Electrical impedance spectroscopic investigations of monodispersed SiO$_2$ nanospheres

A. Sakthisabarimoorthi, S.A. Martin Britto Dhas, M. Jose*

Department of Physics, Sacred Heart College (Autonomous), Tirupattur, Tamilnadu, India

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**Abstract**

Dielectric analysis of uniform and monodispersed SiO$_2$ nanospheres at various temperatures in the frequency range 1 Hz–1 MHz is reported. The high optical transmittance and the presence of silica network in the synthesized product are evident from UV–vis and FTIR spectroscopic techniques respectively. The amorphous structure of SiO$_2$ nanospheres is investigated by powder XRD pattern and uniform spherical morphology is visualized by FESEM analysis. The X-ray photoelectron spectroscopy elucidated the exact valence states of the SiO$_2$ nanospheres. The temperature dependent dielectric parameters such as, dielectric constant ($\varepsilon_r$) and loss factor (tan $\delta$) are decreased with increasing applied frequency and became static at higher frequencies. SiO$_2$ nanospheres exhibited high dielectric constant ($\varepsilon_r = 68$) and low loss factor (tan $\delta = 0.0079$) at 40°C at 1 MHz. The activation energy ($E_a$) and relaxation time constant ($\tau$) are calculated and the equivalent circuit model is developed to describe the electrical behaviour of the material.

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**1. Introduction**

The monodispersed Silicon dioxide nanospheres (SiO$_2$ NSs) occupy a prominent position in the scientific community, owing to their excellent properties such as good biocompatibility, high internal surface area and colloidal stability which have led to applications in wide areas [1]. Since many of the applications are highly dependent on the size and morphology of the nanoparticles, number of synthesis techniques such as, sol-gel process, vapour phase reaction, thermal decomposition and sonochemical method have been employed for the synthesis of differently shaped SiO$_2$ nanostructures [2–4]. The uniform SiO$_2$ NSs were first reported by Stober et al. [5], which involves hydrolysis and condensation of TEOS in a mixture of water and alcohol using ammonia as a catalyst. Later on, monodispersed SiO$_2$ NSs are synthesized in the size ranging from 40 nm to few micrometers by Bogush and Zukoski using modified Stober method [3]. Subsequently, many research groups utilized these monodispersed SiO$_2$ NSs in diverse applications due to their minimum absorption in UV–visible and near-infrared regions, in Industries (electronic devices, insulators, catalysis, etc.), Pharmaceuticals (enzyme encapsulation, drug delivery and cell markers), Stabilizers, Pigments and Chemical mechanical polishing [1,6]. Among all areas, SiO$_2$ NSs are most widely applied to an energy storage dielectric material owing to their high breakdown strength, high resistivity, low defect density at the interface with Si and low loss factor [7,8].

Electrical impedance spectroscopy (EIS) or Dielectric spectroscopy analysis is traditionally used a non-destructive technique to characterize the electro kinetic properties of materials. Materials with high dielectric constant and low tangent loss...
are of great interest for future electronic capacitors with high energy storage densities and low operating voltage. Even though numerous ceramics based high and low dielectric constant (low-K) materials have recently been developed, the outstanding properties of SiO₂ still remains an important dielectric material used in the microelectronics field. Moreover, SiO₂ can be used as a primary substrate based on its dielectric constant value to develop high-K as well as low-K material in the form of interlayer dielectric in transistors. The dielectric constant of SiO₂ can be customized by doping with fluorine (Fluosilicate glass F–SiO₂) and imparting porosity to it [9,10]. In general, the dielectric constant of the amorphous SiO₂ substrate lies between 3.9 and 4.5 depending on the thickness of the film and mode of the deposition cycle. The ultra thin <4 nm SiO₂ films are mainly used in GATE dielectrics but its leakage current is too large. Hence it is necessary to replace thin SiO₂ films with high dielectric constant SiO₂ based oxides or thicker films for GATE dielectrics and other commercial device applications [7]. Moreover, there are no significant dielectric investigations on nanosized SiO₂ particles and hence we have attempted to study the structural and dielectric properties of monodispersed SiO₂ NSs.

This work describes the dielectric behaviour of the SiO₂ NSs at wide frequency range 1 Hz to 1 MHz at selective temperatures 40–90 °C. The changes in electrochemical properties, including impedance (Z’ and Z”), dielectric constant (εr), loss factor (tan δ) and electrical conductivity (σ) of the SiO₂ NSs is described using the equivalent circuit model. The Bode analysis suggests that temperature dependent relaxation process with the different time constant is involved in the material which is attributed to grain boundary effects. The activation energy and relaxation time constant of the material were calculated at selective frequencies and a close resemblance was found in the activation energy of the material from the ac and dc conductivity plots.

2. Experimental

2.1. Materials

The chemicals used as starting materials for the synthesis of monodispersed SiO₂ NSs include Tetraethyl orthosilicate (TEOS) (C₆H₂₅O₄Si), absolute ethanol (C₆H₅OH) and liquid ammonia (NH₃). All reagents were used as received with analytical grade and throughout the experiment double distilled water was used.

2.2. Preparation of SiO₂ NSs

Monodispersed SiO₂ NSs were prepared by adopting modified Stober process [5], which involves hydrolysis and condensation of TEOS in ethanol solution with ammonia as catalyst. The size of the monodispersed SiO₂ NSs was optimized by the selective molar concentrations of TEOS: NH₃: H₂O. Initially, 1 mL of a 0.2 M liquid NH₃ and 1 mL of a H₂O are injected into 30 mL of ethanol solution under continuous magnetic stirring. Subsequently, 2.7 mL of a 0.2 M TEOS was added to the above colloidal solution with gentle stirring. The hydrolysis and condensation process was initiated by the addition of TEOS and the colourless colloidal solution changed slowly to turbid due to the formation of SiO₂ nanoparticles and finally turned into milky white in colour. Then the reaction was allowed to complete the uniform growth for 24 h at room temperature. Finally, the SiO₂ NSs were centrifugally separated from colloidal solution at the rate of 5000 rpm for 10 min and washed several times with ethanol and acetone. The overall chemical reaction leading to the formation of monodispersed SiO₂ NSs may be represented by the following relations [11].

\[
\begin{align*}
\text{Si(C₂H₅O)₄} + H₂O & \xrightarrow{\text{Hydrolysis}} \text{Si(OH)}(C₂H₅OH)₃ + C₂H₅OH \\
\text{Si(OH)}(C₂H₅OH)₃ + C₂H₅OH + H₂O & \xrightarrow{\text{Condensation}} \text{SiO₂} + 3(C₂H₅OH)
\end{align*}
\]

2.3. Characterization

The UV–visible analysis of SiO₂ NSs was examined by Cary Varian 50 Ls UV–visible spectrometer over the spectral range 200–800 nm using a 1 cm path length Suprasil quartz cuvette at room temperature. The FTIR spectrum was obtained by Perkin Elmer spectrophotometer over the wave number region 4000 to 400 cm⁻¹. The structure was analyzed by Enraf Nonius CAD-F Powder X-ray diffractometer with Cukα radiation (λ = 1.540 Å) in the 2 theta range between 10° and 90°. X-ray photoelectron spectroscopy (XPS) analysis was performed to elucidate the chemical states of the element using K-Alpha spectrophotometer with a monochromated Al Kα radiation (Thermo fisher scientific). The morphology and size distribution of the particles were examined by FEI QUANTA FEG-200 field-emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectrometer (EDS). The electrochemical behaviour was analyzed by N4L impedance analyser PSM 1735 LCR meter over the frequency range of 1 Hz to 1 MHz and in the different temperature from 40 to 90 °C at the applied bias voltage of 2 V.
3. Results and discussion

Fig. 1 shows the UV–visible absorption spectrum of the synthesized SiO2 nanocolloids. The SiO2 NSs did not show any absorption band over the entire UV–visible region as is shown in Fig. 1. Since SiO2 NSs are more transparent in UV–vis region owing to their high energy gap and with no imaginary part of the dielectric function. Hence, SiO2 NSs do not exhibit surface plasmon resonance phenomenon [12]. The high transmission in the visible region is more suitable for the electrical and optical communications applications.

The coordination environment of the synthesized SiO2 NSs was investigated by FTIR spectrum (Fig. 2). The absorption band arising at 472 cm⁻¹ corresponds to the rocking vibration of Si–O where the oxygen atom moves perpendicular to the Si–O–Si plane. The band originating at 800 and 946 cm⁻¹ are due to the bending vibrations of Si–O and Si–OH respectively. The very intense and broad absorption band emerging at 1094 cm⁻¹ is due to asymmetric stretching vibration of Si–O–Si [1,13]. The sharp band appearing at 1629 cm⁻¹ is assigned to scissor bending vibration of adsorbed molecular water. The absorption band arising at 2934 cm⁻¹ is assigned to CH₂ which affirms the presence of some unprocessed TEOS in the product. The broad absorption band emerging at 3418 cm⁻¹ is ascribed to O–H stretching vibration mode of Si (OSi)n (OH)4-n (where n = 2–4) linkage of the solid state network structure of silica [14]. The FTIR results clearly evidenced the presence of silica network in the synthesized product.

Fig. 3(a, b) shows the typical powder XRD pattern and chemical composition of the synthesized SiO2 NSs. The diffraction pattern shows a characteristic broad peak which corresponds to the amorphous phase of prepared SiO2 NSs. The absence of any other diffraction peaks confirms that only SiO2 phase is obtained in its amorphous phase. This result reveals that the high percentage of SiO2 NSs is formed as amorphous [13]. The corresponding EDS analysis shows only the presence of SiO2 composition (Si and O only) without having any other organic residues as shown in Fig. 4(b). The appearance of low energy
peak is due to the presence of carbon, which is attributed to the incomplete coverage of the tape surface during sample preparation stage. This result witness the purity of the product is fairly good.

The chemical states of the element corresponding to full width half maximum (FWHM) and percentage of area are obtained by Gaussian curve fitting using casa XPS software with a Shirley type background. Fig. 4 (a, b) depicts the deconvoluted high-resolution XPS spectrum of the O 1s and Si 2p components for SiO$_2$ NSs. As can be seen in Fig. 4 (a), the two deconvoluted peaks of O 1s spectrum shows the binding energies of 532.7 and 534.8 eV, which are ascribed to O–Si and Si–O–Si bridging bonds of SiO$_2$. An analogous phenomenon was observed in the FTIR spectrum and these bridging bonds are in harmony with the XPS analysis as well.
Fig. 6. (a, b) Frequency dependent variation of dielectric constant and loss at various temperatures.
The high-resolution Si 2p spectrum (Fig. 4(b)) could be resolved into four peaks centred at binding energies of 102.5, 103.4, 104.3 and 106.1 eV which are assigned to the oxidation states of Si$^{1+}$, Si$^{2+}$, Si$^{3+}$ and Si$^{4+}$. The various oxidation states of Si elucidate that each Si atom is bound to one, two, three or four oxygen atoms respectively [15]. The position and intensity of each peak are well signalized. The contribution from Si$^{1+}$ and Si$^{4+}$ oxidation states are observed to be very low as compared with other Si$^{2+}$ and Si$^{3+}$ oxidation states. The observed Si 2p peak positioned at 103.4 eV is in good agreement with the standard Si 2p state of SiO$_2$. The absence of peak at 99.4 eV which is the typical binding energy of the oxygen free silicon substantiates that Si atoms are in a bound state with O atoms. These results are further corroborated with the powder XRD and FTIR spectral analysis as well.

The morphology of the synthesized SiO$_2$ NSs is shown in Fig. 5(a and b). Amorphous silica nanoparticles produced by this optimized synthesis condition, have narrow particle size distribution, almost spherical in morphology. The monodispersed nature and exact particle size was evidenced by the relative histogram plot and the resulting particle size is found to be $103 \pm 2.05$ nm as shown in the inset figure. The particle size is well controllable by changing the molar concentrations of TEOS and NH$_3$. Moreover, the figure shows less agglomeration of SiO$_2$ NSs it would be meaningful to high particles stability of the product.

The frequency dependent variation of the dielectric constant ($\varepsilon_r$) and loss factor (tan $\delta$) of the SiO$_2$ NSs in the applied frequency range 1 Hz – 1 MHz is shown in Fig. 6 (a, b). The dielectric constant ($\varepsilon_r$) of the material mainly depends on the following factors, number density of dipoles, various polarization mechanisms (electronic, distortion, orientation), applied frequency and the temperature [11]. The dielectric constant ($\varepsilon_r$) and loss factor (tan $\delta$) show decreasing trend with increasing frequency up to $1 \times 10^3$ Hz and are nearly static on further increasing the frequency. In the low frequency region, the material shows high dielectric constant and dielectric loss due to strong interfacial polarization effects, while the high frequency region shows a dispersive behaviour caused by multiple polarization effects which result in low dielectric constant and dielectric loss [16]. It is observed that both the dielectric constant ($\varepsilon_r$) and dielectric loss factor (tan $\delta$) are found to be decreasing with increase temperature from 40 to 90 °C in the high frequency region. It is clearly shown that the dielectric constant and loss factor are strongly temperature dependent. The dielectric constant of the material is gained from the relation of

$$\varepsilon_r = \frac{ct}{A\varepsilon_0}$$

where $c$ is the capacitance, $t$ and $A$ are the thickness and area of the sample and $\varepsilon_0$ is the absolute permittivity of free space ($8.854 \times 10^{-12}$ F m$^{-1}$). The variation of real and imaginary part of permittivity was also calculated based on impedance values by employing the following relations:

$$\varepsilon' = \frac{Z'}{2\pi f C_0 Z^2}$$

$$\varepsilon'' = \frac{Z''}{2\pi f C_0 Z^2}$$

$$C_0 = \varepsilon_0 \frac{A}{d}$$
where \( C_0 \) is the geometric capacitance, \( \varepsilon_0 \) is the permittivity of vacuum, \( A \) and \( d \) are the area and thickness of the sample. The real \( (\varepsilon'_0) \) and imaginary part \( (\varepsilon''_0) \) of permittivity is directly related to the dielectric constant \( (\varepsilon_r) \) and loss factor \( (\tan \delta) \) respectively which is shown in Fig. 7 (a, b). The calculated temperature dependent variation of dielectric constant and loss factor values are tabulated in Table 1.

**Table 1**
Calculated dielectric parameter values of the SiO2 NSs at selective frequencies for various temperatures.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Temperature (°C)</th>
<th>Resistivity (Ω.m⁻¹)</th>
<th>Capacitance (F)</th>
<th>Dielectric Constant ((\varepsilon_r))</th>
<th>Loss Factor ((\tan \delta))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Hz</td>
<td>40</td>
<td>(1.34 \times 10^5)</td>
<td>(1.95 \times 10^{-9})</td>
<td>2368</td>
<td>56.7180</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>(2.53 \times 10^5)</td>
<td>(1.22 \times 10^{-9})</td>
<td>1488</td>
<td>47.6560</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>(7.89 \times 10^5)</td>
<td>(4.01 \times 10^{-10})</td>
<td>488</td>
<td>46.6580</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>(2.93 \times 10^6)</td>
<td>(1.57 \times 10^{-10})</td>
<td>191</td>
<td>32.0650</td>
</tr>
<tr>
<td>50 Hz</td>
<td>40</td>
<td>(1.39 \times 10^5)</td>
<td>(1.20 \times 10^{-10})</td>
<td>145</td>
<td>15.6420</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>(2.85 \times 10^5)</td>
<td>(1.03 \times 10^{-10})</td>
<td>125</td>
<td>8.8686</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>(9.76 \times 10^5)</td>
<td>(8.69 \times 10^{-11})</td>
<td>105</td>
<td>3.0771</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>(3.26 \times 10^6)</td>
<td>(7.43 \times 10^{-11})</td>
<td>90</td>
<td>1.0780</td>
</tr>
<tr>
<td>1 kHz</td>
<td>40</td>
<td>(1.35 \times 10^5)</td>
<td>(7.28 \times 10^{-11})</td>
<td>88</td>
<td>0.8668</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>(2.84 \times 10^5)</td>
<td>(6.77 \times 10^{-11})</td>
<td>82</td>
<td>0.6889</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>(8.23 \times 10^5)</td>
<td>(6.26 \times 10^{-11})</td>
<td>76</td>
<td>0.2563</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>(2.27 \times 10^6)</td>
<td>(5.86 \times 10^{-11})</td>
<td>71</td>
<td>0.0994</td>
</tr>
<tr>
<td>1 MHz</td>
<td>40</td>
<td>(3.14 \times 10^4)</td>
<td>(5.62 \times 10^{-11})</td>
<td>68</td>
<td>0.0079</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>(6.19 \times 10^4)</td>
<td>(5.58 \times 10^{-11})</td>
<td>67</td>
<td>0.0040</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>(1.40 \times 10^4)</td>
<td>(5.53 \times 10^{-11})</td>
<td>67</td>
<td>0.0018</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>(1.33 \times 10^5)</td>
<td>(5.48 \times 10^{-11})</td>
<td>66</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

Fig. 8 (a, b) represents the variation of real and imaginary parts of impedance which is plotted against the function of frequency at various temperatures. Impedance is a complex number of real part \((Z')\) and imaginary part \((Z''\)), which represents the materials resistance and reactance respectively, i.e. \(Z = Z' + jZ'' \) where \( j = \sqrt{-1} \). Fig. 8(a) illustrates that the magnitude of the real part of impedance \((Z')\) increases in the lower frequencies with an increase in temperatures, which shows a positive temperature coefficient of resistance (PTCR) type behaviour. The fact that the magnitude of \(Z'\) increases with an increase in frequency and temperature suggest that the ac conductivity of the material decreases with increase in frequency as well as temperature. Besides, the \(Z'\) curves for various temperatures merge in higher frequency region which may be due to the release of space charge in the material. Moreover, the imaginary part of impedance \((Z'')\) Vs frequency spectrum (Fig. 8 (b)) reveals the presence of symmetric peak \((Z''_{max})\) at a particular frequency for various temperatures. The decrease in peak

Fig. 8. (a, b) Temperature dependent variation of real and imaginary part of impedance; (c) Nyquist plots (d) Equivalent circuit of SiO2 NSs.
broadening and shift in the peak position ($Z''_{\text{max}}$) on increasing the temperature in lower frequencies indicates the spread of relaxation times i.e. the presence of temperature dependent relaxation process in the material. The relaxation process in the material may be due to the existence of immobile species and defects in lower and higher frequencies respectively. Further, all the curves merge into single curve in higher frequencies which may be due to the accumulation of space charge in the material [17].

A typical shape of Faradaic impedance spectrum, in the form of the Nyquist plot of SiO$_2$ NSs at various temperatures is shown in Fig. 8(c). It is observed from Fig. 8(c) that the radius of the Nyquist plots increases with an increase in temperature which indicates an increase in resistance and consequently decrease in conductivity with increase in temperature of the SiO$_2$ NSs. The semicircle arcs represent the grain boundary effects, which involves a parallel combination of grain boundary resistance and capacitance [18]. The capacitance values for the low and high temperature semicircles are found to be in the range of $10^{-9}$–$10^{-11}$ F, which is further proving the grain boundary effect of the material [19]. Besides, the centre of each semicircle arcs reveal a reasonable shift from the real part of impedance $Z'$, which suggests the occurrence of the non-Debye type of relaxation behaviour in SiO$_2$ NSs. The increase of the radius in each semicircle is a further witness of polarization phenomena with a distribution of relaxation time. Moreover, the angle of each semicircle arcs is directly related to the relaxation time which is further calculated from the Bode plots [20]. The changes in electrochemical properties of the SiO$_2$ NSs at various temperatures could be described from the Nyquist plot using the equivalent circuit model as presented in Fig. 8(d). The simplified equivalent circuit model consists of a parallel combination of two resistors with resistance R, with one capacitor of capacitance C, and one inductor of inductance L (i.e. CRLR model), which represents the grain boundary effects involved in the material. In general, the series resistance is related to the contribution from the electrode, while the parallel resistance in the parallel RC circuit is related to the layer resistance of SiO$_2$ NSs and the parallel capacitance is related to the geometric capacitance of the SiO$_2$ NSs layer [20,21].

The temperature dependent conductivity and resistivity against frequency are shown in Fig. 9 (a, b). In general, the increment of conductivity as a function of frequency is mainly due to the conduction by hopping and a decrement of conductivity as a function of frequency is due to band conduction [22]. The evaluated values of ac and dc conductivity are almost same at lower temperature as a function of frequency, which is due to rapid increase in mobility of charge carriers in the material. As it can be observed in Fig. 9 (a), the ac conductivity increases gradually with increasing frequency which clearly shows that the conduction is mainly due to hopping behaviour. Moreover, the steep rise of conduction in higher frequencies may be due to the formation of polarons, dissociation of cations, enhancement of short range translational motion of charge carriers and hopping behaviour with the adjacent atomic sites [23]. In addition, the temperature dependent ac conductivity behaviour was observed, wherein the ac conductivity decreases gradually with increase in applied temperature as a function of frequency. This result suggests that the electrical conduction in the material is thermally activated process and obeys the Arrhenius law.

The electrical relaxation in the material can also be studied through complex electric modulus plot, which is obtained using the following relation: $M^* = M' + iM''$

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}$$

(5)
The electric modulus plot is especially useful for segregating components with similar resistance but different capacitance. The complex electric modulus ($M^*$) is defined in terms of the reciprocal of the complex permittivity ($\varepsilon^*$):

$$M^* = \frac{\varepsilon^*}{\varepsilon'^2 + \varepsilon''^2}$$  \hspace{1cm} (6)

The electric modulus plot is especially useful for segregating components with similar resistance but different capacitance. The complex electric modulus ($M^*$) is defined in terms of reciprocal of the complex permittivity ($\varepsilon^*$):

$$M^* = \frac{1}{\varepsilon^*}$$  \hspace{1cm} (7)

Fig. 10 (a, b) represents the temperature dependent variation of real ($M'$) and imaginary part ($M''$) of electric modulus as a function of frequency. The real part ($M'$) of electric modulus plot (Fig. 10 (a)) indicates a very low value of $M'$ in low frequency region, representing that electrode polarization is negligible. The continuous dispersion exhibited in the mid frequency region may be due to the short range mobility of charge carriers while the shifting of dispersion towards the high frequency region may be due to long range mobility of charge carriers both contributing to the conduction phenomena. Further, in the high frequency region, the plateau type behaviour is observed indicating the frequency independent electrical conduction in the material. Moreover, the electric modulus peaks (Fig. 10 (b)) shift towards the lower frequency region on increasing the temperature. The peak broadening and asymmetric nature of the peaks suggest the spread of relaxation with different time constants exhibiting non-Debye type relaxation, which is in harmony with the impedance results. Further, the nature of the modulus spectrum confirms the electrical conduction in the material is mainly due to the presence of hopping behaviour. In Fig. 10 (c) the complex electric modulus plots show the overlapping of the semicircles and no difference is observed for all temperatures, which indicates the presence of electrical relaxation phenomena and dynamic process in the material. This characteristic can be associated with the decrease in the contribution of grain boundary resistance to the total modulus resistance with the rise in temperature [17].

The relaxation parameters are acquired from the bode analysis (Fig. 11(a)). The relaxation time of the SiO$_2$ NSs is calculated by using the relation $\tau = \frac{1}{2\pi f_r}$, where $f_r$ is the relaxation frequency. As seen from the figure a single relaxation frequency occurred in the material at various temperature and calculated relaxation time constants are in the order of $10^{-5}$ s. The variation of relaxation time as a function of temperature is shown in Fig. 11(b). Generally, the relaxation time decreases with increasing frequency indicating that the rate of molecular motions increases with frequency.
Fig. 12 (a, b) depicts the linear variation of electrical conductivity as a function of reciprocal temperature (1000/T vs ln $\sigma_{ac}$ and ln $\sigma_{dc}$) with respect to selective frequency. The bulk dc conductivity and ac conductivity of the SiO$_2$ NSs were calculated from the impedance spectrum using the relations,

$$\sigma_{dc} = \frac{t}{R_bA}$$  \hspace{1cm} (8)

$$\sigma_{ac} = 2\pi f\varepsilon_0\varepsilon_r$$  \hspace{1cm} (9)

where $t$ is the thickness, $R_b$ is the bulk resistance, $A$ is the surface area of the sample, $f$ is the frequency, $\varepsilon_0$ is the vacuum permittivity and $\varepsilon_r$ is the dielectric loss [24]. The variation of electrical conductivity plots gives the straight line which shows the Arrhenius type of behaviour. Further, both ac and dc conductivities increase with increasing temperature, suggesting that the electrical conduction phenomenon in the material is a thermally activated process. The activation energy ($E_a$) is determined by the temperature dependent relaxation time constant ($\tau$) which obeys the Arrhenius law by the relation

$$\tau = \tau_0 \exp \left( \frac{E_a}{KT} \right)$$  \hspace{1cm} (10)

where $E_a$ is the activation energy involved in the dielectric relaxation process, $\tau_0$ is the pre-exponential factor, $K$ is the Boltzmann constant and $T$ is the absolute temperature.

Moreover, the slopes taken from the graphs are directly related to the activation energy ($E_a$) of the material and the calculated activation energies ($E_a$) of the SiO$_2$ NSs with respect to selective frequencies are presented in Table 2. A close resemblance found in the activation energy of the material from the dc and ac conductivity plots suggest a hopping mechanism in the material.

Fig. 11. (a, b) Bode plots and corresponding variation of relaxation time of SiO$_2$ NSs.

Fig. 12. (a, b) Arrhenius plots showing the variation of electrical conductivity ($\sigma_{ac}$) and ($\sigma_{dc}$) with respect to selective frequencies.
The activation energy of the material is gradually decreased till 50 KHz followed by gradual increase in the higher frequencies. The calculated $E_a$ value in the low frequency region evidences the predominant hopping conduction behaviour during relaxation consequences. Likewise, the estimated $E_a$ value in the high frequency region is related to the localized oxygen vacancies and cluster of oxygen vacancies [23]. The calculated $E_a$ values are in close resemblance with those reported in the literature for SiO$_2$ NSs, which substantiate that $E_a$ can be varied by changing the degree of hydration, frequency and polymer addition [25–27]. The gradual decrease in $E_a$ at higher frequencies, (at 100 KHz = 0.39 eV) means better electrical conduction as compared with the higher $E_a$ at lower frequencies, which explains the easy migration of charge carriers at higher frequencies.

4. Conclusions

The monodispersed SiO$_2$ NSs with uniform morphology were successfully synthesized by facile stober synthesis process. The presence of functional groups and structure of the synthesized SiO$_2$ NS were confirmed by using FTIR spectroscopy and powder XRD analysis respectively. Further, the chemical states of the element were well elucidated by XPS investigations. The morphology and size of the particles were clearly visualized by FESEM micrographs. The dielectric behaviour of the material in the wide applied frequency range for various temperatures was studied by electrical impedance spectroscopy. A typical Nyquist plot suggests non-Debye type of relaxation behaviour in SiO$_2$ NSs and changes in electrochemical properties was described by an equivalent circuit model. The ac conductivity analysis shows the electrical conduction in the material is a thermally activated process. Further, the complex electric modulus plots indicate the presence of electrical relaxation phenomena and dynamic process in the material. The average life time of electrons from the Bode analysis was found to be in the order of $10^{-3}$ s. This result suggesting that the monodispersed SiO$_2$ NSs can be more beneficial for microelectronic applications.

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References


