Preparation and Surface Modification of Silica Nanoparticles for Superhydrophopic Coating

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Abstract

Silica nanoparticles are well-known to be one of the multifunctional inorganic compounds which are widely used in medical applications. The aim of this study is to prepare the particles of nano silica oxide with particle size ranging from 20-25 nm. In the present study, surface modification of Silica nanoparticles was performed, and influence of modification on the structure and morphological properties was investigated. The resulting nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Silica nanoparticles with the average diameter of about 20 nm were modified with oleic acid, as coupling agents, in order to modify their surface properties and make them more waterproof dispersible in the organic area. Among the results is that the surface modification of the Silica nano-particles leads to more dispersion in the organic medium which indicates better organic synthesis. One of the results obtained, is that modified silica-nanoparticles can be used effectively in environmental and safety applications and can be used in future medical applications as wound stick that prevent water from reaching the wound and then prevent an inflamation.

Keywords: Silica preparation, surface modification; nanoparticles; Oleic acid; Dispersion.

الخلاصة

جسيمات السيلكا النانوية معروفة جيدا لتكون واحدة من المركبات غير العضوية متعددة الوظائف والتي تستخدم على نطاق واسع في التطبيقات الطبية. وتهدف هذه الدراسة إلى تحضير جسيمات أكسيد الزنك النانوي بحجم جسيمي يتراوح (25−20) نانومتر. في الدراسة الحالية، تم إجراء تعديل سطح السيلكا النانوية ، ودراسة تأثير التعديل على الخصائص الهيكلية والتركيبيه. درست خصائص الجسيمات باستخدام حيود الأشعة السينية (XRD) ، المجهر الإلكتروني الماسح (SEM) ومجهرالقوى الذرية(AFM).

تم تعديل جسيمات السيلكا بمتوسط قطر حوالي 20 نانومتر مع حمض الأوليك، كعامل ربط ، من أجل تعديل خصائص سطحها وجعلها أكثر طرد للماء. ومن النتائج التي تم الحصول عليها أن تعديل سطح جسيمات السيلكا النانويه يؤدي الى المزيد من التشتت في الوسائط العضوية والتي تشير إلى توافق عضوي أفضل. من النتائج التي تم الحصول عليها تعديل سطح السيلكا النانوية بحيث يمكن أن تستخدم بشكل فعال في التطبيقات البيئية والسلامة ويمكن أيضا أن تستخدم في التطبيقات الطبية في المستقبل والتي تتضمن لاصقات الجروح التي تمنع وصول الماء للجرح وبالتالي منع الالتهاب.

الكلمات المفتاحية: تحضير السيلكا, تعديل السطح, جسيمات نانوية, حمض الاوليك, تشتت .

Introduction

Superhydrophobic (SH) coating have attracted a huge scientific interest because of their unique charactersitics such as self-cleaning, antiadherence, and contamination control by reducing bacterial attachment in daily used materials, especially those with medical uses, such as textiles and plastics, and as an environmentally friendly water-repellent compounds[Basu and Paranthaman, 2011].

Nanoscience promises to provide a broad range of novel uses and improved technologies for medical and industerial applications. One of the reasons behind the intense interest is that nanotechnology permits the preparation of materials where at least one dimension of the structure is less than 100 nm. This small size is comparable to naturally occurring proteins and molecules in the human cell [Basu, *et al.*, 2014].

Nanoscale particles typically possess a larger percentage of atoms at the material's surface, which can lead to increase surface hydrophobicity [Zimmermann, *et al.*, 2015], and can maximize their ability to dislodge the mousiture from the surfaces. The important use of nanosilica is the hydrophobicity in biomedical and antibacterial applications is gaining interest in the scientific and medical communities, largely due to the physical and chemical properties of nanosilica besides that silica nanoparticles are favored in applications which require transparency and high abrasion resistance such as high performance coatings.

Free silica-nanoparticles cannot be prepared without agglomerates of μm size which inhomogeneously dispersed within the matrix . This would lead to the loss of all the desirable properties of the silica-nanocomposites, so to resolve this issue the surface modification is very important to get the exact nanosize needed for different applications[Burkarter *et al.*, 2013].

Experimental part

A. Materials The materials used in this research are water glass used in the preparation of silica, hydrocloric acid, deionized water imported commercially, silica, which has been prepared in the lab, oleic acid as coupling agent. The polymer materials are room temperature valcanized-silicone rubber RTV-SR

B. Preparation of Silica nanoparticles:

Water glass was used as starting material for preparation of silica nanoparticles. At first, using 300g of water glass by the addition of HCl acid at different addition rates, until silica deposited the precipitated silica is washed with distilled water to remove the formed sodium chloride and excess acid. At this stage, the excess water is removed by evaporation on hot plate, then drying in vacuum oven at temperature 100 ^{o}C for 3 hours. After evaporation of water, material was weighed. The weight of the resulting silica was 120g. At this stage, the silica that has been weighing are ignited at 1000 ^{o}C for a period of one hour to get rid of a moisture completely. Then, silica was weighed again. The weight was 90g.

C. Modification of Silica nanoparticles

We have used oleic acid as coupling agents for the surface modification of silica nano-particles to decrease the surface energy which cause particle agglomeration. Typical 8ml from olic acid was dissolved in 300 ml of o-xylene to form an oleic acid solution. Then, recently prepared silica nano-particles of 10 g were added to the above solution and allowed the reaction to perform at 50 °C under stirring for 2 h. Finally, the particles were separated by centrifuge at 15000 rpm for 10 minutes and washed four times with toluene, to remove the un-reacted coupling agents and then dried at room temperature for one night [X.-M. Li, D. Reinhoudt, and M. Crego-Calama, 2016].

D. Preparation of sheet of RTV-SR/ SiO_2 coating nanocomposites

At the begining we put the RTV-SR at room temperature for 3 hr then we take about 30 g from it and mixied with different weight of silica nanoparticles (2, 4, 6, 8, and 10) g , then poured in oiled mould with the dimension of (3×3×1) mm and left at room temperature for 8 hr at summer and one night in winter to be valcanized to get the fnal shape.

Analysis results of nano-Silica

Scanning Electron Microscopy (SEM):

Figure (1) shows different magnifications of Silica pure and modified nanoparticles surface. The results of this analysis showed the highly agglomeration of silica nanoparticles because it has surface energy that tends to clump together in large particles and this similar to the results of [Zhang, *et al.*, 2016]. It was found that the surface modified silica nanoparticles by coupling agent has reduced the agglomeration by reducing the surface energy. After modification the results showed that the silica nanoparticles were dispersed homogeneously.

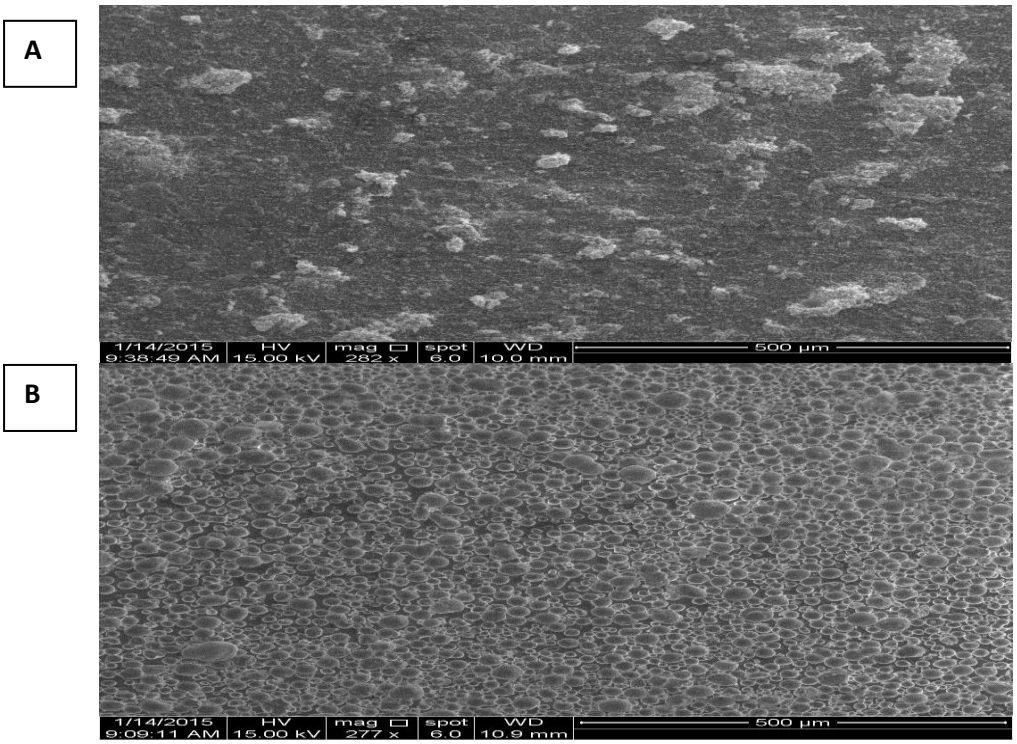

Fig. (1) SEM images of **(A)** pure nano-Silica, and **(B)** nano-Silica after modification

SEM/Energy Dispersive X-Ray Spectroscopy (EDS)

Figure (2) shows that spectrum of crystalline silica nanoparticles. One can conclude from the fig.(2) that the purity of silica nanoparticles is 100% since there is no elements appears in the spectrum and element analysis agrees with the research [Ma and Hill, 2016].

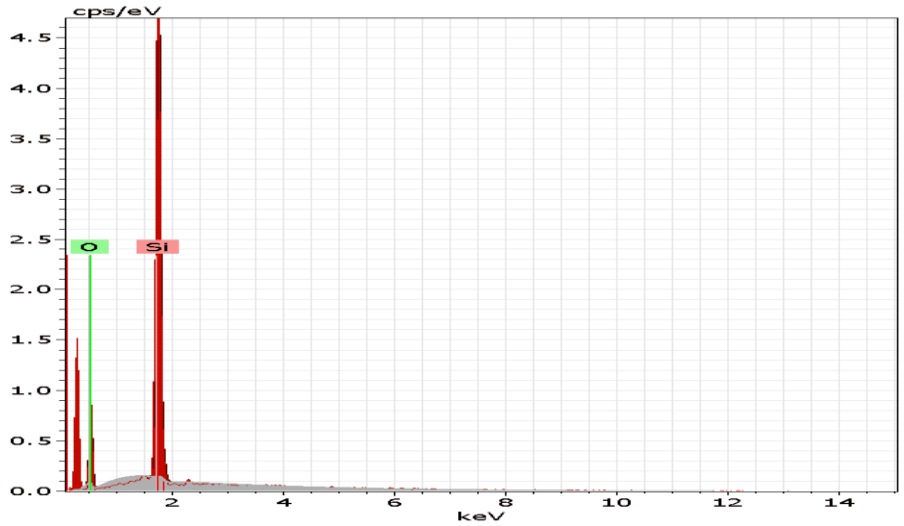

Fig. (2) EDS spectrum of silica modified nanoparticles.

Atomic Force Microscope

Figure (3) shows the AFM (3-D) images of silica unmodified nanoparticles and silica modified nanoparticles. AFM images indicate that the grains are distributed homogeneously within the scanning area (1005.18×1000.25)nm. The average diameter of pure and modified synthesized Silica is measured from AFM analysis using software and is found to be around (20-25) nm depending on preparation conditions**.**

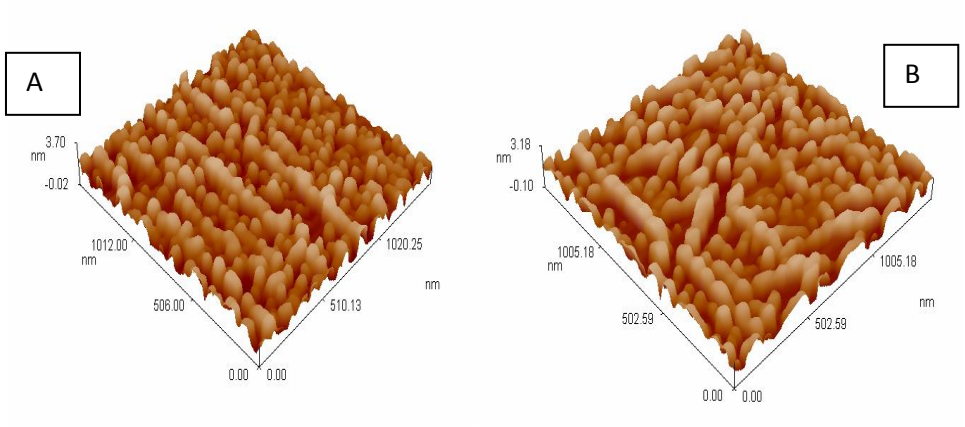

Fig. (3) AFM image of the (A) Pure nano-silica and (B) Modified silica nanoparticles

The surface morphology of the silica unmodified nanoparticles obtained from the AFM analysis in Fig. (3A), Fig. (3 B) shows the AFM images of silica modified nanoparticles. It was mentioned above that the silica modified surface is very smooth as shown in Fig (3B), the average roughness of modified silica is 3.18 nm while in the case of unmodified silica the average roughness is 3.70nm. This result agrees with [Becheri, *et al.*, 2014].

Table (1): The grain size of pure and modified Silica

Sample	*Grain size(average diameter) (nm)*	*Roughness (nm)*
Pure Silica	25	3.70
Modified Silica	20	3.18

X-Ray Diffraction Analysis (XRD)

From the X-ray test figure (4A) of silica unmodified nanoparticles at a diffracted angle (2θ =20˚ - 60˚), a crystalline peak appeared which indicate crystalline structure at (2θ = 23 ˚) which agrees with the results of [Fan Zhang, and Junling Yang, 2009, Sangeetha N. and L.Kumaragura, 2013].

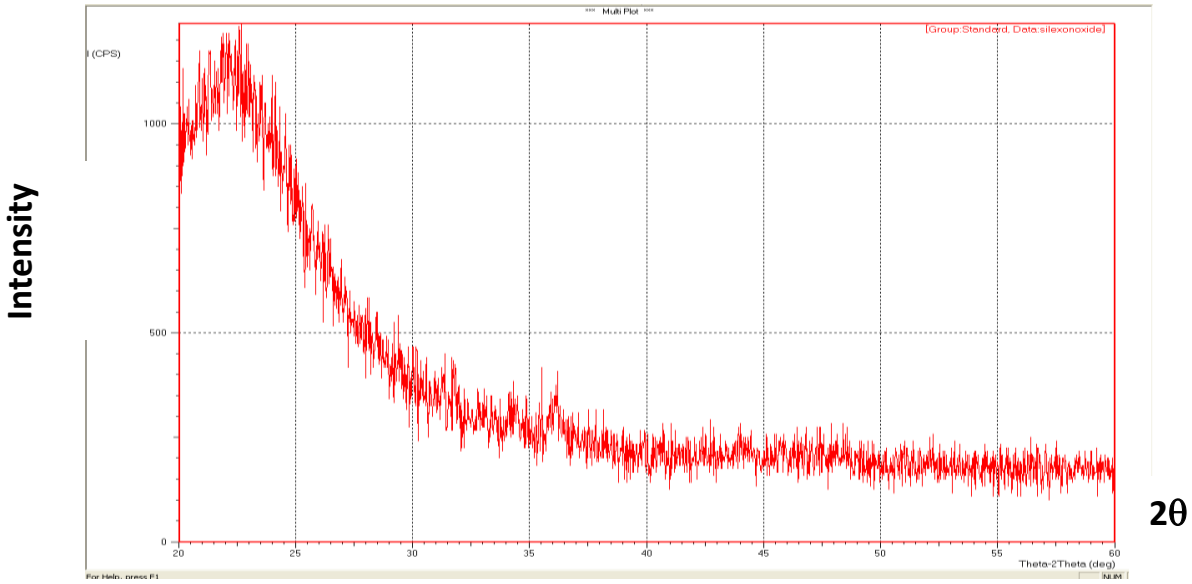

Fig. (4) Analysis of X-ray diffraction for silica modified nanoparticles

Water absorption(Superhydrophobicity) Test

The water absorption test was carried out as described by ASTM D570[ASTMD570-98, 2010]. Samples with dimensions of (3 ×3 ×1) mm immersed in distilled water for two months. Then the samples were collected every 10 days and dried to a constant weight at 40 °C. The percent moisture content/weight gain $\mathbf{M_t}$ is calculated by the following equation [ASTMD570-98, 2010]:

$$M_{t(\%)}=(m_t-m_1/m_1)\times 100.$$

where $\mathbf{m_t}$ is the weight of the sample at time during water immersion and $\mathbf{m_1}$ is the weight of the dry sample at initial time.

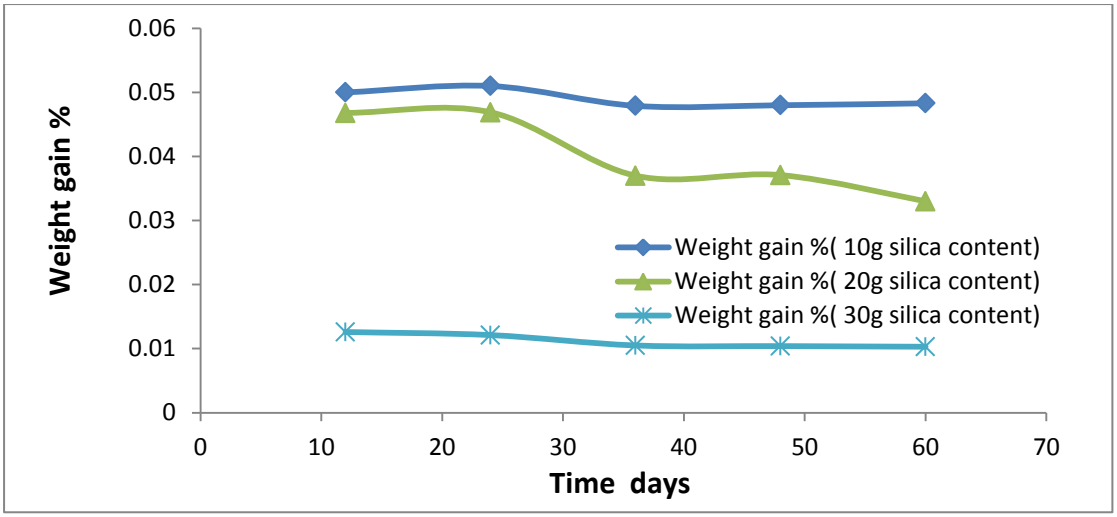

Fig.5 Curves of weight gain(water absorption) for the different load of silica nanoparticles.

From the fig. 5 the results show that the weight gain after immersion in water is decreased with the the increase of loading silica that is the silica nanoparticle will prevent the absorbsion of more water from the enviromental.

Conclusion

According to the results we conclude that:

1. Prepare nano silica by a chemical method which it is easy and non-costly way and the resulting nano silica in acceptable quantity have been successfully developed.
2. It is easy to modify the surface of Silica nano-particles with oleic acid with the aid of toluene and o-xylene.
3. The surface modified nano-particles are able to be uniformly dispersed in different organic media such as medical polymers.
4. Surface modification of Silica nano-particles makes their surface more hydrophobic and makes them compatible with organic media.
5. Oleic acid, as coupling agent was more efficient to modify the surface of nano-particles.
6. Silica nano-particles modified with an oleic acid coupling agent showed the same crystalline structure and morphological properties of pure Silica nanoparticles but with ultrahigh surface area and disagglomeration acceptable range.

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