

Nitrogen Microwave Plasma Flowing Afterglow Polymerization and Deposition of Polypyrrole Films for Preparation of Biocompatible and Conductive Graphene Composite Materials

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Abstract

Statement of background and motivation:

Biological factors such as bio-rejection and scarring are limiting the successful implementation of graphene based interventional technologies, such as graphene electrodes and biosensors [1–4]. The deposition of ordered polymeric coatings for biocompatibility is a relatively simple matter using wet-chemistry, but the issues of medium exchange and chemical residues are still important barriers. Plasma polymerization has thus far been unable to replicate the tightly controlled synthesis mechanisms of wet-chemical polymerization reactions [5]. A new approach has been developed, based on a downstream plasma treatment, to target gas phase plasma polymerization of pyrrole that preserves the aromaticity of the monomer and produces a surface film with the typical molecular structure of polypyrrole (PPY).

Summary of methods and work in progress:

A system comprising a 2.45 GHz microwave source (surfatron) and a low-pressure deposition chamber have been devised to introduce pyrrole vapor into contact with a partially relaxed post-plasma (Fig 1). Liquid pyrrole is introduced into a holding vessel, separated from the vacuum chamber by a narrow orifice valve (0-2 mm). The vessel is brought to vacuum operating pressure (6 torr) and then allowed to equilibrate with the liquid pyrrole, increasing the partial pressure of pyrrole in the vessel. During deposition treatments, 20 sccm of N₂ is introduced through the vessel and into the flowing afterglow at an incident angle normal to the direction of flow. This side flow contains an equilibrium value of pyrrole vapor, allowing for tight control of the pyrrole influx through control of the N₂ flowrate and vessel pressure. To check for plasma chemical considerations, the procedure was examined: a) with pyrrole injected into the late-afterglow directly, b) pyrrole injected into an inert N₂ flow followed by post-treatment by flowing afterglow, and c) pyrrole injected into an inert N₂ flow with no subsequent afterglow treatment.

Results and Discussion:

FTIR measurements of KBr substrates subjected to treatments a)-b) are shown in Fig 2. The injection of pyrrole into the plasma afterglow (a) led to deposition of ordered films showing the characteristic infrared pattern of polypyrrole [6]. These bands were conspicuously absent from post-injection annealed KBr samples (b) and (c). This is an important finding, because polydispersity is a common problem with plasma-synthesized polymer films [7]. Although the bands observed in FTIR are common to nitrogen containing carbonaceous films, the presence of a peak at 1630 cm⁻¹, attributed to a conjugated macromolecular system, confirms that the aromatic structure of pyrrole is preserved in the plasma-synthesized films.

OES measurements of the plasma in operation demonstrate that there is sufficient energy to excite the vibrational levels of C-N. The presence of C-N emission indicates that some of the pyrrole that is injected is dissociated in the afterglow. This further indicates that gas phase chemistry plays an important role in the polymerization process, when considering that procedure (b) yielded no FTIR pattern, as mentioned previously. The energetic considerations of the plasma allow for the precise control of chemical kinetics through tuning the energy density of the plasma afterglow.

Conclusions and Implications:

Polypyrrole has been produced with no significant oxygen content in a one-step plasma deposition mechanism. This procedure allows for the deposition of ppy films directly onto graphene without any wet chemical synthesis or electrochemistry, producing large-area graphene-polymer composite materials with minimal chemical byproducts or process steps.

References

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Figures

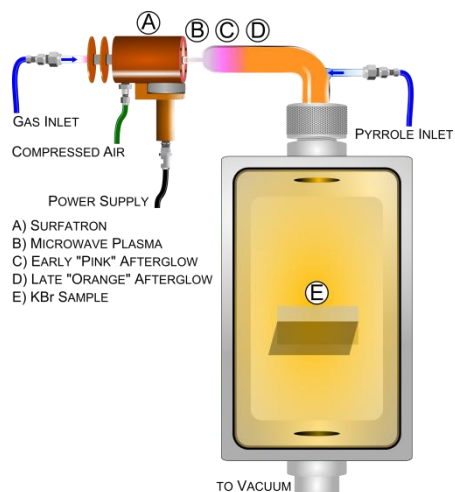


Figure 1. Plasma processing setup for deposition of polypyrrole films. A surface wave microwave discharge is produced at A (2.45 GHz microwave source), and relaxes through internal processes until it produces an early C) and a late D) afterglow. The sample (KBr or Graphene films) is placed in a deposition chamber downstream of the pyrrole injection port. Pyrrole is provided at a controlled concentration through a vaporization chamber (not shown).

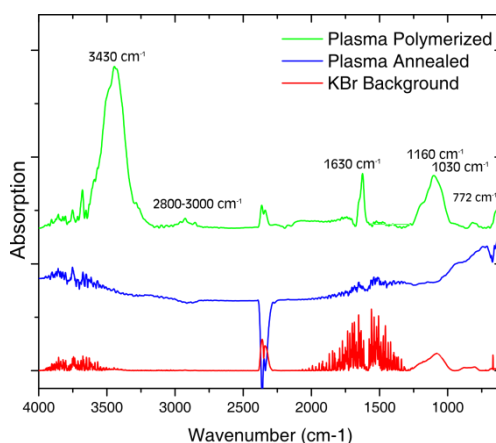


Figure 2. FTIR spectra for KBr windows with deposited films. The peak at 3430 cm^{-1} is assigned to the N-H stretch. The peak at 1630 cm^{-1} is attributed to conjugated structure and the free charge carrier found in PPy. The band at 1160 cm^{-1} results from C-N stretching. The bands of the C-H in-plane stretching vibration and out-plane bending vibration are situated at $2800\text{-}3000\text{ cm}^{-1}$, 1030 cm^{-1} and 772 cm^{-1} . The spectra collected from plasma treated KBr windows were smoothed during post-processing to remove the effect of humidity (seen in the background spectrum).

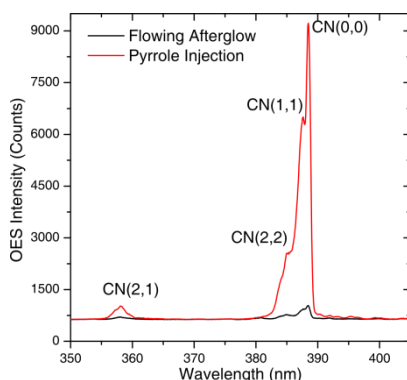


Figure 3. Optical Emission Spectroscopy (OES) measurements of emission from the area of the pyrrole inlet. The characteristic lines of the CN Violet Spectrum are shown to be excited in the flowing afterglow.