SYNTHESIS CHARACTERIZATION AND APPLICATION OF NANO DIMENSIONAL SILVER TUNGSTATE

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ABSTRACT

We report on rapid one step green synthesis of silver tungstate nanoparticle. The characteristics of the obtained nanoparticle was studied using XRD, UV-Vis absorption spectroscopy, FTIR, TG, SEM and EDX. The average diameter of the prepared nanoparticle was about 29 nm. The synthesized particle was orthorhombic in shape. In this study we demonstrate the antimicrobial activity of silver tungstate nanoparticle and compare them with some antibiotics against clinically isolated. This synthesis approach of silver tungstate nanoparticle is cost effective .

Key Words:* *Nanoscience; Silver Tungstate;Paticle Size; Antimicrobial; Antibiotic;

I. INTRODUCTION

Over the past few decades, researchers all over the world were interested in the studies of nanomaterial's and their applications. Nanomaterial's often show unique and considerably changed physical, chemical and biological properties compared to their macro scaled counter parts[1].Nano scale materials have been described as having at least one dimension on the order of approximately 1-100 nanometres [2]. Nanomaterial's have been widely used in various fields, such as photoelectric, recording materials, catalysis, sensors, ceramic materials etc due to their special structures and properties [3,4]. The application of nanomaterial's can be enhanced by decreasing the particle size [5,6].

Metal tungstate's are an important family of inorganic materials that have great application potential in the areas of photoluminescence, optics, humidity sensors, magnetics and catalysis. Silver tungstate (Ag_2WO_4) exists in three phases namely α, β and Ý phases. Several groups have investigatedthe solid-state reactions of silver tungstate with mercuric bromide and mercuric chloride [7,8].

This work reports the synthesis of silver tungstate nanoparticles by sol gel method. Among the various nanomaterial's, silver nanoparticles have attracted increasing technological and industrial interest. This interest has mainly to do with their properties associated with general characteristics such as thermal stability, Mechanical hardness and antimicrobial properties.

Experimental

Synthesis of Tin(IV)phenyl phosphorous acid (SnPN)

It was prepared by reacting AR grade silver nitrate($AgNO_3$) and sodium tungstate (Na_2WO_4) using distilled water as solvent at roomtemperature. The method followed for this synthesis is similar to that used byTakahashi et al.

1.1 Characterization

The particle size was determined from X-ray diffraction data using Scherer equation.SEM image of the sample was obtained using a scanning electron microscope. . UV-Vis spectral analysis was done by using double beam UV-Vis spectrophotometer .Antibacterial activity of the material was determined against Gram positive bacteria BascillusSubtilis and Staphyloicoccusaureus and Gram negative bacteria Pseudomonas aeruginosa and E.Coli. Antifungal activity of the material was determined against Candida albicans and Saccharomyces.It was assayed by so called halo method as follows. A melted beef agar medium was poured into a Petri dish and solidified. Then, the medium containing bacteria was layered over it. The samples were poured into a well cut on the surface. Samples were added in four different amounts viz,5,10,15,20 microliters into each well and then incubated for one day at 37^0C.Antibacterial activity was evaluated by the transparent halo circle around the specimen after incubation. When an agent has antibacterial activity, a halo circle is formed along the periphery of the specimen. When material has an excellent antibacterial activity, the halo ring formed will be very wide.

II. RESULTS AND DISCUSSION

The nano form of silver tungstate was obtained as grey powder. Chemical resistivity of the material assessed in various chemical environments shows that this material is stable in acidic (Conc H_2SO_4 and HNO_3), basic (NaOH and KOH) and organic media (ethanol,glycoletc).

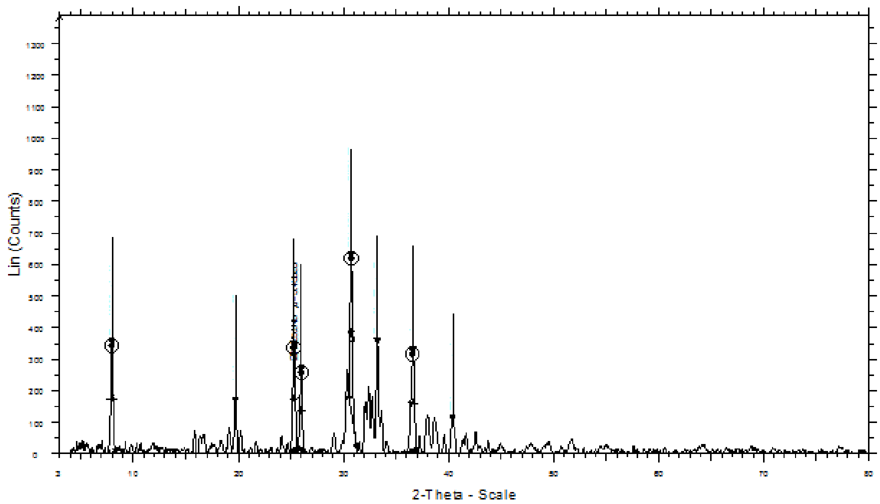

Fig 1 X –Ray Diffraction

Fig I shows the XRD pattern of the silver tungstate. X-ray diffraction shows that Ag_2WO_4 crystallizes in the α-phase and the pattern agrees with the JCPDS file [9]. The crystals are orthorhombic with space group P_n2_n and the lattice parameters are a=10.89 b=12.03 and c=5.920.

In XRD the crystal size can be calculated according to Debye-Scherer formula. $D = 0.9\lambda/\beta \cos\theta$. λ is the wavelength of the Cα-K α radiations. β is the full width at half maximum and θ is the angle obtained from 2θ values corresponding to maximum intensity peak in XRD pattern. The mean crystal size in Ag_2WO_4 nanoparticle was found to be 29nm.

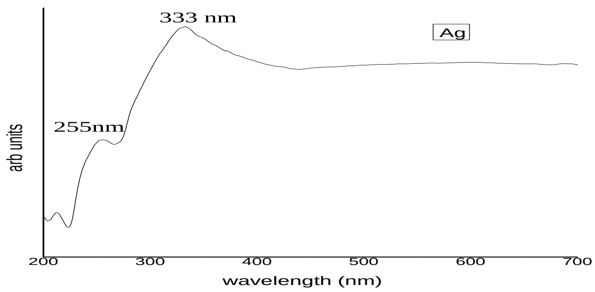

Fig II UV-Vis Spectrum

Fig II represents the UV-Vis absorption spectrum of Silver tungstate. The spectrum was recorded in the range 200-700 nm. The material has two absorption maxima lying at 255 and 333nm. The UV-Vis peak at 255 nm is due to the transition of inner shell electron to the conduction, which is almost reported in the case of UV-Vis absorption of all metal and metal oxide nanoparticles. The absorption peak at 333 nm corresponds to Surface Plasmon absorption peak of Silver tungstate shell layer.

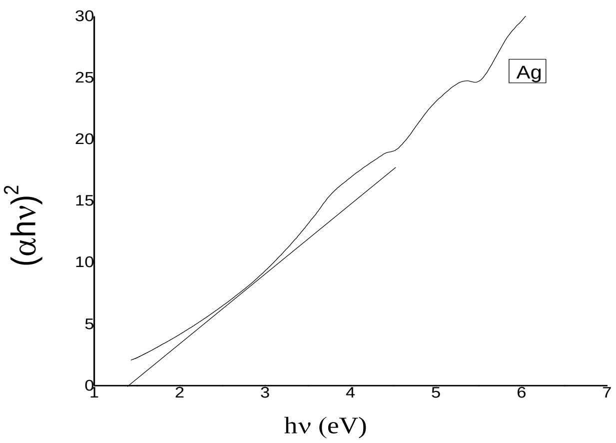

Fig III Tauc Plot

UV Spectra provide important information about the details related with optical band gap of the material.The energy band of the material is related to the absorption coefficient α by the Tauc relation. A graph is plotted by taking $(\alpha h\nu)^2$ versus hν is shown in FigIII.The extrapolation of the straight line to $(\alpha h\nu)^2$ =0 axis gives the value of the energy band .The electronic band gap of the material is 1.45 eV. This is a wide band gap material. Wide band gap typically refers to material with a band gap significantly greater than that of the commonly used semiconductors. Applications include electronic devices such as optoelectronic and power devices.

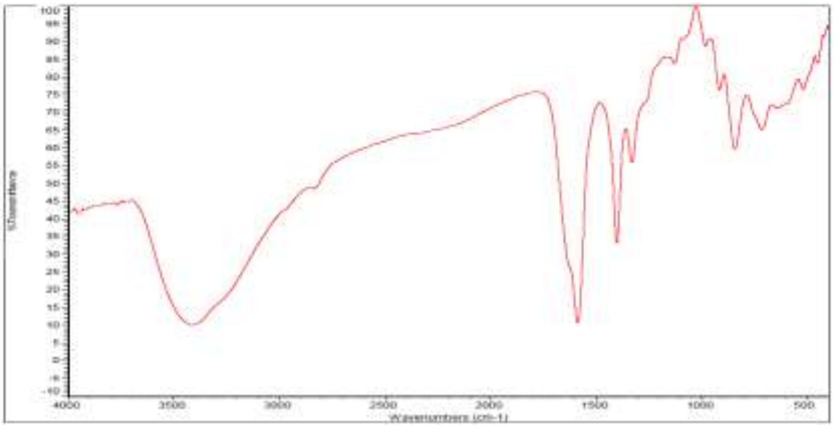

Fig II FTIR Spectrum

FIG 2 shows FTIR spectrum of Ag_2WO_4 at room temperature. The spectrum was recorded in the range of 4000-500cm^{-1}. The peak at 3413.51cm^{-1} and 1587.76cm^{-1} indicates the presence of –OH and C=O residues, probably due to atmospheric moisture and CO_2 respectively. The FTIR spectrum indicate peaks at 715.78, 843.41, 916.21 cm^{-1}. The peaks are due to the W-O-W and O-W-O stretching vibration modes characteristic of tetrahedral tungstate.

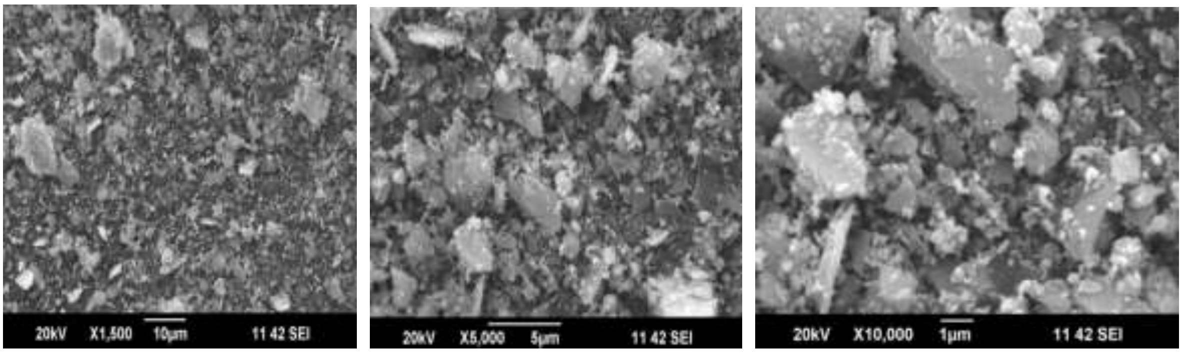

Fig III SEM Images

Fig III indicates the SEM picture of Ag_2WO_4. The surface morphological features of synthesized nanoparticle was studied by scanning electron microscope.

The instrumental parameters, accelerating voltage, spot size, magnification and working substances are indicated on SEM image. The results indicate that mono-dispersive Nano phased Silver tungstate Nano particle was obtained. The appearance of some particles is in spherical shape and some are in rod shape.We can observe that the particles are agglomerated and they are essentially cluster of nanoparticles. The observation of some larger nanoparticles may be attributed to the fact that silver tungstate nanoparticles have a tendency to agglomerate due to their high surface energy and high surface tension of the ultrafine nanoparticle.

Energy dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the chemical analysis or chemical characterization of a sample.It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter analysing X-rays emitted by the matter in response to being hit with charged particles.

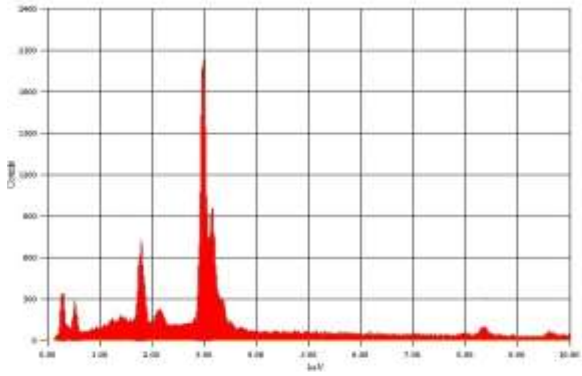

Fig IV

The electron dispersive spectroscopy analysis of these particles in fig. IV indicates the presence of Ag, W and O. Other peaks may be due to some impurities .

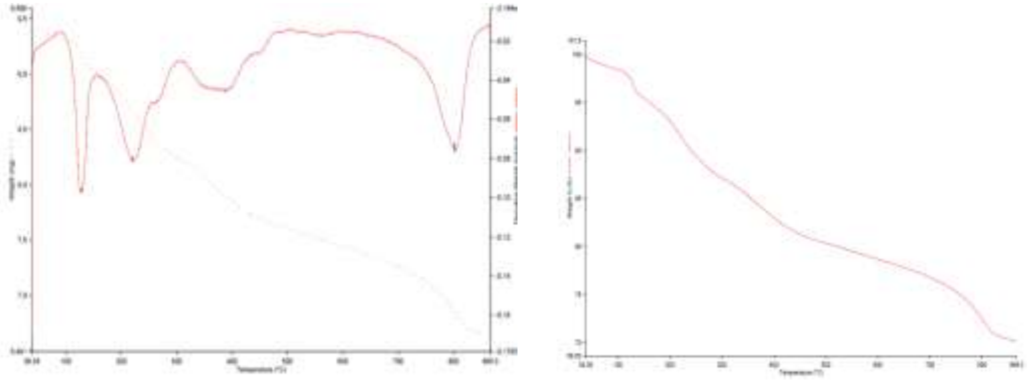

Fig v

Fig V indicates the TGA and DTA curves of Silver tungstate nanoparticle. The TGA curve shows no appreciable weight loss in the temperature range from 30 to 700^{0}C. An endothermic crystalline peak at 800^{0}C is attributed to the melting of the sample. Thermal analysis shows that the silver tungstate nanoparticle is thermally stable up to 700^{0}C.

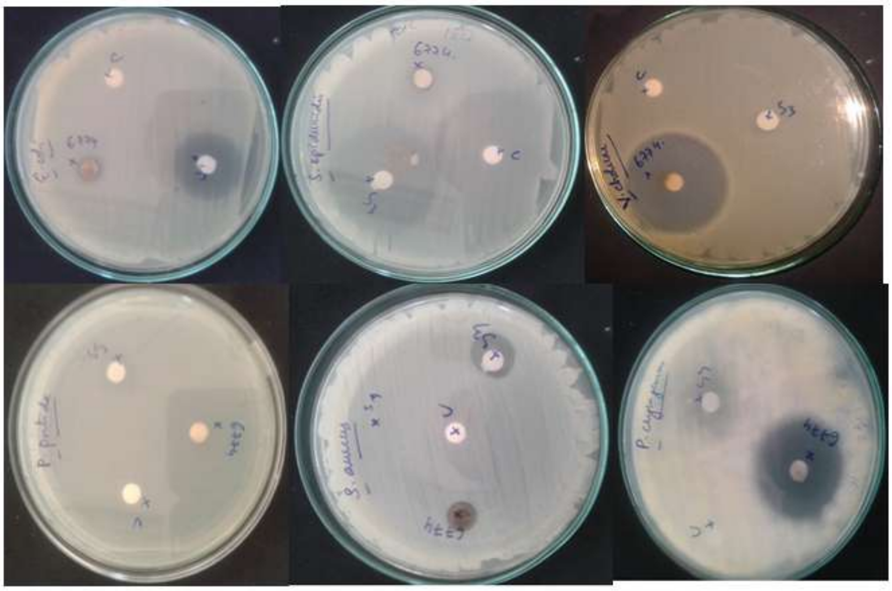

Fig VI

Fig VI represent the antimicrobial activities of silver tungstate nanomaterial. The antimicrobial activity of the sample was determined against Gram positive bacteria, Gram negative bacteria and fungi. It was assayed by so-called halo method as follows. A melted beef agar medium was poured into a Petri dish and solidified. Then, the medium containing bacteria and fungi was layered over it. The samples were poured into a well cut on the surface. Samples were added into each well and then incubated for 1 day at 37^0C.Antimicrobial activity was evaluated by the transparent halo circle around the specimen after incubation. That is to say, when an agent has antimicrobial activity, a halo circle is formed along the periphery of the specimen. When material has an excellent antimicrobial activity, the halo ring formed will be very wide.

The nanomaterial silver tungstate possess antibacterial activity against both Gram positive and Gram negative bacteria. It also possess antifungal activity against PencilliumCrysogenum and Candida alibicans. Greatest antibacterial activity is shown against Vibrio cholera (35mm) while the standard sulphatriad showed only 7mm. Greatest antifungal activity is shown against Pencilliumcrysogenum (30mm).

Table Ihalo Ring Diameter Obtained from Antibacterial Assessment

PARAMETERS	RESULTS
Escherichia coli-Gram negative	Sample -9mm Sulphatriad (Std)-21mm
Vibrio cholera-Gram negative	Sample-35mm Sulphatriad (Std)-7mm
Pseudomonas putida-Gram negative	Sample-NZ Sulphatriad(Std)-12mm
Staphylococcus epidermidis-Gram positive	Sample-8mm Sulphatriad(Std)-35mm
Staphylococcus aureus-Gram positive	Sample-10mm Sulphatriad (Std)-14mm

Halo Ring Diameter Obtained from Antifungal Assessment

PARAMETERS	RESULTS
Pencilliumcrysogenum	Sample-30mm Sulphatriad (Std)-8mm
Candida albicans	Sample-7mm Sulphatriad(Std)-NZ

In the case of silver tungstate nanoparticle Gram positive bacteria ie Staphylococcus epidermidis and Staphylococcus aureus are less susceptible to Ag^+ than Gram negative bacteria (Escherichia coli and Vibrio cholera) while the sample is inactive towards Gram negative bacteria Pseudomonas putida . Gram-positive bacteria have more peptidoglycan than Gram-negative bacteria because of their thicker cell walls, and because peptidoglycan is negatively charged and silver ions are positively charged. More silver may get trapped by peptidoglycan in gram-positive bacteria than in Gram-negative bacteria (Kawahara etal 2000)[10]. The decreased susceptibility of Gram-positive bacteria can also simply be explained by the fact that the cell wall of Gram positive bacteria is thicker than that of Gram-negative bacteria.

An important factor on antibacterial effectiveness is the size of nanoparticles studied by Martinez-Castanonetal [11]. The increased antimicrobial activity of the smaller nanoparticles could be due to the fact that smaller particles have an easier time getting through the cell membrane and cell wall and that relative to larger particles smaller particles have a greater surface area to volume ratio. The greater surface area to volume ratio of smaller nanoparticles means that per unit mass of silver the smaller nanoparticles have more silver atoms in contact with the solution than do larger nano particles. For smaller nanoparticles this means that more of the silver atoms contained in the nanoparticle are able to take part in cell destruction processes. In silver containing nano particles silver ions impart antibacterial properties to a given silver containing material it makes sense that smaller silver nanoparticles have more antimicrobial effectiveness than large silver nanoparticles.

Antifungal activity of the sample was determined against Pencilliumchrysogenum and Candida albicans. Antifungal activity was also evaluated by the transparent halo circle around the specimen. Halo ring having diameter 30 mm was obtained for silver tungstate nano material against Pencilliumchrysogenum while halo ring having diameter only 8mm was obtained in the case of sulphatriade Antibiotic.

III. CONCLUSION

In the present study Silver tungstate was prepared in the Nano form by Sol-Gel method. Characterization of the material was done by using XRD,UV-Vis, SEM,F T I R and TG. The particle size was studied from XRD using Scherrer formula. Owing to the size, their electron structure is easily affected by environments, such as structure and nature of support, substrate etc.

The nanoparticle prepared is of great scientific interest as they effectively bridge between bulk materials and atomic or molecular structures. The prepared nanomaterial is an effective antimicrobial agent. The high antimicrobial activity of this nanomaterial appear promising for Medicinal applications. Hence this material can be used as an antibiotic to treat bacterial as well as fungal infections.

The synthesized material is a semiconductor with electronic band gap 1.45 eV. Applications of such materials include electronic devices such as optoelectronic, power devices and are often utilized in applications in which high temperature operation is important.

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