Renewable Biomaterials to Encapsulate and Align Synthetic Semiconducting Polymers

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This work proposes an environmentally friendly approach to process organic electronics that uses Cerato Ulmin (CU), a natural hydrophobin, to encapsulate and deliver solutions of poly(3-hexylthiophene), P3HT, and cellulose nanocrystals, CNCs. This processing will render a highly conductive P3HT-CNC water-based ink suitable for inkjet printing onto paper substrates.

Introduction

Printed, flexible electronics have gained interest as low-cost, lightweight alternatives to conventional semiconductor devices.

Cellulosic materials can be used as recyclable substrates for large-area, roll-to-roll manufacturing of flexible electronics.

Advantages of paper-based substrates:

- Recyclable/biodegradable
- Amenable to a wide range of printing technologies
- Can be folded to generate 3D structures

The main challenge in producing these flexible devices is the delivery of the semiconducting polymer to the paper substrate.

Objectives

- Design a benign method to deliver semiconducting polymers in aqueous solutions using renewable materials
- Obtain highly conductive dried polymer films

Approach

Pair cellulose nanocrystals with a semiconducting polymer.

Cellulose nanocrystals (CNCs) can be functionalized with a semiconducting polymer, P3HT.

Disperse semiconducting polymer in water.

The P3HT-CNC hybrid can be delivered to cellulosic substrates through a water-based “ink” by encapsulating it in a natural hydrophobin, Cerato Ulmin (CU).

Enforce alignment of polymer chains.

A combination of the ink drying and the constriction of the CU membrane helps to align the P3HT-CNC filaments—increasing the system’s conductivity.

Materials

I. P3HT –semiconducting polymer

- Electrons travel down conjugated backbone and through n–π stacking.
- However, spontaneous self-assembly of P3HT can yield amorphous structures that prevent electron hopping.

II. Cerato Ulmin –encapsulation

- Natural hydrophobin derived from trees.
- Has a hydrophobic and hydrophilic face; self-assembles at phase interfaces.
- Allows for the dispersion of organic substances in water.

III. Cellulose Nanocrystals –long range order

- Rigid, rodlike particles approximately 100-200 nm in length.
- Form a chiral nematic liquid crystal phase in water at ~4.5 wt%.

Preliminary Results

I. Dried P3HT/CNC films show long range order.

II. CU encapsulates P3HT/solvent in elongated bubbles that form a dendritic structure over time.

III. CU encapsulation enhances P3HT alignment.

- Polarized micro-Raman spectroscopy confirmed the anisotropic nature of the P3HT film obtained by drop casting CU-P3HT dispersion.
- UV Vis shows a significant red shift of the specific thiophene ring vibronic peaks when compared to pristine P3HT in TCB.
- Spectral feature at low energy corresponds to planarization of P3HT backbone (red trace).

Future Work

- Functionlize CNCs with P3HT via grafting from polymerization.
- Encapsulate P3HT-CNC hybrid in CU.
- Fabricate organic field-effect transistors (OFETs) and test electronic properties.

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