Journal of Analytical and Applied Pyrolysis 121 (2016) 275–286

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Morphic transitions of nanocarbons via laser pyrolysis of polyimide films

Athanasios Tiliakos[a,*], Cătălin Ceaus[a], Stefan M. Iordache[a], Eugeniu Vasile[b], Ioan Stamatin[a,*]

[a] University of Bucharest, Faculty of Physics, 3Nano-SAE Research Center, Bucharest, Romania
[b] Polytechnic University of Bucharest, Advanced Polymer Materials Group, Bucharest, Romania

ARTICLE INFO

Article history:
Received 27 February 2016
Received in revised form 22 July 2016
Accepted 9 August 2016
Available online 12 August 2016

Keywords:
Carbon nanotubes
Graphene foam
Polyimide
Laser pyrolysis
Surface patterning

ABSTRACT

Attempting a thorough investigation of polyimide pyrolysis via CO_2 lasers, we revisit the Laser-Induced Graphene (LIG) method, and determine the optimal operating window for producing pyrolytic nanocarbons. We design an experimental investigation that targets the full parameter space of available laser operating parameters: laser power, scan rate, and step interval. This allows us to produce different morphic groups of nanocarbons with properties depending on their surface morphology by directly controlling surface patterning. We further establish that the base material comprises a network of vertically aligned graphene channels, hereby referred to as graphene foam, thus readdressing the classification of Multi-Layer Graphene (MLG) given in previous research. We show how the laser pyrolysis method can be adapted for the production of carbon nanotubes (CNTs) via repeated pyrolysis of the starting graphene foam over high laser fluence levels. We characterize the pyrolytic nanocarbons via optical and scanning electron microscopy, Raman and UV–vis spectroscopy, surface tension measurements, and thermogravimetric analysis.

1. Introduction

Carbon-based solid-state supercapacitors have a long history that has seen the employment of various forms of carbon as electrode materials [1,2]. Starting from porous activated carbon, current research efforts have shifted towards exploiting the properties of graphene and carbon nanotubes (CNTs) to initiate new chapters in supercapacitor technology [3–7]. One of the latest trends has seen the use of lasers to inscribe electrode designs directly onto carbon-based substrates by reducing the starting material to multi-layered porous graphene. Initial implementations employed self-standing graphene oxide (GO) films and computerized numerically-controlled (CNC) CO_2 laser engravers (Reduced Graphite Oxide – RGO method) [8]. Later implementations succeeded in utilizing affordable commercial technology (LightScribe drives, IR laser at 780 nm) to reduce GO films deposited on optical media (Laser Scribed Graphene – LSG method) [9–11]. The latest advances have abandoned GO as a precursor –thus avoiding the time and cost for the production of the material- in favor of polyimide (PI) films used as substrates for producing Laser-Induced Graphene (LIG method) via CNC CO_2 lasers [12,13].

Carbonic materials produced via the above laser scribing/induction methods generally fall under the classification of multi-layered graphene (MLG), comprised of stacks of graphene sheets adding to a total width of a few microns [9–13]. Morphology and structure of end-products are influenced by both the precursor material and the processing method. MLG produced by chemical reduction of exfoliated GO constitutes a disordered material comprised of crumpled graphene sheets and thin aggregates [14]. GO nanosheets are hydrophilic: water molecules intercalate within the basal planes, which are decorated with epoxy and hydroxyl groups, with carbonyl and carboxyl groups decorating the edges, in agreement with the Lerf-Klinovski model [15,16]. GO hydrophilicity (allowing wet processing and deposition on flexible films), along with its capability for full or partial reduction to graphene by a diversity of methods (including thermal annealing, microwave and photo reduction [17]), have paved the way for the latest laser-printing methods that produce highly porous RGO/LSG with graphene sheets ordered in layered formations [8–11].

Polyimides ($C_{22}H_{10}O_5N_2$) have been in mass production since 1955; they are lightweight, flexible, resistant to heat and chem-

* Corresponding authors.
E-mail addresses: tiliakos@3nanosae.org (A. Tiliakos), istarom@3nanosae.org (I. Stamatin).

http://dx.doi.org/10.1016/j.jaap.2016.08.007
0165-2370/

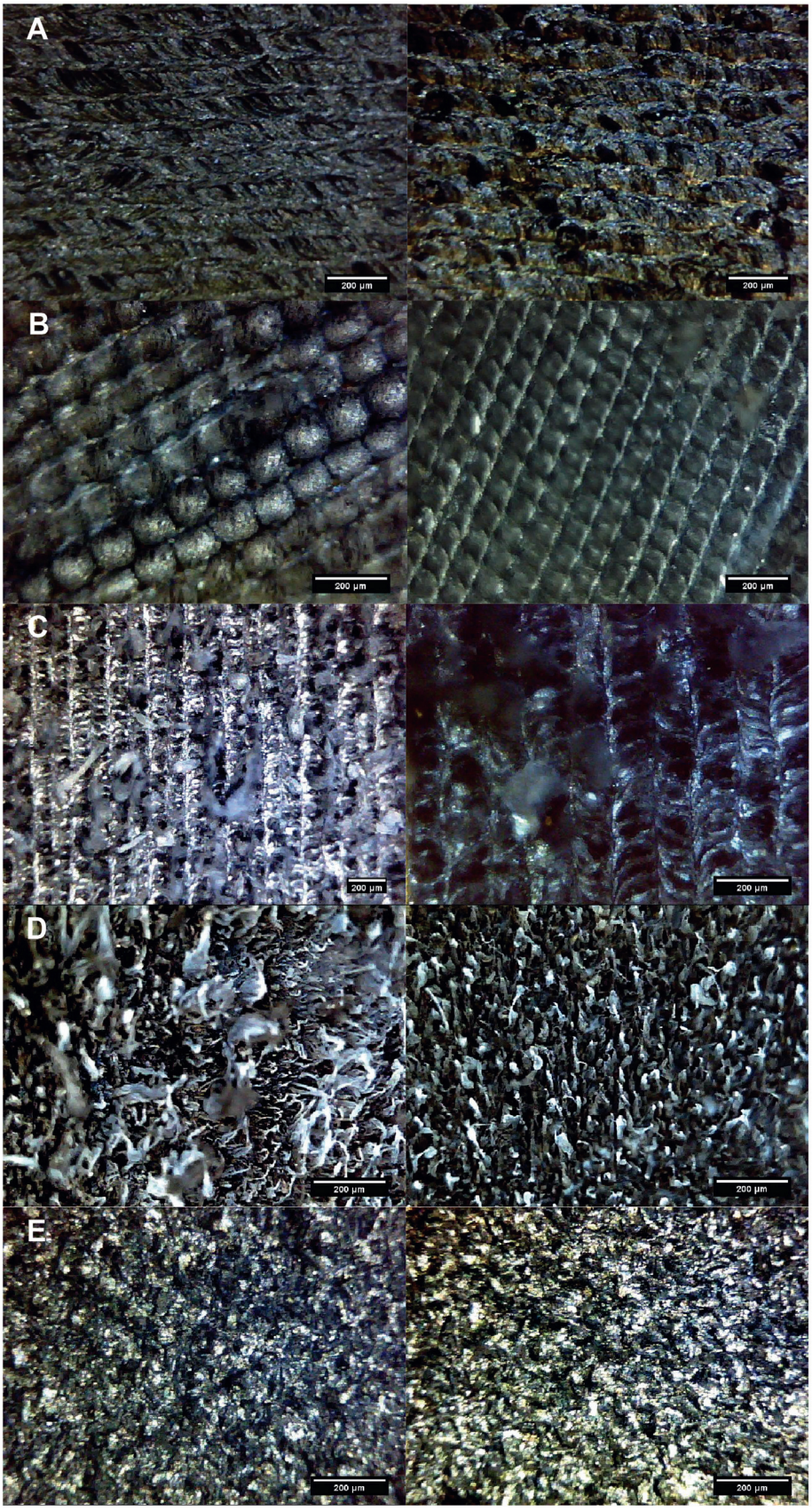

Fig. 1. Optical microscopy images of LIG morphic groups produced under different sets of laser parameters: A) irregular light contouring without emerging patterns; B) ordered ribbons, rhomboids and scales at constant spacing; C) chain meshes and dendrites emerging from parallel axes, decorated with glassy nanocarbons at elevated planes; D) tendrils growing out of the surface at random orientations; and E) amorphous configurations with no discernible pattern or structure at the optical level. Scale bar at 200 μm.