# Cooperative Learning of Nanomaterials Manufacturing and Characterization through High Impact Practices

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## Abstract

High-impact practices such as first-year seminars, learning communities, service learning, undergraduate research, and capstone experiences are effective on enhancing learning. In this paper, we will present how to improve undergraduate student education through high impact activities in a cooperative learning setting. Specifically, scalable, low cost manufacturing process for making high performance energy conversion nanomaterials is dealt with. Cooperative learning on several upper division general engineering courses including Independent Research and Studies, Senior Capstone Design, Special Topics on Nanotechnology is investigated. Several scalable, low cost manufacturing research tasks are adopted to enhance the context learning through cooperative learning approach that integrates advanced manufacturing research activities into both academic and social learning experiences. Team-based research projects are implemented. Meanwhile, structuring positive interdependence of students is emphasized. The main content includes: (1) low cost, scalable manufacturing process leading to various nanomaterials research, (2) nanomaterials property characterization, and (3) cooperative learning effectiveness evaluation. The paper addresses fundamental issues including how to allow undergraduate students learning better through cooperative learning approach, how to effectively develop workforce in several priority fields in this country such as advanced manufacturing and nanotechnology, and how to end social inequality in engineering education and practice. The research work focuses on low cost, scalable nanomanufacturing. Nanoporous materials, electrospun nanofibers, and nanoparticles for energy conversions are studied. Students learn multidisciplinary science and engineering knowledge through four focused research projects i.e. (1) nanoporous materials processing and characterization, (2) nanomaterials for energy conversions, (3) nanofibers for photoelectrochemical energy conversion and (4) superparamagnetic nanoparticles for biomedical applications including high resolution magnetic resonance imaging and hyperthermia therapy. Synthesis of nanoporous materials with high surface area for nanosensor applications was performed. The morphology of the nanoporous materials was characterized. Self-assembled nanostructures for energy conversion were investigated. Multilayered structures containing nanoarchitectured fiber arrays were designed and fabricated. The structures are capable to absorb solar rays, and convert the radiation energies into heat and electricity. Students also learned how to make photochemical catalysis electrode. Fundamentals of oxide materials' response to external magnetic field is studied to explore new biomedical imaging agents with controlled nanostructures. Synthesis of superparamagnetic oxide multilayer nanotubes with enhanced hyperthermia was performed. Evaluation on the learning outcomes is provided. Both formative evaluation and summative evaluation results are presented to support the collaborative learning.

## Introduction

In next decade, over millions of undergraduates will be trained in engineering fields all over the country. It is, therefore, imperative to implement effective learning methodologies to enhance education in engineering. Nanomaterials and related manufacturing technology with the multidisciplinary nature are viewed as important areas in engineering filed. Universities should provide students in-depth knowledge and opportunities and allow them to practice multidisciplinary concepts and team working. The cooperative learning setting may allow students to enjoy unique learning experience. Since the industry and academia require students with both practical and analytical skills, undergraduate student learning through the exposure of scientific research is adopted. The pedagogical effort focuses on knowledge obtaining and skill acquiring.

In this work, we practice the project-based cooperative learning. The learning context includes experiments to address nanomaterials synthesis, nanomanufacturing processes, and characterization. Such an approach is implemented in a wide spectrum of upper division courses including the Independent Research/Study, Nanotechnology, and Senior Capstone Design.

## Cooperative Learning Context

The cooperative learning was conducted through several small research projects. In the first team project, the development of a nanomaterial sensor using a quartz crystal microbalance (QCM) to determine the concentration and the rate of decomposition of ammonium nitrate ($NH_4NO_3$) in water is performed. Results are presented for the sensor readings for dilute solutions of ammonium nitrate ($NH_4NO_3$) in various concentrations. The participating students show a very good correlation of concentration level with the output response of the QCM. The students also find that QCM is very sensitive to the scan rate of the voltage potential.

Ammonium nitrate has long been used as a high nitrogen fertilizer in the agriculture industry. In the 1950's it was discovered that ammonium nitrate mixed with fuel oil (ANFO) provided an excellent explosive that could be used in the mining industry. Since ANFO and ammonium nitrate are so commonly used in industry, there have been several instances of accidents and malicious use. The most notable malicious use of ammonium nitrate as an explosive for a terrorist attack was the 1995 Oklahoma City Bombing. In order to reduce the danger associated with this chemical there needs to be a reliable method to detect and determine the concentration of ammonium nitrate.

One possible method to detect ammonium nitrate is through the use of an electrochemical quartz crystal microbalance. A QCM is a sensor composed of a thin slice of a single crystal of quart between two gold electrodes which resonates at a known frequency. When the crystal is in contact with a solution, the molecules that are dissolved in the solution can deposit themselves on the surface of the crystal and cause a change the resonating frequency which can be measured and recorded. A QCM has been used previously in experimentation to detect gaseous ammonia ($NH_3$) in the air[1]. Most of the research before 1980 involving QCM sensors was conducted in a vacuum environment and used for the detection of gasses. In the 1980's there are several

examples of experiments successfully being conducted with the QCM in contact with liquids[2]. There have also been successful experiments using a QCM to determine the concentration of methanol ($CH_3OH$) in liquid form[3]. The purpose and scope of this experiment was to determine a method for explosive detection and mitigation using a QCM as a sensor. The QCM is used in conjunction with two electrodes supplying varying voltage potential to the solution of ammonium nitrate to cause decomposition. There have been other methods of decomposing ammonium nitrate which require significant temperature and pressure to sustain[4]. This experiment attempts to use electrical potential along with a platinum electrode as a catalyst to cause decomposition of the ammonium nitrate.

The students designed an experimental approach for explosive detection and mitigation using quartz crystal microbalance (QCM). The purpose of this experiment was to do explosive detection and mitigation using a QCM as a sensor platform. The QCM is used in conjunction with two electrodes supplying varying voltage potential to the solution of ammonium nitrate to cause decomposition of the explosive. There have been other methods of decomposing ammonium nitrate which require significant temperature and pressure to sustain. This experiment attempts to use electrical potential along with a platinum electrode as a count electrode to cause decomposition of the ammonium nitrate. The experimental procedures are fairly simple and the equipment and solutions used for this experiment included:

1. Electrochemical Analyzer – CH Instruments Model CHI440C
2. Quartz Crystal Microbalance (QCM) oscillator
3. Aqueous ammonium nitrate solutions in 0.1 M, 0.5 M, and 1.0 M concentrations
4. Platinum electrode
5. Reference electrode – Silver/Silver chloride (AgCl) in KCl

Three samples of ammonium nitrate with varied concentrations were prepared for this experiment. Approximately 20 mL of each sample was tested individually by putting it into the QCM test cell. The QCM test cell consisted of the plastic housing to hold the solution and the quartz crystal inside and ports to connect the QCM to the analysis equipment. The Platinum electrode was inserted into the solution and connected to the voltage supply. The silver reference electrode immersed in silver chloride was also inserted into the solution and connected to the opposite lead of the voltage supply. For this experiment an electrochemical analyzer (CH Instruments Model CHI 440C) was used to set the parameters of the testing and for data acquisition. See *Figure 1* for experimental set-up.

For each concentration of ammonium nitrate and the control (de-ionized water) the voltage potential was scanned between 0 volts to 0.5 volts and back to 0 volts in a cycle. The time interval between each incremental voltage change was also independently varied to later determine the time effect and response of the sensor. The parameters of the testing along with the corresponding ammonium nitrate solution concentrations are shown in *Table 1*. The current response was measured and recorded with the corresponding potential. The change in frequency of the QCM was also measure and recorded.

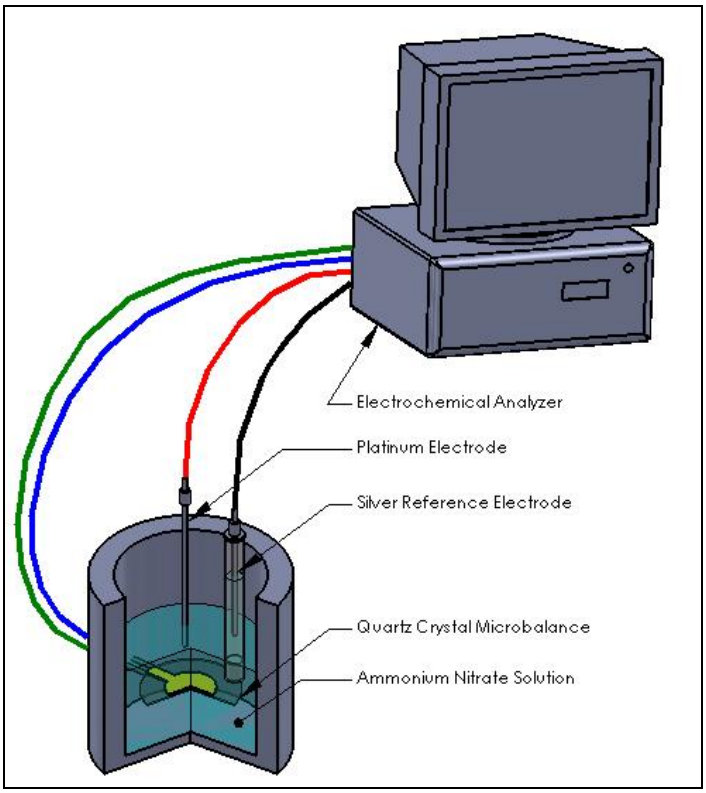


Figure 1: Experimental set-up

Table 1: Test parameters and ammonium nitrate solution concentrations

| Concentration (M) | 0.5 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 1.0 | 1.0 | 1.0 | water | water | water |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Init E (V) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| High E (V) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Low E (V) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Scan Rate (V/s) | 0.01 | 0.1 | 0.01 | 0.005 | 0.001 | 0.001 | 0.1 | 0.01 | 0.001 | 0.1 | 0.01 | 0.001 |
| Sample Interval (V) | 0.001 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.001 | 0.001 | 0.01 | 0.001 | 0.001 |
| Sensitivity (A/V) | 1.0E-06 | 1.0E-06 | 1.0E-06 | 1.0E-06 | 1.0E-06 | 1.0E-06 | 1.0E-06 | 1.0E-06 | 1.0E-06 | 1.0E-06 | 1.0E-06 | 1.0E-06 |
| QCM Init Freq (Hz) | 7864227 | 7842048 | 7834305 | 7852789 | 7813336 | 7816129 | 7982896 | 7982881 | 7982783 | 7865140 | 7864816 | 7818423 |

*Figure 2* shows the results of the experiment with each concentration of ammonium nitrate and water samples. As the voltage potential was varied from 0 to 0.5 volts and back to 0 volts the natural resonance frequency of the QCM increased both during the rising voltage potential and during the falling voltage potential interval. It is also clear from *Figure 2* that with each concentration of Ammonium Nitrate there is a distinct shift in the change in frequency. As the concentration is stronger the natural frequency becomes lower relative to the natural frequency of the crystal in water. This phenomenon is caused by the increased density of each more concentrated solution. Since the density is higher with higher concentrations, the thin film of solution that is in contact with the crystal also has a density and reduces the natural frequency of the crystal.

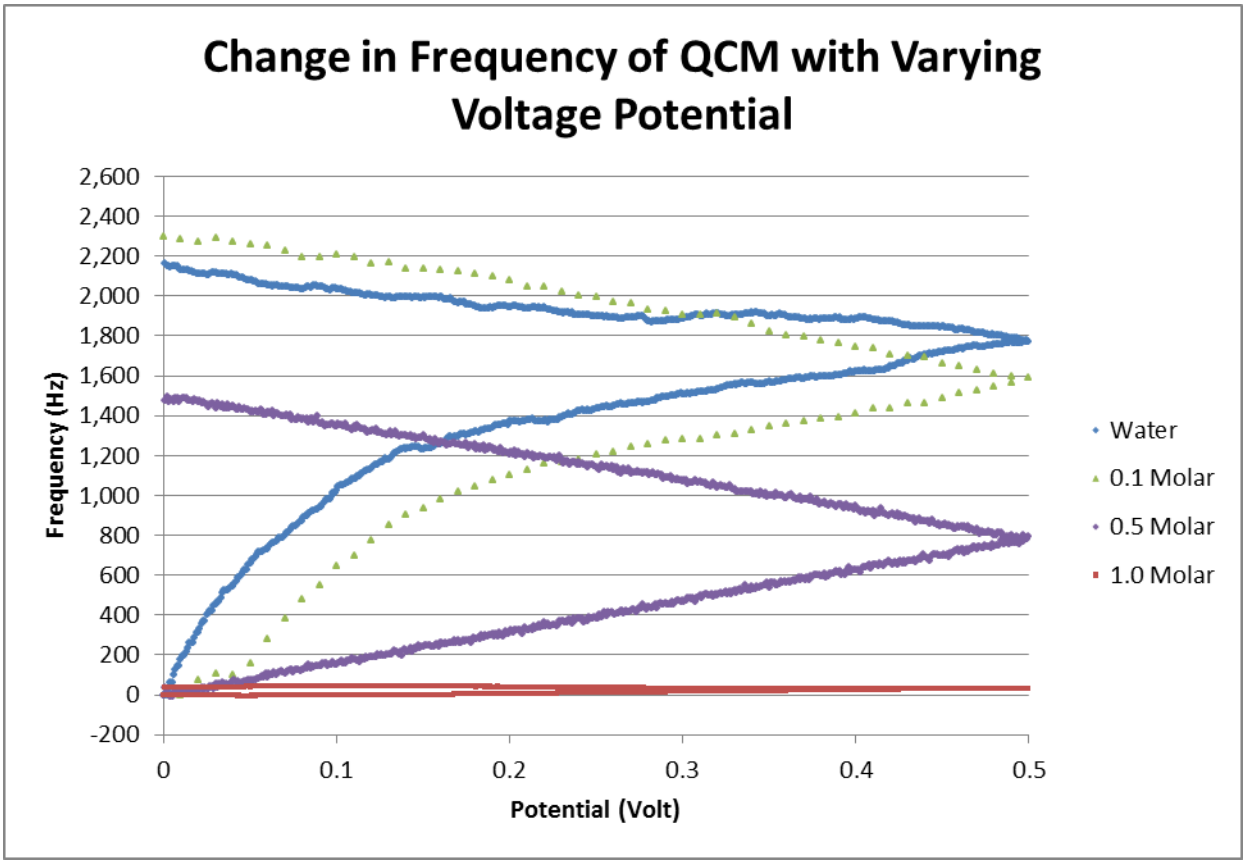


Figure 2: Change in frequency of the QCM measured with varying voltage potential for different concentrations of ammonium nitrate

From the data it appears that initially the change in frequency is increasing logarithmically with a very rapid increase at first and gradually trending toward a steady frequency. This trend can be more easily seen when the frequency change is plotted against the time duration of each experimental analysis.

As a concluding remark, this experiment was a successful test of sensing ammonium nitrate in liquid form using a QCM as the sensor platform. There were clear frequency changes or shifts that could be used to determine the concentration with proper calibration. There are also several limits to this technique of sensing including the rate of voltage potential scanning has a significant impact on the resulting measurements. The clearest most distinct trends occurred with the slowest scan rates for the voltage. There did not seem to be measurable difference in concentration caused by decomposition induced by the potential and the electrodes. This could be due to the small scale of the experiment. Future testing could be conducted using constant voltage and measuring the variables against time to get more steady results. Also acquiring a larger sample size would be beneficial in determining stronger correlations.

The second project is on electrospinning nanofibers for medical applications. Electrospinning has been researched for the past thirty years. In its growth, it uses in the electrical field with sensor materials; the medical field with tissue scaffolding as well as drug delivery. As shown by Sill and von Recum's research, by attaching specific proteins to electrospun matrices, they were able

to help with decreasing the spreading rate of an infection[5]. The research with electrospinning continues today with its growing applications across many engineering practices. The purpose of this project was to produce a quality, electrospun fiber that would later lead to possible medical applications. There are needs for drug delivery in which manufacturing the product may be difficult. Electrospinning offers one method in which nanofibers are relatively easily produced and very helpful in drug delivery. On the same note, producing nanofibers can also create small meshes of grafts that can react to external energies such as microwaves. With the right materials, a microwave can cause a reaction and by design activate the nanofibers. This is the main goal of the project. The experiment will begin with spinning iron based nanofibers with other materials, and observing its reactions to external electromagnetic waves.

The first material tested was the polyvinylpyrrolidone (PVP) solution. The samples were used as the baseline control group of the experiment. Ethanol alcohol was mixed with 10% PVP synthesizing approximately 5 mL of the solution. It should be noted that a small trace of food coloring was added to the control solution so that the fibers would later be easily observed. The PVP solution was poured into a 10 mL syringe using a 24 gage needle. In the second test, a second batch of PVP and ethanol was prepared with the addition of 0.1 g of pure fine iron. To thoroughly mix the solution with the iron particles, an ultrasonic processor was used. Due to the grain size and viscosity of the second and third solution, a larger 22 gage needle would be used on a 1 mL syringe. There was some concern in the possibility of a particle clogging within the syringe during the electrospinning. Lastly, for the third test 0.1 g of iron and 0.05 grams of oxide powder were added to the 1 mL of PVP ethanol alcohol solution. It should be noted that although oxide was added for the third test, a similar gage needle was used as in the second test. The third solution was not mixed with the ultrasonic processor, but plainly mixed by thoroughly stirring.

The solutions were prepared in small glass beakers. Upon mixing the samples, the solutions were poured into their respective syringes which would be later inserted into the medical pump. The Chemyx Fusion 200 Classic syringe pump was chosen due to its precise control of flow rate. For this experiment, there were occasions where a flow rate of .001 mL/min was desired and was easily achieved due to the syringe pump's wide range of speeds. The syringe pump was then placed on top of a stable metal stand. Once the syringe was securely clamped into the pump, the receiving plate was placed approximately 7 to 9 cm directly in front of the syringe. Two glass slides were placed over a paper towel on the receiving plate to act as targets and collectors catching the spinning fibers. With the receiving plate being mounted to a vice, the glass slides were held in place, clamped by magnets.

The next step was to then set up the electrical system. The electrical components consisted of a RSR DC Power Supply which was connected to a Hewlett Packard E3615A Power Supply then connected to the CZE2000. The CZE2000 was used as a magnifier to increase the power to the needed 15 kV. The positive end of the power supply was connected to the needle of the syringe and the ground end was connected to the back of the receiving plate. Careful precautions were taken to minimize any risk of the wires shorting on the metal stand or the ground. The positive wire was connected to the syringe tip while the negative, ground end was connected to the back of the receiving plate. This enclosed the magnetic field which would provide the bridge for the fibers to move across.

Table 2-A through 2-D show the temperatures recorded as well as the changes in temperature with respect to the given time affected by microwaves. While ethanol alcohol was present during the synthesis of all solutions, with the process of electrospinning the alcohol actually gasifies and evaporates. Thus the liquid should theoretically have no effect in the microwaving process. The temperature ranges were normally within 3 degrees of the average. The data curves show that the nanoparticles of the iron and oxide do have thermal effects on the fibers. The temperature effects are not drastically different from the control temperatures. In comparison to the PVP the test fibers lost around 20%- 30% in heat gained through the microwave.

**Table 2-A: Control substrate test results**

| Control: Glass Plate | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time (s) | Temperature ( ˚C ) | | | | | Avg T (˚C ) | ΔT (˚C) |
| 0.0 | 22.0 | 22.0 | 22.0 | 22.0 | 22.0 | 22.0 | |
| 5.0 | 23.2 | 23.0 | 22.0 | 23.0 | 23.2 | 22.9 | 2.6 |
| 10.0 | 25.4 | 26.0 | 25.8 | 25.8 | 26.6 | 25.9 | 5.7 |
| 15.0 | 28.6 | 28.8 | 30.0 | 28.4 | 28.2 | 28.8 | 8.6 |
| 20.0 | 35.0 | 35.6 | 35.6 | 34.6 | 36.0 | 35.4 | 15.1 |
| 25.0 | 41.0 | 45.0 | 46.0 | 45.0 | 41.0 | 43.6 | 23.4 |
| 30.0 | 45.0 | 48.0 | 46.0 | 42.4 | 43.0 | 44.9 | 24.6 |

**Table 2-B: PVP nanofiber responses**

| Test 2: PVP | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time (s) | Temperature ( ˚C ) | | | | | Avg T (˚C ) | ΔT (˚C) |
| 0.0 | 22.2 | 21.0 | 22.0 | 21.8 | 21.8 | 21.8 | |
| 5.0 | 23.0 | 21.8 | 24.0 | 24.0 | 23.6 | 23.3 | 3.0 |
| 10.0 | 25.8 | 25.2 | 24.3 | 26.6 | 26.2 | 25.6 | 5.4 |
| 15.0 | 37.0 | 38.0 | 36.0 | 37.2 | 37.8 | 37.2 | 17.0 |
| 20.0 | 40.6 | 41.0 | 39.8 | 41.0 | 40.6 | 40.6 | 20.4 |
| 25.0 | 49.0 | 49.2 | 49.2 | 49.0 | 48.8 | 49.0 | 28.8 |
| 30.0 | 47.6 | 47.0 | 45.6 | 47.6 | 48.0 | 47.2 | 26.9 |

**Table 2-C: Iron particle-containing PVP nanofibers**

| Test 2: PVP + Fe | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time (s) | Temperature ( ˚C ) | | | | | Avg T (˚C ) | ΔT (˚C) |
| 0.0 | 21.8 | 21.8 | 21.8 | 21.8 | 21.8 | 21.8 | |
| 5.0 | 22.6 | 22.8 | 20.2 | 22.2 | 22.2 | 22.0 | 1.8 |
| 10.0 | 26.0 | 24.8 | 25.0 | 25.0 | 25.0 | 25.2 | 4.9 |
| 15.0 | 32.0 | 30.4 | 31.2 | 29.8 | 30.0 | 30.7 | 10.4 |
| 20.0 | 34.0 | 33.0 | 33.8 | 32.2 | 33.8 | 33.4 | 13.1 |
| 25.0 | 36.8 | 37.4 | 38.6 | 37.2 | 36.6 | 37.3 | 17.1 |
| 30.0 | 39.0 | 42.0 | 41.6 | 38.0 | 40.0 | 40.1 | 19.9 |

**Table 2-D: Iron oxide containing PVP nanofibers**

| Test 3: PVP + Fe + O | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time (s) | Temperature ( ˚C ) | | | | | Avg T (˚C ) | ΔT (˚C) |
| 0.0 | 20.0 | 19.6 | 19.6 | 19.6 | 19.6 | 20.2 | |
| 5.0 | 20.6 | 19.8 | 20.8 | 20.0 | 20.0 | 20.8 | 0.6 |
| 10.0 | 21.4 | 20.0 | 21.0 | 20.8 | 21.0 | 23.7 | 3.4 |
| 15.0 | 25.0 | 24.8 | 22.0 | 23.0 | 23.6 | 33.9 | 13.7 |
| 20.0 | 33.6 | 34.0 | 33.6 | 33.6 | 34.8 | 33.9 | 13.7 |
| 25.0 | 36.6 | 35.6 | 36.2 | 35.8 | 36.4 | 36.1 | 15.9 |
| 30.0 | 36.6 | 35.2 | 36.8 | 36.4 | 37.0 | 36.4 | 16.2 |

The results confirm that it is definitely possible to use electrospinning to produce iron-containing nanofibers as opposed to other techniques. If these materials were to be used to produce a mesh that can be placed within the human body, its properties can react to a magnetic field produced by an magnetic resonance imaging (MRI) machine which would be useful in future applications.

**Evaluation on the learning outcomes**

Evaluation on the learning outcomes is conducted. Both formative evaluation and summative evaluation were made to examine the effectiveness of the collaborative learning. By the time of finishing the team projects, two of the students have been on the full time positions. One was accepted by graduate program and started the Master Degree project. One student is at the senior level and will continue his capstone design project on the similar topic. The team projects helped three students to meet the requirements of the graduation and obtaining the BS degrees.

**Conclusions**

Undergraduate research and capstone experiences are effective on enhancement of learning. Improving undergraduate student education through high impact activities in a cooperative learning setting is a way worthy of exploring. Specifically, scalable, low cost manufacturing process for making high performance energy conversion nanomaterials is dealt with in our studies. Cooperative learning on several upper division general engineering courses including Independent Research and Studies, Senior Capstone Design, Special Topics on Nanotechnology generates the outcome of improving the graduation rate. Several scalable, low cost manufacturing research tasks are adopted to enhance the context learning through cooperative learning approach that integrates advanced manufacturing research activities into both academic and social learning experiences. The student groups enjoyed the team-based research projects and generated meaningful results.

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