

# STRUCTURAL DEVELOPMENT OF HEAT-TREATED POLYPARAPHENYLENE-BASED CARBONS

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Research and development of lithium ion batteries, having a carbon host doped with lithium as the anode, is currently a very active research field because of the general need for light weight, safe, rechargeable battery cells for portable electronic devices.<sup>1-3</sup> Previous studies on PPP heat treated up to temperatures  $T_{HT} \sim 3000^\circ\text{C}$  have examined the electronic properties<sup>4,5</sup> and structural characteristics<sup>5,6</sup> of PPP-based carbons. In this work we examine the optical properties of PPP-based carbons heat-treated to various temperatures, using Raman scattering as a probe of the vibrational spectra, and photoluminescence (PL) to study the electronic structure related to the complicated defect structure within the carbon-polymer matrix. Our goal is to understand why PPP heat treated to  $700^\circ\text{C}$  has such a high lithium uptake.<sup>7</sup>

The granular PPP was synthesized by the Kovacic method<sup>8</sup>, pressed into  $\sim 15\text{mm}$  diameter discs, and heat treated to various temperatures between  $600$  and  $750^\circ\text{C}$  for 1 hour in high purity argon gas, using a conventional resistance furnace. PL spectra ( $\lambda_{exc} = 350\text{ nm}$ ) were collected from samples heat treated at  $T_{HT} = 600^\circ\text{C}$ ,  $650^\circ\text{C}$ ,  $675^\circ\text{C}$  and  $700^\circ\text{C}$  as well as from the polymer prior to heat-treatment (pristine PPP). The PL results are shown in Fig. 1. The PL spectra from the pristine PPP sample showed spectral features in the blue-green located at  $426\text{ nm}$ ,  $453\text{ nm}$ ,  $480\text{ nm}$  and  $515\text{ nm}$ , along with a dominant, broad, red PL structure centered at  $668\text{ nm}$  with lesser contributions at  $619\text{ nm}$  and  $726\text{ nm}$ . The PL from the PPP-600 sample consisted of similar spectral features but the broad red PL structure was much reduced in intensity, and the structure in the red was no longer distinct. The PL intensity from the PPP-650 sample was much smaller than from the PPP-600 sample and the features in the blue-green can no longer be clearly seen.

PL provides an effective probe of the presence of the polymer in the samples after the heat-treatments, since the polymer fragments exhibit strong PL emissions, but the disordered carbon regions formed from the polymer precursor generally will not luminesce. Our experimental results clearly indicate the presence of the polymer in PPP samples with  $T_{HT} \leq 675^\circ\text{C}$ .

Raman spectra of all heat-treated samples were collected using excitation wavelengths,  $\lambda_{exc}$ , equal to  $488.0\text{ nm}$  and  $514.5\text{ nm}$ . Figure 2 shows Raman spectra for all samples excited at  $514.5\text{ nm}$ . A single well-

defined band at  $1605\text{ cm}^{-1}$  is observed, along with weaker bands in the range  $1200\text{--}1500\text{ cm}^{-1}$ . The high-frequency band at  $1605\text{ cm}^{-1}$  broadens with increasing  $T_{HT}$ , with a full-width-half-maximum (FWHM) ranging from  $25$  to  $49\text{ cm}^{-1}$  for samples PPP-650 through PPP-750, respectively. As  $T_{HT}$  is increased above  $700^\circ\text{C}$ , the low-frequency structure in the Raman spectrum becomes less defined, leading to a single, broad peak near  $1330\text{ cm}^{-1}$ . For samples PPP-650 and PPP-675, structure at  $1244$ ,  $1271$  and  $1331\text{ cm}^{-1}$  are well resolved using  $\lambda_{exc}$  at both  $514.5\text{ nm}$  and  $488.0\text{ nm}$ .

A detailed least-squares fit to Raman data collected at  $488.0\text{ nm}$  indicates the presence of several low frequency peaks in samples PPP-650, PPP-675 and PPP-700. Figure 3 shows the results for PPP-650. All peaks are well described by Lorentzian lineshapes, after subtraction of a linear background term in the fitting routine. The aforementioned bands ( $\sim 1240$ ,  $\sim 1270$  and  $\sim 1330\text{ cm}^{-1}$ ) are well accounted for by the fit, but a better fit is obtained if small Lorentzians centered at  $1216$  and  $1360\text{ cm}^{-1}$  are also used to fit the PPP-650 and PPP-675 spectra.

The vibrational spectra of pristine PPP has been studied extensively.<sup>9-12</sup> A planarized PPP molecule in its ground state possesses  $D_{2h}$  symmetry, yielding the following in-plane modes at  $k=0$ :

$$5A_g + 5B_{1g} + 4B_{2u} + 4B_{3u}.$$

Of these, 3  $A_g$  modes produce strong Raman lines in the range  $1100\text{ cm}^{-1}$  to  $1800\text{ cm}^{-1}$ , namely at  $\sim 1220\text{ cm}^{-1}$ ,  $\sim 1280\text{ cm}^{-1}$  and  $\sim 1600\text{ cm}^{-1}$  for a benzenoid configuration. It is also well known that a (higher energy) quinoid state exists for the molecule, producing Raman lines near  $1240\text{ cm}^{-1}$  and  $1330\text{ cm}^{-1}$ , slightly higher in frequency from those for the benzenoid system due to a redistribution of C-C double-bonds. Such an excited (doping-induced) molecular state has previously been observed optically.<sup>13</sup>

We conjecture that the Raman spectra for PPP heat-treated near  $700^\circ\text{C}$  is the result of a superposition of peaks derived from both quinoid and benzenoid segments, the former being induced by disorder. Ultimately, a planar configuration of phenyl groups is energetically favored as the heat treated solid loses more hydrogen and forms small graphene ribbons and segments.

Raman studies reveal that, for PPP samples with  $T_{HT} \sim 700^\circ\text{C}$ , features in the Raman spectrum between  $1200\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$  may be identified with modes derived from each of the resonant PPP molecular structures. Thus, at low  $T_{HT}$ , we find the co-existence of a mostly quinoid-like disordered PPP material with smaller amounts of benzenoid-PPP and turbostratic graphene constituents. The crosslinking of polymer chains that occurs with heat-treatment results in pockets of polymer surrounded by regions of the turbostratic graphene constituents. It seems that in PPP-700,  $\pi$ -electron delocalization over the polymer chains and between chain segments prevents strong luminescence. However, phonon modes in conjugated polymers are more strongly influenced by the rearrangement of  $\sigma$ -electrons as opposed to  $\pi$ -electrons, thereby allowing a quinoid-like PPP skeleton to exist in PPP-700 which is confirmed by the observed Raman spectrum.

The various regions within the PPP-700 material provide a variety of sites for binding lithium. The turbostratic graphene regions would provide sites similar to those observed in first stage Li intercalated graphite intercalation compounds (GIC). The many edge sites from the disordered polymer and the pre-graphitic clusters also provide binding sites for lithium.

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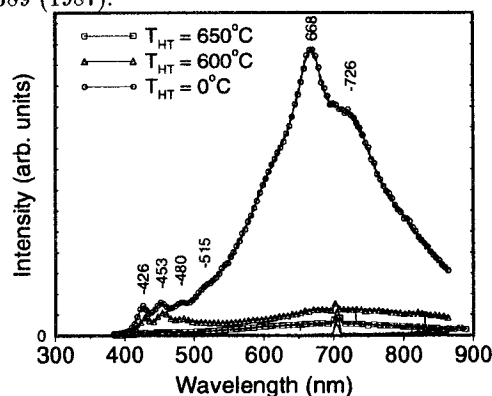


FIG. 1. Plot of PL emission vs. wavelength for samples of PPP subjected to different heat treatment temperatures ( $T_{HT}=0^\circ\text{C}$ ,  $600^\circ\text{C}$ ,  $650^\circ\text{C}$ ,  $675^\circ\text{C}$ ,  $700^\circ\text{C}$ ). Excitation was at  $3.54\text{ eV}$  ( $350\text{ nm}$ ).

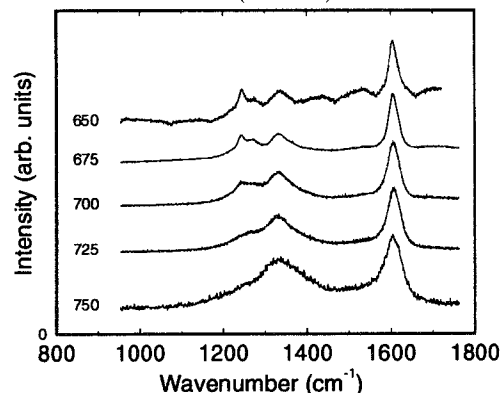


FIG. 2. Raman spectra for  $\lambda_{exc} = 514.5\text{ nm}$  of poly-paraphenylene (PPP) heat treated to (a)  $650^\circ\text{C}$ , (b)  $675^\circ\text{C}$ , (c)  $700^\circ\text{C}$ , (d)  $725^\circ\text{C}$  and (e)  $750^\circ\text{C}$  showing the evolution of the Raman peaks over a narrow  $\Delta T_{HT}$  range.

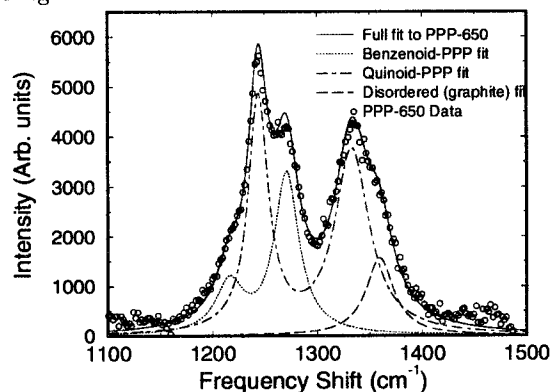


FIG. 3. Low frequency Raman spectra of PPP-650 showing the superposition of several peaks, presumably due to the coexistence of benzenoid and quinoid segments (see text).