

Synthesis and Characterization of Silica Nanoparticles and Study of Impurity Removal from Silica Nanoparticles by Acid Leaching

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Abstract: Water in oil reverse microemulsion synthesis and characterization of silica nanoparticles and removal of impurity from silica nanoparticles have been focused. A study has been established for the synthesis of non-agglomerated spherical silica nanoparticles. These nanoparticles were characterized using SEM-EDS, XRD, and TGA. After purification silica nanoparticles were characterized by UV and ICP-MS. SEM image reveals that spherical particle size of Silica nanoparticles are obtained in about 1 nanometer scale in a non-agglomerated form. The elemental composition of $\text{SiCl}_4 \cdot 5\text{H}_2\text{O}$ was determined using EDS. The major elements are 3.33 of O and 0.2 of Si (% by weight). Sharp XRD pattern confirms crystalline structure of Silica nanoparticles. There is presence of other phase's peaks due to impurities into Silica nanoparticles. TGA explain that weight loss has occurred around 100°C of silica nanoparticles indicates the removal of absorbed and residual water. The data reveals that a total mass loss of 29.23% and 48.63% at around 100°C for the SiO_2 NPs. The impurities in chemically treated silica nanoparticles before and after purification were analyzed by UV-vis and ICP-MS method. It was found that chemical treatment is very pronounced by ICP-MS in the removal of certain impurities such as aluminum and Sodium but other impurity Fe is less affected. The effects of acids on the removal of impurity from Silica NPs have been studied using acid leaching: successive two mixtures composed of HCl; HCl: HNO_3 with a volume composition of 1; (2:1) respectively. UV-visible light absorption measurements were applied for the evaluation of the nature and the concentration of the dissolved impurities.

Keywords: Synthesis, Silica Nanoparticles, Characterization, Impurity Removal, Acid Leaching

1. Introduction

Because of candidate of silica nanoparticles for drug delivery, the detection of biomolecules and bioimaging [1, 2], Silica nanoparticles (SiO_2 NPs) have received more attention. The SiO_2 NPs can be used to deliver drugs such as antibiotics because of high thermal, high surface area [3].

Silica can be produced using several methods such as sol-gel, precipitation, microemulsion and so on. By conventional industrial, sodium carbonate reacts with quartz after at a high temperature, as a consequence sodium silicate solution creates and the precipitated silica is formed between sodium silicate solution and sulfuric acid. This method is hazardous responsible to resultant disposal and environmental pollution

problems, e.g. carbon dioxide (CO_2) and waste water. Huge amount of energy is consumed because of the reaction occurs at a very high temperature [4]. Limitations of other production method is the use of high-cost of tetraethylorthosilicate (TEOS), which consuming large amounts energy, and disadvantage related to size and shape. A cheaper and environmentally friendly method needs for the preparation of nanosilica from silicon-containing materials. Low-cost materials can reduce production cost [5]. Pure SiO_2 with crystalline phase can be used as the production material in semiconductor electronic devices, film substrates, ceramics etc. [6].

Nanosilica extraction from rice husk ash (RHA) using simple method which is used as corrosion inhibitor for brass plates was done in the literature [7]. Environmental consequences because of corrosion have attained a major challenge to engineers [8]. Corrosion inhibitors were extracted from plants now a days [9-11].

Synthesis of silica from NaSiO_4 solution by carbonation method was done in literature [11]. Preparation of silica nanoparticles are also produced by alkaline solution [12].

Pure Silica is more used in many products e.g. semiconductor chips and aerospace materials [13, 14]. Natural silica cannot be used directly due to impurities (Fe, Al, Na, K) [15]. The chemical methods can be used different organic acids (oxalic and acetic) and inorganic acids (hydrochloric and nitric) to remove iron impurity. Researchers used the effect of combination of different kinds of acids (H_2SO_4 , HCl , HNO_3) and the results in nitric acid and sulfuric acid have very good results in removal of iron [16].

Various processes were discovered about twenty years ago to purify silica and these processes are very expensive because of losses of material. To reduce the cost of the final product and to enhance the purity of silica, one can purify silica [17].

Many researches had been done in this field but preparation of silica nanoparticles from SiCl_4 by chemically was not found in the literature.

The first objective of this study is to prepare silica nanoparticles from SiCl_4 . The second aim of this research is to monitor the high effectiveness of several acids for the removal of impurities e.g. iron and aluminium, sodium from silica nanoparticles by a simple acid leaching method.

2. Experimental

2.1. Materials

Cetyltrimethylammoniumbromide (CTAB), cyclohexane, 1-butanol used are analytical grade and were used without any further purifications from Merck Germany. Precursor SiCl_4 and reducing agent NaBH_4 were used from Merck Germany and double distilled deionized water was used for cleaning and all preparations.

2.2. Methods

Reverse microemulsions given in Table 1 at water to surfactant mole ratio, $w_0=1$ and $w_0=2$ were considered to be prepared by composed of and homogeneously mixing up Cetyltrimethylammoniumbromide (CTAB), cyclohexane, 1-butanol and de-ionized water using Microprocess controlled bench-top Ultrasonic Cleaner (model no. powersonic 410). Equal amounts of water in oil microemulsions at $w_0=1$ were placed in two beakers and prepared 0.1M SiCl_4 solutions were injected into one beaker by pipettes and Microlitre Syringes (Hamilton Bonadus AG)) and 5% (w/v) NaBH_4 solution directly incorporated into another beaker using pipettes. Microemulsion at $w_0=2$, mentioned process was flowed. The resulting Silica nanoparticles were left for settledown and proceed for calcination in Furnace (Nabertherm, geprüfte Sicherheit) at 1300°C for about 4 h to exhaust adsorbed chemicals and water. Produced Silica nanoparticles were taken to analyze by SEM (JEOL JSM 5410LV), Energy Dispersive X-ray Spectroscopy (EDS), XRD (Bruker D8 Advance) and TGA. And then proceed for two successive acids leaching of Silica nanoparticles.

Table 1. Composition of prepared reverse microemulsion for synthesis silica nanoparticles.

w/o microemulsion number	% weight				w_0 , water to surfactant mole ratio
	CTAB	1-butanol	cyclohexane	water	
1.	15	74.26	10	0.74	1
2.	15	73.52	10	1.48	2

2.3. Acid Leaching

Silica nanoparticles were dipped for about one hour in an acid HCl and mixture solution $\text{HCl}:\text{HNO}_3$ with volume (2:1) to remove metallic impurities. UV-vis was measured by Lambda 950 UV-vis spectrophotometer in the spectral range from 190 to 1100 nm. UV-visible light absorption measurements are applied to evaluate the nature and the concentration of the dissolved impurities. ICP-MS is applied for investigation how much impurities are reduced in the first and second acid leaching.

3. Results and Discussion

Figure 1(a) and 1(b) explain the XRD images of Silica nanoparticles at $w_0=1$ and $w_0=2$ respectively. The data were in good agreement with standard JCPDS pattern file no. 96-

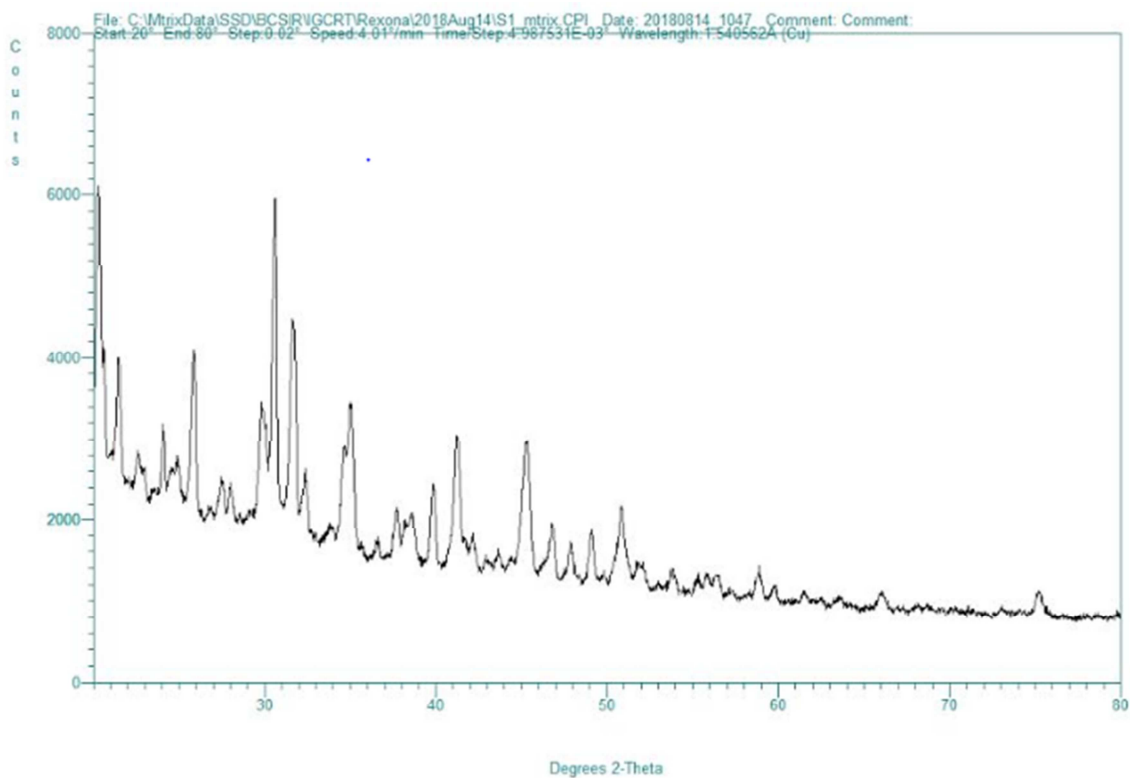
154-0288 of nano crystalline structure of Silica nanoparticles. There is presence of other phase's peaks due to impurities into Silica nanoparticles. There is a sharp peak at $\sim 30^\circ$ two theta. This sharp peak confirmed the presence of crystalline silica phase.

Figure 2 demonstrates the SEM photographs of Silica nanoparticles at $w_0=1$ and elucidates the spherical crystalline size of Silica nanoparticles with diameter about 1 nm. Figure 2 represent the particle size of nanosilica was obtained in nanometer scale in a non-agglomerated form.

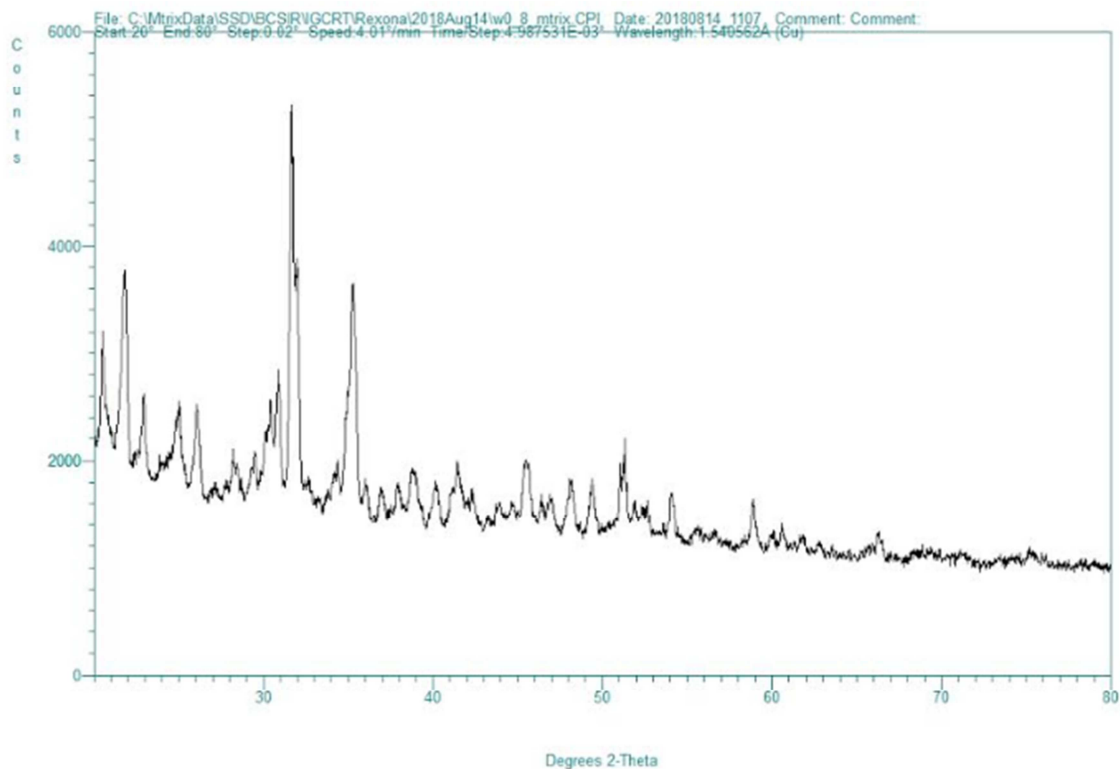
Figure 3 pictures the EDS which confirms the preparation of Silica nanoparticles. There is presence of other elements because of impurities. The elemental composition of $\text{SiCl}_4 \cdot 5\text{H}_2\text{O}$ was determined using EDS and the major elements found were 3.33 of O and 0.2 of Si (% by weight).

Figure 4(a) and 4(b) exemplify the TGA graphs of Silica nanoparticles at $w_0=1$ and $w_0=2$ respectively. TGA results illustrate the weight loss of Silica nanoparticles during

thermal analysis. TGA data plots demonstrate that weight loss has occurred around 100°C, as a consequence indicating the removal of absorbed and residual water.



(a)



(b)

Figure 1. XRD patterns of Silica nanoparticles at $w_0=1$ and $w_0=2$.

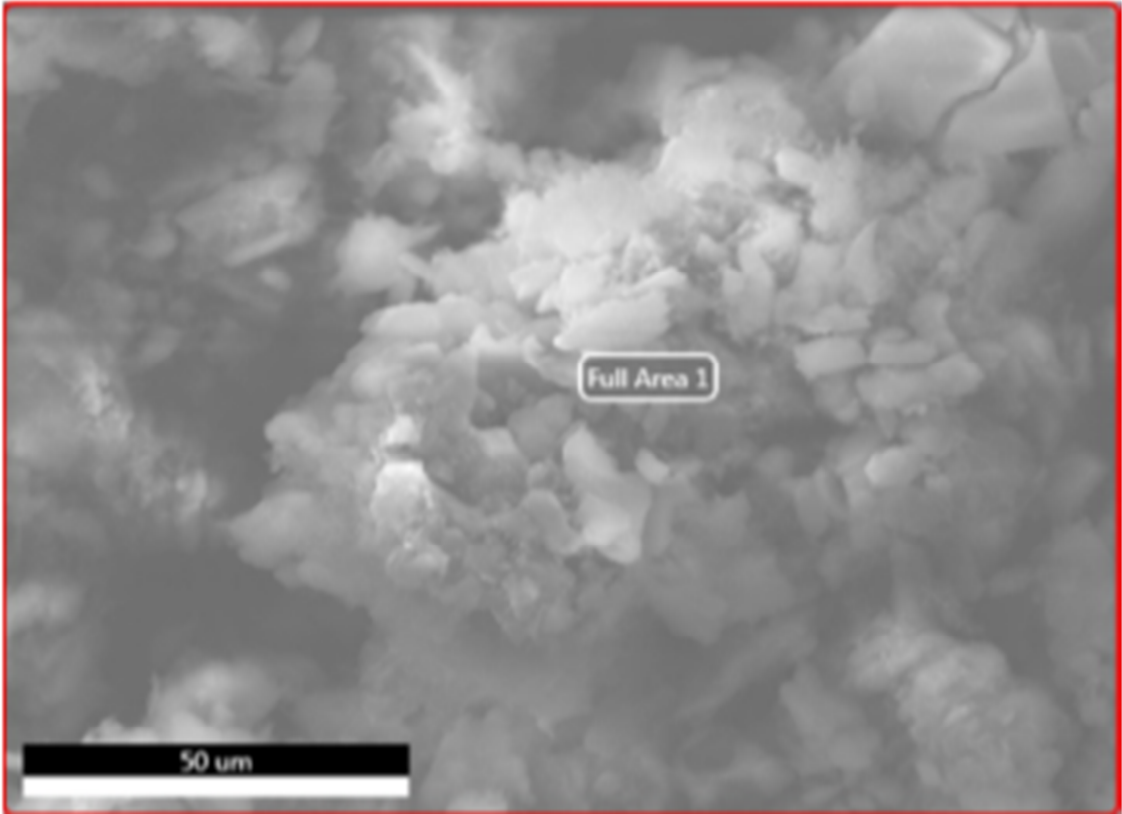


Figure 2. EM photographs of Silica nanoparticles at $w_0 = 1$.

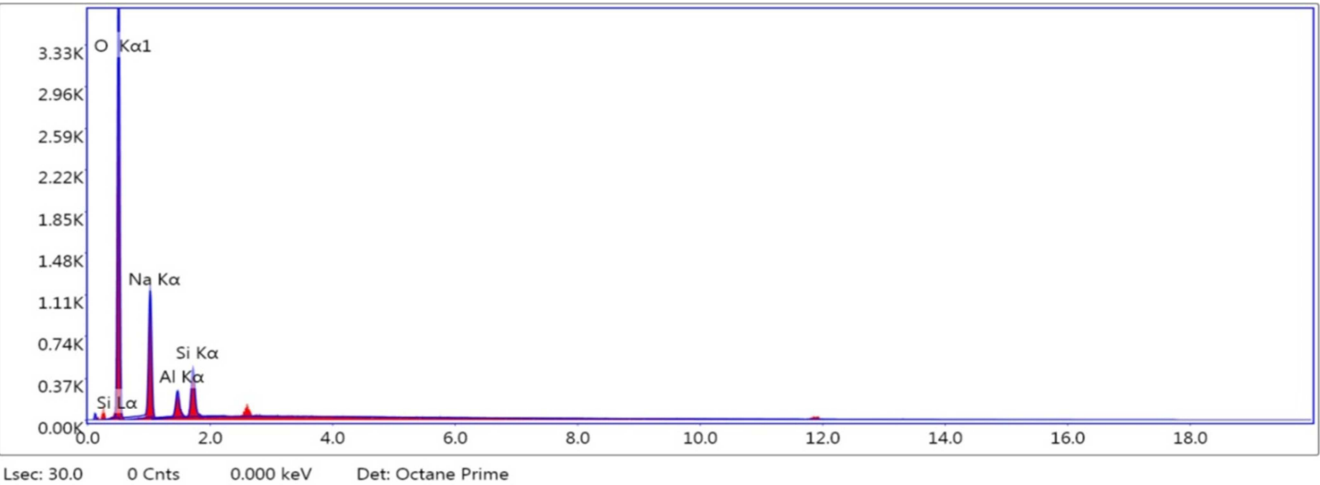
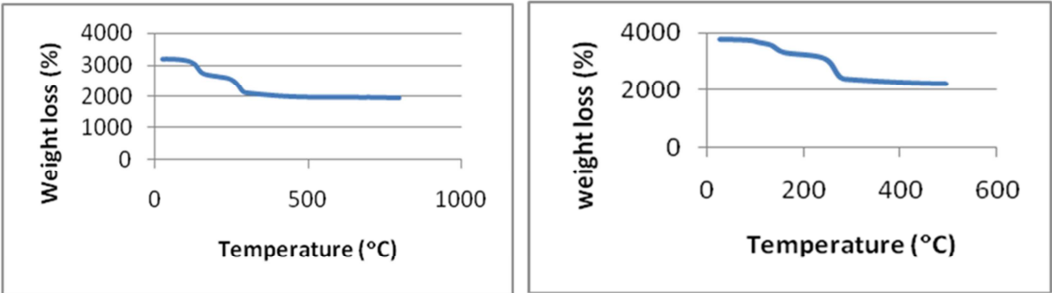


Figure 3. EDS plots of Silica nanoparticles at $w_0 = 1$.



4(a)

4(b)

Figure 4. TGA graphs of Silica Nanoparticles at $w_0 = 1$ and $w_0 = 2$.

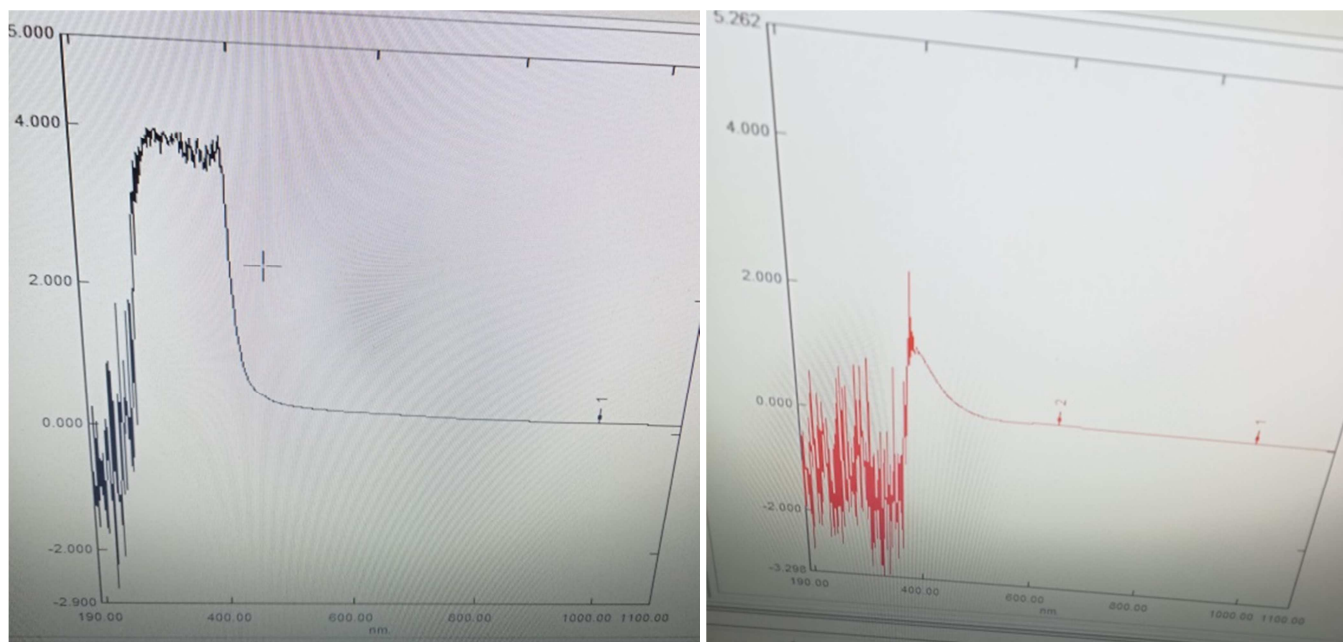


Figure 5. UV plots of two successive acid leaching.

Figure 5 explains the first leaching (black curve) reveals strong and broad UV absorption in the range from 190 to 1100 nm with a broad band located at about 230 nm to 400nm. This strong UV absorption is because of the presence of Fe and for the second acid leaching (red curve) we exhibit a decrease in the intensity of the peak at 330nm. Those results represent that the impurities are present on the grain and concentration are decreasing and the majority of impurities are eliminated after the second leaching.

Table 2 depicts the ICP-MS results for the natural silica nanoparticles and purified silica nanoparticles. The most impurities of the silica nanoparticles are: Al, Fe, Na and

results in after two acids leaching of silica nanoparticles, the total impurities concentration is reduced in the second leaching. The concentrations of Fe are less reduced after second purification process. Al concentration is largely reduced from 631 ppm to 76 ppm and the sodium is completely removed due to their oxides in the leaching solution.

These test data is result in after purification of silica nanoparticles are significantly removed after second leaching by the acid combination of HCl and HNO₃. Fe is reduced from 250 ppm to 150 ppm and Na is reduced from 140 ppm to 0 ppm which is completely removed.

Table 2. Concentrations (ppm) of impurities present in the silica nanoparticles before and after purification.

sample	Impurities concentration (in ppm)			total
	Fe	Na	Al	
SiO ₂ nanoparticles	250	140	631	1021
Purified SiO ₂ nanoparticles	150	0	76	226

4. Conclusions

Silica nanoparticles have been successfully synthesized by a simple chemical low-cost, efficient reverse microemulsion that is w/o microemulsion method. Characterization and acid leaching of silica nanoparticles were investigated. Characterization was studied by SEM-EDS, XRD and TGA. SEM explains that non-agglomerated spherical nano crystalline particles of Silica with diameter about 1 nm. The elemental composition of SiCl₄·5H₂O was determined using EDS. The major elements were 3.33 of O and 0.2 of Si (% by weight). EDS results out confirm the preparation of Silica nanoparticles. XRD pattern exhibits crystalline structure of Silica nanoparticles. Sharp peak confirmed the presence of crystalline silica phase. There is presence of other phase's

peaks due to impurities into Silica nanoparticles. TGA depicts that weight loss has occurred around 100°C of Silica nanoparticles occurred, as a result indicating the removal of absorbed and residual water. The impurities in treated silica nanoparticles were analyzed by UV-vis and ICP-MS. It was result out that chemical treatment is very efficient in the removal of aluminum and sodium but Fe is less affected. After the technique of removal impurities from nano silica, photo voltaic researchers will get the opportunity for their research work in this field.

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