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 day, 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 adhesion¹, biocompatibility² and aqueous stability³ 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/M² 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.

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 monochromated Al K α source. A Bruker 1 95 9760 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 Figure 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 micron 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 (Figure 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.

3.2 X-Ray Photoelectron Spectroscopy

Survey scans and high resolution regional XPS scans were taken for each of the samples. The N 1s, Ga 2p and Al 2p region scans provided evidence of the species present on the surface of each of the samples. In the Al 2p (Figure 3(a)) regional scan, the AlOOH sample has a peak near 74 eV which is not present in the AlOOH-lysine composite. It is believed that this is due to the AlOOH nanorods being buried in the lysine matrix along with the reduced response of Al in XPS when compared to Ga. The GaOOH and GaOOH-lysine composite both have a peak in the Ga 2p (Figure 3(b)) regional scan which is located near 1118 eV. Figure 3 (c) shows the N 1s regional scans of the various species indicating evidence of lysine presence in both the AlOOH and GaOOH containing lysine composites. This is based on the presence of two peaks near 399 and 400 eV on the composites as well as on the L-lysine standard.¹⁹ No N 1s peak is present in

the AlOOH sample and two peaks are present in the GaOOH at about 395 and 392 eV. These peaks are attributed to the Auger peaks Ga LMM 1 and 2.

3.3 Fourier-Transformed Infrared Spectroscopy

In order to evaluate the nature of the vibrational frequencies of the chemical species within the samples, FT-IR was used. The FT-IR spectra of both GaOOH²⁰ and AlOOH²¹ nanostructured samples have previously been reported. Figure 4 displays the spectra of each of the four synthesized samples as well as of the lysine standard. The spectrum of the synthesized GaOOH nanorods contains expected peaks near 1030, 950, 690 and 630 cm⁻¹.²² Peaks that are corresponding to the carboxylic acid group on lysine are found near 1600-1300 cm⁻¹ in the spectrum of the standard. These peaks are also observed in the spectra of both of the lysine containing composites. In the AlOOH sample, peaks are seen near 1165, 1071, 737, 610 and 478 cm⁻¹, consistent with previously reported results.²¹ The peaks from AlOOH or GaOOH are

difficult to resolve in the composite materials due to their high level of overlap with the characteristic peaks of the organic material.

3.4 Inductively Coupled Plasma-Mass Spectrometry Aqueous Stability

The leaching characteristics of the nanocrystalline materials and composites were investigated to determine the effect of the surface modification with lysine. Solutions of the various materials encompassed by DI water, soaked over periods of 1, 5 and 7 days, were measured with ICP-MS for Al and Ga leaching concentrations. The initial concentrations of GaOOH, GaOOH-lysine, AlOOH, Al-lysine were 8.7 mg, 9.1 mg, 9.4 mg and 8.6 mg in 10 mL, respectively. Table 1 shows the average and standard deviation. It is observed that the presence of lysine does not reduce the presence of Ga leaching in the GaOOH samples and that these materials are relatively stable over time. In the AlOOH samples, however, the level of Al leached into solution is significantly less for the lysine functionalized composites. Statistical analysis was

performed to determine if leaching levels over time were significantly different. These statistical tests are presented in the supplemental information. The values of leaching observed in the AlOOH were above reported toxicity values of between 50-200 ppb²³ and 9 ppm.²⁴ The values of observed leaching for the AlOOH-lysine composite were below this, indicating the advantage of functionalizing the aluminum containing nanostructures with lysine.

4. Conclusions

An environmentally friendly inorganic synthesis and functionalization process was followed to make GaOOH and AlOOH composites with lysine. Nanostructured forms of the oxide materials were synthesized using a microwave hydrothermal process. The chemical and crystallographic nature of the composite was explored with XPS, FT-IR and XRD. The leaching characteristics of the composites were characterized using ICP-MS of DI water solution over a period of 7 days. The results indicated that the lysine incorporation on the AlOOH nanostructured materials improved the aqueous stability of the particles over a 7 day period. Understanding the effects of surface modification of nanostructured semiconductors provides pivotal information for future implementation of these composites into biomolecule based devices such as bacteriostatic glasses containing Ga.²⁵

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References

1. Kuddannaya, S.; Bao, J. N.; Zhang, Y. L., Enhanced in Vitro Biocompatibility of Chemically Modified Poly(dimethylsiloxane) Surfaces for Stable Adhesion and Long-term Investigation of Brain Cerebral Cortex Cells. *ACS Appl. Mater. Interfaces* **2015**, 7 (45), 25529-25538.
2. Pla-Roca, M.; Isa, L.; Kumar, K.; Reimhult, E., Selective (Bio)Functionalization of Solid-State Nanopores. *ACS Appl. Mater. Interfaces* **2015**, 7 (11), 6030-6035.
3. Shan, C. S.; Yang, H. F.; Han, D. X.; Zhang, Q. X.; Ivaska, A.; Niu, L., Water-Soluble Graphene Covalently Functionalized by Biocompatible Poly-L-lysine. *Langmuir* **2009**, 25 (20), 12030-12033.
4. Alexander, M. R.; Beamson, G.; Blomfield, C. J.; Leggett, G.; Duc, T. M., Interaction of carboxylic acids with the oxyhydroxide surface of aluminium: poly(acrylic acid), acetic acid and propionic acid on pseudoboehmite. *J. Electron Spectrosc. Relat. Phenom.* **2001**, 121 (1-3), 19-32.
5. (a) Shahid, N.; Villate, R. G.; Barron, A. R., Chemically functionalized alumina nanoparticle effect on carbon fiber/epoxy composites. *Compos. Sci. Technol.* **2005**, 65 (14), 2250-2258; (b) Omrani, A.; Simon, L. C.; Rostami, A. A., The effects of alumina nanoparticle on the properties of an epoxy resin system. *Mater. Chem. Phys.* **2009**, 114 (1), 145-150.
6. Zhang, T.; Go, M. A.; Stricker, C.; Daria, V. R.; Tricoli, A., Low-cost photo-responsive nanocarriers by one-step functionalization of flame-made titania agglomerates with L-Lysine. *J. Mat. Chem. B* **2015**, 3 (8), 1677-1687.
7. Shakiba, A.; Jamison, A. C.; Lee, T. R., Poly(L-lysine) Interfaces via Dual Click Reactions on Surface-Bound Custom-Designed Dithiol Adsorbates. *Langmuir* **2015**, 31 (22), 6154-6163.
8. Hussain, N.; Singh, B.; Sakthivel, T.; Florence, A. T., Formulation and stability of surface-tethered DNA-gold-dendron nanoparticles. *Int. J. Pharm.* **2003**, 254 (1), 27-31.
9. Pasche, S.; De Paul, S. M.; Voros, J.; Spencer, N. D.; Textor, M., Poly(L-lysine)-graft-poly(ethylene glycol) assembled monolayers on niobium oxide surfaces: A quantitative study of the influence of polymer interfacial architecture on resistance to protein adsorption by ToF-SIMS and in situ OWLS. *Langmuir* **2003**, 19 (22), 9216-9225.
10. Duan, X. C.; Kim, T.; Li, D.; Ma, J. M.; Zheng, W. J., Understanding the Effect Models of Ionic Liquids in the Synthesis of NH₄-Dw and gamma-AlOOH Nanostructures and Their Conversion into Porous gamma-Al₂O₃. *Chem.-Eur. J.* **2013**, 19 (19), 5924-5937.
11. 이재범; Tai, K. S., Synthesis of AlN powders from AlOOH. *Korean Journal of Materials Research* **2006**, 16 (12), 771-776.
12. Muruganandham, M.; Amutha, R.; Wahed, M.; Ahmmad, B.; Kuroda, Y.; Suri, R. P. S.; Wu, J. J.; Sillanpaa, M. E. T., Controlled Fabrication of alpha-GaOOH and alpha-Ga₂O₃ Self-Assembly and Its Superior Photocatalytic Activity. *J. Phys. Chem. C* **2012**, 116 (1), 44-53.
13. Liu, G. C.; Duan, X. C.; Li, H. B.; Liang, D., Preparation and photoluminescence properties of Eu-doped Ga₂O₃ nanorods. *Mater. Chem. Phys.* **2008**, 110 (2-3), 206-211.
14. Pearce, B. L.; Wilkins, S. J.; Rahn, M. S.; Ivanisevic, A., In situ functionalization of gallium nitride powder with a porphyrin dye. *J. Mater. Res.* **2015**, 30 (19), 2910-2918.

15. Kelsen, D. P.; Alcock, N.; Yeh, S.; Brown, J.; Young, C., PHARMACOKINETICS OF GALLIUM NITRATE IN MAN. *Cancer* **1980**, *46* (9), 2009-2013.
16. Takeno, N., Atlas of Eh-pH diagrams: Intercomparison of thermodynamic databases. Environments, R. C. f. D. G., Ed. National Institute of Advanced Industrial Science and Technology: Japan, 2005.
17. Sun, M.; Li, D. Z.; Zhang, W. J.; Fu, X. Z.; Shao, Y.; Li, W. J.; Xiao, G. C.; He, Y. H., Rapid microwave hydrothermal synthesis of GaOOH nanorods with photocatalytic activity toward aromatic compounds. *Nanotechnology* **2010**, *21* (35).
18. Vogelson, C. T.; Koide, Y.; Alemany, L. B.; Barron, A. R., Inorganic-organic hybrid and composite resin materials using carboxylate-alumoxanes as functionalized cross-linking agents. *Chem. Mat.* **2000**, *12* (3), 795-804.
19. Niedzialkowski, P.; Ossowski, T.; Zieba, P.; Cirocka, A.; Rochowski, P.; Pogorzelski, S. J.; Ryl, J.; Sobaszek, M.; Bogdanowicz, R., Poly-L-lysine-modified boron-doped diamond electrodes for the amperometric detection of nucleic acid bases. *J. Electroanal. Chem.* **2015**, *756*, 84-93.
20. Huang, C. C.; Yeh, C. S.; Ho, C. J., Laser ablation synthesis of spindle-like gallium oxide hydroxide nanoparticles with the presence of cationic cetyltrimethylammonium bromide. *J. Phys. Chem. B* **2004**, *108* (16), 4940-4945.
21. Music, S.; Dragcevic, D.; Popovic, S.; Vdovic, N., Microstructural properties of boehmite formed under hydrothermal conditions. *Mater. Sci. Eng. B-Solid State Mater. Adv. Technol.* **1998**, *52* (2-3), 145-153.
22. Zhao, Y. Y.; Frost, R. L.; Yang, J.; Martens, W. N., Size and morphology control of gallium oxide hydroxide GaO(OH), nano- to micro-sized particles by soft-chemistry route without surfactant. *J. Phys. Chem. C* **2008**, *112* (10), 3568-3579.
23. Willhite, C. C.; Ball, G. L.; McLellan, C. J., Total allowable concentrations of monomeric inorganic aluminum and hydrated aluminum silicates in drinking water. *Crit. Rev. Toxicol.* **2012**, *42* (5), 358-442.
24. Water, O., 2012 Edition of the Drinking Water Standards and Health Advisories.
25. Mourino, V.; Newby, P.; Pishbin, F.; Cattalini, J. P.; Lucangioli, S.; Boccaccini, A. R., Physicochemical, biological and drug-release properties of gallium crosslinked alginate/nanoparticulate bioactive glass composite films. *Soft Matter* **2011**, *7* (14), 6705-6712.

Figure Captions

Figure 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.

Figure 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.

Figure 3. Depicted are the high resolution XPS spectra of various samples for a) Al 2p, b) Ga 2p and c) N 1s.

Figure 4. Shown are the FT-IR spectra of the various samples including the L-lysine standard, the AlOOH and GaOOH composites and the clean nanostructure materials.

Tables

Table 1. Displayed is the ICP-MS data for Day 1, 5 and 7 of the various solutions of the submerged materials and the measured Ga or Al concentrations and percent of starting material leached.

Sample Type	Day 1		Day 5		Day 7	
	Ga Concentration (ppm)	Percent Leached (%)	Ga Concentration (ppm)	Percent Leached (%)	Ga Concentration (ppm)	Percent Leached (%)
GaOOH	1.487±0.036	0.2517±0.0060	1.187±0.036	0.2011±0.0054	1.092±0.024	0.1849±0.0040
GaOOH-Lysine	6.400±0.030	2.521±0.012	6.86±0.17	2.691±0.065	7.400±0.054	2.920±0.021
	Al Concentration (ppm)	Percent Leached (%)	Al Concentration (ppm)	Percent Leached (%)	Al Concentration (ppm)	Percent Leached (%)
AlOOH	24±20	5.6±4.7	31±16	7.7±3.9	25±22	6.0±5.2
AlOOH-Lysine	0.49±0.24	0.43±0.22	0.2093±0.0049	0.1860±0.0043	0.2110±0.0013	0.1885±0.0045