



University of Dayton  
Office of Technology Partnerships  
937.229.3469

## **Hydrogen Gas Generation From Aluminum Nanoparticles And Room Temperature Water**

Case #: UD-515

US Patent Serial #: [12/791,900](#)

Inventor: Chris Bunker, Elena Guliants, et. al.

## Point-Source Hydrogen Production for Battlefield Power Generation

### (Hydrogen from Room Temperature Tap Water)

POC: Christopher E. Bunker, AFRL/RZPF, 5-6935

In-the-field generation of hydrogen is a key enabler for advanced energy concepts that support the war fighter. Efforts to replace batteries (heavy, bulky, costly) with energy-on-demand fuel cell technologies are on-going; however, little is gained if hydrogen storage via metal hydrides (heavy, bulky, costly) or hydrogen from liquid hydrocarbons (fuel storage, transport, logistics) is required to operate the fuel cells. Recently, we discovered a new class of energetic nanoparticles capable of splitting hydrogen from water with no additional additives (i.e., no co-reactants or strong alkali solutions are required) that can generate large quantities of hydrogen (hundreds of liters) at operational pressures (> 50 psi) in a short period of time (minutes). The nanoparticles are composed of an aluminum core protected by a unique, two component shell that prevents oxidation of the aluminum in ambient air, but readily allows the oxidation of the aluminum in water to yield hydrogen gas.

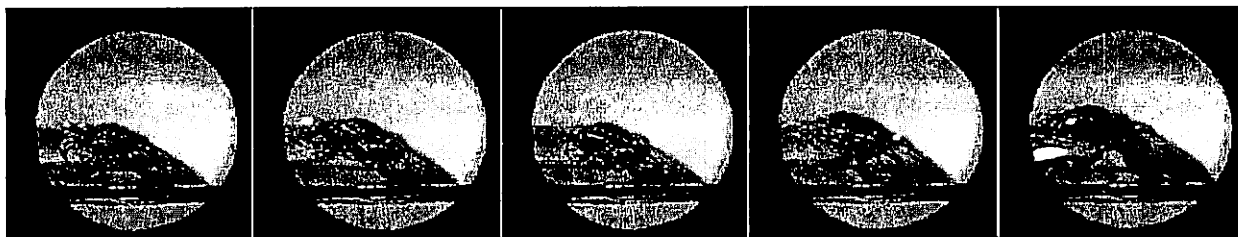
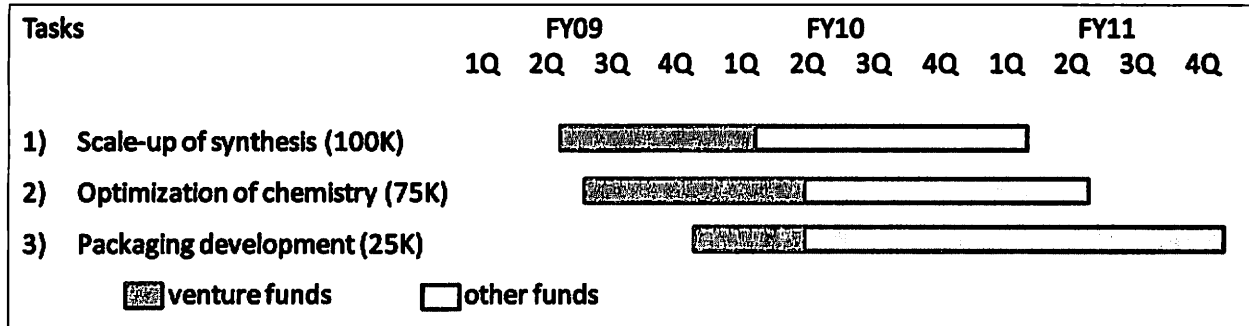


Figure 1. A series of magnified images showing hydrogen gas evolution from a water droplet containing a small piece of the reactive nanoparticles.

This technology would provide the war fighter, equipped with a compact fuel cell, the ability to produce hydrogen from plain water and our nanoparticles. From our initial studies, we estimate *10 grams of our compound combined with 1 mL of water yields 1 liter of hydrogen gas*. For a fuel cell operating at 100 ml/min, this would provide 10 min of operation time. One kilogram (roughly the size of a baseball) of our nanoparticles with 100 mL of water would yield ~16 hrs of operation. Such a capability should be considered a game-changer for a soldier in the field.

Funds are requested to support further development of this technology; specifically, three tasks are identified for support, 1) scale-up of the reactive nanoparticles to support larger testing, 2) optimization of the nanoparticle chemistry to increase efficiency, and 3) packaging of the reactive nanoparticles for optimal field utilization. It is expected that venture fund support would initiate this program and that other sources of funding would be sought to cover the out years.

Nominal Plan: 200K Venture Funds



Venture funds to be expended by 2Q FY10. Other funds TBD.

Task Details:

Task 1. Scale-up of synthesis – the reactive nanoparticles are synthesized using sonochemistry. Currently, samples of 30 to 200 mg per reaction are possible at 3 to 5 reactions per day. It is anticipated that routine use of gram quantities will be required to support both optimization and package development. We anticipate an order of magnitude increase in quantity is required to support further development. To achieve this goal, we will explore the scale-up potential of the sonochemical method to workable limits (we predict ~ 500 mg per sample as a best case as too large a sample can alter the chemical properties of the nanoparticles). To further expand the production quantities, we will also explore the scale-out potential of sonochemistry through the matrixing of multiple instruments coupled with robotic control. This technique should allow for continuous synthesis with gram quantity production.

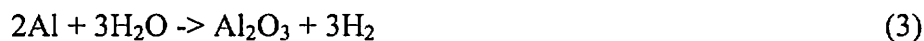
Task 2. Optimization of chemistry – the current sample consists of nanoparticles that are of a core-shell geometry. The core, which is the reactive aluminum, currently accounts for only 40% of the particle mass. The remaining 60% represents the protective shell. Research under this task will be focused on increasing the aluminum content on the particles without degrading the superior action of the protective shell. One possible approach will be to increase the size of the nanoparticles, as increasing the size reduces the percentage of the protective shell to the total mass. However, this must be balanced against any loss of efficiency in the reaction of the aluminum to generate hydrogen gas due to the decrease in surface area.

Task 3. Packaging development – the reactive nanoparticles will ultimately require formulation such that they are readily applied to hydrogen gas generation given the constraints of in-the-field operation. This includes storage, transport, usage, and control. The initial goal is a battery-like configuration where a simple method for water injection will allow controlled quantities of hydrogen to be generated. By controlling the amount of water, the operator would control the amount of hydrogen, the rate of formation, the pressure generated, and the power generated.

**16 a:** The development of technologies that would lead toward adoption of a hydrogen economy requires readily available and safe access to hydrogen. The reaction of aluminum with water is one potential source for this hydrogen; however, the protective nature and the stability of aluminum oxide is a clear detriment to the application of the aluminum-water reaction. Here, we demonstrate the generation of hydrogen gas from ordinary room-temperature tap water when combined with aluminum-oleic acid core-shell nanoparticles. The reaction is found to be near-complete (> 85% yield hydrogen) and the rate dependent on sample mass. The potential of these nanoparticles as a source of hydrogen gas for power generation is demonstrated using a simple fuel cell with an applied load.

## **Introduction**

In obtaining hydrogen from water, it is well known that Al metal will react with water to yield H<sub>2</sub> gas;



However, these reactions are limited in their utility due to the natural occurrence of a protective aluminum oxide shell on the surface of the aluminum. The stability of the aluminum oxide prevents air and moisture from accessing the underlying aluminum metal. To circumvent this problem, researchers have applied various reaction-promoting schemes, including the addition of

peroxides or alkalis,<sup>ref</sup> or the application of high temperature.<sup>ref</sup> Recently, Woodall demonstrated hydrogen generation from gallium/aluminum solutions with water.<sup>ref</sup> By dissolving the aluminum in liquid gallium, the researchers prevented the formation of the aluminum oxide shell, thus allowing the aluminum-water reaction to proceed. While capable of providing hydrogen from the aluminum-water reaction, these approaches involve greater complexity than the equations for the reaction would seem to require. A more simple solution might be achieved if the nature of the protective aluminum oxide shell could be altered. Recent research on the combustion of aluminum nanoparticles protected by aluminum oxide shells suggests this may be possible with data demonstrating enhanced reactivities over micron- or bulk-scale aluminum.<sup>ref</sup> These results have been attributed to the role surfaces and interfaces play in aluminum oxidation, noting that as particle size decreases, the surface and interfacial areas increase and become dominant in determining the physical and chemical properties. However, having particles on the nano-scale alone is not sufficient—commercial aluminum nanoparticles possessing an aluminum oxide shell will not react in water under ambient conditions. In fact, the mixing of commercial aluminum nanoparticles with liquid water or water ice (ALICE) is being investigated as potential propellant formulations for underwater or space applications.<sup>ref</sup>

To achieve our desired goal, chemical modification of the aluminum oxide shell is required. Previously, we reported the synthesis of air stable aluminum-oleic acid (AIOA) core-shell nanoparticles via a sonochemically-assisted thermal decomposition of alane in the presence of the catalyst titanium (iv) isopropoxide.<sup>ref</sup> The particles consist of an inner aluminum core surrounded by an oxide shell, followed by an outer organic shell, each accounting for ~40, 25, and 35% of the total particle mass, respectively. The oxide shell is believed to have formed from the oxygen atoms brought to the aluminum surface by the capping agent oleic acid; hence, it was

termed an organic-provided oxide shell. Thermal analysis of these particles demonstrated that this oxide does not behave as natural aluminum oxide, instead reacting at a much lower temperature ( $\sim 420$  °C) vs. standard aluminum nanoparticles ( $\sim 600$  °C).<sup>ref</sup> Yet, this oxide shell prevents oxidation of the aluminum metal under ambient conditions, with samples remaining viable after months of storage with no special precautions (*i.e.*, stored in glass bottles sitting out on countertops). It should be noted that nanoparticles prepared via a standard thermal decomposition of alane do not exhibit the stability achieved using sonochemistry. The samples will oxidize within minutes to days. While we are still unclear as to why such a difference exists, there are a number of unique aspects to the sonochemical process that might influence the properties of the nanoparticles; for example, sonochemistry generates extreme temperature regions ( $\sim 5000$ K) with very rapid cooling rates ( $\sim 10^{10}$  K/sec),<sup>ref</sup> promotes radical formation,<sup>ref</sup> and displays the phenomenon of jetting (harsh impacting of material on the micron scale).<sup>ref</sup>

In examining the stability of the AlOA nanoparticles, samples ( $\sim 30$  mg) were suspended in a series of solvents (10 mL) and agitated in a simple sonic bath for 90 min. The solvents included non-polar hydrocarbons (hexane, toluene), mildly acidic hydrocarbons (chloroform), and polar solvents (ethanol, methanol, and water). In all cases but one, the particles remained unchanged as measured by powder x-ray diffraction (Figure 1, A). Only water showed a change in the particles with a significantly altered x-ray spectrum (Figure 1, B). The spectrum is not identifiable as a single aluminum oxide material, but the main peaks may suggest formation of xxx, xxx, and xxx. Clearly, water is oxidizing the aluminum metal. To test the reaction, a small quantity of sample (20 mg) was mixed with water (5 mL) and the headspace sampled with a home-assembled quadrupole mass spectrometer. After subtraction of a background spectrum, the data showed a strong signal for hydrogen gas (supplemental on-line material, SOM, Fig. S1).

It should be noted that in the above experiments, the AlOA to water mass ratio is fairly small ( $\text{AlOA:H}_2\text{O} = 10^{-3}$ ). When performed at a much larger value (e.g., 0.5), the reaction appeared far more vigorous and generated considerable heat. The x-ray spectrum of the oxide product formed under those conditions is quite different (Fig. 1, C), demonstrating a clear pattern for boehmite (eq. 2). To further elucidate the meaning of these observations, a small-scale temperature measurement system was assembled (SOM, Fig. S2) using a thermocouple affixed to an alumina cup. Water (a constant 60  $\mu\text{L}$ ) was added to AlOA samples varying in mass from  $\sim 2$  mg to 15 mg ( $\text{AlOA:H}_2\text{O} = 0.03$  to 0.25). Temperature was then recorded as a function of time, and the data is plotted in Fig 2. The traces of temperature vs. time are all similar in that they exhibit an induction phase, a rapid rise, a maximum, and they then a steady decrease, eventually returning to room temperature. A plot of the slopes obtained from the rapid rise section of each trace vs. sample mass is shown in Fig. 2, inset (SOM Fig. S3 shows the plots of temperature vs. time with the linear fits). The data indicates that as mass increases, the rate at which the sample reaches its maximum temperature increases non-linearly. Such an observation is indicative of a self-heating reaction; as the sample reacts, the heat generated accelerates the reaction. This effect is amplified as the sample mass increases (note: such a reaction must be considered hazardous for in the case of a run-away reaction, the processes won't stop until the starting materials are fully consumed). Also shown in Fig. 2, inset are the values for maximum temperature vs. sample mass. The plot is linear, indicating the reaction yield is constant.

To obtain a value for the yield, we require a different experimental system, since thermal absorption and loss are not easily calibrated for this setup. Instead, we perform the same basic experiment using a 25 mL pressure vessel coupled to a digital pressure meter. To the vessel was added 1 mg of sample and 2 mL of water ( $\text{AlOA:H}_2\text{O} = 0.5$ ), resulting in a rapid increase in

pressure due to hydrogen gas generation. The pressure is plotted vs. time in Fig 3B and shows a rapid rise that then slows to reach a plateau. The pressure at the plateau is 309 psi, or 21 atm. From the knowledge that our samples are ~40% aluminum metal, using the stoichiometry of eq. 2, and applying the ideal gas law, we calculate an ~90% yield for the formation of hydrogen gas. The utility of this hydrogen is demonstrated in Fig. 3A where just after the plateau is reached, the pressure vessel is placed in-line with a fuel cell (SOM, Fig. 4) using a pressure regulator set to deliver under 5 psi hydrogen. The attached to the fuel cell is a simple computer fan to serve as the electrical load, and the voltage and current are recorded as the hydrogen is consumed. As can be seen from the figure, once the hydrogen is delivered to the cell, the voltage and current quickly reach stable working values (~13 v and 0.15 amp). The power consumed by this system is ~ 2 w for a continuous 2.3 min. Obviously, the power generated is a function of the fuel cell, not the hydrogen; however, greater power would certainly result in faster consumption of the hydrogen. For real applications, a larger quantity of hydrogen will be required. Fortunately, from the data presented here, this reaction should be easily scalable. In addition, the exothermic property and the self-heating nature of this reaction offers one the possibility to control the rate of the reaction through manipulation of the system temperature. For example, if active cooling could be applied, one might be able to slowly deliver the hydrogen as it is produced, negating the need for a high pressure vessel and improving the safety of the system.

## **Acknowledgements**

Financial support provided by:



Air Force Research Laboratory (AFRL, F33615-03-2-2347)

Defense Threat Reduction Agency (DTRA, grant #HDTRA-07-1-0026)

Dayton Area Graduate Studies Institute (DAGSI, RH5-UD-08-2)

## **References**

## **Inventor's Roles**

Idea, determination, understanding of hydrogen generation from ALOA particles:

Christopher E. Bunker

Idea, development, planning, directing of research focused on highly energetic core-shell nanoparticles where the shell provides protection under ambient conditions but becomes active under other conditions (i.e., temp or water).

Christopher E. Bunker, Elena A. Gulians

Development of the thermal and sonochemical syntheses, understanding and practice, that lead to the current particles that exhibit the hydrogen generating properties:

K. A. Shiral Fernando, Marcus J. Smith, Barbara A. Harruff

## Experimental

**Materials.** Alane *N,N*-dimethylethylamine in a 0.4 M toluene solution, titanium (iv) isopropoxide (98%), oleic acid (99%), and dodecane (99% and anhydrous) were all obtained from Aldrich and used as received. Hexane (Optima grade) was obtained from Fisher Scientific.

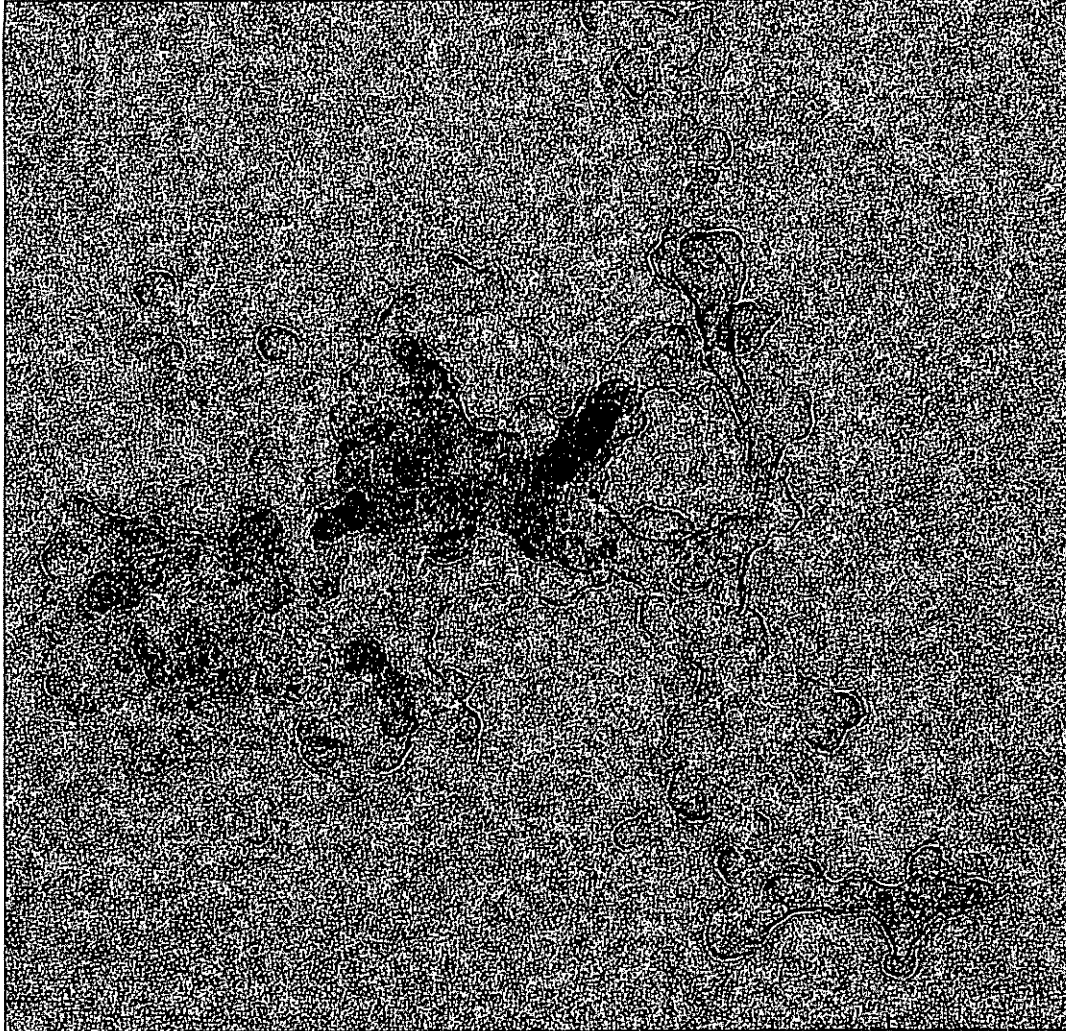
**Synthesis.** A detailed procedure for the synthesis of these aluminum-oleic acid core-shell nanoparticles was reported elsewhere. Only minor modification to that synthesis was made to achieve a larger sample mass. Briefly, four mL of a deoxygenated solution of oleic acid in dodecane (xx M) was combined with 10 mL of a solution of alane *N,N*-dimethylethylamine in toluene (0.4 M). To this combined solution was added titanium (iv) isopropoxide such that the final concentration was 55 M. The working solution was then sonicated for 7.5 min active time at an amplitude of ~46% (~22W) following a one-second-on, one-second-off procedure. The above conditions produced a black colored solution that gradually precipitated yielding a grayish-black powder. The powder was recovered by evaporation of the solvent under vacuum followed by repeated washings with hexane. The reaction yielded between 200 and 250 mg per synthesis.

**Measurements.** X-ray powder diffraction (XRD) analysis was performed on a Bruker D8-Advanced equipped with a Cu $\alpha$  source, monochromator, and a Sol-X detector. Identification of the observed patterns was accomplished by comparison to the ICDDs crystallographic database. TEM (transmission electron microscopy) images were obtained using a Hitachi H-7600 operated at 100 kV. Samples were prepared from solution by drip spotting on carbon coated copper grids. Hydrogen mass spectrum was obtained using a home-built molecular beam

quadrupole mass spectrometer. Pressure was recorded using a Heise PM digital pressure gauge and temperature measured using a Fluke 8846a volt meter with a K-type thermal couple.

## Figure Captions

1. TEM image of Al-oleic acid nanoparticles from the sonochemical reaction of alane with titanium catalyst. Size bar indicates 100 nm.
2. Mass spectra demonstrating hydrogen production from the reaction of the aluminum-oleic acid nanoparticles and water: (top) background spectrum; (middle) reaction spectrum; (bottom) background-subtracted spectrum.
3. Powder x-ray diffraction spectra for the aluminum-oleic acid nanoparticles (top, identified as fcc aluminum) and the product of their reaction with water (bottom, identified as boehmite).
4. Plot of temperature vs. time for the reaction of the aluminum-oleic acid nanoparticles with water. The different curves represent different amounts of sample (solid line bottom to top – 3.0, 4.9, 5.0, 6.4, 7.1, 11.3, and 14.7 mg; dashed line bottom to top – 7.3, and 13.7 mg). Inset depicts the maximum temperature vs. sample mass and the change in temperature per change in time for the rapid rise section of the curves vs. sample mass.
5. Plots of pressure vs. time (bottom) and voltage and current vs. time (top) for the reaction of 1.0 gm of the aluminum-oleic acid nanoparticles with 2.0 mL of water in a 0.025 L pressure vessel. The pressure was allowed to stabilize before the fuel cell was brought on-line. The operating power was approximately 2 W.



TH20BH47.tif

Aluminum

SG30MS1

Print Mag: 185000x @ 7.0 in

11:52 08/20/07

TEM Mode: Imaging

100 nm

HV=100kV

Direct Mag: 50000x

X: 54.7 Y: 397.1 T:0.0

NEST

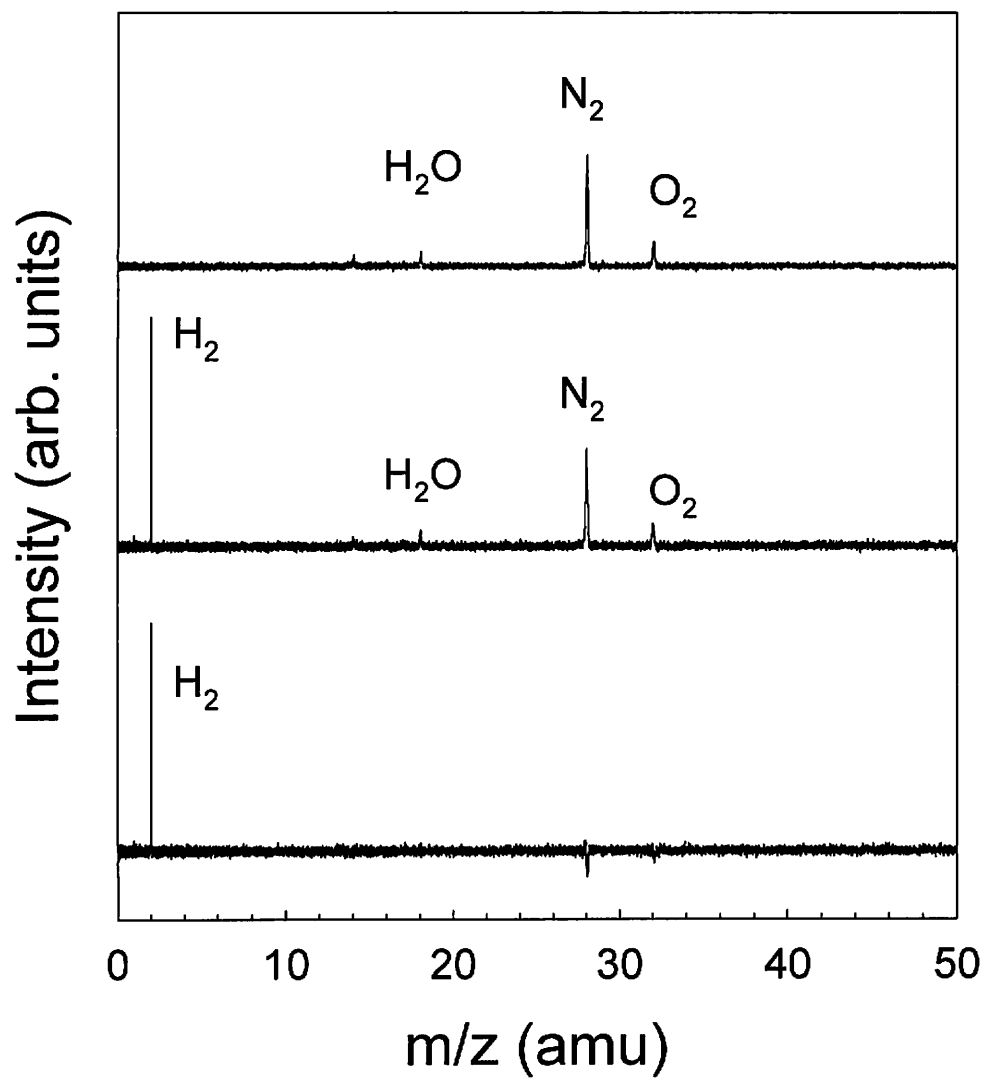


Figure 2.

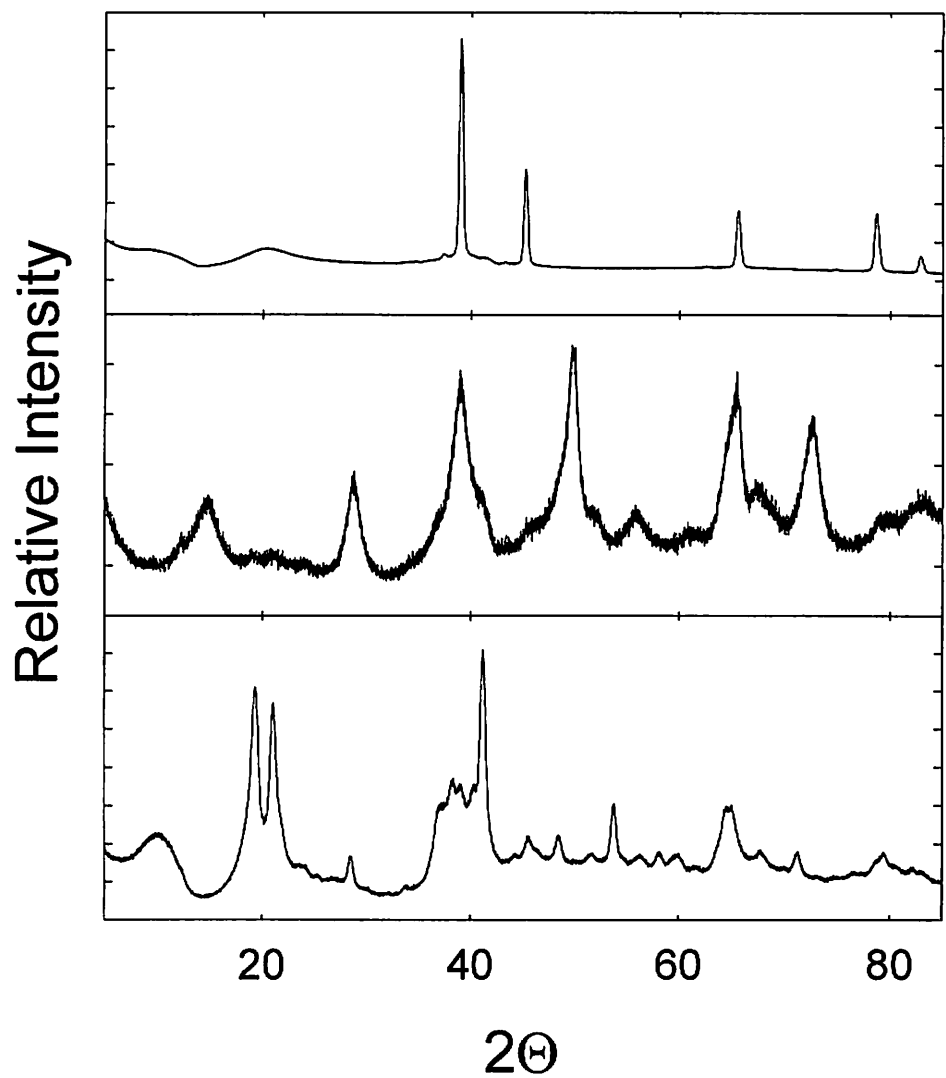


Figure 3.

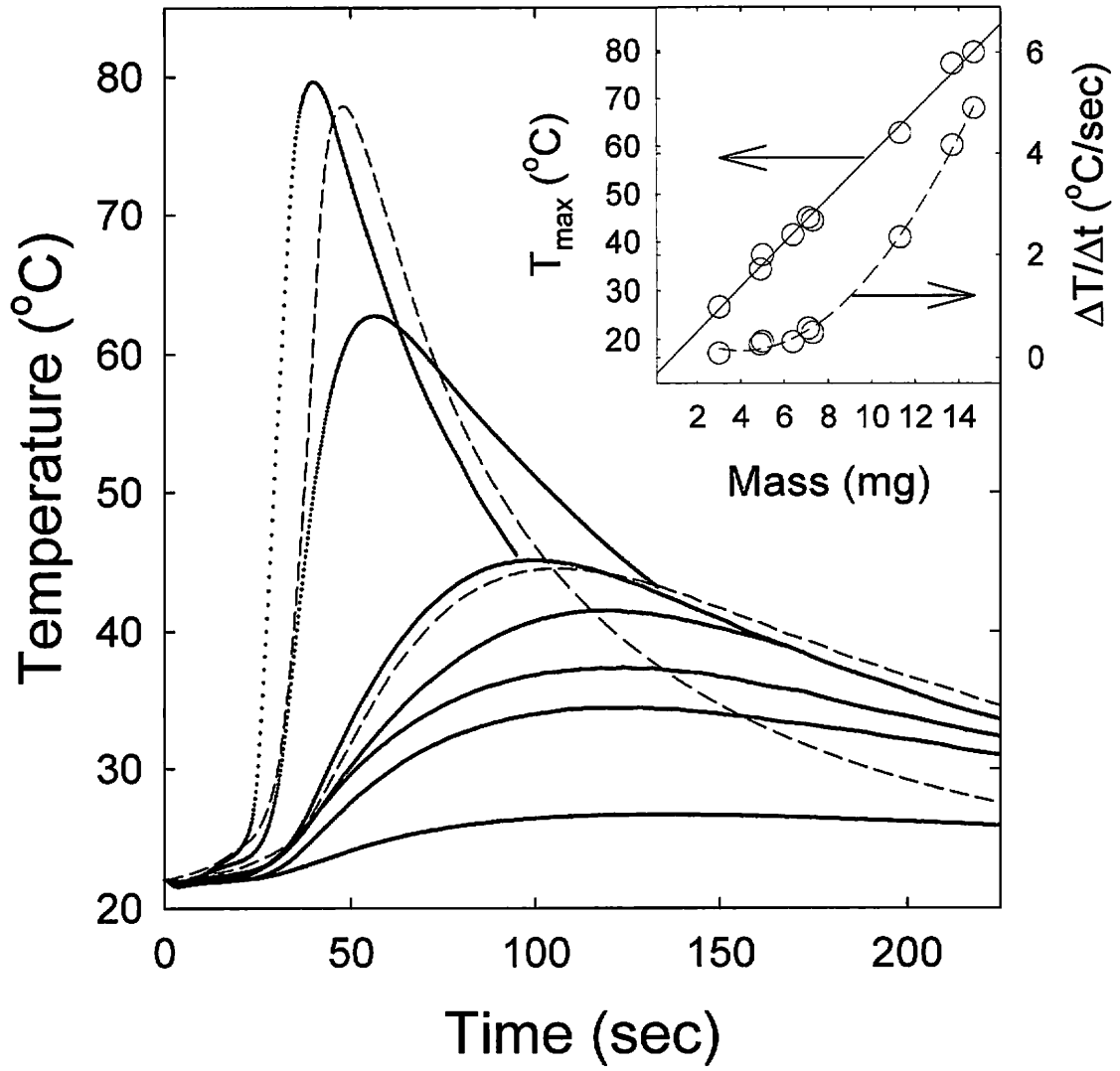


Figure 4.



