Solid State Science and Technology, Vol. 24, No 2 (2016) 61-70
ISSN 0128-7389 | *http://journal.masshp.net*

CHARACTERIZATION OF SILVER NANOPARTICLES DISPERSED IN ORGANIC COMPOUND AND NATURAL POLYMER SOLUTIONS USING LASER ABLATION

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ABSTRACT

The present work investigated about morphology of Silver nanoparticles by using laser ablation which is a green technique. A Q-Switched Nd: YAG pulsed laser with 532 nm wavelength and 360 mJ/pulse energy used for synthesis of silver nanoparticles from silver plate with 99% purity for 30 min in organic compound such as ethylene glycol and natural polymer such as chitosan. The media (Ethylene glycol and chitosan) allowed the formation of nanoparticles with well dispersed. The spherical silver nanoparticles with different sizes obtained in various liquid media that was changed just over from 22 nm to about 10 nm in ethylene glycol and chitosan solution respectively. Additionally, the morphology of nanoparticles was compared with distilled water as a reference. The results showed silver nanoparticles proficiently dispersal in the chitosan solution with a considerable size reduction in comparison with other media.

Keywords: Silver nanoparticles (Ag-NPs); Organic compound (ethylene glycol); Natural polymer (chitosan); Laser ablation (LA);

INTRODUCTION

Recently, a lot of researches interested in metallic nanostructure materials have come up due to their unusual properties which are different from their bulk materials such as their electronic, optical, magnetic and chemical properties [1]. Due to these properties the main attraction for scientists is applications of these nanoparticles (NPs) in technology which nanocomposite fabrications and antibacterial are some of the most noticeable applications of silver NPs (Ag-NPs) [2, 4]. Hence, various NPs or nanocomposite materials have been investigated for their antimicrobial activity as growth inhibitors [5]. During the past years many methods such as chemical methods, sol gel, sono-chemical method were used to synthesize of Ag-NPs that among these techniques laser ablation (LA) was more flexible to fabricate Ag-NPs [6, 9]. Nevertheless, such chemical reduction method is not recommended since the chemicals

are highly reactive and known to pose a potential environmental hazard and biological risks. Instead, a variety of green technologies for the preparation of Ag-NPs have been developed [10]. Recently, plasma assisted methods based in LA, whilst the laser beam interacted with a solid target the plasma plum is formed above the surface of target that is called break-down phase. The advantage of LA compares to chemical synthesis is the simplicity of the procedure and also absence of chemical reagents in solution. Furthermore, the laser pulse has appeared to be more flexible and promising technique because of it is able to ablate metals, ceramic and polymer considers the ultra-high energy density. In LA, the control over the growth process were provided by manipulating the process parameters like irradiation time, duration, energy density and wavelength, etc [12]. LA technique is based on ablating a solid target in a gas or a liquid environment. The more effective collection of synthesized NPs can be achieved by LA in liquid phase. Scientists have studied about different features of LA technique regarding to the aqueous media that it had a dramatic affect on particle size and stability of NPs [13, 14]. Recently, using an organic solvent as a stabilizer for synthesis of NPs has been investigated [15, 16]. Among all organic solvent, ethylene glycol (EG) ($HOCH_2CH_2OH$) got more attraction due to its chemical and physical properties. EG is a colorless, practically odorless, relatively low-volatility, and hygroscopic liquid with low viscosity. Indeed, it is completely miscible with water, many organic liquids and many polar solvents (e. g alcohols, glycol, ethers, and acetone), and vaguely soluble in non-polar solvent such as toluene, benzene, chloroform [17, 20].

On the other hand, among the natural polymers, chitosan is the second most naturally abundant polysaccharide that it can be easily isolated from crustacean shell. The chitosan is non-toxic and it has been approved by food and drug administration (FDA) [21]. In this case, the dispersed Ag-NPs in chitosan solution is not necessarily to be separated and purified [22].

This work preformed LA silver plate in EG and chitosan to prepare Ag-NPs. In the LA process, we hypothesized that the Ag-NPs size decreases. Conversely, the stability of NPs increases in these media to compare with distilled water (DW).

EXPERIMENTAL

A pulsed Q-Switched Nd: YAG laser (SL400/SL800 system) with pulse duration of 10 ns and 30 Hz repetition rate at a second harmonic wavelength (532 nm) was applied to prepare the Ag-NPs. The schematic diagram of the LA experimental set-up is illustrated in Figure 1. A silver plate with high purity (Sigma Aldrich) was placed in glass cubic glass cell containing 15 ml of EG, chitosan and distilled water. Amounts of 0.2 g chitosan was dissolved separately 100 ml in distilled water at 60 ^oC and stirred for 1 hr. Prior to ablation, the silver plate was cleaned by using an ultrasonic bath for 30 min, and it was immersed in the solution. The solution was magnetically stirred at room temperature during the ablation process to disperse the produced NPs. The laser output power 35 mJ/pulse was measured by the optical power detector. The laser beam was focused on the silver target by a 25 cm focal length lens. The ablation was carried out

at room temperature for 30 min. The prepared samples have been characterized using a UV-visible, double beam photo-spectrometer (UV -1650 PC, Shimadzu) with 1 cm optical path cell, transmission electron microscopy (TEM, Hitachi H-7100; Hitachi) at 120 KV accelerating voltages and Fourier transform Infrared (FT-IR) spectrometer (1650; Perkin Elmer, Waltham, MA).

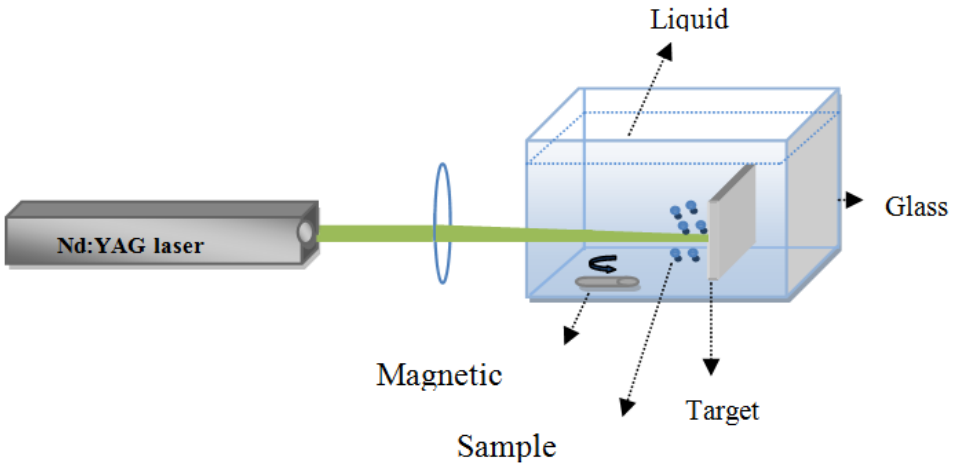

Figure 1: The LA setup for the colloidal NPs production

RESULTS AND DISCUSSION

The solutions are observed to change color from its colorless and transparent form to slightly yellowish after a few minutes during the ablation of the silver plate. The dark yellow will achieve for higher concentration. This was also confirmed by UV-visible absorption spectra. Figure 2, indicates the optical absorption spectra of the solutions containing Ag-NPs. The peak at 400 nm is the signature of plasmon peak of Ag-NPs which confirmed the Ag-NPs was formed inside the aqueous media. The peak intensity considerably increased with slightly blue shift toward high energy in chitosan solution in comparison with DW [23] which indicates a dramatic growth in the formation efficiency of the NPs, while the blue shift shows a decline in the particle size with regard to the Mie theory [24]. Furthermore, the spectrum peaks at this wavelength signifies that the NPs in the solutions are spherical which is confirmed by TEM results shown in Figure 3 and 4 [25]. From Figure 2, the intensity of absorption peak at 400 nm was increased that can conclude the number of generated NPs was also increased. The increase of formation efficiency is owing to the increment of the density and viscosity of solvent.

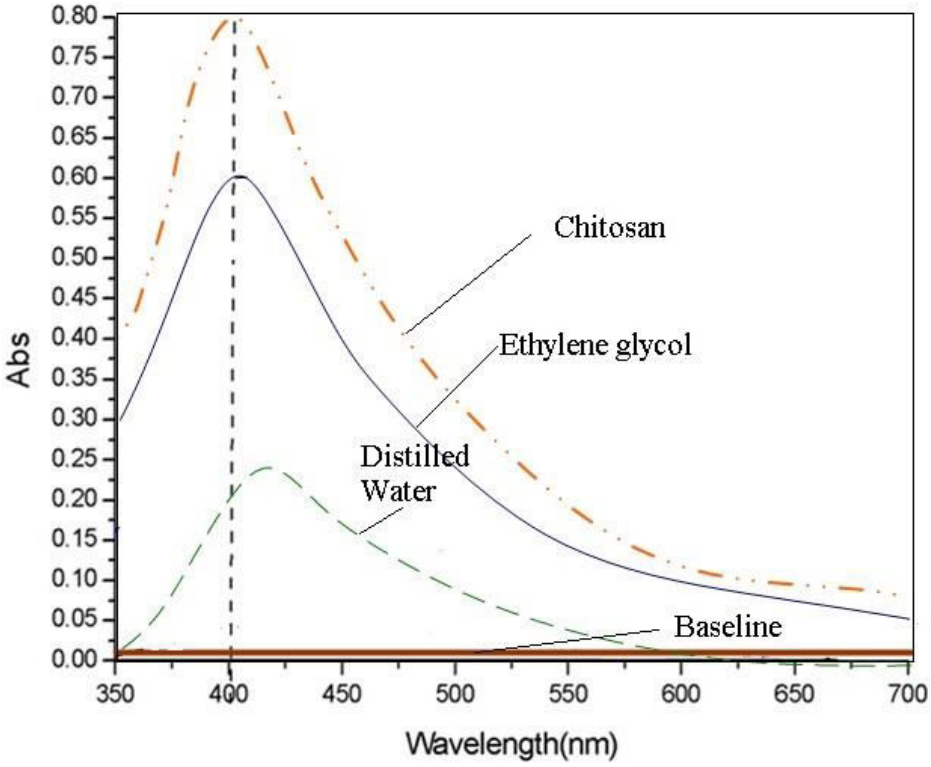

Figure 2: UV-visible absorption spectra of Ag-NPs prepared for 30 min ablation times in EG, chitosan and DW

In contrast, in Figure 4.a size reduction can be explained by the interaction between the EG molecules and laser products. In this step silver atoms interact with EG molecules therefore; the initial silver particles are formed because of this inter-atomic interaction. The mechanism of protecting particles from aggregation by EG can be explained by the hydroxyl group. In the fact of competition, the EG molecules now can absorb particle and prevent them from aggregation and growth [26]. On the other hand, Figure 4.c shows Ag-NPs in chitosan and their corresponding size distribution that the obtained mean particle size is about 10.5 nm. Referring to Figure 4.c, TEM analysis also indicates that Ag-NPs are well dispersed with spherical morphology and there is no evidence of agglomeration.

Figure 3 depicts the TEM images indicate the spherical shape of Ag-NPs [27]. This type of NPs shaped is suitable for drug loading and most biological applications, such as antibacterial properties [28]. Measurement the mean size of Ag-NPs are 22.08 nm in EG and in chitosan are about 10.5 nm and the mean size of Ag-NPs are 27.41.nm in DW which ablation time for all cases completed in 30 min. Indeed, confirms the observation of particle size decrement with respect to the media as shown in Table 1. The formation efficiency of NPs in chitosan is higher than in EG and EG is higher than in DW (chitosan >EG >DW) due to the confinement on the Ag plate produced by ablation and it becomes stronger with the increase of solvent density and viscosity. In

this case, chitosan has higher density and viscosity than other solutions for these reasons it is observed the effect of size decrement for Ag-NPs. The plasma generated close to the plate with high pressure, which is confined surface and it can etch the surface to make NPs [29-30]. The procedure called secondary ablation [31] can improve efficiency of the formation Ag-NPs. On the other hand, the number of NPs had an upward trend due to rise the density and viscosity of aqueous media (Table 1), whereas the plasmon peak shifts toward higher energies.

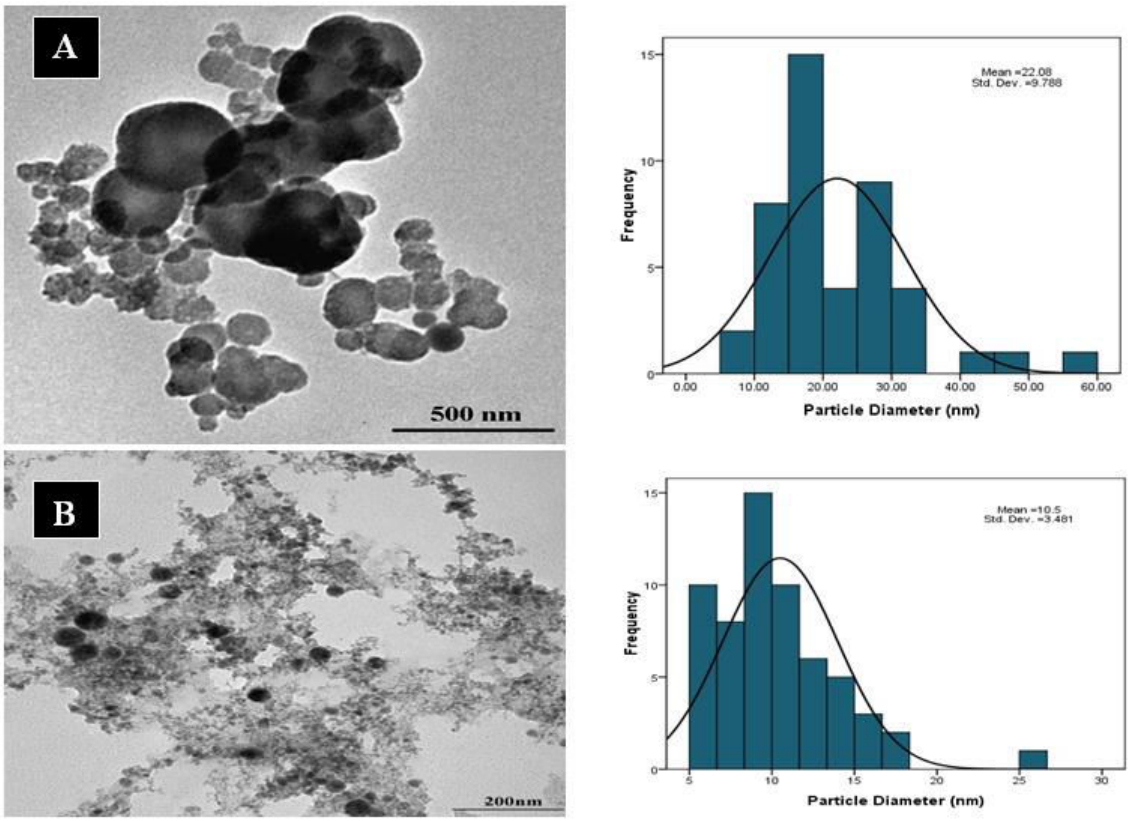

Figure 3**:** TEM image and typical of statistical graph for Ag-NPs produced in (**A**).EG, (B) in Chitosan and (C) in DW under 30.min ablation times in temperature room

Table 1: Particle size and volume fraction of Ag-NPs in various liquid media at 30 min ablation time

Media	**Particle size (nm)**	**Volume fraction (10^{-7})**
Ethylene glycol	22.08	4.8
Chitosan	10.50	8.4
Distilled water	27.41	2.8

Infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. FT-IR spectra in Figure 4, confirms the formation Ag NPs inside the solutions. The spectrum in Figure 5.a indicates that absorption peak at about 512.07 cm^{-1} which is a signature of Ag-NPs bonding with oxygen from hydroxyl groups [32] and Figure 5 shows the mechanism of protecting particles from aggregation by this stabilizer. The absorption peaks at about 3296.48, 1660.69 cm^{-1} which presented O-H groups. Furthermore, the peaks in 2936.57, 2875.14 cm^{-1} were assigned to symmetric and asymmetric of C-H_2 stretching [33] the band at 1410.27 cm^{-1} corresponds to C-H_2 bending. While, the peak at 1205.34 cm^{-1} corresponds to C-H stretching [32] and the peak at 1080.10 cm^{-1} indicates to the bending of C-C-O [33].

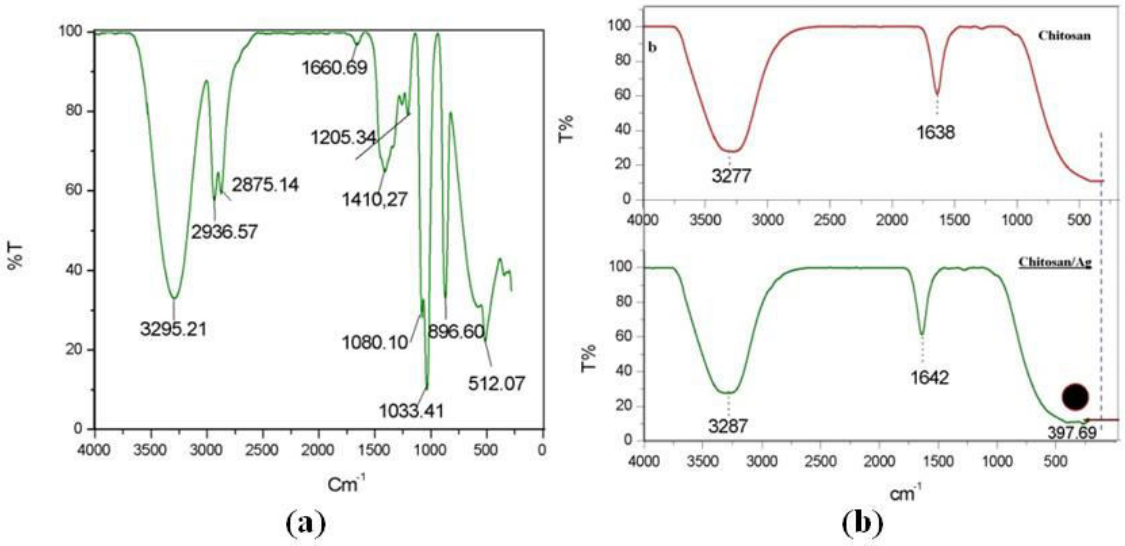

Figure 4: FT-IR spectra of Ag-NPs in (a) EG and (b) chitosan using LA

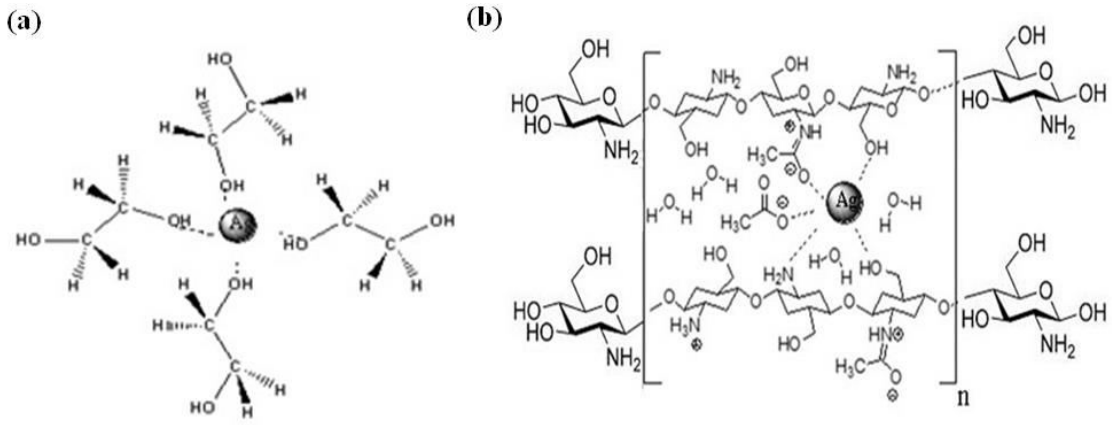

Figure 5: Mechanism of capping Ag-NPs by (a) ethylene glycol and (b) chitosan

In competition, the chitosan molecules can absorb particle and prevent their aggregation and growth [34]. The mechanism of protecting particles from aggregation by chitosan can be explained by those nitrogen atoms of amino group in chitosan hold a free electron doublet that it is responsible for the uptake of NPs by chelating mechanism [35]. Some researchers have attributed a key role to the amine in the Ag+ reduction due to its decrease in the potential of Ag+/Ag (EAg+/Ag) promoting the reaction [36]. However, there is still no substantial evidence that confirms this assumption. The stability of Ag-NPs was examined after one month. The UV-visible spectra of the Ag-NPs in EG, chitosan and in the water were measured after 1 month to investigate the capability of fluids as a stabilizer. The absorption spectrum in the Figure 6 does not show a significant change in the fresh sample compared to old sample in chitosan , but a large reduction can be seen in EG and water. It shows the Ag-NPs in chitosan were stable. Moreover, there is a red shift which indicates some agglomeration of the Ag-NPs in EG and water, hence the vaguely descent in the absorption intensity is due to the slight sedimentation of the larger particles [37].

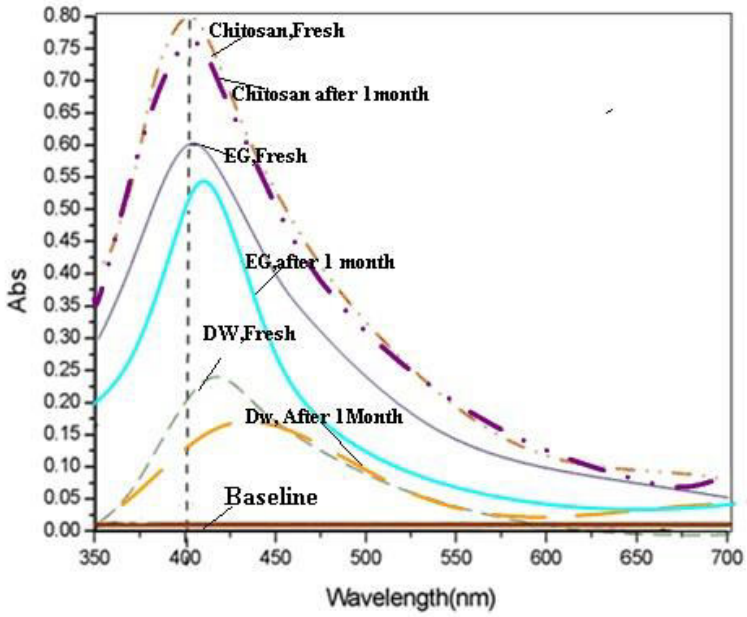

Figure 6: UV-visible absorption spectra of Ag-NPs in EG, DW and chitosan for freshly prepared and after 1 month

Although, FESEM image after one month confirms UV-Visible spectra observations which it's indicated of Ag-NPs in chitosan were still well dispersed, whereby some of the particle aggregated over a long period of time (Figure 7). This confirms the current hypothesis that stability can be achieved over quite long period of time.

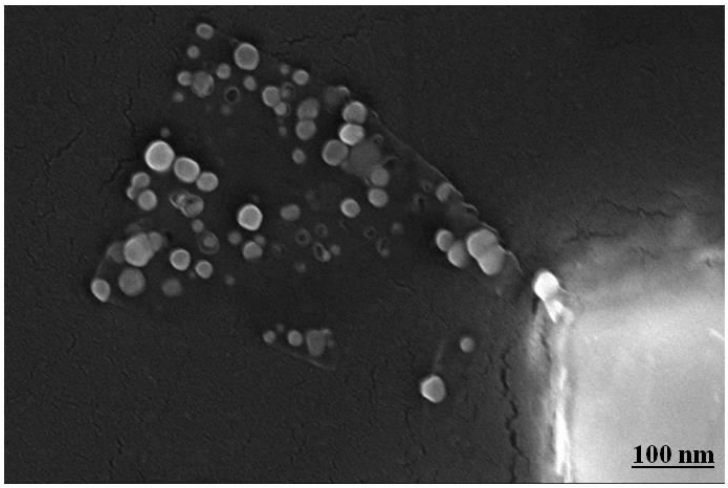

Figure 7: FESEM image of Ag-NPs in chitosan solution after one month

CONCLUSIONS

Characterization of Ag-NPs dispersed in various liquid media was presented as simple and green method. At the same ablation time, the obtained results indicated the size of Ag-NPs in chitosan solution was smaller than other media. In this case, liquid media has an effect on a size reduction in comparison with pure water. Finally, Ag-NPs were stable over long time storage in chitosan because it controls the particle from agglomeration.

ACKNOWLEDGMENT

The authors gratefully acknowledged the financial support for this work from the Fundamental Research Grant Scheme (FRGS) of Project No. 01-02-13-1345FR.

REFERENCES

[1]. J. Lin, S.F. Lim, S. Mahmood, T.L. Tan, S.V. Springham, P. Lee and R.S. Rawat. Synthsis and characterization of FeCo nanoparticle colloid by pulsed laser ablation in Distilled Water. ECA 30I, 2006, P 2-087.

[2]. C. Song, D. Wang, Y. Lin, Z. Hu, G. Gu, X. Fu. *Nanotechnology.* **15** 962–965 (2004)

[3]. M. Kokkoris, CC. Trapalis, SK.Kossionides, RBS and HIRBS. *Phys Res B.* **188** 67–72 (2005)

[4]. DP. Dowling, AJ. Betts, C. Pope, ML. McConnell, R. Eloy, MN. Artnauld. *Surf Coat Technol.* **637** 163–164 (2003)

[5]. J.W. Rhim, L.F. Wang, S.I. Hong. *Food Hydrocolloids* **33** 327-335 2013

[6]. ZS. Pillai, PV.Kamat, *J Phys Chem B.* **108** 945–951 2004

[7]. M. Brust, M. Walker, D. Bethel, D. Schiffrin, DJR. Whyman. *J Chem Soc Chem Commun.* 15 801–802 (1994)

[8]. I. Pastoriza-Santos, LM. Lis-Marzan. *Langmuir.* **15** 948–951 (1999)
[9]. F. Bonet, V. Delmas, S. Grugeon, R. Herrera Urbina, PY. Silvert, K.Tekaia-Elhsissen. *Nanostruct Mater.* **11** 1277–1284 (1999)
[10]. Habbalalu, D., Lalley, J., Nadagouda, M. N., & Varma, R. S. *Sustainable Chemistry & Engineering*. **1** 703–712 2013
[11]. A. Simakin, V. Voronov, G. Shafeev, R. Brayner, F. BozonVerduraz, *Chem. Phys. Lett.* **348** 182 (2001)
[12]. M. Yamamoto, M. Nakamato. *J Mater Chem.* **13** 2064–2065 (2003)
[13]. V. Amendola, S. Polizzi, M.Meneghetti. *Langmuir.* **23** 6766–6770 (2007)
[14]. V. Amendola, M. Meneghetti. *Phys Chem Chem Phy.* **11** 3805–3821 2009
[15]. Wu N, Fu L, Aslam M, Wong KC, Dravid VW. *Nano Lett.* **4** 383–386 2004
[16]. HT. Song, YM. Huh, S. Kim, WW. Jun, JS. Suh, J.Cheon. *J Am Chem Soc.* **127** 9992–9993 (2005)
[17]. E. Canada and H. Canada, Canadian Environmental Protection Act, 2000.
[18]. M. W. Forkner, J. H. Robson, W. M. Snelling, A. E. Martin, F. H. Murphy and T. E. Parsons, Glycols–Ethylene Glycols, 2004.
[19]. R. Gomes, R. Liteplo and M. E. Meek, World Health Organization, Geneva, 2002, CICADS 45.
[20]. R.A. Ganeev, M. Baba, A.I. Ryasnyansky, M. Suzuki, H. Kuroda, *Optics Communications.* **240** 437–448 (2004)
[21]. Pradip Kumar Dutta, Joy deep Dutta and V S Tripathi. *Jornal of Scientific and Industrial Research.* **63** 20-31 (2004)
[22]. Yoksan, R. and Chirachanchai, S. *Materials Chemistry and Physics.* **15** 296-302 (2009)
[23]. M. Kerker. *J. ColloidInterf. Sci,* **105** 297-314 (1985)
[24]. R. Zamiri, B. Z. Azmi, A. R. Sadrolhosseini, H. AbbastabarAhangar, A. W. Zaidan1,M. A. Mahdi. *International Journal of Nanomedicine.* **6** 71–75 (2011)
[25]. T. Tsuji, K. Iryo, N. Watanabe, M. Tsuji. *Appl Surf Sci.* 202 80–85 (2002)
[26]. F. Mafune, J. Kohno, Y. Takeda and T. Kondow. *J. Phy. Chem. B,* **104** 9111-9117 (2000)
[27]. F. Hajiesmaeilbaigi, A. Mohammadalipour, J. Sabbaghzadeh, S. Hoseinkhani, HR. Fallah. *Laser Phys Lett.* **5** 252–256 (2006)
[28]. PK. Khanna, CKK. Nair. *International Journal of Green Nanotechnology: Physics and Chemistry.* **1** 3–9 (2009)
[29]. Y. Kawaguchi, X. Ding, A. Narazaki, T. Sato, H. Niino. *Appl Phys A.* **80** 275–281 (2005)
[30]. Y. Tomita, PB. Robinson, RP. Tong, JR. Blake. *J Fluid Mech.* **466** 259–283 (2002)
[31]. Kabashin AV, Meunier M. *J Appl Phys.* **94** 7941–7944 (2003)
[32]. K. Shameli, M. B. Ahmad, S. D. Jazayeri, S. Sedaghat, P. Shabanzadeh, H. Jahangirian, M. Mahdavi and Y. Abdollahi. *Int. J. Mol. Sci.* 2012, 13, 6639-6650; doi:10.3390/ijms13066639
[33]. L. Ramajo, R. Parra, M. Reboredo and M. Castro. *J. Chem. Sci.,* **121** (1) 83–87 (2009)
[34]. Mafune, F., Kohno, J., Takeda, Y. and Kondow, T. *J. Phys. Chem. B,* **104**

9111-9117 (2000)
[35]. Silva, S. S., Ferreira, R.A.S., Fu, L., Carlos, L.D.,Mano, J.F. and Reis, R. L. *J . Materials Chemistry,* **15**, 3952-3961 (2005)
[36]. Ramojo, R Parra, M Reboredo and M Castro. *J. Chem. Sci.* **121** 83–87 (2009)
[37]. R. Zamiri, B. Z. Azmi, H. Abbastabar, M. Darroudi, M. Shahril Husin, M. Adzir Mahdi. *International Journal of Nanomedicine,* **6** 565–568 (2011)