Laser pruning of Poly(p-phenylene vinylene) nanostructures

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ABSTRACT

We have expanded on recently conducted research, which discovered that pruning Poly(p-phenylene vinylene) (PPV) nanostructures with a focused 662nm (red) laser alters their photoluminescence (PL) spectra. Using red, green, and violet lasers at various powers, we pruned PPV nanotubes and nanowires of different lengths. We found their PL spectra exhibited peaks at fixed wavelengths, regardless of the original morphology and other variables. Exposure to laser light resulted in an increase in the relative intensity of peaks at longer wavelengths, giving the appearance of a red-shifted spectrum. Our findings suggest that the photoluminescence of PPV originates from independent chemical processes of differing energy, with morphology affecting the activity of these processes. Thus, exposure to laser light inhibits high-energy processes and/or enhances low-energy processes.

INTRODUCTION

It has been observed on many occasions that the electrical, thermodynamic, optical, and magnetic properties of materials often behave differently, sometimes dramatically so, at the micro- and nanoscopic scale. However, much of this research has focused on inorganic materials, with carbon fullerenes being one notable exception to this. Considering the broad range of applications for organic polymers at the macroscopic scale, it is plausible that they should find equally far-reaching application in the growing field of nanotechnology.

One material that has been demonstrated to exhibit various potentially useful optical and electronic properties is the conducting polymer Poly(p-phenylene vinylene) (PPV), of the rigid-rod polymer host family. Among its other bulk properties, it has been shown to display photoluminescence (PL) (Bradley et al., 1987). It has recently been noted by Chin et al. (2009) that the PL spectra of PPV nanowires (NWs) and nanotubes (NTs) show some curious differences from their bulk film counterparts. They found that the spectrum generated from a nanowire array using a 325nm (UV) excitation source appeared red-shifted relative to the film’s spectrum. Additionally, it was discovered that cutting the nanowires with a 662nm (red) laser caused the spectrum be further red-shifted. Our investigation was concerned with determining the variables affecting this phenomenon to try to uncover its source. We conducted trials using

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nanotubes (NTs) and nanowires (NWs) of varying length and cut the nanostructures using lasers of a range of wavelengths and power settings.

MATERIALS AND METHODS

Samples and Equipment

The poly(p-phenylenevinylene) nanowires and nanotubes used for this experiment were produced in the manner described by Chin et al. (2009). We produced NTs of length ~0.8µm, ~1.6µm and ~3.1µm and NWs of length ~0.9µm and ~1.2µm. Since nanowires were the subject of the previous investigation, only the short NWs were used for most tests, for comparison. The NTs and NWs had a diameter of 0.2-0.3µm while the NTs had walls ~0.1µm thick.

Three lasers of wavelengths spanning the visible EM spectrum were used for pruning: 655nm (red), 532nm (green) and 405nm (violet). The nanostructures were visually characterized using the SSL scanning electron microscope, a JEOL JSM 6700-F with operational parameters of 10µA and 5.0kV. PL spectra were then obtained using a Renishaw inVia Raman Microscope at room temperature and an excitation wavelength of 325nm.

Procedures

For each laser wavelength, three separate areas were cut. For the red and green lasers, whose power output could be controllably varied, the three areas were cut with three different powers. The violet laser operates at a fixed output, and so it was simply scanned over each area a different number of times. The parameters are summarized below:

<table>
<thead>
<tr>
<th>laser/area</th>
<th>Area 1</th>
<th>Area 2</th>
<th>Area 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>655nm (red)</td>
<td>20mW, one scan</td>
<td>30mW, one scan</td>
<td>40mW, one scan</td>
</tr>
<tr>
<td>532nm (green)</td>
<td>3.1mW, one scan</td>
<td>3.8mW, one scan</td>
<td>9.9mW, one scan</td>
</tr>
<tr>
<td>405nm (violet)</td>
<td>6.0mW, one scan</td>
<td>6.0mW, two scans</td>
<td>6.0mW, three scans</td>
</tr>
</tbody>
</table>

Following laser pruning, the samples were characterized unaltered with SEM, with the exception of edge-view images. In order to obtain an edge-view, the sample was sputtered with platinum at 7.5Pa using a JEOL JFC-1600 Auto Fine Coater, operating at 20mA for 45s to improve the conductance of the surface. This was done at the conclusion of the experiment so as not to interfere with the results.

RESULTS AND DISCUSSION

One of the most important discoveries over the course of this investigation was that PPV seems to contain peaks which are fixed from spectrum to spectrum, regardless of the sample, laser wavelength, or laser power. When occurring near the spectrum’s maximum amplitude, these peaks were local maxima. When far from the universal maximum, they corresponded to rapid changes in slope. This is illustrated in Fig. (1), below. The vertical grey lines correspond to one such feature, a particularly prominent one, at 574nm. The vertical axis is the intensity of the emission, and should be read as being in arbitrary units.
Each individual spectrum is normalized such that the mean intensity over all the data points is 1.0 units of intensity. Thus, a lower maximum corresponds to a broader spectrum. These spectra show the effect that laser cutting at the highest power had on the PL spectra. They are colour coded in Fig. (1) according to the laser used, with black being the uncut spectrum. In total, there were seven easily identified peaks at the same wavelength in every spectrum, shown below:

Fig. (2) shows the spectra obtained from the various uncut nanostructures. With this data, the nature of the spectral changes following laser pruning are easy to describe: the fixed peaks corresponding to higher wavelengths became more intense compared with the lower wavelengths. When comparisons were made between PL spectra of the same sample and laser, varying only the laser power, we frequently observed that the amount of apparent red shift increased with laser power and that the spectra were broadened the most at low power cuts.

The nature of the interaction between the laser and the nanostructures was characterized with SEM, as shown in Fig. (3). We were able to observe the extent to which the NTs were cut.
CONCLUSIONS

The confirmation that PPV PL spectra exhibit fixed peaks regardless of structure suggests that a chemical process is at the very core of the phenomenon. Following laser pruning, the high-energy processes become inhibited and/or the lower energy processes become enhanced. This results in the higher wavelength peaks increasing in relative intensity, causing the spectrum to appear red-shifted. Often, this effect became more pronounced with exposure to more intense laser light or repeated exposure to the same. Thus, the spectra frequently passed through an intermediate phase where a number of the peaks had comparable intensities. This gave the spectra a broadened appearance after pruning at the lower energy laser settings.

We suggest the possibility that it is interactions with atmospheric gases at the surface of the nanostructure, as in the formation of singlet O₂ (Clough et al., 1995), that leads to this inhibition/enhancement of certain chemical processes. We recommend further inquiry along these lines. Poly(p-phenylene vinylene) shows promising potential for integration into nanoscale devices. First, however, there is a great deal more we must learn about its properties.

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REFERENCES

