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Development of Narrow Size Distribution Silver Nanoparticles as Standard Reference Material/Bhartiya Nideshak Dravay for TEM/HRTEM and Particle Size Analyzer Instruments

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Abstract:- Silver nano particles (Ag NPs) with narrow size distribution were derived chemically by sol-gel process and characterized by XRD, and highresolution transmission electron microscopy (HRTEM) techniques to confirm their formation, morphology, particle size and distribution properties. The variation in size of as prepared Ag NPs were monitored periodically every month by HRTEM for the last six months to check the stability of nanoparticles with time to assign the shelf life of Bhartiya NideshakDravay (BND) and estimated the overall expanded uncertainty in size of nanoparticles. The traceability of the developed silver nanoparticles will be derived from the NIST standard reference materialor from other NMI which established facility for assigning particle size. Such Ag NPs BNDs of different particle sizes can be used for calibration of instruments like TEM/HRTEM and particle size analyzersfor research and find usagein many industrial applications with global acceptance.

Keywords: *Silver nanoparticles, Sol-gel, Uncertainty measurement, HRTEM, Particle Size analyzer.*

I. INTRODUCTION

The vast emergence in the field nanoscience and nanotechnology has encouraged development of variety of nanomaterials for application in many existing and new advanced technologies in all walks of life. As we know that nanomaterials have one dimension in nanometer range and acquire different morphological forms like nanoparticles, nanorods, nanowire, nanotube, flower/ring/spring or in quantum dot form etc. These nanoparticles are prepared by physical/chemical/green chemistry route. The sizeand morphology of nanomaterials are controlled by the selection of appropriate synthesis route and operating parameters as they are very important for their device application. The structure, shape, size and distribution of nanoparticles prepared by different routes is very precisely and accurately measured by transmission electron microscope (TEM)/HRTEM techniques. While the other indirect measurement technique e.g. particle size analyzer gives information of particles size only and do not provide information about the shape, and structure of nanoparticles. That's why TEM/HRTEM are the most preferred techniques for the nanoparticles size and size distribution estimation. For this and global acceptance of data, the instruments in use should be calibrated and the record for its periodical calibration as recommended by the company should also be maintained to keep the performance of instrument at par.The sample used for calibration of TEM/HRTEMshould have the capability of image resolution calibration for recording images, the camera constant calibration for indexing diffraction patterns, and the image/diffraction pattern rotation calibration for crystal directions viewed in the image[1-3].The different magnification standards have beenproposed for different magnification ranges. For example in HRTEM, magnification exceeds 300000 times when thin cross-sections of single crystals and single-crystalline gold islands are used. In single crystals e.g. gold and silver, the magnification calibration is done via lattice-plane spacing. The optics aberration correction and image reconstruction methodshave markedly improved the point resolution of TEM to ~ 0.05nm.

The magnification and resolution are interrelated to each other and reveals the efficiency of the microscope. At present polystyrene spheres are used but they are damagedeither by the radiation or the grating.The resolution of TEM and HRTEM is evaluated by lattice imaging of the standard Au and Ag nano particles. This problem encouraged researchers for the development of new robust materials which can toleratethe variations in temperature or radiation [2]. The noble gold nanoparticlesare considered to bear such adverse conditions for the calibration of TEM instrument. In this work, the use of economic Ag NPs derived by sol-gel method under optimized conditions is proposed as a secondary standard reference material/BND for the calibration of TEM/HRTEM or particle size analyzer instruments. The uncertainty in as prepared silver nanoparticles size from recorded TEM/HRTEM image is evaluated as per standard GUM and Eurachem guidelines for the measurement of overall uncertainty.

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II. EXPERIMENTAL MEASUREMENTS

A. Synthesis of Ag NPs:

The monodispersed silver nanoparticles were prepared by a sol-gel method, the aqueous solution of $AgNO_3$as silver precursor was prepared and stored in dark brown colored bottle. Trisodium citrate (TSC) solution in water was heated at 90 °C having teflon coated magnetic stirrer for 30 minutes to undergo reduction reaction. To this hot solution $AgNO_3$ was added dropwise in dark with continuous stirring and pH of solution was maintained at 10.5 by adding 0.1 M NaOH aqueous solution. On further heating for 20 minutes, the reaction completed and solution color changed to yellow color. In this reaction, TSC plays dual role (i) as reductant and (ii) as stabilizing agent and performed in dark to restrict oxidation of $AgNO_3$ on exposure to air. Then suspension was cooled to room temperature homogenous solution and centrifuged at 12000 rpm for 15 minutes to separate out Ag NPs and washed several time with DI water to remove excessive unreacted salts. The as obtained Ag NPs wereagain dispersed in DI water to obtain stable aqueous suspension for storage. These suspensions are keptin refrigerator for further use.

B. Measurements:

The formation of Ag NPs is confirmed from XRD pattern recorded on Bruker d8 Advance X-ray diffractometer, using CuKα radiation (λ = 1.5406 Å), 40 kV-30mA in 2θ range of 30° to 90°. The recorded XRD pattern is presented in Figure 1.

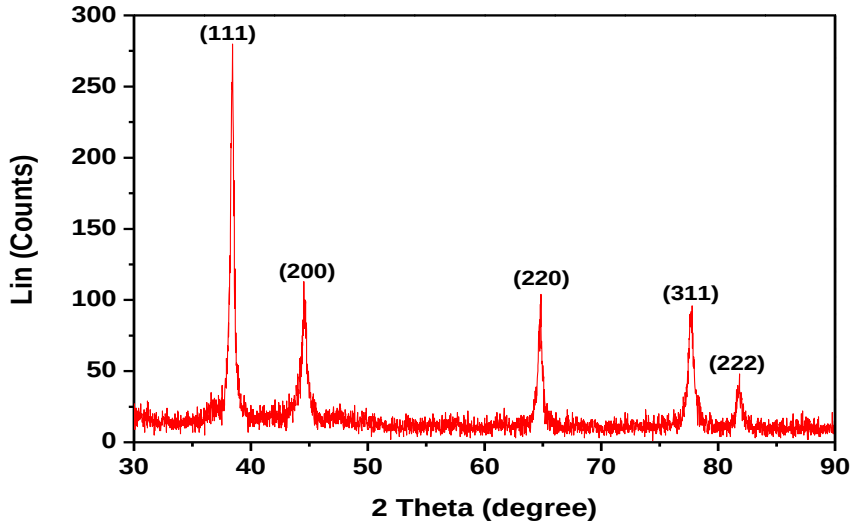

Fig. 1: XRD pattern of Ag NPs

The five peaks pertaining to silver at 2θ values of 38.2209°, 44.5253°, 64.9748°, 77.7057°and 81.8620°of (111), (200), (220), (311) and (222) planes respectively are observed in diffraction pattern. These peaks match well as reported in the standard powder diffraction card of JCPDS, silver file No. 04-0783.

HRTEM images of Ag NPs suspension were recorded in different intervals on M/S Technai G2 F30 STWIN HRTEM to reveal the particle size, distribution and uncertainty measurement.

III. RESULTS AND DISCUSSION

The aim of present work is to develop different size Ag NPs BNDs for the calibration of TEM/HRTEM instruments available in different laboratories/ institute/universities in India as well as outside. These are extensively used for the characterization of nanomaterials. For the global acceptance of data as per ISO 17025 standard guidelines, all the assigned values to any parameter should be accompanied by the uncertainty value and its traceability to some standard issued by apex body or NMI of any country where such type of work is going on. The size of any type of procured or developed nanoparticle is generally measured by TEM/HRTEM instruments. To check the accuracy of data obtained from these instruments need calibration these instruments. For this purpose, CSIR-NPL, New Delhi initiated project on the development of BNDs in lab pertaining to different activities in lab and in India to aware materials research community for the need of these standards and to earn revenue to become self sustainable lab in India.

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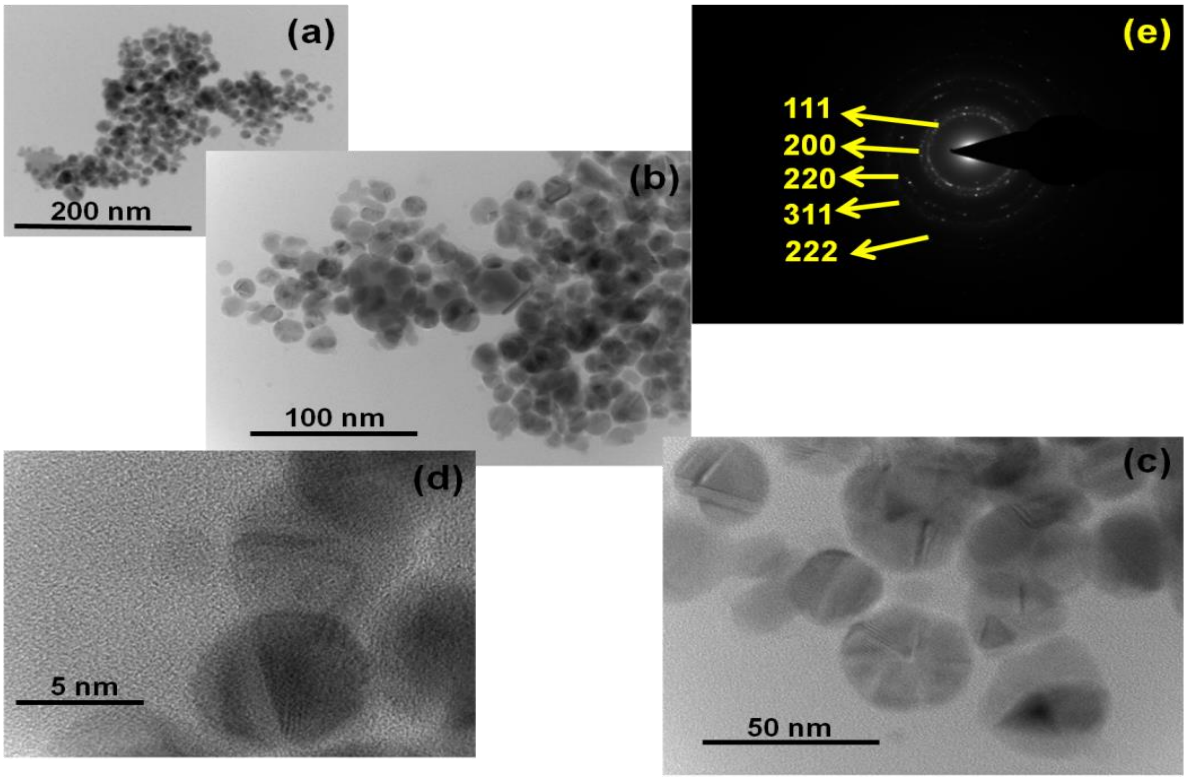

Fig. 2: TEM images (a, b, c. d) of as prepared Ag NPs under different resolutions and (e) SAEDP of crystalline ring structure

HRTEM images of the as prepared Ag NPs were recorded under different resolution along with specific area electron diffraction pattern at (20 ± 2) °C temperature and (45 ± 5) % relative humidity are presented in Fig. 2 (a, b, c, d, e). The tentative planes of silver are mentioned pertaining to different rings. The images exhibit the spherical shape nanoparticles with size in the range of 10 nm to 30 nm range (10 ± 2 nm, 18 ± 2 nm and 25 ± 2 nm) with the dominance of 10± 2 nm size particles.

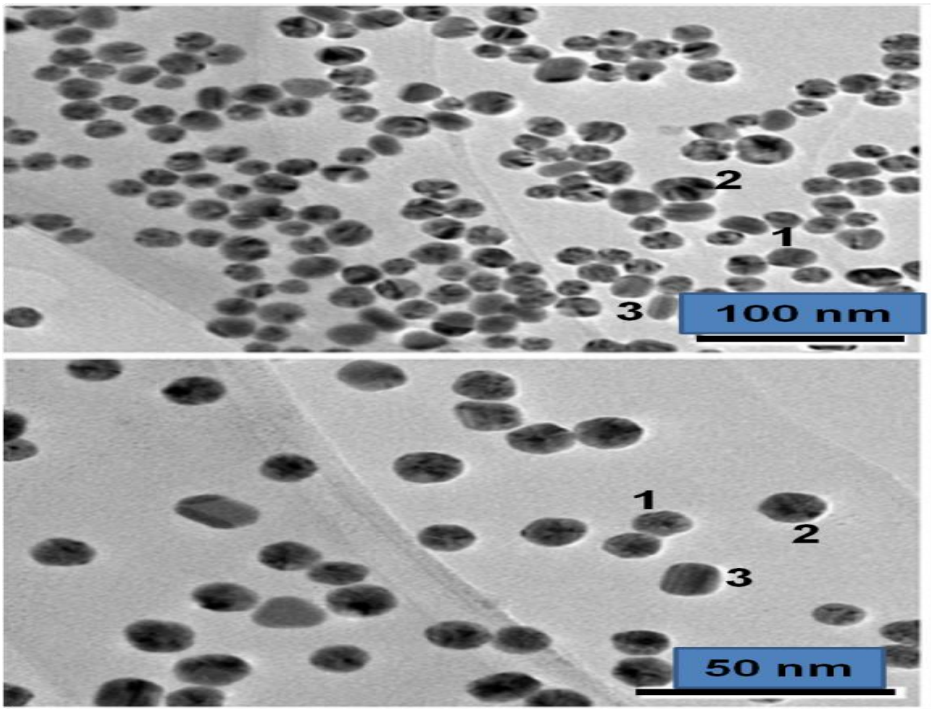

Fig. 3: TEM image of Ag NPs under 100 nm and 50 nm resolution with particles marked 1, 2 and 3 for uncertainty measurements

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As per EAL, ISO, GUM or NIST guidelines [4-15] for evaluation of the overall uncertainty, this can be divided into two sections: Type A (random errors) and Type B (systematic errors). Uncertainty evaluated from experimental data statistically, repeated number of times under substantially similar conditions comes under Type A category. This comprised of small independent random variables like measuring process, environmental conditions, inherent instability of the instrument, personal judgment of the operator etc. The random component of uncertainty, generally for infinite number of observations gives information about the population of results. But practically, a finite number of measurements were carried out to evaluate a particular parameter as defined in standard procedure [6-9, 11-15]. Type B uncertainty was evaluated from the contribution of three main sources (i) measuring instrument, (ii) operating procedure and (iii) characteristics of the sample under calibration. Uncertainty value for these components were generally taken from the calibration certificate provided by the manufacturer/ literature available. The variations in uncertainty from systematic errors generally follows normal, rectangular or triangular probability distribution and to calculate their uncertainty values, divide their uncertainty value by 2, √3 and √6 respectively. Sometimes contribution to the systematic uncertainty do not follow rectangular distribution and in such cases the standard deviation should be determined separately for each contribution and assign values. Then Type A (random errors) and Type B (systematic errors) components of uncertainty were combined for the estimation of single value of uncertainty i.e. overall uncertainty. The final result was expressed as overall uncertainty at 95% confidence level.

To estimate the overall uncertainty in particle size measurement, all the electron microscopic images are recorded under same environmental conditions and instrumental parameter settings to nullify/minimize their effects on measurements and contribution in uncertainty. For uncertainty calculations, the following Ag NPs picture (Figure 3) at 100 nm and 50 nm resolution is selected. This figure clearly depicts three different sized nanoparticles labeled as 1, 2, 3 with the dominance of smaller size nanoparticles i.e. 1. While number 3 labeled are least.

The images are scanned at the same position and repeated ten times to observe the variation in image. Then in the image similar size nanoparticles are marked and through statistical standard deviation calculations Type A uncertainty (u_A) value is obtained. The instrumental parameters, environmental conditions, human effects come under Type B uncertainty. Since all the measurements were carried out by the same operator under same environmental conditions, that's why their contribution in uncertainty measurement is ignored and considered only instrumental parameters contribution. These are given as:

- Uncertainty in layer thickness (u_{B1}) of reference standard provided by the supplier i.e. 0.02 nm. Used triangular distribution $u_1(\delta r1) = 0.02\sqrt{6} = 0.008165$ nm with degree of freedom ($\nu 1$) = ∞.
- Uncertainty in TEM Point Resolution: TEM point resolution value of is 0.205 nm for HRTEM as provided by the supplier for thickness in 50 nm to150 nm. By using normal distribution, standard uncertainty in the value of measurement of particle size by this resolution: $u2(\delta r2) = 0.205/2 = 0.1025$ nm with degree of freedom ($\nu 2$) = ∞.
- Uncertainty in TEM Line Resolution: TEM Line resolution value of is 0.144 nm i.e. 0.144 x 10^{-9} m for thickness in the range of 50 to 150 nm for HRTEM as provided by the supplier. By assuming normal distribution, standard uncertainty in the value of measurement of particle size by this resolution: $u3(\delta r3) = 0.144/2 = 0.072$ nm with degree of freedom ($\nu 3$) = ∞.
- Uncertainty in STEM resolution: STEM resolution value of is 0.17 nm i.e. 0.17 x 10^{-9} m for HRTEM as provided by the supplier. By assuming normal distribution, standard uncertainty in the value of measurement of particle size by this resolution: $u4(\delta 43) = 0.17/2 = 0.085$ nm with degree of freedom ($\nu 3$) = ∞.

By estimating the values of Type A and Type B uncertainty components then combined uncertainty value is obtained by using the following equation:

Combined uncertainty (uc) = [(uA(x))^2 + (u1(δr1))^2 + (u2 (δr2))^2 + (u3(δr3))^2+ (u4(δr4))^2]1/2

Overall Expanded uncertainty is U = 2*uc at 95 % confidence level, and Coverage factor (K) : 2

In the present case of sol-gel derived Ag NPs, the size of three different size nanoparticles along with overall uncertainty estimated values at 95% confidence level are summarized in the following Table1as:

Particles label	Size (nm)	Overalluncertainty (nm)
1	8.458	0.0368
2	17.162	0.0419
3	26.249	0.0467

Table 1: Particle labeled in Figure 3, Size and overall uncertainty of prepared Ag NPs

IV. CONCLUSION

These preliminary investigations report the synthesis of Ag NPs with optimized parameters to get desired size nanoparticles with narrow size distribution. These nanoparticles are characterized by XRD and HRTEM techniques to confirm their formation and particle size and shape evaluation. The uncertainty in particle size is estimated and the stability of nanoparticles in suspension is derived by recording their HRTEM images in regular interval of time which in turn helps in assigning their shelf life an important parameter required for releasing BND.

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