Synthesis and preparation of Nano-silica particles from Iraqi western region silica sand via SOL-GEL method

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Abstract. Nano-silica particles have been successfully synthesized from Iraqi western region sand (Al-anbar sand) by SOL-GEL method, the raw materials for this work were sodium hydroxide, concentrated sulfuric acid, de-ionized water in addition to the Iraqi sand. In this method; solid sodium silicate is dissolved in deionized water and then precipitated by adding concentrated sulfuric acid. The selection of the used Iraqi sand based on XRF analysis, then the produced Sample was studied using XRD, BET surface area, AFM, FT-IR, and SEM analysis, BET Surface area and average particle size were (438,215 m²/g) and (6 nm) respectively.

Key words: nano-silica, Iraqi sand, SOL-GEL method

1. Introduction

Silica is included in rice husks, coffee husks, wheat husks, sugar cane bagasse, corn cob ash, and fly ash, as well as being a major component of sand in nature. Tetra ethoxysilane, for example, is a well-known compound that contains silica (TEOS), which can be further removed. Silica is also used for adsorption, structural uses, glass processing, water filtration, medical additives, composite material fillers, and synthetic source partner. Because of its adaptable properties, In the fields of electronics and photonics, energy harvesting and storage, drug delivery, bio sensing and catalytic application, building, and other fields, nano-silica has been the focus of extensive research. Composites and ceramics are examples of materials, as well as packaging. Since it can be used in a variety of ways, silica sand is used. Bear in mind that silica sand contains inorganic impurities such as Fe, Mg, K, and Ca, the majority of which are metallic, when using it in research and applications. As a consequence, these impurities can have an adverse effect on the product's properties, resulting in harm or failure to achieve the desired output.

Because of their low toxicity, high physical and chemical stability, broad surface area to volume ratio, and direct surface chemistry, they can be combined or functionalized with a wide range of functional species or molecules. Chemical methods for processing Nano silica include sol-gel, micro emulsion, chemical vapor deposition (CVD), hydrothermal, and co precipitation. The sol-gel method is the most popular chemical method for preparing Nano-
silica because of its simplicity and ability to monitor particle size, distribution, and morphology.

By applying 50 percent sulphuric acid to a sodium meta silicate solution, Chlomach and Kind (2004) precipitated and obtained silica. The primary silica particles were uniformly 22.7 nm in size.

Carbon dioxide was used by Cai et al. (2009) to precipitate silica from a sodium metasilicate solution. The aggregated SiO_2 particles obtained through dynamic light scattering were around 160 nm in size. By transforming natural chrysotile asbestos into amorphous nanofibrillar silica, amorphous nanofibrillar silica was developed. Wang et al. (2006) and Liu et al. (2006) are two examples (2006). The year was 2007. Jesionowski (2001) investigated the precipitation of silica in emulsions using sodium metasilicate and sulfuric acid. Jesionowski (2002) used hydrochloric acid to precipitate silica from sodium metasilicate solution, non-ionic surfactants, polydisperse mono(4-nonylphenyl) polyoxylethylene glycol ethers as emulsifiers, and an ultrasonic wash to create spherical silica particles. The precipitated silica had a specific surface area of 120-260 m²/g.

Synthetic conditions such as synthesis temperature, precipitation time, PH, coagulant addition, and washing and drying methods all had a major impact on the properties of precipitated nano-silica. The size, aggregation, and specific surface area of nano-silica particles are all affected by these variables. [11,12]

### 2. EXPERIMENTAL WORK

#### 2.1. Materials

In this work, the materials used for nano-silica synthesis shown in table below:

| Table.1 Materials used for nano-silica synthesis |
|--------------------------------------------------|
| Materials | Source(company) | Purity |
| Sodium hydroxide | Alpha chemika | 99 % |
| Sulfuric acid | Sigma Aldrich | 98 % |
| Deionized water | - | - |

#### 2.2. Raw materials

Iraqi sand was used as silica natural source, the selection of the Iraqi sand was based on XRF analysis which considered the best analysis to determine the elemental composition of the material, so it will be done to investigate the rich silica sand type.

| Table.2 Composition of two different types of Iraqi sand by XRF analysis |
|-------------------------------------------------------------|
| Type of sand | SiO_2 (wt.%) | Impurities (wt.%) |
| | | Al_2O_3 | CaO | SO_3 | MgO | other compounds |
| ordinary building sand | 34.23 | 0.91 | 55.79 | 4.91 | 1.38 | 2.78 |
| western region Al-anbar sand | 96.97 | 1.14 | 1.20 | 0.29 | 0.0041 | 0.39 |
2.3. Procedure

In a typical preparation of nano-silica, the following procedure should be followed:
1. 40 g of Sand is crushed using laboratory solid material grinder, then sieved to a particle size of 45 nm or smaller using sieving machine.
2. 125 g of sodium hydroxide pellets is crushed well using pestle and mortar.
3. Sand and sodium hydroxide were mixed well and calcined at 500 C° for 30 min in a programmable electrical furnace to produce solid sodium silicate.
4. After calcination, the solid silicate is crushed and transferred to a 800 ml beaker.
5. Hot deionized water at 60 C° is added to the beaker with a vigorous stirring using a magnetic stirrer, when the reaction occur, it produces green and homogenous solution.
6. Concentrated sulfuric acid (98%) is added intermittently and slowly with continuous stirring at 400 rpm so that a white gel is obtained.
7. The mother liquor was separated from the solid obtained gel using filter paper and Buckner funnel with the aid of vacuum pump.
8. The obtained gel is dried at 110 C° overnight in an electrical laboratory dryer.
9. Then the product is washed with a hot deionized water at 60 C° until PH reaches 2.
10. For checking the presence of SO₃²⁻, test 10 ml of the liquid filtrate from step 9 by adding a few drops of barium chloride BaCl₂.
11. If white crystalline BaSO₄ is precipitated, washing process should be continued.
12. The obtained solid product should be dried at 110 °C overnight after washing; the end product is nano-silica powder.

2.4. Procedure flow chart steps
3. Results and Discussion

3.1. Structure and pattern identification

The XRD analysis is one of the most important techniques for powder sample preparation. Figure 4 shows that the formed sample has a quartz structure with the highest peak at $2\theta = 22.4^\circ$, which is characteristic of an amorphous structure. Martinez et al. (2006) used the sol-gel technique to make amorphous nano-silica from a special form of sand and thermal treatment in his work; an amorphous peak was focused at $2\theta = 23$. This peak was shifted to lower 20 values with increased heating temperature, depending on the molar ratio of water to tetraethoxysilane (TEOS) and the heating temperature. Zhang et al. (2008) discovered an amorphous nano-silica broadened XRD peak with a value of 2 that was close to ours.

![XRD analysis of the prepared nano-silica sample](image)

3.2. BET surface area analysis

The sample was dried and degassed at 120 C° under helium for 3-4 hours, then submerged in cooled liquid nitrogen at -196 C°, where the analyzer measured and registered the nitrogen adsorbed at different pressures. The total BET surface area for the prepared sample was 438.215 m$^2$/g.

Hyeon-Lee et al. (1997) used the aerosol-gel method to make nano-silica powder with a high specific surface area of 400 m$^2$/g$^{-1}$. Martinez et al. (2006) used a chemical method to achieve a total surface area of up to 130 m$^2$/g$^{-1}$, indicating that the Nano-silica prepared from Iraqi sand has a greater total surface area than Martinez et al. (2006) and Hyeon –Lee et al (1997).
3.3. The composition of the produced nano-silica

Table 3 below shows the elemental composition of the produced sample, the silica content is increased due to the formation of silica nano particles during the reaction, while the compounds which is considered as impurities is decreased, so it is obvious that the chemical SOL-GEL method is a good example of decreasing the impurities.

| Type of sand            | SiO₂ (wt.%) | Impurities (wt%) |
|-------------------------|-------------|------------------|
|                         |             | Al₂O₃   | CaO    | SO₃    | MgO    | other compounds |
| Prepared nano-silica    | 98.67       | 0.0045  | 0.23   | 0.0005 | 0.0040 | 1.09            |

3.4. Atomic force microscopy and Average particle size

The topography of the prepared sample in its atmosphere is imaged using atomic force microscopy analysis. This technique has been shown to be useful in distinguishing between amorphous and crystalline phases, as well as measuring the fundamental properties of sample surfaces.

The average particle size of the prepared sample is found to be 6 nm, as shown in the granularity cumulative distribution map in fig.6.

Each silica sand particle has a different length, width, and height, implying that the nano-silica made from Iraqi sand has a smaller particle size than Cia et al (160 nm).
This study clearly shows the topography of the nano-silica surface in 2-Dimensional and 3-Dimensional images, as shown in fig. 7.
3.5. FT-IR analysis

Is an analytical technique that scans research samples and observes chemical properties with infrared light, then measures the sample absorbance of infrared light at different wavelengths to determine the molecular composition and structure of the substance. Figure 8 shows the FT-IR spectrum of the shaped nano-silica, with the stretching vibration of H$_2$O molecules at 3419 cm$^{-1}$, the bending vibration of H$_2$O molecules at 1643 cm$^{-1}$ and the shoulder at 3246 cm$^{-1}$, which corresponds to the stretching vibrations of Si—OH groups in the amorphous SiO$_2$ structure. The Si—OH group is confirmed to be bounded water, and the very solid and deep IR band at 1095 Cm$^{-1}$, with a shoulder at 1188 Cm$^{-1}$, is usually assigned to the TO and LO modes of the Si—O—Si asymmetric stretching vibrations, while the IR band at 956 Cm$^{-1}$ can be assigned to the silanol groups, and the IR band at 800 Cm$^{-1}$ is attributed to Si—O—Si symmetric stretching vibrations.

Murphy and Greytak (1979) assigned the Si—OH wagging mode to the IR band at 380 Cm$^{-1}$, but in this analysis, the IR band is recorded at a shoulder at 378 Cm$^{-1}$.

Bock and Su (1970) measured the IR spectrum of fused silica and compared it to the effects of vibrational measurements; the IR bands for fused silica were 377, 465, 800, 950, 1100, and 1190 Cm$^{-1}$.

Amorphous SiO$_2$ precipitated by carbonation has a spectrum that closely matches the FT-IR spectrum shown in fig.8 (Cai et al. 2009).
3.6. SEM

The surface morphology and structural measurements of raw silica sand were examined using scanning electron microscopy. As shown in fig.8, SEM images of unit compositions, which are amorphous alumino-silicate materials, reveal irregular size and structure. On SEM (halite, NaCl), nano-silica agglomerates and a cubic-like structure can also be seen. A course of action Many studies [1,2,5] have supported the agglomeration of Nano-silica particles. This halite crystal shaped as a byproduct of the Nano-silica powder preparation [8]. Halite was found in the final Nano-silica powder sample after washing because some NaCl persisted, and these primary particles had a proclivity to accumulate.

![Fig.9. Scanning Electron microscopy for the prepared sample](image)

4. Conclusion

The nano-silica particles were chemically synthesized using Iraqi western region silica sand using the SOL-GEL process. The final nano-silica particle has a total BET surface area of 438.215 m²/g and an average particle size of 6 nm. The highest peak of 2θ=22.4° in XRD study reveals quartz nano-silica structure, according to SEM study, silica nano-particles were globular, agglomerated, and irregular in form, silica sand is a good alternative precursor that can be used as a silica source and chemically prepared to generate nano-silica particles.

5. References

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