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Gallium Nanoparticle Formation and Doping of Nanocrystalline Alumina from a Ga−Al Liquid Metal Hydrogen Generating Reaction

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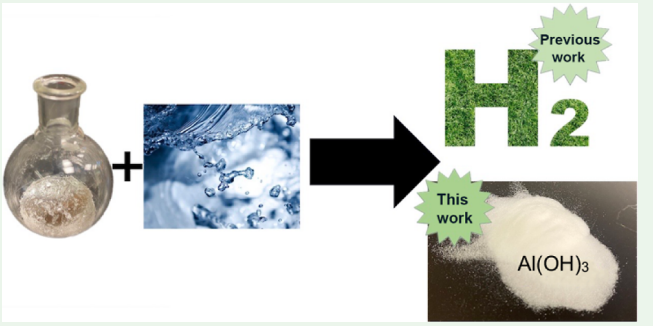
ABSTRACT: We report a liquid metal gallium−aluminum (Ga−Al) composite water splitting reaction, where gallium nanoparticles (Ga NPs) and nanocrystalline aluminum hydroxide [$Al(OH)_3$] are generated simultaneously with the coproduction of green H_2 fuel. This reaction involves the formation of Ga NPs originating from Lewis acid−base nanoclusters composed of Ga and Al NPs. The initial Ga−Al NP liquid composite possesses the ability to cleave the H−O−H bonds of water, resulting in the formation of Ga−H and Al−OH bonds. Under ambient conditions, the Ga−H bonds subsequently metathesize into Ga NPs and H_2. Interestingly, these Ga NPs undergo gradual oxidation in air, resulting in the doping of the nanoaluminum hydroxide byproduct. Remarkably, this reaction occurs under atmospheric conditions without the need for caustic chemicals, electrolysis, reverse osmosis, inert atmosphere, or external energy input. The reaction products were characterized using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), powder X-ray diffraction (PXRD), and inductively coupled plasma-optical emission spectroscopy (ICP-OES). We further investigated the influence of various reaction conditions, such as composition of the binary alloy, volume of water used, and temperature, on the resulting byproducts. The nano-$Al(OH)_3$ byproduct could be successfully calcined to value-added nanocrystalline α-Al_2O_3 at 1100 °C.



KEYWORDS: *gallium nanoparticles, hydrogen generation, aluminum nanoparticles, liquid metal composite, water splitting, bayerite, aluminum hydroxide*

INTRODUCTION

The development of efficient ways to split water for the generation of hydrogen gas (H_2) is essential for the widespread adoption of a hydrogen economy. Currently, over 95% of H_2 production relies on fossil fuels, such as the steam reforming of natural gas.[1] Unfortunately, this process also produces large quantities of carbon dioxide, greatly offsetting the environmental benefits of H_2.[2] The gravimetric energy density of H_2 is 120 MJ/kg, and the sole combustion product is water.[3] The gravimetric energy density of gasoline is only 44 MJ/kg, while being highly polluting.[4] The volumetric energy density of H_2 at 700 bar, the typical on-board gas storage pressure for H_2 fueled vehicles, is only 5.6 MJ/L and is far less than the 32.0 MJ/L for gasoline.[5] Nevertheless, H_2 holds immense promise for the widespread production of clean energy.

An unadopted method for potential H_2 generation utilizes Al metal, which is capable of spontaneously splitting water to produce H_2 fuel and nano-$Al(OH)_3$ as a byproduct.[6−8] Common Al products do not undergo this reaction due to its passivating oxide layer that prevents water from contacting the pure Al metal.[9] If this passivating layer is removed, then water can freely react with Al to produce hydrogen gas and nano-$Al(OH)_3$. A simple and effective way to remove the passivating oxide layer and produce Al nanoparticles is to dissolve Al metal in liquid gallium (Ga) to form a gallium−aluminum (Ga−Al) binary composite.

We recently reported that liquid Ga metal breaks up bulk Al metal into Al nanoparticles free of any passivating oxide layer.[10] The Al nanoparticles function as a Lewis acid−base pair, reacting with water *via* a Grotthuss mechanism.[11−14] This reaction produces byproduct hydrated Al [$Al(OH)_3$ and AlO(OH)], which are important industrial commodities. They are the raw materials for Al metal in addition to alpha alumina (α-Al_2O_3), which has vast and diverse applications ranging from ceramics and catalysis to packaging and electronics.[15−17] At present, all primary Al productions relies on the Bayer process for extracting $Al(OH)_3$ from bauxite ore. This highly polluting and energy-intensive process requires caustic chemicals that produce vast pools of environmentally

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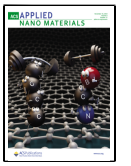
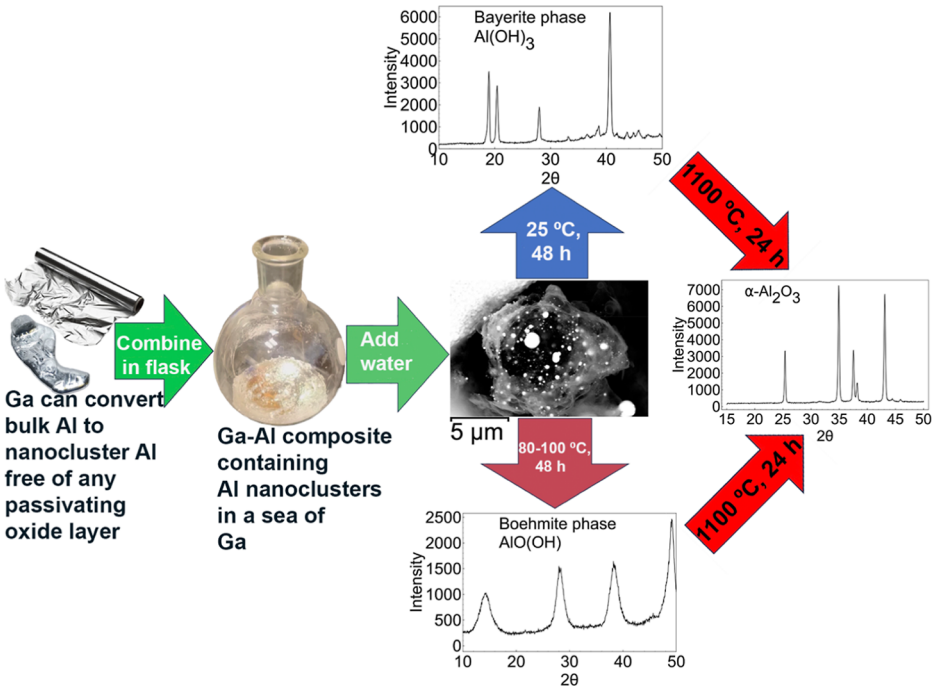


Scheme 1. Schematic Diagram Showing the Initially Formed Ga NP/Hydrated Aluminum Hydrogel Formed when Ga−Al Composites are Combined With Water and How Reaction Conditions Effect By-Product Formation



toxic red mud.[18] The process ultimately isolates Al from bauxite ore as gibbsite phase $Al(OH)_3$, which can then be calcined to industrially valuable α-Al_2O_3.[19]

Water splitting *via* a Ga−Al composite offers a nonpolluting route to nano-$Al(OH)_3$ from postconsumer Al, in addition to producing economically and environmentally valuable H_2 fuel.[10] The reaction also serves as a simple and quick method for the synthesis of Ga NPs, which, in addition to other liquid metal nanoparticles, have attracted attention in a wide variety of fields from biomedicine to catalysis.[20−26] Additionally, the current literature lacks a comprehensive investigation into the production of aluminum hydroxide/oxyhydroxide through liquid metal water splitting reactions, particularly involving simple and efficient binary Ga−Al composites (Scheme 1).

Our binary metal composites offer a sustainable and environmentally friendly approach to produce H_2 and obtain valuable nano-$Al(OH)_3$ or nano-AlO(OH) with the coproduction of Ga NPs, all achieved without the need for corrosive chemicals, electrolytic solutions, electrolyzers, reverse osmosis, or elevated temperature/pressure. Herein, we report a comprehensive analysis of the intricate process involved in the synthesis of nano-$Al(OH)_3$ and nano-AlO(OH) with the simultaneous production of Ga nanoparticles (Ga NPs) under various reaction conditions. Our investigation focuses on elucidating the oxidation behavior of the generated Ga NPs and their consequential impact on the doping of byproduct nano-$Al(OH)_3$ and subsequently calcined α-Al_2O_3.

EXPERIMENTAL SECTION

Materials. All chemicals and reagents were purchased and used without further purification. Ga ingot (99.99% metal basis) was purchased from Alfa Aesar. Reynold's brand Aluminum foil, free of any nonstick chemicals, was purchased from a local supermarket. $GaCl_3$ (99.99% trace metal basis) was purchased from Thermo Scientific. $NaBH_4$ powder was purchased from Fisher Scientific. Lab grade $Al(OH)_3$ was purchased from Fisher Science Education. CaH_2 was purchased from Oakwood Chemical. Dry tetrahydrofuran (THF) was obtained by passing previously degassed THF through activated alumina columns. Pyridine, of ACS grade, was supplied by Acros Organics.

Characterization. PXRD was measured on a Rigaku Americas Miniflex Plus diffractometer with a scan rate of 2°·min^{-1} and a 0.04° step size using 13 kV, 15 mA Cu Kα radiation (λ = 1.5418 Å). Samples were imaged in an FEI Quanta 3D Dualbeam SEM operating at 10 kV and 11.7 pA equipped with both secondary electron and STEM detectors. SEM-EDS was performed using a Thermo Scientific Apreo scanning electron microscope with an EDS attachment operating at 20 kV and 1 nA. Quantitative elemental analysis was carried out using a Thermo iCap 7400 radial view ICP-OES after sample digestion with conc. HCl followed by dilution to within the dynamic range. A Lindberg/Blue M tube furnace was used for sample calcination. ^{11}B NMR was performed by using a Bruker 500 MHz spectrometer at 25 °C using a composite pulse sequence. Signals were recorded at 160, 500, and 152 MHz for ^{11}B, ^{1}H, and ^{71}Ga, respectively. ^{11}B, ^{1}H, and ^{71}Ga NMR chemical shifts were measured relative to the external standards BF_3:OEt_2 (δ = 0 ppm), TMS (δ = 0 ppm), and $Ga(NO_3)_3$ (δ = 0 ppm), respectively.

General Procedure to Prepare the Ga−Al Composite. For the production of a 3:1 atom % Ga/Al composite, to a 50 mL round-bottom flask was added loosely crumpled aluminum foil (0.108 g, 4.0 mmol) was added. Gallium metal (0.837 g, 12 mmol) was briefly heated using a heat gun until it became a liquid and was added using a syringe to the same flask. The crumpled foil was then mixed into the gallium with a combination of pressing and stirring for 3 min or until the composite appeared as a homogeneous shiny coating on the bottom of the flask. Mixing over a heat gun on low heat ensured that the composite remained liquid during preparation. This procedure was also used to prepare Ga/Al composites of 6:1, 1:1, and 1:2 atom %.

Method for Ga NP and H_2 Production Using Gallium Chloride ($GaCl_3$) and Sodium Borohydride ($NaBH_4$). Under a nitrogen atmosphere, solid $GaCl_3$ (0.131 g, 0.75 mmol) and $NaBH_4$ (0.085 g, 2.3 mmol) were added to a two-neck 100 mL round-bottom flask equipped with rubber stoppers. The flask was then placed under positive nitrogen pressure and quickly connected to a buret equipped with a dry ice trap to measure H_2 evolution (Figure S1). The system

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was flushed with nitrogen to remove any air from the flask-buret system. To the 100 mL flask was added 5 mL of dry THF kept over calcium hydride (CaH_2) using a syringe filter to remove any suspended CaH_2. Use caution! The addition of THF to a solid mixture of $GaCl_3$ and $NaBH_4$ can produce diborane (B_2H_6), which can spontaneously explode upon contact with air. For this reason, we advise that THF be added quickly and that the system be thoroughly flushed with an inert gas. Evolution of H_2 ceased approximately 5 min after the addition of THF with a total of 20 mL (0.80 mmol) H_2 produced. The supernatant was transferred to an NMR tube under a nitrogen atmosphere for the ^{11}B NMR analysis. The resultant gray solid was isolated and analyzed using SEM-EDS.

In order to trap GaH_3 and prevent its decomposition at room temperature, $GaCl_3$ (0.334 g, 1.9 mmol) was dissolved in 2 mL of pyridine and added to a pyridine (2 mL) slurry containing $NaBH_4$ (0.215 g, 5.6 mmol) at room temperature. An aliquot (0.1 mL) of the reaction mixture was collected 15 min later and dissolved in $CDCl_3$ (0.5 mL) for analysis by ^{71}Ga and ^{11}B NMR spectroscopy.

Procedure for Monitoring the Effects of Ga−Al Composite Ratio on the Nature of Al Oxide-hydroxide Byproducts. To four separate 100 mL round-bottom flask containing either Ga/Al 6:1 atom %, (3.348 g:0.108 g; 24 mmol:4.0 mmol), 3:1 atom % (0.837 g:0.108 g; 12 mmol:4.0 mmol), 1:1 atom % (0.279 g:0.108 g; 4 mmol:4.0 mmol), or 1:2 atom % (0.279 g:0.216 g; 4.0 mmol:8.0 mmol) composite, 10 mL of deionized (DI) water was added at 25 °C without stirring. Hydrogen gas evolved rapidly upon the addition of water, and the regenerated Ga from the composites was removed after 15 min by supernatant decanting. Isolated Ga was rinsed with DI water and stored in a separate container. The samples were then filtered, and the solid was dried in a vacuum oven connected to the house vacuum (30 Torr) at 100 °C for a minimum of 15 min.

Method for Monitoring the Effects of Reaction Time on the Nature of Al Oxide-hydroxide Byproducts. To a flask containing a Ga/Al (3:1 atom %, 0.837 g:0.108 g; 12 mmol:4.0 mmol) composite, DI water (10 mL) was added at 25 °C without stirring. The regenerated Ga from the reaction mixture was removed 15 min after the addition of water to the composite, rinsed with copious amounts of DI water, and stored in a separate container for reuse. The supernatant suspension was then set aside, without stirring, at 25 °C. Aliquots were withdrawn from the suspension after 24 and 48 h. The aliquots were then filtered, and the solid was dried in a vacuum oven connected to house vacuum at 100 °C and dried for a minimum of 15 min.

Technique for Monitoring the Effects of Volume of Water on the Nature of Al Oxide-hydroxide Byproducts. To four 50 mL flasks containing Ga/Al (3:1 atom %, 0.837 g:0.108 g; 12 mmol:4.0 mmol) composite, 3, 5, 10, or 20 mL of water was added at 25 °C without stirring. Hydrogen gas evolved rapidly, and the regenerated Ga from the composites was removed after 15 min, rinsed with DI water, weighed, and stored in a separate container. The resulting supernatant suspension was then set aside, without stirring, at 25 °C for 48 h, and filtered, and the solid was dried in a vacuum oven at 100 °C for a minimum of 15 min.

Procedure for Monitoring the Effects of Hydrolysis Temperature on the Composition of Al Oxide-hydroxide Byproducts. To five 50 mL flasks containing Ga/Al (3:1 atom %, 0.837 g:0.108 g; 12 mmol:4.0 mmol) composites, DI water (10 mL) was added without stirring and maintained at 25, 40, 60, 80, or 100 °C. The regenerated Ga from the reaction mixture was removed after 15 min, rinsed with copious amounts of DI water, and stored in a separate container. The supernatant suspensions were then set aside, without stirring, at 25, 40, 60, 80, or 100 °C for 48 h and filtered, and the solid was dried in a vacuum oven at 100 °C for a minimum of 15 min.

Method for Isolating the Regenerated Ga from the Reaction Mixture. The regenerated Ga collected at the bottom of the reaction flask as a liquid and was removed from the reaction mixtures at 25 °C by decanting the supernatant. The Ga remaining in the flask was transferred to a glass vial and rinsed with DI water (~10 mL) until it became a shiny solid. Additional scratching of the reaction flask was occasionally necessary to induce solidification.

Recyclability of Composite Ga. To a 50 mL flask containing Ga/Al (3:1 atom %, 0.837 g:0.108 g; 12 mmol:4.0 mmol) composite, DI water (10 mL) was added at 25 °C without stirring. The regenerated Ga from the composite was removed 15 min after water was added and rinsed with DI water, as described above. The supernatant suspension was then set aside, without stirring at 25 °C for 48 h, and was isolated by vacuum filtration and dried in a vacuum oven at 100 °C. Regenerated Ga was recycled from three separate experiments and was used to make three additional Ga/Al (3:1 atom %) composites.

Calcination of Nano-$Al(OH)_3$ and Nano-AlO(OH) to α-Al_2O_3. Approximately 50 mg of either $Al(OH)_3$ or AlO(OH) solid were placed in a ceramic boat in a tube furnace at 1100 °C. The solid was spread out in the boat to maximize the surface area, and all samples were preground using a mortar and pestle. Samples were not further ground when PXRD was used to check the status of calcination at 2 and 24 h.

RESULTS AND DISCUSSION

Formation of Gallium Nanoparticles and Gallium Doping in Byproduct Aluminum Hydroxide. Our recent report describing the generation of green hydrogen has significant potential for the hydrogen economy.[10] While the hydrogen-generating portion of this reaction has been explored, a detailed investigation into the nature of the byproduct(s) under various conditions has remained unexplored. The Ga−Al composites are produced directly in a round-bottom flask by using a spatula to press lightly crumpled spheres of Al foil into a bead of liquid Ga. Immediately upon the addition of water to the Ga/Al composite, the supernatant became a dark gray-colored suspension. The hydrated aluminum byproducts of the reaction [$Al(OH)_3$ and AlO(OH)] are white solids and thus do not account for the gray color of the reaction mixture, which gradually turns white over approximately 48 h. This intriguing observation warranted further analysis of the gray solids using SEM-EDS. It was determined the color does not originate from any Al-based byproduct but is due to Ga NPs as evidenced by SEM-EDS (Figure 1). Additional SEM micrographs showed distinct Ga NPs with a wide range of sizes (Figure S2) suspended in the bayerite hydrogel collected 15 min after water was added to the composite.

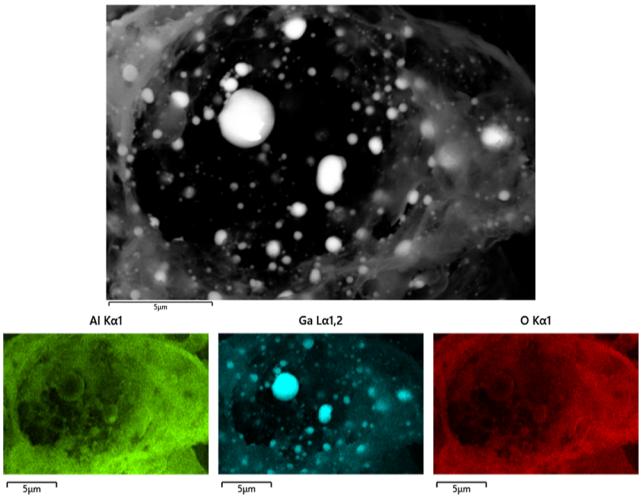

Figure 1. SEM-EDS images showing Ga NPs suspended in a bayerite hydrogel 15 min after water was introduced to the composite (Al: green; Ga: cyan; O: red).

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These Ga NPs likely originated from a side reaction produced by Lewis acid−base pairs of Al and Ga nanoclusters formed when the binary-metal composites were made. We propose Ga and Al nanoclusters can split water by polarizing the H−O−H bonds of H_2O, resulting in new Ga−H and Al−OH bonds on the surface of the nanoclusters, analogous to the Al Lewis acid−base pair splitting of water previously reported.[11−14] Repetition of this process an additional two times can result in the formation of gallane (GaH_3) and $Al(OH)_3$. We suggest that Ga−H bonds of GaH_3 subsequently metathesize into Ga NPs and H_2, as established in literature.[27−29]

To verify the plausibility of this pathway to Ga NPs from the corresponding hydride, we carried out a novel reaction in which gallium chloride ($GaCl_3$) and sodium borohydride ($NaBH_4$) were combined at 25 °C in THF. We anticipated that $NaBH_4$ could reduce $GaCl_3$ to GaH_3 and simultaneously form BH_3:THF. The GaH_3 thus formed was expected to decompose to Ga metal NPs and H_2 at room temperature. This new reaction proceeded as predicted and afforded Ga NPs and BH_3:THF at room temperature. In this event, combining $GaCl_3$ and $NaBH_4$ in THF immediately evolved H_2 gas, followed by the formation of a gray precipitate. SEM showed that the gray solid is composed of Ga NPs (Figure 2),

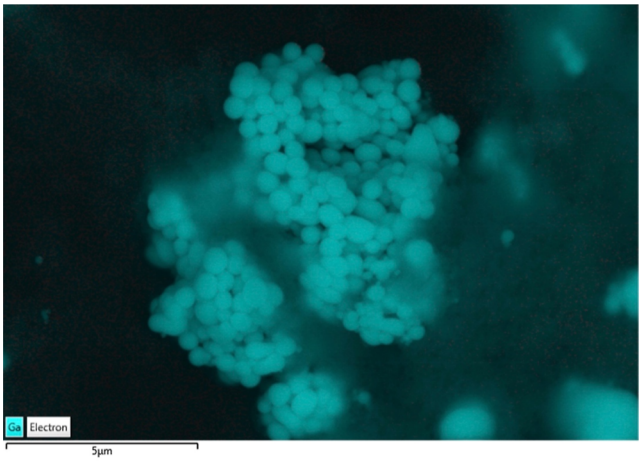

Figure 2. SEM-EDS micrograph of the Ga NPs resulting from the addition of THF to a solid mixture of $GaCl_3$ and $NaBH_4$ (Ga: cyan).

and ^{11}B NMR of the supernatant solution showed the presence of BH_3:THF (Figure S3). This is tenable evidence that GaH_3 is produced from the Ga−Al composite water splitting reaction and is responsible for the formation of the Ga NPs observed in the reaction. Further evidence for the formation of GaH_3 from the reaction between the Ga−Al composite and water was given by an additional novel reaction between $NaBH_4$ and $GaCl_3$ in a pyridine solvent. These conditions allowed GaH_3 to be trapped by pyridine as a GaH_3:pyridine adduct at room temperature and was observed using ^{71}Ga NMR (Figure S4).

As the supernatant suspension is allowed to age, it is gradually transforms from gray to white, and the SEM-EDS imaging showed the initial Ga NPs are absent in the supernatant suspension after 48 h (Figure 3). Additionally, EDS mapping showed Ga evenly distributed among the byproduct bayerite (Figure 3). Another sample is shown at a higher magnification in Figure S5. EDS is a reliable technique for mapping Al, Ga, and O since electronic transitions

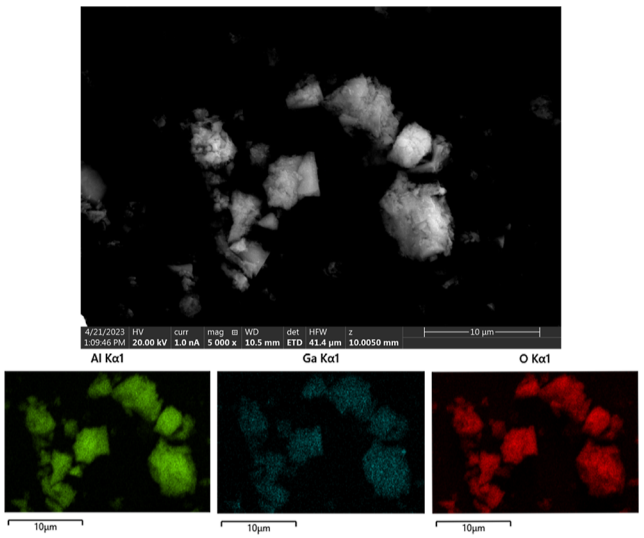

Figure 3. Top: SEM image of nanobayerite, $Al(OH)_3$, collected 48 h after combining water and the composite; bottom: accompanying EDS maps showing Ga does not exist as individual crystals but is evenly distributed among the nanobayerite $Al(OH)_3$ due to Ga doping (Al: green; Ga: cyan; O: red).

associated with the elements that are detected by EDS do not overlap, and thus each can be clearly resolved. We show these transitions in addition to a semiquantitative elemental analysis in Figure S6. We suggest that the initially formed Ga NPs oxidize to Ga^{3+} over the duration of 48 h and become incorporated into the nanobayerite structure. Ga metal does not readily oxidize under ambient conditions, but since it exists as Ga NPs in the reaction mixture, oxidation is readily achievable due to the greatly increased surface area.[30] This offers an explanation for the change in color of the supernatant suspension from gray to white over the course of 48 h and the even distribution of hydrated Ga among the resultant nano-$Al(OH)_3$. Due to the similar ionic radius and chemical nature of Ga^{3+} and Al^{3+}, it is plausible that they form a mixed oxide, as has been reported for a wide variety of scientific applications.[31−33]

Armed with the knowledge that Ga dopes the produced nano-$Al(OH)_3$, we set out to investigate the key variables that affect the byproduct of this Ga−Al water splitting reaction. These variables include: (i) Ga/Al atom % ratio of composite; (ii) effect of reaction time; (iii) volume of water introduced to the composite; (iv) reaction temperature; (v) effect of recycled Ga for composite construction. Additionally, byproduct nano-$Al(OH)_3$ was calcined, and the resulting α-Al_2O_3 was analyzed using PXRD and SEM-EDS. We also demonstrated that postconsumer Al could be used to make the composites with no effect on byproduct formation at room temperature (Figure S7).

Effect of Composite Ga/Al Atom % Ratio on Byproduct Formation. Our previous report showed that a composite of 3:1 (Ga/Al atom %) had the best hydrogen generating ability at 25 °C. For completeness, here we investigated the effects on byproduct formation of lesser-performing Ga/Al ratios at 25 °C. The byproduct collected was determined to be nanobayerite $Al(OH)_3$ for all ratios explored. Since the Ga/Al composite ratio did not affect the nature of the byproduct formed (Figure 4) and the 3:1 (Ga/Al

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atom %) composite evolved the largest volume of hydrogen, this composite ratio was selected for further investigation.

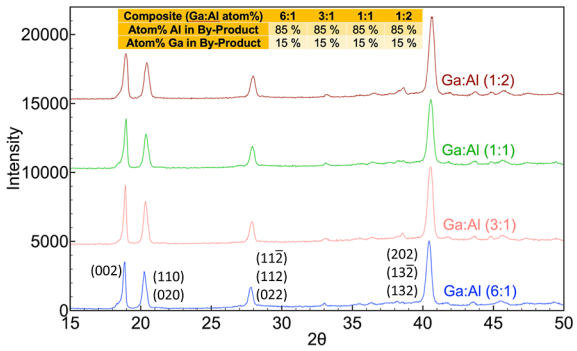

Figure 4. PXRD evidence showing minimal effect of Ga/Al atom % ratio on bayerite (COD ID: 9010964) formation. The inset displays the Al and Ga atom % of the byproduct bayerite as determined by ICP-OES.

Effect of Reaction Time on Byproduct Formation. Earlier, we reported that the hydrogen evolution reaction was 80% complete within 15 min after water was added to the 3:1 (Ga/Al atom %) composite at 25 °C. In order to scale up this reaction, one would need to remove the regenerated Ga from the reaction mixture as quickly as possible so it can be recycled for subsequent reactions and continue to generate hydrogen. For this reason, we allowed the water to react with the composite for 15 min before removing the Ga (Experimental Section) and allowed the supernatant to set for 48 h at the initial reaction temperature. At no point during the progress of the reaction was mechanical stirring employed since it was shown to have no effect on the nature of the byproduct formed (Figure S8). Since these conditions incorporate the highest-performing composite ratio for hydrogen generation and allow for the quick recovery of Ga in the absence of any stirring, we will refer to these conditions as "standard conditions" for the duration of this paper. Under standard conditions with 10 mL of water and a constant temperature of 25 °C, it takes 48 h for the initially produced $Al(OH)_3$ hydrogel to assemble into the crystalline bayerite phase nano-$Al(OH)_3$. Consequently, we let all supernatant reaction mixtures set for 48 h after the addition of water to the Ga−Al composite before isolating the crystalline nano-$Al(OH)_3$ byproduct (Figure 5).

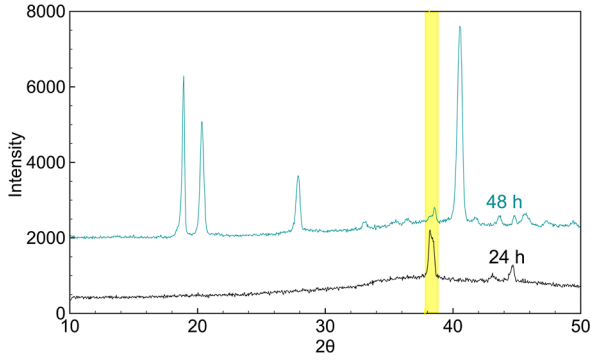

Figure 5. PXRD showing an amorphous byproduct after 24 h and converting into crystalline nanobayerite after aging for 48 h. The peaks highlighted in yellow arise from the Al sample holder.

Effect of Water Volume on Byproduct Formation. Different volumes of water were added to 3:1 (Ga/Al atom %) composites under standard conditions at 25 °C. The volume of water used was varied (3, 5, 10, and 20 mL), and any effects on the structure, crystallinity, and percent Ga doping of the resultant nano-$Al(OH)_3$ were recorded (Figure 6). The

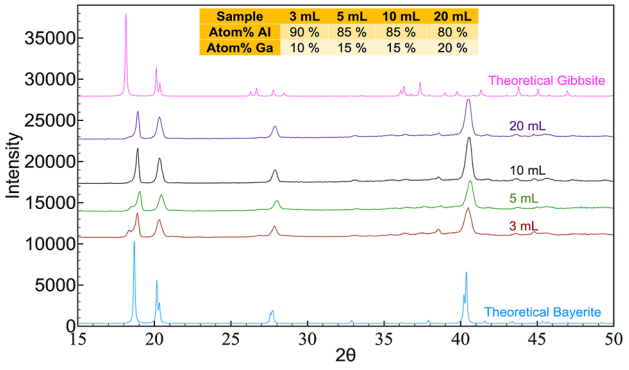

Figure 6. PXRD showing the effects of the volume of water on the nature of the byproduct nano-$Al(OH)_3$ produced under standard conditions at 25 °C. The inset displays the Ga and Al atom % of the byproduct nanobayerite as determined by ICP-OES.

addition of water is immediately followed by the release of hydrogen that bubbles through the gray supernatant suspension. Solid byproduct was isolated as described earlier, and the PXRD spectrum confirmed that bayerite $Al(OH)_3$ was the major product for each trial. PXRD of the solid byproduct from the 3 mL water sample and, to a lesser extent, from the 5 mL sample, however, showed a peak associated with gibbsite $Al(OH)_3$ at 18.3° (2θ) as a shoulder on the lowest-angle bayerite peak at 18.9° (2θ).

Effect of Reaction Temperature on Byproduct Formation. With the effects of the volume of water on the composition of the byproduct having been determined, we systematically investigated the effect of reaction temperature on the composition and level of metal doping of the nano-$Al(OH)_3$ byproduct. These experiments were performed by introducing 10 mL of water to our composite under standard conditions at 40, 60, 80, and 100 °C. Until this point, all experiments were carried out at 25 °C, and all produced bayerite phase nano-$Al(OH)_3$ as the major byproduct. Under no conditions at 25 °C was boehmite phase AlO(OH) ever produced. Boehmite phase nano-AlO(OH), however, was readily synthesized as the exclusive byproduct by elevating the reaction temperatures to 80−100 °C. When hydrolysis was carried out at 40 °C, bayerite was still the dominant byproduct with gibbsite present in minor amounts. For the hydrolysis reaction at 60 °C, bayerite and gibbsite were both present, in addition to the initial formation of broad peaks associated with boehmite (Figure 7). As a control, previously synthesized bayerite was introduced to water at 100 °C for 48 h to observe whether it would convert into boehmite. After 48 h, the collected product remained bayerite with only minor blips associated with boehmite arising (Figure S9). This evidence shows that the temperature of water used during the composite's introduction and the 48 h aging process plays a crucial role in promoting the formation of nano-AlO(OH).

Recyclability of Ga from Spent Reaction Mixtures. All experiments exploring the varying conditions discussed thus far utilized fresh Ga metal for synthesizing the binary composites.

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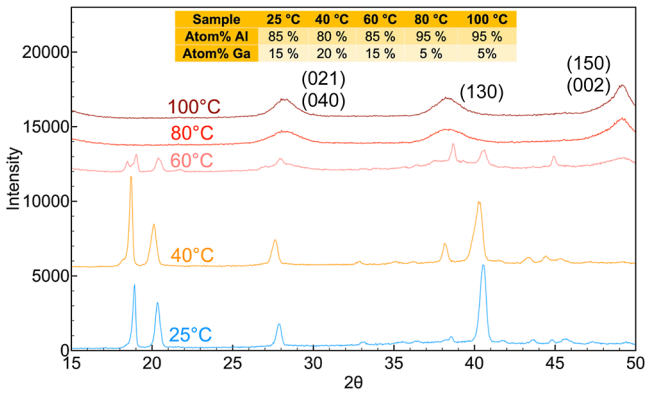

Figure 7. PXRD illustrating the transition from bayerite phase nano-$Al(OH)_3$ to boehmite phase nano-AlO(OH) (COD 9012250) as the reaction temperature is increased. The inset displays the Ga and Al atom % of the aluminum hydroxide and aluminum oxyhydroxide byproducts as determined by ICP-OES.

In order for this process to be industrially feasible and environmentally friendly, it is essential to reuse Ga collected from previous reactions. To test if Ga recovered from the reaction could be used to construct new composites without influencing the byproduct, Ga collected from previous experiments was used to construct new 3:1 (Ga/Al atom %) composites (see Experimental Section). These composites, made from recycled Ga metal, were then introduced into 10 mL of water at 25 °C under standard conditions. The Ga metal was collected again to make another recycled Ga/Al composite to repeat the reaction and determine whether there was any change in the nature of the byproduct. This process was repeated three times for proof of concept (Figure 8). As can be

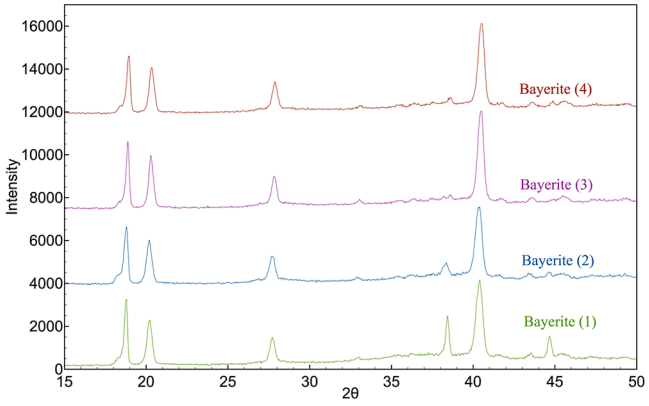

Figure 8. PXRD spectra showing that recycled Ga metal has no effect on the production of nanobayerite under standard conditions after four reaction cycles.

seen, recycled Ga metal from previous reactions can be collected and recycled to make new composites without influencing the amount of hydrogen generated (Figure S10) or the nature of the resultant nano-$Al(OH)_3$. Additionally, recovered Ga is essentially pure, ~0.1% Al in most samples, as observed by ICP-OES.

Formation of α-Al_2O_3. The dehydration of bayerite/gibbsite $Al(OH)_3$ through calcination is used industrially to produce valuable α-Al_2O_3 with applications ranging from catalytic supports to electronics and abrasives. Obtaining α-Al_2O_3 is still a highly polluting process since it is manufactured from $Al(OH)_3$ through the Bayer process. The Ga−Al composite described in this paper produces green nano-$Al(OH)_3$ or nano-AlO(OH) and thus the resulting α-Al_2O_3 produced is highly green in nature. When byproduct nano-$Al(OH)_3$ and nano-AlO(OH) is calcined for 2 to 24 h at 1100 °C in a tube furnace, the original bayerite structure is converted to α-Al_2O_3 (Figure 9). It was observed that the nano-$Al(OH)_3$ and nano-AlO(OH) phases are transformed to majority phase α-Al_2O_3 after only 2 h, as evidenced by PXRD (Figure S11).

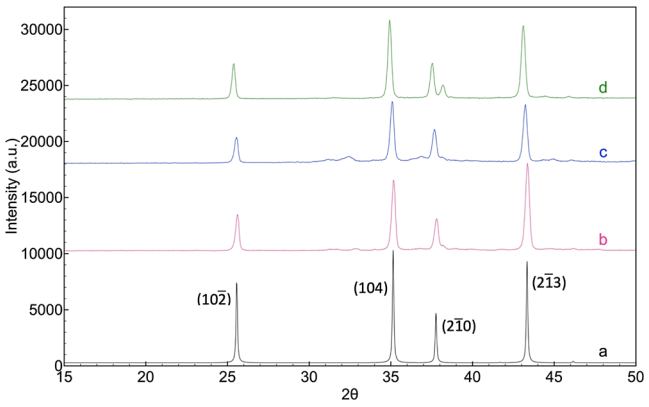

Figure 9. PXRD patterns of: (a) literature α-Al_2O_3 (COD ID: 9007496); (b) product after 24 h of calcination at 1100 °C for commercially purchased $Al(OH)_3$; (c) calcination of byproduct nano-$Al(OH)_3$ under the same conditions as (b,d) calcination of nano-AlO(OH) byproduct under the same conditions as (b).

SEM was employed to observe microstructural differences between α-Al_2O_3 synthesized from bayerite under our standard conditions and boehmite obtained from reactions performed at 80 °C. SEM micrographs revealed that the α-Al_2O_3 morphology varies depending on the starting material. Figure 10a shows the starting bayerite, while Figure 10c shows the resultant α-Al_2O_3 produced by calcination at 1100 °C for 24 h. The starting nano-$Al(OH)_3$ phase bayerite has multiple jagged regions protruding from a smooth and nonporous surface. The resultant α-Al_2O_3 no longer has a smooth underlayer like the starting nano-$Al(OH)_3$ but has been transformed to a porous solid, in which jagged features emerge. In Figure 10b, we see the starting boehmite, and Figure 10d shows the α-Al_2O_3 product obtained from calcination at 1100 °C for 24 h. The starting boehmite has a highly fine, fibrous surface with few features visibly extending outward. There are, however, valleys and hills on the surface that become more apparent in the product α-Al_2O_3. The surface of the α-Al_2O_3 is porous, similar to α-Al_2O_3 derived from nano-$Al(OH)_3$, while the surface of α-Al_2O_3 from the nano-AlO(OH) phase boehmite is significantly smoother. Its surface lacks the jagged features that are ubiquitous on α-Al_2O_3 derived from nano-$Al(OH)_3$. The highly topographical nano-$Al(OH)_3$ produces a similar α-Al_2O_3 surface, while the smoother, highly fibrous nano-AlO(OH) leads to a more even α-Al_2O_3 surface with less microstructural diversity (Figure 10).

EDS analysis provided confirmation that Ga and Al are again evenly dispersed in the samples of α-Al_2O_3, much like they are in the initial nano-$Al(OH)_3$ and nano-AlO(OH) (Figure S12). EDS was employed to estimate the Ga and Al atom % of the samples rather than ICP-OES due to the difficulty of digesting α-Al_2O_3. The results demonstrated that the Ga and Al atom %

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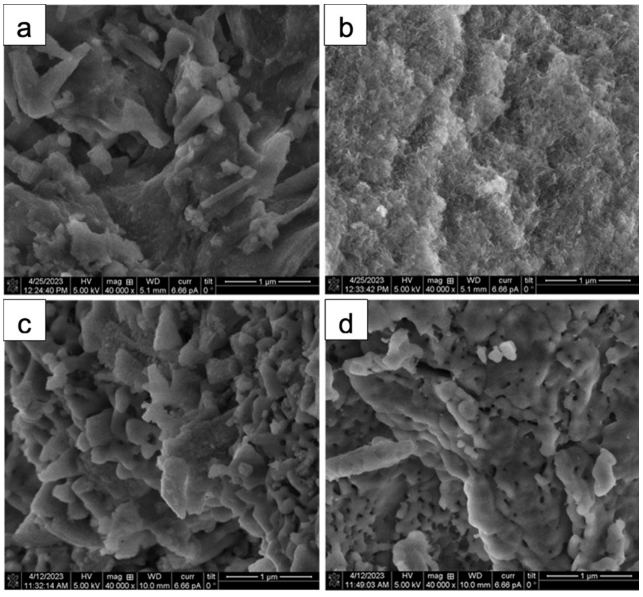

Figure 10. SEM images of: (a) nano-$Al(OH)_3$ produced under standard conditions; (b) nano-AlO(OH) produced at 80 °C; (c) the resultant α-Al_2O_3 from calcination of nano-$Al(OH)_3$ at 1100 °C for 24 h; (d) the resultant α-Al_2O_3 from calcination of nano-AlO(OH) synthesized at 80 °C.

values of the resultant α-Al_2O_3 are identical to those of the starting nano-$Al(OH)_3$ and nano-AlO(OH). The process of calcination thus influences neither the distribution nor the atomic ratios of Ga and Al compared to those of the initial materials.

CONCLUSIONS

The use of Ga to activate Al for water splitting is an effective and green method for the production of the nano-$Al(OH)_3$ phase bayerite and nano-AlO(OH) phase boehmite, in addition to green hydrogen. The generation of H_2 is accompanied by the formation of Ga NPs and an amorphous hydrogel composed of hydrated Al. The hydrogel transforms into crystalline bayerite phase nano-$Al(OH)_3$ after 2 days under ambient conditions. If the Ga NPs are left in the supernatant suspension, they will undergo oxidation to Ga^{3+}, thereby facilitating incorporation into the resulting nano-$Al(OH)_3$. The Ga NPs likely originated from a side reaction where Al and Ga nanoclusters act as a Lewis acid−base pair capable of splitting water to form new Ga−H and Al−OH bonds and eventually GaH_3 and $Al(OH)_3$. The GaH_3 metathesizes into Ga NPs and H_2. Additionally, the effects of various reaction conditions on the Ga−Al water splitting reaction were explored. Ga/Al (atom %) composite ratios of 6:1, 1:1, and 1:2 all produced nano-$Al(OH)_3$ under ambient conditions. Volumes of water ranging from 3 to 20 mL also produced nano-$Al(OH)_3$ when reacted with a 3:1 composite under standard conditions at 25 °C. The hydrated aluminum byproduct phase is highly dependent on temperature, with nano-AlO(OH) being the sole phase between 80 and 100 °C. We also showed nano-$Al(OH)_3$ and nano-AlO(OH) byproducts could be fully converted to α-Al_2O_3 at 1100 °C in 24 h, with α-Al_2O_3 peaks dominating the PXRD spectra after just 2 h. The Ga metal used for the composites can be recovered from spent reaction mixtures in its pure state and can be recycled to make additional binary metal composites without any influence on the reaction. The process requires no energy input and produces only green hydrogen and value-added Ga-doped nano-$Al(OH)_3$ or nano-AlO(OH), as precursors to green α-Al_2O_3.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.3c04751.

Further details on experimental setup, physical characterization, and results (PDF)

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Notes

The authors declare no competing financial interest.

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