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Properties of carbon nanostructures prepared by polyaniline carbonization

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Abstract. Nanometric sponge-like structures have been prepared from the carburization of polyaniline-(emeradine salt) using a rapid immersion in hot-filament system fed with carbon dioxide, ethyl alcohol and argon. Fiber-like fragments of width in the range of 20 – 40 nm have been observed by field emission scanning electron microscopy (FESEM). Raman measurements suggested that benzenoid rings and amide were present in the carburized samples. Lowest threshold achieved for field emission was 23.5 V/ μm .

1. Introduction

Research on the development of new nanostructured carbon based materials, such as carbon nanotubes [1-2], fullerenes, nanodiamonds [3-4] and conducting polymers [5] has been going on intensively because of their potential applications in nanoelectronics, solar cells and field emission displays.

There is also a considerable effort to integrate these materials on the nano-size level. Coating of carbon nanotubes with conducting polymers [6], integration in nanocomposites [7-8], or preparing nanotubes and nanofibers from conducting polymers [9-10], have been demonstrated.

In this work, we report the fabrication of sponge-like nanostructures from the carburization of polyaniline-(emeraldine base) after rapid immersion in a hot-filament system fed with CO₂, ethyl alcohol and argon. Polyaniline-(emeraldine base) has been chosen due to its good chemical stability and remarkable electronic conduction. Field emission scanning electron microscopy (FESEM) and Raman spectroscopic analyses and field emission properties of the samples are presented and discussed.

2. Experimental Details

Polished copper foils (10 mm x 10 mm square) of 0.5 mm thickness, were used as substrates. The polymer solution was prepared from 2 g of polyaniline-(emeraldine base), diluted in 100 ml of dimethylformamide in ultrasound for 10 min. The substrates were coated by the polymer solution without spinning and then dried in a hot-plate in air at 373 K for 120 min. In the sequence, the samples were immersed for 2 min. in the reaction chamber of a hot-filament reactor system fed with carbon dioxide (14.5 % vol.), ethyl alcohol vapor, and argon. (85 % vol.). A total pressure of about 20 Torr and a total flow rate of about 100 sccm were maintained throughout. The temperature as measured by a thermocouple placed on the underside of the copper substrates was 683 K.

Morphological analyses were made by Field Emission Scanning Electron Microscope (FESEM) using a JEOL JSM-6330F operated at 5 kV, 8 μA . Raman spectra were recorded at the ambient temperature using a Renishaw microprobe system, employing an Argon laser for excitation ($\lambda = 514.5$ nm) at a laser power of about 6 mW.

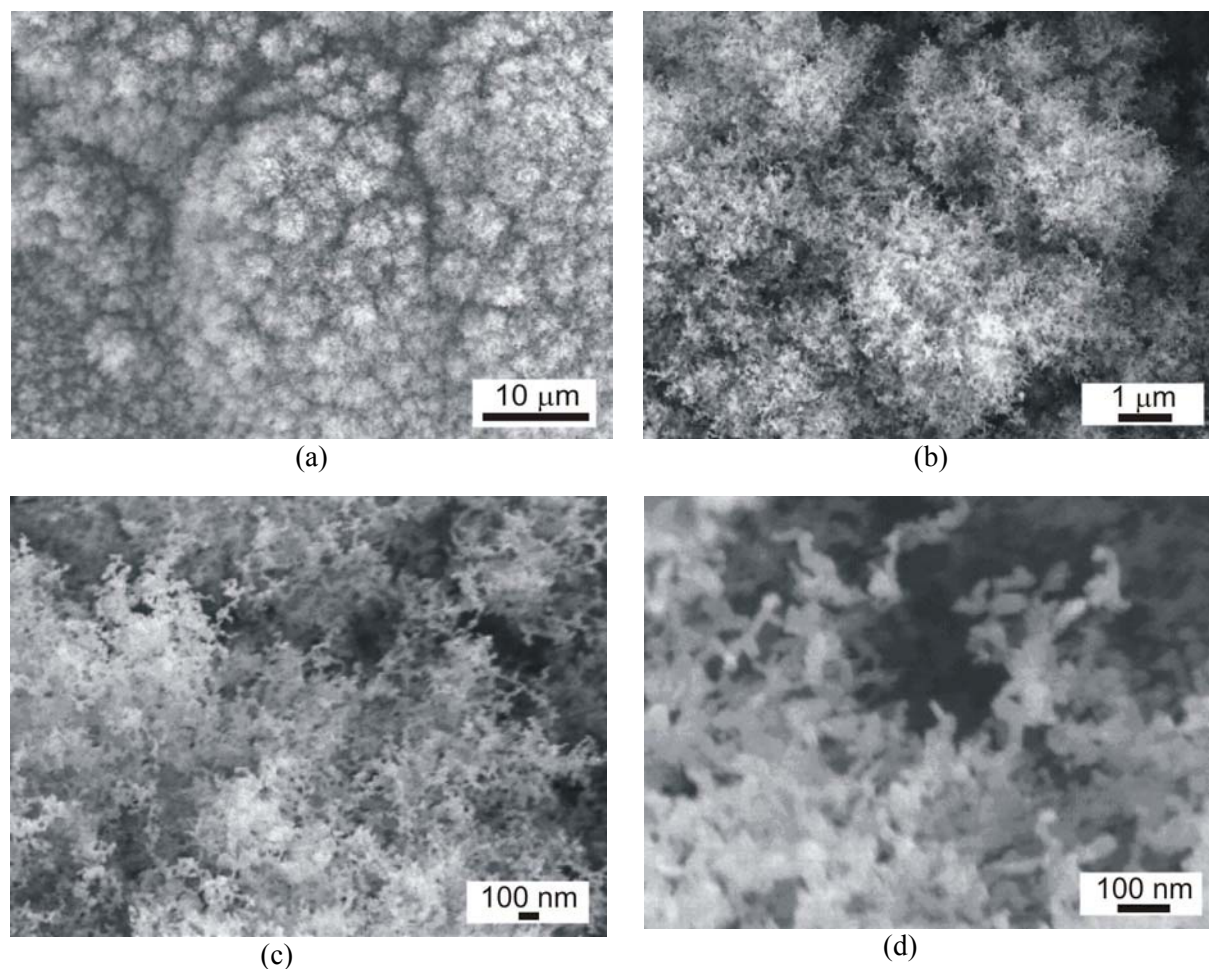


Figure 1. Typical FESEM images of carbonized polyaniline samples at different magnifications

Field emission properties were characterized in a specially designed vacuum system by controlling the distance (d) and the parallelism between anode-cathode (samples) surfaces using a precisely combined XYZ-angular micrometer stage. A Cu rod of 3 mm diameter was used as anode in parallel plate configuration with the samples (cathode). The threshold field (E_{th}) for electron emission was measured by the slope of the bias (for a standard electron current density of 500 nAcm^{-2}) versus anode-cathode distance curves, fitted to straight lines.

3. Results and Discussion

Typical FESEM images are presented in Figure 1 (a)-(d), at different magnifications. Scale bars are from 10 μm to 100 nm, respectively. The images clearly show that the deposited samples consist of sponge-like structures, covering the substrate surface (see Figure 1 (a)) with random agglomeration and high porosity (see Figure 1 (b)-(c)). Magnification of Figure 1 (c) image (see Figure 1 (d)) shows that no identifiable form is apparent besides some fiber-like segments of width in the range of 20 – 40 nm.

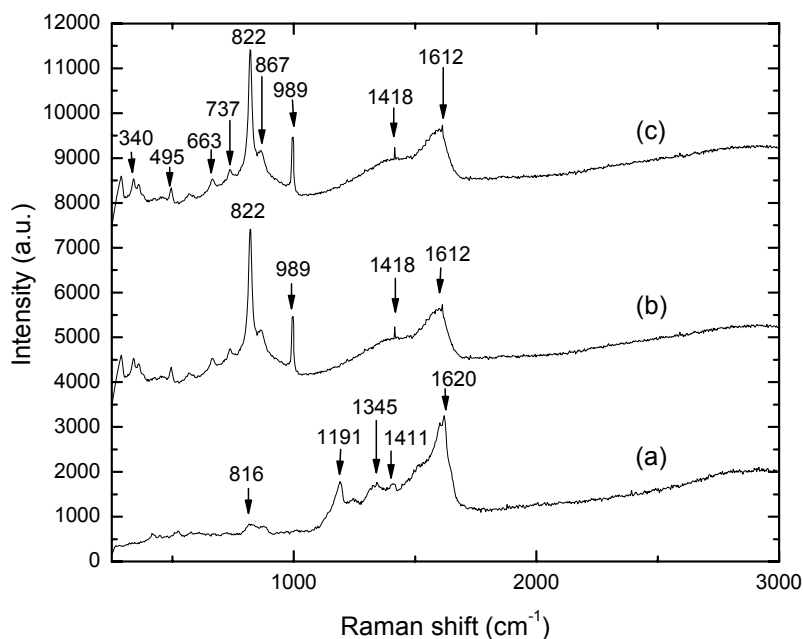


Figure 2. Typical Raman spectra from (a) polyaniline-(emeraldine base) after hot-plate drying and (b-c) from hot-filament processed samples, taken with a laser wavelength of 514.5 nm.

Figure 2 shows typical Raman spectra of the samples. Spectrum (a) was taken from polyaniline-(emeraldine base) after hot-plate drying and spectra (b-c) are those of hot-filament processed samples. Spectrum (a) shows peaks at 816 cm^{-1} , 1191 cm^{-1} , 1345 cm^{-1} , 1411 cm^{-1} and 1620 cm^{-1} . These peaks may be associated with deformation in amine ($\sim 822 \text{ cm}^{-1}$), C-H bending in quinoid rings ($\sim 1160 \text{ cm}^{-1}$), C-C stretching in quinoid rings ($\sim 1372 \text{ cm}^{-1}$), C-H bending in benzenoid rings ($\sim 1420 \text{ cm}^{-1}$) and C-C stretching deformation in benzenoid rings ($\sim 1620 \text{ cm}^{-1}$) [7, 11-12]. The spectra of the CVD processed samples show additional peaks at 340 cm^{-1} , 495 cm^{-1} , 663 cm^{-1} , 737 cm^{-1} , 822 cm^{-1} , 867 cm^{-1} , 989 cm^{-1} , 1418 cm^{-1} and 1612 cm^{-1} . These peaks may be associated to benzenoid ring deformation ($\sim 506 \text{ cm}^{-1}$, $\sim 630 \text{ cm}^{-1}$ and $\sim 870 \text{ cm}^{-1}$), imine deformation ($\sim 734 \text{ cm}^{-1}$), amine deformation ($\sim 822 \text{ cm}^{-1}$), C-H bending in benzenoid rings ($\sim 1420 \text{ cm}^{-1}$) and C-C stretching deformation in benzenoid rings ($\sim 1620 \text{ cm}^{-1}$) [7, 11-12]. However, we could not make a clear identification of the peaks at 340 cm^{-1} and at 989 cm^{-1} .

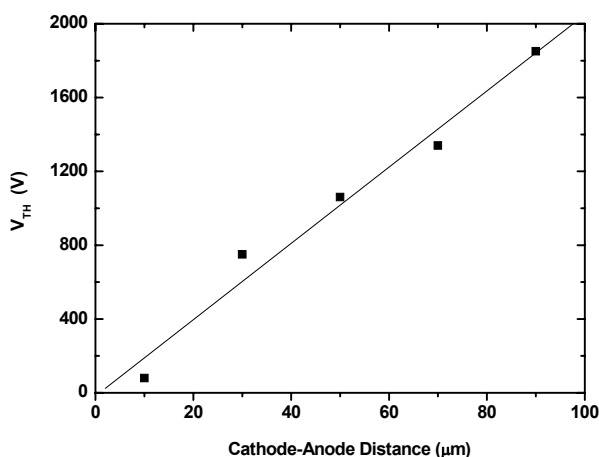


Figure 3. Typical field emission threshold voltage (V_{th}) versus distance necessary to produce a standard threshold current density of about 500 nAcm^{-2} .

Typical electron emission results are shown in Figure 3 by plotting the threshold voltage (V_{th}) versus cathode-anode distance necessary to produce a standard threshold current density of about 500 nAcm^{-2} . A linear fit to this data yields the typical threshold field (E_{th}) for each sample. The lowest threshold field achieved was $23.5 \text{ V}/\mu\text{m}$. The best values of threshold fields for electron emission of nanotubes, graphenes and nanostructured diamond reported in literature are in the range of 1- $10 \text{ V}/\mu\text{m}$ [13-18].

The differences in the Raman spectra of polyaniline-(emeraldine base) after hot-plate drying and from hot-filament processed samples suggested that the polymer suffered a profound transformation in the hot-filament processing although structures of benzenoid rings and amine were likely to be present in the carbonized material. This transformation is also evidenced by the sponge-like structures, revealed by the FESEM images. For field emission applications, rough geometrical structures results in localized discharge of electrons, but in sponge-like materials the amount of field enhancement is limited due to electrostatic screening effects of neighboring tips.

4. Conclusions

Carburization of polyaniline-(emeraldine base) deposited on copper substrates have been studied using a hot-filament system. The samples exhibited a sponge-like morphology, with fiber-like fragments of width in the range of 20 – 40 nm. Raman measurements suggested that benzenoid rings and amide are present in the carburized samples. The lowest threshold field achieved was $23.5 \text{ V}/\mu\text{m}$. We suggest that the effective field enhancement may be low because of electrostatic screening effects. Potential nanotechnology applications for this material include the fabrication of field-electron sources, fuel-cell electrodes, bio-chemical sensors, filter membranes, catalyst supports, and scaffolds for cell growth.

Acknowledgments

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