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Structural Characterization of Silver Nanoparticles Synthesized by Micro emulsion Route

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Abstract*−** **Silver *nanoparticles were synthesized by micro emulsion route in W/S ratio of 5 at room temperature. X-ray diffraction (XRD) pattern reveals FCC structure of Ag nanoparticles. Spherical shape of Ag nanoparticles of average particle size 5.0 to 12.0 nm were observed by transmission electron microscopy. FTIR spectra confirmed the presence of Ag−O bonding. Thermal studies were carried out by the differential scanning calorimeter (DSC) techniques. In addition, UV-Visible spectra were employed to estimate the band gap energy of Ag nanoparticles.

***Keywords*: Nanostructure, Micro emulsion, XRD, Optical properties.**

I. INTRODUCTION

In recent years, noble metal nanoparticles have been the subject of focused research due to their unique electronic, optical, mechanical, magnetic and chemical properties that are significantly different from those of bulk counterpart [1-5]. Now-a-days, silver Nanoparticles has gain tremendous popularity in the world in the field of sensors because of outstanding significance optical, electronic and chemical properties [6-8]. Silver nanoparticles exhibit new optical properties, which are observed neither in molecules nor in bulk metals. One example is presence of absorption band in visible light region. This band appears due to the surfaceplasmon-oscillation modes of conduction electrons which are coupled through the surface to external electromagnetic fields [9]. Silver exhibits the highest electrical and thermal conductivities among all the metals [10].

A variety of preparation routes have been reported for the preparation of metal oxide nanoparticle[3, 4] notable examples include, reverse micelles process [5, 11], salt reduction [12], microwave dielectric heating reduction[13], ultrasonic irradiation [14], radiolysis [15, 16], solvothermal synthesis[17], electrochemical synthesis [18, 19] etc.

Compare to other methods, the reverse micelle method is one of the most promising wet chemistry synthesis approaches of synthesis of metal nanoparticles [20]. This method provides a favorable microenvironment for controlling the chemical reaction. As such the reaction rate can be easily controlled, and it is possible to obtain a narrow nanoparticle size distribution [21]. Reverse micelle micro emulsions are transparent, isotropic, and thermodynamically stable [22, 23].

In continuation to our earlier research work [24-26], present work reports synthesis of Ag nanoparticles by micro emulsion route. Characterization of Ag nanoparticles were carried out by XRD, TEM, DSC, FTIR and UV-Visible spectroscopy.

II. EXPERIMENTAL

A. Materials and method

All chemicals used in experiment were of analytical grade. The stable reverse micelle micro emulsion was prepared by mixing a non-ionic surfactant, Triton X-100 [$(C_{14}H_{22}O\ (C_2H_4O)_n)$] (Qualigen Chem. Pvt. Ltd., Mumbai), Polyvinyl pyrollidone (PVP) (K85-95) (Merk, India) and 1:9 ratio of cyclohexane (Qualigen Chem. Pvt. Ltd., Mumbai) and triple distilled water (conductivity less than 1×10^{-6} S cm^{-1}). The micro emulsion was mixed rapidly with continuous stirring for five minutes. $AgNO_3$ (Qualigen Chem. Pvt. Ltd., Mumbai) solution (0.5 M) was added drop by drop to micro emulsion with continuous stirring. A colorless mixture was obtained. PVP was used as a stabilizing agent. After half an hour of equilibration, 1.0 M hydrazine hydrate (Qualigen Chem. Pvt. Ltd., Mumbai) solution was added drop by drop with continuous stirring at room temperature. Synthesis of silver nanoparticles was carried out in dark room. The reverse micelles were broken by adding THF (Merk, India).

Ag nanoparticles were subsequently washed with ethanol and triple distilled water to remove residual surfactant molecules. After washing Ag nanoparticles were dried in oven at 100.0 °C for 48 hours.

B. Characterization techniques

Structural and optical properties of the Ag nanoparticles were determined by using Transmission Electron Microscopy (TEM) (Hitachi: H-7500; Resolution: 2 Å), X-ray Diffraction (XRD) (Rikagu Mini-2 using CuKα1, λ = 0.15406 nm radiations), Differential Scanning Colorimetery (DSC) (TA Instruments USA, DSC Q10) in the range 50-600 °C, Fourier Transform Infra-Red spectroscopy (FTIR) (Thermo-USA, FTIR-380) in the wavelength range of 400 - 4000 cm^{-1} and UV-Visible spectroscopy (Systronic-2203).

III. RESULT AND DESCUSSION

A. Synthesis

Due to the solvating action, $AgNO_3$ dissolves in water to produce the colorless solution which is due to the presence of $[Ag(H_2O)]^{+1}$ ions. Addition of $N_2H_4.H_2O$ to the aqueous solutions of silver nitrate results to production of grey precipitates of Ag nanoparticles inside the miceller core. PVP act as stabilizer for these Ag nanoparticles. The surfactant and PVP molecules adhere to the surface of nanoparticles which serve as a protective layer to prevent the further reaction.

The TEM images are also confirm the coating of PVP surrounding the spherical Ag nanopartilcles.The reaction profile of formation Ag nanoparticles can be illustrated as:

$$2AgNO_3(aq) + N_2H_4 + H_2O(l)$$

$$\rightarrow 2Ag(s) + [(N_2H_5)(NO_3)_2]^{+}(aq) + OH^{-}(aq) \qquad (1)$$

There are two important factors that affect the exchange rate of reverse micelles in micro emulsions; the stability of the dimer form and the size of channels between the two dimmers [27]. The dimer stability, which depends on the intermicellar attractive potential, determines the interdroplet transfer of reactants. On the other hand, the size of channels which depends on the rigidity of interfacial film in the micro emulsion, determines the Ostwald ripening contribution [28].

B. X-ray diffraction analysis

Data for some 2θ range has given in Table1. Indexing process of powder diffraction pattern was done and Miller Indices (h k l) to each peak was assigned. All Miller Indices (h k l) reveal the FCC structure of Ag nanoparticles. Table 2 shows the full width half maxima, d-spacing, Miller indices and grain size of Ag particles nanoparticles.

Table. 1 Simple peak indexing

Peak Positon(2θ) (deg)	1000 × Sin²θ	1000 × Sin²θ/35	Reflection	Remarks
38.46	108	3	(111)	$(1^2+1^2+1^2)$
44.44	143	4	(200)	$(2^2+0^2+0^2)$
64.56	285	8	(220)	$(2^2+2^2+0^2)$
78.00	396	11	(311)	$(3^2+1^2+1^2)$

Table. 2 The particle size of Ag nanoparticles.

2θ of the intense peak (deg)	(h k l)	FWHM of intense peak (β) in radian	Size of the particle (D) nm	d-spacing nm
38.46	(111)	0.0275	5.3	0.2338
44.44	(200)	0.0183	8.2	0.2039
64.56	(220)	0.0321	5.1	0.1443
78.00	(311)	0.0238	6.5	0.1224

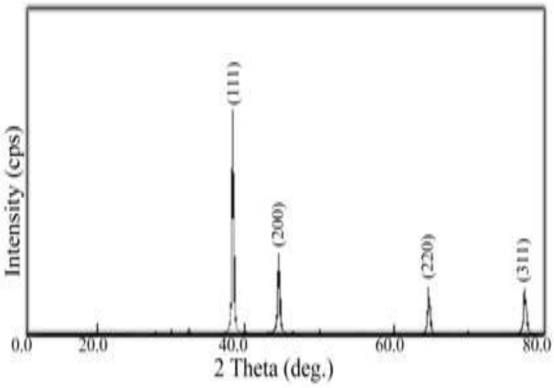

Fig. 1 XRD pattern of Ag nanoparticle.

Figure 1 shows XRD diffraction pattern of Ag nanoparticles. All diffraction peaks of sample correspond to the characteristic face centered cubic structure of Ag nanoparticles (a = 0.407 nm) [29]. Average particle size of Ag nanoparticles is found to be 6.4 nm using Scherrer equation [30]. Diffraction pattern corresponding to impurities are found to be absent. This proves that pure Ag nanoparticles were as synthesized.

C. Transmission electron microscopy

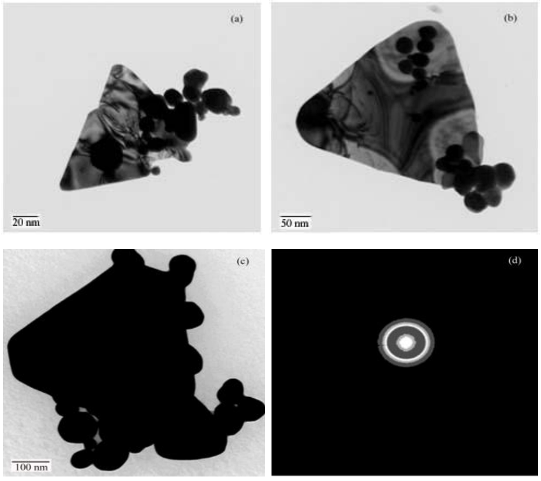

Fig. 2 TEM images of Ag nanoparticles (a, b, c) and its selected area electron diffraction image (d).

Figure 2 (a, b & c) show the TEM images of Ag nanoparticles. Spherical shape Ag nanoparticles were observed in TEM images of average size in the range of 5.0–12.0 nm. From the TEM images, it is clear that PVP provide a triangular coating on the surface of Ag nanopaticles. This prevents the further agglomeration of Ag nanoparticles. Figure 2 (d) shows the selected area diffraction pattern (SAED) of Ag nanoparticles. It shows that the particles are well crystallized. The diffraction rings on SAED image matches with the peaks in XRD pattern which also proves the FCC structure of Ag nanoparticles.

D. FTIR spectroscopy

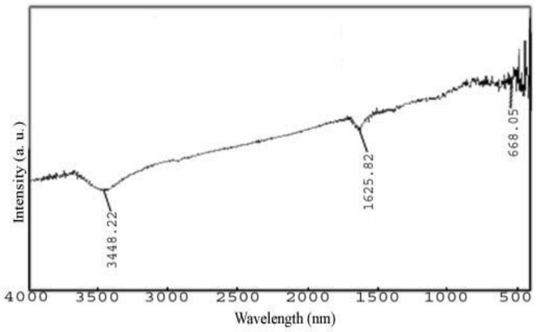

Fig. 2 FTIR spectra of Ag nanoparticle

Figure 3 shows FTIR spectra of Ag nanoparticles. Infrared studies were carried out in order to ascertain the purity and nature of the metal nanoparticles. Metal generally give absorption bands in fingerprint region i.e. below 1000 cm^{-1} arising from inter-atomic vibrations. The peak observed at 3448.22 cm^{-1} are may be due to O-H stretching and deformation, respectively assigned to the water adsorption on the metal surface. The peaks at 1625.82 and 668.05 cm^{-1} are corresponding to Ag−O stretching and deformation vibration, respectively. The metal-oxygen frequencies observed nm for the respective metal oxides are in accordance with literature values [31]. Similar FTIR studies of silver nanoparticles were reported by N. D. Singho and his coworkers [32] favor the results.

E. UV-Visible spectroscopy

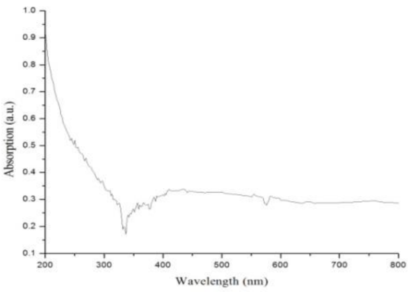

Fig. 4 (a) Absorption spectra of Ag nanoparticle as a function of wavelength

The optical characterization of the sample was recorded on UV-Vis absorption spectrophotometer Figure 4 (a) shows the UV-Visible absorption spectra of Ag nanoparticles as a function of wavelength. The UV-Visible absorption spectroscopy of Ag nanoparticles in ethanol solvent does not show any sharp absorption peak. This result shows that silver nanoparticles were stabilized by the PVP coating. Due to which transition of electrons from the surface of silver nanoparticles is not possible.

Absorption coefficient (α) associated with the strong absorption region of the sample was calculated from absorbent (A) and the sample thickness (t) by using the relation:

$$\alpha = 2.303A/t \qquad (3)$$

While the optical band gap of Ag nanoparticles is calculated using the Tauc relation [33]:

$$\alpha = \frac{B(h\nu - E_g)^n}{h\nu} \qquad (4)$$

Where, α is the absorption coefficient, B is a constant, $h\nu$ is the energy of incident photons and exponents n whose value depends upon the type the transition which may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively [34].

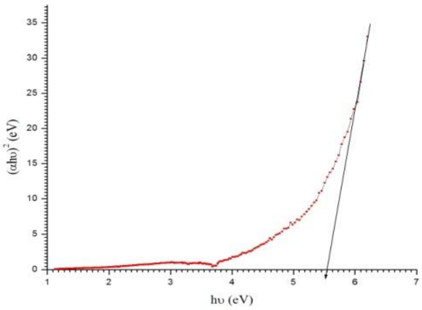

Fig. 4 (b) Variation of $(\alpha h\nu)^2$ with $h\nu$ for Ag nanoparticles as a function of Wavelength at n value of 1/2.

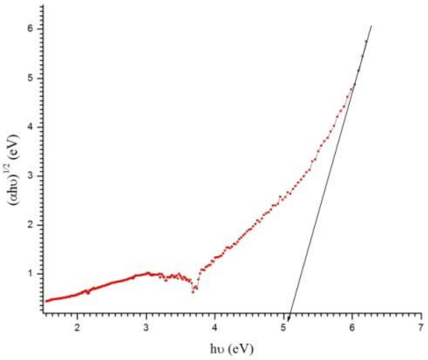

Fig. 4 (c) Variation of $(\alpha h\nu)^{1/2}$ with $h\nu$ for Ag nanoparticles as a function of Wavelength at n value of 2

Figure 4 (b & c) show the variation of $(\alpha\ h\nu)^{1/n}$ vs. photon energy, $h\nu$ for Ag nanoparticles with n values of 1/2 and 2, respectively . Allowed direct and indirect band gap of Ag nanoparticles are calculated to be 5.6 and 5.1 eV, respectively. This is very higher than reported values as zero eV in bulk silver and 2.6 eV in silver dimer nanoparticles [35]. The increase in the band gap of the Ag nanoparticles with the decrease in particle size may be due to a quantum confinement effect [36].

F. DSC analysis

The isothermal behavior of Ag nanoparticles has been investigated using DSC technique over a temperature range of 50-600 °C in ambient air.

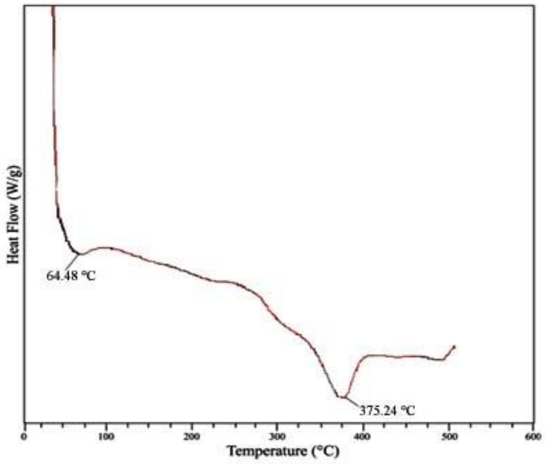

Fig. 5 DSC curve of Ag nanoparticles

Figure 5 shows DSC curve of Ag nanoparticles. A small low temperature endothermic peak at 64.48 ºC is due to loss of water molecule adsorbed on the surface of Ag nanoparticles during synthesis conditions. A large high temperature endothermic peak at 375.24 ºC is assigned the conversion of PVP−Ag−PVP to Ag nanoparticles.

IV. CONCLUSION

Ag nanoparticles of FCC structure are synthesized by microemulsion technique. From TEM study, it is found that Ag nanoparticles are of spherical shape coated by PVP with average size of 5.0–15.0 nm. The FTIR spectral analysis reveals the characteristic peaks for Ag−O stretching. The absorption of water molecules on the Ag nanoparticles is confirmed by FTIR spectra. The UV-Visible study is not showing any sharp absorption. Allowed direct and indirect band gap energy of Ag nanoparticles are found to be higher as compared to their bulk counter part. Thermal studies are carried out by DSC technique which further confirms the formation of Ag nanoparticles.

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