Optical and Morphological Characteristics for Silicon Dioxide NPs Prepared by Sol-Gel Method

Suma H. AL-Shaikh Hussin[(1)], Ali H. AL-Hamdani[(2)], Alaa N. Abdalgaffar[(3)]

Abstract— Silicon dioxide (SiO_2) nanoparticle prepare via sol –gel method by mixing isopropanol alcohol (IPA) with deionization water (DW) and using tetraethelyorth silicate (TEOS) with nitric acid (HNO_3).The optical properties and the optical constant absorbance (A), transmittance(T%), refractive index (n), absorption coefficient (α) and optical energy gap (E_g) were studied. The results for SiO_2-sol nanoparticale prepare by sol-gel method indicate that, the wavelength for maximum absorbance is (λ_{max}=235 nm). The transmittance range (80-95)% in wavelengths (400-1100)(nm), the refractive index of SiO_2-sol was (n=1.3796). The indirect allowed energy gap is optimum (E_g=4.9 eV).

Index Terms— sol-gel, SiO_2 optical properties, morphological properties of SiO_2-sol, Dynamic light scattering (DLS) of SiO_2-sol, .

1 INTRODUCTION

mprovement nanotechnology has led to creation of nanosized silica (SiO2) which has been widely used as filler in engineering compound. The (SiO2) particles educed from natural resources contains metal impurities and not favorable for advanced scientific and industrial applications. Therefore, focus is given to synthetic silica (colloidal silica, silica gels, pyrogenic silica, and precipitated silica), which is pure and produced mostly in amorphous powder forms compared to natural mineral silica (quartz, tridymite, cristobalite) which are in crystalline forms [1]. There are many methods that have been used to obtain silica particles can be categorized into two main approaches: top-down and bottom-up. Top-down is characterized by decreasing the dimension of the original size by utilizing special size decrease techniques 'physical approach'. Bottom-up or chemical approach involves a common route used to produce silica nanoparticles from atomic or molecular scale. Some of the widely used methods to synthesize silica nanoparticles are sol-gel process, reverse microemulsion, and flame synthesis. The sol-gel process is extensively used to produce pure silica particles owing to its ability to control the particle size, size distribution and morphology through systematic monitoring of reaction parameters. Sol-gel identified as transformation of starting material solution "precursor" into an inorganic solid by inorganic polymerization reactions induced by water.There are two important process in sol-gel reaction to formalization of an inorganic polymer are hydrolysis and condensation reactions. Hydrolysis from a sol a dispersion of colloidal particles in a liquid and otherwise condensation feedbacks in a gel, an interconnected tough and porous inorganic network assuage a continuous liquid phase. This conversion is called the sol-gel transition.Depend on on the detailed reaction conditions, condensation may begin before hydrolysis is complete[2]. A common sketch for sol-gel process which leads to the production SiO2 using TEOS is shown in figure 1 [3].

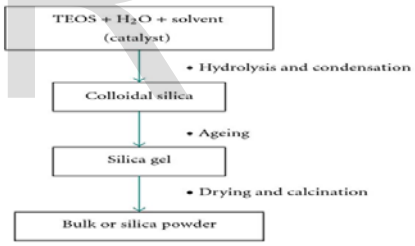

Fig 1: A sketch of sol-gel process

.

In the sol-gel process for silicon dioxide using tetra-ethyl-ortho silicate (TEOS) as precursor, the sol-gel transformation of metal alkoxides or Si-alkoxide (Si(OR)4) contributes two essential reaction types; hydrolysis and condensation show in fallowing (1,2,3) [4]:

(I) hydrolysis

Si-OC2H 5 + H2O ~ Si-OH + C2H5OH … (1)

(II) alcohol condensation

Si-OC2H 5 + HO ~ Si-O- + C2H5OH … (2)

(III) water condensation

Si-OH + HO-Si ~ Si-O-Si + H2O … (3)

One of the most important parameters in the sol-gel process is the pH of the starting solution. The isoelectric point of silica, at which the electron mobility and the surface charge is zero, occurs at approximately pH = 2. This pH value forms the boundary between so-called acid catalysis of the polymerization process (pH < 2) and base catalysis (pH > 2). Acid catalysis is associated with fast hydrolysis rates and relatively long gel times whereas, under basic conditions, hydrolysis is slow and condensation rates are faster, giving rise to shorter

gel times. In the limit of low pH (< 2) and low R (R < 2), the gel evolves as a weakly branched microporous structure with pore sizes < 2 nm [5]. In conditions of pH > 2 and R > 2, a particulate gel is formed with larger pores. Increasing the ratio (R) value increases the hydrolysis rate for a particular pH value.

2 Experimental

Prepare silicon dioxide (SiO_2) by sol –gel method by mixes in the stirrer with high speed the isopropanol alcohol (IPA), (C_3H_8O), from Marck of (15.4 ml) in 1(ml) deionization water (DW) and using tetraethelyorth silicate (TEOS), [$Si(OC2H_5)_4$], purity 98%, from Sigma Aldrich of (4.4 ml) with (IPA) of (15.6 ml) both solution at temperature (0C), then added (0.8 ml) of nitric acid (HNO_3), purity 65% , from Sigma Aldrich. The resultant solution was stirred for (2h) yielding transparence sol. Figure 2 shown the sketch of prepare silicon dioxide (SiO_2).

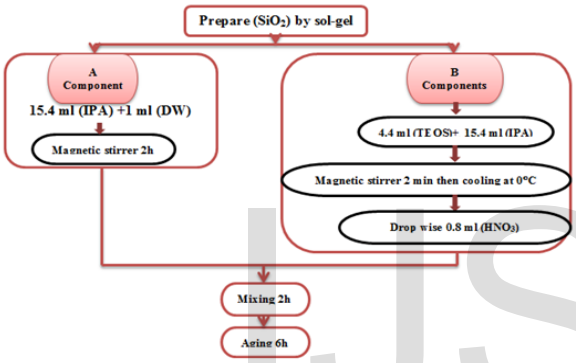

Figure 2: The sketch of Prepare silicon dioxide (SiO2).

3 Result and Discussion

3.1 The optical properties of SiO2-Sol

In the present work the optical characterizations of SiO_2-sol {absorbance (A), transmittance (T%), refractive index (n), absorption coefficient (α) and optical energy gap (E_g)} were measured. Figure 3, 4 show the absorption and transmission spectra measured by double beam spectrophotometer(CECIL,UK and CE7200). Where figure 3, indicates that the peak absorption at a wavelength (λ_{max}= 235 nm). While figure 4 shows the SiO_2 have transmittance about (75-100)% in wavelengths range (400-1100)(nm).

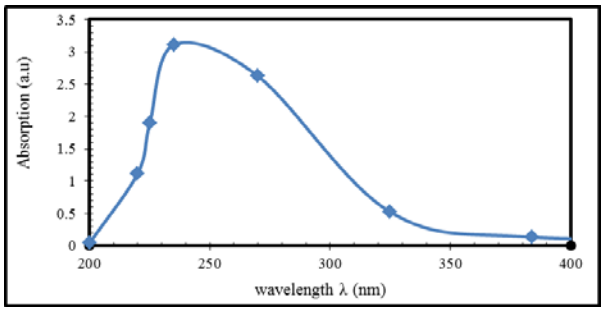

Fig 3: The absorption spectrum for SiO2- sol nanoparticles and the maximum absorption wavelength in λmax=235 (nm).

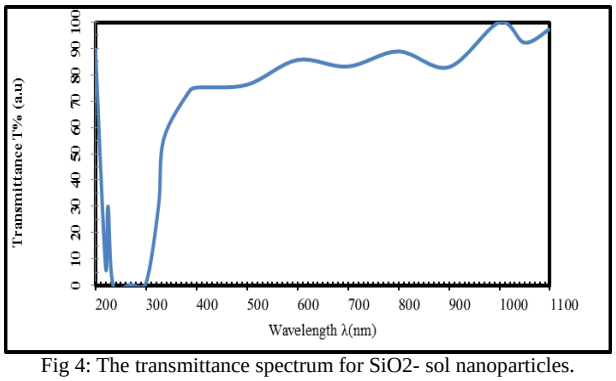

Fig 4: The transmittance spectrum for SiO2- sol nanoparticles.

SiO_2-sol refractive index (n=1.3796) was measure by refractometer-AR4 from Germany. To characterize the various absorption edge structures observed, band gap energies were determined by fitting the absorption edge using either direct or indirect band gap models using linear fit in region of interest to a plot of (α E)2, where α is the absorption coefficient in (cm^{-1}) and E is energy in (eV) [6,7].

$$\alpha = 2.303\frac{A}{T} \qquad \ldots (4)$$

$$\lambda = \frac{hc}{E_g} = \frac{1240}{E_g} \qquad \ldots (5)$$

Here we using the direct and indirect models only as a tool to characterize the complex absorption edge behavior of these samples, and draw on the crystalline band gap models because the shape of the absorption edges measured are reminiscent of those found in crystalline materials. The direct and indirect gap fitting has been used previously for characterizing the changes in the absorption edge in amorphous materials such as silicon and other amorphous semiconductors and has been found useful to characterize the observed changes in the electronic structure that shown in figure 5. An absorption edge of semiconductors corresponds to the threshold of charge transition between the highest nearly filled band and the lowest nearly empty band. The optical band is [8]:

$$\alpha\, h\nu = \delta(h\nu - E_g)^z \qquad \ldots (6)$$

where δ is the probability parameter for the transition, also the constant δ is a measure of the disorder of the material [9] .

$$\delta = 4\pi\lambda_{min}/nc\Delta E \qquad \ldots (7)$$

where λ_{min} is the minimum metallic conductivity, n is the refractive index, c is the light-velocity, and $\Delta E = \Delta E_c - \Delta E_v$ represents the band tailing E_g is the optical band gap of the material, hυ is the incident photon energy; z is the transition coefficient and show in table1.

Table I :The direct and indirect band gaps of SiO_2-sol nanoparticle .

Transition coefficient (z)	Transition mode	Energy gap according to fig. 5
1/2	Direct allowed	4.5
3/2	Direct forbidden	4.8
2	Indirect allowed	4.9
3	Indirect forbidden	4.6

Fig 5: The energy gap direct and indirect of SiO-sol in $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^{3/2}$, $(\alpha h\nu)^{2}$ and $(\alpha h\nu)^{3}$.

3.2 The morphological properties of SiO_2-sol.

The morphological properties of SiO_2-sol was investigated by Dynamic light scattering (DLS) and Transmission Electron Microscopy (TEM).

3.2.1 Dynamic light scattering (DLS) of SiO2-sol.

The zetasizer nano range of instruments provides the ability to measure three characteristics of particles or molecules in a liquid medium.

These two fundamental parameters are particle size by{ dynamic light scattering (DLS)} , zeta potential by {laser doppler electrophoresis (LDE)}. By using the unique technology within the zetasizer system these parameters can be measured over a wide range of concentrations [10].

To calculate the particle size we use the dynamic light scattering (DLS) from (company Malvern, model ZEN 3600, Bertrand Floure Inc.) and that obtain by statistics graph and curve which describe the following measurement :-

1. Size distribution by intensity shown in figure 6.
2. Size distribution by number shown in figure 7.
3. Size distribution by volume shown in figure 8.
4. Diffusion distribution shown in figure 9.
5. Relaxation times distribution shown in figure 10.
6. Zeta potential shown in figure 11.

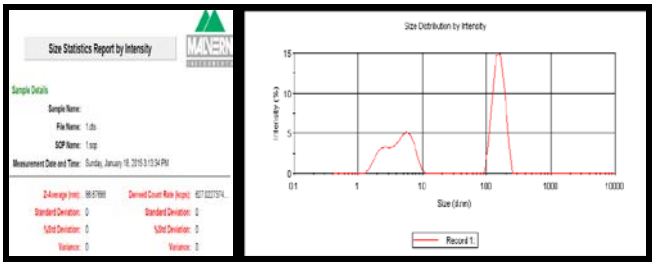

Fig 6: Size distribution by intensity statistics and curve diagrams.

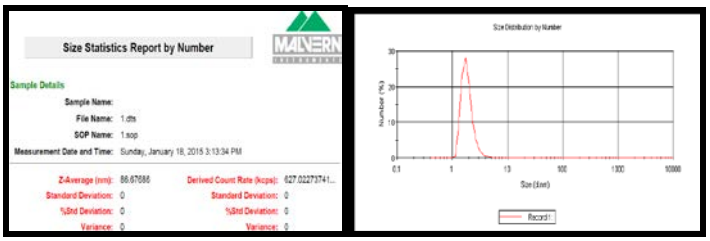

Fig 7: Size distribution by number statistics and curve diagrams.

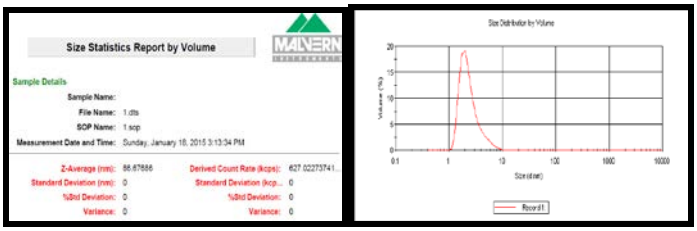

Fig 8: Size distribution by intensity statistics and curve diagrams.

From calculate size distribution by (intensity, number and volume) shown in figures 6, 7, 8 respectively found grain size for SiO2 nanoparticle(= 86.676 nm) and these diagrams shows the properties of the material are correct.

From figure11 show the diffusion distribution by intensity for first peak around (1µm2/s) the intensity 15% and for second peak between (10-100)(µm2/s) the intensity 5% so that the diffusion distribution in first peak better than second peak.

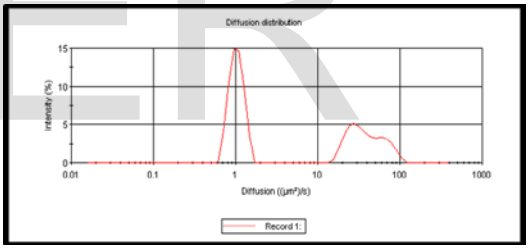

Fig 9 :Diffusion distribution by intensity diagrams.

Figure 10 show the relaxation time distrbution btween the first peak and secound peak.

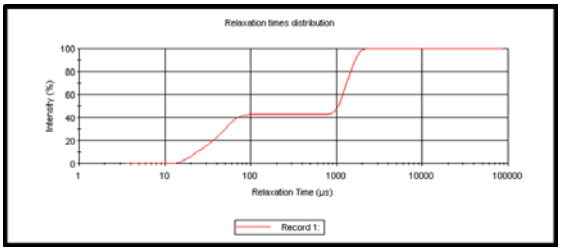

Fig 10:Relaxation times distribution by intensity diagrams.

The magnitude of the electrostatic interactions between particles can be determined by measuring the zeta potential of the particle dispersion.

Zeta potential is the overall charge a particle acquires in a particular medium. It depends on both the chemistry of the surface and the dispersant. The zeta potential measurements can be used to predict dispersion stability and hence product

shelf life. To measure zeta potential use Laser Doppler Electrophoresis. The conductivity of SiO2 nanoparticle thin films is (3.28 ms/cm) at temperature (25 C˚) from figure 10. The zeta potential is not the charge of the particle; it is the charge of the particle in a specific medium at a certain distance of the particle surface.

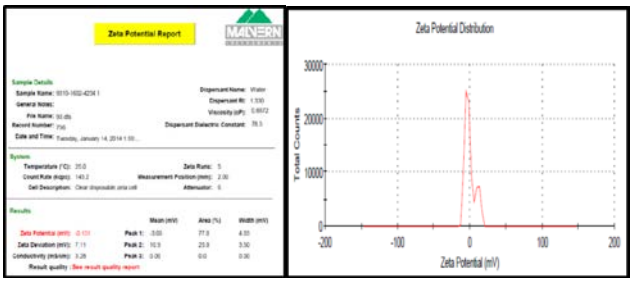

Fig 11: The Zeta potential distribution statistics and curve diagrams of SiO2 nanoparticle thin films.

From finger 11 the high zeta potential value will result in a high repulsion force, particle will tend to repel each other. Low zeta potential value will result in low repulsion force and then particle will attract each other [11] . Zeta potential is not the charge of the particle. It is the charge of the particle in a specific medium at a certain distance of the particle surface.

3.2.2 Transmission Electron Microscopy (TEM) of SiO2-sol.

The transmission electron microscopy (TEM) was investigate by (Phillips, model EM208) voltage at 100(KeV) device. In the sol step from short axes of (25-50)(nm) shown in figure 12. The (TEM) shows the shape and size nanoparticle in solution seems like bees wax shape with particle size in range of (80-90)(nm).

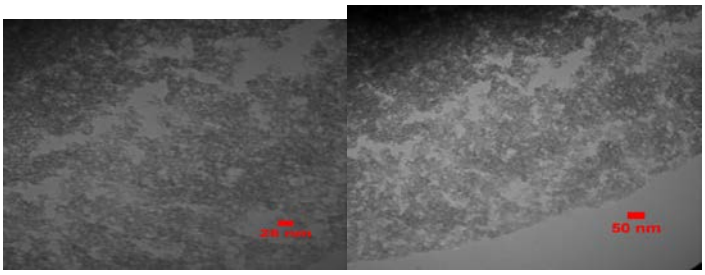

Fig 12: The transmission electron microscopy (TEM) for (SiO2) in the sol step.

4 Conclusion

SiO2-sol nanoparticale prepare by sol-gel method. The wavelength for maximum absorbance is (λmax=235 nm). The transmittance range (80-95)% in wavelengths (400-1100)(nm), the refractive decrease when wavelength increase, the refractive index of SiO2-sol was (n=1.3796). The reflective spectrum about (17.7-4.2)% in wavelengths (325-1050)(nm) respectively. The indirect allowed energy gap is optimum (Eg=4.9 eV). The grain size of SiO2-sol measure by (DLS) is (d=86.67686 nm) from (intensity, number and volume) tests and the conductivity (3.28 ms/cm)measure by zeta-potential. The (TEM) shows the shape and size nanoparticle in solution seems like bees wax shape with particle size in range of (80-90)(nm).

Reference

[1] C.Huan and S. Shu-Qing ," Silicon nanoparticles: Preparation, properties, and applications", Chin. Phys. B, 23, 8 (2014) 88-102.
[2] S. Okumoto and N.Fujita, " Theoretical Study of Hydrolysis and Condensation of Silicon Alkoxides", J. Phys. Chem. A, 102 , 22 , (1998) 3991–3998.
[3] P.Sai, J.Rao, C.Devarayapalli, K.Sharma," Preparation and Characterization of TiO2-SiO2 Sol-Gel Anti Reflection Coatings on Multi Crystalline Silicon Solar Cell", International Journal of Engineering and Advanced Technology (IJEAT) 3,1(2013).
[4] R. Lenza and W. Vasconcelos," Synthesis of Titania-Silica Materials by Sol-Gel", Material Research ,5 , 4 , (2002) 497-502.
[5] . Besbes, N. Fakhfakh, M. Benzina, "Characterization of silica gel prepared by using sol-gel process", Physics Procedia ,2 (2009) 1087–1095.
[6] Daram, K.R. AL- Rawi and S.H. ALShaikh Hussin," Improve the performance efficiency of solar cell by using epoxy plates doped with Rhodamine 6G dye," Indian Journal of Science and Technology, 4 , 12 (2011) 1726-1731.
[7] R. Nandanwar1, P. Singh1 and F. Z. Haque," Synthesis and Characterization of SiO2Nanoparticles by Sol-Gel Process and ItsDegradation of Methylene Blue", American Chemical Science Journal, 5, 1(2015) 1-10.
[8] S.H. Al-Shaik Hussin, " Study the Optical Properties of Transparent Epoxy Resin (Epoprimer) Plates ", Journal Baghdad of science, Department of Physics, University of Baghdad (Iraq), 1, 7 (2010) 20-30.
[9] M. Dongol, A. El-Denglawey, M. Abd El Sadek, I.Yahia," Thermal annealing effect on the structural and the optical propertiesof Nano CdTe films", Optik 126 (2015) 1352–1357.
[10] B. Maxit, " Particle size measurements of dark and concentrated dispersions bydynamic light scattering", Cordouan Technologies, France, (2011)1-19.
[11] Dejan Arzenšek, Rudolf Podgornik, Drago Kuzman," Dynamic light cattering and application to proteins in solutions", University of Ljubljana, department of physics (2010)1-19.