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A green facile one-pot approach to the phytochemical assisted synthesis of 3-D Silicon(IV) oxide nanosheets using the aqueous leaf extract of *Azadirachta indica* (Neem)

O. S. Bankole-Ojo[1], F. O. Oyedeji[2]

[1] *Department of Physical Science, Crawford University, Faith city, Igbesa, Ogun State, Nigeria.*
[2] *Department of Chemistry, University of Ibadan, Ibadan, Oyo State, Nigeria.*

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sciforch@hotmail.com ;
Phone: +2348034501256

Abstract

The present study reports on a green approach for the synthesis of silicon(IV) oxide (SiO_2) nanoparticles from SiF_6^{2-} complexes using phytochemicals from *Azadirachta indica* as capping and stabilizing agents. The Ultraviolet-Visible spectroscopic analysis indicated a broad peak at 380 nm which increased as reaction time increased. Fourier Transform Infrared analysis revealed the presence of Si-O-Si content, and the appearance of phytochemicals such as primary amine and alcohol groups as capping agents. X-ray Diffraction studies showed sharp peaks that confirmed that the nanoparticles were crystalline. Scanning Electron Microscopy analysis showed the formation of sheets of SiO_2 nanoparticles arranged in a pattern with the sides facing up and sheet thickness ranging from 35 to 50 nm without any agglomeration among the particles. Energy dispersive X-ray analysis showed a 38 weight percentage of silicon content in the sample and a complete absence of fluorine and potassium which indicated a complete hydrolysis of the precursor.

1. Introduction

Silicon(IV) oxide (SiO_2) is the most abundant oxide on earth [1]. SiO_2 exists as quartz, tridymite and cristobalite. It is used in many personal and healthcare products, food and pharmaceutical applications and as a precursor to glass [2].

SiO_2 nanoparticles have attained great importance in all spheres of science. The nanoparticles are used for specific protein adsorption and separation, nucleic acid detection and purification, drug and gene delivery, imaging contrast agents construction, strengthening composites and impartation of super-hydrophobicity on surfaces [3]. SiO_2 nanoparticles have been synthesized mostly by using hydrothermal [4], micro-emulsion [5], flame synthesis [6] and sol-gel methods [7]. The biological methods were developed to eliminate the use of extreme temperature conditions, thus, there has been an explosion in the use of biological agents like bacteria, fungi, algae and plants. Plants have been particularly favoured because of the absence of cultures, speed of synthesis and up-scalability. SiO_2 nanoparticles have been synthesized from bamboo and rice husks, however, these processes involve pyrolysis at very high temperatures and a laborious multi-step procedure [8]. Thus, the foregoing highlights the need for a facile one-step procedure for the synthesis of SiO_2 using a biological route. SiO_2 nanoparticles have also been synthesized by reacting Tetraethyl orthosilicate (TEOS) with the aqueous leaf extracts of *Thuja orientalis* and *Azadirachta indica* [9,10]. Little work has been done on the synthesis of SiO_2 nanoparticles using SiF_6^{2-} complexes. SiO_2 nanoparticles have been synthesized from the aqueous anionic complexes of SiF_6^{2-} by using the fungus *Fusarium oxysporum* [11] and the bacterium *Actinobacter sp*. [12]. *Azadirachta indica* (Figure

1) was chosen because of its wide distribution along the tropics and its high antioxidant properties [13]. To the best of our knowledge, this study presents the first attempt at synthesizing SiO_2 nanoparticles through a phytochemical mediated hydrolysis of SiF_6^{2-} complexes.

Figure 1: *Azadirachta indica leaf*

2. Material and Methods

2.1. Material

Analytical grade chemicals were used. De-ionised water was used in preparing all reagents and solutions. Potassium hexafluorosilicate (K_2SiF_6) was used as received without further purification. The *Azadirachta indica* (Neem) leaves harvested at CSIR-IICT botanical garden, Tarnaka, Hyderabad, India (17º25'28.9"N, 78º.32'17.8"E) between 12 noon and 4pm. Taxonomic identification was done by Dr. G. Baskar Rajan, the head of the botanical garden.

2.2. Preparation of plant materials

The leaves were washed with double distilled water and air dried for four days. A dedicated domestic blender was used to pulverise the leaves. Pulverised leaves were stored at 4ºC in an air-tight glass container for further use.

2.3. Preparation of aqueous plant extract

0.5 g/ml suspension of the pulverised leaves was heated under reflux at 100ºC for 30 minutes and thereafter, allowed to cool. 11µm pore size filter paper was used for filtration. The filtrate was centrifuged at 10,000 rpm at 15ºC for 10 minutes. This was done to remove heavy biomolecules that might precipitate with nanoparticles during the purification process. The supernatant was obtained after decantation and filtered to separate any remaining plant particle.

2.4. Synthesis of nanoparticles

25ml of the plant extract was slowly added in a dropwise manner under intensive stirring to 50ml of 1mM aqueous solution of K_2SiF_6. Drops of 0.1M H_2SO_4 solution were added to achieve a pH of 3. The colour of the solution changed from magenta to orange after 6 hours of reaction. The nanoparticles were precipitated out of solution via centrifugation at 10,000rpm at 15ºC for 10 minutes and re-dispersed in absolute ethanol while being sonicated using a bath sonicator for 10 minutes. The centrifugation-dispersion cycle was carried out three times to remove organic groups loosely adsorbed to the nanoparticle surface. The ethanolic suspension was evaporated at 60ºC in a vacuum oven for 6 hours.

2.5. Characterizations and instruments

Shimadzu UV-160 spectrophotometer was used for UV-Visible spectroscopic analysis. FTIR spectra were measured on a Thermo Nicolet Nexus 670 spectrophotometer. XRD analysis was carried out on a X-ray diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm)) with an operating voltage of 30 mA, 45 kV. XRD data were recorded with 2θ ranging from 10º to 70º. SEM was used to study the particle size and morphology of nanoparticles using an Olympus BX-51 scanning electron microscope.

3. Results and discussion

UV-Visible spectra was recorded for the reaction medium as a function of the time of reaction (Fig. 2). It was observed that the SiO_2 surface plasmon band occurs at 380 nm. There was further hydrolysis of the SiF_6^{2-} complexes to produce more SiO_2 with increase in reaction time.

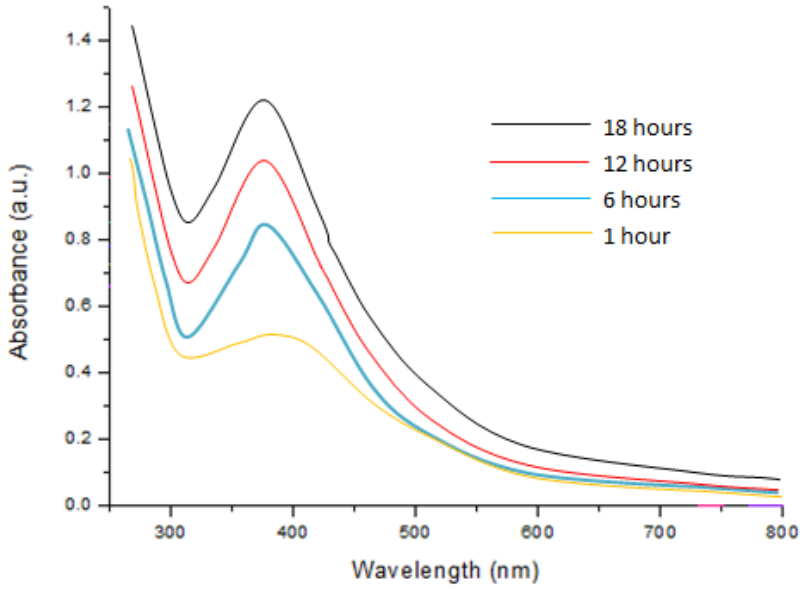

Fig 2: UV-Visible spectroscopic analysis

The FTIR spectroscopy was used to monitor the reaction. FTIR spectroscopic measurements were performed at 0h, 1h, 6 h, 12 h and 18 h of reaction (Fig. 3). The strong 1086 cm^{-1} band is attributed to excitation of the antisymmetric Si–O–Si stretching mode of vibration. A gradual and monotonic increase at 1086 cm^{-1} that is accompanied by a decrease in intensity of the resonance at 750 cm^{-1} with time clearly indicates the hydrolysis of SiF_6^{2-} ions into SiO_2.

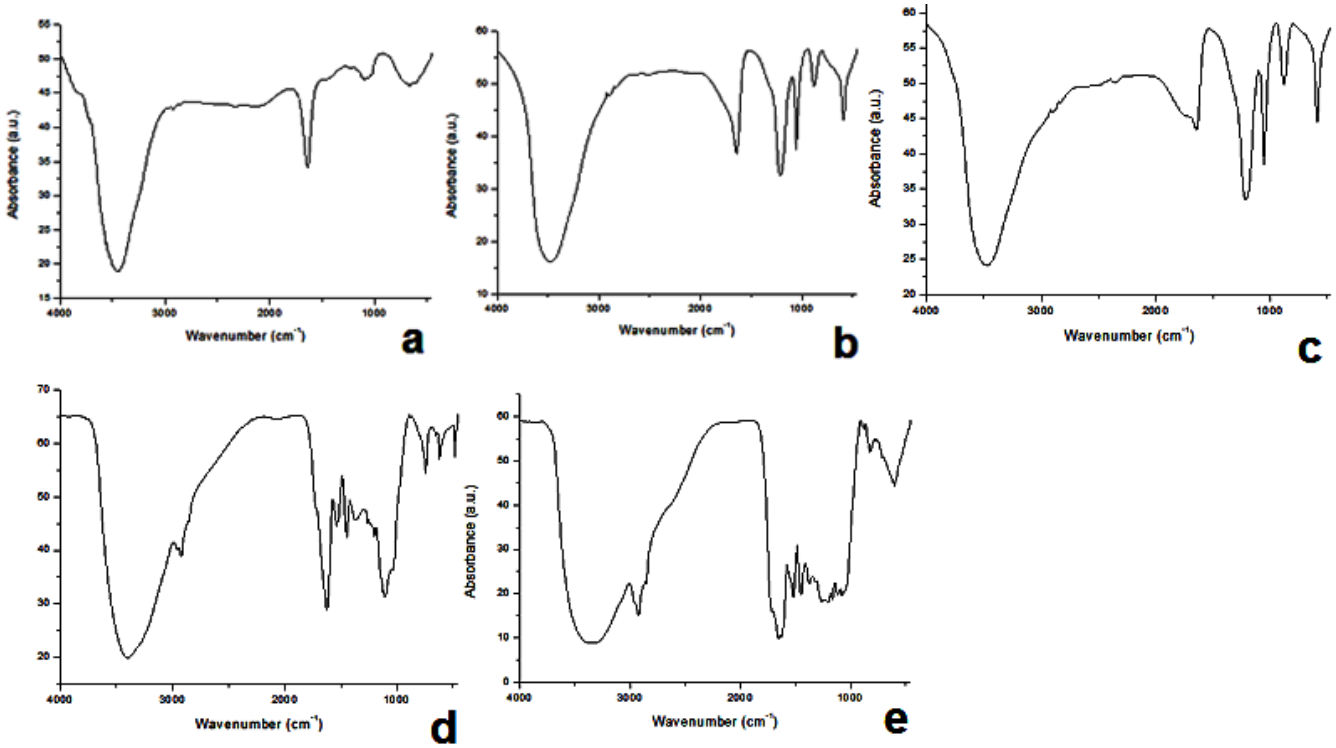

Fig 3: Time dependent FTIR spectra of reaction at a) 0 hours b) 1 hours c) 6 hours d) 12 hours e) 18 hours

Sharp peaks were observed for the as-synthesized SiO_2 nanoparticles indicating their crystalline nature from the XRD data (Fig. 4). The most prominent peaks were located at 2θ= 29.6988 and 30.7304 corresponding to crystallite sizes of 38.81nm and 36.11 nm respectively.

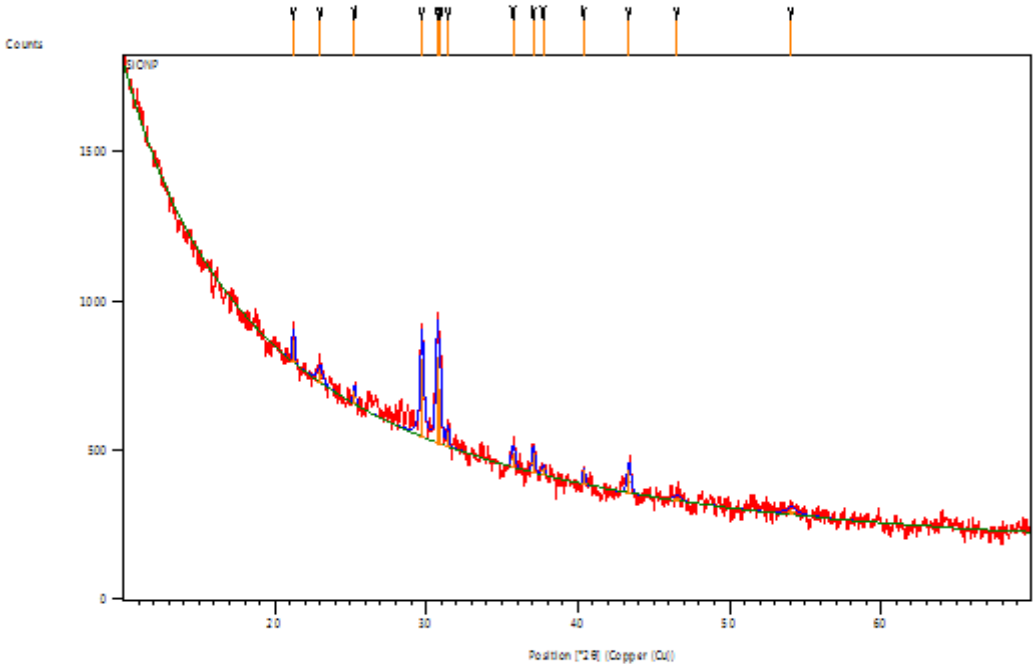

Figure 4: XRD data for as-synthesized SiO_2 nanoparticles

The surface morphology of the SiO_2 nanoparticles were studied by scanning electron microscopy method (Fig. 5). The SEM image of the SiO_2 nanoparticles showed three dimensional nanosheets arranged in patterns with most of the sheets vertically positioned having sheet thickness between 40nm-55nm.

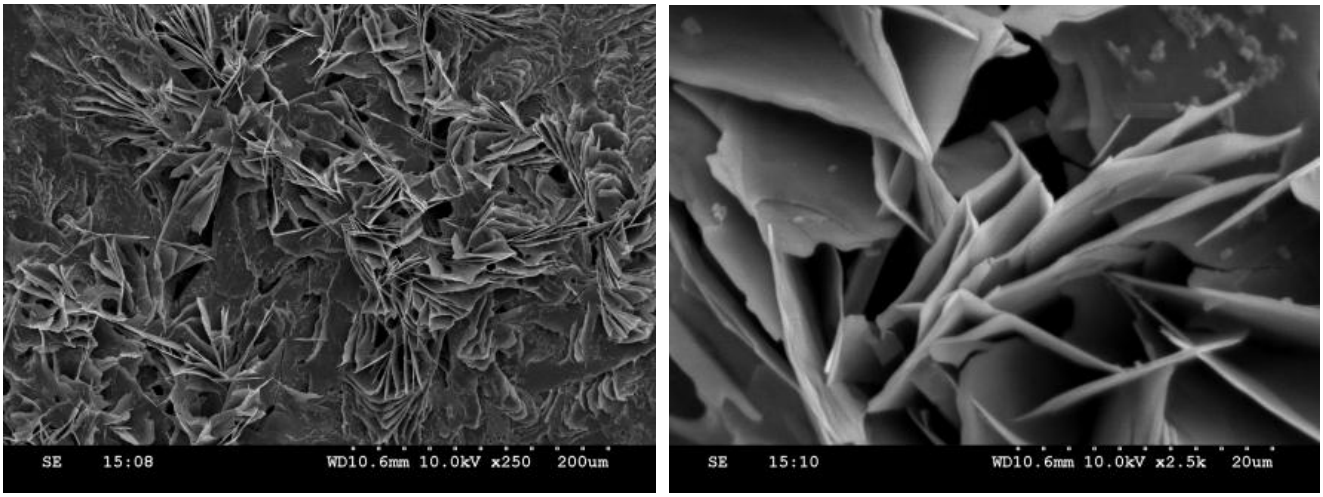

Fig 5: SEM images of as-synthesized SiO_2 nanoparticles

Energy dispersive analysis of X-rays (EDAX) measurements showed the presence of Si and O (Fig. 6). The absence of potassium and fluorine from the precursor, K_2SiF_6 showed the complete transformation of K_2SiF_6 into SiO_2 with 38 weight percentage for silicon. The high percentage of carbon and the presence of impurities may be as a result of plant use.

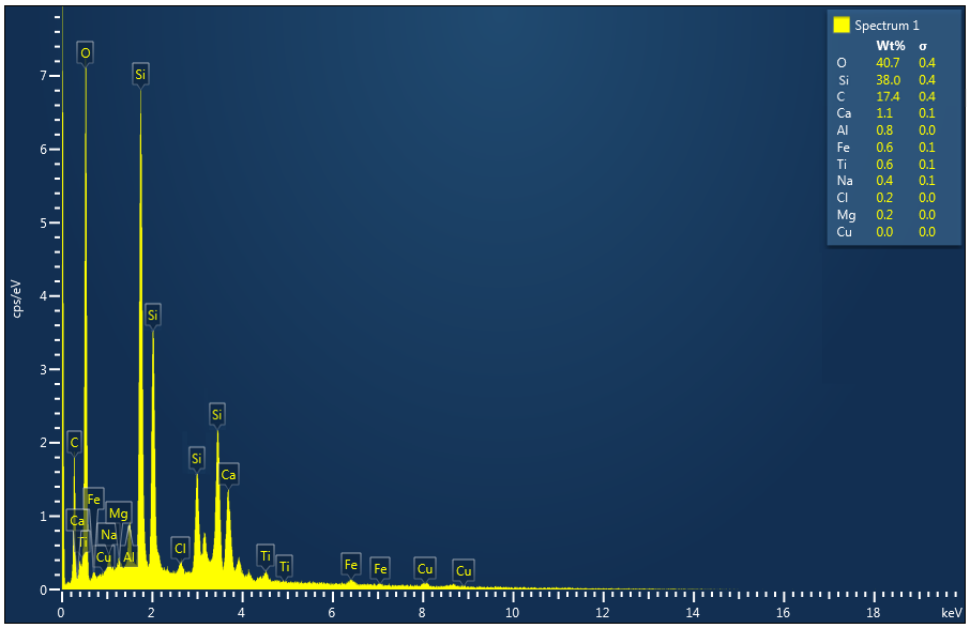

Fig 6: EDAX image of as-synthesized SiO_2 nanoparticles

Conclusion

In this study, SiO_2 nanoparticles were synthesized from the aqueous extract of the leaves of *A. indica* through an environmentally benign route without the involvement of toxic chemicals or corrosive gases at ambient temperature. The synthesized SiO_2 nanoparticles using *A. indica* were obtained as 3-dimensional nanosheets with sheet thickness of 42nm without any further agglomeration between the particles. In this study, FT-IR studies showed an incremental production of SiO_2 content with increasing reaction time in the form of growing Si–O–Si bands and EDAX studies showed 38.0 weight percentage of silicon content. Sharp peaks were observed in XRD studies, which revealed that the particles were crystalline in nature. The present synthesis route is devoid of the use of the calcination procedure. We conclude that the plant *A. indica* acts as an excellent capping and stabilizing agent for the production of SiO_2 nanoparticles and this paves a futuristic way for synthesizing SiO_2 nanoparticles using SiF_6^{2-} precursors via a phytochemical mediated route.

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