Final Report on the SPS Chapter Award 2014

Funded by SPS, American Institute of Physics

TITLE OF RESEARCH PROJECT: High-Throughput Synthesis and Characterization Studies of Novel Nanoscale Hydrogen Storage Systems

DURATION OF THE ENTIRE PROJECT: January 1 – December 31, 2014

SPS CHAPTER, Physics Department, Tuskegee University: ZONE: 06, SPS Chapter #7446

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PROJECT PARTICIPANTS: Undergraduate Physics Majors:

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FUNDING AGENCY: American Institute of Physics, SPS, ΣΠΣ

ABSTRACT

The objective of this SPS-SPS Undergraduate Proposal is to investigate high throughput synthesis and characterization of novel nanoscale hydrogen storage systems for stationary and mobile applications. In this propose work, the synthesis procedures will be optimized by combintorial methods of tailoring the composition, and catalyst doping concentrations.

PROJECT OBJECTIVES

Hydrogen can be stored in many ways such as (i) gas in high pressure cylinders, (ii) liquid at cryogenic temperatures, and (iii) interstitials atoms or molecular hydrogen species in solid state material hydrides. The long term stability and safety of storing hydrogen in solid state materials such as complex metal hydrides nanocomposites, has undoubtedly surpassed the other two options mentioned above. The research goals of the proposed investigation are to synthesize and characterize the pristine and nanomaterials doped complex hydride, Li-nMg-B-N-H employing high energy mechanical milling. The nanomaterials doping and compositional modifications on the bulk structure of these hydrides demand for high throughput synthesis procedures.

AWARD ACTIVITY

Hydrogen storage in solid state materials offers a long term solution for the sustainable and alternate fuel usage. Complex chemical hydrides (e.g. sodium or lithium alanates, borohydrides, mixed complex/metal hydrides) [1-3] have demonstrated with higher theoretical storage capacity at temperatures >350^{o}C. To reduce the thermal decomposition temperature of these complex hydrides, a destabilization strategy was adopted using metal hydrides. Based on the literature survey, we have successfully formulated the hydrogen sorption characteristics of complex hydrides ($LiBH_4/2LiNH_2$) using nanocrystalline MgH_2 and synthesized via a high energy planetary milling process [4,5]. Thus obtained NC MgH_2 assisted ternary hydride Li-B-N-H demonstrated reversible hydrogen storage capacity of ~5.2 wt.% at 175 ^{o}C as shown in pressure-composition isotherms (PCI) Figure 1. Whereas for the case of LiBNH ternary hydride without MgH_2, showed a irreversible H_2 storage capacity of 4wt.% at 250 ^{o}C and for the case of commercial MgH_2 ad-mixed LiBNH, showed reversible capacity of only 3wt% at 175 ^{o}C.

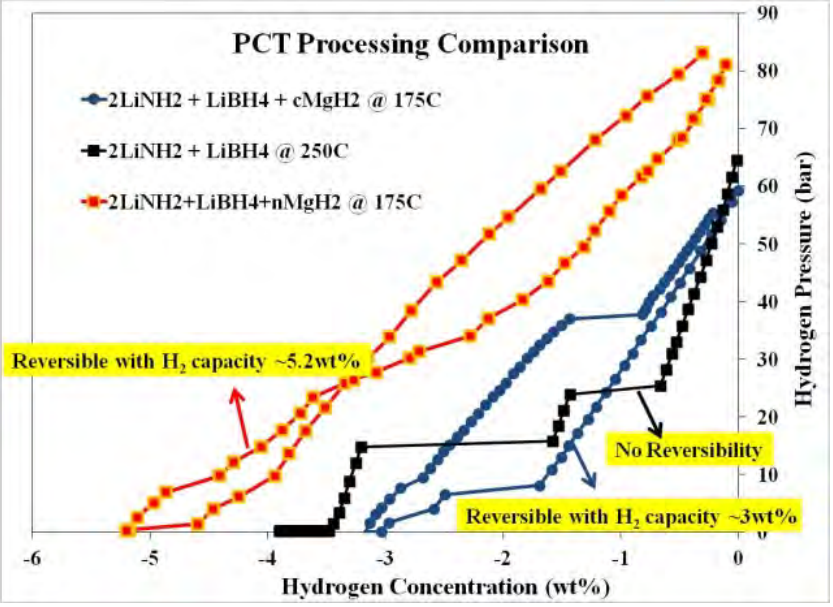

FIGURE 1. PCI of $2LiNH_2+LiBH_4$ with (a) No MgH_2 (b) Commercial MgH_2 and (c) nano MgH_2

The higher reversible hydrogen capacity of ~5.2wt.% at temperature of 175^{o}C, as demonstrated in Figure 1, was obviously due to the crystallite size of both quaternary hydride (LiBNH) and magnesium hydride (MgH_2) and their optimum size difference. For example, the sample of $2LiNH_2+LiBH_4$+nanoMgH_2 after synthesis, demonstrated with crystallite size difference of ~18.8 nm (LiBNH ~28nm and nMgH_2 ~9.2nm) as shown in Figure 2 below. On the other hand, the commercial magnesium/complex hydride (LicMgBNH) mixture synthesized via all-in-one method showed the size difference of ~3.3 nm (ie LiBNH ~40 nm and cMgH_2 ~36.7nm) and showed capacity of only 3wt%.

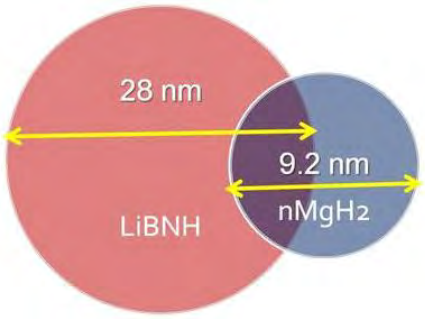

FIGURE 2. Crystallite size difference of complex hydride and metal hydride for hydrogen storage

The hydrogen release from the $2LiNH_2+LiBH_4$+nMgH_2 complex hydrides occur at two different temperatures such as 150 and 300 ^{o}C. Though the first step hydrogen release kinetics not much affected, the doping of nanocatalysts (~2 mol%) such as nanoMn and nanoNi enhances

the reaction rate at lower temperatures (230-270 ^{o}C) as demonstrated in Figure 3. The presence of 3d transition metal of Mn and Ni in nanostructure forms (1-3 nm) thus dissociates the hydrogen molecule in to H-atom and facilitate catalytic enhancement of hydrogen absorption and desorption at moderate temperatures.

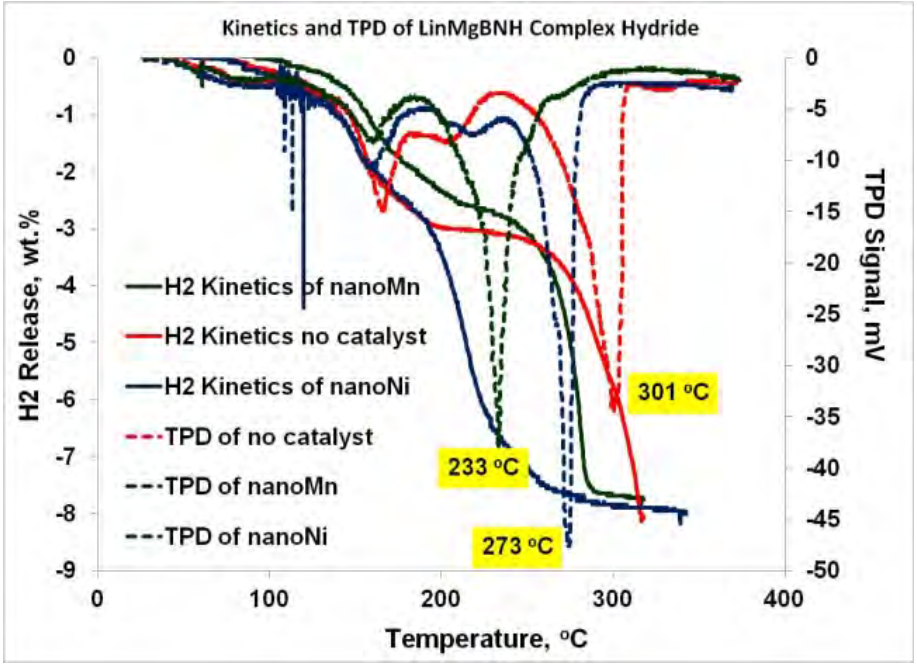

FIGURE 3. H_2 release kinetics and TPD profiles of $2LiNH_2+LiBH_4+nMgH_2$ with (a) No catalyst (b) nano Mn and (c) nano Ni [6]

NF & NS FOR H_2 STORAGE

Polymer nanostructrues such as polyaniline (PANI) nanofibers and nanospheres have recently explored for hydrogen storage. Polyaniline in its bulk form, has shown with hydrogen storage capacity of ~0.5 wt.%. However, polyaniline nanostructures prepared by both chemical and electrospinning routes, have resulted in reversible hydrogen storage characteristics in terms of both physisorption and chemisorption processes. Figure 4 represents the SEM morphology of the polyaniline nanostructures before and after hydrogen sorption. A ballooning or bulging effect, fibrous expansion and micro-cracks propagation due to H_2 interaction are visible from Figure 4. Table 1 summarizes the results of hydrogen storage characteristics of PANI in its bulk and nanostructure forms. PANI nanostructure forms exhibits higher capacity of 2-8 wt% with reversibility at T<150 ^{o}C.

TABLE 1. H_2 storage characteristics of Polyaniline [7]

Material	H_2 Capacity	Temperature
Bulk PANI	0.4wt%	125°C
PANI-NS	2-4wt%	30°C
PANI- NF	3-9wt%	30-100°C

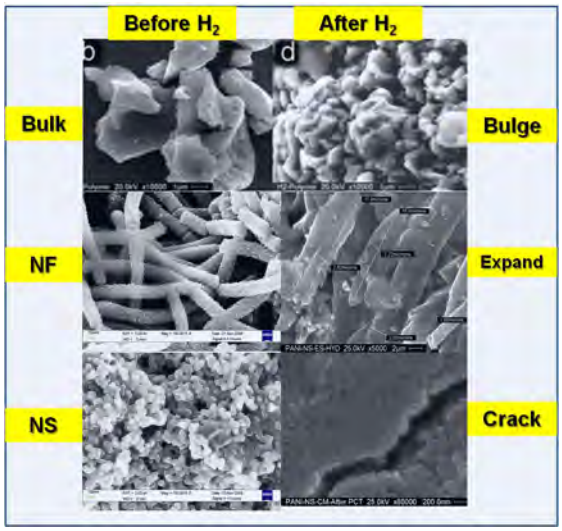

FIGURE 4. SEM morphology of (a) Bulk, (b) NF and (c) NS Polyaniline Materials

SYNERGISTIC EFFECTS OF NP & NT

This section introduces the concept of two different nanostructures, for example nanotubes and nanoparticles have exhibited superior performance on the hydrogen uptake and release characteristics when compared to their individual counterpart. We have chosen Nb_2O_5 nanoparticles and multiwall carbon nanotubes (MWCNT) for doping the host complex hydride $2LiNH_2/LiBH_4/nMgH_2$. The concentrations of both Nb_2O_5 and MWCNT have been optimized for greater hydrogenation and dehydrogenation characteristics at lower temperature. From the thermal programmed desorption (TPD) profiles shown in Figure 5, it is unambiguously seen that the Nb_2O_5 of 2wt% and MWCNT of 10wt% doped on the Li-nMg-B-N-H host hydride excelled in terms of thermal decomposition of hydrogen both at low (<200 °C) and high temperatures (<350 °C) regimes.

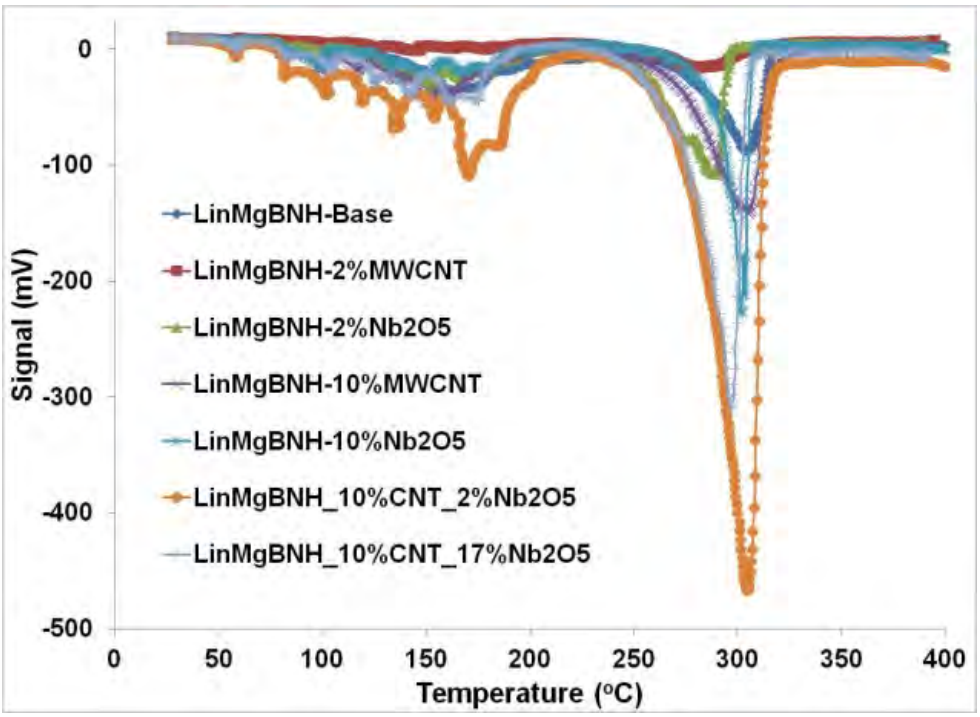

FIGURE 5. TPD signal of Nb_2O_5 and MWCNT doped complex hydrides (Li-nMg-B-N-H)

Figure 6 represents the schematic diagram of the interaction of H_2 molecule on the surface of nanoparticle to dissociate in to H atoms and further transported via nanotubes for the effective hydrogen absorption by the host complex hydride.

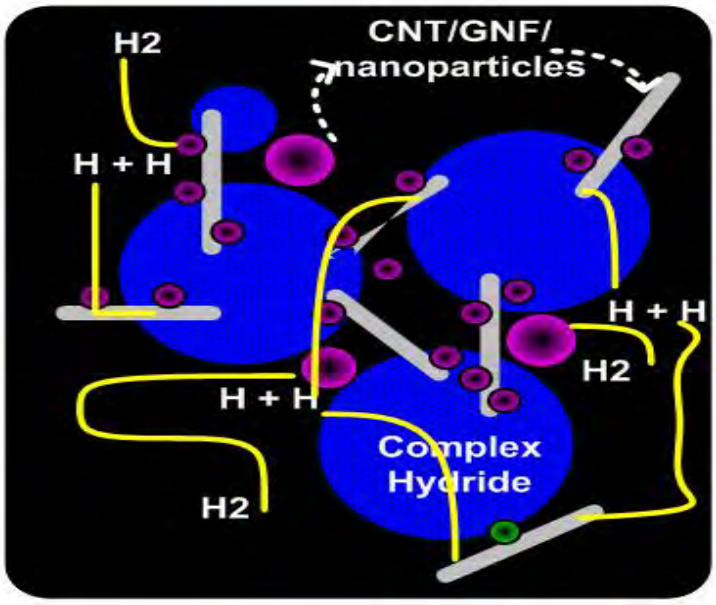

FIGURE 6. Schematics of H_2 dissociation and atomic hydrogen transport via NP and NT

RESULTS AND DISCUSSIONS

In conclusion, nanomaterials by their unique size and shape have demonstrated excellent properties and behavior for versatile applications in clean energy, environment and health science. Some of the potential uses and applications of nanostructured materials for hydrogen production and storage, solar assisted photocatalysis are discussed in this paper. Nanoparticles of ruthenium oxide (RuO_2) coated on the silicon electrodes or sandwiched with CoS_2 nanoparticles have proved to be an effective electrocatalysts that can work under low bias voltage for the splitting of water of H_2S to hydrogen and oxygen (sulfur or sulfuric acid). For the hydrogen storage in solid state complex hydrides, the role of nanocrystalline MgH_2, and nanocatalysts such as Mn, Ni etc. are phenomenal to improve both the thermodynamics and kinetics of hydrogen sorption reactions. Moreover, the advantage of having both Nb_2O_5 nanoparticles and multi wall carbon nanotubes (MWCNT) on the high reversible hydrogen storage have established via the synergistic mechanism of H_2 dissociation and the effective hydrogen atom transport. We have developed earth benign nanoparticles of TiO_2, $InVO_4$ and $ZnFe_2O_4$ for the water or air detoxification applications. However, these materials either due to their high energy band gap or inappropriate band edge positions often showed poor visible light assisted photocatalytic performances. To utilize the entire solar spectrum for higher quantum efficiency, we have adopted two approaches (i) semiconductor coupling to produce nanocomposites of $TiO_2/InVO_4$, $TiO_2/ZnFe_2O_4$ and (ii) anion (carbon, nitrogen) doping of TiO_2. In both cases, because of the band gap tailoring and optimization, a blue or "anomalous" red shift of the absorption edge was observed. Hence, an enhancement of photo-oxidation and/or photo-reduction processes was successfully demonstrated using UV-Visible light irradiation. We will further explore and research other attractive properties and applications of nanomaterials.

DISSIMINATION OF RESULTS

The following methods will be applied to inform the results of this work to the scientific community: (i) by presenting work in science related meetings and conferences and (ii) by publishing in scientific journals.

REFERENCES

1. P.C. Sharma and S. Srinivasan, Development of Novel Nanostructures and Nanoscale Complex Hydrides for Reversible Hydrogen Storage, *InTech Publications*, http://dx.doi.org/10.5772/50171, 25 pages, (2012).
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IMPACT ASSESSMENT

The work was discussed in the Tuskegee University Society for Physics Students and presented at different forum. The TUSSP members were influenced and motivated to involve in such research projects. It is expected that it would help increase the SPS membership in fall semester. A better assessment can only be made in next semester by analyzing the chapter's activities.

ACKNOWLEDGEMENTS

The project participants, faculty mentors and SPS TU chapter advisors are grateful to the American Institute of Physics (AIP), Society for Physics Students (SPS) and Sigma Pi Sigma (ΣΠΣ), National Science Foundation (Energy Sustainability) for financial support.

PUBLICATIONS/CONFERENCE PRESENTATIONS

1. STUDENT POSTER/ORAL COMPETITIONS AT THE 90TH ALABAMA ACADEMY OF SCIENCES (AUBURN UNIVERSITY)
   (i) Invited Talk: Synergistic Effects of nanotubes and nanoparticles for reversible hydrogen storage, P. C. Sharma, S. Srinivasan et. al. 91st Annual Meeting of AAS, Auburn University, March 12-14, 2014.
   (ii) Title: Synthesize and characterize the pristine and nanomaterials doped complex hydride, 91st Annual Meeting of AAS, Auburn University, March 12-14, 2014.

2. STUDENT POSTER/ORAL COMPETITIONS AT THE 5TH JOINT ANNUAL RESEARCH SYMPOSIUM (TUSKEGEE UNIVERSITY)
   (i) Oral Presentation Title: The long term stability and safety of storing hydrogen in solid state materials, Tim Powell and P.C. Sharma, 5th Joint Annual Research Symposium (JARS), March 6, 2014.

Tuskegee University SPS Advisors: Dr. P. C. Sharma (Left) and Dr. Akshaya Kumar (Right)

Tuskegee University President presenting AAS Awards to Tuskegee University SPS Members

Faculty, Tuskegee University SPS members and the President

Tuskegee University SPS Students discussing physics with local school students

Tuskegee University SPS selected members with Provost Hill and other faculty members