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OPTICAL, THERMAL AND DIELECTRIC STUDIES OF SILVER-SILICA NANOPARTICLES SYNTHESIZED VIA SOL-GEL TECHNIQUE

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Abstract. Silver-silica nanocomposites (Ag-SiO_2NCs), with unique properties such as highly resonant particle plasmons, conductivity and potential applications in optics and various nanoelectronics are very attractive materials for sensing probes in biotechnology. Ag-SiO_2NCs with various compositions were synthesized through sol-gel technique. The morphology, optical and thermal stability of the nanocomposite were investigated and was compared with pure sol-gel to determine the effects of the nanoparticles. Transmission electron microscopy (TEM) confirmed that SiO_2 was encapsulated Ag with mean size of 30 nm. Uv-vis spectroscopy shows that the surface plasmon resonance (SPR) peak show Ag-SiO_2 NCs were greatly reduce due to the SiO_2 particles. The permittivity and refractive index were decreased as the composition of Ag was increased at composition of 60% silver. The real permittivity is negative along the visible region. The trend stability of Ag-SiO_2NCs were increased with the increased amount of silver.

Introduction

Silver nanoparticles (AgNPs) are widely investigated due to their remarkable optical, electronic, magnetic and catalytic properties, which depends on their size and shape [1,2]. These materials shows surface plasmon resonance (SPR) in visible region[3]. The SPR phenomenon is due to the collective oscillation by the free electron of the metal nanoparticles which is in resonance with the frequency of the lightwave which interact with the metal nanoparticles. The SPR peak is usually used as a primary signature of metal nanoparticle formation. Collective coherent excitation of the free electrons in the conductive band are responsible for the strong absorption of the light by the particle [4]. AgNPs in a dispersed system has greatly changed the refractive index in the visible range by doping the nanoparticles due to the plasmonic resonance [5]. Poldolskiy et al predicted that the AgNPs could be the basis for negative refraction at visible wavelength [6].

The use of tetraethyl orthosilicate (TEOS) sol gel as the dielectric host is due to the lower temperature needed for the sol-gel process and the absence of aggressive reaction poducts. These

are the main advantages of using TEOS instead of the traditional precursors such as silane or tetrachlorosilane and also due to its controllable hydrolysis reaction rate, which could assist the possibility of incorporating of silver nanoparticles into the system. In addition, the mechanical and electrical properties of SiO_2 films deposited from TEOS are very good.[7]. The sol-gel processing is one recommended approach because of (a) high optical quality of materials produced and (b) freedom to impregnate them with a variety of additives to modify their optical characteristics. The sol-gel reaction is a technique to make metal oxide and non-metal oxide nanocomposites through chemical reactions, without high temperature processing [8]. In this study, we will investigate the effects of silver nanoparticles dispersed in TEOS to further study the characteristic of metamaterial. Since the objective of this study is an easy method toward producing one-dimension isotropic metamaterials, the methodology should be emphasized on the realization of negative permittivity during the synthesis of nanocomposite. It is assumed that the size, shape and morphology as well as the volume concentration satisfy with the conditions of applicability of Maxwell-garnett model.

Experimental

Materials and reagents

All chemicals were used without further purification. Daxad 19 (Sodium Salt of polynaphthalene sulfonate formaldehyde condensate) MW800) (Canamara united supply company) as a stabilizer. Silver Nitrate ($AgNO_3$) (RM Chemicals) as the silver source. Polyethylene glycol (PEG) (Fisher Scientific) as the reducing agent. Tetraethyl Orthosilicate (TEOS)(Aldrich) sol gel as dielectric host. A mixture of aqueous Ammonia (Aldrich), Ammonium Fluoride (Fisher Scientific) and Ethanol(Aldrich) for the catalyst. Deionized water was used in all preparation for aqueous solution.

Silver nanoparticles (AgNPs) preparation through reduction technique

4.5g of Polyethylene glycol (PEG) and 5g of Daxad 19 were dissolved through dioinized water under magnetic stirring. The solution turn to light brown color and heated to 80° C. Then, 4g $AgNO_3$ is dissolved into the solution. The mixed solution turn to gray-black color indicated the formation of AgNPs. The solution is then stirred for 1h with the temperature is maintain at 80° C. After the solution is cooled at room temperature, it was then centrifuged (6000 rpm) and washed with distilled water and acetone for several times. The precipatation is dried at room temperature which is grey-white shinning color.

Silver-Silica nanocomposites (Ag-SiO_2 NCs) preparation through sol-gel method:

A solution containing 12.5 mL of Tetraethyl Orthosilicate (TEOS) and 10 mL of ethanol is prepared. Different volume of AgNPs solution (50mM) is mixed into the solution with vigorous magnetic stirring and sonicated for 45-60 min. Then, a catalyst solution containing 9 mL of ethanol, 18 mL of distilled water, 0.07 mL of 35% aqueous ammonia, and 0.3 mL of 0.5 M ammonium fluoride was slowly added into the silica solution by injection by the rate of 70 mL/hr. Right after the injection, the mixture was poured into a plastic dish and sonicated again for 60 min. This is to ensure the particles are well dispersed. The composite is then dried at room temperature for several days. Table 1 shows the ratio between AgNPs and TEOS for the sol-gel preparation.

Thin film preparation

Glass slide coated with Indium Tin Oxide (ITO) is used as substrate for the composite deposition [9,10]. ITO is used since it's conductive to perform the electrophoresis process. In this process, Ag-SiO_2 NCs is crushed into powder and dissolved with deionized water. The solution is then mixed

with 2-propanol as the main solution for electrophoresis process. ITO is used as electrode for the deposition of the composite. Ag-SiO_2 NCs is then deposited as thin film on one of the electrode and dried at room temperature.

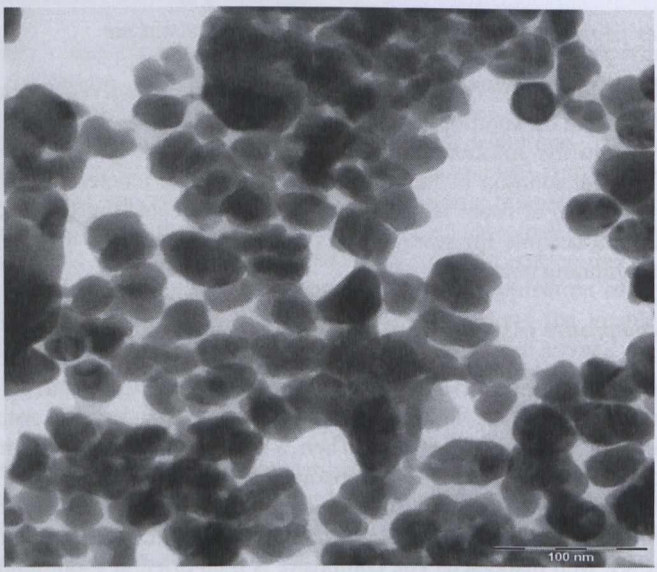
Table 1 : Details paramaters of Sol-gel preparation

AgNP (50mM) (mL)	TEOS (mL)	Total Volume (ml)	Fraction AgNPs/TEOS
2.5	12.5	15	0.2
5	12.5	17.5	0.4
7.5	12.5	20	0.6
10	12.5	22.5	0.8
12.5	12.5	25	1.0

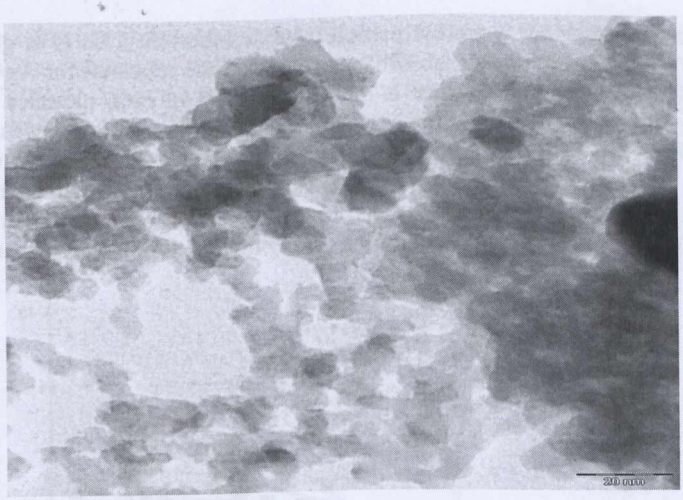
Characterization

AgNPs and Ag-SiO_2NCs were characterized by LEO LIBRA transmission electron microscopy (TEM) operated at 120 kV for physical morphology and Biocary 50 Varian ultraviolet (UV)-visible spectrophotometer for optical properties. HORIBA JOBIN YVON ellipsometer spectroscopy is used to study the dielectric properties of the Ag-SiO_2 NCs.

Results and discussion



(a)



(b)

Figure 1. TEM images of (a) Silver nanoparticles (AgNPs) ; (b) Silver-Silica Nanocomposites (Ag-SiO_2 NCs)

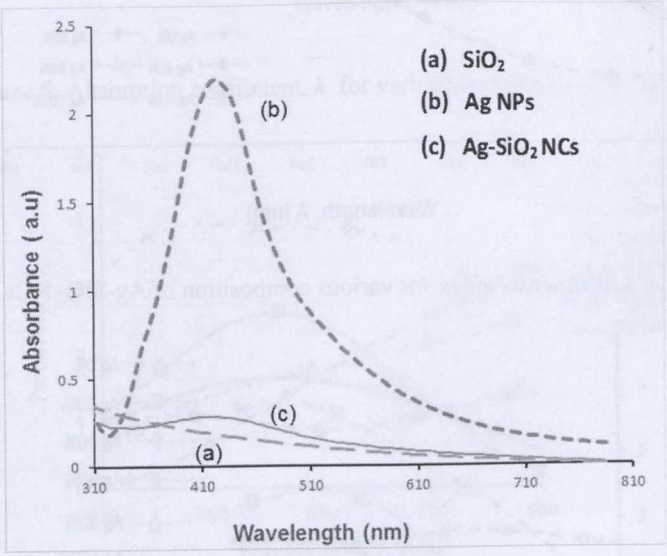


Figure 2. UV-visible absorption spectra of (a) SiO_2 , (b) AgNPs and (c) Ag-SiO_2 NCs.

Fig. 1 shows the TEM images of AgNPs and Ag-SiO_2 NCs. AgNPs are well dispersed with 30 nm of mean diameter. The specific size of AgNPs in this process is very important and that is why the reactant temperature should be maintained at 80° C. The absorption spectra of AgNPs, which plasmon-derived resonance, become distinct and stronger for AgNPs as the size of the particles grew at the reactant temperature[11]. The homogeneity of AgNPs distribution is important to ensure that plasmonic behaviour plays a role all over the area.. Fig. 2 shows the absorption spectra of SiO_2, AgNPs and Ag-SiO_2 NCs. SiO_2 particles show no peak since it is non absorbance materials. However, AgNPs shows a high intense surface plasmon resonance (SPR) peak at 423 nm. The SPR

peak is symmetrical indicates a narrow particle size distribution. This is in good agreement with TEM image in Figure 1(a). A lower absorbance of SPR peak appeared for Ag-SiO_2 NCs as shown in Fig. 2 (c). The reduce in absorbance is due to the effect of SiO_2 particles which encapsulated AgNPs. The spectrum's also blue shifted towards 420 nm. This shift happens because of particle size changes. It has been shown that higher AgNPs concentration leads particles size increment [12]. The size and shape depends on the reactant temperature which will give variations to SPR. The increase in reactant temperature will lead to a peak shift towards a longer wavelength[13]. In addition, coatings with higher Ag concentrations show increased of absorption intensities [14].

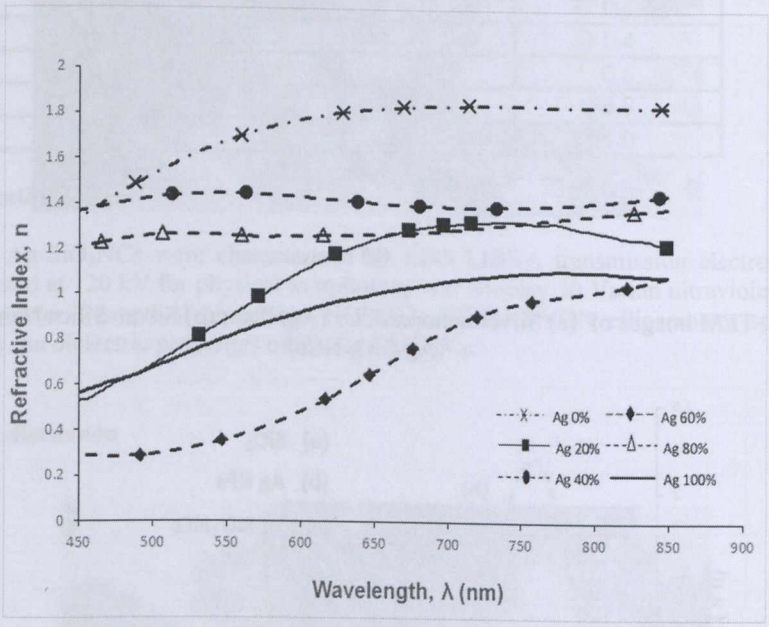


Figure 3. Refractive index for various composition of Ag-SiO_2 NCs.

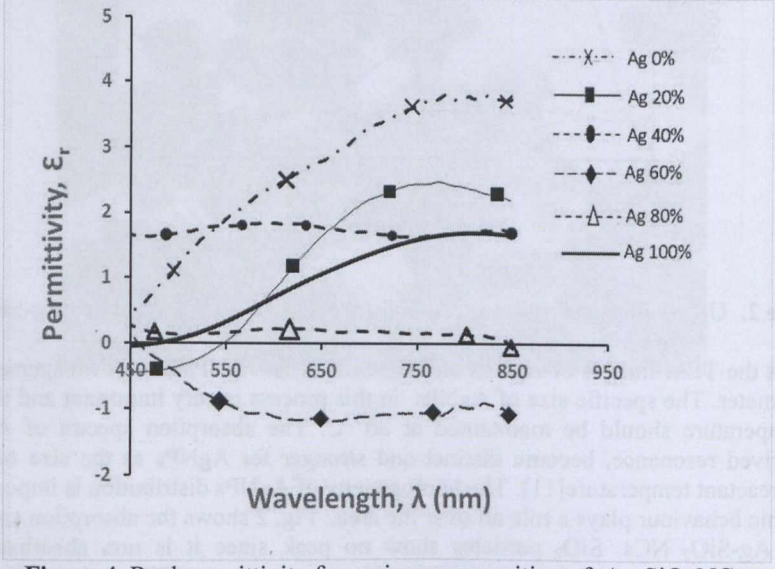


Figure 4. Real permittivity for various composition of Ag-SiO_2 NCs.

Figure 3 shows the refractive index decreases with the presence of AgNPs in the composites. The presence of AgNPs also reduces the real permittivity of the nanocomposites. Meanwhile, it figure 4, the composition of 60% of Ag in the composite produce metamaterial properties with negative real permittivity in the visible range. This is due to the Drude-type response of free electrons in Ag at long wavelengths. Any changes in dielectric of composites comes mainly from interfacial polarization effect[14].

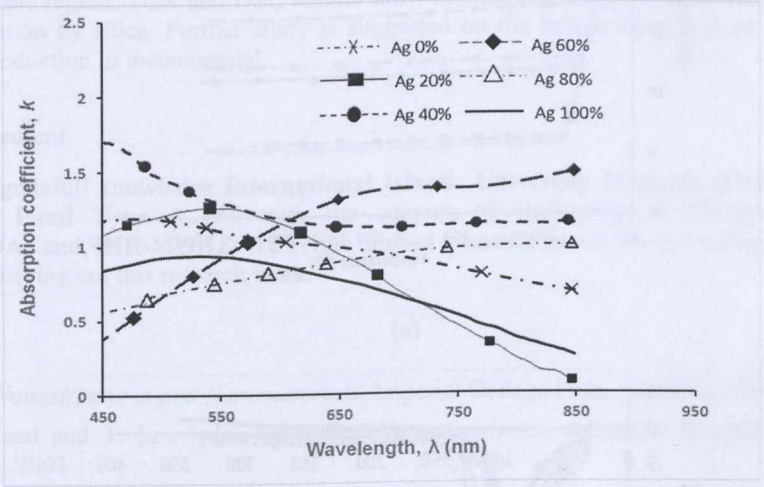


Figure 5. Absorption coefficient, k for various composition of Ag-SiO_2 NCs.

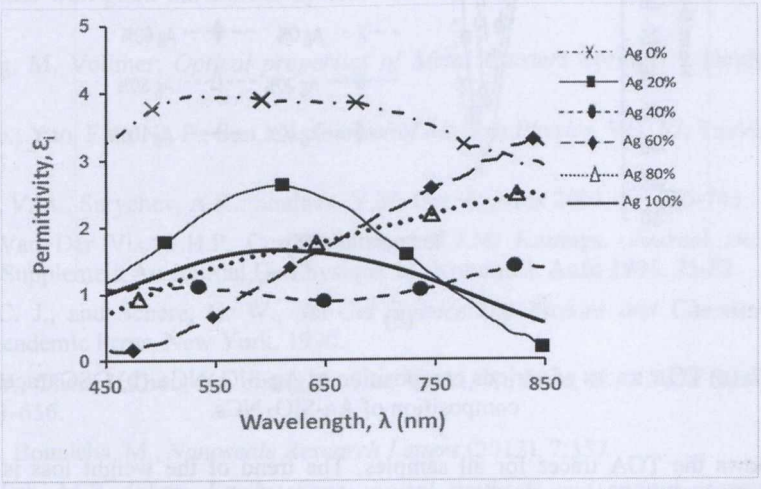
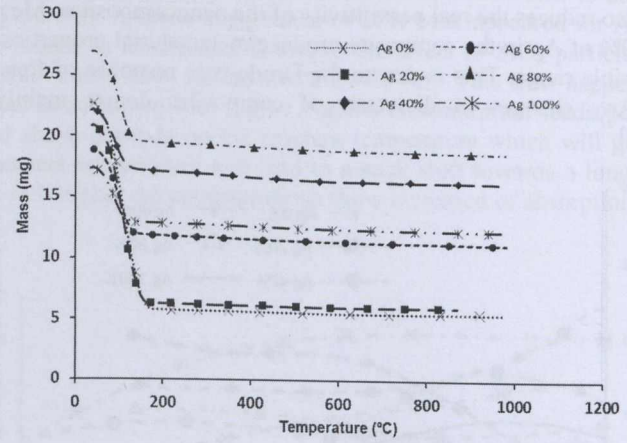
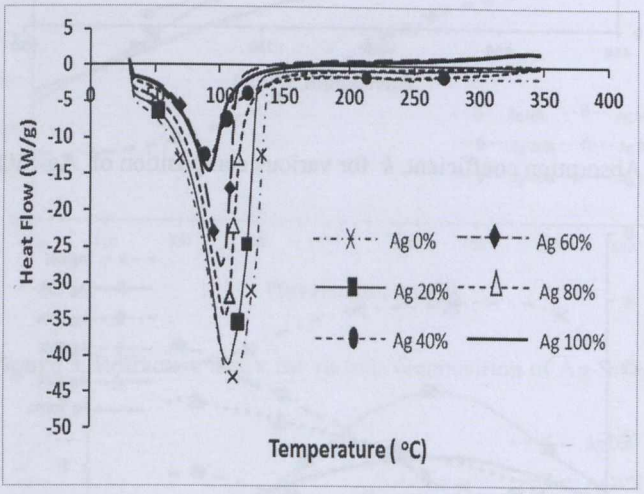


Figure 6. Imaginary permittivity of various composition of Ag-SiO_2 NCs.

Fig. 5 shows the absorption coefficient of the nanocomposite. Ag-SiO_2 NCs with 40%, 60% and 80% of AgNPs shows a consistent trend along the visible region while the other composition shows the decreasing trend. This is due to the dispersions of AgNPs in the dielectric host which effect the thickness of the thin film during electrophoresis process. Fig. 6 shows the imaginary permittivity of the nanocomposites. Pure Silica possess the highest permittivity compare to the nanocomposites. Meanwhile, the 60% of Ag in the composite shows rapid increasing of permittivity along the visible region. The changes are stronger, particularly those at longer wavelength due to the electric and magnetic losses and gains in the material.



(a)



(b)

Figure 7. (a) TGA traces of various composition of Ag-SiO_2 NCs. (b) DSC traces of various composition of Ag-SiO_2 NCs.

Fig. 7(a) shows the TGA traces for all samples. The trend of the weight loss is similar for all samples, at which all samples are having a single step weight loss. This is due to the decomposition of solvent and water evaporation. From the curves, the weight loss is recorded to start at around 50° C and ended at around 140°C. The stability of the Ag-SiO_2 NCs were maintained until 1000 °C. This shows that the thermal stability of the composite is increased. This can be explained with the analysis from TEM images. The surface of AgNPs were encapsulated with silica nanoparticles. The presence of silica nanoparticles has increase the thermal stability of AgNPs. Fig. 7(b) shows the DSC results for all samples. The graph shows high endothermic peak which falls in the range of 60°C to 130°C. This results is a good agreement with TGA results with single step profile of composition. Thus, we can assume that the endothermic peak is caused by absorption of energy to evaporate water and solvent. No other peak were observed in the DSC curves.

Conclusions

The effect on AgNPs on silica was studied. AgNPs with the range of size 25-32 nm in diameter were dispersed in silica gel while gelation process. The results indicate considerable drop in permittivity, refractive index and the absorption of light compared to pure silica. At 60% composition of Ag, the metamaterial properties were achive when the real permittivity is negative along the visible region. TGA and DSC results show that the AgNPs stability is much higher with the encapsulation by silica. Further study is suggested on the best composition of Ag-SiO_2 NCs toward the production of metamaterial.

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References

[1] G. Cao, *Nanostructures and Nanomaterials*, Imperial College Press, London, 2004.

[2] M.A. Reed and T. Lee (eds) *Molecular Nanoelectronics*, American Scientific Publishers, Valencia, CA, 2003.

[3] L. Pei, W. Xiang, X. Zhao, X. Liang, X. Yang, H. Liu, Z. Chen, C. Xie, X. Maa, C. Zhang, L. Maa, J. Zhao, *Sol–gel synthesis of silver nanocrystals embedded in sodium borosilicate monolithic transparent glass with giant third-order optical nonlinearities*, Mater. Res. Bull. 59 (2014) 154–161.

[4] U. Kreibig. M. Vollmer: *Optical properties of Metal Clusters* Springer – Heidelberg. Berlin (1995)

[5] Pei, Yanbo.; Yao, F.F.; Ni, P.; Sun, X. *Journal of Modern Physics*. Vol. 57, Taylor and Francis, 2010. 872-875.

[6] Podolskiy, V. A., Sarychev, A.K.; Shalaev, V.M. *Opt. Express* 2003, 11, 735-745.

[7] M.G.M. Van Der Vis, E.H.P. Cordfunke And R.J.M. Konings, .*Journal De Physique IV Colloque* C3, Supplement Au Journal De Physique 11, Volume 3, Aofit 1993 75-82

[8] Brinker, C. J., and Schere, G. W., *Sol-Gel Science:The Physics and Chemistry of Sol-Gel Processing*, Academic Press, New York, 1990.

[9] Tan, W. W., Chen, J.,Zhou, X., Zhang, J., Lin, Y., Li, X., Xiao, X., J *Solid State Electrochem* (2009) 13: 651-656.

[10] G, Najla., Bouaicha, M., *Nanoscale Research Letters* (2012), 7:357

[11] N.A.C. Lah, M.R. Johan, *Facile shape control synthesis and optical properties of silver nanoparticles stabilized by Daxad 19 surfactant*, App. Surface Sci. 257 (2011) 7494–7500

[12] A. Babapour, O. Akhavan, A. Z. Moshfegh and A.A. Hosseini, *Thin Solid Films,* **515,** 771 – 774(2006)

[13] N. A. C. Lah, M. R. Johan., *Applied Surface Science* 257 (2011) 7494 - 7500

[14] A. Babapour, B. Yang, S. Bahang, and W. Cao, *Biocide silver nanoparticles in two different silica-based coating*,AIP Conf. Proc. 1482, 681 (2012)

[15] W.Q. Ni,X.H.Zheng,J.C.Yu,*Sintering effects on structure and Dielectric properties of dielectrics* $CaCu_3Ti_4O_{12}$, J.Mater.Sci.42(3) (2007) 1037–1041.