1-D Structures of Metal Oxides Templated via Electro-Hydrodynamic Micro-Flows (EHμFs)

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Electro-hydrodynamic micro-flows (EHμFs) of highly viscous liquids (i.e., polymer melts or solutions), also known as electrospinning, are commonly used as templates to form solid 1-D nanostructures, such as nanofibers and nanoribbons. EHμFs have been applied to template 1-D structures of a wide variety of materials ranging from metal oxides (MOs) to organic/inorganic composites. Because of their extensive technological applications in sensors and photocatalysis with UV light, 1-D mats of TiO_2, ZnO, and SnO_2 are the metal oxides most commonly templated via EHμFs. In comparison with, for instance, a nanocrystalline porous film, a 1-D structure has the advantage of a faster electron transport rate while maintaining a relatively high surface area for chemical reactions [1]. Nevertheless, other materials such as *copper oxide*, with *semiconducting properties* and *light absorption in the visible regime*, are being investigated for applications in sensors, batteries, and photocatalytic processes using sunlight. As some works suggest, there is vast room for the investigation and improvement of the physicochemical properties of copper oxide 1-D nanostructures with a high length/diameter ratio (≥ 10^5) [2, 3].

EHμFs are formed upon the application of a high voltage (typically kilovolts) to a liquid flowing out of a capillary tube. At a given voltage, the viscous liquid forms a conical shape, a “Taylor cone”, and emits a charged liquid jet. As the jet elongates, driven by electrostatic forces towards a collector surface, the jet solidifies and can form various *highly monodisperse* 1-D structures, depending on the solution physicochemical properties and process parameters. Because of the inherent high-charge state of the 1-D structures, their trajectory can be controlled using electric fields and/or by mechanical methods, to form patterns onto either conductive or insulating substrates [4]. Furthermore, one can produce mats made of either uniaxially aligned or randomly oriented 1-D structures through manipulation of the collection process and the electric field intensity[5].

Here we report the application an EHμF technique to produce fiber mats of polymer/CuAc (copper acetate) composites made of (i) long (up to 5 cm), highly aligned and (ii) randomly oriented fibers (Figures 1a-c). The high alignment of the composite fibers was achieved through simultaneous focusing the liquid jet by electrostatic means using a “back electrode” and pulling the jet mechanically with a rotating cylinder collector [5]. Randomly oriented composite fibers were readily obtained by collecting the fibers on a static collector. The MO 1-D structures are obtained after calcination of the polymer matrix and simultaneous decomposition of the MO precursor, followed by nucleation and growth of the MO phase. The polymer tested as template materials were PVAc [Polyvinyl acetate; M_w 100 kDa], PMMA [Poly(methyl methacrylate); M_w 350 kDa], PAN [Poly(acrylonitrile); M_w 150 kDa], and a blend of PVA [Polyvinyl alcohol, M_w 31-50 kDa] and PEO [Poly(ethylene oxide); M_w 5000 kDa]. Although all the electrospun polymer/CuAc solutions had a polymer concentration greater than 10 wt % (suitable for electrospinning), high fiber alignment was only possible for the PVAc/CuAc and PMMA/CuAc solutions. EHμFs of the PVA/PEO/CuAc and PAN/CuAc solutions resulted in randomly oriented fiber mats even at high both electric field intensity and cylinder rotation speed. Subsequent calcination at 500 ºC or higher temperatures of the polymer/CuAc composite fibers formed 1-D nanostructures of copper oxide. Randomly oriented fiber mats of *pristine copper oxide,* as demonstrated by electron dispersive spectroscopic (EDS) analyses, with fiber diameters in the nanometric range, were obtained from

PVA/PEO/CuAc composite fibers (Figure 2a). Conversely, calcination of the 1-D structures of PMMA/CuAc composites on a mica substrate resulted in uniaxially aligned copper oxide 1-D structures (Figure 2b); however, they were cracked in several places along the length of the structures, possibly caused by mechanical stresses during sample manipulation post-calcination. In the case of PAN/CuAc composite fibers "ribbon-like" structures were observed post-calcination. Furthermore, uniaxially aligned fibers of PMMA/CuAc collected on a Si wafer led to collapsed copper oxide 1-D patterns (Figure 2c). A similar phenomenon was observed for the PVAc/CuAc solution. The low melting point of PMMA (~160 ºC) and PVAc (less than 100 ºC) may have played a role in the formation of these 1-D patterns.

The current work presents a methodology for producing fiber mats of copper oxide with various morphologies, depending on the EHµF conditions and the polymer template. The technique can be extended to other MOs by appropriate selection of uniformly mixed polymer/MO precursor solutions. The formation of 1-D patterns of semiconductor materials onto both, conductive and insulating substrates have implications in key technological areas such as solar energy harvesting and storage, nanopatterning, and nanoimprinting.

References

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Figures

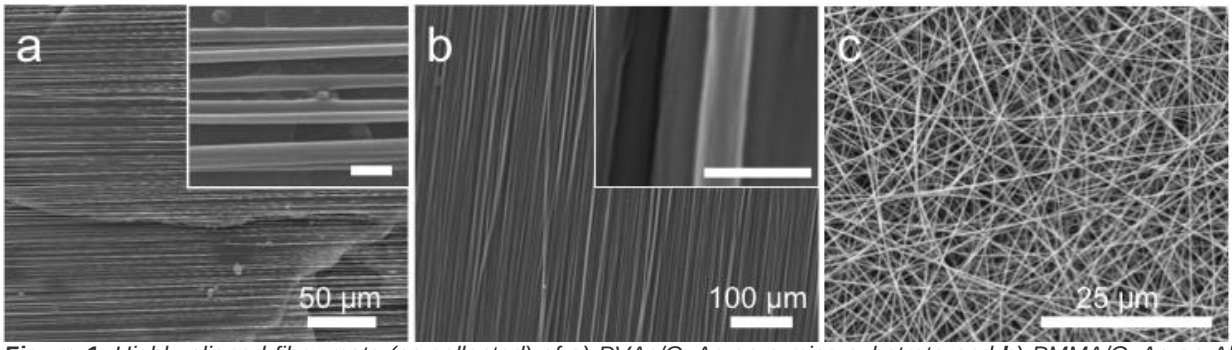

***Figure 1**. Highly aligned fiber mats (as collected) of **a**) PVAc/CuAc on a mica substrate and **b**) PMMA/CuAc on Al foil, and **c**) randomly oriented fiber mats of PVA/PEO/CuAc on Al foil. The white bar in the insets represents 2 µm.*

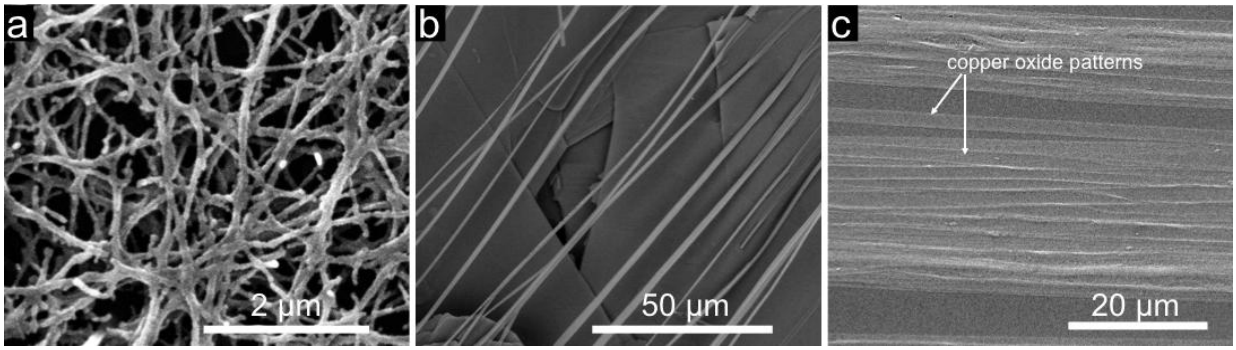

***Figure 2**. **a**) Randomly oriented fibers of copper oxide on Al foil, **b**) aligned fibers of copper oxide on a mica substrate, and **c**) collapsed copper oxide patterns on Si wafer formed by of calcination of the polymer 1-D template.*

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