

Influence of molecular structure on plasma carbonization of organic semiconductor molecules

Toshihiro Shimada^{1,2}, Naoki Muraya³, Jun Tomita³, Takashi Yanase⁴,
Taro Nagahama¹

¹ Division of Materials Chemistry, Faculty of Engineering, Hokkaido University,
Kita-ku, Sapporo, Hokkaido 060-8628, Japan

² CREST-JST, Gobancho, Chiyoda-ku, Tokyo 100-0013, Japan

³ Graduate School of Chemical Science and Engineering, Hokkaido University, Kita-ku,
Sapporo,
Hokkaido 060-8628, Japan

⁴ Frontier Chemistry Center, Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo,
Hokkaido 060-8628, Japan

Abstract

The plasma treatment of organic semiconductor molecules includes issues related with nanoscale plasma interfaces. The process was examined by optical emission spectroscopy. It was found that molecules are sublimed by the heat and decomposed by the interaction with the plasma. The product carbon solids were examined by Raman spectroscopy. The Raman spectra are strongly dependent on the molecular structures. The carbon solids which does not show graphitic Raman spectra have nanostructures originating from initial molecules.

1. Introduction

Carbon materials with controlled nanostructure are gathering much attention recently for the application in electrode materials for rechargeable batteries[1], carbon-based catalysis[2] and new semiconductors such as carbon nanotubes (CNTs)[3] and graphene[4]. However, the strategy for finely control the nanostructure is rather limited so far, for example calcination of polymers with various functional moieties[5], diameter control of the CNTs by controlling the size of the catalysts[6], and doping of other elements during the growth[7]. In order to explore the possibility of producing nanostructured carbon from organic molecules, we have studied the high temperature treatment of the molecules by vacuum deposition at 1800 °C[8]. However, the amount of the product was too small to allow detailed systematic examination. We here report the study on the possibility of synthesizing carbon materials with well-defined nanostructures by treating organic semiconductor molecules with plasma. Recent advances in the organic electronics, various molecules with wide p-electron systems have been synthesized. By exposing these molecules to plasma, radicals and ions of these molecules will be formed and they will polymerize to make a solid. It is expected that the product may contain the structure of the initial organic semiconductor molecules. In this paper, we examined the effect of microwave plasma by optical emission spectroscopy of the plasma and Raman spectroscopy of the product solids.



2. Experiment

The organic semiconductor molecules used as the raw materials in this study are shown in Fig. 1. They are solid powders at room temperature and used as purchased. 1~2 mg of the powder was sealed in a quartz tube (4mm OD, 2.5mm ID, 4 cm length) and the gas inside the tube was replaced with 99.9% N₂. It was pumped by a rotary pump to the pressure of 100 Pa and then sealed by fusing an oxygen burner. It was observed that the molecules are sublimed in the tube when the tube was heated to 100 ~ 300 °C (the temperatures are dependent on the molecules). The tube was set to a surfatron reactor shown in Fig. 2. Microwave (~ 500 W) from magnetron was irradiated and the

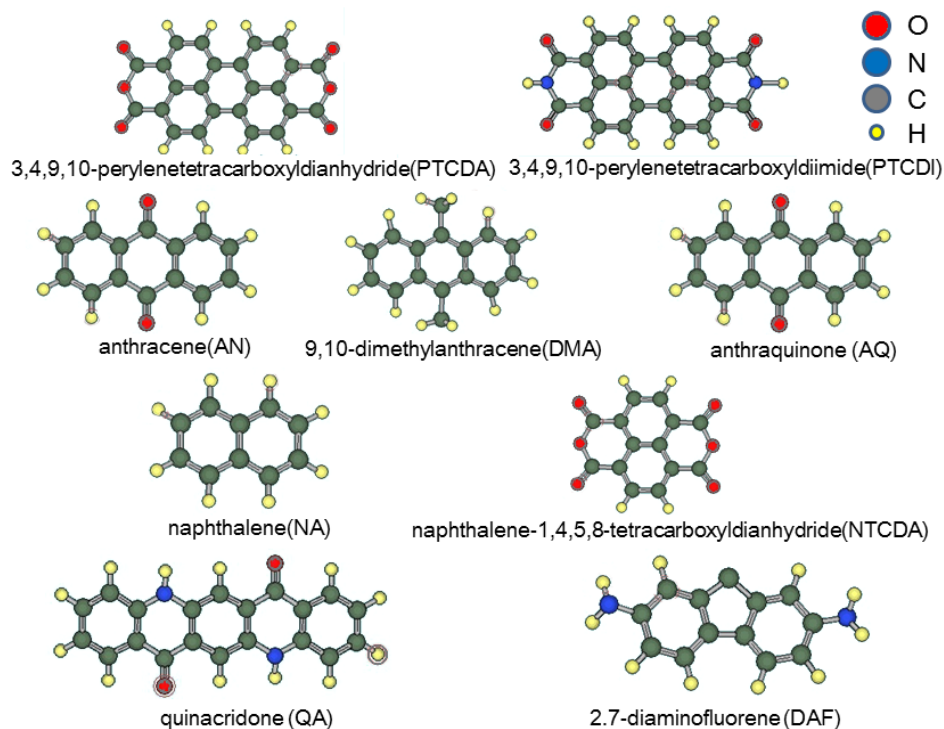


Fig. 1: Structure of the molecules used as source materials.

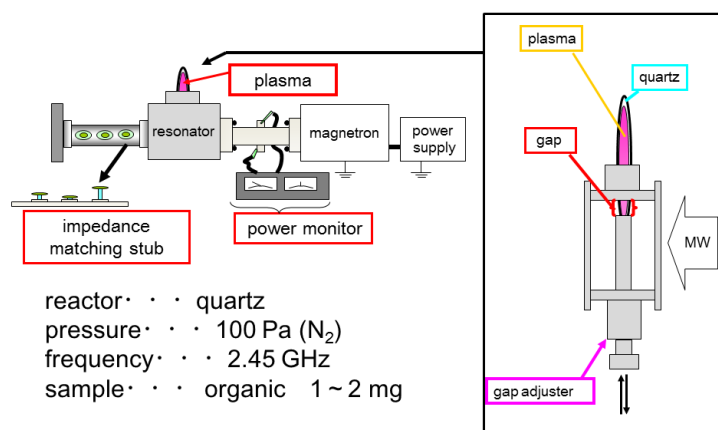


Fig. 2: Schematic drawing of the surfatron reactor.

plasma was excited. The colour of the plasma changed as the time elapsed and the plasma ceased eventually. The optical emission spectra were monitored by a fibre optic spectrometer (Ocean Optics

USB-2000) which was calibrated by emission wavelengths of neon. After the plasma treatment, the inside of the tube turned brown or black colour. The obtained solids were examined by Raman spectroscopy using Renishaw Invia spectrometer using 532 nm or 780 nm laser excitation. The laser wavelength was chosen to achieve high resolution spectra while avoiding fluorescence.

3. Results and discussion

The typical time evolution of optical emission spectra during the plasma treatment is shown in Fig. 3. The molecule was PTCDA. After the plasma ignition, emission peaks arising from the N₂ gas plasma

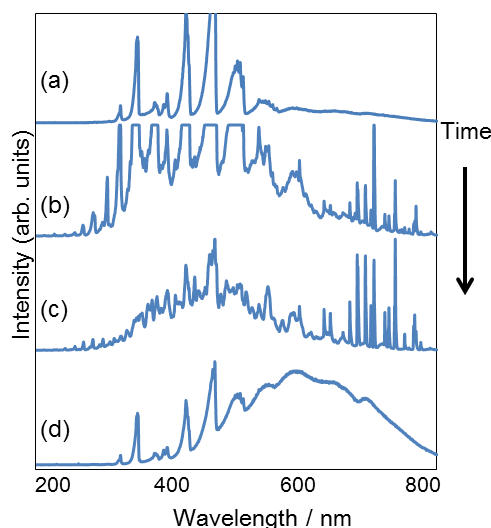


Fig. 3: Optical emission spectra from PTCDA- containing tube during the plasma treatment.

was observed (Fig. 3(a)). After several second, the quartz tube was heated by microwave and the plasma, and molecules are vaporized. Corresponding emission was appears as peaks in visible region (Fig.3(b)). When the molecule contains oxygen, as in the case of PTCDA, peaks around 700-800 nm appears. It shows the decomposition at the oxygen containing part of the molecule. After several seconds, the N-originated peaks diminished and the many small peaks were observed in the visible region(Fig.3(c)). Finally a broad peak appeared from infrared region and shifted toward the visible region(Fig.3(d)). At this moment, the quartz tube glowed and sometimes it deformed. We consider that the broad peak was the blackbody radiation from the quartz tube and the sample. It is supposed that the temperature was elevated to the glass transition temperature of the quartz glass (~1000 °C).

We found that the molecules are categorized into three groups. The first group is easily graphitized molecules. Figure 4 shows the Raman spectra of the product obtained from DAF and PTCDA. D peak (~1350 cm⁻¹) and G peak (~1580cm⁻¹) are observed clearly and no other peaks are noticeable. It is the signature of the formation of graphite-like carbon. The broadness of the D and G peaks and their ratio indicates that the size of the graphite is very small, probably not far beyond the size of the molecules [9]. It is noticed that PTCDA shows sharper peaks than DAF, which is in accordance with the fact that PTCDA easily produces graphemes by CVD [10]. The broad background peak observed in the Raman spectra of these materials probably correspond to various ill-defined structures having various vibration frequencies. It is difficult to analyze the structure because fluorescence is also present even with infrared (780nm) excitation.

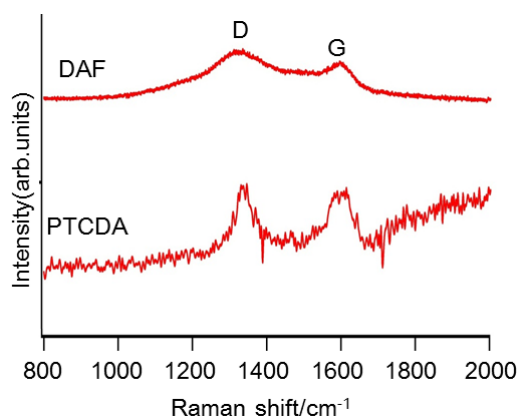


Fig. 4: Raman spectra of solids obtained from the plasma treatment of DAF and PTCDA (group 1).

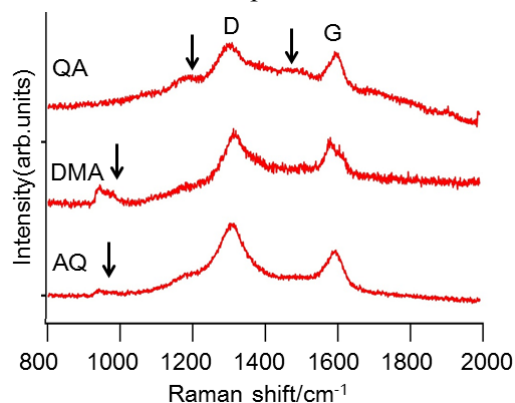


Fig. 5: Raman spectra of solids obtained from the plasma treatment of QA, DMA and AQ (group 2).

Figure 5 shows the Raman spectra of the second group, i.e., giving strong single D and G peaks with additional peaks, indicated by arrows, originating from substitution groups. These molecules have linearly fused benzene rings. It is considered that these molecules are decomposed to give graphite-like carbons but substantial amount are not incorporated in the graphite lattice. Although the origin of the additional peaks are still under investigation, preliminary quantum chemical simulation suggests that vibration of the CH_3 - group coupled with that of the fused benzene rings corresponds to the peak around 900 cm^{-1} .

The third group is shown in Fig. 6. They show strong additional peaks with D and G peaks weaker and broader than other groups. The initial molecules are derivative of small linear aromatics. It shows that these molecules are not easily graphitized. The striking difference is the difference between NTCDA and PTCDA, both having the carboxylic dianhydride structure. It is noticed that the size of the core aromatics is very important.

4. Conclusion

We investigated the plasma treatment of organic semiconductor molecules. We found that molecules are sublimed by the heat and decomposed by the interaction with the plasma. The product carbon solids were examined by Raman spectroscopy and whether the graphitic carbon is formed or not is strongly dependent on the molecular structure. The carbon solid which does not show graphitic Raman spectra have nanostructures probably originating from initial molecules and its functions as an electrode or catalyst are promising.

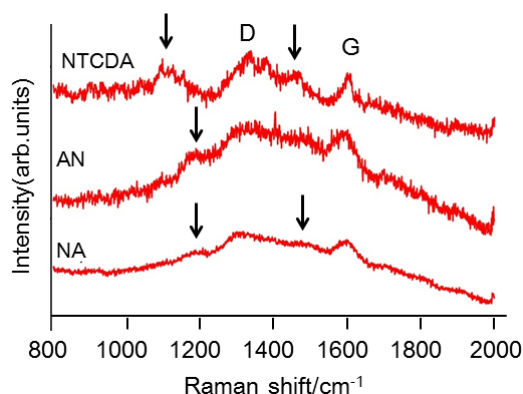


Fig. 6: Raman spectra of solids obtained from the plasma treatment of NTCDA, AN and NA (group3).

Acknowledgments

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References

- [1] Liwen Ji , Zhan Lin, Mataz Alcoutlabi and Xiangwu Zhang 2011 *Energy Environ. Sci.* **4** 2682.
- [2] Ozaki J., Tanifuji S., Kimura N., Furuuchi A. and Oya A 2006 *Carbon* **44** 1324.
- [3] Baughman R.H., Zakhidov A.A., de Heer W.A. 2002 *Science* **297** 787.
- [4] Novoselov K.S. et al. 2004 *Science* **306** 666.
- [5] Meng Y. et al. 2006 *Chem. Mater.* **18** 4447.
- [6] Terrones M et al. 1997 *Nature* **388** 52.
- [7] Lin Y.C. et al. 2010 *Appl. Phys. Lett.* **96** 133110.
- [8] Noguchi T., Shimada T., Hanzawa A. and Hasegawa T. 2009 *Thin Solid Films* **518** 778.
- [9] Concardo L.G. et al. 2006 *Appl. Phys. Lett.* **88** 163106.
- [10] Yudasaka M. et al. 1994 *Appl. Phys. Lett.*, **64** 3237.