ACS APPLIED NANO MATERIALS

www.acsanm.org Article

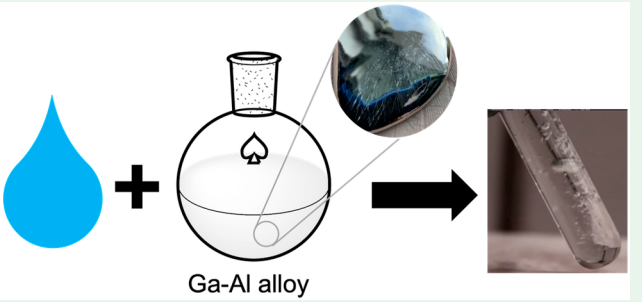
Aluminum Nanoparticles from a Ga−Al Composite for Water Splitting and Hydrogen Generation

Gabriella Amberchan, Isai Lopez, Beatriz Ehlke, Jeremy Barnett, Neo Y. Bao, A'Lester Allen, Bakthan Singaram,* and Scott R. J. Oliver*

Cite This: *ACS Appl. Nano Mater.* 2022, 5, 2636−2643 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: We report the use of a gallium (Ga)-rich aluminum (Al) composite to enhance the formation of Al nanoparticles and to facilitate its ability to split water to generate hydrogen at ambient conditions. The synthesis of this Ga−Al composite occurs without the need of an inert atmosphere or mechanical aid. Commercial Al can be used, including postconsumer aluminum foil that is usually discarded. Characterization of the Ga−Al composite with scanning electron microscopy, energy-dispersive X-ray spectroscopy, and powder X-ray diffraction illustrates that the Ga acts to dissolve the aluminum oxide coating of the Al nanoparticles. The pristine nanoparticles are then available for continuous water splitting and on-demand hydrogen generation through the Grotthuss mechanism. The water-splitting reaction does not require an applied potential and functions at ambient conditions and neutral pH to rapidly generate 130 mL (5.4 mmol) of hydrogen per gram of alloy. Any available source of water can be used including wastewater, commercial beverages, or even ocean water, with no generation of chlorine gas, as confirmed by gas chromatography−mass spectrometry. In addition, Ga remains intact, allowing it to be collected and reused indefinitely. The Ga−Al alloy is stable under cyclohexane for at least 3 months so it can be preprepared for a later use. As an initial example of the application of evolved hydrogen, we show a hydrogenation reaction.



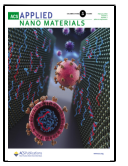
KEYWORDS: *water splitting, hydrogen generation, gallium, environmental chemistry, waste prevention*

INTRODUCTION

Aluminum (Al) nanoparticles have gained wide application in plasmonics, propellants, and hydrogen generation.[1,2] This is largely due to the abundance of Al in the earth's crust, making it a more economic option than other metals. The methods employed to make Al nanoparticles are classified into two major categories: gas phase and liquid phase. Gas-phase methods involve the electroexplosion of Al wires at high pressure and temperature. Liquid-phase methods usually employ electrochemical template deposition but generally have low yields and need a large excess of substrate solutions. In general, the synthesis of Al nanoparticles is quite challenging, and only a few manipulation methods have been developed, such as modification of the Al source, solvent system, or ligands to achieve different shapes and sizes.[1] Common Al precursors include $LiAlH_4$, alane, AlH_3/N-(Me_2Et), triisobutylaluminum (TIBA), and diisobutylaluminum hydride (DIBAL) to synthesize Al nanoparticles.[3−5] While making Al nanoparticles from AlH_3/N(Me_2Et) is interesting, aluminum hydride derivatives are explosive. Both TIBA and DIBAL are expensive and pyrophoric reagents. Interestingly, when TIBA decomposes, it generates DIBAL, which, in turn, decomposes to give metallic Al, isobutylene, and hydrogen. None of these methods are effective at making Al nanoparticles at 25 °C.[6]

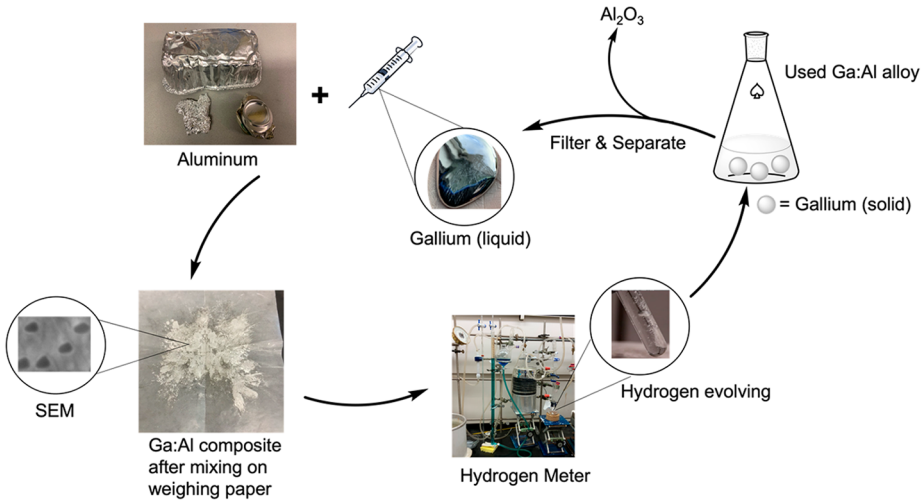
Pure Al can also be used to obtain nanoparticles; however, the challenge with using Al is its almost immediate surface oxidation in air to produce oxide products, such as Al_2O_3. This oxide coating passivates Al from useful reactions, such as hydrogen evolution from water. Therefore, many of the reported processes require nanoparticle synthesis in an inert atmosphere to prevent decomposition of the starting reagents and formation of the Al_2O_3 layer. Mechanical manipulation has also been reported to produce Al nanoparticles, either through pulsed laser ablation[7] or ball milling,[8] but again caution must be taken to inhibit formation of the oxide layer. Alternatively, room temperature liquid metal alloys, such as GaInSn, have been reported to simultaneously dissolve Al,[9] create Al nanoparticles, and remove the passivation layer.[9−14] Some of the most effective Al composites for splitting water contain

Received: December 14, 2021
Accepted: January 31, 2022
Published: February 14, 2022



https://doi.org/10.1021/acsanm.1c04331
ACS Appl. Nano Mater. 2022, 5, 2636−2643

Scheme 1. Schematic Diagram of the Synthesis of the Ga−Al Composite, Hydrogen Evolution, and Recycling of Ga



bimetallic and trimetallic composites. These have included mixing Al with gallium (Ga), indium (In), tin (Sn), and bismuth (Bi) in various ratios to obtain ternary,[10] quaternary,[11] and quinary[12] alloys. The composites are then used to conduct water-splitting reactions on the surface of pristine Al. This reaction produces substantial amounts of hydrogen, while producing only aluminum oxide as the byproduct (eq 1).[15] However, these composites make it difficult to recover and recycle the many components from the spent metal composites.

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \quad (1)$$

While previous work focused on employing Al-rich alloys,[11,12] the production of hydrogen from water at ambient temperature was too low and too slow for practical applications. We conjectured that varying the amount of Ga in a Ga−Al composite could be modulated to increase the reactivity of Al toward its ability to split water. More specifically, we wondered whether changing the elemental composition of a Ga−Al composite could be a modular approach to enhancing the formation of Al nanoparticles by simple mechanical mixing. During a systematic study, we found that the change in the atom ratio of Ga to Al could ultimately lead to a bimetallic composite that is highly active for water-splitting reactions from various sources of water. We postulated that liquid Ga metal, which has the ability to remove the passive oxide coating on Al, would lead to a system capable of producing nanoclusters of Al when used in a larger amount. To test this hypothesis, we conducted a series of water-splitting experiments using binary alloys with various atom ratios of Al to Ga to assess the best ratio of Ga to Al to produce the maximum possible amount of hydrogen from a given volume of water. It was also found that these alloys produced hydrogen in far greater yield and rate from water at ambient conditions. We also examined the application of this Ga-rich alloy to generate hydrogen on-demand from water and its effectiveness as a hydrogen source in a hydrogenation reaction. Because the cost of Ga would be an economic barrier for widespread use, we developed a method of recycling Ga and reusing it for multiple alloy synthesis reactions. Herein, we report our results on generating Al nanoparticles in a sea of Ga by simple mixing of waste Al with Ga at room temperature, as observed through multiple characterization techniques (Scheme 1). Further application of the Al nanoparticles as an on-demand hydrogen generator was also explored.

EXPERIMENTAL SECTION

Materials. All chemicals and reagents were purchased without further purification. Ga (99.9999%), Bi, In powder, and 4-phenyl-1-buten-4-ol were purchased from Fisher Scientific. Aluminum foil was purchased from Safeway.

General Procedure for Preparing the Ga−Al Composite. On a piece of weighing paper, the aluminum foil (0.108 g, 4 mmol) was shaped into a cup, and to the center of the aluminum cup was added using a syringe weighed warm liquid Ga (0.837 g, 12 mmol). The aluminum foil was wrapped around the Ga, the weighing paper was folded into fourths, and the metals were pressed from the outside edges to the center to keep the Ga from spilling. The Ga was continuously pressed into the Al for 10 min or until the composite appeared to be homogeneous and shiny in color. Once all of the Al was dissolved by the Ga, the weighing paper was folded in half and a dry ice pellet was pressed over the weighing paper to solidify the composite. Cooling should start from the outside edges to the center to keep the liquid composite from spilling. The Ga−Al composite appeared to be dull gray when it hardened. Using a razor blade, the composite was delicately peeled off the weighing paper and placed into a weighed flask for hydrogen generation or stored under cyclohexane for future use. This procedure was used to prepare the Ga−Al mixtures of different atom ratios used in this study.

General Procedure for Preparing the Alternative Composites. On a piece of weighing paper, the aluminum foil (0.108 g, 4 mmol) was shaped into a cup, and to the center of the aluminum cup was added the secondary metal. The aluminum foil was wrapped around the secondary metal, the weighing paper was folded into fourths, and the metals were pressed from the outside edges to the center to keep the composite from spilling out. The composite was continuously pressed for 10 min or until the composite appeared to be homogeneous and shiny in color. Once all of the Al was dissolved, the weighing paper was folded in half and a dry ice pellet was pressed over the weighing paper to solidify the composite. Cooling should start from the outside edges to the center to keep the liquid composite from spilling. The composite appeared to be dull gray when it hardened. Using a razor blade, the composite was delicately peeled off the weighing paper and placed into a weighed flask for hydrogen generation.

General Procedure for Measuring Hydrogen Evolution by a Gas Buret.[16] A Ga−Al nugget was placed in a round-bottom flask containing a magnetic stirbar still warm from a drying oven, the heat from which "melted" the alloy in ∼1 min. The flask was connected to a gas buret reservoir via a cannula (Figure S1). Deionized (DI) water

https://doi.org/10.1021/acsanm.1c04331
ACS Appl. Nano Mater. 2022, 5, 2636−2643

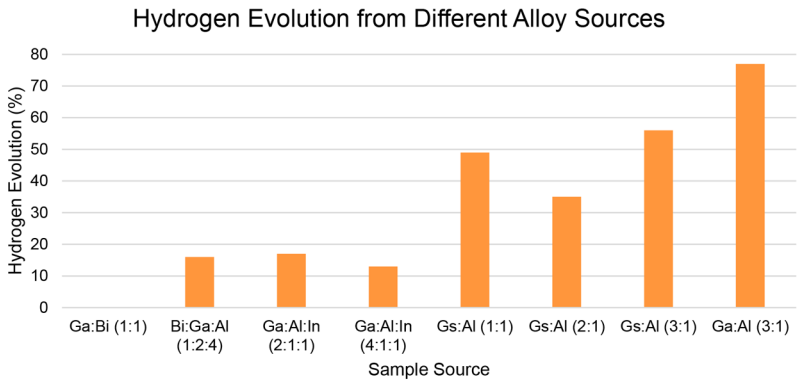


Figure 1. Hydrogen evolution from different alloy sources and their atomic ratios. The percent of hydrogen evolved was calculated after 15 min of reaction with DI water. All of the composites were comprised of 4 mmol of Al.

(10 mL) was added to the flask containing the composite, causing hydrogen gas to evolve immediately. Volume measurements were taken after it appeared that all of the material had reacted, ca. 15 min. By controlled release of the pressure in the closed system into a graduated cylinder, the volume of gas generated was measured by water displacement. The temperature of the displaced water and barometric pressure were also measured. The quantity of hydrogen produced was determined by following a previously published method.[16]

Procedure for Recycling Ga. The initial spent reaction mixture containing residual Al particles was left at room temperature in a flask for 12 h to convert all of the Al particles into aluminum oxide. Then the flask was gently warmed to aggregate liquid Ga beads and cooled to 0 °C to solidify Ga into nuggets. The suspension of Al_2O_3 and solid Ga was then filtered, and tweezers was then used to gather the shiny Ga metal from Al_2O_3 solids in the residue. We could routinely isolate >95% of Ga. The used Ga was then stored in a vial for future use.

Characterization of the Ga−Al Composites. The morphology and composition of the composite was investigated on a Thermo Scientific Apreo scanning electron microscope. Powder X-ray diffraction (PXRD) was performed on a Rigaku SmartLab X-ray diffractometer with Cu Kα radiation (1.5418 Å). Samples were analyzed in a parallel beam mode from 10 to 80° (2θ) with a step size of 3 min^{-1}.

Residual Water Analysis. The Ga and Al concentrations were obtained by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis on a Thermo Scientific iCAP 7000 Series ICP spectrometer using scandium and yttrium as internal standards. The calibration curves for Al and Ga were prepared using external standards.

General Methods for NMR Analysis. 1-Phenyl-1-butanol was confirmed by NMR spectroscopy, measured in parts per million. ^{1}H NMR spectra (Figure S2) were recorded on a Bruker 500 MHz spectrometer at 297 K and calibrated using residual $CDCl_3$ (δ = 7.26 ppm) as an internal standard. ^{13}C NMR spectra (Figure S3) were analyzed at 125.7 MHz (297 K) and calibrated using $CDCl_3$ (δ = 77.0 ppm) as an internal standard. The coupling constants (J) are given in hertz, and the signal multiplicities are abbreviated as s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad.

Procedure for the Hydrogenation of 4-Phenyl-1-buten-4-ol Using a Nickel (Ni) Catalyst.[17] In a 100 mL round-bottomed flask, $NaBH_4$ (1.0 g, 26.43 mmol) was suspended in ethanol (EtOH; 24 mL) and 2 M NaOH (1.25 mL, 2.5 mmol) with stirring. In a separate 100 mL round-bottomed flask, nickel(II) acetate tetrahydrate (0.314 g, 1.25 mmol) was dissolved in EtOH (12.5 mL). To the Ni solution, the $NaBH_4$ solution (1.25 mL, 1.38 mmol) was added slowly via a syringe (***Caution!*** *H_2 is evolved*). Once the hydrogen evolution abated, the stirring was stopped, the alkene 4-phenyl-1-buten-4-ol (0.187 mL, 1.25 mmol) was added to the reaction flask, and a balloon was then connected to the reaction flask. One Ga−Al nugget (0.945 g, 4 mmol, of theoretical H_2) was placed in a separate round-bottomed flask, melted with a warm stirbar, and then connected via a cannula to the reaction flask containing the Ni catalyst and alkene. With both flasks being stirred, DI water (5 mL) was added to the Ga−Al flask to generate hydrogen, which was then led into the reaction flask. After 15 min, the two flasks were disconnected, a third flask containing another Ga−Al nugget (0.945 g, 4 mmol, of theoretical H_2) was attached, and the same procedure as that above was conducted to generate hydrogen gas. After the hydrogen had evolved, the reaction mixture was allowed to stir for 1 h. The reaction mixture was then centrifuged and the supernatant decanted. The solid catalyst was rinsed with diethyl ether (2 × 10 mL) and centrifuged and the supernatant decanted. The combined supernatants were then concentrated by rotary evaporation to afford essentially a pure product, 1-phenyl-1-butanol (0.170 g, 90% yield).

1-Phenyl-1-butanol.[18] ^{1}H NMR (500 MHz, chloroform-d): δ 7.35 (d, J = 5.5 Hz, 4H), 7.30−7.26 (m, 1H), 4.66 (dd, J = 7.5 and 5.8 Hz, 1H), 2.12 (s, 1H), 1.83−1.76 (m, 1H), 1.72−1.65 (m, 1H), 1.47−1.40 (m, 1H), 1.35−1.28 (m, 1H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-d): δ 144.99, 128.41, 127.45, 125.93, 74.40, 41.26, 19.05, 13.99.

RESULTS AND DISCUSSION

We were intrigued by the various reports describing the ability of a room temperature liquid material, when mixed with Al, to split water.[11,12] As shown in Figure 1, different metal composites were tested to find a mixture that evolved substantial amounts of hydrogen in under 15 min. The Ga−Bi (1:1) composite produced 0% hydrogen, highlighting the importance of Al for the reduction of water (eq 1). All other Al-based composites produced hydrogen, with the greatest amounts coming from Ga or Ga-based sources. Galinstan (Gs), an alloy composed of Ga, In, and Sn, was thought to aid in the reduction of water; however, the ternary alloy only produced 56% hydrogen at its best ratio (3:1 Gs−Al). This result compared to the simpler binary, Ga−Al (3:1), composite produced much higher yields of hydrogen (77%) after 15 min. Therefore, the rest of the study focused on understanding the Ga−Al composite for hydrogen evolution.

Most of these studies focused on Al-rich composites and Al−Ga weight ratios. These reports attributed the main role of Ga to cleaning up the surface of the dominant Al by removing the passivating layer of Al_2O_3. We postulated that larger amounts of liquid Ga metal, besides removing the passive oxide coating on Al, would also lead to a system of producing nanoclusters of Al. Consequently, we initiated a study examining the water-splitting ability of various Ga and Al composites. We explored the atomic ratio rather than the weight ratio reported earlier, in order to find the most effective

https://doi.org/10.1021/acsanm.1c04331
ACS Appl. Nano Mater. 2022, 5, 2636−2643

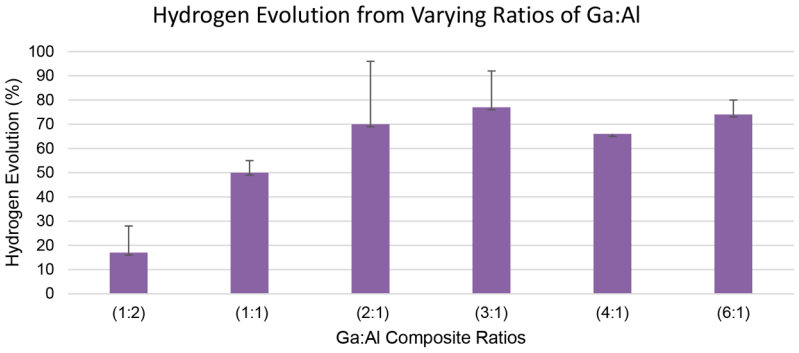


Figure 2. Average hydrogen gas production generated from various Ga−Al atomic ratio composites. The generation of hydrogen was obtained after 15 min of reaction with DI water. All composites used 4 mmol of Al. Ga−Al (3:1) produces 90% hydrogen after 30 min, and then the hydrogen evolution slows.

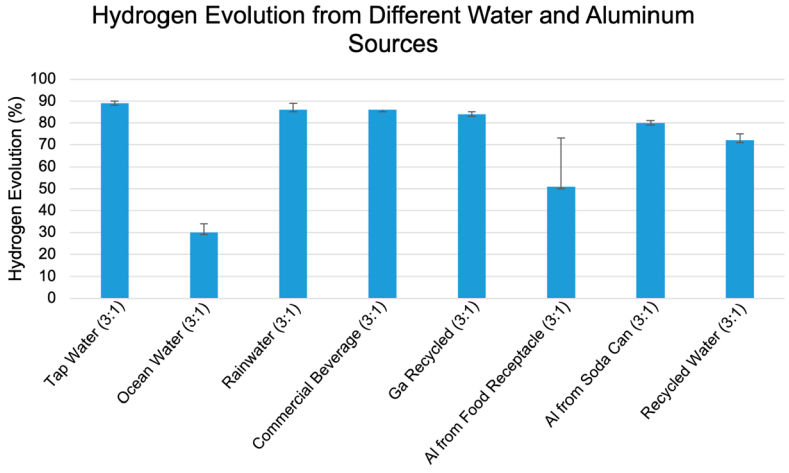


Figure 3. Quantitation of hydrogen evolution from the Ga−Al composite using different water and Al sources. Reactions ran for 15 min before hydrogen gas was quantified.

Ga−Al composite to split water (DI water), including Ga-rich mixtures. Accordingly, various atomic ratios of the Ga−Al composites were generated to optimize the production of hydrogen from water at ambient conditions. We were pleased to find that Ga-rich ratios produced the greatest amount of hydrogen, compared to Al-rich composites (Figure 2). The more economical 3:1 atomic ratio alloy outperformed the 4:1 alloy, and so 3:1 was used for all subsequent experiments. Not only do the Ga:Al (3:1) composites have enough Al to maximize hydrogen production, but also we surmised that they keep the Al particles from aggregating. Because of the high cost of Ga, we developed a method for its recovery from the used composite (unoptimized recovery ∼98%) by simple filtration and aqueous rinsing. It was found that the recycled Ga has no depreciating effect for its ability to produce hydrogen (>85% of the theoretical amount; Figure 2).

Pristine aluminum foil was initially used to optimize the composite ratio, but expansion to waste Al in the form of commercial baking trays and food wrappers demonstrated that hydrogen is efficiently generated regardless of the Al source (50%; Figure 3). In the U.S., the most recycled source of Al is beverage cans, and as such, we wanted to demonstrate that hydrogen can also be produced from a composite comprised of this ubiquitous source.[19] The top and bottom of a standard soda can contain over 90% Al, and far less paint and polymer coating resides in those areas. When the soda can lid was tested, it was discovered that a higher ratio of Ga was necessary (Figure 3) to dissolve the Al completely because of its greater thickness. Subsequent hydrogen studies revealed that the Ga−Al composite made using a soda can lid produced 80% of the theoretical amount of hydrogen, again demonstrating that recycled Al is a viable material for the composite.

In addition to DI water, other water sources proved to be successful in generating hydrogen using the optimized 3:1 composite. Tap water produced substantial amounts of hydrogen, much like DI water (89%; Figure 3). Ocean water produced ∼30% hydrogen (Figure 3), and a visual comparison showed a much less vigorous reaction for the composite in ocean water than in DI water. The slower production of hydrogen could be due to the presence of sodium chloride (NaCl).[20,21] Gas chromatography−mass spectrometry confirms that no chlorine gas was formed, a pervasive problem that prevents the use of electrode-based ocean water splitting.[22,23] In an effort to identify the cause for the reduced yield, a NaCl solution (0.33 M) was made to mimic the salt content of ocean water. It too showed lower hydrogen generation similar to ocean water, indicating that the salt was the likely culprit for the decreased hydrogen yield in ocean water splitting. Nevertheless, ocean water still gives rise to greater hydrogen volumes than Al-rich composites. Degassed commercial soda yielded 86% hydrogen, showing that sweetener does not impede the reaction. On average, the 3:1 Ga−Al composite

https://doi.org/10.1021/acsanm.1c04331
ACS Appl. Nano Mater. 2022, 5, 2636−2643

generates 109 mL of hydrogen within 15 min (see the Supporting Information and Movies S1–S5), whereas the common water-splitting techniques of electrolysis and photocatalysis produce only 2–9 mL of hydrogen in 50–180 min, depending on the catalyst.[24−27] Our studies demonstrate that the Ga–Al alloy maintains excellent hydrogen production regardless of Al or water source (Figure 3).

As stated earlier, after the hydrogen evolution reaction is complete, the Ga can be easily recycled and reused for multiple composite synthesis reactions (Figure 4); the aluminum oxide

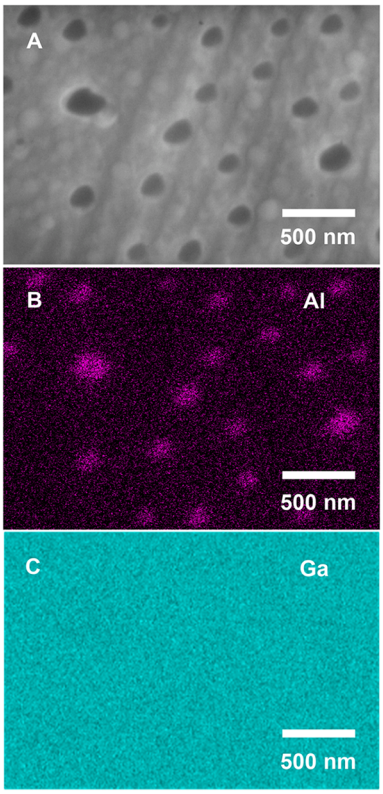


Figure 4. SEM image (A) and corresponding EDX maps (B and C) revealing discrete Al nanoparticles (B, magenta) in a Ga medium (C, cyan).

byproduct is readily separated as well. The water can also be collected and reused in subsequent reactions, producing 72% hydrogen. ICP-OES analysis of the residual water confirmed the low metal concentrations of 12.8 ppm of Ga and 9.2 ppm of Al.

Storage of the Ga–Al composite was an initial challenge because moisture from the atmosphere gradually degraded the efficacy of the material. It was found that the Ga–Al composite can be stored as pellets under cyclohexane and used when needed. Samples of nuggets stored under cyclohexane were tested periodically over several months of storage for their hydrogen production. We found that we could maintain an average yield of 82% of hydrogen production from these pellets. The composites can therefore be stored and used on-demand when needed without fear of oxidation or premature hydrogen generation.

We speculated that by mixing Ga with Al, the Ga dissolves the Al to create Al nanoparticles within the Ga. Different Ga–Al ratios were examined to identify the critical amount of Ga that is required to cause Al nanoparticle formation. On the basis of the hydrogen evolution data and the scanning electron microscopy–energy-dispersive X-ray (SEM-EDX) spectra, the optimal ratio was determined to be a 3:1 Ga–Al composite, which revealed nanoparticles of Al of ∼80–150 nm diameter (dark regions; Figure 4a). The corresponding EDX maps confirm that these regions are Al (Figure 4b) in a Ga medium (Figure 4c). Structural analysis of the composites at various Ga–Al ratios was performed using PXRD (Figure 5). The 3:1 Ga–Al composite is clearly a mixture of the two metals [cubic Al, *Fm*3*m*, 38.5°, 44.7°, 65.1°, and 75.3° (2θ); orthorhombic Ga, *Cmca*, 30.3°, 30.6°, 45.4°, 46.4°, 57.6°, 63.6°, 76.3°, and 77.0° (2θ)]. The ratio of the peak intensities for each phase approximately follows the expected ratio based on the atomic ratio (6:1 to 1:4 Ga–Al; Figure 5). The Al and Ga diffraction peaks are conserved after mixing. The lack of any major peak broadening or shifting suggests that the original crystal structures are intact and a lack of homogeneous alloy formation. The major product after hydrogen production ceases is proposed to be primarily $Al_2O_3{\cdot}5H_2O$ (ICSD 28379; Figure 6). Because of its low diffraction intensity and quasi amorphous nature, full phase identification was not possible.

It is generally believed that hydrogen generation occurs at the interface between Al and water, thus requiring a pristine Al surface with high surface area. Bulk commercial aluminum foil will not generate hydrogen gas because its passivating oxide layer and macrosurface area prevents any reaction from occurring with water. According to the data presented above, we propose that Ga not only dissolves Al to create clusters of nanoparticles but also removes any passivating aluminum oxide film. SEM clearly indicates that Al nanoparticles form within a sea of Ga by simple mechanical mixing in a 3:1 atomic ratio of Ga to Al (Figure 4). Each element maintains their individual crystal structures, as seen in the PXRD data (Figure 5). Therefore, Al exists as nanoparticles/clusters and is floating on a "sea" of Ga. They do not mix, and there is a distinct grain boundary between the Al and Ga metals. The sea of Ga keeps the Al nanoclusters from agglomerating. It is not just pristine Al that is reacting with water to produce hydrogen, it must be Al in its nanoform that is responsible for the splitting of water. At these nano-Al sites, a series of hydrogen-bond exchanges occur to liberate hydrogen.[28−31] The Al_2O_3 byproduct is fibrous and gets swept away by the agitation of bubble formation, exposing a new surface of Al on the nanoparticles for further reaction. These observations are in qualitative agreement with the theoretical calculations previously reported in which Al nanoparticles can split water by the Grotthuss mechanism.[29−32] Density functional theory calculations on 13-atom clusters such as Al_{13} and $GaAl_{12}$, as well as an in-depth analysis of complementary Lewis acid/base pairs of these metal clusters, reveal that doping of Ga in an Al_{13} cluster reduces the transition state barrier for the reduction of water via the simultaneous breaking of O–H and Al–H bonds.

In addition to the synthesis of the composite, we wanted to demonstrate the utility of the composite for actual use in a research setting. The hydrogenation of alkenes is a classic reaction in organic synthesis. These reactions traditionally use a metal catalyst under pressurized hydrogen and heat to induce the transformation.[33] Because of the safety issues surrounding pressurized hydrogen, there is a need to avoid cylinders for an alternate, safe, and efficient hydrogen production. Consequently, we used the Ga–Al composite to generate hydrogen under atmospheric pressure and room temperature conditions. The alkene 4-phenyl-1-buten-4-ol was used as a representative

https://doi.org/10.1021/acsanm.1c04331
ACS Appl. Nano Mater. 2022, 5, 2636−2643

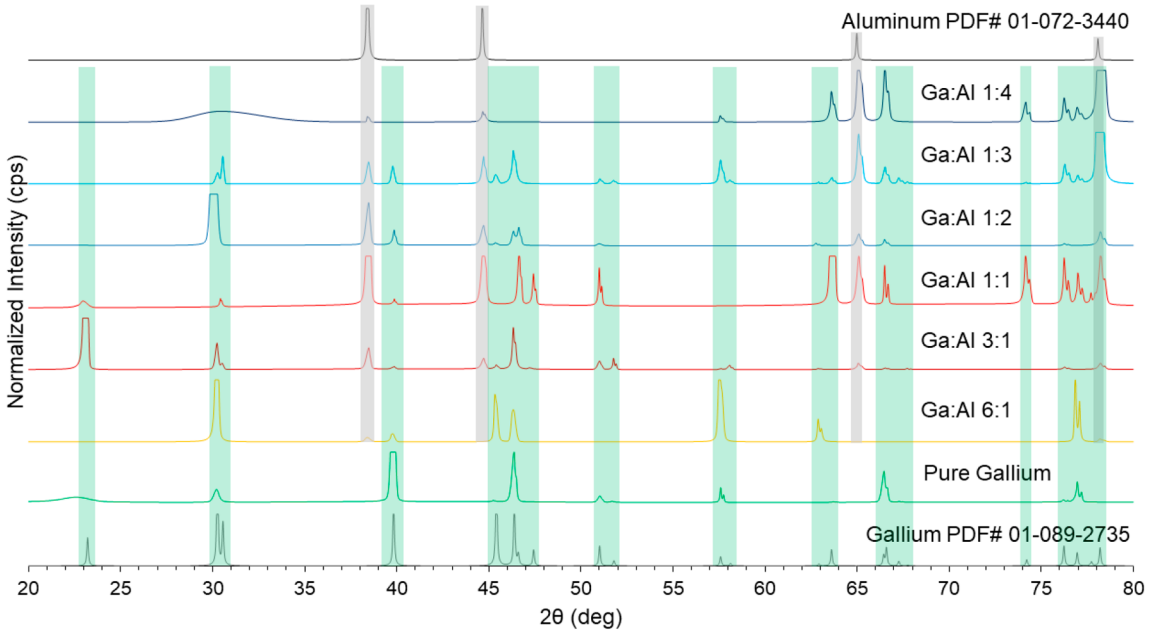


Figure 5. PXRD patterns for varying Ga−Al ratios and the theoretical patterns calculated from single-crystal data for pure Al (PDF 01-072-3440; ICSD 240129) and Ga (PDF 01-089-2735; ICSD 43388).

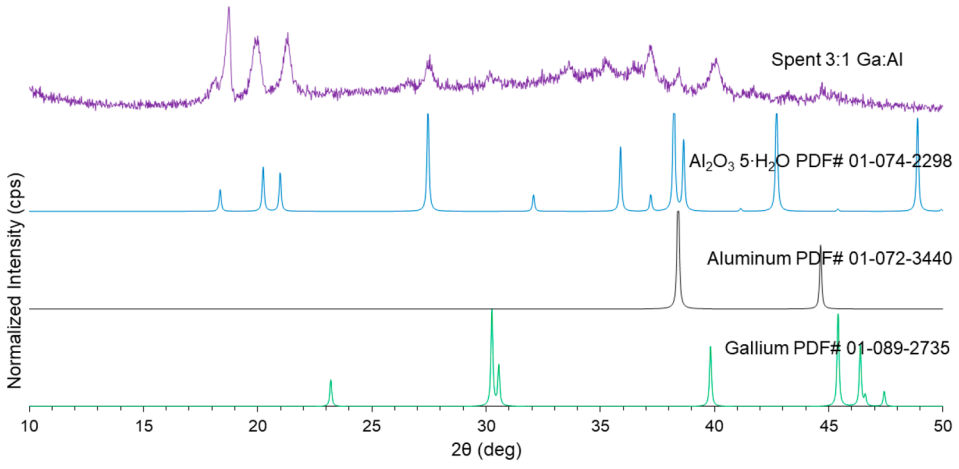
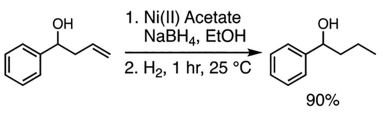


Figure 6. PXRD pattern after hydrogen production in water (spent 3:1 Ga−Al; top) and the proposed primary aluminum oxide phase (PDF 01-070-7848; ICSD 160680).

hydrogenation substrate with a Ni catalyst. Hydrogen was generated ex situ and then transferred via a cannula into the reaction mixture. The alkene was hydrogenated in 1 h, and the product was isolated in very high yield and purity (Scheme 2). Previous hydrogenation reactions of this alkene have been reported to produce the saturated compound in similar yields but required pressurized systems and/or extreme temperature.[33−35]

Scheme 2. Reduction of 4-Phenyl-1-buten-4-ol (1.25 mmol) with a Ni Catalyst (1.25 mmol) in EtOH, Followed by Reaction with Composite-Generated Hydrogen (9.0 mmol, 2.6 g) in DI Water (5 mL)



CONCLUSIONS

Ga-rich Ga−Al composites are highly efficient in generating hydrogen and require simple mixing of liquid Ga with waste Al at ambient temperature. Our findings show that Ga acts as a solvent to dissolve the waste Al into nano-Al sites in a Ga matrix. This happens at room temperature and requires minimal energy input. Through SEM, EDX, and PXRD analysis, we were able to visualize the Al nanoparticles formed within a sea of Ga, while simultaneously removing the passivating oxide layer. Application of the bimetallic composite for hydrogen generation from water demonstrates that substantial amounts of hydrogen can be obtained in under 15 min at ambient conditions. Waste Al sources, such as soda cans, were found to form the same Al nanoparticles without requiring the waste Al to be precleaned. The Ga selectively dissolves the Al to form the nano-Al sites necessary for hydrogen generation. Furthermore, it was found that similar

https://doi.org/10.1021/acsanm.1c04331
ACS Appl. Nano Mater. 2022, 5, 2636−2643

yields of hydrogen were obtained regardless of the Al or water source. To expand upon the utility of the bimetallic composite, a simple hydrogenation reaction was performed with the Ga−Al/H_2O mixture as the hydrogen source. This reaction demonstrated that the Ga−Al mixture can be used without the need to pressurize or heat the hydrogen generation source. Once spent, the product can be easily separated and recovered into aluminum oxide and pure Ga. The recovered Ga was found to be pure and reusable in subsequent Al nanoparticle generations. The aluminum oxide was separated from the Ga and could act as an Al source for smelting plants. The alloys formed from recycled Ga saw no decrease in their ability to generate hydrogen gas. Overall, the Ga-rich Ga−Al mixture produces substantial amounts of hydrogen at room temperature with no energy input, material manipulation, or pH modification.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.1c04331.

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

Movie S1 showing a series of clips from a zoomed-in video of the water splitting (MP4)

Movie S2 showing hydrogen release as additional water is added (MP4)

Movie S3 showing a huge release of hydrogen after a water droplet reaches the surface of the alloy (MP4)

Movie S4 showing the reaction when water is added to a 3:1 Ga−Al composite (MP4)

Movie S5 showing the reactions when water is added to a series of test tubes containing Ga−Al composites of various ratios (MP4)

■ AUTHOR INFORMATION

Corresponding Authors

Bakthan Singaram − *Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, California 95064, United States;* orcid.org/0000-0002-3986-6528; Email: singaram@ucsc.edu

Scott R. J. Oliver − *Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, California 95064, United States;* orcid.org/0000-0002-6160-1518; Email: soliver@ucsc.edu

Authors

Gabriella Amberchan − *Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, California 95064, United States;* orcid.org/0000-0001-7923-8385

Isai Lopez − *Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, California 95064, United States*

Beatriz Ehlke − *Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, California 95064, United States*

Jeremy Barnett − *Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, California 95064, United States*

Neo Y. Bao − *Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, California 95064, United States*

A'Lester Allen − *Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, California 95064, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsanm.1c04331

Author Contributions

Conceptualization: I.L. and B.S. Investigation: all authors. Supervision: B.S. and S.R.J.O. Writing the original draft: all authors. Writing the review and editing: all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Brandon Cheney for his aid in SEM−EDX, Dr. Tom Yuzvinsky and the W. M. Keck Center for Nanoscale Optofluidics for help with SEM imaging, and Dr. Brian Dreyer for his help with ICP-OES. This work was partially supported by funds from The Ima Hernandez Foundation (to I.L.).

■ REFERENCES

(1) Jacobson, C. R.; Solti, D.; Renard, D.; Yuan, L.; Lou, M.; Halas, N. J. Shining Light on Aluminum Nanoparticle Synthesis. *Acc. Chem. Res.* **2020**, *53*, 2020−2030.

(2) Baldé, C. P.; Hereijgers, B. P. C.; Bitter, J. H.; de Jong, K. P. Facilitated Hydrogen Storage in $NaAlH_4$ Supported on Carbon Nanofibers. *Angew. Chem., Int. Ed.* **2006**, *45*, 3501−3503.

(3) Haber, J. A.; Buhro, W. E. Kinetic Instability of Nanocrystalline Aluminum Prepared by Chemical Synthesis; Facile Room-Temperature Grain Growth. *J. Am. Chem. Soc.* **1998**, *120*, 10847−10855.

(4) Clark, B. D.; Jacobson, C. R.; Lou, M.; Renard, D.; Wu, G.; Bursi, L.; Ali, A. S.; Swearer, D. F.; Tsai, A.-L.; Nordlander, P.; Halas, N. J. Aluminum Nanocubes Have Sharp Corners. *ACS Nano* **2019**, *13*, 9682−9691.

(5) Clark, B. D.; Jacobson, C. R.; Lou, M.; Yang, J.; Zhou, L.; Gottheim, S.; DeSantis, C. J.; Nordlander, P.; Halas, N. J. Aluminum Nanorods. *Nano Lett.* **2018**, *18*, 1234−1240.

(6) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. Surface Organometallic Chemistry in the Vapor Deposition of Aluminum Films Using Triisobutylaluminum: β-Hydride and β-Alkyl Elimination Reactions of Surface Alkyl Intermediates. *J. Am. Chem. Soc.* **1989**, *111*, 1634−1644.

(7) Altuwirqi, R. M.; Baatiyah, B.; Nugali, E.; Hashim, Z.; Al-Jawhari, H. Synthesis and Characterization of Aluminum Nanoparticles Prepared in Vinegar Using a Pulsed Laser Ablation Technique. *J. Nanomaterials* **2020**, *2020*, 1−5.

(8) Jiang, A.; Wang, F.; Xia, D.; Li, M.; Qiang, L.; Zhu, Z.; Wang, P.; Fan, R.; Lin, K.; Yang, Y. Aluminum nanoparticles manufactured using a ball-milling method with ammonium chloride as a grinding aid: achieving energy release at low temperature. *New J. Chem.* **2019**, *43*, 1851−1856.

(9) Meroueh, L.; Neil, L.; Eagar, T. W.; Hart, D. P. Leveraging Grain Size Effects on Hydrogen Generated via Doped Aluminum-Water Reactions Enabled by a Liquid Metal. *ACS Appl. Energy Mater.* **2021**, *4*, 275−285.

(10) Wang, W.; Chen, D. M.; Yang, K. Investigation on microstructure and hydrogen generation performance of Al-rich alloys. *Int. J. Hydrogen Energy* **2010**, *35*, 12011−12019.

(11) Ziebarth, J. T.; Woodall, J. M.; Kramer, R. A.; Choi, G. Liquid phase-enabled reaction of Al-Ga and Al-Ga-In-Sn alloys with water. *Int. J. Hydrogen Energy* **2011**, *36*, 5271−5279.

(12) Huang, T.; Gao, Q.; Liu, D.; Xu, S.; Guo, C.; Zou, J.; Wei, C. Preparation of Al-Ga-In-Sn-Bi quinary alloy and its hydrogen production via water splitting. *Int. J. Hydrogen Energy* **2015**, *40*, 2354−2362.
(13) Razavi-Tousi, S. S.; Szpunar, J. A. Effect of structural evolution of aluminum powder during ball milling on hydrogen generation in aluminum-water reaction. *Int. J. Hydrogen Energy* **2013**, *38*, 795−806.
(14) Irankhah, A.; Seyed Fattahi, S. M.; Salem, M. Hydrogen generation using activated aluminum/water reaction. *Int. J. Hydrogen Energy* **2018**, *43*, 15739−15748.
(15) Xu, S.; Zhao, X.; Liu, J. Liquid metal activated aluminum-water reaction for direct hydrogen generation at room temperature. *Renewable and Sustainable Energy Rev.* **2018**, *92*, 17−37.
(16) Clary, J. W.; Rettenmaier, T. J.; Snelling, R.; Bryks, W.; Banwell, J.; Wipke, W. T.; Singaram, B. Hydride as a Leaving Group in the Reaction of Pinacolborane with Halides under Ambient Grignard and Barbier Conditions. One-Pot Synthesis of Alkyl, Aryl, Heteroaryl, Vinyl, and Allyl Pinacolboronic Esters. *J. Org. Chem.* **2011**, *76*, 9602−9610.
(17) Brown, C. A.; Ahuja, V. K. The reaction of sodium borohydride with nickel salts in ethanol solution. P-2 nickel, a highly convenient, new, selective hydrogenation catalyst with great sensitivity to substrate structure. *J. Org. Chem.* **1973**, *38*, 2226−2230.
(18) Shi, L.; Tu, Y.-Q.; Wang, M.; Zhang, F.-M.; Fan, C.-A.; Zhao, Y.-M.; Xia, W.-J. A reaction for sp^3-sp^3 C-C bond formation via cooperation of Lewis Acid-promoted/Rh-catalyzed C-H bond activation. *J. Am. Chem. Soc.* **2005**, *127*, 10836−10837.
(19) *Containers and Packaging: Product-Specific Date, Aluminum Containers and Packaging*. United States Environmental Protection Agency, https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/containers-and-packaging-product-specific-data (accessed September 4, 2020).
(20) Lu, J.; Yu, W.; Tan, S.; Wang, L.; Yang, X.; Liu, J. Controlled hydrogen generation using interaction of artificial seawater with aluminum plates activated by liquid Ga-In alloy. *RSC Adv.* **2017**, *7*, 30839−30844.
(21) Jovanovič, P.; Može, M.; Gričar, E.; Šala, M.; Ruiz-Zepeda, F.; Bele, M.; Marolt, G.; Hodnik, N. Effect of Particle Size on the Corrosion Behavior of Gold in the Presence of Chloride Impurities: An EFC-ICP-MS Potentiodynamic Study. *Coatings* **2019**, *9*, 10.
(22) Dresp, S.; Dionigi, F.; Klingenhof, M.; Strasser, P. Direct electrolytic splitting of seawater: opportunities and challenges. *ACS Energy Lett.* **2019**, *4*, 933−942.
(23) Zheng, J.; Zhao, Y.; Xi, H.; Li, C. Seawater splitting for hydrogen evolution by robust electrocatalysts from secondary M (M = Cr, Fe, Co, Ni, Mo) incorporated Pt. *RSC Adv.* **2018**, *8*, 9423−9429.
(24) Merki, D.; Fierro, S.; Vrubel, H.; Hu, X. Amorphous molybdenum sulfide films as catalysts for electrochemical hydrogen production in water. *Chem. Sci.* **2011**, *2*, 1262−1267.
(25) Sun, Y.; Liu, C.; Grauer, D. C.; Yano, J.; Long, J. R.; Yang, P.; Chang, C. J. Electrodeposited Cobalt-Sulfide Catalyst for Electrochemical and Photochemical Hydrogen Generation from Water. *J. Am. Chem. Soc.* **2013**, *135*, 17699−17702.
(26) Kiran, V.; Mukherjee, D.; Jenjeti, R. N.; Sampath, S. Active guests in the MoS_2/$MoSe_2$ host lattice: efficient hydrogen evolution using few-layer alloys of $MoS_{2(1-x)}Se_{2x}$. *Nanoscale* **2014**, *6*, 12856−12863.
(27) Vrubel, H.; Hu, X. Molybdenum Boride and Carbide Catalyze Hydrogen Evolution in both Acidic and Basic Solutions. *Angew. Chem., Int. Ed.* **2012**, *51*, 12703−12706.
(28) Reber, A. R.; Khanna, S. N.; Roach, P. J.; Woodward, W. H.; Castleman, A. W. Reactivity of aluminum cluster anions with water: Origins of reactivity and mechanisms for H_2 release. *J. Phys. Chem. A* **2010**, *114*, 6071−608.
(29) Shimojo, F.; Ohmura, S.; Kalia, R. K.; Nakano, A.; Vashishta, P. Molecular dynamics simulations of rapid hydrogen production from water using aluminum clusters as catalyzers. *Phys. Rev. Lett.* **2010**, *104*, 126102.
(30) Vashishta, P.; Shimojo, F.; Ohmura, S.; Shimamura, K.; Mou, W.; Kalia, R. K.; Nakano, A. Rapid hydrogen production from water using aluminum nanoclusters: A quantum molecular dynamics simulation study. *Solid State Ionics* **2014**, *262*, 908−910.
(31) Chen, J.; Luo, Z. Single-point Attack of Two H_2O Molecules towards a Lewis Acid Site on the $GaAl_{12}$ Clusters for Hydrogen Evolution. *ChemPhysChem* **2019**, *20*, 499−505.
(32) Roach, P. J.; Woodward, W. H.; Castleman, A. W., Jr; Reber, A. C.; Khanna, S. N. Complementary Active Sites Cause Size-Selective Reactivity of Aluminum Cluster Anions with Water. *Science* **2009**, *323*, 492−495.
(33) Ghosh, A. K.; Krishnan, K. Chemoselective catalytic hydrogenation of alkenes by Lindlar catalyst. *Tett. Lett.* **1998**, *39*, 947−948.
(34) Adair, G. R. A.; Williams, J. M. J. Chemoselective catalytic hydrogenation of alkenes by Lindlar catalyst. *Chem. Commun.* **2007**, 2608−2609.
(35) Maytum, H. C.; Francos, J.; Whatrup, D. J.; Williams, J. M. J. 1,4-Butanediol as a Reducing Agent in Transfer Hydrogenation Reactions. *Chem. Asian J.* **2010**, *5*, 538−542.

https://doi.org/10.1021/acsanm.1c04331
ACS Appl. Nano Mater. 2022, 5, 2636−2643