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A green and fast approach to nanoporous carbons with tuned porosity: UV-assisted condensation of organic compounds at room temperature

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ABSTRACT

This work reports a green and fast approach to the synthesis of nanoporous carbon materials based on the UV-assisted condensation of organic compounds as precursors. This new approach offers several improvements over the classical soft template and sol-gel routes for the synthesis of materials: versatility of organic precursors, shorter synthesis time, and ambient conditions. Owing to the specificity of the UV-assisted reactions mechanisms, organic compounds of varied chemical composition can be used as precursors in the preparation of nanoporous carbons with tuned porous features. The method consisted in the exposure of an aqueous solution of the organic precursors to UV light for 60 min at room temperature in the absence of a catalyst, allowing an outstanding shortening of the synthesis time compared to sol-gel routes. Furthermore, UV irradiation promoted the cross-linking of the polymer chains of precursors at room temperature, as opposed to classical methods that require an additional step at mild/high temperatures. By changing the chemistry of the organic compound used as precursor, it was possible to modulate the surface area (from 10 to 720 $m^2\ g^{-1}$) and the porosity of the synthesized carbons within the micro-/mesopore range. The obtained carbons also presented varied morphology depending on the precursor, from dense aggregates to ordered hexagonal arrangements of nanometric dimensions.

1. Introduction

Photochemical reactions are those caused by absorption of UV, visible of infrared radiation [1] and many of them occur in nature, such as photosynthesis in plants, human skin production of vitamin D, ozone formation and dissociation in the atmosphere, or photochemical smog (air pollution due to reaction of nitrogen oxides and some volatile organic compounds with sunlight). Most of them proceed through the formation of thermodynamically instable compounds (excited state species usually more reactive than the corresponding ground ones), allowing reactivity otherwise inaccessible by conventional methods [2–4].

In materials' chemistry, photochemical reactions are useful since many molecules and atoms are capable of undergoing chemical changes upon light absorption. Indeed, light-induced transformation of materials is a common phenomenon and the study of light-matter interactions has led to advances in several fields (heterogeneous catalysts, therapeutic applications, patterning of materials for semiconductor applications), and many ground-state reactions have also been studied (e.g. photocycloadditions, photodecarbonylations, photoenolizations, photoisomerizations, photoreductions) [2–6].

Recently, considerable efforts are being devoted to the fabrication of highly featured nanoporous carbon materials with a precise control of their physicochemical, textural and structural properties (uniformity in pore architectures, composition, particle size and shapes), due to their versatility and potential applications in multidisciplinary science and engineering fields (adsorption and separation, catalysis, sensing, energy storage [7,8]. The combination of large specific surface areas (microporosity) and pore volumes along with an adequate network of transport pores (mesopores) is most desirable to favor diffusion and/or adsorption of bulky

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molecules of strategic interest in multidisciplinary fields covering environmental remediation (e.g., hormones, pharmaceuticals, dyes), energy storage and conversion (e.g. electrocatalysis, supercapacitors) and sensing applications (e.g., immobilization of enzymes) [9,10]. In this context, the preparation of nanoporous carbons with well-defined pore architectures in the full micro-/mesopore range has become a subject of great interest. Porous carbon materials typically have relatively broad pore-size distributions, being the porosity mainly dominated by the micropore structure with classical methods showing almost no control over the porous features of the resulting carbons [11,12]. The control over the porous features of the carbons can be achieved to a certain extent by means of nanocasting procedures (soft and hard templating), self-assembling and sol-gel polycondensation reactions, among most representatives [13–16]. However, these are usually time consuming and complex reactions, therefore with quite scarce impact in the large-scale production and commercialization perspectives.

Recently, the use of light-induced reactions has become an interesting tool for the preparation and modification of carbon materials. For instance, Cao et al. showed a localized photothermal growth of carbon nanotubes and silicon nanowires on metal nanoparticles exposed to a focused light beam [17] due to the heat generated at the metallic surface plasmons exposed to irradiation. The same principle based on the light absorption properties of a metallic component has been used to induce the phase transformation of amorphous carbon deposited on nanoparticulated metal films, thereby obtaining carbon materials with enhanced electrical properties (graphitization) [18]. Vinu et al. reported the photofunctionalization of a carbon matrix with carboxylic moieties by exposing the sample to UV light and oxygen at room temperature [19]. The preparation of ordered porous carbons using phloroglucinol as precursor based on photoinduced evaporation reactions has also been reported [20] using a triblock copolymer as sacrificial template. The main advantage of the photoinduced synthesis, compared to the conventional endotemplating route (using the same precursors) is the time scale, since the aging step needed to induce the cross-linking of the polymeric precursor is significantly reduced due to the energy provided by the UV irradiation. Here, we demonstrate a fast and highly localized phase transformation of polyhydroxylated aromatic precursors on liquid phase by irradiation through condensation and spinodal decomposition of the precursor mixtures, to render aromatic resins and ultimately nanoporous carbons after a thermal treatment at 600 °C. We highlight the critical role of the polymeric precursors used in the homogenous liquid phase in bringing about a well connected network, sufficiently cross-linked to render a nanoporous carbon solid after densification of the resin. The difference in yields and porosity of the phenolic resins upon the pyrolytic treatment clearly demonstrates the role of the precursor on the photoassisted phase transformation and cross-linking of the polymers. Changes in composition, nanotexture and microstructure of the materials obtained after irradiation of the precursors were evaluated using Raman spectroscopy, solid state NMR and gas adsorption of several probes at various temperatures.

2. Experimental

2.1. Chemicals

Gallacetophenone (GA), 2,3-dihydroxynaphtalene (DN), pyrogallol (PG) and bisphenol A (BP), Pluronic F127 (poly(ethylene oxide)-block-poly(propylene oxide)-block-poly-(ethylene oxide, $PEO_{106}PPO_{70}PEO_{106}$, $Mw = 12\ 600$ Da), glyoxal aqueous solution (40%, $C_2H_2O_2$), absolute ethanol (C_2H_6O), and HCl (37%) were purchased from Sigma-Aldrich. The chemicals were used as received without any further purification.

2.2. Synthesis

GA, DN, PG and BP were selected as polymeric precursors for the photoassisted synthesis of nanoporous carbons. In a typical synthesis, the precursors (1.6 g) and the surfactant (3.2 g) were dissolved in ethanol containing HCl (37%). After complete dissolution at room temperature, a certain amount of glyoxal (1.6 mL) aqueous solution was added. Afterwards, the solutions were transferred to glass dishes and exposed to UV light for various periods (i.e., up to 70 min). The light source was a lightning cure device fitted with a 365 nm elliptical reflector. An anticaloric filter was used to avoid heating and evaporation during irradiation (monitored temperature was constant). The progress of the photoassisted reaction was monitored via UV–visible absorption spectroscopy using a Thermo Fisher Scientific Evolution 200 spectrophotometer.

The brownish viscous solids obtained after the irradiation were recovered from the dishes and further pyrolyzed at 600 °C under inert atmosphere (i.e., 120 ml/min Ar, heating rate 2°C/min, dwelling time 2 h) to allow the decomposition of the organic resins in carbon materials, and the generation of porosity. The nomenclature assigned for the resins after UV exposure is MM, where MM stands for the organic precursor (GA, PG, BP, DN); when the resins are carbonized, the nomenclature is MM-c600. To evaluate the eventual cross-linking of the organic precursors in the absence of UV light, blank reactions in were carried out for all the studied precursors (allowing the reaction to occur under darkness for several days).

2.3. Characterization techniques

The porosity of all the samples was determined by means of N_2 adsorption/desorption isotherms at -196 °C in a volumetric analyzer (Micromeritics). Before the experiments, the samples were outgassed at 120 °C for 17 h under vacuum (10^{-4} Torr). The specific surface area, S_{BET} and total pore volume, V_{total}, were calculated from the N_2 adsorption data. The pore size distribution in the full micro-/mesopore range was calculated from the N_2 adsorption isotherms using the 2D-NLDFT-HS (www.NLDFT.com) model assuming surface heterogeneity of carbon pores [21]. This model has been validated for the characterization of nanoporous carbons with similar porous features [21–23], and was chosen following IUPAC recommendations to use advanced methods based on NLDFT for the determination of pore size distributions of nanoporous carbons, rather than BJH method that underestimates the pore size for narrow mesopores [24]. The narrow microporosity was further assessed by CO_2 adsorption isotherms at 0 °C using the Dubinin-Radushkevich (DR) equation. All the gases were supplied by Air Products with ultrahigh purity (i.e., 99.995%).

Raman spectroscopy was performed by excitation with green laser light (532 nm) in the range between 1000 and 2000 cm^{-1} (InVia Raman Microscope, equipped with a Leica microscope). The samples were scanned between 10° and 90° (2θ) at a 0.02°/12 s scan rate.

Samples were chemically characterized by elemental analysis. The determination of carbon, hydrogen and nitrogen was carried out by a LECO CHNS-932 and oxygen was measured in a LECO VTF-900 CHNS-932 microanalayzer.

The surface pH of the carbon samples was measured in an aqueous suspension containing 0.4 g of carbon sample powder added to 20 mL of distilled water. After equilibration under stirring overnight, the pH value was measured using a glass electrode.

Thermogravimetric (TG) curves of all the samples were obtained