



Physical & enhanced photocatalytic properties of green synthesized SnO₂ nanoparticles via *Aspalathus linearis*



A. Diallo ^{a, b}, E. Manikandan ^{a, b}, V. Rajendran ^{a, b, c}, M. Maaza ^{a, b, *}

^a UNESCO-UNISA Africa Chair in Nanosciences-Nanotechnology, College of Graduate Studies, University of South Africa, Muckleneuk Ridge, PO Box 392, Pretoria, South Africa

^b Nanosciences African Network (NANOAFNET), iThemba LABS-National Research Foundation, 1 Old Faure Road, Somerset West 7129, PO Box 722, Somerset West, Western Cape, South Africa

^c Centre for Nano Science and Nanotechnology, K.S. Rangasamy College of Technology, Tiruchengode 63721, Tamil Nadu, India

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ABSTRACT

This contribution reports on the synthesis and the main physical properties of n-type SnO₂ nanoparticles synthesized for the first time by a completely green chemistry process using *Aspalathus linearis*'s natural extract as an effective chelating agent. Their surface/interface and volume properties by X-rays diffraction, Raman, X-rays photoemission & photoluminescence spectroscopies are reported. Their average diameter ranging from 2.1 to 19.3 nm follows a thermal governed equation of $\langle \phi_{\text{particles}} \rangle = 1.048 \cdot 10^{-5} T^2 - 4.92 \cdot 10^{-3} T + 2.84$. The smallest SnO₂ nanoparticles exhibit effective photocatalytic responses to Methylene blue, Congo red and Eosin Y.

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1. Introduction

There are two normal oxidation states of tin cation, known as stannous ion (Sn²⁺, SnO) and stannic ion (Sn⁴⁺, SnO₂). Compounds of these two oxidation states which have attracted interest as early as the 40s, exhibit quite different physico-chemical characteristics and have different applications [1,2]. In addition to these two different oxidation states, metastable mixed-valent tin oxides, such as Sn₅O₆, Sn₃O₄ and Sn₂O₃, have dissimilar properties compared to that of stannous or stannic oxides. Despite this mixed-valent tin oxide phases, the focus of the scientific community is geared mainly towards SnO₂. This latter is a transparent, n-type semiconductor with a bandgap of ~3.6 eV [3–7]. Once doped, it is a material of choice due to the ability to tailor its electrical and microstructural properties, making it useful in several applications such as transparent conducting oxides, varistors, gas sensors, thick film resistors, and electrochemical devices as well as effective

photocatalysts [8–18]. Much of the ability to tailor SnO₂'s properties comes from the multi-valence ability of the tin atom related to the Sn⁴⁺ reduction to Sn²⁺ & vice-versa. Reduction of the surface will lead to formation of Sn 5s derived surface states that lie deep within the band gap and also cause a lowering of the work function [19]. An additional singularity of SnO₂ lies in the surface oxygen atoms' coordination. More precisely, a theoretical study has shown that energetically favorable reconstructions of the SnO₂ (110) and (101) surfaces result in surface oxygen deficiency [23–25]. Consequently, SnO₂'s surface will act as a sink for vacancies.

In terms of synthesis, nanosized SnO₂ particles and systems of various shapes and sizes were prepared via a large and rich set of physical or chemical methodologies. This includes thermal evaporation, sputtering, e-beam, pulsed laser ablation, spark processing, glow discharge growth, rapid oxidation of metal tin, microwave mediated synthesis, hydrothermal, solvothermal, colloidal growth, sol-gel, chemical vapor deposition, spray pyrolysis, sonochemistry, hydrolysis, self-assembly, electrodeposition, electrospinning and carbothermal reduction processes among others [4,20–36]. However, relatively high temperatures and/or elaborated stages during the synthesis are necessary for these methods and further thermal annealing is usually necessary to obtain good crystalline samples. In addition, it is extremely difficult if not challenging to synthesize

* Corresponding author. UNESCO-UNISA Africa Chair in Nanosciences-Nanotechnology, College of Graduate Studies, University of South Africa, Muckleneuk Ridge, PO Box 392, Pretoria, South Africa.

E-mail addresses: Maaza@tllabs.ac.za, Maazam@unisa.ac.za (M. Maaza).

crystalline nano-scaled SnO_2 particles smaller than 2.7 nm in diameter. Such nano-crystals with a diameter less than the exciton Bohr radius would manifest quantum confinement effects such as the blue shift of the band edge transition energy among other unusual structural and optical properties which can be sensed [37]. Recently, in addition to the physical and chemical methodologies, green processes using natural extracts as chelating agents have been demonstrated to be very effective in the synthesis of a variety of nano-scaled oxides with average nanoparticles' size as small as 2.1 nm in ($\langle \phi_{\text{particles}} \rangle$) [38–45].

This contribution reports on the synthesis and the main physical properties of nano-scaled pure and single phase Cassiterite SnO_2 particles synthesized for the first time by a completely green process using *Aspalathus linearis*' natural extract as an effective chelating agent without addition of any acid or base standard compounds. The average diameter of the as prepared Cassiterite can be as small as ($\langle \phi_{\text{particles}} \rangle$) ~2.12 nm which can be controlled/increased via an annealing treatment. Such small nanoparticles exhibit an enhanced photocatalytic responses for several organic water contaminants such as Methylene blue, red Congo and Eosin Y.

2. Experiments, results and discussion

2.1. Synthesis of single phase cassiterite SnO_2 nanoparticles & characterization

Aspalathus linearis of the family Fabaceae, also known as Rooibos, is a plant which is originally found in the Southern Africa. As summarized in Fig. 1, *Aspalathus linearis*' extract contains, among others, two unique phenolic compounds, namely aspalathin, a dihydrochalcone C-glucoside, and aspalalinin, a cyclic dihydrochalcone. Other major phenolic compounds present include flavones (orientin, isoorientin, vitexin, isovitexin, luteolin, chrysoeriol), flavanones (dihydro-orientin, dihydro-isoorientin, hemiphlorin) and flavonols (quercetin, hyperoside, isoquercitrin, rutin) [46,47]. It is established that Aspalathin, which is a rare C–C dihydrochalcone glycoside, and the two structurally related chalcones (nothofagin and aspalalinin) are the most bioactive compounds. These bioactive components are believed to be potential

chemical chelting agents [46]. While the mechanism of formation and the dynamic of growth of the SnO_2 nanoparticles via the reaction of the Tin Chloride precursor with the set of bioactive compounds from the *Aspalathus linearis* natural extract is of a major importance, it will be presented thoroughly in a follow up paper.

High quality dried *Aspalathus linearis*' leaves powder was weighted and initially cleaned extensively with cold H_2O (15 °C). Following a drying phase under sunny conditions at ambient temperature, the samples were ground. 8 g of *Aspalathus linearis* leaves powder was mixed with 450 ml of de-ionised H_2O each for 48 h. The duration of 48 h was considered to ensure the maximum extraction of the bioactive compounds (highlighted in Fig. 1) from the *Aspalathus linearis* leaves powders. This later maximum extraction of the bioactive compound was verified by UV-VIS spectroscopy. The optical absorbance spectrum does not change for high periods of extraction. The brown solution was filtered 3 times to eliminate residual solid if any. The pH of the extracted naturel dye pH was 5.01 at room temperature. It was used to reduce chelate several Tin based salts including SnCl_4 , SnCl_2 , and SnNO_3 , as well as Sn-Ammonium hydrate based precursors. This communication focuses on the green chelation of SnCl_4 Chloride pentahydrate precursor ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) as a proof of concept of synthesis of single phase SnO_2 nanoparticles. Analytical grade reagent $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ from Sigma -Aldrich was used. A fixed amount of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (4 g) was dissolved in 400 ml the above considered *Aspalathus linearis* extract solution. Subsequently, a white deposit was observed at the bottom after 10 min approximately. The solution with the deposit was submitted 3 times to a centrifugation process at 1000 rpm for 10 min each. The collected white deposit was dried at about ~80 °C. Following this drying phase, the corresponding powder was annealed at various temperature during 4 h at 400, 700 and 900 °C in air within a standard oven unit.

Following such a step, various characterization were carried out on the dried and the 3 annealed powders. For the High Resolution Transmission Electron Microscopy (HRTEM) and Selected Area Electron Diffraction (SAED) a Joel JEM 4000EX electron microscopy unit with a resolution limit of about 0.12 nm, equipped with a Gatan digital camera, was used. Image analysis was carried out using image J software. The Dispersive X-ray Spectroscopy (EDS)

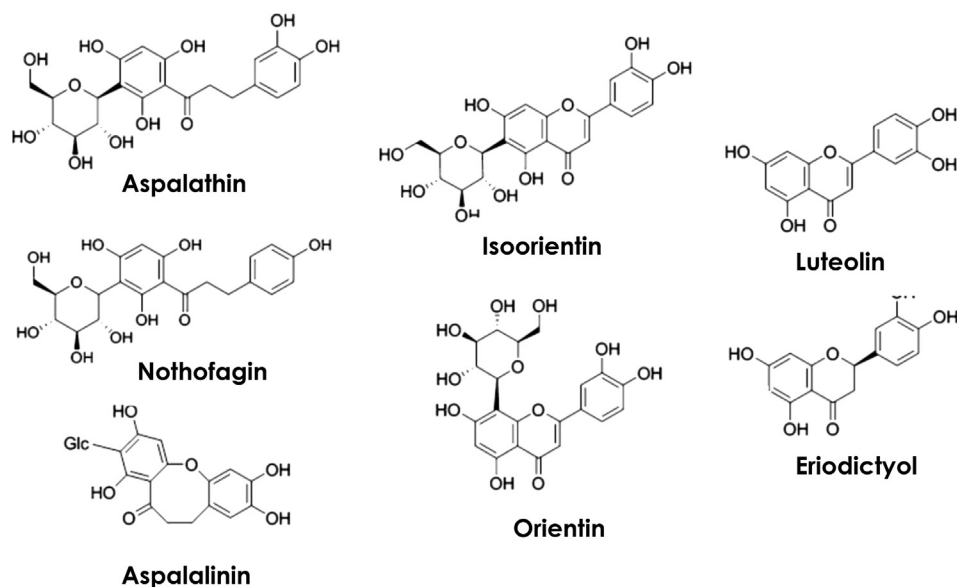


Fig. 1. Chemical structure of the various active molecular compounds within the *Aspalathus linearis* natural extract. [Adapted from Ref. [46]].

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