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Journal of Materials Research and Technology
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Original Article

TEM and SEM study of nano SiO_2 particles exposed to influence of neutron flux

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ARTICLE INFO

Article history:
Received 23 April 2015
Accepted 1 November 2015
Available online 11 December 2015

Keywords:
Nano SiO_2
TEM
SEM
Neutron irradiation
Nanopowder

ABSTRACT

Before and after neutron irradiation, in order to identify the "adhesion" in silica nanoparticles, analyses have been conducted on transmission electron microscope (TEM) at small nano dimensions. Simultaneously, at relatively larger nano dimensions, the surfaces of the samples were observed by the scanning electron microscope (SEM). Moreover, analyses of the samples with SAED (selected area electron diffraction) technology on TEM device used for determining the structure of the nanomaterial. From TEM analyses, it has been found that little "adhesion" is observed at small dimensions (maximum 70 nm) under the influence of neutron irradiation and this "adhesion" directly influences the electrophysical properties of nanomaterials.

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Take home message

- Silica nanoparticles analyzed with TEM, SAED and SEM.
- Study neutron flux effects on silica nanoparticles.
- After radiation determined "adhesion" of nanoparticles.

1. Introduction

Recently, nanomaterials have been widely used in computer, telephone, satellite technology, different types of detectors and other various fields of industry for their unique features [1–4]. Size effects of inorganic nanoparticles increase their application possibilities in nano dimensions [5,6]. Nano SiO_2 compound used in the experiment has a wide application

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http://dx.doi.org/10.1016/j.jmrt.2015.11.001
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fields in space electronics and nuclear technology in macro and micro sizes. Recently, the application of these nano-size materials in space and nuclear technologies are very topical, therefore we have studied stability of these materials after neutron irradiation. As mentioned before, the size effect of nanomaterials influence to their application possibilities. Therefore, on the SEM and TEM devices we have studied the "adhesion" process, which can be formed in big and small size nanomaterials after influence of neutron flux. Moreover, we have determined nanoparticles sizes in the local state by TEM device and the nature of nanoparticles by selected area electron diffraction (SAED) technology. The samples used within the experiments have been irradiated by neutron flux (2×10^{13} n cm^{-2} s^{-1}) in the central channel (Channel A1) of the TRIGA Mark II light water pool-type research reactor at full power (250 kW) in Jozef Stefan Institute (JSI). TEM analyses (images and SAED) have been carried out on "Jeol JEM-2100" device and SEM analyses on "Jeol JSM-7600F" device for all samples (initial circumstance and after continuously 5, 10, 15 and 20 h irradiated by neutrons), in the "Department of Nanostructured Materials – K7" at JSI in Ljubljana, Slovenia.

TEM equipment has been used for observing nanomaterials with size smaller than 100 nm and obtaining quantitative results [7–9]. The main reason, minimum 100 keV of the accelerated electrons energy on TEM devices and its increases several times the degree of sensitivity in small sizes of the TEM devices relatively to SEM devices. There are some problems for observation far background of the samples operating on the basis of high-energy electrons TEM devices. In this case, it is advisable to use SEM device operating with maximum 30–50 keV energy electron flux. Taking into account these properties for TEM and SEM devices, we have used both of the devices for completely observing nano SiO_2 samples. Thus, we have reviewed the images of SiO_2 nanoparticles at the relatively far background (SEM capabilities) and at small sizes (TEM capabilities), taking advantage of both devices.

2. Theoretical frameworks

In this section, we will review briefly and simply the dependence on external potential of the wave property of electron flux used on SEM and TEM technologies. For this reason, first of all, it should be mentioned the influence of wave properties on growing and resolution. The shortest distance between two points, which can be distinguished from each other, is called resolution. For example, the average resolution for the human eye is approximately 0.1–0.2 mm and the resolution in optic microscopes is much smaller than this value. In the general case, we can calculate the resolution of the microscope with the following equation: $\delta = (0.61\lambda/\mu \sin\beta)$ (here λ – wavelength, μ – refraction index and β – observation angle in zoom lens) [10].

We can say that, resolution of microscope dependence on the wavelength which directly used beam if we consider the refraction index and sinus of observation angle change very little in most cases. So, with an increase of wavelength, the numerical value of microscope resolution increases and thus its zoom decreases. For example, using a wavelength of 550 nm for optic microscopes in the best case, we will get at least 300 nm for its resolution and it does not allow us to see the distance of 0.2 nm (or small nanoparticles of which size is in nano order) between two atoms. During the SEM and TEM analyses, electron flux is used and this time wave properties of electron directly influence the device resolution. Thus, according to dual property of the particles we can write $\lambda = (h/p) = (hc/E)$ for de-Broglie wavelength of the electron. This equation indicates the wavelength of the E energy (or impulse is p) electron. It should be mentioned that, it is obtained $\lambda = 1.22/E^{1/2}$ expression in accordance with the last relation, without consideration of relativistic effects in well-known de-Broglie's expression for wave property of the electron [10]. Here E – energy of the electron, which is expressed with eV, λ – de-Broglie wavelength expressed with nm. In the SEM and TEM devices, the electron moves in V potential field and in this case, its kinetic energy (eV) is defined as $eV = (m_0 v^2/2)$. Making some simplicities in this equation, we can define the electron impulse as $p = m_0 v = (2m_0 eV)^{1/2}$. We will get the expression $\lambda = h/\sqrt{2m_0 eV}$ in simple case for its wavelength while moving in V potential inside electron microscope. From the expression, it is seen that the potential of the field is inversely proportional to wavelength and by changing the potential at SEM or TEM device, we can control the wavelength. It should be mentioned that in previous expressions we have not considered the relativistic movement of electron but the electron moves relativistic in reality. The relativistic effect is usually observed on TEM devices, so on TEM devices the speed of electron at potentials more than 100 kV is higher than the half of light speed. Consequently, we can write the equation $\lambda = h/(\sqrt{2m_0 eV(1 + (eV/2m_0 c^2))})$ for relativistic state [10]. A bit more potential is required which is calculated with the initial equation at the relativistic state. If we consider the potential is 100 keV in the last equation, then we will find that the resolution for TEM is 0.0037 nm, and it allows us to observe nano and angstrom sizes at atomic level. It should be mentioned that on TEM devices it can be used more potential than SEM devices and that is why magnification capacity of TEM devices is larger than SEM devices.

3. Materials and methods

At the presented work, it has been investigated the transmission electron microscope (TEM) analyses and scanning electron microscope (SEM) images of SiO_2 nanoparticles before and after neutron irradiation. In this research we have chosen SiO_2 nanoparticles with 160 m^2 g^{-1} specific surface area (SSA), 20 nm particle size and some parameters of the used sample has been studied [11–15]. Simultaneously, it has been carried out "selected area electron diffraction" (SAED) analyses of SiO_2 nanoparticles before and after neutron irradiation on TEM device. The samples have been irradiated by neutron flux (2×10^{13} n cm^{-2} s^{-1}) in the central channel of the TRIGA Mark II research reactor at full power.

It is important to note that the JSI TRIGA reactor has been thoroughly characterized [16,17] and the computational model used for computational characterization has been thoroughly verified and validated against several experiments [18–21]. In addition, the model has been used to support

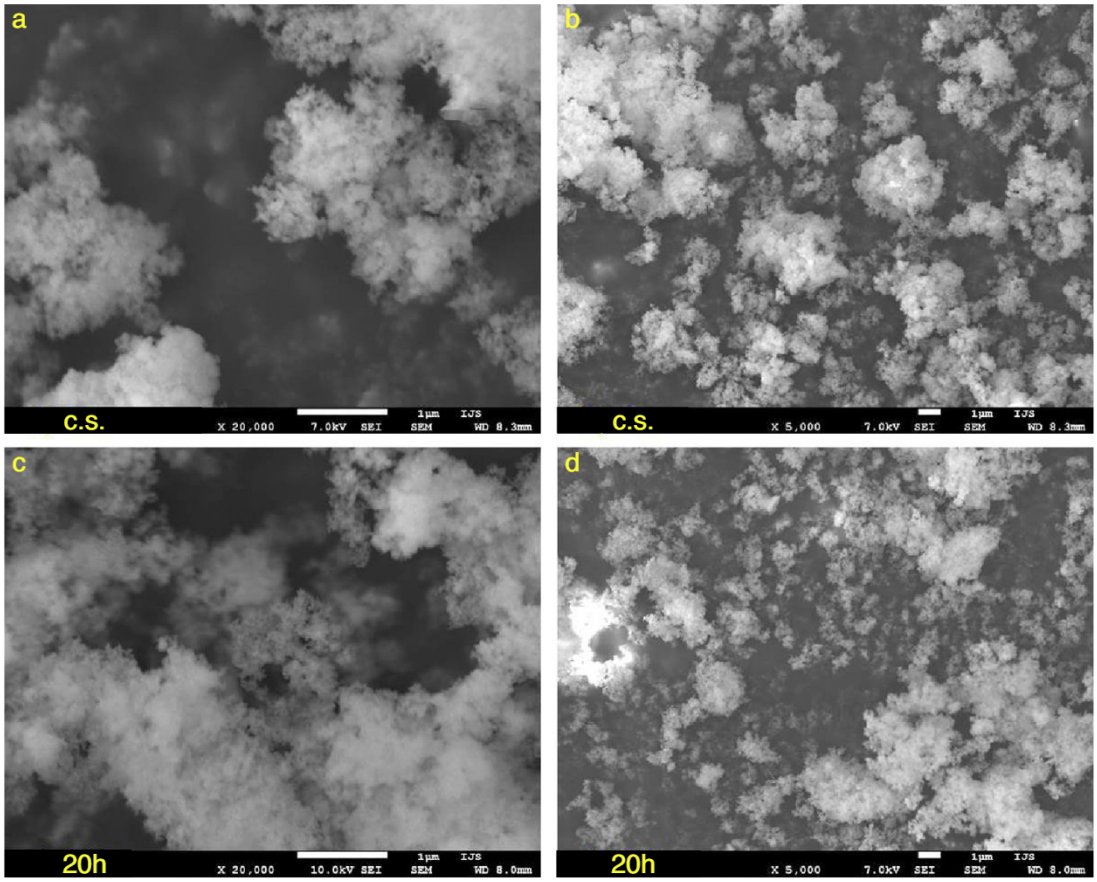

Fig. 1 – SEM images of SiO_2 nanoparticles before irradiation (a and b) and after neutron irradiation (c and d).

many experimental campaign and projects to calculate reactor parameters [22–27].

The irradiation parameters in the central channel at full power (250 kW) are as follows: thermal ($E_n < 0.625$ eV) neutron flux is 5.107×10^{12} n cm^{-2} s^{-1} (1 ± 0.0008), epithermal ($E_n \sim 0.625$ eV–0.1 MeV) neutron flux is 6.502×10^{12} n cm^{-2} s^{-1} (1 ± 0.0008), fast ($E_n > 0.1$ MeV) neutron flux is 7.585×10^{12} n cm^{-2} s^{-1} (1 ± 0.0007), and the total neutron flux in the central channel is 1.920×10^{13} n cm^{-2} s^{-1} (1 ± 0.0005). SiO_2 nanoparticles have been filled in aluminum containers with high purity as powder at the special condition and prepared appropriately to the reactor channels. Firstly, the prepared sample has been irradiated for 5 min and activity analyses have been conducted. Then the other four samples have been separated into four groups and each of them has been separately continuously irradiated at various times such as 5, 10, 15 and 20 h by neutron flux (2×10^{13} n cm^{-2} s^{-1}). TEM analyses of the samples (before and after neutron irradiation) have been carried out at the 200 kV efficient voltage on "Jeol JEM-2100" device. Moreover, SEM images of the samples have

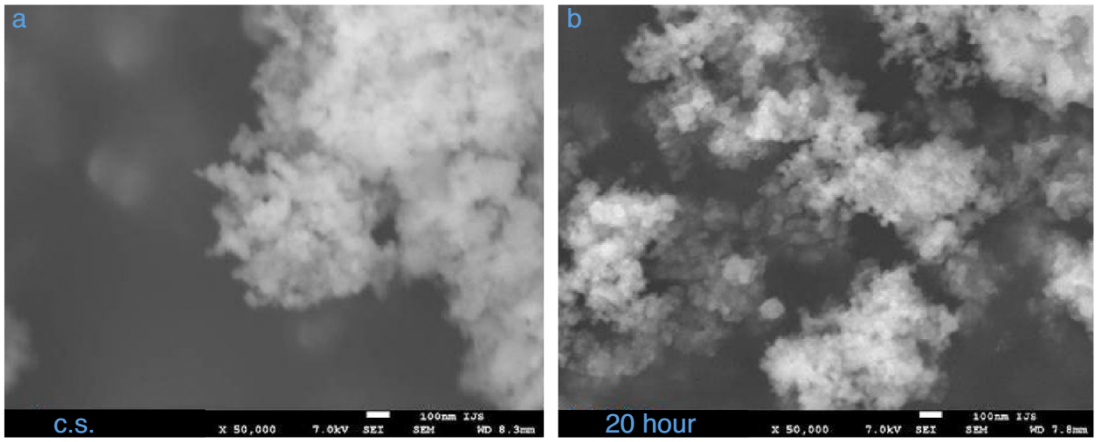

Fig. 2 – SEM images of SiO_2 nanoparticles before irradiation (a) and after neutron irradiation (b) (×50.000 and 100 nm).

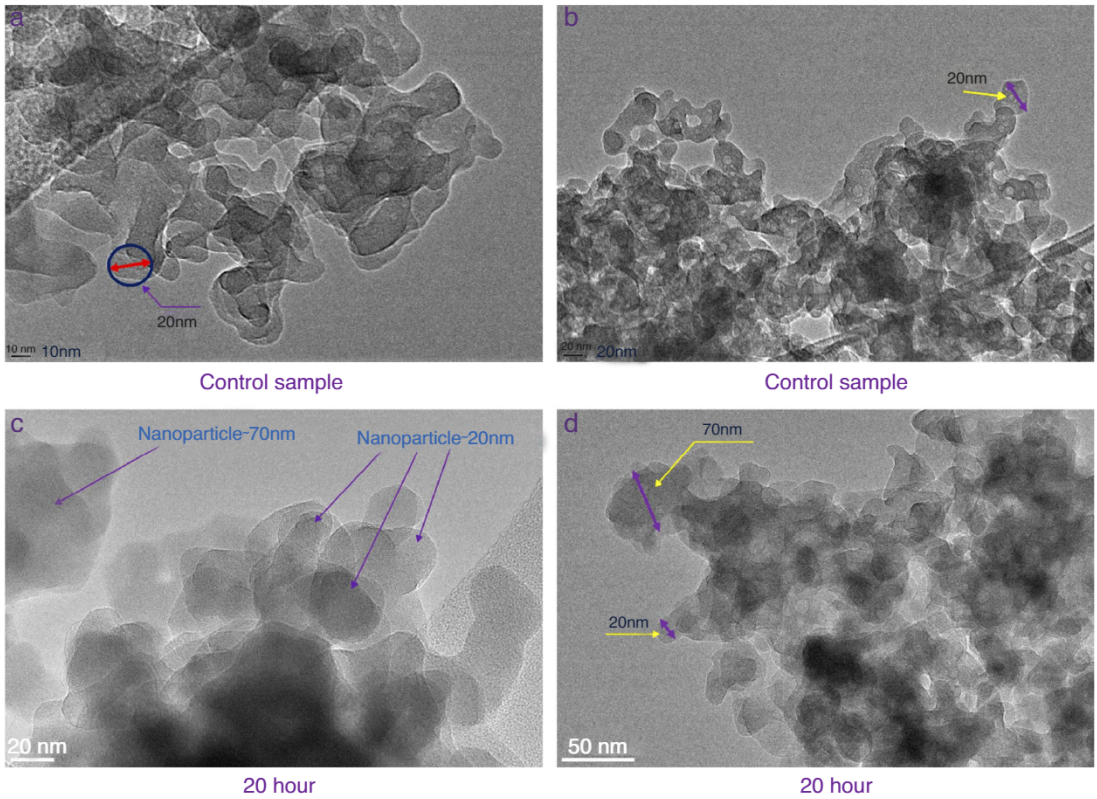

Fig. 3 – TEM images of SiO_2 nanoparticles at initial (a and b) and irradiated with neutron flux (c and d).

been taken on "Jeol JSM-7600F" device at the 7–10 kV efficient voltage and 8 mm working distance for initial circumstance and after neutron flux.

4. Result and discussion

During the experiments, SEM and TEM images of SiO_2 nanoparticles have been taken in different magnification. The main purpose of scanning the images in low magnification orders is to observe the nanoparticles adhesion in micron size in the samples. So, if nanoparticles changed to micro-size cluster by adhesion, in this case, it is impossible to observe the existing clusters in nano images in ×50.000 and more magnification. Therefore, first let us review SEM images scanning with micron-size images and ×5.000 and ×20.000 magnification (1 μm index) (Fig. 1).

From the figures, it is seen that before (control sample) and after irradiation there is not any change in the general background of the image (Fig. 1a–d). According to SEM images shown in Fig. 1, we can say that SiO_2 nanoparticles do not change to large-size "combination" (clusters) under the influence of neutron flux. And now let us review relatively big magnification in order to observe the clusters that can be generated in several hundred nanometer (Fig. 2).

So, in this case, we will review SEM images taken with ×50.000 magnification (100 nm index). In this case, it is possible to observe bigger nanoclusters, which can be formed in nano size, however in this case also the clusters are not observed. Obviously, to these SEM images clusters with the sizes of 200 nm to 1 μm are not observed.

Now let us review TEM images for analyzing the compound of the nanoparticles (2–5 nanoparticles with the diameter of 50 nm) in the smaller size (Fig. 3).

TEM images shown in Fig. 3, have been taken up to ×1.200.000 magnification (10 nm index). From TEM images (Fig. 3a and b) of the initial nanoparticles it is seen that, all particles has 20 nm size in the samples. This shows that practically the process of "adhesion" does not occur in the initial sample without external influence. In other words, the experimental sample consists of pure nanoparticles, which has 20 nm particles diameter. Moreover, other two TEM images shown in Fig. 3c and d, we can say that new nanoparticles with about 70 nm size are generated in the sample by very little "adhesion" under the influence of neutron irradiation. And this small amount "adhesion" direct influence to electrophysical properties of nanomaterials [11–14]. Furthermore, in order to study the lattice structure of SiO_2 nanoparticles, it has been carried out SAED analyses for the samples exposed to neutron flux influence and initial circumstance in TEM device (Fig. 4).

As a result of the analyses, it has been revealed that the sample has not changed its state before and after irradiation, that is the sample keeps its amorphous feature before and after irradiation. It can be easily observed in SAED images taken in TEM device. Thus, from general analyses of the nanoparticles it has been revealed that macro or micro-size "adhesion" is not observed in SiO_2 nanoparticles after neutron irradiation. So, if not to consider the small-size nano

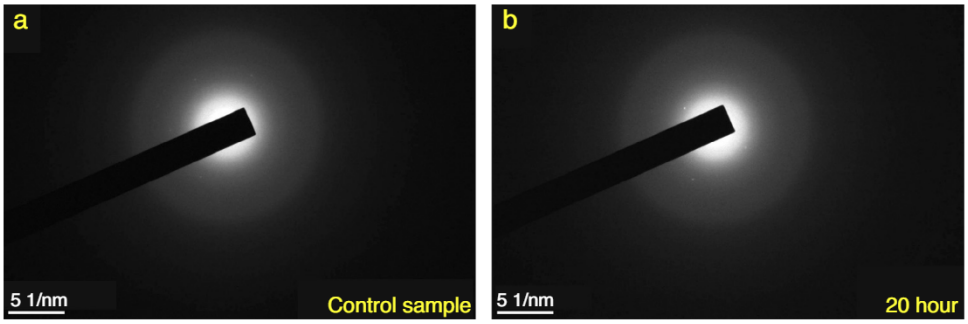

Fig. 4 – SAED study of SiO_2 nanoparticles in TEM device at initial (a) and irradiated with neutron flux (b).

"adhesion", practically, the nanoparticles keep its nano feature before and after irradiation.

5. Conclusion

From SEM analyses of nano SiO_2 samples, it has been revealed that nanoparticles does not "adhesion" macro or micro dimensions before and after neutron irradiation. In order to determine the "adhesion" and crystalline structure of nanomaterial at low nano sizes, the samples have been analyzed on TEM device and SAED technology. It has been found by TEM analyses that very little "adhesion" is observed at small dimensions (maximum 70 nm order) under the neutron irradiation. And this small amount "adhesion" directly influence to electrophysical properties of nanomaterials. Simultaneously, from the SAED studies in TEM device, it has been revealed that the presented sample possess an amorphous structure before and after neutron irradiation.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

The work has been conducted following the agreement signed between the Institute of Radiation Problems (IRP) of Azerbaijan National Academy of Sciences (ANAS), and Jožef Stefan Institute (JSI), Slovenia. We gratefully acknowledge the assistance of our colleagues from IRP of ANAS and "Reactor Infrastructure Centre (RIC)" and "Department for Nanostructured Materials – K7" at JSI. We would like to thank Asst. Prof. Dr. Luka Snoj and Anze Jazbec for providing irradiated samples in TRIGA Mark II type research reactor.

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