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Aqueous stability of nanostructured aluminum and gallium oxyhydroxide before and after functionalization with lysine

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ABSTRACT

Composites of nanostructured aluminum and gallium oxyhydroxide (AlOOH and GaOOH) and L-lysine were synthesized using an environmentally friendly approach. These composites were investigated to determine the effects of the functionalization on the aqueous stability and leaching of aluminum and gallium. The organic and inorganic components present in the samples were assessed with X-Ray photoelectron spectroscopy (XPS) and Fourier transformed-infrared spectroscopy (FT-IR). In the GaOOH-lysine composite, XPS provided evidence of both the presence of gallium and lysine. Crystallographic information was gathered using X-Ray diffraction (XRD). The FT-IR and XRD spectra of the composite materials were dominated by peaks related to lysine, due to the nature of these samples. Inductively coupled plasma-mass spectrometry (ICP-MS) data were collected of the functionalized and non-functionalized samples left in solution for periods of 1 days, 5 days and 7 days. This provided evidence of improved aqueous stability of the AlOOH-lysine composite with no effect seen in the GaOOH-lysine composite. The findings of this study will be used in determining the importance of lysine functionalization for future biomolecule-nanomaterial composites.

1. Introduction

The incorporation of the amino acid lysine to various functional materials to increase cell adhesion [1], biocompatibility [2] and aqueous stability [3] is of interest for a variety of applications including biosensors and targeted radiation therapy. The use of carboxylic acid containing molecules for bonding with materials such as AlOOH has been previously explored [4]. Lysine-alumoxane hybrid resins have been investigated to determine their effects on carbon fibers and epoxies [5]. For applications such as drug delivery, lysine can provide a means for specific drug transport across the blood-brain-barrier [6]. Lysine has proven to be an effective linker of various biomolecules to the surfaces of various gold samples for device capabilities such as biosensing [7]. The dendrimer structures of lysine have shown to provide an attachment mechanism for gold nanoparticles and DNA [8]. Graft polymers consisting of lysine and poly(ethylene glycol) (PEG) were investigated for adsorption on niobium oxide layers where altering the ratio of lysine to PEG directly affected the surface adhesion [9].

The use of nanocrystalline materials for functionalization with organic moieties provides increased surface area for functional group attachment to the surface of the material. The materials of interest for this study, AlOOH and GaOOH, are typically researched for their effectiveness as precursors for conversion into Al_2O_3 [10], AlN [11], Ga_2O_3 [12] and GaN [13]. In addition to this, there are a number of reasons for considering these materials as the inorganic component of organic-inorganic composites. Particularly, the native hydroxide layer present on the materials provides an effective site for the attachment of organic molecules with functional side groups such as phosphonic and carboxylic groups [14]. The surface attachment ensures long term stability of the interface between the two molecules. In this study, the functionalization of AlOOH and GaOOH nanostructured materials with L-lysine was performed. Toxicity occurs in biological systems at 700 mg/M^2 of gallium nitrate [15]. The importance of the surface functionalization of aluminum and gallium materials can be seen in Pourbaix diagrams [16]. The passivation of Al and Ga occurs in small pH window. Due to this, functionalization with molecules capable of improving the stability of these materials is of particular interest.

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2. Materials and methods

2.1. Synthesis of AlOOH and GaOOH nanostructured materials and lysine composites

Gallium nitrate hydrate, aluminum nitrate nonahydrate and sodium hydroxide, from Sigma Aldrich, were used as precursors for the formation of GaOOH and AlOOH nanorods using a previously reported hydrothermal microwave process [17]. This specific technique has not been reported for the synthesis of AlOOH nanorods. Due to the colloidal nature of the AlOOH solutions after microwaving, centrifugation was done in place of filtration. The oxide-lysine composites were made using a previously reported reflux reaction [18]. The L-lysine standard was obtained from Sigma Aldrich.

2.2. Characterization

X-ray Diffraction (XRD) spectra were obtained on a Rigaku SmartLab XRD. A Kratos Analytical Axis Ultra XPS provided surface sensitive information about the samples using a monchromated Al Kα source. A Bruker 1 959760 ALPHA FT-IR spectrometer equipped with a KBr beam splitter was used to gather FT-IR spectra in transmittance mode.

3. Results and discussion

The nanomaterial synthesis and functionalization was done via a more environmentally green approach using water as a solvent and remaining at relatively low temperatures. A schematic representation of the various steps performed is shown in Fig. 1. Included with this is SEM images of the GaOOH nanorods before and after functionalization. The nanorods are around 80 nm in width and 1 μm in length. To the best of our knowledge, this is the first reported use of GaOOH for this reaction in place of AlOOH.

3.1. X-ray diffraction

The XRD spectra of the synthesized GaOOH and AlOOH nanorods and lysine composites showed the effectiveness of the reflux reaction (Fig. 2). The GaOOH nanorods matched with the standard spectrum; however the AlOOH spectrum showed peaks consistent with possible leftover precursor material. The peaks attributed to AlOOH in this sample were significantly broad, which is attributed to the nano scale nature of the material. The significantly broader peaks in the AlOOH sample provide some evidence of smaller crystallite sizes in this sample when compared to the GaOOH. The composite materials both contained peaks that are consistent with the L-lysine standard which is also presented in the figure. The lack of any significant, observable crystallographic contributions from the GaOOH and AlOOH in the composites is attributed to the nature of the samples. It is hypothesized that the nanostructured oxides are surrounded by a crystalline lysine matrix whose XRD peaks are of significantly higher intensity.

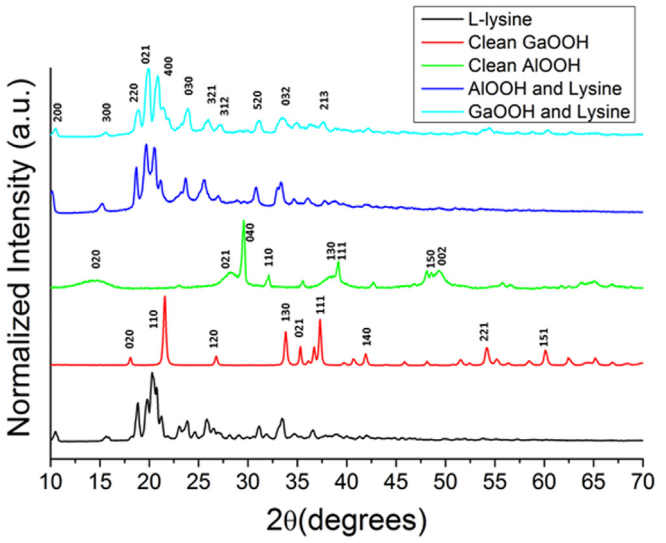

Fig. 2. Displayed are the XRD spectra of the various samples including the L-lysine standard, the AlOOH and GaOOH composites and the clean nanostructured materials.

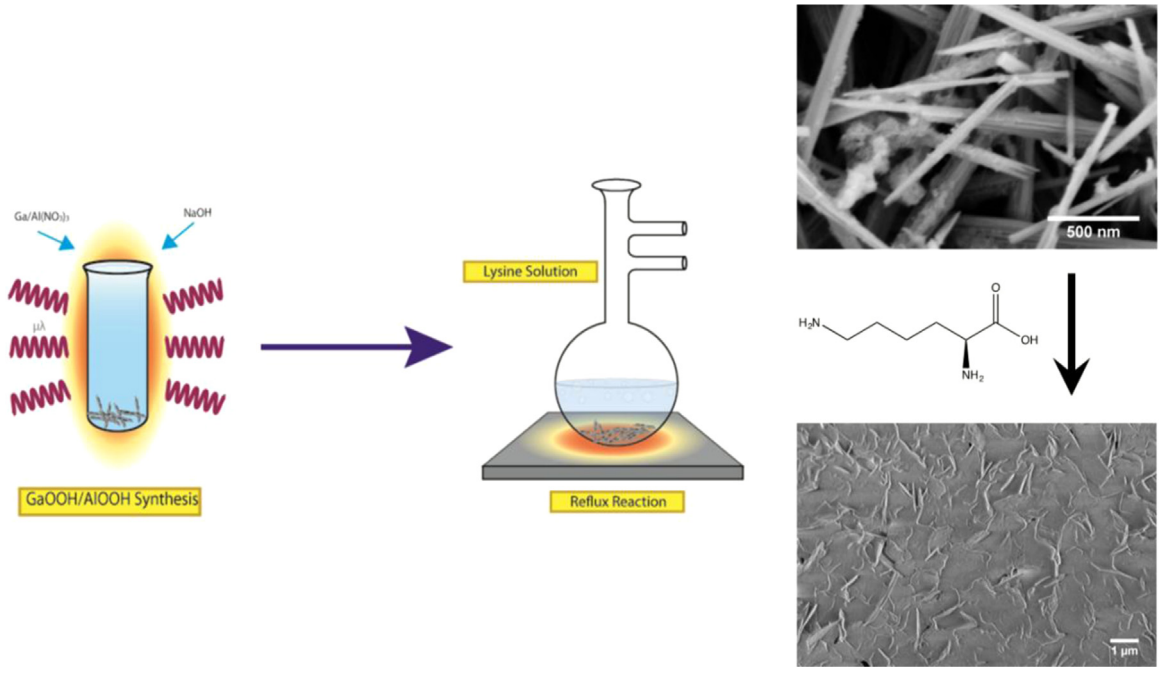

Fig. 1. A graphical schematic depicting the processes followed for the synthesis of the composite materials. Included are SEM images of the GaOOH nanorods before and after lysine functionalization.