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Microwave Synthesis of Oleylamine-capped Ag Nanoparticles in Aqueous Solution

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Ag nanoparticles have been synthesized using microwave irradiation. Oleylamine (OA) was used as stabilizer and capping agent, dimethylformamide (DMF) as reducing agent and deionized water as solvent. UV-Vis spectroscopy was used for the observation of absorbance peak as a sign of nanoparticle formation and size distribution. The synthetic parameters: OA/Ag, DMF, Ag concentration and the microwave irradiation power and time were optimized systematically. It was found that with the increase of OA/Ag mole ratio up to 100, the size of nanoparticles decreases up to 10 nm. The excess of OA in the solution plays a disturbing role in covering Ag nanoparticles and causes agglomeration and growth of nanoparticles. Optimized mole ratio of OA/Ag is accompanied with the use of 0.05 ml of DMF at 540 W microwave irradiation power for 30 sec. Transmission electron microscopy was employed to give clear evidence of nanoparticle formation with the sizes range from 10 nm – 20 nm. Fourier Transformed Infra-Red spectroscopy demonstrated that the particles have been capped successfully with OA in aqueous solution. The capped nanoparticles are polar and can be used in biological applications and also for the deposition of metal-oxide shells on their surface.

Keywords: hydrophilic Ag nanoparticle, oleyamine, microwave, plasmon.

1. INTRODUCTION

Ag nanoparticles have attracted many attentions due to their visible-light plasmon resonance for many years [1 – 10]. They have found versatile applications in different areas of science and technology such as biology [11, 12], sensor design [13], optics [14] and energy conversion [15 – 18]. There are many reports on the synthesis of Ag nano structures with different methods but there are few about microwave irradiation method [19 – 21]. Nanoparticles represent metastable clusters exhibiting the fundamental property to aggregate. Thus, the stabilization of the nanoparticles against aggregation is a fundamental prerequisite in nanoparticle science and technology. The stabilization of nanoparticles may be accomplished by the capping of the nanoparticles with weakly, electrostatically-bound ions (e. g. citrate stabilized Ag particles) [22], by molecular ligands [23], and the protection of the nanoparticles in polymer matrices [24]. Ag nanoparticles have also been functionalized by different capping agents to improve or facilitate their usage. Ashrafi et al. have functionalized Ag with rhodamine B isothiocyanate in an Igepal CO-520 and cyclohexane solution [12]. Nishioka et al. and Thi My Dung et al. have prepared Ag capped nanoparticles with the help of poly(vinylpyrrolidone) (PVP) and ethylene glycol as solvent [25, 26]. The use of non-polar solvents in the synthesis procedures limits their applications in various biomedical and clinical areas [12]. Recently oleylamine (OA) has been employed for a vast and versatile synthesis of nanoparticles ranging from metallic to oxide particles with a variety of morphologies and shapes [27]. Oleylamine (OAm) is another long-chain primary alkylamine, such as ODA or hexadecylamine (HDA), which can act as electron donor at elevated temperatures. Interestingly, commercial OAm has a much lower cost than commonly used pure alkylamines, though some concerns regarding purity and reproducibility have also been raised. Moreover, OAm is liquid at room temperature, which may simplify the washing procedures that follow the chemical synthesis of nanoparticles. OA exhibit alkalinity and affinity to metals through their NH_2 from one side of molecule and can be dispersed in water or bonds to metal-oxides such as SiO_2, TiO_2 and ZnO through OH from the other side [27]. Although it has been used to synthesis noble plasmonic metals [28 – 31], there are few reports on the synthesis of Ag nanoparticles with OA in non-polar solvent. Chen et al. have reported functionalization of Ag nanoparticles using OA with the aid of paraffin as solvent [31]. On the other hand, when the prepared Ag nanoparticles are used for the fabrication of different core-shell materials such as Ag@SiO_2 [11, 13] and Ag@TiO_2 [18], one must extract the Ag particles from the initial solution and re-disperse them in a new medium. This causes an agglomeration of the nanoparticles and the prolongation of the synthesis process of final product. In this work, we present a fast and facile method for the synthesis of well-controllable size of capped-Ag nanoparticles in an aqueous solution to be used for different synthetic purposes without the need of any further treatment.

2. EXPERIMENTAL METHOD

The microwave synthesis of Ag nanoparticles was performed using Shikoku Keisoku SMW 064, with a 2.45 GHz working frequency, attached with a refluxing system. This system had maximum power of 1000 W and a built-in magnetic stirring system. The temperature was controlled using feedback system with a thermocouple.

$Ag(NO_3)$ (Merck) was used as starting material. oleylamine (Sigma-Aldrich) has been applied as stabilizer

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and capping agent. Dimethylformamide (DMF) was employed to reduce Ag ions and deionized water (18.3 MΩ) was used as the solvent. To synthesis Ag nanoparticles, $Ag(NO_3)$ was dissolved in 20 ml deionized water and stirred for 5 minutes. Then, oleylamine (OA) was added to the initial solution and stirred for another 5 minutes. Finally, DMF was injected to the secondary solution and stirred for 5 minutes. The prepared transparent solution was exposed to microwave irradiation until it yields a transparent yellow solution.

The characteristic plasmon resonance of Ag nanoparticle was confirmed by UV-Vis spectroscopy with the help of AvaSpec-ULS3648TEC in the wavelength range of 200 nm – 1100 nm. The Fourier transformed infrared (FTIR) data were collected using an AVATAR-370-FTIR THERMONICOLET spectrometer using two separate procedures. Sample was unpacked into a tablet shape and put onto a polished silicon wafer before analysis. To obtain Transmission Electron Microscope (TEM) images, we used a LEO912 AB Electron Microscope operating at a bias voltage of 200 kV.

3. RESULTS AND DISCUSSION

OA-functionalized Ag nanoparticles have been prepared using a new combination of chemical materials. Although there are few reports on the preparation of Ag nanoparticles in ethanolic solution using microwave irradiation [9, 19], functionalization of Ag nanoparticles in aqueous solution by microwave has not been reported to the best of our knowledge. Thus, it is necessary to optimize the effective parameters of the method. A set of experiments were performed by changing one parameter at the same time while the rest of parameters are fixed. Finally, a sample was prepared with the optimized parameters and used for TEM and FTIR measurements. It should be notified that all the samples were prepared using a constant volume of 20 ml deionized water. The effect of different parameters has been studied on the formation of Ag nanoparticles and their average size distribution from section 3.1 through 3.5.

3.1. OA/Ag mole ratio

A set of nanoparticles were prepared with the mole ratios of [OA/Ag: 20, 30, 40, 100 & 200]. Microwave power, irradiation time, Ag concentration, and DMF were kept at 540 W, 30 sec, 0.00125 gr/ml and 0.05 ml, respectively. Fig. 1 shows that the Gaussian peak appears for 30 mole ratio and increases with the increase of OA.

Metallic nanoparticles of Ag have a plasmon peak in absorption spectrum that the wavelength of the peak is highly related to their size distribution. With the increase of particle's size, the wavelength of plasmon peak shifts to larger wavelengths or it is called a "red shift". The width of the peak shows the size distribution of particles. Ag nanoparticles with uniform size have narrow width. Thus, the peak position and peak width obtains the average size and the size distribution of particles [32]. The peak is centered at 412 nm for 40 mole ratio and shifts down to 407 nm for 100 mole ratio. The best value is 100, which results in appearance of a plasmon peak at 407 nm with a narrow size distribution.

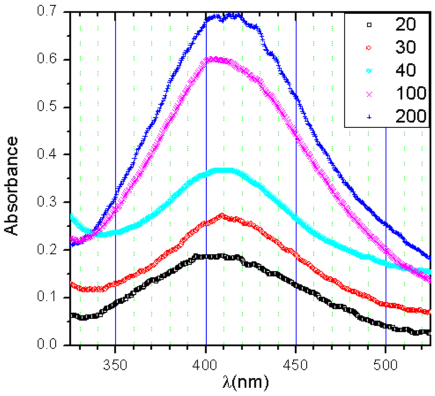

Fig. 1. Absorbance spectra of the nanoparticles synthesized with different OA/Ag mole ratios

A further increase of OA/Ag up to 200 results in a red shift of the peak, which is a sign of the increase of the nanoparticles' size. Thus, the best choice for OA/Ag mole ratio is 100. It could be due to the fact that OA molecules aggregate in the solution when their OA/Ag value increases more than 100 and consequently could not cover Ag surfaces completely and, results in the formation of larger nanoparticles.

3.2. Dimethylformamide

Dimethylformamide (DMF) was used as reduction agent to boost the formation of metallic Ag from Ag^+ ions. Microwave power, irradiation time, Ag concentration and OA/Ag were kept 540 W, 30 sec, 0.00125 gr/ml and 100, respectively at this step. Fig. 2 demonstrates that the more DMF is used, the higher is the Gaussian peak.

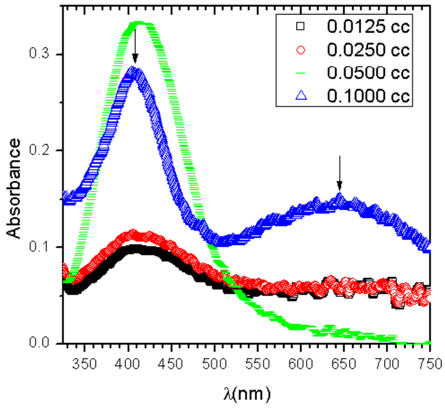

Fig. 2. Absorbance spectra of samples with different DMF values

It means that a larger number of Ag nanoparticles has been formed. However, application of 0.1 gr DMF resulted in an inhomogeneous formation of Ag nanoparticles and a yellow-black solution was obtained (indicated by arrows). The increase of DMF over 0.05 gr gives rise to the formation of big Ag particles along with nanoparticles. For the fixed parameters, the best result was obtained using 0.05 gr DMF, which results a plasmon peak at 407 nm.

3.3. Microwave power and irradiation time

In order to optimize the microwave irradiation power, the irradiation time was kept at 30 sec, then different irradiation time was also applied for different powers to obtain an appropriate irradiation time for each power.

OA/Ag mole ratio, Ag concentration and DMF were kept at 100, 0.00125 gr/ml, 0.05 ml, respectively. Fig. 3 exhibits that the absorption peak increases with the increase of power, continuously. An increase of power from 540 W to 900 W results in 10 nm shift of plasmon peak to higher wavelengths as well as broadening of the peak. It states that very high irradiation power accelerates Ag ion agglomeration and cluster formation. By continuing irradiation time up to 60 sec for 900 W and 540 W irradiation powers, the Ag solutions turned from light-yellow in 30 sec into dark-yellow and subsequently became black in the next 30 sec. The least of the irradiation time for the formation of Ag nanoparticles for high microwave powers such as 540 W is 20 sec (Fig. 4).

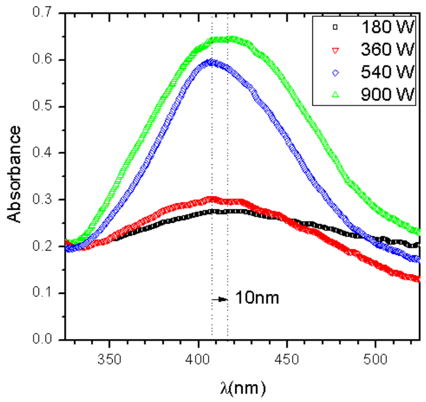

Fig. 3. The comparison of absorbance spectra of Ag nanoparticles prepared with different microwave powers for 30 sec

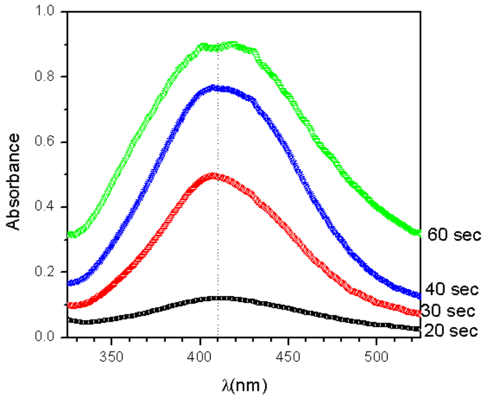

Fig. 4. Absorbance spectra of nanoparticles synthesized using the 540 W power and different irradiation times

The same experiment was done for 360 W and 180 W irradiation power but they are only different from the 540 W case in the time of formation. It is because the total energy delivered to the solution in microwave process is obtained by multiplying irradiation time and irradiation power; thus, the total energy is 540 W · 30 sec = 16200 W·sec. If one calculates the equivalent time of the same energy value for the power of 360 W, it results 45 sec. Nevertheless, the best times for the formation of yellow colored solution with a plasmon peak at 410 nm (not shown) are 90 sec and 120 sec for 360 W and 180 W microwave powers, respectively. It shows that in microwave synthesis process, it is not only the total energy transfer to the solution that furthers a chemical reaction but also, the interaction of electromagnetic wave with matter plays an essential role.

3.4. Ag concentration

Since functionalization of Ag nanoparticles is dependent to the accessibility of surface of nanoparticles to surrounding OA molecules, Ag concentration is a crucial parameter. To seek the effect, the mole ratio of OA/Ag must be kept fixed at 100. Microwave power, irradiation time, and DMF were kept 900 W, 30 sec and 0.05 gr, respectively. Fig. 5 indicates that in very low concentration of Ag atoms, Ag nanoparticles would not be formed.

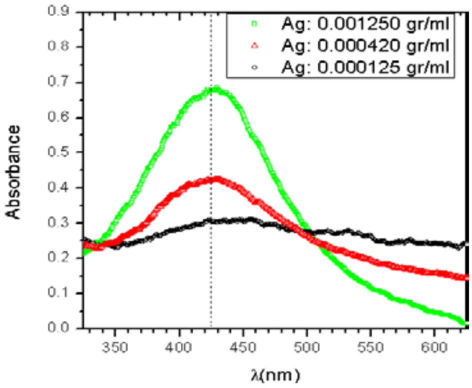

Fig. 5. Effect of Ag concentration on the absorbance of the nanoparticles

It could be attributed to the large distances between Ag ions and disability of DMF in reduction of Ag ions at the presence of capping agent. It is also inferred that high concentration of Ag could results in the formation of large nanoparticles.

3.5. Stability of prepared nanoparticles

The sample which was prepared with the synthetic parameters of, microwave power, irradiation time, Ag concentration, DMF and OA/Ag as 540 W, 30 sec, 0.00125 gr/ml, 0.05 and 100, respectively, was kept sealed in a dark stored place for 80 days. The comparison of the samples' absorbance (Fig. 6) indicates that in the course of time the plasmon peak does not shift to higher wavelengths significantly.

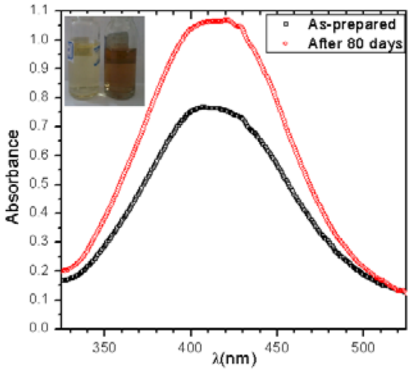

Fig. 6. Effect of aging time on the absorbance of Ag nanoparticles

It demonstrates a negligible red shift in the plasmon peak of the aged sample compare to the as-prepared sample. Thus, OA effectively covers the surface of particles and inhibits their agglomeration and the growth of particles' size. The increase in the intensity could be due to some partial formation of new particles and/or water evaporation.

3.6. TEM & FTIR characterization

The Ag nanoparticles-with the preparation parameters: 540 W & 30 sec microwave power & time, respectively, OA/Ag: 100, DMF: 0.05 gr. were dispersed in ethanol, then centrifuged and dried at room temperature for further characterization. TEM image (Fig. 7) shows the formation of Ag nanoparticles with average size of ~15 nm. FTIR analysis (Fig. 8) shows that there are various types of bounds on the surface of Ag nanoparticles.

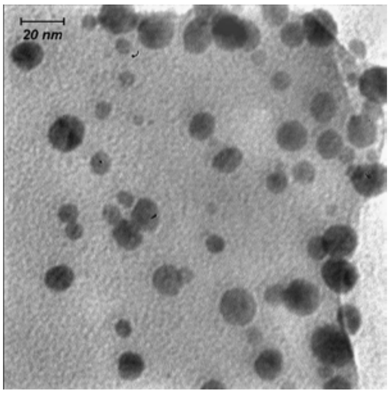

Fig. 7. TEM image of Ag nanoparticles prepared with the optimized parameters

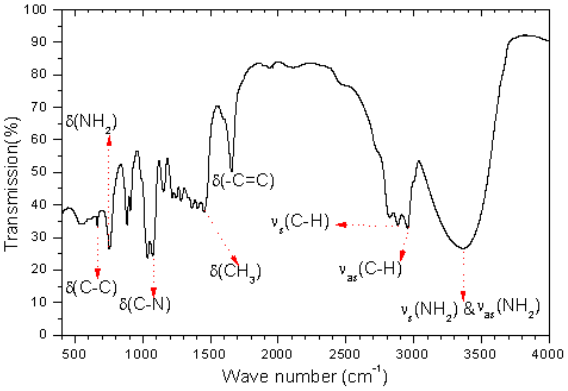

Fig. 8. FTIR spectrum of the Ag nanoparticles with the synthesis parameters of 540 W & 30 sec, OA/Ag: 100, DMF: 0.05 gr. (ν_s = symmetric stretching vibration; ν_{as} = asymmetric stretching vibration; δ = bending vibration)

Peaks at 722, 795, 1071, 1647, 2854, 2922, 3006, 3300 and 3376 cm^{-1} are attributed to OA molecular structure [27]. It indicates that Ag nanoparticles have been capped successfully with OA.

4. CONCLUSIONS

Oleylamine-capped Ag nanoparticles were successfully synthesized using microwave irradiation in aqueous solution for the first time. Although oleylamine is hydrophobic, it has functionalized Ag particles in an aqueous media. FTIR study shows that the presence of CH bounds on the surface of nanoparticles has made them hydrophilic and the particles are capable of bonding to metal oxide compounds such as TiO_2 and SiO_2. Study of various parameters showed that the optimized parameters for the synthesis of Ag nanoparticles with the average size of 10 nm – 15 nm with the plasmon peak at 407 nm are as following: microwave power: 540 W, irradiation time: 30 sec, OA/Ag:100, DMF: 0.05 gr in 20 ml of deionized water. The prepared nanoparticles are stable for at least 80 days. The prepared nanoparticles could be directly used for the preparation of biological samples or different core-shell structures without any further treatment such as centrifuging the solution and re-dispersing the Ag nanoparticles in water.

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