

ELECTRICAL CHARACTERIZATION OF CARBONACEOUS PARTICLES COLLECTED FROM PREMIXED LAMINAR FLAMES

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Abstract

The aim of this study is the characterization of combustion-formed particulate matter for possible applications as optoelectronic organic materials. UV-visible absorption spectroscopy analysis has been used to calculate the optical band-gaps of the materials by reporting the optical spectra in the Tauc plot. The I-V characteristics, i.e. current vs. voltage plots, have been measured in order to estimate the electrical conductivity. Three different sampling procedures have been developed. A quartz substrate was rapidly inserted in flame, to collect by thermophoresis the carbon particulate matter, containing two main different classes of materials: soot and nanoparticles of organic carbon (NOC). The first class has a band-gap between 0.1 eV and 0.8 eV and a fair electrical conductivity, while the second class has a band-gap between 1.9 eV and 3 eV and a low electrical conductivity. The optical band-gap was investigated under varying flame conditions (C/O ratio and height above the burner) and residence time of substrate in flame. A probe located in flame and a particles impactor was used to sample NOC separated by total particulate matter. Soluble organic fraction (SOF) was chemically extracted from sampled particulate; electrical characterization showed an unusual presence of a hysteresis in the I quadrant of the I-V characteristic of SOF. Finally by using a theoretical model, obtained from literature, the phenomenon of electrical conduction through a soot particles layer is probably attributed to tunneling effect.

1. Introduction

Carbon particulate matter derived from combustion consists of a variety of organic compounds, which often have features similar to polymers and molecules used as photoactive layers in the most common organic solar cells [1]. This consideration has recently provided the inspiration to check out the possible applications of these products in the photovoltaic technology. In this manuscript, combustion-formed carbonaceous materials were collected from various fuel-rich premixed flames of ethylene and air, in order to characterize both optical and electrical properties. The flame-formed carbon particulate matter contain two main different classes of

materials: soot and NOC [2]. To obtain carbon materials with different properties, three different sampling procedures were used: 1. Thermophoretic sampling via rapid insertion of a quartz substrate; 2. Probe sampling followed by collection via particles impactor; 3. Chemical extraction of the soluble organic fraction (SOF).

UV-visible absorption spectroscopy analysis has been conducted to obtain the optical spectra, from which the values of the band-gap (E_g) has been derived by means of the well-known Tauc relation [3]; this equation connects together the absorbance (A), the energy of the incident photon (E) and the optical band-gap (E_g), through a constant of proportionality (B): $(A \cdot E)^{0.5} = B \cdot (E - E_g)$. The electrical conductivity characterization has been performed by measuring the current-voltage characteristics of the materials.

2. Experimental

2.1 Thermophoretic sampling via rapid insertion of a quartz substrate

The experimental combustion system consists of a McKenna burner with a flat atmospheric pressure laminar flame, it was used to generate five fuel-rich flames of ethylene and air, reported in Table 1, at different C/O ratios, and at different heights above the burner HAB. Particulates were thermophoretically sampled via rapid insertions of a quartz substrate in the flame; for all the flames, were varied both the time of each insertion, from 30 ms to 100 ms, and the number of insertions, up to a maximum of 100 total insertions.

Table 1. Investigated flame conditions.

	<i>Flame #1</i>	<i>Flame #2</i>	<i>Flame #3</i>	<i>Flame #4</i>	<i>Flame #5</i>
C/O ratio	0.65	0.72	0.77	0.85	0.85
HAB, mm	10	10	10	10	15

The UV-visible spectra of the carbon materials collected have been measured in the 190–1100 nm wavelength range on an Agilent 8453 spectrophotometer; the spectra obtained were then processed with the Agilent UV-Vis ChemStation software.

In order to make measurements of electrical conductivity, three substrates provided with aluminum metal electrodes were prepared by etching, sputtering and photolithography techniques. The I-V measurements were carried out by using a picoammeter/voltage source Keithley 6487, and a probe station Signatone H-150.

2.2 Probe sampling followed by collection via particles impactor

The experimental combustion system consists of a laminar flame McKenna burner, at atmospheric pressure, used to generate a flame of ethylene and air with a C/O ratio equal to 0.72. In this flame has been inserted a probe, at a height above the burner of 6 mm, in which nitrogen flowed; the probe consists of a stainless steel tube 20 cm long, with a side hole ($d=2.5$ mm) through which nitrogen sampled the

combustion gases, and connected to a particles impactor, that collected particles with a given distribution function. The UV-visible spectra and the I-V current-voltage characteristics were obtained as described above.

2.3 Chemical extraction of the soluble organic fraction (SOF)

The experimental combustion system consists of a McKenna burner with a flat laminar flame, at atmospheric pressure, used to generate a flame of ethylene and air with a C/O ratio equal to 0.85; carbonaceous particulate was thermophoretically sampled via rapid insertions of a quartz substrate in the flame, at a height above the burner of 15 mm, and immersed in a solution of dichloromethane (DCM). The soluble organic fraction was then chemically extracted from the total particulate matter by using an ultrasonic bath Elmasonic S 40 H, with a work frequency of 37 kHz. The UV-visible spectra and the I-V current-voltage characteristics were obtained as described above.

3. Results and discussion

3.1 Thermophoretic sampling via rapid insertion of a quartz substrate

The Flame #1 was too poor in fuel, so was not possible to collect enough material to measure an optical spectrum suitable for our goals. For the other flames, UV-visible spectra have been measured at different residence times, by varying both the time of each insertion and the total number. Increasing the total residence times, the amount of particulate matter sampled increases, and all the spectra become higher in absorbance. The optical gap analysis were performed based on the absorption spectra reported in the Tauc domain. On the Tauc plots has been identified two different regimes, each corresponding to a different value of the optical gap (E_g), obtained by extrapolating the intercept with the x-axis; the two values of the band-gap have been named E_{g1} (the lowest) and E_{g2} (the highest). By this sampling procedure, two different classes of materials were collected, with different molecular structure and energetic characteristics. Values of the E_{g1} as a function of the number of insertions of the substrate in flame is reported in Figure 1a; as the number of insertions increases, collected particulate undergoes an annealing phenomenon, which involves the reduction of the optical band-gap.

The range of E_{g1} is between 0.1 eV and 0.8 eV, typical of materials with a high percentage of sp^2 hybridization; the first class of material is thus made up of particles of soot, which have a graphite-like structure. Values of the band-gap E_{g2} as a function of the number of insertions of the substrate in the flame is reported in Figure 1b; as before, the optical band-gap decreases as the number of insertions increases, due to an annealing phenomenon. The range of E_{g2} is between 1.9 eV and 3 eV, higher than the range of E_{g1} ; the second class of material collected is made up of nanoparticles of organic carbon (NOC), with a high molecular weight. Figure 2 reports the measured I-V characteristics for flame #3 (C/O ratio 0.77, HAB 10 mm), and for flame #5 (C/O ratio 0.85, HAB 15 mm); both curves are symmetrical and non-linear, indicating a non-ohmic electrical behavior. Particulate

matter sampled from flame #5, with a higher C/O ratio than flame #3, is richer in soot, and so has a higher electrical conductivity, due to the small values of the optical band-gap.

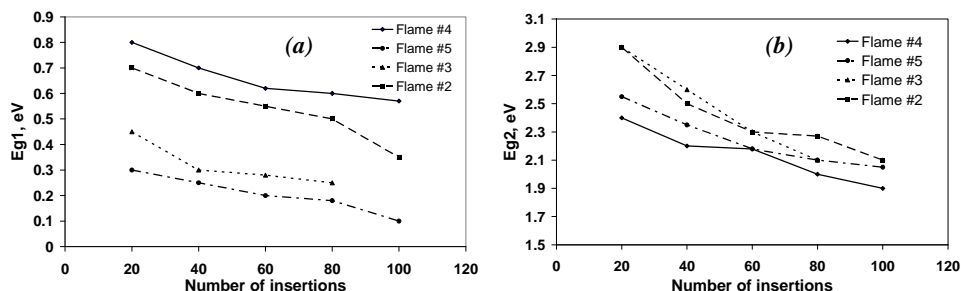


Figure 1. E_{g1} (a) and E_{g2} (b) as a function of the number of insertions of the substrate in the flame.

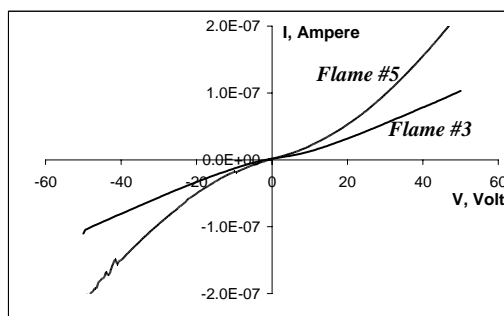


Figure 2. I-V characteristics for two different flames.

3.2 Probe sampling followed by collection via particles impactor

The probe and the particles impactor have allowed to separate nanoparticles of organic carbon from soot, in order to collect mainly NOC. UV-visible spectra has been measured at different total sampling times; all spectra show only a monotonous decreasing trend, with a different slope from the previous case. The optical gap analysis has been performed on the absorption spectra reported in the Tauc domain, as before. Only one regime has been identified, corresponding to a single value of the optical gap (E_g) of about 2 eV; by this sampling procedure, one single class of materials has been collected, made up of nanoparticles of organic carbon (NOC), with a high molecular weight. As before, optical band-gap decreases as the total time of sampling rises.

Figure 3a reports the measured I/V characteristics for carbonaceous material collected with probe and particulate impactor. Particulate matter sampled has a very low electrical conductivity, due to the high values of the optical band-gap.

3.3 Chemical extraction of the soluble organic fraction (SOF)

By chemical extraction, has been separated from the total particulate matter the whole organic fraction, whose characteristics are therefore those of the class with optical band-gap E_g . An UV-Visible spectrum has been measured and reported in the Tauc plot, obtaining a single value of the optical gap E_g of about 1.8 eV.

Figure 3b reports the measured I/V characteristics for the chemically extracted fraction, which shows a very unusual electrical behavior. For positive applied tensions, there is a hysteresis, asymmetric to the rest of the curve, and independent from the previous application of negative currents.

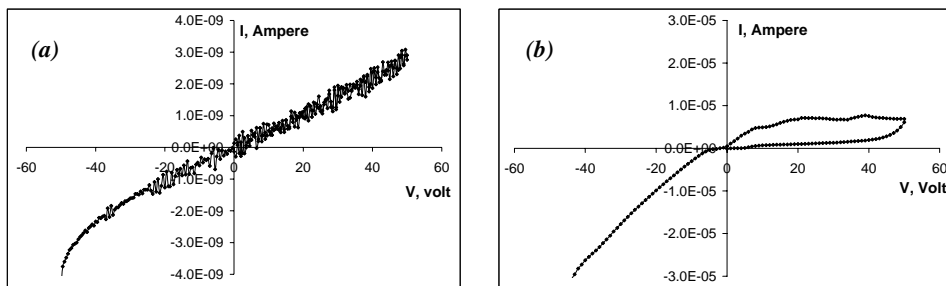


Figure 3. I-V characteristics of NOC sampled with probe and particles impactor (a). I-V characteristics of the soluble organic fraction SOF (b).

3.4 Electrical conduction between soot particles

Current/voltage characteristics reported in Figure 2 seem to show an electrical behavior similar to that of non-ohmic granular system [4]. In this kind of materials, it is possible to assume that the electrical conduction is due to the tunneling of electrons between neighboring particles. Bruschi and Nannini [5] obtained a theoretical equation, that predicts the I/V characteristic of a material in which the electrical conduction is governed by tunneling effect:

$$I = C \left[\frac{A - BV}{\exp\left\{\frac{(A - BV)}{T} - 1\right\}} - \frac{A + BV}{\exp\left\{\frac{(A + BV)}{T} - 1\right\}} \right] \quad (1)$$

where A is proportional to the activation energy of the process, B is a constant depending on the material and C is inversely proportional to the tunneling distance. Equation 2 has been used to fit experimental I/V characteristics of soot, such as those reported in Figure 2; it was observed that equation 1 approximates satisfactorily the experimental data. Values of parameters A and C have been obtained from the fit, and reported in Figure 4 (a and b), as a function of the number of insertions of the substrate in flame.

Values of parameter A are not much affected by increasing the number of insertion, so the activation energy of the process is quite independent of the total amount of sampled material. Parameter C increases as the number of insertion increases; as

more material is present on the substrate, the more particles are close together, decreasing tunneling distance.

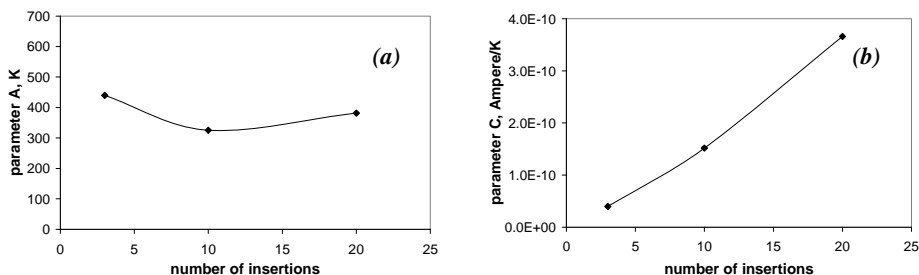


Figure 4. Parameter A (a) and parameter C (b) as a function of the total number of insertions of the substrate in flame.

4. Conclusions

The analysis of different combustion-formed carbonaceous materials has been carried out by investigating optical and electrical properties. Two different classes of material have been identified, with values of optical band-gap of about 0.5 eV and 2 eV, corresponding to soot and nanoparticles of organic carbon, respectively; the optical band gap can be adjusted depending on the flame condition and the sampling procedure. Soot has shown a fair electrical conductivity, while NOC has shown a low electrical conductivity, to be verified in heterojunction with commercial polymers. SOF has shown a very unusual electrical behavior, to be explored for possible application. A theoretical model for the interpretation of the electrical characteristics of carbon materials, based on the tunneling effect, has been deepened.

References

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