

# Large Scale Composite Nanowires and 3D Nanostructures for Energy Conversion and Storage

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## Introduction

Composites of functional materials have long been synthesized for achieving enhanced physical and chemical properties such that they serve improved functions for a range of nanoelectronic devices and architectures. This is because many nanoelectronic devices demands materials of multiple functions including high conductivity and high surface area. In particular, these two functions are mutually competing in nanostructured materials – when the surface area increases as a result of nanostructuring processes, the increased surface fraction imposes surface states that lie within the bandgap of the material and subsequently the electrical conductivity is lowered.<sup>[1]</sup> Many attempts have been adopted in the past to have high surface area and highly conducting materials in the single material system; however, making a composite is the most simple one and could be industrially accepted. Composite properties are achieved through many methods such as physical mixing of its components, chemical methods such as core/shell, hierarchical structures, nanoparticle-decorated nanowires, and carbon-reinforced porous materials are few examples.<sup>[2,3]</sup> However, preparing a composite in the form of a nanowire or a 3D nanoflower is relatively new.

Given the paramount importance of energy, recently energy conversion and storage devices are researched globally with high intensity. Optical transparency and workability at low light conditions enable the dye-sensitized solar cells (DSSCs) and the perovskite solar cells (PSCs) as desirable choice as smart windows in modern buildings for adding aesthetics with diverse choice of colors while producing clean electricity so as to realize zero-energy buildings.<sup>[4]</sup> In both of these solar cells, the photoactive material is chemically developed from solutions on a wide bandgap material, known as photoelectrode. The photoelectrode influence the performance of the solar cells in many ways as they are either the charge separation medium or the charge transport medium or both. Commercially available mesoporous TiO<sub>2</sub> has been a widely investigated material; but the sluggish charge kinetics due to the surface charges and intrinsic poor electrical conductivity triggered an intensive search on new materials worldwide. As a result many materials and materials architectures are developed with superior properties than the commercial choice; however, most of new materials are hardly scalable to the industrial levels. Among them, nanowires and 3D nanostructures such as flowers offer many advantages such as anisotropic charge dynamics, large surface area, and high crystallinity. Again, most of the materials synthesized thereby are through hardly scalable chemical processes.<sup>[5,6]</sup> Similarly, storage of electrical energy in media and protocols with high energy and power densities have received a revived interest due to high power mobile electrical devices, electric vehicles, and other disconnected from grid but electrically powered technologies such as drones and robots. As a result, many new battery concepts such as sodium batteries, lithium-air, and lithium-Sulphur are currently under intensive research as a replacement for traditional lithium ion batteries.<sup>[7]</sup> One of the promising replacement for batteries is battery-supercapacitor hybrids (BSHs) owing to its potentially higher power density (<5 kW kg<sup>-1</sup>) and longer life cycle (>100,000) compared to that of batteries; however, their energy density is rather unimpressive because of the sluggish charge kinetics of the electrode materials used. Therefore, making a composite with a highly conductive material with a highly electrochemically active material is a potential remedy.

In the course of our research on the development of materials for energy conversion and storage, we have developed a range of composite materials in large quantities as nanobelts, nanowires and 3D nanoflowers through multineedle electrospinning techniques. The resulting materials performed synergistically and the energy conversion and storage devices fabricated using them gave superior properties than those fabricated using their constituents.

## Experiment

In general, the procedure for electrospinning of inorganic materials starts with preparation of a polymeric solution containing

precursors of the required inorganic solid. The solutions were then electrospun to get a nanofibrous polymeric mat, which is appropriately annealed to synthesize the inorganic solid. The difference in morphology was created by interfering in the nucleation event. In the conventional electrospinning to synthesize inorganic nanowires, the metal precursor dispersed in the polymeric fiber is allowed to nucleate and grow at appropriate conditions – which took place at equilibrium conditions, i.e., the growth vessel (the polymeric fiber) is large enough to accommodate the nuclei. On the other hand, to synthesize composite nanoflowers a non-equilibrium situation is produced such that the nuclei developed could not be located within the growth vessel such that growth requires an expansion of space. Details of synthesis, characterization methods adopted, and instruments and protocols used are in our published works.

## Results and Discussion

Fig.1 schematically explains the difference in the formation of nanowires and nanoflowers. The flower is formed because of the increase in activation energy for nucleation and subsequent crystallization when large amount of precursor is enclosed in a tiny polymeric template; on the other hand, a lower precursor concentration leads the formation of the usual electrospun fiber morphology.

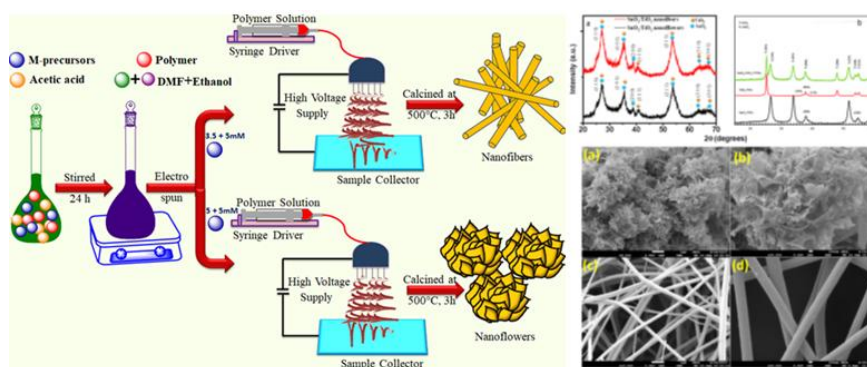


Figure 1: Schematics synthesis of nanowires and nanoflowers by changing precursors concentration via electrospinning technique (left panel). Right Top Panel: XRD patterns of the composite flowers and wires compared with their single component counterparts; Right Bottom Panel: SEM images of the flowers and wires

The similarity of chemical nature and difference in morphology of nanowires and nanoflowers are shown in Figure 1. The top panel shows the XRD patterns of a typical  $\text{SnO}_2/\text{TiO}_2$  composite nanowires and nanoflowers (left panel), which are identical; the right panel compares the XRD patterns of the  $\text{SnO}_2/\text{TiO}_2$  composite nanowires with that of its constituents – the XRD pattern of the composite does not display any peaks other than its constituents, i.e.,  $\text{TiO}_2$  and  $\text{SnO}_2$ . The bottom panels show the FE-SEM images of the composite nanowires and nanoflowers. The flowers had a size of  $\sim 2\text{-}5\ \mu\text{m}$ , each flower is composed of petals of thickness  $< 100\ \text{nm}$ ; whereas the diameter of the wires are  $100\text{-}150\ \text{nm}$ . The surface properties and electrochemical properties were further verified by a range of techniques including X-ray photoelectron spectroscopy, gas adsorption measurements, energy dispersive X-ray analysis, cyclic voltammetry, linear sweep voltammetry etc.

A comparative device performance is shown in Figure 2; the top panel represents the changes in the optical absorption (top left), changes in the redox potentials representing shift in band edge energies (top middle), and changes in the photovoltaic performance (top right) of the  $\text{SnO}_2/\text{TiO}_2$  composite nanowires compared to that of its binary counterparts. All these data indicated that the composite wire behaved like a single material system and the beneficial properties of the component binary metal oxides are synergistically combined in the composite wires. Perovskite solar cells are also fabricated using flowers and wires; the devices fabricated using the 3D nanoflowers showed superior photovoltaic properties than those of the nanowires; the best performing device in this study is a perovskite solar cell with a photo conversion efficiency of 17.25%, open circuit voltage of  $\sim 1\ \text{V}$ , short circuit current density of  $\sim 23.73\ \text{mA}/\text{cm}^2$  and fill factor 73.07%. The origin of improved performance of the devices has been systematically studied using electrochemical impedance spectroscopy.

In the case of energy storage devices, the composite showed synergistic properties. The bottom left panel compares the discharge current density of a typical  $\text{CuO}/\text{Co}_3\text{O}_4$  nanowire compared with its component wires; the bottom middle panel of Figure 2 shows discharge density as a function of current density of the composite wires and the bottom right panel represents the capacitive

charge stored in the composite wires. Obviously, the charge storage in the composite wires are superior than its component wires.

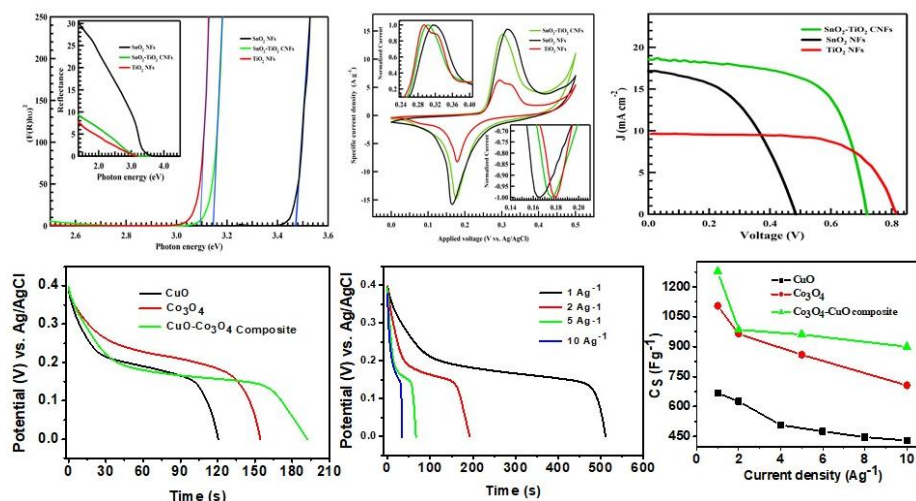


Figure 2: Top left: Absorption spectra of the  $\text{TiO}_2/\text{SnO}_2$  composite nanowires compared with that of pure  $\text{TiO}_2$  and pure  $\text{SnO}_2$  nanowires; Top middle: Corresponding cyclic voltammograms; Top right: comparison of current – voltage characteristics of the composite nanowire based solar cells with that fabricated using its component materials. Bottom Left: Charge/discharge characteristics of  $\text{CuO}/\text{Co}_3\text{O}_4$  composite wires compared with its component nanowires; Bottom Middle: Charge/discharge characteristics of the composite wires as a function of current density; Bottom right: capacitive charge storage comparison between composite and component nanowires.

## Conclusions

In conclusion, we have developed a number of nanowires and 3D nanoflowers of composite materials in large quantities by multi-needle electrospinning technique. The materials showed synergistic properties when used as an electrode for solar cells or energy storage devices. In the case of energy conversion devices, so far, the best performing device was a perovskite solar cell fabricated using 3D composite nanoflowers with a photo conversion efficiency of 17.25%, open circuit voltage of  $\sim 1$  V, short circuit current density of  $\sim 23.73$   $\text{mA}/\text{cm}^2$  and fill factor 73.07%. The best performing morphology for the energy storage device was nanobelts composing  $\text{NiO}$  and  $\text{CoO}_3$  nanoparticles. Using appropriate electrolyte, the nanobelts offer possibilities of fabrication of battery-supercapacitor hybrid devices with energy density similar to batteries and power density similar to supercapacitors.

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