

Electrospinning of Ceramic Nanofibers (Kanchan Mondal)

Traditional synthetic materials are constructed to yield desirable thermal and mechanical properties. To this end, the conventional route was to embed a stiff material in a matrix. The advent of nanocomposites has shown significant improvement in the functional capability and mechanical toughness compared to larger volumes of reinforcement in traditional materials. However, they still pale in comparison to the natural composites in terms of functional and organizational complexity. One of the reasons for this difference is that most natural composites are based on nanofibers that provide the basic platform on which the other components are organized. Electrospinning provides a route to produce non-woven fibers that are submicron in diameter and significantly long. The first patent on electrospinning was issued in 1902¹. However, it was only recently that there was revived interest in the technique, primarily due to the growing interest in nanotechnology. Although previously used for the synthesis of polymer structures, the method has been adapted for the production of ceramic nanofibers. The key to this transition is the selection of a polymer solution with desired viscosity and surface tension containing the ceramic precursor. The electrospun product is then calcined to produce crystalline or amorphous ceramics. Porous nanofibers (for gas membrane applications) can be either produced as a result of phase separation or due to the evaporation of a second more volatile component in the precursor solution. Nonetheless, this results in a tremendous increase in the surface area. One of the main challenges in electrospinning is to produce ordered assemblies with controlled porosity. Conventional set-up allows only for non-woven meshes since the electrospinning path is very chaotic. However, researchers have devised techniques to attain some degree of order in the fibers. The common methods used are to control the electric field, use of dynamic collector such as a rotating drum or a combination of both. In addition, path modulators such as auxiliary electrodes may also be used.

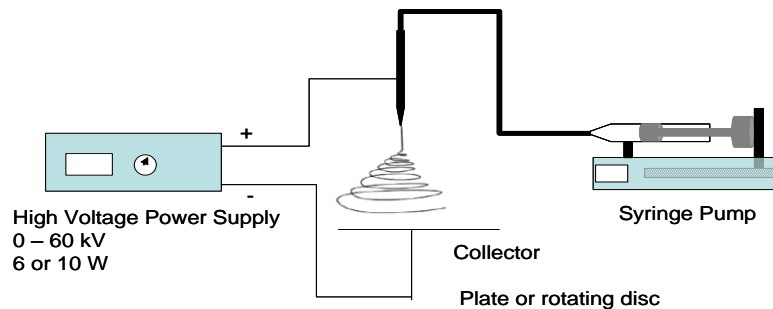


Figure Electrospinning Setup

Electrospinning allows extensive tunability in the materials properties and functions through selection of polymeric nanofibers, ceramic nanofibers, metallic nanofibers or composite nanofibers. Such non-specific material selection for electrospinning is because any solution or liquid, which can carry electrical charges and with sufficient viscosity to be stretched, have the potential to be electrospun into fibers. The next step is to fabricate fibers with in-built functionality. The objective of research relates to the development of isothermal selective emitters for harvesting thermal energy and to the development of coaxial nanofibers with upconverting components for the upconversion for visible light to ultraviolet range. The primary hypothesis is that the new design of the spinneret (designed with the help of undergraduate researcher Jana Aylsworth and fabricated by Dolomite, UK), the unique solution delivery, the choice of precursors and the use of rotating electrode technique, it is possible to

create aligned core-sheath structured ceramic nanofibers with multi-functionality. Dr Mondal and his graduate student, George Trifon (previously undergraduate student help, currently masters student and admitted to the PhD program under Dr Mondal's supervision) has developed rare earth doped titania and rare earth doped pyrochlore nanofibers for application as selective emitter in thermophotovoltaic devices. They are currently designing a thermophotovoltaic device.

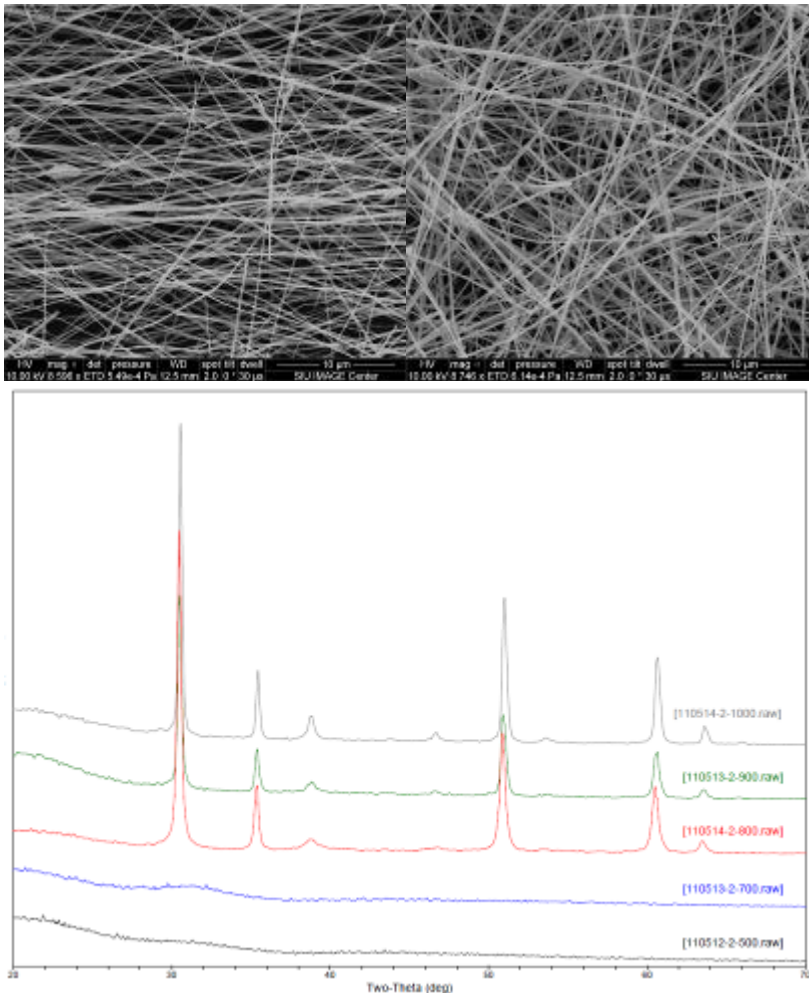


Figure Electrospun nanofibers and effect of calcinations temperature on crystallinity of RE doped pyrochlore ($\text{Er}_x\text{Y}_{2-x}\text{Ti}_2\text{O}_7$)

The REU students will utilize above techniques to develop RE doped ceramic nanofibers for upconversion of visible light to ultraviolet region. They will synthesize core shell structures for concomitant and sequential upconversion. Various techniques will be used for aligning the nanofibers. These nanofibers will be used with CdSe based photovoltaic cells for high efficiency solar cells.

Carbon Nanotube Catalyzed CO Hydro de-oxygenation (Kanchan Mondal and Saikat Talapatra)

Fischer Tropsch Synthesis (FTS) is complex set of reactions which can essentially be viewed as the chain growth of hydro-deoxygenated of CO. The mechanism of FTS

requires the presence of transition metals in its reduced state as a catalyst. In general, the CO is reduced by hydrogen to CH₂ monomers which then grows into larger chains. As a result, long chain hydrocarbons are formed. An incomplete hydro de-oxygenation lead to the formation of oxygenates. The presence of transition metal sites allow the weakening of the triple bonds for hydrogenation to occur. In 2008, Mondal and Talapatra began

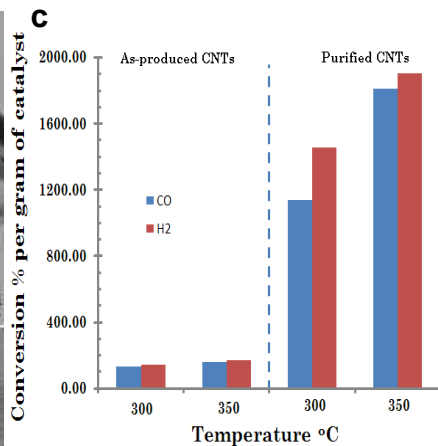
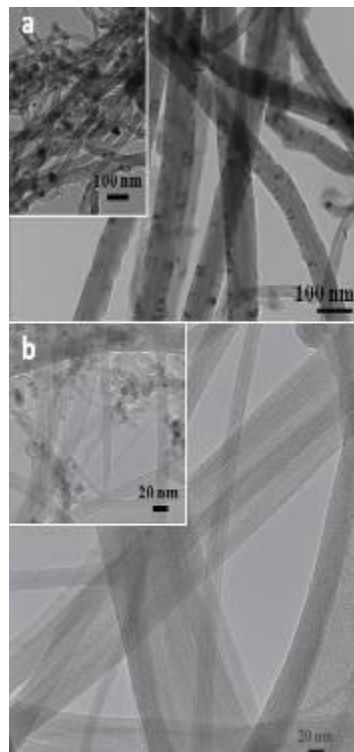


Figure Shows the effect of purification on the CNT samples. It is clear from the images that the majority of the iron particles present in CNTs (see inset of a & b) are removed after purification. (c) Comparison of FT synthesis results on as produced and purified CNTs.

investigations on CNT-based catalysts for FT synthesis. It was during these investigations that the authors found compelling evidence that CO hydrogenation could be catalyzed by as-produced CNTs with or without H₂ activation. In fact, the CO conversion on as-produced CNTs were two orders greater than an Fe-Zn-K/γ alumina catalyst and significantly higher than the cases where the CNTs were used as supports for Co and Fe catalysts. In order to further reduce the iron content, the as-produced CNTs were peroxide and acid treated and then dried. The FT synthesis tests revealed an additional order enhancement in CO conversion on the post treated CNTs. Another significant finding was that the CNT preparation conditions did not significantly alter the conversion nor the product distribution^{ii, iii}. On the other hand, when the CNTs were pretreated with a CO/H₂ mixture at 450 °C before conducting the FT experiments, the product distributions changed from predominantly alcohols to hydrocarbons and the conversions were observed to increase for the pretreated sample. The above results show that as-produced CNTs by the method employed by the proposers can effect CO hydrogenation at rates comparable to industrial catalysts and pretreatment - by acid treatment or heat treatment in a reducing atmosphere - enhances the activity and alters the selectivity of the process. The hypothesis is that the unique chemical and electronic properties of carbon nanotubes (CNTs) and the presence of defects (functional groups) afford the CNTs catalytic properties. The objective of the research is to conclusively prove the hypothesis and identify the useful functional groups. Mondal and Talapatra currently have an NSF –CBET proposal on this topic that has been recommended for funding in this cycle. Two undergraduate researchers will be hired as a part of this project.

The REU students will employ an air assisted vapor phase catalyst delivery CVD method for growing CNTs. In the experiments, ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$, contains iron as the catalyst) and xylene (carbon source) will be employed for growing vertically aligned CNTs. In addition, the REU students will produce new families of doped CNTs with nitrogen-phosphorous using the CVD approach indicated above. In particular, we will work with various compounds containing P such as silane, $P(\text{C}_6\text{H}_5)_3$. The REU student will also synthesize COH and COOH functionalized CNTs by employing the same ultrasonic sprayer but in this case with solutions of ferrocene (FeCp_2), toluene (C_7H_8) and different concentrations of ethanol (Et-OH). The catalytic activities of these arrays will be tested. Both Mondal and Talapatra will mentor the students. Talapatra will be responsible for CNT growth and functionalization and Mondal will be responsible for mentoring the student in catalysis.

ⁱ Morton, W. J., Method of Dispersing Fluids, US Patent 705,691, (1902)

ⁱⁱ Talapatra, S., K. Mondal, "Single Step Synthesis of Carbon Nanotube Based Fischer Tropsch Catalyst", patent disclosure (2009)

ⁱⁱⁱ Mondal, K., S. Talapatra, M. Jeffers, X. F. Zhang, J. Gautam, "Fischer Tropsch Synthesis on CNT based Catalysts", The 35th International Technical Conference on Clean Coal and Fuel Systems, Coal:Rising to New Challenges, June 6th – 10th, Clearwater, FL, 2010