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Synthesis and characterization of nanophased silver tungstate

THRESIAMMA GEORGE[1], SUNNY JOSEPH[1] and SURESH MATHEW[2,*]
[1]Nirmala College, Muvattupuzha 686 661, India
[2]School of Chemical Sciences, Mahatma Gandhi University, Kottayam 686 560, India
*Corresponding author. E-mail: sureshmathew@sancharnet.in; tresasunny@gmail.com

Abstract. Silver tungstate (Ag_2WO_4) nanoparticles in two different morphologies are prepared by controlling the reaction kinetics of aqueous precipitation. X-ray diffraction studies reveal that the silver tungstate nanoparticles are in the α-phase. SEM images show the rod-like and fiber-like morphologies of the nanoparticles with high aspect ratios. The TGA and DTA studies show the high thermal stability of the nanorods. The average crystallite sizes (20–30 nm) of the rod-like silver tungstate estimated from TEM is consistent with the XRD results.

Keywords. Nanomaterials; soft chemistry; silver tungstate.

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1. Introduction

Nanotechnology has been viewed as the 'little big science' which is considered as the impetus for the next industrial revolution. The core of nanoscale science is to create large structures with fundamentally new functions and properties. Searching for new strategies toward nanosized building blocks such as nanorods, nanowires, nanotubes and nanobelts have attracted intensive interest because of their distinctive geometries, novel physical and chemical properties and potential applications in nanodevices [1]. The main synthesis techniques for nanostructures include template directed growth methods, vapour–liquid–solid (VLS) mechanism, soft-chemistry methods like sol–gel synthesis, hydrothermal synthesis and chemical precipitation. Recently, our group has investigated the microwave properties of nanocrystalline copper ferrite synthesized by sol–gel method [2]. The soft-chemistry (chimie douce) method has the advantage that the reaction takes place at much lower temperatures compared to normal solid-state reaction procedures. New metastable phases, which cannot be prepared by other routes, can be isolated using these methods. The new phases therefore have unusual structures and interesting properties [3].

Today tungstate ceramics are getting attention due to a variety of applications such as photoluminescence, microwave applications, optical fibers, scintillator materials, humidity sensors and catalysis. Silver tungstate (Ag_2WO_4) exists in three phases, namely α-, β- and γ-phases. The phase diagram and the ionic conductivity of Na_2WO_4–Ag_2WO_4 system are described in [4]. Several groups have investigated heat capacity studies of silver tungstate, kinetics and mechanisms of solid-state reactions of silver tungstate with mercuric bromoiodide and mercuric chlorobromide and also the solid-state reactions of silver tungstate with mercuric bromide and mercuric chloride [5–7].

The kinetics of nucleation and particle growth in homogeneous solutions can be adjusted by the controlled release of the anions and cations. The particle size is influenced by the reactant concentration, pH and temperature [8]. In the present work, we report a successful room temperature synthesis of rod-like and fiber-like silver tungstate nanoparticles, adopting careful control of the reaction kinetics of aqueous precipitation. Aqueous precipitation route is simple, ecofriendly, inexpensive, highly reproducible and provides us a new strategy to synthesise other materials of similar nature. The method is suitable for the large-scale preparation of silver tungstate nanoparticles.

2. Experimental

Silver tungstate nanoparticles were synthesized by reacting AR grade silver nitrate ($AgNO_3$) and sodium tungstate (Na_2WO_4) using distilled water as solvent at room temperature. The method followed for this synthesis is similar to that used by Takahashi *et al* [9]. However, their investigation was limited to an electrochemical study of $Ag_6I_4WO_4$ and no attempt was made to study the nature of silver tungstate phase, which they prepared as an intermediate.

In the first part of the investigation, two stoichiometric concentrations of the aqueous solutions were used as reactants: (a) 0.009 M silver nitrate and 0.0045 M sodium tungstate, (b) 0.018 M silver nitrate and 0.009 M sodium tungstate. After sudden mixing of the reactants the evolved precipitate was centrifuged, filtered and washed in distilled water a number of times and dried in a vacuum desiccator to get fine white rod-like silver tungstate nanoparticles.

The X-ray diffraction pattern of the nanoparticles was taken using Bruker D8-Advance, powder X-ray diffractometer using Cu K_α radiation ($\lambda = 1.5406$ Å). The thermal behavior of the sample was analyzed by thermogravimetric analyser (TGA) and differential thermal analyzer (DTA) using a Shimadzu DTG 60, at a heating rate of 10°C min^{-1} from ambient to 900°C. The FTIR spectrum in the range 600–4000 cm^{-1} was taken using Shimadzu infra-red spectrophotometer (8400-S) using KBr pellet.

During the second part of the investigation, when the reactant concentration was kept below 0.003 M for silver nitrate and 0.0015 M for sodium tungstate, the precipitates get suspended without settling in the reaction mixture for a long time. During that time the pH of the solution was slightly alkaline. When such a solution was kept overnight for more than 12 h at room temperature (30°C), fiber-like growth resembling cotton bundles or grass-like features were observed in the solution. The fibrous structures were separated and gently washed in distilled water and dried in vacuum.

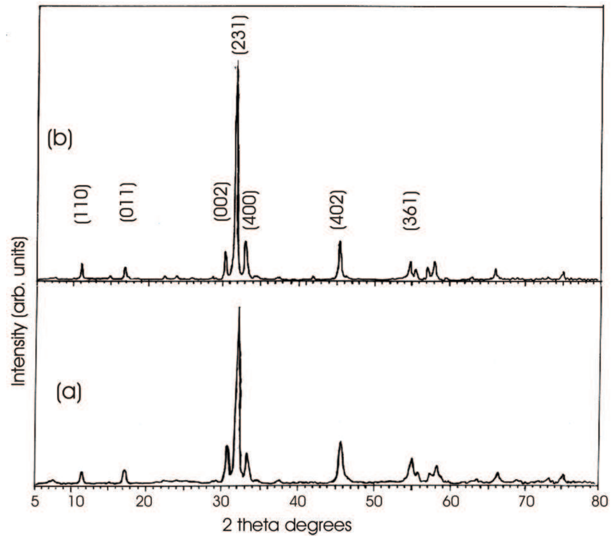

Figure 1. X-ray diffraction of rod-like silver tungstate nanoparticles synthesized from (**a**) 0.009 M $AgNO_3$ and 0.0045 M Na_2WO_4 and (**b**) 0.018 M $AgNO_3$ and 0.009 M Na_2WO_4.

The structure and the morphology of the rod-like and fiber-like silver tungstate nanoparticles were examined with scanning electron microscope (A Lieca Stereoscan 440 model SEM) at an accelerating voltage of 20 kV and a working distance of 15 mm. The samples were dispersed in isopropyl alcohol and drop-casted on the sample holder and allowed to dry in air for SEM measurement. TEM images were collected on a Jeol 1200 EX instrument operating at 120 kV. Samples for TEM analysis were prepared by ultrasonicating the nanoparticles in ethanol and evaporating a drop of the solution on a carbon-coated copper grid.

3. Discussion

Figure 1 shows the XRD patterns of the rod-like silver tungstate synthesized from two reactant concentrations, namely (a) 0.009 M silver nitrate and 0.0045 M sodium tungstate, (b) 0.018 M silver nitrate and 0.009 M sodium tungstate. X-ray diffraction shows that Ag_2WO_4 crystallizes in the α-phase and the pattern agrees well with the JCPDS file [10]. The crystals are orthorhombic with space group Pn2n and the lattice parameters are $a = 10.82, b = 12.01$ and $c = 5.9$ Å. The average particle sizes were found to be 20 nm for sample a and 30 nm for sample b. The XRD pattern of the fiber-like silver tungstate also matches well with that of the JCPDS file [10].

Figure 2 shows the SEM image of rod-like Ag_2WO_4 nanoparticles (sample b). The SEM image shows the uniformly size distributed and non-agglomerated rod-like Ag_2WO_4 nanoparticles. The TEM image shown in figure 3 shows the rod-like nature of the silver tungstate (sample b) without any ambiguity. The particles are

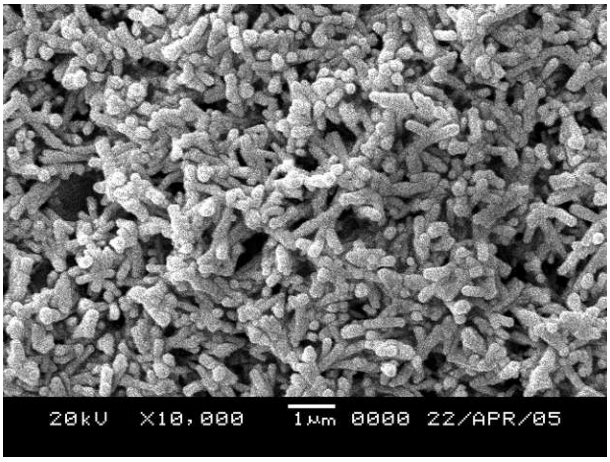

Figure 2. SEM image of rod-like nanocrystalline silver tungstate.

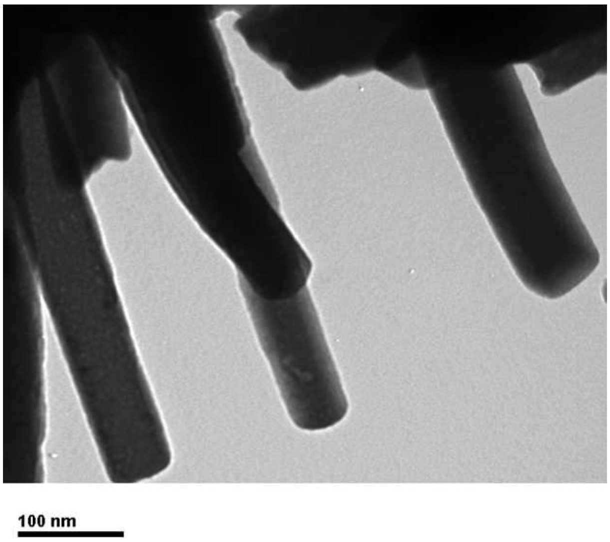

Figure 3. TEM image of rod-like nanocrystalline silver tungstate.

not agglomerated and their average diameter can be determined as about 30 nm, which is in good consistency with the data calculated from XRD.

Figure 4 shows the SEM image of the fiber-like Ag_2WO_4 nanoparticles. Each fiber is having an average diameter of 0.50 μm and length approximately 100 μm showing a high aspect ratio. The long fiber growth is observed only in a particular range of concentration, viz., 0.003–0.001 M $AgNO_3$ and 0.0015–0.0005 M Na_2WO_4 and when the reaction mixture is kept intact for a long time. Below this concentration limit the fibrous growth is not visible. But, above this concentration limit a sudden

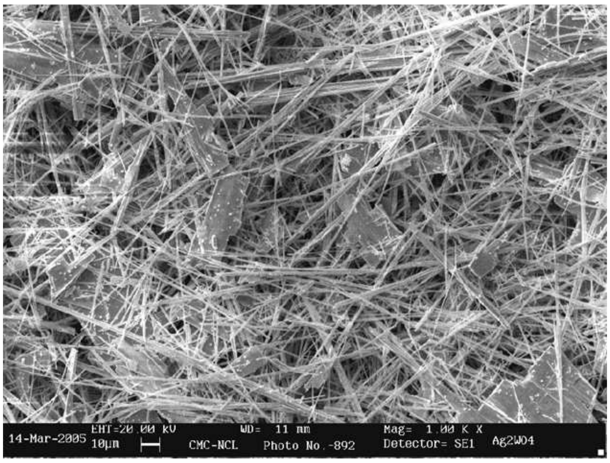

Figure 4. SEM image of fiber-like nanocrystalline silver tungstate.

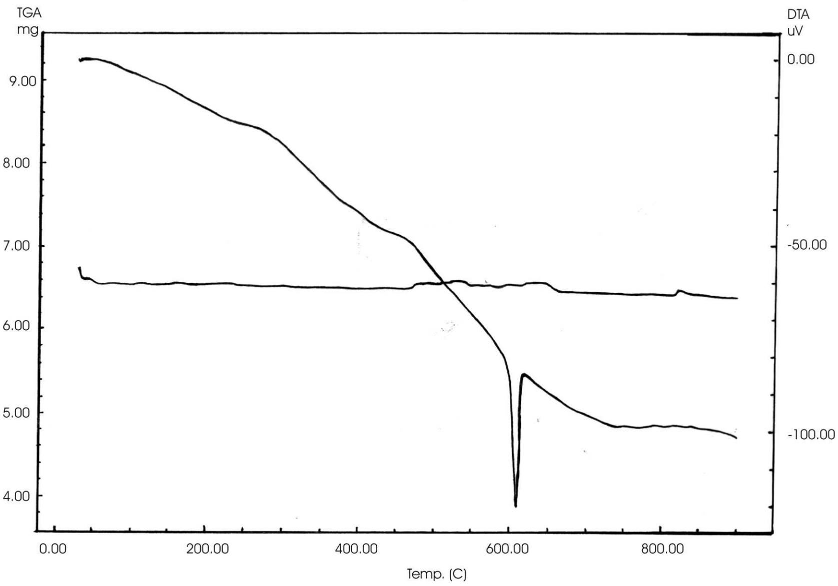

Figure 5. TGA and DTA curves of rod-like silver tungstate.

precipitation of silver tungstate occurs and the precipitate settles down, which hinders long fiber growth. This simple aqueous precipitation method avoids the use of any costly capping agents or surfactants resulting in stable rod-like and fiber-like nanoparticles of silver tungstate without agglomeration.

Figure 5 indicates the TGA and DTA curves of rod-like silver tungstate nanoparticles. The TGA curve shows no appreciable weight loss in the temperature range from 30 to 900°C, barring a slight weight loss initially due to the drying of the

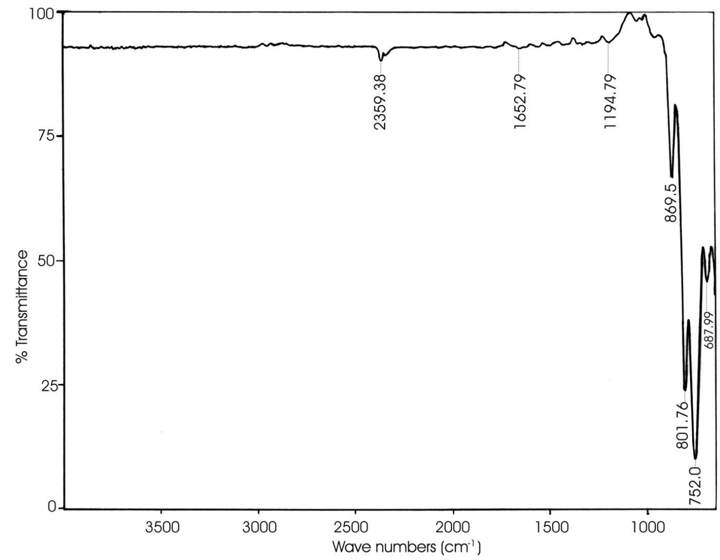

Figure 6. FTIR spectra of rod-like silver tungstate.

sample. The DTA endothermic peak at 609°C is attributed to the melting of the sample. Exothermic crystallization peak reported at 220°C is not observed in the DTA curve [11]. This observation may be due to the crystallization of the synthesized nanoparticles at room temperature. Thermal analysis shows that the silver tungstate nanoparticles are thermally stable up to 609°C.

Figure 6 shows the FTIR spectra of the rod-like silver tungstate nanoparticles. The FTIR spectra indicate intense peaks at 687.9, 752, 801.7 and 869.5 cm^{-1}. The peaks are due to the W–O–W and O–W–O stretching vibration modes characteristic of tetrahedral tungstate [4,11].

These nanostructures can be embedded into resin to produce conducting resin nanocomposite, which can give different electrical conducting performances. Further work is in progress.

4. Conclusions

Silver tungstate (Ag_2WO_4) nanoparticles in two different morphologies (rod-like and fiber-like) are prepared by a simple aqueous chemical route. The average particle sizes of the synthesized rod-like nanoparticles estimated from XRD are consistent with the TEM result. Thermal analysis shows that the compound is thermally stable up to 609°C. The surface morphology studies using SEM image reveals rod-like and fiber-like nanoparticles with high aspect ratio. The synthesized silver tungstate nanoparticles are quite stable without agglomeration. Moreover, the method is simple and inexpensive because one does not have to use any costly capping agents or surfactants.

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