# THERMOELECTRIC ENERGY CONVERSION POLYANILINE MADE BY ELECTRIC FORCE ASSISTAED CENTRIFUGAL NANOCASTING

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## ABSTRACT

In this paper, a composite material containing conducting polymer, polyaniline nanofibers and nanoparticles was made by electric force assisted nanocasting. The thermoelectric behavior of the composite material was characterized. The conducting polymer (polyaniline) was electrosprayed onto a glass plate. The dispersion of the polymer nanofibers and nanoparticles on the glass plate was achieved via electric field assisted nanocasting. The Seebeck coefficient and electrical resistance measurement experiments were performed. The experimental results were used to test the hypothesis that electric force facilitates the uniform distribution of nanofibers and nanoparticles to form a composite material. It is found that the manufactured composite material possesses thermoelectric energy conversion property.

## INTRODUCTION

Nanocasting has the capability of generating well-ordered, very fine entities such as nanofibers or nanorods, coaxial nanotubes, and porous architectures. Traditional casting refers to the solidification process whereby a molten metal is transferred into the cavity of a mold [1]. Casting is considered as a cost-effective technique for manufacturing various parts [2]. Casting can be combined with rolling, which is the semisolid casting. The molten metal is cast into a large ingot. The ingot is subjected to a hot-rolling process. In some cases, the molten metal is cast into the space of water cooled dies so that the metal is in a mixed liquid and solid state. The semisolid slurry is under the subsequent extrusion or rolling, thus, segregation is inhibited. Chemical composition and mechanical properties are more uniform [3]. Inspired by the casting technique, researchers have considered making nanoscale components or features using the similar process. This is the origin of nanocasting technology. Nanocasting deals mainly with nonmetallic material processing. For example, oligomeric surfactants and block copolymers have been used to cast nanoporous materials [4] [5] [6] [7] [8]. Porous silica materials were obtained via nanocasting on a pseudopolyrotaxanes template synthesized from α-cyclodextrin and polyamines [9]. Nanocasting two-dimensionally (2D) ordered porous arrays using monolayer colloidal crystal templates has the advantage of generating hierarchical structures at micro and nanometer length scales. Polystyrene (PS) beads with the size of 1 micron were used to form 2D ordered arrays [10]. The arrays were served as the casting molds to make $Co_3O_4$ hierarchical structures.

The external force-assisted nanocasting or spinning concept has been proposed for years [11] [12] [13] [14]. This technique has been studied for making polymer fibers [11] [13] [15]. The principles have also been explored for manufacturing ceramic fibers [11] [14]. By extending the external force-assisted nanocasting process concept to various material systems, it is possible to synthesize fibers as suitable organic-inorganic composites. Up to now, there is very limited research work done on electric force assisted centrifugal nanocasting thermoelectric composite materials. The challenges of this new technology include: the use of a single step process to manufacture large scale fiber reinforced materials; increasing the production rate of the nanostructures while keeping the cost associated with the manufacturing process reasonable; and most importantly, to manufacture heterogeneous material-supported composites with controlled architectures for thermoelectric energy conversion. The objective of this work is to understand the fundamentals of electric force assisted nanocasting manufacturing process and to use this new approach to make organic-inorganic composites.

## MATERIALS AND EXPERIMENTAL METHODS

All the materials used in this work were purchased from Alfa Aesar. Fig. 1(a) shows the schematic of the electric force assisted nanocasting experimental set-up. A precision auto lapping/polishing machine was used as the main part. This machine contains a rotating platform whose speed can be well controlled. A Shimpo tachometer was used to measure its rotating speed. The $TiO_2$ nanotube specimen was put at the two ends of a plastic pipe being fixed on the rotating platform. High voltage of 15 kV was applied across the aniline solution. Aniline was electrochemically polymerized in the $TiO_2$ nanotubes because the titanium plates, as anodes, were connected by two carbon fiber brushes to the outer ring which serves as the positive electrode of the DC power source. Under the combined electric and mechanical forces, the polymerized polyaniline was cast into nanofibers within the $TiO_2$ nanotubes. The centrifugal casting principle is shown in Fig. 1(b).

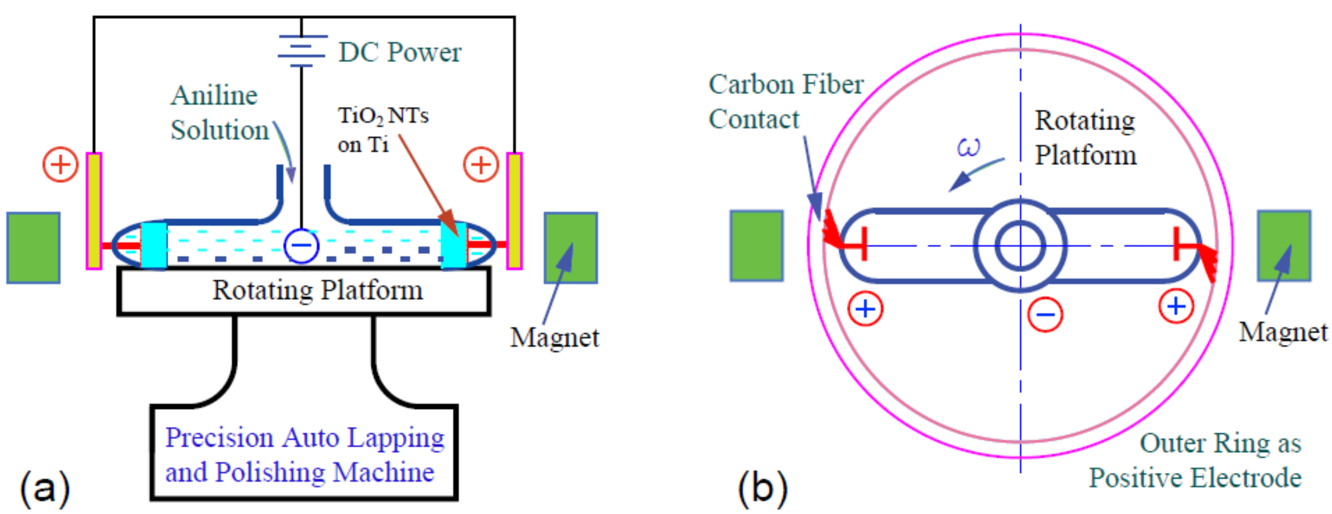


Fig. 1 Electric force assisted nanocasting experimental set-up and the working principle.
(a) the rotating platform holds the nanocasting uint, (b) nanocasting under external forces.

The Seebeck coefficient of the nanofiber composite was measured using a self-build measurement system containing a Talboys heat platform with temperature control and a mode 410 Extech Multimeter. The nanofiber composite was clamped onto two strips of aluminum tape for voltage measurement. The temperature difference was imposed at the two ends of the specimen. The absolute values of the Seebeck coefficients obtained at different measuring temperature ranges were obtained and plotted. The resistance of the composite material was also measured by the two point method using a CHI 600E electrochemical workstation running under the linear scanning mode.

## RESULTS AND DISCUSSION

Without combined electric and centrifugal forces, the electrochemically plolymerized polyaniline started growing just at the surface of the titanium dioxide nanotubes as revealed by both the scanning electron microscopic (SEM) image of Fig. 2(a) and the transmission electron microscopic (TEM) image of Fig. 2(b). Because the aniline solution is hydrophobic, it tends to stay on the top surface of the titania nanotubes which are hydrophic. Therefore, electrocentrifugal nanocasting has to be used to draw the aniline into the nanotubes under coupled electric and mechanical forces.

The thermoelectric nanoparticles was made by the Galvanic displacement method similar to that as reported in [16] [17] [18]. In [16] and [17], Ni-Fe alloy was used as the raw material. But in this work, Ni and Co nanoparticles were used as the precursors to form core shell particels due to the better controllability. The surface layer was BiTe alloy and the core was Ni or Co. BiTe alloy is used because it is considered as one of the best materials with high value of Seebeck coefficient in a wide temperature range. Since Ni or Co tends to be attracked by magnetic force, the BiTe/Ni shell-core nanoparticle clusters (as shown in Fig. 3a) in the aniline solution held by the plastic container (as shown in Fig. 3b) move outwardly towads the $TiO_2$ nanotubes. Te size of the nanoparticles, 4 nm, as seen from Fig. 3(a), is much smaller that the inner diameter of the nanotubes, which is about 120 nm as can be seen from Fig. 3(c). Obviously, the external field helped the thermoelectric nanoparticles go into the nanotubes.

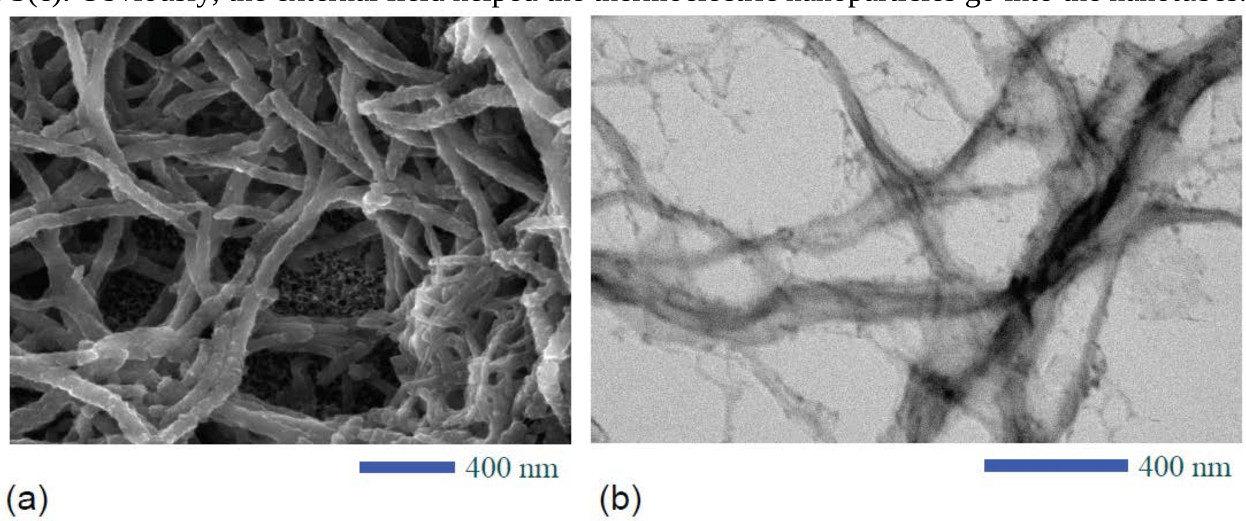


Fig. 2: Images of polyaniline nanofibers on titanium dioxide nanotubes: (a) SEM, and (b) TEM.

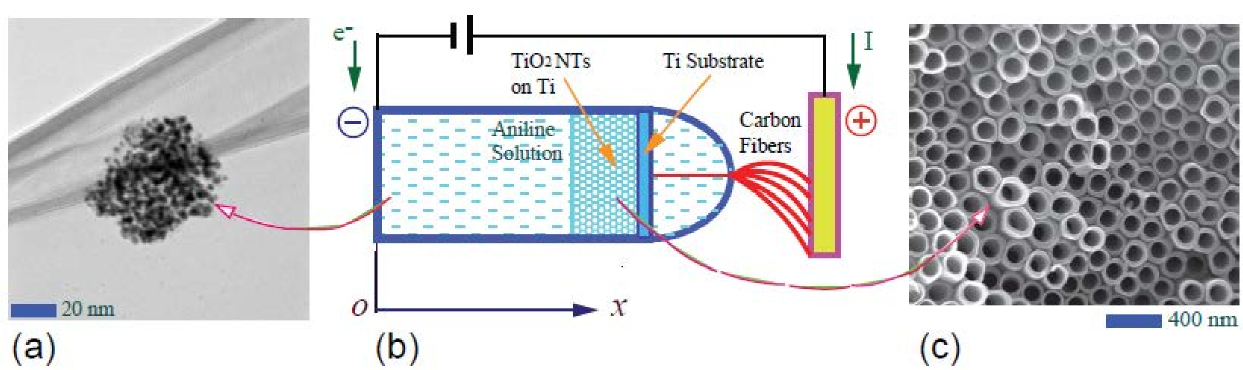


Fig. 3: (a) TEM image of a BiTe/Ni shell-core nanoparticle cluster generated by Galvanic displacement, (b) BiTe/Ni in aniline solution (c) SEM image of titanium dioxide nanotubes.

It is found that the average Seebeck value for the polyaniline nanofiber is -10 μV/K. The negative sign means that the material shows *n*-type behavior. As compared with the inorganic semiconducting material, bulky silicon crystalline material, the nanofiber has three times lower value of Seebeck coefficient. The measured Seebeck value of the silicon bulk material is as high as -40 μV/K under the same measurement conditions. Therefore, further improvement on the thermoelectric property of the polymeric nanomaterial is needed. The electrical resistance of the nanocast polyaniline nanofiber was measured at the room temperature of 25$^{o}$C. The material shows the resistance of 35 MΩ, which is in the range of those typical semiconducting materials.

## CONCLUDING REMARKS AND FUTURE WORK

Polymer based composite nanomaterial can be processed under the assistance of high electric field. The nanocomposite shows *n*-type property with an average Seebeck value of -10 μV/K. The electrical resistance of the composite is about 35 MΩ. The preliminary results from this work show the promising of the electric force assisted nanocasting. Future work will be on developing a commercially viable, scalable manufacturing process ensuring high process yield, process and product repeatability and reproducibility, along with optimized quality control. The scalable manufacturing process should be further tested for producing functional nanocomposites for high efficiency thermoelectric energy conversion.

## ACKNOWLEDGEMENTS

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