

Impact of non-thermal plasma on SiO₂ nano particles synthesized by rice husk

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Silicon dioxide (SiO₂) is the most plentiful mineral in the world. Plants are the basis of this mineral. In recent periods, with the development of nanotechnology, silica nano particles have been establish new applications in solar cell. Rice husk and straw are rich causes of silica. In this study, amorphous silica nano particles were made from RH by chemical reduction method, and the surface of the material is improved by using DC glow discharge plasma. The synthesized samples were characterized by FTIR, XRD, EDAX, UV , FESEM and the results of both plasma treated and untreated samples were compared.

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1. Introduction

Rice husks(or rice hulls) are the rigid shielding of grains of rice. Rice husk is an agricultural residue profusely available in rice manufacturing countries. Husk Formed is around 20% of total rice production. Rice husk is usually not recommended as cattle feed meanwhile its cellulose and other sugar contents are very low, it is a partial source of energy for body. Furfural and rice brand oil are removed from rice husk. Industries use rice husk as fuel in boilers and other power production. Among the different types of biomass used for coal gas, rice husk has a high ash content fluctuating from 18 – 20 % and Silica is the major basic of rice husk ash[1].

Rice Research Institute of Iran conveyed that the annual paddy production in Iran reaches 3 million tons containing of 65% white rice, 20% husk and 15% bran. SiO₂ is obtainable in two forms amorphous and crystalline. A number of products colloidal silica, highly-pure silica and silica gel can be acquired by processing silica. These applications coatings, rubbers, electronics, and optics. At the same time, it is extensively used in synthesis of chemicals like sodium silicate, highly-pure silicon, silicon nitride, and silicon carbide. High-tech industries are needing silica nano particles, driven by their unique properties (Kalapathy et al., 2000).

2. Experimental details

2.1. Materials & Methods

RH is 13% to 29% minerals, 87% to 97% of amorphous silica. Main impurities of RH are sodium, potassium, calcium and iron.

Different methods have been described for synthesis of nanosilica particles from RH, including Chemical Vapor Deposition (CVD), sol-gel (Liou, 2004). The production costs have extended its application (Liou, 2004).

Two models exist to define the structure of amorphous SiO₂, the continuous random network model suggested by Zachariasen[7]) and the microcrystalline model of Randall[8]. In this first model, the local structural unit (SiO₄ tetrahedron)remains unchanged, with each tetrahedron corner divided with another tetrahedron, as in the crystalline forms. In the second model, the SiO₂ is set from microcrystallites of allotropic forms of crystalline SiO₂ .

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The synthesized SiO_2 nano particles was exposed to air plasma. The plasma surface modification method is ecologically friendly and nontoxic.

Rice husks (RH) were collected from a local rice mill with the husk dimension of 7-10 mm long, 1.5-2.5 mm wide and 0.10-0.16 mm thick. Dry raw rice husks were washed with water to remove the soil and other impurities and then dried in the sunlight for 24 hrs. These were labelled as raw rice husk (RRH). Acid bleaching was accomplished by treating the RRH with dilute HCl (1:1) and distilled water for 2 hour, followed by dilute ammonia solution (10 vol. %) for 1 hr to remove the traces of acid. The treated husk was taken out and washed with distilled water monitored by drying air for 24 hrs. About 5 g samples of RRH and acid-treated rice husk (ARH) were presented into a muffle furnace for pyrolysis at different temperatures varying from 800°C . The Black ash (Sic) and White ash (SiO_2), powders were prepared[2].

Non-thermal plasma was caused using a dc glow discharge chamber. Atmospheric air was used as a plasma. The discharge chamber was first cleaned and air tightened. Air in the chamber was evacuated using vacuum pump. The required air pressure was permitted through gas needle valve and the pressure was measured by pirani gauge. The electrodes inside the chamber was fitted perpendicular to the axis and were divided by a distance of 6 cm. The distance from the electrode to the sample is 3 cm. The potential of 400V is applied to electrodes. After steady discharge plasma RRH ash was exposed perpendicular to the axis through Teflon stick. Treatments were completed under the discharge potential of 400V with 15 mins exposure time. The result of the treated RRH ash was compared with that of the untreated RRH ash.

3. Results and discussion

3.1. Structural analysis

The XRD technique was applied to detect the crystalline phase of sample. The diffraction pattern improved a wide peak with its center at $2\theta = 22^\circ$, which is related to the values obtained. This figure[1] shows an amorphous structure with no crystalline pattern in both plasma treated and untreated sample. It is clearly seen that there is no significant change in position of the diffraction peaks except that the peak is more intense for the plasma treated film. It is observed from the XRD pattern that there is no secondary phase that indicates particles that has been incorporated into the lattice as a substitutional atom. The increase in intensity of the Si-O bond after plasma treatment indicates the reaction of oxygen atoms with the Si atoms during the plasma-treatment process. The plasma discharge limited active species that lead to the formation of radicals. Further O_2 atoms attaching to Si atoms in an increase in the concentration of Si-O bonds[3].

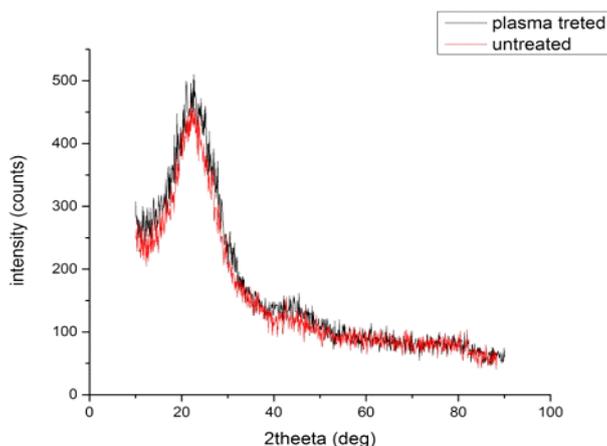


Fig 1. XRD pattern of SiO_2 at room temperature with 400 volt and 15 mins for plasma treated and untreated

3.2. Surface chemical analysis

Fourier Transform Infrared Spectra search changes the response of functional elements against IR irradiation. The functional behavior of fundamental elements in the spectra on the other hand reveals the structural modification.

Fig. 2 shows the FTIR spectra of amorphous SiO_2 rice husk powder heated at 800°C , 2h and treat with plasma of 400V at 15 mins in the range of $4000\text{--}400\text{ cm}^{-1}$. The FTIR spectra of the samples show a series of bond in the mid-infrared region. A large broad band around 3521.20 cm^{-1} and a band centered at 1589.41 cm^{-1} . In Fig. 2a is due to the stretching and bending vibration of the O-H bond from Si groups (Si-OH) and is credited to the absorbed water molecule on the silica surface[4]. The sharp peak band at 1100.44 cm^{-1} is due to the Si-O-Si asymmetric stretching vibration, whereas the band at 800.49 cm^{-1} has been allocated to the network Si-O-Si symmetric bending vibration[5]. The band peak at 463.90 cm^{-1} is accompanying with bending frequency of O-Si-O. The stretching band at 3418.21 cm^{-1} and libration bond at 468.61 cm^{-1} showed in Fig. 2b is attributed to absorbed water originate from OH- groups, approves highly condensed silica network in Amorphous silica. No peak was initiate between $2800\text{--}3000\text{ cm}^{-1}$. It means that there were no original organic compounds in silica before and after plasma treatment.

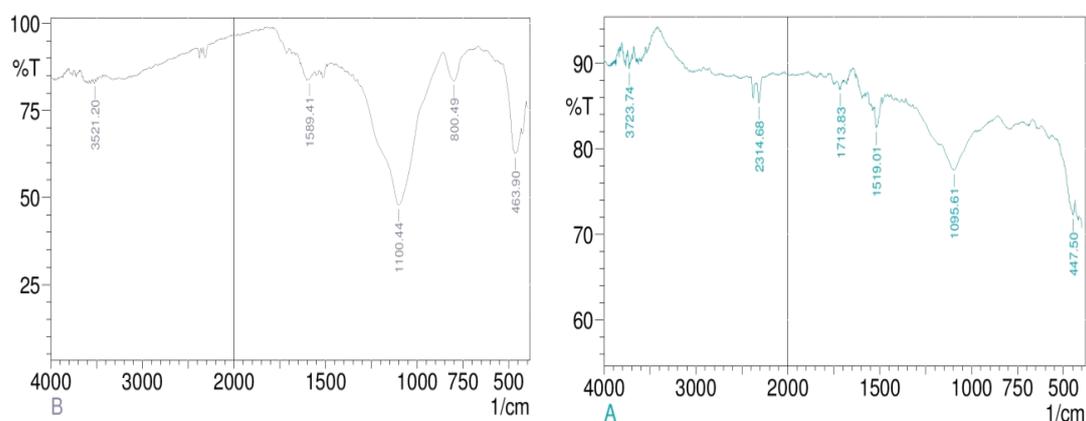


Fig. 2. (a). FTIR Spectrum of SiO_2 at room temperature for untreated; (b) FTIR Spectrum of SiO_2 at room temperature with 400 volt and 15 mins for plasma treated.

3.3. Surface morphology analysis

FESEM micrographs of the nano particles before and after the plasma treatment is shown in fig(3a and 3b). This reveals that the untreated nano particles are porous, with an asymmetrical surface structure. This type of structure lead to the accumulation and catching of static charges, thus resulting in agglomeration. The particles were fascinated to one another via static charges on the particles surfaces. From the figures (3b), the plasma-treated nano particles had moderately smoother surfaces compared to the untreated samples. The plasma treatment enhanced the surface compatibility, compact agglomeration, altered the interfaces, and increased the surface area. These actions resulted in a hardening of the bonding and adhesion at the interfaces of the nanoparticles[6].

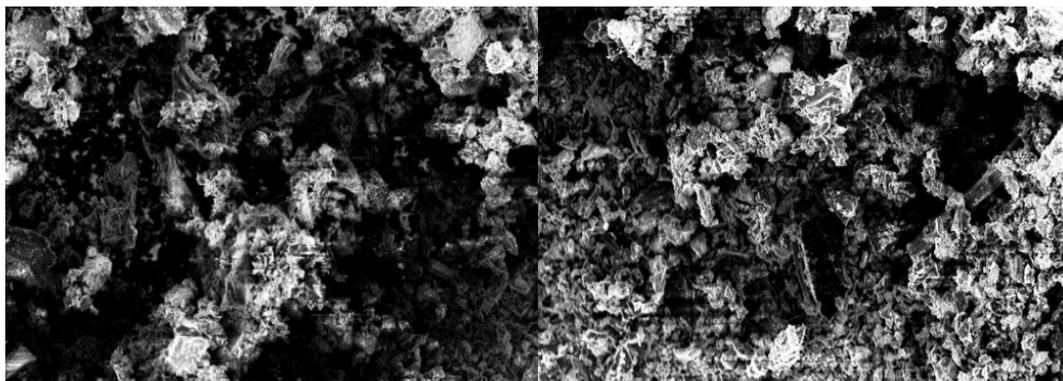


Fig. 3.(a) FESEM photograph of SiO_2 for Untreated; (b) FESEM photograph of SiO_2 for Air plasma treated.

3.4. Chemical composition analysis

The SiO_2 nano particles were characterized by using EDX to observe the changes in their chemical composition after plasma treatment. Table 2 shows measurable atomic percentage of the nano particles after plasma treatment. After plasma treatment, their oxygen (O) content increased, while their silicon (Si) content decreased. The O_2 content in the sample increased from 66.76% to 70.71 % after plasma treatment [7]. Plasma treatment modified the surface of the nano particles contained with the interaction process of plasma discharge. In plasma many active species, such as ions, electrons, and photons, the bombardment of which lead to the creation of radicals. The recombination of radicals are caused a change in surface morphology of the nanoparticles. During the discharge, however, some of the active species reacted with oxygen holding radicals. As a result, increased to uptake of oxygen. This increase in O_2 content after the plasma treatment specifies that surface oxidation. This result is in arrangement with research by Fang et al[8].

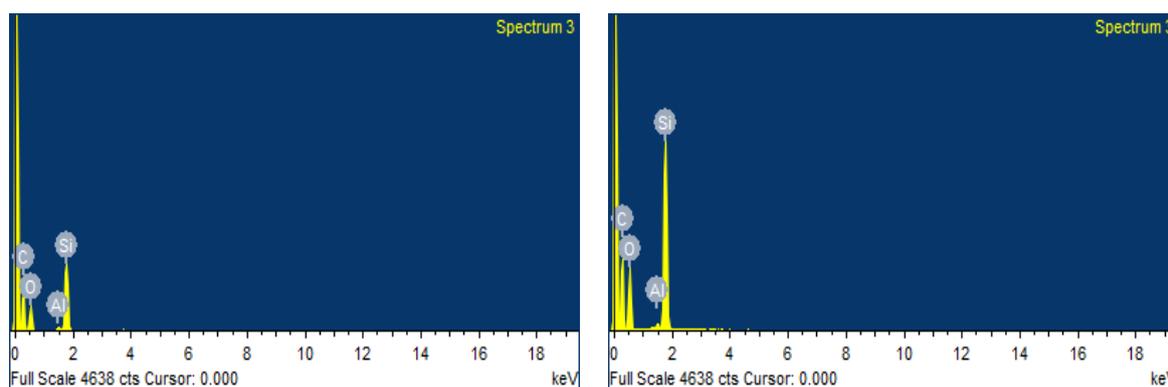


Fig. 4.(a) EDAX pattern of SiO_2 for Untreated; (b) EDAX pattern of SiO_2 for Air plasma treated

Table 2. Atomic concentrations of nanoparticles after plasma treatment.

Samples	Atomic content (%)
untreated	C- 22.48
	O- 66.76
	Si- 10.72
	Al-0.04
Air Plasma treated	C- 20.26
	O- 70.71
	Si- 9.01
	Al-0.02

3.5. Optical analysis

Optical characterization of the present samples engaged using UV-VIS Spectroscopic analysis. Using the resultant spectra, the behaviour of samples against the irradiation of optical source of various wavelengths has been detected. The spectra exhibits absorption bands around the wavelength 200-300 nm both plasma treated and untreated can be ascribed to the electronic transition from the π - π^* states[9]. Hypochromic shift exposes the decreasing absorption ability of sample due to the compositional changes.

The spectra explore the charge transfer between the HOMO-LUMO levels of nano particles result of electromagnetic irradiations. By observing decrease in band gap value for plasma treated sample 5.14eV and untreated sample 5.28eV is due to the reductions in imperfect sites in nanoparticles. The reduction in the unsaturated bonds and thereby reductions in the density of localized energy state lead the optical band gap develop narrower[10].

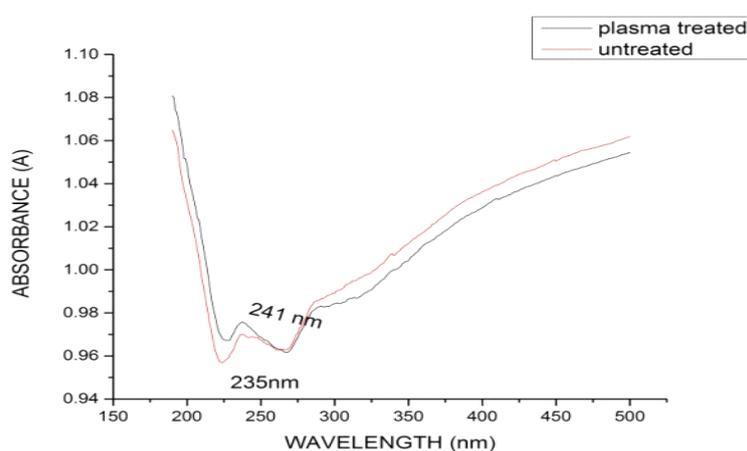


Fig. 5. Ultra violet-visible spectrum of SiO_2 at room temperature with 400 volt and 15 mins for plasma treated and untreated.

4. Conclusions

Investigating the properties of plasma treated SiO_2 nano particles such as physical, structural, optical, thermal at the function of compositional changes.

Structural features of samples are analysed using XRD studies, it has been found that SiO_2 is amorphous structure. The FESEM-EDAX observations engaged on the samples exhibit different morphological images, These micrographs expose the increasing formation of tiny granule morphology of the plasma treated SiO_2 . The observed EDAX analysis confirmed the increasing quantity of SiO_2 and thereby corresponding changes in compositions in the samples. UV-vis spectroscopic analysis display spectral absorptions of each sample at selective wavelength. The samples exhibit two different bands of absorptions around 235nm and 241nm. FTIR observations are used to search the response of functional elements and their relative bonding structure against IR irradiation. These spectroscopic observation confirmed the structural regulation due to compositional changes by exhibiting sharp and deepened transmission peaks.

Acknowledgments

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