

Kinetically Controlled Formation of Deposited Polymer Nanomaterials with Unique Surface Substructures

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ABSTRACT

One-dimensional (1D) electronic materials with inherent nanoscale features are considered to be promising components for achieving unprecedented future technologies. Much effort has been devoted to the synthesis of inorganic nanomaterials and, as a result, unique size- and structure-dependent properties have been identified in those nanomaterials. Owing to the technical difficulties in fabricating and manipulating them, however, relatively little research has been done on the applications of polymeric nanomaterials. Moreover, there is still a lack of a theoretical interpretation as to how the polymerization proceeds at the nanometer regime. Conducting polymers may be an alternative materials against metals and inorganic semiconductors in future applications. Here, we prepare multidimensional conducting polymer nanomaterials using single-nozzle co-electrospinning, followed by vapor-deposition polymerization. We, for the first time, suggest the concept that the morphology of deposited polymer nanomaterials is subject to substrate curvature, as well as synthetic conditions. Nanonodules and nanorods were grown on a nanofiber surface by controlling critical kinetic factors such as temperature and pressure during vapor deposition polymerization, leading to the formation of multidimensional polymer nanostructures. On the other hand, no remarkable nanostructures were generated on bulk flat substrate under the same conditions. Multidimensional poly(3,4-ethylenedioxythiophene) (PEDOT) nanofibers were fabricated successfully, and their hollow nanostructures were also prepared by a core-etching process. It is anticipated that the multidimensional polymeric nanomaterials will have advantages when used as structures for filtration, separation, sensing, and energy conversion/storage.

Keywords: multidimensional, vapor-deposition, nanofibers, poly(3,4-ethylenedioxythiophene)

1 FABRICATION OF MULTIDIMENSIONAL PEDOT NANOSTRUCTURES.

Poly(methyl methacrylate) (PMMA) has polar groups that can interact with metal cations and is also soluble in various organic solvents. Thus, PMMA (1 g, $M_w = 350\,000$, Aldrich) was dissolved in dimethyl formamide (DMF) at 70–80 °C, and PMMA nanofibers were electrospun from the PMMA/DMF solution. In the electrospinning process, the solution was injected through a stainless steel needle (22 gauge) that was connected to a high-voltage dc power supply (Nano NC 60 kV/2 mA). The solution was continuously fed through the nozzle connected with syringe pump (Kd scientific) at a rate of $12\ \mu\text{m}\ \text{min}^{-1}$. High voltage (15 kV) was applied between the needle and the grounded collector (the distance was 15 cm). As a result, PMMA nanofibers were continuously ejected from the nozzle and accumulated on a cellulose substrate. The thickness of the nanofiber network film was controlled by adjusting the accumulation time. The resulting PMMA nanofibers were immersed into ferric chloride/methanol solution (40 mL). After drying under vacuum, the nanofibers were placed in the pressure-controllable reactor. Then, the 3,4-ethylenedioxythiophene (EDOT) monomer (Aldrich) was injected at a controlled reactor pressure and temperature, which resulted in the formation of PEDOT-coated PMMA nanofibers. The PEDOT nanotubular structures were obtained by dissolving the PMMA core with DMF solution. The final products were washed by suction filtration of water and methanol to remove residual reagents, and the energy-dispersive X-ray spectroscopy (EDS) analysis demonstrated that there were no impurities in the nanostructures. The four-probe conductivities of the nanostructures were 2×100 to $6 \times 101\ \text{S}\ \text{cm}^{-1}$.

2 RESULTS AND DISCUSSION

Figure 1 outlines the synthetic procedure for multidimensional nanofibers and nanotubes under three representative vapordeposition polymerization (VDP) conditions. Polymer nanofibers were fabricated by electrospinning, and then conducting polymer was introduced onto the nanofiber surface through VDP. During this process, the electrospun nanofibers serve as both template and substrate for the growth or assembly of nanobuilding blocks (from oligomer to polymer). More

specifically, PMMA nanofibers were accumulated on electrically conductive collectors by electrospinning.

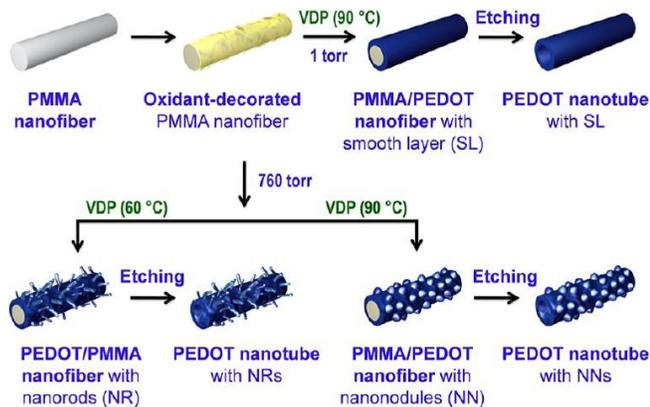


Figure 1: schematic illustration of the synthetic routes to multidimensional PEDOT nanostructures. PMMA nanofibers were accumulated on the collector by electrospinning, in which PMMA solution was supplied to the syringe tip at $5 \mu\text{m min}^{-1}$ and an electric field of 15 kV was applied between the tip and the grounded collector (distance, 15 cm). The PMMA nanofibers function as template as well as substrate for the growth of PEDOT under different synthetic conditions (temperature and pressure).

3 CONCLUSIONS

We created a new synthetic process that allows tailoring the surface morphology of 1D conducting polymer nanomaterials. Novel nanonodule and nanorod substructures were grown on the surface of electrospun polymer nanofiber substrate by controlling pressure and temperature. The kinetic model developed showed that slower polymerization kinetics were favorable to the growth of the unique substrates on the nanofiber surface. Several other potentially critical variables remain, which can affect the formation of the surface nanostructures, such as the reactivity of monomer and the interfacial tensions of monomer and substrate. Thus, there is an ongoing effort to develop a more generalized kinetic model. Lastly, it is expected that the multidimensional polymer nanostructures can have additional advantages when used as structures for superhydrophobic coatings, adhesion enhancement, separation, and energy conversion/storage.

4. REFERENCES

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