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Novel synthesis of ultra-fine Sb_2O_3 nanocubes using plant extract

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Abstract: In this study, the synthesis of ultra-fine grade antimony trioxide (Sb_2O_3) using plant extract for the first time is reported. Antimony chloride was used as a starting material and *Dioscorea alata* tuber extract was used as a reducing and capping agent. The synthesised nanoparticles were characterised by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), dynamic light scattering (DLS), and Fourier transform infrared spectroscopy. XRD analysis indicates the formation of pure Sb_2O_3 nanoparticles. The result from FE-SEM and DLS showed that the particles have a cube-like morphology and have an average size of 346.4 nm which falls within the range of ultra-fine grade Sb_2O_3.

1 Introduction

Antimony trioxide (Sb_2O_3) is the most important commercial compound of antimony [1]. Its global production was 130,000 tonnes in 2012 which is increasing every year. The safety of the Sb_2O_3 was confirmed by World Health Organization (WHO) (2003) [2] and the European Food safety authority (2004) [3]. It has wide applications in industries and used as an excellent catalyst to accelerate the polymerisation in polyester manufacturing. In ceramic industries, it is used as an improver while glass manufacturer uses it as a degassing agent. It is also used as an opacifier in porcelain and enamelling products. In titanium dioxide production, it is incorporated as a flocculent [4]. In lubricants, it is added to increase stability. In fluorescent light bulbs, it is used as a phosphorescent agent [5]. Sodium stibogluconate has been used as medicine since 1940 which is synthesised using Sb_2O_3. It is on WHO list of essential medicine [6], the most effective and safe medicine used for the treatment of leishmaniasis [7, 8].

Since ancient times, Sb_2O_3 is used as a white pigment. The pigmentation of antimony in plastics can be controlled and adjusted by selecting a proper grade of Sb_2O_3 having a specific particle size. The product with smaller particle size will impart the whitest colour and highest opacity to plastic. Translucent plastic can be prepared using large particles. Particle size during manufacturing is controlled by adjusting temperature and rate at which antimony vapour are precipitated as these vapours exist furnace. The grades of commercially available Sb_2O_3 are ultra-fine (particle size 250–450 nm), high tint (800–1800 nm), and low tint (1900–3200 nm) [9].

Sb_2O_3 is used as a flame retardant synergist with halogenated hydrocarbon compounds in plastic industries to provide maximum flame retardancy in synthetic plastic and resin such as high impact polystyrene, polypropylene, polyethylene, and synthetic textile fibres such as modacrylic. Addition of any type of additive to plastic usually alters the physical properties of the original plastic. Hence, it is always desired to improve flame retardancy while minimising the effect on physical properties of the plastic substrate. It is been proposed that when Sb_2O_3 is finely divided and distributed in plastic, the physical properties are less affected. Blizzard and Martin have demonstrated a method and apparatus for making Sb_2O_3 powder having a specific sub-micron size. Sb_2O_3 powder was prepared using a plasma arc process using vaporisation and condensation of crude Sb_2O_3. This complex system requires sophisticated instrumentation and very high operating temperature. Particles of 320 nm were obtained by this process [10].

Conventionally, Sb_2O_3 is produced by high-temperature smelting using antimony trisulphide as a starting material. The main drawback of this process is the release of sulfur dioxide which leads to acid production which has a detrimental effect on the environment. In a typical conventional technology for manufacturing of Sb_2O_3, the capital cost of scrubbing SO_2 emission will be double than the capital cost of production of Sb_2O_3. Other methods for synthesis of Sb_2O_3 nanoparticles are hydrothermal [11], gamma radiation-oxidation [12], micro-emulsion [13], solution phase reduction [14], thermal oxidation [15], vacuum evaporation [16], ultra-sound [17], and biosynthesis [18]. In spite of the success of all these methods, there are several drawbacks such as the requirement of high temperature and pressure, sophisticated instrumentation, extensive use of solvents, expensive raw materials, tedious procedures, long incubation times etc. All these factors add cost to the final product.

Dean Thibault *et al* have also demonstrated a two-step method for synthesis of Sb_2O_3. The first step comprises production of antimony trichloride by reacting antimony trisulphide and iron (III) chloride. The second step comprises hydrolysis of antimony trichloride for production of Sb_2O_3 [19].

Green synthesis of nanoparticles is an eco-friendly, cost-effective approach in which plant extract can be effectively used as reducing and stabilising agents for the synthesis of metal and metal oxide nanoparticles. This way we can adapt the benign synthesis approach that uses non-toxic reactions and maintains mild reaction conditions [20]. Plants are capable of generating a wide variety of nanostructures matching the elegance of current engineered materials. Water-soluble plant metabolites (such as alkaloids, phenolics, flavonoids, terpenoids, and catechins) are responsible for reduction [21]. Green route eliminates or minimise the use of the harmful polluting substance in the synthesis of nanomaterials.

Dioscorea is a genus of flowering plants with over 600 species in the family *Dioscoreaceae*. *Dioscorea alata* is one such edible species which has the highest yield among all *Dioscorea* species and can be stored for a relatively longer period [22]. It is a rich source of phytochemical such as flavonoids, phenolics, alkaloids,

saponin etc. and is also rich in vitamin and mineral contents [23]. As *Dioscorea* species are rich in polyphenolic content and thus can be used for bio-reduction of metal to nanoparticles [24]. We have successfully synthesised bismuth trioxide nanoparticles using *D. alata* tuber extract [25].

Particle size is an important criterion for industrial application of Sb_2O_3. In this paper, we have proposed a rapid, cost-effective, green-route for the synthesis of ultra-fine Sb_2O_3 nanoparticles.

2 Materials and method

2.1 Chemicals

Antimony trichloride ($SbCl_3$) and ethanol were procured from S.D. Fine-Chem India. All reagents used in the experiment were of analytical grade and used without further purification.

2.2 Collection of plant material

D. alata tubers were collected from the field and identified in Botany Department, Shivaji University, Kolhapur, India.

2.3 Preparation of plant extract

Initially, *D. alata* tubers were thoroughly washed with water, then peeled off and diced into small pieces, and dried in a hot air oven. Dried tubers were pulverised and the powder was stored at room temperature. For the preparation of plant extract, the dried powder (5 g) was weighed and transferred to 500 mL of Erlenmeyer flask containing 100 mL of deionised water, mixed using magnetic stirrer for 10 min and then transferred to preheated water bath at 80°C and incubated for 15 min. The extract was stained using a sieve, and then centrifuged at 8000 rpm for 15 min and the supernatant was filtered through Whatman no. 1 filter paper. The clear filtrate was collected and used for synthesis.

2.4 Synthesis of Sb_2O_3 nanocubes

For the synthesis of Sb_2O_3, 0.456 g (0.1M) of antimony trichloride was dissolved in 20 mL of 70% ethanol. Then 50 mL of tuber extract was added dropwise under constant stirring. After addition of tuber extract, the mixture turns turbid. After mixing for 20 min, culture bottles were autoclaved at 121°C at 15 lbs for 21 min. The obtained solution was cooled at room temperature and the precipitate was isolated by centrifugation. The obtained pellet was washed using ethanol and water thrice. Then dried in a vacuum desiccator for 6 h. The resultant white colour powder was used as it is for X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. KBr pellet method was used for Fourier transform infrared (FTIR) analysis.

2.5 Characterisation of Sb_2O_3 nanocubes

XRD was measured on Bruker AXS D2 phaser diffractometer using Cu k_α radiation (k = 1.5406 Å). Field emission scanning electron microscopy (FE-SEM) by Mira-3 Tescan and dynamic light scattering (DLS) by Malvern instrument Zetasizer Nano ZS-90 was used to investigate the morphology and particle size distribution of synthesised nanoparticles. FTIR spectroscopy was done using the Shimadzu FTIR spectrophotometer.

3 Result and discussion

White colour is a characteristic property of Sb_2O_3 nanoparticles which was obtained after completion of the reaction. The obtained sample was marginally soluble in water and ethanol, this is also a characteristic property of Sb_2O_3 nanoparticles [26].

3.1 XRD analysis

To evaluate the crystalline size and phase of Sb_2O_3, the XRD pattern (Fig. 1) was recorded. The observed pattern was identified with the α phase of antimony oxide using *JCPDS* data card (card no. 00-003-0530) with reveals high purity of Sb_2O_3. From intense peak (1 2 1), the grain size was estimated using the Scherrer formula [27]. The average grain size was found to be 305.81 nm.

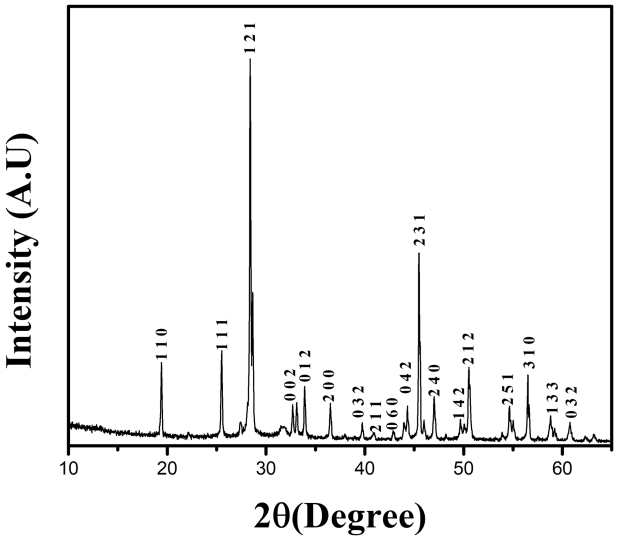

Fig. 1 *XRD pattern of synthesised Sb_2O_3 nanocubes*

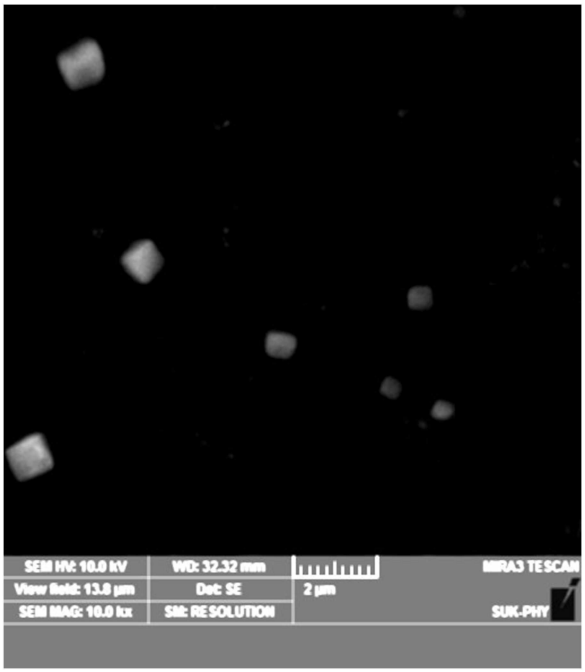

Fig. 2 *FE-SEM of Sb_2O_3 nanocubes*

3.2 Field emission scanning electron microscope

FE-SEM reveals the formation of morphology and particle size. Cube-like structures are shown in Fig. 2. The FE-SEM was analysed on ImageJ 1.50i software. These measurement states that the nanocubes have a wide distribution range from 200 to 800 nm. The same trend is seen in the DLS histogram. The morphology of synthesised material matches with morphology reported in the literature [28–32].

3.3 DLS

The histogram in Fig. 3. shows the distribution of particle size which indicates that the particles have a wide size distribution from 10 to 1000 nm. The mean diameter of nanoparticles obtained from the Gaussian fit of the histogram is 346.4 nm. The size of commercial ultra-fine Sb_2O_3 powder ranges from 250 to 450 nm. The mean size obtained from DLS falls within the range of ultra-fine grade of Sb_2O_3.

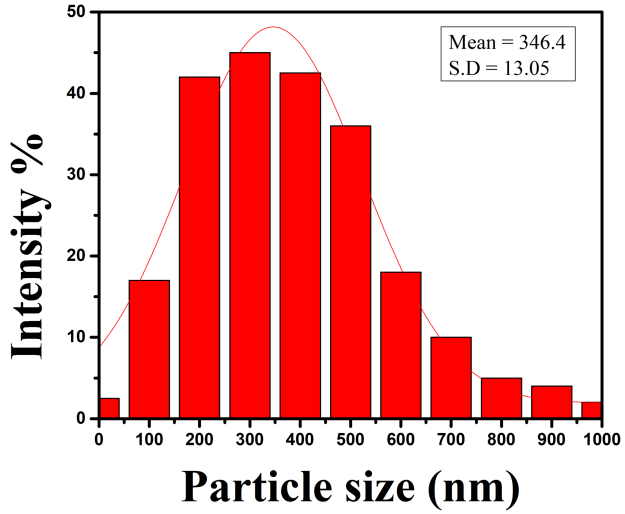

Fig. 3 *DLS histogram of the size distribution of Sb_2O_3 nanocubes*

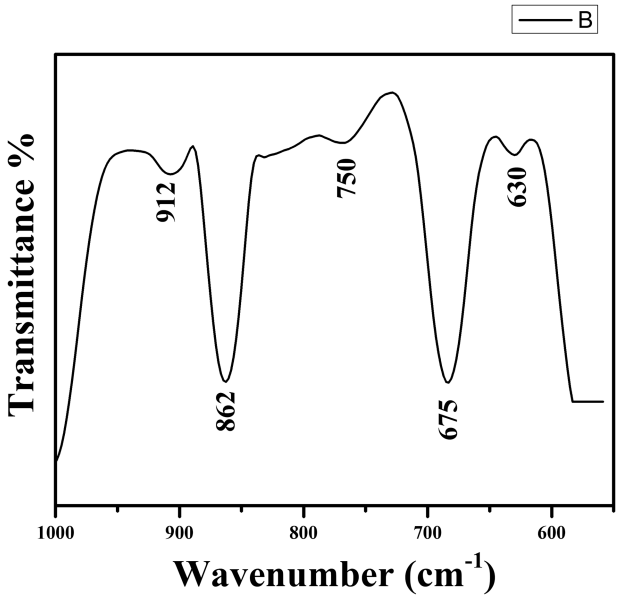

Fig. 4 *FTIR spectra of Sb_2O_3 nanocubes*

3.4 FTIR analysis

FTIR spectrum in Fig. 4. reveals the chemical groups and characteristic bands of Sb_2O_3 nanoparticles. The peaks obtained at 750 and 912 cm^{-1} correspond to symmetric stretching (V_s) and overtone ($V_s + V_{as}$) vibrations. The sharp peak at 675 and 862 cm^{-1} and peak at 630 cm^{-1} correspond to symmetric and asymmetric bending, respectively [33–35].

Dean Thibault *et al* in their patent WO1998011021A1 demonstrated a two-step process to eliminate impurities present in the starting material $SbCl_3$ [19]. The same starting material was used in our process. The XRD pattern as well as the FTIR spectra did not show any impurity. This confirms that pure Sb_2O_3 nanoparticles are synthesised by a green route.

Flame retardancy decreases when particle size is <250 nm [36]. The nanoparticles synthesised by gamma radiation-oxidation [12], solution phase reduction [14], thermal oxidation [15], vacuum evaporation [16], ultra-sound [17], and biosynthesis [18] have size distribution from 2 to 100 nm.

Blizzard and Martin in their patent US4347060A [10] have synthesised Sb_2O_3 powder of size 320 nm. This process requires very high operating temperature, which increases the cost of the final product. In this paper, we have demonstrated eco-friendly prices operating at ambient temperature and pressure. The final product was obtained within 6 hours. Due to these parameters, the cost of the final product will decrease, which will benefit the industry.

4 Conclusion

For the first time, ultra-fine Sb_2O_3 nanoparticles were successfully synthesised using plant extract. *D. alata* tuber extract is a promising reducing and capping agent in the synthesis of metal oxide nanoparticles. This green approach overcomes the drawbacks of conventional methods such as incubation time, high temperatures and pressure conditions, complex and expensive equipment, and use of toxic precursors.

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