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Digital light processing for the fabrication of 3D intrinsically conductive polymer structures

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ABSTRACT

Conventional methods to fabricate intrinsically conductive polymer actuators result in planar morphologies that limit fabricated devices to simplistic linear or bending actuation modes. In this study, we report a conductive polymer formulation and associated 3D printing fabrication method capable of realizing three-dimensional conductive polymer structures that are not subject to such geometric limitations. A light-based 3D printing technique known as digital light processing is employed due to its ability to fabricate complex microscale features in conjunction with a specially-formulated photosensitive polypyrrole resin. The performance of this fabrication system is characterized via feature resolution and depth of cure experiments, and the results are subsequently applied to the fabrication of 3D components. This technique enables the fabrication of novel electroactive polymer structures and provides a framework for advanced 3D electroactive polymer-enabled devices capable of complex modes of sensing and actuation.

1. Introduction

The alternating single and double bonds along the backbone of intrinsically conductive polymers (ICP, also known as conjugated polymers) provide this class of materials with electrical and ionic conductivity properties [1]. The electrical conductivity property has applications with organic electronic devices [2–5] while the ionic conductivity property has been used to create actuators due to an ion-driven volumetric expansion and contraction [6,7]. Thus, ICP have garnered research interest because of their capacity for advanced sensing and actuation technologies.

The insoluble and infusible properties of the ICP polypyrrole (PPy) have prevented it from being fabricated by traditional polymer forming methods. Alternatively, in situ polymerization techniques such as chemical, electrochemical, and photopolymerization must be employed to create polypyrrole structures [8–13]. Electropolymerization is commonly used to fabricate PPy actuators in the form of thin polymer films or coatings with desirable electro-mechanical properties [6,14]. The electropolymerized polymer is constrained to simple linear or bending actuation modes due to the monolithic nature of these films. Developing novel fabrication methods for the synthesis of PPy in the form of active 3D structures will enable more complex actuation modes, such as torsion or multiple degree of freedom motions that further exploit the actuation potential of these materials.

Our group aims to fabricate 3D ICP structures via the development of specialized 3D printing techniques, and have previously reported the initial development towards 3D printing ICP devices [15–17]. The digital light processing (DLP) 3D printing technology, also referred to as projection micro-stereolithography, is a particularly attractive technique as it is capable of producing structures with microscale features [18,19]. This technique uses a DLP projector to selectively cure 2D layers of a photosensitive polymer to build up 3D objects layer-by-layer. The fabrication of objects with fine features is desirable as the response time of ICP devices is highly dependent on the diffusion distance of ions through the material [20]. Hence, a new class of high-performance ICP devices that are capable of producing more complex actuation tasks will be possible with 3D ICP structures.

The fabrication of 3D ICP structures using two photon stereolithography techniques has been reported [21–23]. While this method is capable of producing complex 3D structures with sub-micron features, it is limited to producing structures within a support material. Microfabrication techniques have also been utilized to fabricate bilayer polypyrrole micro actuators for their potential in lab-on-a-chip technologies [6,24]. This study aims to extend these advances in the production of 3D polypyrrole microstructures with the DLP fabrication technique that will enable the direct fabrication of freestanding ICP devices with improved throughput. In this investigation, the capabilities of the fabrication system and photopolymer formulation are characterized by means of depth of cure and feature resolution experiments. The results of these experiments are then applied to the

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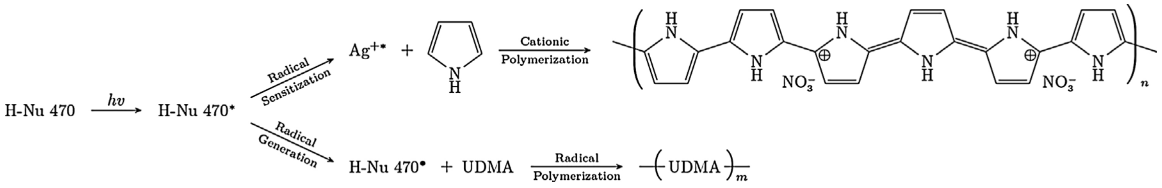

Scheme 1. Proposed reaction scheme for the two-component photoinitiating system.

fabrication of 3D polypyrrole structures with microscale features. The photopolymerized polymer is characterized with FTIR, optical and scanning electron microscopy, electrochemical and electrical conductivity techniques.

2. Polymer formulation

The polymer formulation contained the following reagents: pyrrole (Sigma Aldrich, 131709), extended urethane dimethylacrylate (UDMA, Esstech Inc. X-726-0000), silver nitrate (Sigma Aldrich, 209139), propylene carbonate (Sigma Aldrich, P52652) and 5,7-diiodo-3-butoxy-6-fluorone (H-Nu 470, Spectra Group Limited Inc.).

A photosensitive PPy formulation is required to fabricate structures with the DLP 3D printing technique. While photosensitive formulations exist for other conjugated polymers such as polyaniline and polythiophene, polypyrrole was selected due to its superior actuation performance which will be beneficial for the future development of 3D conjugated polymer actuators [25]. Various approaches have been reported on the photopolymerization of PPy [10–13,26–30]. One of the major challenges with using photosensitive formulations that enable the selective polymerization of polypyrrole is the brittle nature of the resulting polymer. This challenge prevents these PPy formulations from being directly used with the DLP additive fabrication technique since the forces on the produced structures during fabrication cause the material to fail. Efforts have been made to improve their mechanical properties by incorporating large surfactant anions [13] or simultaneous polymerization of pyrrole with another polymer [12,27–30]. These hybrid polymer systems enable the overall material to take on the smart material properties of PPy and the mechanical properties of the secondary polymer.

A UDMA polymer was incorporated into the formulation to yield a hybrid polymer to improve the mechanical properties. UDMA was selected to impart flexibility in the polymer upon curing. It is anticipated that the flexible property will be beneficial when the hybrid polymer is used to create ICP actuators since these devices require large volume expansion and contraction. Various concentrations of UDMA in the photopolymer formulation were investigated. At high UDMA concentrations, the polymer formulation became very viscous, making it difficult to dispense into thin layers. To compensate for this effect, the UDMA was diluted with 20 wt% propylene carbonate.

The hybrid polymer formulation requires a photoinitiating system to generate reactive species that initiate polymerization of both the pyrrole and UDMA monomers when irradiated with light. Pyrrole is known to polymerize with an oxidation reaction that can be initiated by a cationic photoinitiator [12] while UDMA requires a radical photoinitiator [31]. These requirements can be met with a two-component photoinitiating system that relies on radical sensitization of a cationic photoinitiator [32]. This photoinitiating system uses a radical photoinitiator that is initiated by light from the DLP projector to both directly initiate polymerization of the UDMA polymer and sensitizes a cationic photoinitiator to initiate polymerization of the pyrrole. Silver nitrate has been reported for use as the cationic photoinitiator in PPy photopolymer formulations [13,26,30]. Silver salts can be directly used as a photoinitiator for pyrrole due to the former's UV absorption, but radical sensitization is required for the proposed DLP 3D printing technique due to the visible light emission spectrum of the DLP projector. The silver ion is a weak oxidant that will polymerize the pyrrole monomer over the course of several days. The oxidation reaction speed is greatly increased when the silver ions are sensitized by a radical photoinitiator. The nitrate anion becomes incorporated along the polymer chain as a dopant [33]. Thermal energy can also increase the reactivity of the silver ions to polymerize PPy. Heating of the photopolymer due to irradiation should be mitigated to minimize the polymerization of PPy outside the irradiated area. An 8:1 molar ratio of pyrrole to silver nitrate was used for all formulations as this ratio has been found to produce polypyrrole films with the greatest electrical conductivity [13]. Scheme 1 illustrates the proposed two-component photoinitiating system.

The radical photoinitiator is required to have a strong absorbance overlap with the emission spectrum of the light source. This requirement limits the number of available photoinitiators since most are initiated by UV irradiation and the emission spectrum of the projector is within the visible light spectrum. The H-Nu 470 radical photoinitiator was chosen due to its visible light absorbance up to 700 nm which has a strong overlap with the emission spectrum of the DLP projector. The absorbance spectrum of the H-Nu 470 photoinitiator and emission spectrum are shown in Fig. 1. This photoinitiator is known to be efficient and requires much lower concentrations compared to UV photoinitiators [34]. A photoinitiator concentration of 0.1 wt% was used in this formulation. Due to the absorption of light within the visible spectrum, the polymer formulations were prepared under red light to prevent premature initiation.

3. DLP fabrication

The 3D fabrication system incorporates a DLP projector to generate patterns that selectively photopolymerize thin polymer layers. The optics of the projector produce a projected pixel size of approximately 40 μm at the surface of polymerization. The workflow for the 3D fabrication initiates with a 3D model of the desired geometry. The geometry is then discretized into thin layers and represented as binary images. The images are then displayed for the prescribed cure time to photopolymerize each layer of the discretized 3D object. The fabricated structures were washed with acetone to remove any uncured polymer resin.

DLP 3D printing systems typically use either a fixed-surface or free-

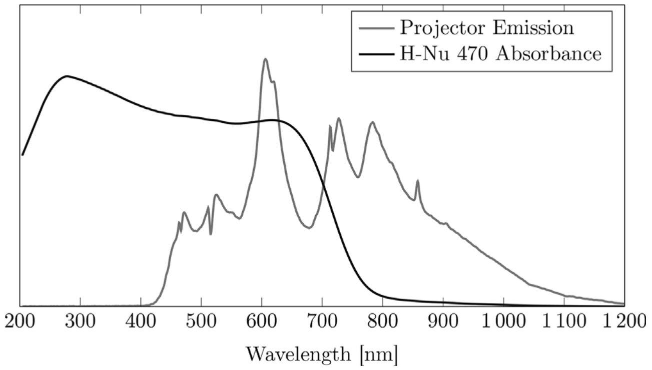

Fig. 1. Emission spectrum of the projector and absorption spectrum of the H-Nu 470 photoinitiator. The intensity and absorbance axes have been normalized.

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