Nanostructured Oxides Containing Ga: Materials with Unique Properties for Aqueous-Based Applications

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ABSTRACT: Oxides containing Ga have been studied by various research communities due to their stability under harsh conditions as well as conductivity and luminescence properties. Nanostructured forms of such oxides can be fabricated by a variety of methods. Advances in synthesis approaches have focused on control over size and shape that can permit adaptation in applied interfaces related to medicine, energy, and the environment. Chemical functionalization can enhance the stability of nanostructured oxides containing Ga in aqueous solutions. In this prospective, we summarize progress in making these materials as well as functionalizing them in water solutions. The prospective also identifies future opportunities with these materials in applied and fundamental materials chemistry research.

I. INTRODUCTION

Prior to this decade, Ga containing materials have been predominantly used in microelectronics. For instance, the optoelectronics community is currently addressing the need to produce single crystal Ga2O3 with specific characteristics (i.e., p-type doping and improved thermal conductivity) that are essential for fabricating devices for power electronics.1 However, advances in the synthesis of nanostructured Ga-based oxide materials has expanded their utility.2,3 Currently, there is an emphasis on understanding their properties in the context of catalysis,4 sensors,5 and biomedical modalities,6 such as targeted drug delivery, chemo/thermal/photodynamic therapy, and in vivo imaging. Properties of particular interest include unique conductivity7 and photoluminescence.8 Additionally, these nanostructured oxides are often incorporated into specific processing where cost-effective, large scale production is essential along with chemical and thermal stabilities over broad ranges and conditions9 as well as high transparency and tunable luminescence.

The potential applications of these materials have prompted a number of efforts to improve the materials’ synthesis using several general routes. Table 1. Ga-based oxides have been primarily studied in two forms: Ga2O3 and GaOOH. Recent work has focused on controlling their size, aspect ratio, as well as processing-based parameters, such as the use or elimination of surfactant during synthesis in the solution. The prospective will focus on the challenges and opportunities associated with not only making these materials but also modifying them via chemical functionalization.10 Additional surface chemistry on Ga2O3 and GaOOH can improve their stability in aqueous solutions.11 However, surface passivation is not the only motivation for the development of surface chemistry routes to alter them. Additional optical properties that can change include photoluminescence12 and persistent photoluminescence.13

There are unique materials chemistry aspects that one needs to consider in tailoring the properties of Ga2O3 and GaOOH in aqueous-based applications. For example, as-synthesized Ga2O3 and GaOOH are negatively charged, and their surface can readily be coronated by proteins when introduced into the conditions associated with in vitro or in vivo studies. Furthermore, already modified Ga2O3 and GaOOH nanostructured particles can experience dissociation of weakly bound ligands in aqueous solutions under different temperatures and pHs. This dissociation can lead to agglomeration, alter desired properties, and lead to irreproducibility during processing procedures. Combined computational and experimental studies have highlighted the importance of surface structure and reactivity of the oxide surface with respect to stability of specific ligand attachment in water.14 This prospective will appeal to a wide audience due to the emerging use in Ga2O3 and GaOOH in many fields where low inorganic materials’ toxicity and preparation in environmentally friendly solvents such as water is desired. We summarize current efforts to improve the utility of Ga containing oxides in aqueous solutions to achieve desired stability as well as optical characteristics that are needed in areas ranging from environmental monitoring in extremely harsh environments to solution-based biochemical sensors.

II. SYNTHESIS OF GA CONTAINING OXIDES

Table 1 summarizes representative examples of Ga containing oxides that have been reported in the literature. In several instances, these oxides are subsequently converted to other products (i.e., GaN). A few of the synthesis methods offer...
Table 1. Summary of Representative Methods Used to Fabricate Ga Containing Oxides

| product | precursors | processing technique | refs |
|---------|------------|----------------------|------|
| mixed oxyhydroxide | metal nitrates, weak base | sol−gel/hydrothermal | 12, 35, 36 |
| Ga₂O₃:MO₂ | metal nitrates, Si(OCH₃)₄, Ti(OCH₃)₄ | sol−gel | 37, 33 |
| Dy–β-Ga₂O₃ | Dy₂O₃ , β–Ga₂O₃ , citric acid (C₆H₈O₇) , poly(ethylene glycol) | sol−gel 75 °C | 38 |
| β–Ga₂O₃ | β–Ga₂O₃ | single crystal growth | 39 |
| β–Ga₂O₃ | GaAs, N ion, air (oxygen) | ion implantation | 40, 41 |
| β–Ga₂O₃ | GaCl₃, NaOH | combustion synthesis | 20, 42–46 |
| γ–Ga₂O₃ | Ga metal, (patterned p-Si substrate), (Au NP) | chemical vapor deposition | 47, 48, 3, 5, 49–51 |
| γ–Ga₂O₃ | Ga salt, base | hydrothermal → calcination | 52, 8 |
| γ–Ga₂O₃ | Ga salt, base, organic template | wet chemistry (template optional) | 53–55, 27 |
| eutectic-GaIn, Ga | Ga, In, organic stabilizing ligand (thiol, phenol) | liquid metal ultrasonication | 30, 56, 32 |
| eutectic-GaIn | In, Ga | high temperature oxidation | 29 |
| Gd–Al–Ga₂O₃ | Gd₂O₃, Ga₂O₃, (NH₄)Al(SO₄)₂, HNO₃, NH₃, NH₄HCO₃ | co-precipitation | 57 |
| GaON | Ga(NO₃)₃, (CH₂)₆N₄ | hydrothermal | 9 |
| GaOOH | Ga metal | laser ablation | 58 |
| GaOOH | GaCl₃ | sonochemical | 59 |
| GaOOH | GaN | ball mill | 60 |
| GaOOH | Ga(NO₃)₃, (NaOH) | hydrothermal | 16, 61–64, 2 |
| GaOOH | Ga metal | ultrasonication | 4 |
| GaZnON | Ga₂O₃, ZnO, HCl, NaOH, Na₂CO₃ | hydrothermal | 65 |
| In/Ga/InGa oxide | In, Ga, lysozyme | hydrothermal with surfactant | 31 |
| LaGaO₃ | La, Ga, C₅H₇O₂ | chemical vapor synthesis | 66 |
| Nd:Gd–Ga₂O₃ | Ga₂O₃, Gd₂O₃, Nd₂O₃ | microwave combustion of gel | 67 |

Table 2. Summary of Representative Sizes and Shapes of Reported Ga Containing Oxides along with Methods for Their Characterization

| Ga containing oxide | shape | size | analytical characterization | refs |
|---------------------|-------|------|-----------------------------|------|
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | sphere | 2–15 nm | A, B, D, E, F, N, P, R, S, T, U, †, ‡ | 37, 32 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | sphere | 15–80 nm | A, B, D, E, F, P, R, S, T | 43, 35 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | sphere | 100–200 nm | D, F, N, P, R, S, T, U, †, ‡ | 55 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | rice/orzo | 200 nm to 1 μm length | D, F, I, S, T | 68 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | rice/orzo | 1–4 μm | D, E, F, P, S, U, †, ‡ | 54 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | rod | 80 × 30 nm length × width | D, †, ‡ | 69 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | rod | 200–1000 × 50–100 nm | D, P, R, U, †, ‡ | 70 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | rod | 1–4 μm × 100–500 nm | D, E, F, N, P, R, S, U, †, ‡ | 54 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | wire/needle | 30–100 nm diameter | D, P, R, S, †, ‡ | 47 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | wire/needle | 200–500 nm diameter | D, I, L, P, S | 5 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | knotted chain | knots 400 nm, spindle 50 nm | D, E, S, T, † | 49 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | ribbon | 1–3 μm wide | P, R, S, † | 41 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | ribbon | 10 μm wide | R | 50 |
| β–Ga₂O₃ or β–Ga₂O₃:MyOx | plate | 8 mm | D, S | 39 |
| Ga oxides on liquid metal | sphere | 1–2 nm | S, † | 30 |
| Ga oxides on liquid metal | sphere | 30–50 nm | E, S, T, ‡ | 31 |
| Ga oxides on liquid metal | sphere | 1–5 μm | E, M, S, †, ‡ | 29 |
| GaOOH | spindles | 1–2 μm | D, F, U | 71 |
| GaOOH | rice/orzo | 250 × 450 nm | D, F, N, † | 58 |
| GaOOH | rice/orzo | 1–2 μm | D, F, U | 72 |
| GaOOH | rod | 500–1000 nm | D, E, F, N, S, T, †, ‡ | 53 |
| GaOOH | rod | 100–200 nm | D, F, P, S, U, †, ‡ | 60 |
| GaOOH | wire/needle | 3–1.5 μm × 300–500 nm | D, U, † | 61 |
| GaZnON | porous surface | 50–100 nm diameter | D, P, T, U, † | 65 |
| GaON | spheroid | 50–80 nm crystallite | D, † | 9 |
| Ga–Al–Ga₂O₃ | rough sphere | 10–2 nm | D, F, S, U, † | 57 |
| Nd:Gd–Ga₂O₃ | sphere/dendrite | 30 nm | D, F, S | 67 |

“A–Absorption/emission, B–Brunauer–Emmett–Teller, D–X-ray diffraction, E–energy dispersive X-ray, F–Fourier transform infrared spectroscopy, I–inductively coupled plasma mass spectroscopy, L–dynamic light scattering, M–atomic force microscopy, N–nuclear magnetic resonance, P–photoluminescence, R–Raman, S–scanning electron microscopy, T–transmission electron microscopy, U–ultraviolet visible spectroscopy, †–X-ray photoelectron spectroscopy, ‡–selected area electron diffraction, L–differential scanning calorimetry-thermal gravimetric analysis.

specific advantages when adapting Ga containing oxides for aqueous-based applications. A number of reports describe solution-based techniques resulting in Ga containing nanostructured materials. Examples include microemulsion, sol–gel,
hydrothermal, and ultrasonic-assisted fabrication. Furthermore, researchers have performed the hydrothermal synthesis under microwave radiation in an effort to improve final yield while reducing reaction times. Column 2 of Table 1 identifies metal nitrate salts as one of the more commonly used precursors to make these materials. The formation of the final materials proceeds in two steps where a hydrolysis of the salt results in the formation of a metal hydroxide. Subsequently, the hydroxide is dehydrated, a precipitate is observed, and further drying yields the metal oxide. The two reactions are summarized, as described by Hayashi et al.15

\[
\text{M(NO}_3\text{)}_x + x\text{H}_2\text{O} \rightarrow \text{M(OH)}_x + x\text{HNO}_3
\]  

(1)

\[
\text{M(OH)}_x \rightarrow \text{MO}_{x/2} + \frac{x}{2}\text{H}_2\text{O}
\]  

(2)

Surfactant molecules have also been utilized during the synthesis of these materials. During this process, the surfactant is used together with a stabilizer often referred to as an emulsifier. The molecule chosen as a stabilizer has a polar head group and nonpolar tail. During the synthesis of the Ga containing oxides, the surfactant, and emulsifier are mixed together with the metal salt precursors. As the mixture is formed, the emulsifier is using its nonpolar tail to face toward the surfactant, whereas its polar head group orients toward the aqueous solution containing the precursor materials. During this process, the size and shape of the Ga containing oxide are controlled by the emulsifier which is around the reaction solution where the product crystallizes.

Another methodology used to control the size of Ga containing particles is via a sol–gel where a polymerization reaction takes place. The chosen precursor materials identified in Table 1 form gels through a hydrolysis reaction. One can tune the size of the particles by controlling the rate of the hydrolysis reaction in addition to any condensation that might take place. A drawback of this methodology is the need to remove solvents by calcination which requires elevated temperatures. A methodology that does not require any additional heat or pressure is the sonochemical route where chemical reactions are initiated by ultrasonic radiation. The use of ultrasound promotes the formation of bubbles in the solution which continue to grow until they collapse. These bubbles are thought to produce extremely high temperatures during the process of their collapse which are then rapidly cooled back to the ambient solution temperature.

By far, the most widely used route to make Ga containing oxides in a number of papers is the traditional hydrothermal synthesis technique where a solution of precursors is sealed and placed into an autoclave. The reaction can take up to 24 h. However, if one replaces the autoclave with a microwave, these reactions can be done in less than an hour. Additional advantages include is the elimination of the need for a surfactant and the use of deionized water as a solvent. Literature sources cite the reduced reaction time as the key advantage of the microwave synthesis.

Many of the summarized synthetic methods have focused on controlling shape and size. Table 2 lists the ranges of sizes and examples of shapes reported in the literature. The use of general terms such as “base” or “weak base” is intended to denote that a wide range of chemicals can be used to perform the synthesis. The Ga containing oxide particles dimensions and geometrical variations have been linked to specific properties quantified by a wealth of analytical techniques listed in the last column of the table. In addition to control the over surface to volume ratios, size and shape have been linked to a number of anisotropy-dependent properties. Ga containing oxides can adopt different shapes during the different synthesis steps and show shape-dependent stability in aqueous solutions. Differences in stability are particularly noteworthy in complex biological solutions where release of Ga ions can lead to variable physiological responses of cells.16 In addition to stability, the thermal, spectral, and photocatalytic properties of Ga containing nanostructure are also size and shape dependent.17 β-Ga$_2$O$_3$ nanobelts obtained via mechanical exfoliation under room temperature and humidity conditions have been incorporated into devices that show remarkable radiation tolerance.18 Many of the spectroscopic studies summarized in Table 2 have examined the role of water hydrogen bonded to the Ga$_2$O$_3$- and GaOOH- nanostructured materials. Infrared bands associated with bonding to hydroxyl units are reported to be sensitive to synthesis conditions.19 Additional spectroscopic studies have concluded that the luminescence of these materials is nanocrystalline size dependent, and the location of the emission peak is in the blue-green region.20 The intensity and the broadness of the emission peak of Ga containing oxides are not altered in aqueous solutions, and its after-glow or persistent luminescent properties are showing promise in preclinical in vitro and in vivo imaging studies.21

Figure 1. Possible binding modes of thiol (1), carboxylic acid (2), and phosphonic acid adsorbates (3: monodentate; 4, 6: bidentate; 5: tridentate) to surfaces terminated on Ga containing oxides.
Chemical functionalization not only improves the stability of Ga containing oxides in aqueous solutions but can also add to their functionality by tailoring properties such as emission and chemical recognition. Certain surface planes have been shown to be more stable than others as is the case for $\beta$-Ga$_2$O$_3$(100)-B which can lead to difficulties in the development of successful functionalization routes. In many instances, the hydroxide groups present on the surface have proven effective moieties for the covalent modification of the surface with a number of moieties. Typical adsorbates considered in the literature include thiols, alcohols, carboxylic acid, and phosphonic acid derivatives. Some of these adsorbates can engage in various modes of binding to the Ga oxide containing surface, Figure 1. The desired chemisorption can be accomplished ex situ by taking the already made nanostructured Ga containing oxide and exposing it to the chosen adsorbate. Procedures can focus on tuning incubation times, temperature, and ligand concentration. The mode of binding of each type of adsorbate is dependent on what type of surface structure is energetically more favorable, though experimental results report observations of multiple modes of binding with specific ligands.

With respect to functionalization, recent work has focused on a different approach to modify the nanostructured Ga containing oxides. The so-called in situ procedure modifies the material during the synthesis. Several advantages are cited including ease of preparation, shorter time needed to prepare the final product, and the use of water as a solvent when the Ga salt precursor is mixed with a solution containing water soluble adsorbates with functional groups that have an affinity for the oxide. During the in situ protocol, it is important to consider the Pourbaix diagram for Ga. This element is passivated in small pH windows, and during the in situ procedure varying pH values can result in leaching of Ga.

During the in situ procedure, as the Ga$_2$O$_3$ or GaOOH is formed, the inherent presence of oxides eliminates the need for an etchant which is required for the in situ modification of other Ga containing materials, such as GaN. This process represents a highly scalable and environmentally friendly technique for forming organic/inorganic hybrids with long term interface stability. Representative literature reports have used cyclo-dextrin, phosphonic acid, and carboxylic acid derivatives for in situ functionalization of Ga-containing oxides. In the cases of phosphonic acid derivatives, the passivation achieved via the in situ procedure resulted in exceptional ligand stability compared to passivation done ex situ. Water soluble dye molecules with carboxylic acid moieties have been also utilized to modify GaOOH in situ and ex situ. In contrast to other organic acid derivatives the ones containing carboxylic acids showed excellent stability in water regardless of what method was used for their preparation. These results support the notion that carboxylic acid derivatives have greater affinity for Ga containing oxides surfaces compared to other ligands with other functional groups.

It is important to note in the context of in situ functionalization of Ga containing oxides the recent interest in understanding of how to control the complex oxides that include gallium when nanostructured materials are formed from liquid metals. Representative ligands used to control the synthesis of these materials and to modify the nanostructured Ga containing oxide shell of these materials include: thiols, cetrionium bromide, poly(4-vinyl-1-methyl-pyridinium bromide), lysozyme, oleic acid, and dodecylamine. Not all studies have focused on understanding the nature of the bonding between the oxide and the chosen ligand, but they have all demonstrated that the ligands do control the desired shape and size.

**IV. APPLIED INTERFACES BASED ON GA CONTAINING OXIDES IN AQUEOUS SOLUTIONS**

We highlight three recent examples published in the last 20 months of incorporating Ga containing oxides in interfaces that benefit from preparation or use in aqueous solutions. The chosen examples are representative of the unique properties associated with the oxides. We have specifically chosen examples that derive the materials through methods other than liquid metal approaches because these have been the subject of other recent extensive reviews in the literature.

The synthesis of metal oxides is often motivated by their potential to perform better in photocatalytic applications. Ismail et al. have prepared mesoporous Ga$_2$O$_3$−TiO$_2$ nanocomposites and have demonstrated its efficient photodecomposition of a herbicide. The method used to make the Ga containing oxide is based on the solution−gel in the presence of copolymer. The amount of Ga$_2$O$_3$ was tuned during the synthesis by controlling the starting amount of Ga salt used. The unique structure and composition of the composite contributed to its mechanism of action, Figure 2A. Specifically, the increased amounts of defects associated with a large content of Ga$_2$O$_3$ is attributed to superior ability to trap holes and prevent recombination. The authors concluded that the improved photocatalytic performance can be traced to the greater number of acceptor states with respect to Ga$_2$O$_3$ present in the amorphous phase. This conclusion was supported by luminescence measurements. Additional attributes of the Ga containing oxide composite are fabrication reproducibility and stability of the water, as well as the fact that it can be recycled in multiple cycle while maintaining high efficiency.

Nanostructured Ga containing oxides have recently shown promise in lithium-ion batteries. The methodology is depicted in Figure 2B. We summarize key features associated with the use of Ga oxides in this example. The particles are prepared via a hydrothermal carbonization method that controls their size to 2.6 nm and ensures the formation of a carbon shell around each particle. The key feature is that during the lithiation process the carbon shell prevents the particles from aggregation. Because lithium-ion batteries are intended to be rechargeable, stability and lack of aggregates is key during the cycling evaluation of anode and cathode materials. The reported Ga$_2$O$_3$ based anode showed superior characteristics due to its ability to prevent the formation of surface aggregates while still forming Ga during the lithiation process.

In biomedical applications ability to control the optical properties of nanostructured materials is valuable in designing imaging and targeting applications. Nanostructured Ga containing oxides show particularly noteworthy promise for these applications due to their persistent luminescence properties. A recent advance in particle design showed that nanostructured particles with hollow cavities that are decorated with Ga oxides show an afterglow effect due to their persistent photoluminescence, Figure 2C. These Ga oxide-containing particles are amenable to other aqueous solution processing that can enhance their chemo and photodynamic attributes, in addition to the promise they show in imaging. Most importantly for these types of applications the particle stability was verified in...
functional groups. Taken together current and future advances in the field of Ga containing oxides are projected to increase their potential for practical applications.

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Figure 2. Recent applied studies with Ga containing oxides: (A) mesoporous Ga2O3−TiO2 nanocomposite for efficient photodecomposition of herbicide imazapyr (copyright 2018 Elsevier); (B) fabrication and testing of Ga2O3 anode for lithium-ion batteries (copyright 2018 American Chemical Society); (C) persistent luminescent nanoparticles containing Ga oxides that can be used in cancer theranostic applications after chemical functionalization (copyright 2018 American Chemical Society).
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