

LIGHT-INDUCED SYNTHESIS OF ORDERED MESOPOROUS CARBONS

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Introduction

As porosity has an specific impact on the materials properties and therefore their applications, the preparation of activated carbons with specific textural properties and pores architectures represents a classical concern in materials science; a great deal of work has been done to enhance and, above all, to control the porosity of the carbon adsorbents. As conventional activation methods do not allow the precise control of the pore size and volume¹⁻², a rational design that allow controlling the porosity at the nanometric scale has aroused much attention during the last decades, and several new strategies (e.g. nanocasting, hard- or soft-template...) have been developed. Furthermore, since ordered mesoporous materials appears³ and after that, the first ordered mesoporous carbons (OMC) were prepared⁴ by templating, using mesoporous silica molecular sieves as hard-template, the synthesis of OMC are awaking a great interest, triggered by their unique properties in different fields (catalysis, electrochemistry, drug release). Soft-templating approaches are more interesting ones as they overcome the limitations of high cost and the removal of the template. In this regard, the use of light has emerged as a powerful strategy in material's synthesis^{3,4}, as it offer several advantages over conventional approaches such as a shorter time scale (several minutes), or the versatility of precursors that can be used, since these reactions do not require especial/controlled pressure or temperature conditions and can be/are performed under ambient conditions. Following our recent studies on the use of light to accelerate self-assembly reactions of polyhydroxylated compounds, we herein report the synthesis of OMC by the photoinduced assembly of adequate organic precursors following optimized synthetic conditions.

Materials and Methods

1,2,3-trihydroxybenzene (pyrogallol), 2,3,4-trihydroxyacetophenone (gallacetophenone), 2,3,4-trihydroxybenzoic acid (pyrogallol-4-carboxylic acid) and 2,4,6-trihydroxybenzoic acid, were selected as organic precursors. Glyoxal (40 wt.% aqueous solution) was used as linker, [4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone as photoinitiator (Chr.) and Pluronic F127 as surfactant. In a typical synthesis⁴, about 0.83 g of the precursor and 1.64 g of Pluronic F127 were dissolved in ethanol (when required, HCl and/or Chr are also added in this stage) and then 0.8 mL of glyoxal are added and magnetically stirred for 60 min. The mixture was transferred to glass dishes and exposed to light from 30 to 60 min, using a 365 nm lamp provided with an anticaloric filter. The brownish viscous solid obtained was pyrolysed at 600 °C under inert atmosphere (ca. 120 ml/min, heating rate 2 °C/min) during 2 hours. The resulting materials were thoroughly characterized using various complementary techniques such as gas adsorption of various probes and at various temperatures, TEM, surface pH measurement, solid state NRM,

among most representatives.

Results and Discussion

The precursor's mixture (precursor, surfactant and/or acid and photoinitiator) were exposed to light, and a gradual darkening was observed for all of them, indicating a photopolymerization reaction. After 60 min of irradiation, a brownish viscous resin was formed as a result of the cross-linking of the reactants, with the exception of THBA that rendered a denser resin. Carbonization yields ranging from 9 to 24 wt.% were obtained. The textural characterization of the carbonized materials showed large gas uptakes for all of the studied samples, confirming their nanoporous nature. Most of them showed a well-developed mesoporosity, with differences in the total pore volume and position of the hysteresis loop. The shape of these loops depends on the organic precursor photopolymerized, and defines the average mesopores size and the preparation of carbons with uniform/heterogeneous mesopore size distributions. TEM images of the carbons revealed important differences among the samples; some carbons presented the typical wormhole-like morphology of amorphous carbons, while others displayed an ordered pattern of well-aligned parallel channels. A closer inspection of these materials showed that they are composed of an ordered arrangement of large mesopores, in agreement with the pore structure from the textural characterization.

Conclusions

We have developed an effective method for the synthesis of nanoporous carbons with high mesoporous features and ordered structure based on the UV assisted condensation of organic polymeric precursors at room temperature. The cross-linking of the mixtures is determined by the nature and location of the functional moieties of the organic precursor. In general, non-conjugated hydroxyl groups give rise to highly crosslinked and dense structures mainly composed of narrow micropores, whereas conjugated groups create more open mesopore structures, rendering in some cases an ordered mesopore structure.

Acknowledgments

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