the amorphous phase to the polycrystalline phase with the domination of cristobalite crystal structure, tridymite, and quartz. The calcination process definitely influenced the change of the amorphous phase to the crystal and the particle grain size of SiO$_2$ was bigger and the particle grain border disappeared.

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References

[1] Munasir, A. Sultan, Triwikantoro, M. Zainuri, Darminto, Synthesis of silica nanopowder produced from Indonesian natural sand via alkali fusion route, in: AIP Conf. Proc., AIP Publishing, 2013: pp. 28–31. doi:10.1063/1.4820986.

[2] M. Taxarchou, D. Panias, I. Douni, I. Paspaliaris, A. Kontopoulos, Removal of iron from silica sand by leaching with oxalic acid, Hydrometallurgy. 46 (1997) 215–227. doi:10.1016/S0304-886X(97)00015-7.

[3] A. Sdiri, T. Higashi, S. Bouaziz, M. Benzaïna, Synthesis and characterization of silica gel from siliceous sands of southern Tunisia, Arab. J. Chem. 7 (2014) 486–493. doi:10.1016/j.arabjc.2010.11.007.

[4] M. Dapaggi, L. Pagliari, A. Pavese, L. Sciascia, M. Merli, F. Francescon, The formation of silica high temperature polymorphs from quartz: Influence of grain size and mineralising agents, J. Eur. Ceram. Soc. 35 (2015) 4547–4555. doi:10.1016/j.jeurceramsec.2015.08.015.

[5] C.S. Marians, L.W. Hobbs, Network properties of crystalline polymorphs of silica, J. Non-Cryst. Solids. 124 (1990) 242–253. doi:10.1016/0022-3093(90)90269-R.

[6] L. Guttman, Ring structure of the crystalline and amorphous forms of silicon dioxide, J. Non-Cryst. Solids. 116 (1990) 145–147. doi:10.1016/0022-3093(90)90686-G.

[7] W. Tabelski, M. Benzaïna, S. Bouaziz, Physico-chemical characterisation of the Douiret sand (Southern Tunisia): Valorisation for the production of Silica Gel, Phys. Procedia. 2 (2009) 1461–1467. doi:10.1016/j.phpro.2009.11.117.

[8] H. Mori, Extraction of silicon dioxide from waste colored glasses by alkali fusion using potassium hydroxide, J. Mater. Sci. 38 (2003) 3461–3468. doi:10.1023/A:1025100901693.

[9] U. Zulfiqar, T. Subhani, S.W. Husain, Synthesis and characterization of silica nanoparticles from clay, J. Asian Ceram. Soc. 4 (2016) 91–96. doi:10.1016/j.jascer.2015.12.001.

[10] Q. Guo, D. Huang, X. Kou, W. Cao, L. Li, L. Ge, J. Li, Synthesis of disperse amorphous SiO2 nanoparticles via sol-gel process, Ceram. Int. 43 (2017) 192–196. doi:10.1016/j.ceramint.2016.09.133.

[11] Munasir, Triwikantoro, M. Zainuri, Darminto, Synthesis of SiO2 nanopowders containing quartz and cristobalite phases from silica sands, Mater. Sci.-Pol. 33 (2015) 47–55. doi:10.1515/msp-2015-0008.

[12] A.M. Said, M.S. Zeidan, M.T. Bassuoni, Y. Tian, Properties of concrete incorporating nano-silica, Constr. Build. Mater. 36 (2012) 838–844. doi:10.1016/j.conbuildmat.2012.06.044.

[13] M. Heikal, S. Abd El Aleem, W.M. Morsi, Characteristics of blended cements containing nano-silica, HBRC J. 9 (2013) 243–255. doi:10.1016/j hbrcj.2013.09.001.

[14] Y. Chen, Z. Peng, L.X. Kong, M.F. Huang, P.W. Li, Natural rubber nanocomposite reinforced with nano silica, Polym. Eng. Sci. 48 (2008) 1674–1677. doi:10.1002/pen.20997.

[15] T. Mizutani, K. Arai, M. Miyamoto, Y. Kimura, Application of silica-containing nano-composite emulsion to wall paint: A new environmentally safe paint of high performance, Prog. Org. Coat. 55 (2006) 276–283. doi:10.1016/j.porgcoat.2005.12.001.

[16] C. Fruijtj-Põlloho, The toxicological mode of action and the safety of synthetic amorphous silica—A nanostructured material, Toxicology. 294 (2012) 61–79. doi:10.1016/j.tox.2012.02.001.

[17] S. Wang, W. Hou, L. Wei, H. Jia, X. Liu, B. Xu, Antibacterial activity of nano-SiO2 antibacterial agent grafted on wool surface, Surf. Coat. Technol. 202 (2007) 460–465. doi:10.1016/j.surfcoat.2007.06.012.

[18] Z. Luo, Y. Xu, Q. Ye, Effect of nano-SiO2-LDPE packaging on biochemical, sensory, and microbiological quality of Pacific white shrimp Penaeus vannamei during chilled storage, Fish. Sci. 81 (2015) 983–993. doi:10.1007/s12562-015-0914-3.

[19] Q. Zhu, Q. Gao, Y. Guo, C.Q. Yang, L. Shen, Modified Silica Sol Coatings for Highly Hydrophobic Cotton and Polyester Fabrics Using a One-Step Procedure, Ind. Eng. Chem. Res. 50 (2011) 5881–5888. doi:10.1021/ie101825d.
[20] M.D. Teli, B.N. Annaldewar, Superhydrophobic and ultraviolet protective nylon fabrics by modified nano silica coating. J. Text. Inst. 108 (2017) 460–466. doi:10.1080/00405000.2016.1171028.

[21] P.-H. Chen, C.-C. Hsu, P.-S. Lee, C.-S. Lin, Fabrication of semi-transparent super-hydrophobic surface based on silica hierarchical structures. J. Mech. Sci. Technol. 25 (2011) 43–47. doi:10.1007/s12206-010-0113-0.

[22] B. Qiao, Y. Liang, T.-J. Wang, Y. Jiang, Surface modification to produce hydrophobic nano-silica particles using sodium dodecyl sulfate as a modifier. Appl. Surf. Sci. 364 (2016) 103–109. doi:10.1016/j.apsusc.2015.12.116.

[23] Z. Favors, W. Wang, H.H. Bay, Z. Mutlu, K. Ahmed, C. Liu, M. Ozkan, C.S. Ozkan, Scalable Synthesis of Nano-Silicon from Beach Sand for Long Cycle Life Li-ion Batteries. Sci. Rep. 4 (2014). doi:10.1038/srep05623.

[24] X. He, Q. Shi, X. Zhou, C. Wan, C. Jiang, In situ composite of nano SiO$_2$-P(VDF-HFP) porous polymer electrolytes for Li-ion batteries. Electrochimica Acta. 51 (2005) 1069–1075. doi:10.1016/j.electacta.2005.04.048.

[25] J.T. Park, K.J. Lee, M.-S. Kang, Y.S. Kang, J.H. Kim, Nanocomposite polymer electrolytes containing silica nanoparticles: Comparison between poly(ethylene glycol) and poly(ethylene oxide) dimethyl ether. J. Appl. Polym. Sci. 106 (2007) 4083–4090. doi:10.1002/app.26951.

[26] D. Fu, B. Luan, S. Argue, M.N. Bureau, I.J. Davidson, Nano SiO$_2$ particle formation and deposition on polypropylene separators for lithium-ion batteries, J. Power Sources. 206 (2012) 325–333. doi:10.1016/j.jpowsour.2011.10.130.

[27] S. Affandi, H. Setyawan, S. Winardi, A. Purwanto, R. Balgis, A facile method for production of high-purity silica xerogels from bagasse ash, Adv. Powder Technol. 20 (2009) 468–472. doi:10.1016/j.apt.2009.03.008.

[28] U. Kalapathy, A. Proctor, J. Shultz, An improved method for production of silica from rice hull ash, Bioresour. Technol. 85 (2002) 285–289. doi:10.1016/S0960-8524(02)00116-5.

[29] I.A. Rahman, V. Padavettan, Synthesis of Silica Nanoparticles by Sol-Gel: Size-Dependent Properties, Surface Modification, and Applications in Silica-Polymer Nanocomposites—A Review. J. Nanomater. 2012 (2012) 1–15. doi:10.1155/2012/132424.

[30] M. A Akl, H. Aly, H. M.A. Sholiman, A.M.A. Abd-Elrahman, A.I. Abd-ElRahman, Preparation and Characterization of Silica Nanoparticles by Wet Mechanical Attrition of White and Yellow Sand, J. Nanomedicine Nanotechnol. 04 (2013). doi:10.4172/2157-7439.1000183.

[31] F.M. Wahle, R.E. Grim, R.B. Grab, Phase Transformation in Silica as Examined by Continuous X-Ray Diffraction, The American Mineralogist, 46(1961), 196-208.

[32] M.E. Kjelstadli, Kinetic and Mechanism of Phase Transformation from Quartz to Cristobalite, NTNU, Norwegian University Science and Technology, Juni 2016.

[33] A. A Reka, B. Palovski, T. Anovski, Phase Transformations of Amorphous SiO$_2$ in Diatomite at Temperature age 1000-1200°C, Geologia Macedonica, 29(1) (2015), 87-92.

[34] C. Jiang, Y. Zhang, Q. Wang, T. Wang, Superhydrophobic polyurethane and silica nanoparticles coating with high transparency and fluorescence, J. Appl. Polym. Sci. 129 (2013) 2959–2965. doi:10.1002/app.39024.

[35] R.K. Nariyal, P. Kothari, B. Bisht, FTIR Measurements of SiO$_2$ Glass Prepared by Sol-Gel Technique, Chem. Sci. Trans. (2014). doi:10.7598/cst2014.816.

[36] N. Dhiman, B.P. Singh, A.K.G. Gathania, Synthesis and characterization of dye-doped TiO$_2$-SiO$_2$ core-shell composite microspheres, J. Nanophotonics. 6 (2012) 063511. doi:10.1117/1.JNP.6.063511.

[37] A.N. Nittaya Thudadij, Preparation of Nanosilica Powder from Rice Husk Ash by Precipitation Method, Chiang Mai J. Sci. 35 (2008) 206–211.

[38] I.A. Rahman, V. Padavettan, Synthesis of Silica Nanoparticles by Sol-Gel: Size-Dependent Properties, Surface Modification, and Applications in Silica-Polymer Nanocomposites—A Review, J. Nanomater. 2012 (2012) 1–15. doi:10.1155/2012/132424.
[39] P.K. Jal, M. Sudarshan, A. Saha, S. Patel, B.K. Mishra, Synthesis and characterization of nanosilica prepared by precipitation method, Colloids Surf. Physicochem. Eng. Asp. 240 (2004) 173–178. doi:10.1016/j.colsurfa.2004.03.021.

[40] S. Basu, ed., Crystalline Silicon - Properties and Uses, InTech, 2011. doi:10.5772/844.

[41] K.S. Rao, K. El-Hami, T. Kodaki, K. Matsushige, K. Makino, A novel method for synthesis of silica nanoparticles, J. Colloid Interface Sci. 289 (2005) 125–131. doi:10.1016/j.jcis.2005.02.019.