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Synthesis and characterization high purity alumina nanorods by a novel and simple method using nanocellulose aerogel template

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ABSTRACT

Highly porous nanofibrillated cellulose aerogel fibers (NFCA) prepared from bagasse pulp was used as a template for *in situ* preparation of alumina nanorods. NFCA was soaked in aluminum nitrate aqueous solution followed by soaking in ammonium hydroxide solution to generate aluminum hydroxide within the porous structure and at surface of NFCA. Sintering of NFCA/Al $(OH)_3$ was carried out at 1100 °C to produce nano-sized alumina with rod-like structure. The synthesized Al_2O_3 nanorods were investigated using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and high resolution transmitted electron microscope (HR-TEM). The Al_2O_3 rods had width from 123 to 86 nm while their length was in the micrometer range, as shown from SEM and HR-TEM images. The selected area X-ray diffraction (SEAD) showed rhombohedral crystal structure. XRD pattern confirmed formation of α-alumina. Energy dispersive X-ray spectroscopy (EDX) showed purity of the prepared Al_2O_3.

1. Introduction

Preparation of inorganic nanomaterials with different shapes and geometry is an attractive area of research due to the unique properties of nanomaterials due to their nano-size compared to their bulk counterparts. Inorganic nano tubes, rods and particles can find different uses in drug delivery systems, nano electronics, reinforcing elements to improve mechanical properties, and optoelectronics. Novel and simple methods are needed to overcome the high cost of preparation of these nanomaterials.

Alumina, especially α-alumina, is characterized by high chemical stability, inertness, hardness, high melting point, high optical transmission range, and wide band gap. Alumina finds different applications in implants, semiconductors, opt-electronics, and as reinforcing elements in composites [1, 2]. Alumina nanoparticles, nanotubes, and nanofibers have interesting properties due to their nano-size and the aforementioned properties of alumina.

During recent years, different routes toward alumina nano-objects were investigated such as use of laser ablation [3, 4, 5, 6], liquid-feed flame spray pyrolysis [7], and precipitation techniques [8]. The use of templates for formation of alumina nanoparticles is another attractive route since the templates used are usually cheap and/or produce specific nanostructure. These templates could be nanoporous membranes or nanofibers. In this context, aerogels could be used as facile highly porous templates for nanostructured alumina [9, 10, 11, 12].

Cellulose is the most abundant polymer on earth. It has many attractive advantages such wide availability of raw materials (wood, agricultural residues, agro-based fibers, grasses) biodegradability, non-toxicity, ability for chemical modification. The utilization of agricultural wastes for isolation of cellulose is one of the potential ways to minimize the pollutants and save our environment. Cellulose and cellulose derivatives aerogels have been used as templates for preparation of different metal oxide [13] and ceramics [14] particles having micro to nano-size range. Regarding the use of cellulose and cellulose derivatives for preparation of alumina, cellulose pulp from softwood, cyanoethyl-, amidoethyl- and carboxy methylcellulose were synthesized from bleached softwood pulp and used as templates for alumina materials preparation [15]. The cellulosic materials were impregnated with aluminum chloride and sintered at 600–700 °C to produce alumina particles having micrometer size. In another study, alumina fibres were prepared by sol-gel process using aluminum-tri-isopropoxide as a precursor and hydroxyethyl cellulose as a template [16]. The gel containing HEC was spun by a syringe in ammonia solution to form fibers which were sintered at 1600 °C to obtain α-alumina fibers with diameter in the micrometer range. Transparent alumina film and fiber were prepared

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using basic aluminum chloride and methyl cellulose as template [17]. The composite dried film of basic aluminum chloride and methyl cellulose was heated up to 1150 °C to obtain α-alumina film. For obtaining alumina fibers, the mixture of basic aluminum chloride and methyl cellulose was spun in ammonia solution into wet fibers that were dried and heated up to 1150 °C to form alumina fibers. The thickness of the alumina film obtained was about 40 μm while the diameter of the alumina fibers was about 80 μm.

Cellulosic nanomatierals, e.g., cellulose nanofibers and cellulose nanocrystals, are a new class of materials with interesting properties [18]. They could be isolated from different agricultural residues such as bagasse, rice straw, and other agricultural and wood residues [19, 20].

Cellulose nanofibers could be used to prepare highly porous aerogels by different drying methods for different applications [21, 22, 23, 24, 25, 26]. The unique architecture and porous structure of cellulose aerogel made it excellent template for preparation of other inorganic materials with specific shapes and dimensions (from micro-to nano-size) where the porous structure act as a template for controlling shape and dimension of the in-situ prepared inorganic materials [27].

Regarding use of nanocellulose for preparation of alumina nanoparticles, few studies have been conducted so far. For example, aerogel prepared from nanocellulose was used as a template for preparation oxides of alumina and titania nanotubes using atomic layer deposition technology [28, 29] where the oxides of alumina and titania were evaporated onto the surface of nanocellulose areogel followed by sintering to produce alumina and titania nanotubes with diameter in the nano-size range. Using a different approach, alumina suspension was mixed with cellulose nanofibers and the mixture was calcined to form hollow rods of alumina nanoparticles.

In the current study, freeze-dried aerogel from cellulose nanofibers isolated from bagasse pulp was used as template for preparation of alumina nano-rods using simple precursors (aluminum nitrate and ammonium hydroxide) and method (soaking-drying-sintering).

2. Experimental

2.1. Materials

Aluminum nitrate nonahydrate (Al $(NO_3)_3$. $9H_2O$) of 98% purity was used in this study (Loba Chemie Pvt Ltd, Mumbai, India) and porous nanocellulose aerogel fibers as template. Ammonia solution (Merk 25%) was used for gel precipitation. Bleached kraft bagasse pulp was kindly supplied by Qena Company for Pulp and Paper, Qena, Egypt. The chemical composition of the pulp was α-cellulose 70.6%, pentosans 26.8%, ash 0.82%, and degree of polymerization (DP) of 1174.

2.2. Preparation of NFC and NFCA

To prepare porous nanocellulose aerogel, nanofibrillatred cellulose (NFC) was first isolated from bagasse by chemical treatment of bagasse pulp with 2,2,6,6-tetramethyl-1-piperidinyloxy radical, sodium bromide, and sodium hypochlorite as previously described [30]: Bleached pulp (3 g) was dispersed in distilled water (400 mL) with TEMPO (0.048 g, 0.3 mmol) and sodium bromide (0.48 g, 4.8 mmol). Then, 30 mL of sodium hypochlorite solution was then added with stirring, and the pH was adjusted to 10. At the end of reaction, the pH was adjusted to 7, and the product was centrifuged at 10 000 rpm. The product was further purified by repeatedly adding water, dispersion, and centrifugation. Finally, the product was purified by dialysis for one week against de-ionized water with 3500 MWCO Spectra/Por dialysis tubing. To isolate the nanofibers, TEMPO-oxidized fibers were homogenized by mechanical disintegration at 15000 rpm using CAT unidrive 1000 high shear homogenizer (CAT Scientific Inc., USA) after being diluted with water to 1% consistency. Carboxylic content of the oxidized nanofibers was 0.64 mmol/g according to the Technical Association of the Pulp and Paper Industry test method T237 cm-98.

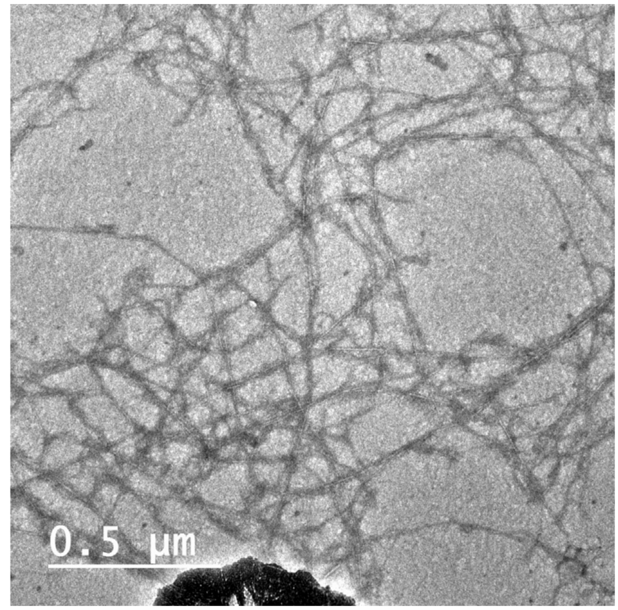

Fig. 1. TEM images of NFC isolated from bagasse.

The produced NFC gel was freeze dried using Alpha 1–4 LSCplus CHRIST freeze dryer (Martin Christ Gefriertrocknungsanlagen GmbH, Germany) at -60 °C, 10^{-3} mbar for 12 hours to form porous nanofibrillated cellulose aerogel (NFCA). Porosity of NFCA was calculated based on the following equation (Eq. 1):

$$\text{Porosity} = 1 - (\rho/\rho_s) \qquad \text{(Eq. 1)}$$

where ρ and ρ_s are the densities of the aerogel and cellulose fibrils (skeletal density). The value for ρ_s is 1.5 g cm^{-3} [31].

To prepare alumina nanorods, 0.1 M aluminum nitrate solution was prepared then NFCA (0.5 g) was soaked in 50 ml the nitrate solution in a petri dish for 30 min at 25 °C. The soaked NFCA was then immersed in ammonia solution (pH 8.8). The NFCA/$Al(OH)_3$ was removed from reaction mixture, drained, and dried overnight at 100 °C. The dried samples were put inside muffle furnace and the temperature was raised up to 1100 °C at a heating rate of 5 °C/min and the sample was kept at that temperature for 1 hour.

2.3. Characterization of NFC, NFCA, and alumina

The morphology of prepared NFC and alumina was investigated using high resolution transmission electron microscopy (JEM-2100 transmission electron microscope, JEOL, Japan) with acceleration voltage 100 kV. Scanning electron microscopy SEM coupled with energy-dispersive spectroscopy EDX (Quanta 200 scanning electron microscope, FEI Company BV, Netherlands) with an acceleration voltage of 20 kV was used to determine purity of prepared alumina and investigate morphology of alumina nanoparticles and NFCA. X-ray diffraction pattern of the prepared alumina was recorded using Empyrean X-ray diffractometer (PANalytical, Netherlands). Scherrer equation was applied to estimate the crystallite size of alumina the as shown in the following equation (Eq. 2):

$$D = K\,\lambda\,/\,\beta\cos\theta \qquad \text{(Eq. 2)}$$

The crystallite size (D) was calculated using the X-ray wavelength (λ), the peak full width at half maximum (β), the Bragg angle (θ) and the Scherrer constant value (K ~0.9).

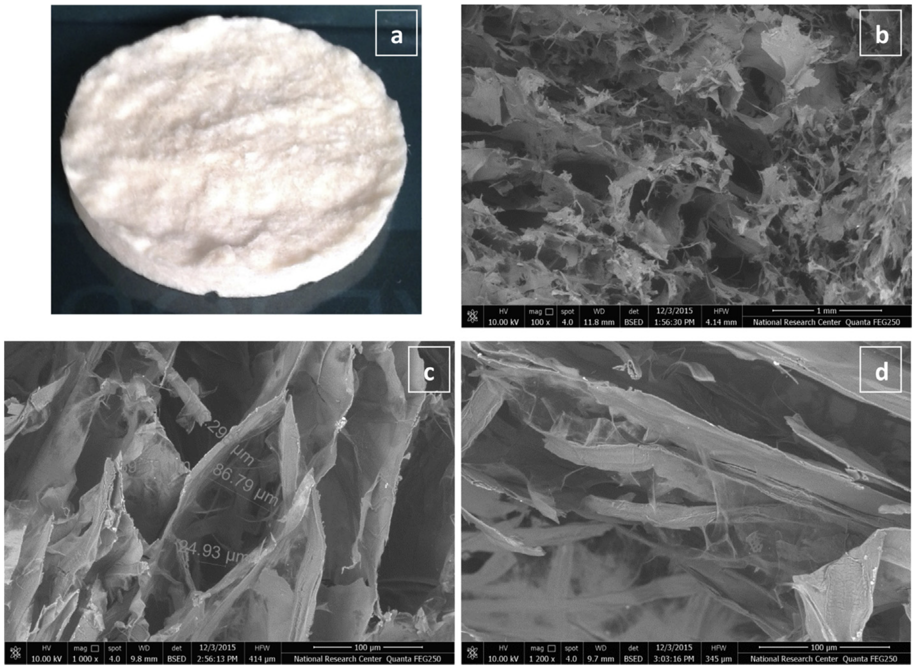

Fig. 2. photo of NFCA (a) and SEM of NFCA cross-section at 200, 1000, and 1200x magnifications (b, c, and d).

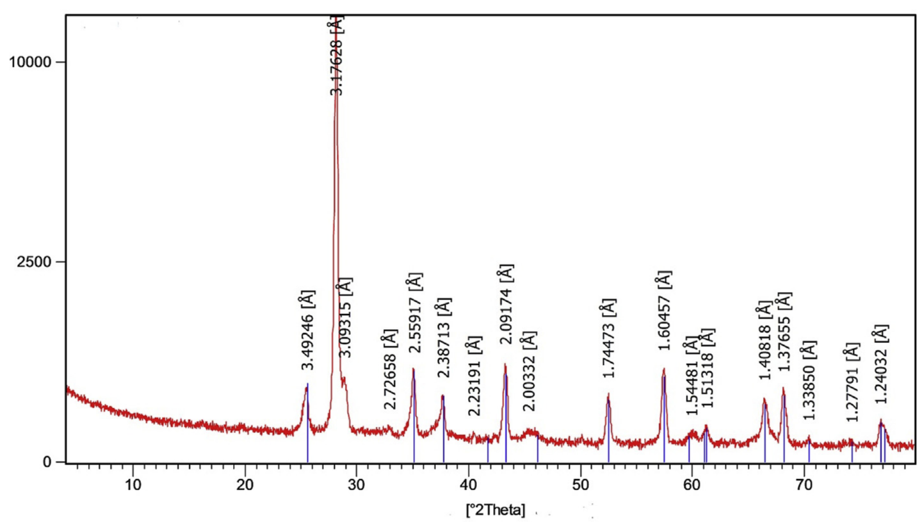

Fig. 3. XRD pattern of the α- Al_2O_3 nanorods .

3. Results and discusion

3.1. Characterization of NFC and NFCA

Fig. 1 showed TEM image of NFC isolated from bagasse pulp. The thickness of the prepared NFC was in the range of 3–5 nm while the length was several microns. The obtained NFC thickness is in accordance with previously prepared NFC from other lignocellulosic materials such as palm, rice straw, and wood [19, 30, 32, 33].

Freeze-drying of the produced gel-like NFC produced areogel disks with very low density of 0.03 g/cm^3. The density of the produced NFCA is similar to others prepared from other lignocellulosic materials [21]. According to the density value obtained, porosity of about 98% could be estimated.

Fig. 2 shows SEM image of cross section of the produced NFCA produced by freeze drying. As shown in the images, highly porous structure was formed with micro-size voids and pores. The diameter of these pores ranged from 25 to 87 μm. The thickness of walls, which consist of NFC was in the range from 3 to 8 μm. These walls have nanoporous structure, i.e., nanoscale porosity [21].

3.2. Characterization of alumina nanorods

NFCA was used as a template for *in situ* formation of alumina nanorods. NFCA were soaked in aluminum nitrate solution, drained, and soaked in ammonia solution to form aluminum hydroxide within the porous structure of the NFCA. Sintering NFCA/aluminum hydroxide produced scaffold of nano-sized alumina with rod-like shape.

Fig. 3 shows XRD pattern of Al_2O_3 nanorods. The XRD pattern shows all peaks corresponding to α-alumina with rhombohedral crystal system; the sample was matched with the ASTM cards 01-080-0786. Calculation of crystallite size by Sherrer equation showed that the crystallite sizes of the alumina nanorods was in the range from 60 to 35 nm.

Scanning Electron Microscopy (SEM) with EDX was used to

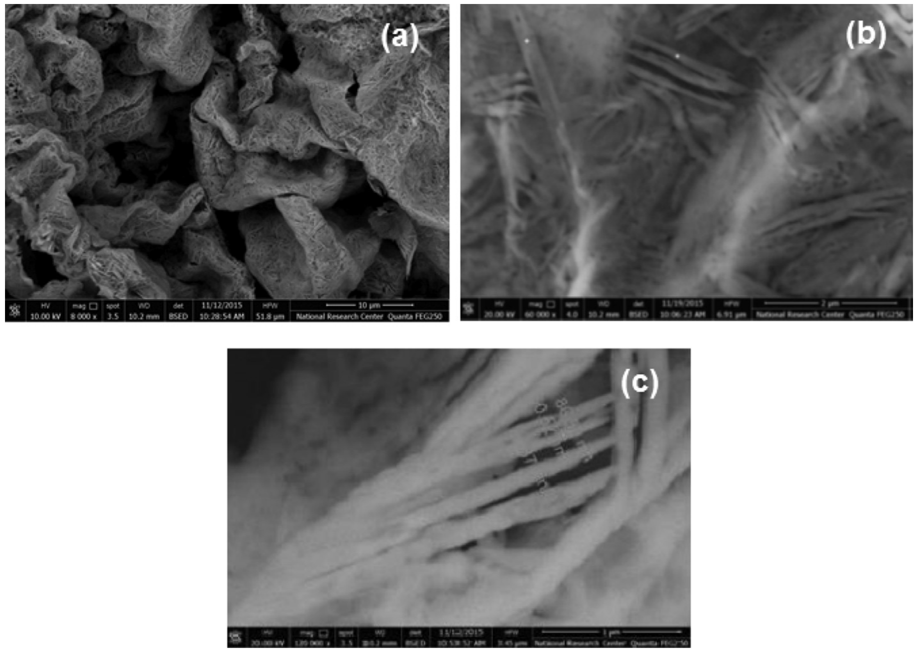

Fig. 4. SEM images of alumina at (a) 8000x, (b) 60000x, and (c) 200000x magnifications.

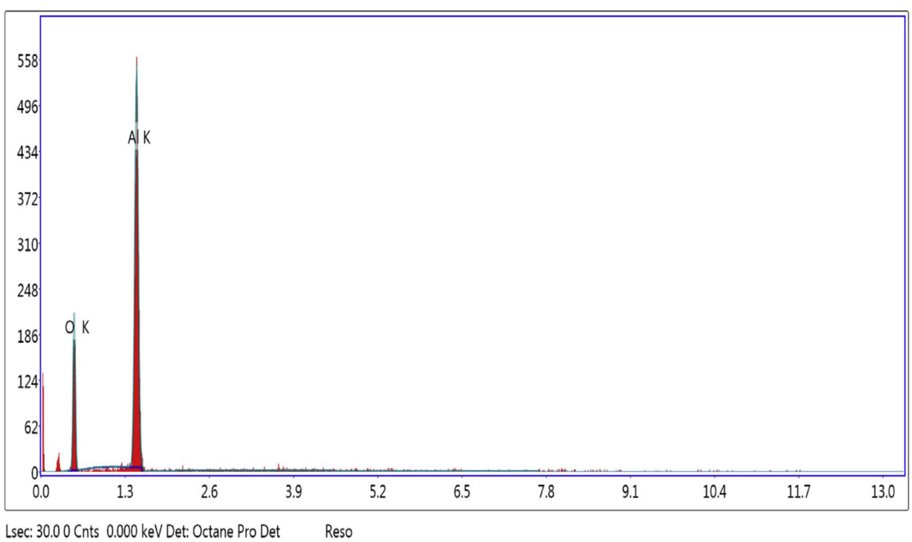

Fig. 5. EDX spectrum of Al_2O_3 nanorods.

investigate purity and morphology of the prepared scaffold. As shown in Fig. 4, sintering of NFCA/aluminum hydroxide resulted in alumina with rod-like structure with diameter ranged from 86-123 nm and several microns in length. These nano-size dimensions means that most of the aluminum hydroxide formed upon soaking NFCA/Aluminum nitrate in ammonia was inside the nano-porous walls of the NFCA. The diameter of the pores in the aerogel ranged from 25 to 87 μm, and the thickness of walls of that areogel, which consist of NFC was in the range from 3 to 8 μm. Therefore, the wall is expected to have porous structure in the nano-size formed by the NFC. After firstly soaking NFCA in aluminum nitrate, it was drained from excess nitrate solution and then soaked in ammonia. Therefore, aluminum hydroxide will be in situ precipitated mainly within the walls of the aerogel or at their surfaces. The presence of hydroxyl and carboxylate functional groups at the surface of NFC plays an important role in controlling nucleation and growth of the nanoparticles by complexation/solvation of metal cations [13, 14, 27].

The EDX spectrum in Fig. 5 confirmed high purity of Al_2O_3 and reveals that nanorods composed of Al and O elements. Elemental analysis showed atomic ratio of Al to O of 1.38 (atomic ratio was 58% and 42% for Al and O, respectively) while the theoretical atomic ratio of alumina is 1.5.

Further investigation of the morphology of alumina nanorods was carried out using HR-TEM. The alumina scaffold was treated in ultrasonic water bath before carrying out the investigation to separate the rods forming the scaffold. As seen in Fig. 6, the nanorods had rectangular shape with width close to that observed by SEM. These rectangular nanorods are formed from the rhombohedral alumina crystallites. TEM images also showed bundles of multi-layered overlapped well-arranged Al_2O_3 nanorods. The selected area X-ray diffraction (SEAD) confirmed also formation pattern of hexagonal crystallographic planes for α-Al_2O_3: 012 planes (d = 3.4 Å), 116 plane (d = 1.63 Å), and 1010 plane (d = 1.2 Å). The strong diffraction spots indicate a single-crystal structure in the nanorods of rhombohedral crystal structure (Fig. 7).

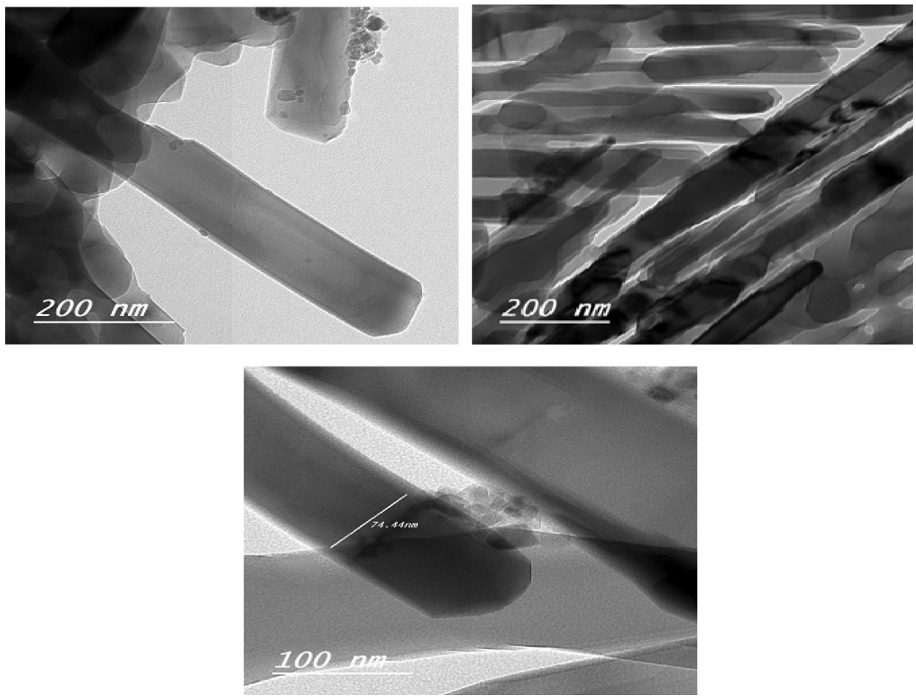

Fig. 6. HR-TEM images of alumina nanorods sintered at 1100°C

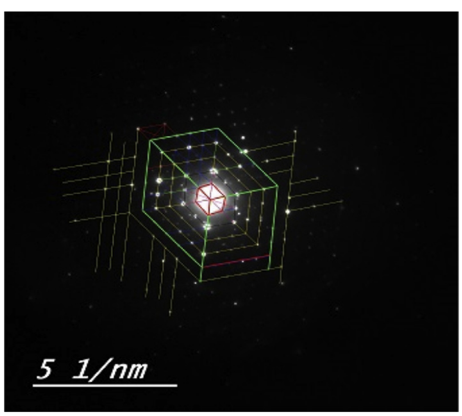

Fig. 7. SAED pattern of Al_2O_3 nano rods with different planes and d-spacing.

4. Conclusions

The present work showed possibility of preparation α-Al_2O_3 nanorods from aluminum nitrate using aerogel nanocellulose fibers as template through the co-precipitation route. The method is simple and could be followed for preparation of similar oxides such as ZrO_2, TiO_2, Mullite, and Al_2O_3-ZrO_2 nanomaterials, which are currently under investigation.

Declarations

Author contribution statement

Sayed H. Kenawy, Mohammad L. Hassan: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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