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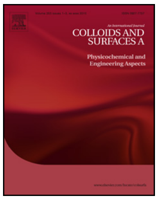

Carbon based porous materials from particle stabilized wet foams

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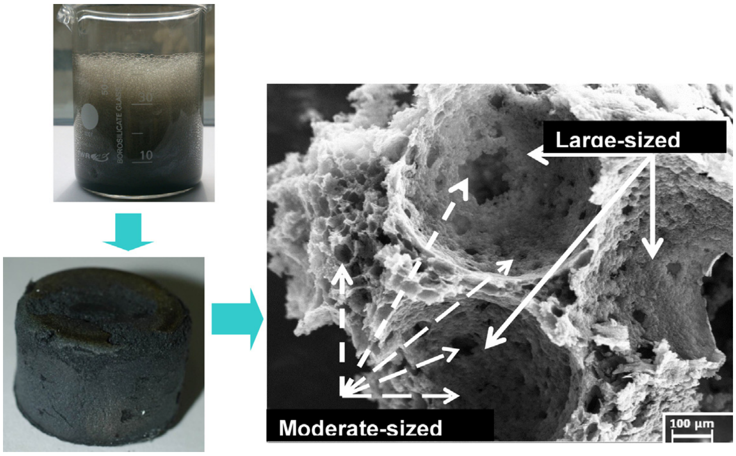
HIGHLIGHTS

- Methods combining direct foaming with gel-casting are effective to produce carbon solid foams.
- Foams stabilized by carbon particles associated to ionic surfactant as precursor to porous materials.
- High temperature treatments provide materials with hierarchical multi-porous structure.
- The morphology and the specific area of the porous materials can be tailored changing the composition of the precursor.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a method is proposed for the production of carbon porous materials based on the foaming of a carbon colloidal dispersion in the presence of a short chain ionic surfactant (CTAB) and Poly(vinyl alcohol) followed by the in situ polymerization by cross-linking with 2,5-dimethoxy-2,5-dihydrofuran (DHF). The particle stabilized wet foams are used as templates for the gel-casting providing porous materials with carbon particles mainly distributed at the surface of the cells. This sample so obtained is then submitted to a high temperature treatment to remove all organic components from the matrix and get a compact carbon solid foam. The morphology of the samples obtained according to this procedure have been analyzed via Scanning Electron Microscopy (SEM) and different aspects regarding both the procedure and the composition of the initial dispersion have been investigated such as the role of the surfactant, the dependence on the particle concentration and the temperature adopted during the thermal treatment.

1. Introduction

Carbon is an essential element for industrial applications, more and more exploited in the last years in many technological fields. Besides the different crystalline form used, such as crystalline phase of graphite, diamond and fullerene, also many amorphous carbons are employed, like the here investigated activated carbon which is used in a wide range of applications [1–3]. For example, depending on its porosity and surface chemical activity, it is employed for gas adsorption, waste treatment, chemical recovery operations, industrial purification [4–7], but also the sheet of micro-graphite find special applications

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in the field of electronics, optical spectra or field emission [8,9].

Recently, carbon-based porous materials have attracted attention in the scientific community and different methods for their fabrication have been proposed [10–15]. On the other hand, the methods based on the solidification of particle-stabilized wet foams which are mainly applied for the synthesis of porous ceramic materials [16–19] are very promising also for carbon.

In this work a method is proposed, based on the direct foaming of carbon dispersion combined with gel-casting. According to this method, wet foams stabilized by carbon colloidal particles are used as template where the gelling reaction occurs by in situ polymerization of organic monomers, previously dissolved in the liquid phase [20,21]. The samples so prepared are then treated at high temperature to eliminate the organic components and obtain a solid carbon foam.

As already pointed out in our previous study [19], the structure of the final porous materials strongly depends on the composition of the adsorption layers stabilizing the precursor foams. In this work the formulation of the initial dispersion has been established on the bases of the results obtained in ref. [22], where a systematic characterization of the surface properties of carbon particle dispersions in association to short chain ionic surfactants was performed, crossed with the characterization of the bulk dispersion by Dynamic Light Scattering (DLS) and ζ-potential measurements. The results obtained allowed us to select the best conditions favoring the transfer of particles at the liquid–air interfaces providing stable foams suitable for the further processing.

Aim of this work is to deepen the relationship between the morphological properties of the final porous materials and the formulation of the carbon particle stabilized foams used as precursor. By this way the method will be appropriate to produce carbon based porous materials with specific characteristics, such as high specific surface area and open cell structure, for application in the field of gas adsorption, CO_2 capture or as materials for chemical catalysis and for industrial purification devices.

2. Materials

Carbon soot (CS) was a commercial carbon particulate, purchased from Sigma-Aldrich. It is an activated carbon composed of micro-graphite in nanometer scale with short-range order which is produced by resistive heating of graphite and presents a density of 1.7 g/mL at 25 °C and specific surface area (BET) of 319 m^2/g. As shown in ref. [22], CS is well dispersible in pure water where presents a single particle size population centered around 100 nm, checked by Dynamic Light Scattering (DLS) measurements, and ξ-potential around – 16 ± 5 mV.

The cationic surfactant, hexadecyltrimethylammonium- bromide (CTAB) as well as the other components used to produce the foams, that are, partially hydrolyzed Polyvinyl alcohol (PVA), cross-linker 2,5-dimethoxy-2,5-dihydrofuran (DHF) and Nitric acid (HNO_3) in purity of 70–89%, were supplied by Sigma–Aldrich (Germany) and used as received.

Water used for dispersions was obtained by a multi-cartridge system (Millipore, Elix plus Milli-Q), providing a resistivity greater than 18 MΩ cm and surface tension of 72,5 mN m^{-1} without any appreciable kinetics over several hours.

3. Method

3.1. Preparation of the green body

Mixed CTAB carbon particle dispersions are prepared, as in Ref. [22], adding drop by drop the surfactant solution to the carbon dispersion, previously prepared in an ultrasound bath. A volume of PVA solution at concentration of 3.9 wt% is then added drop by drop to the same volume of dispersion, always maintained under stirring. The stirring is then continued for 1 h. Without surfactant the PVA is added in the same way to the carbon particle in water dispersion.

Foams are produced by aerating the above dispersions by using a mixer IKA ULTRA TERPAX T25, at 8000 rpm for 2–4 min. To activate the in situ polymerization process, 10 min before foaming, 1 cm^3 of nitric acid was incorporated into 10 cm^3 of dispersion. Then immediately before foaming, a given amount of 1.2 cm^3 of the cross-linking agent, DHF, is added to the dispersions under stirring.

The foam is then immediately transferred inside an oven and left for 3–4 h at temperature of 80 °C until the gelation was complete. The materials obtained at this stage, which are ready for further high temperature treatments, are called here and in the following “green bodies” in analogy with the terminology related to the sintering of ceramic materials. The volumes of the green body obtained were typically around 50 cm^3.

More in detail, the furan ring opening responsible of the activation of gelling process is induced by the presence of the nitric acid. As described elsewhere [23–25], DHF exposed to an acidic media opens the furan ring to form the di-aldehyde butenedial, which in turn, acts as a di-functional cross-linking agent able to gel the PVA in particle-surfactant-polymer dispersion. Butenedial reacts with the alcohol groups of two polymer chains of PVA to give an acetal. On this way a low-viscosity particle dispersion behavior change from liquid-like to solid-like, “freezing” the structure of the freshly generated wet foam.

The obtained green bodies were left to cool at room temperature, then removed from beakers and dried in the air for at least 2 days.

3.2. High temperature treatment

The green bodies obtained according to the above procedure are submitted to a high temperature treatment, in argon atmosphere aimed to remove all organic components from the matrix and obtain a solid carbon porous material, or solid foam. Such thermal treatment was optimized in order to obtain compact materials, stable during the whole process, avoiding mechanical breakage and combustion.

The heating/cooling procedure is sketched in Fig. 1. The temperature was increased at a constant rate of 5 K/min up to 500 °C or 900 °C. The chamber containing the samples of internal volume of about 6.7×10^{-3} m^3, was flowed by argon since at least 1 h before the beginning of the heating till the completion of the cooling, in order to maintain the sample in the same inert atmosphere during the whole treatment. Different flow rates were checked as well as different supports for the sample in order to find the most appropriate conditions as discussed in next paragraphs.

The aim of this thermal treatment is the complete removal of the organic compounds from the final material avoiding, at the same time, the combustion of carbon. On the bases of the literature results in the field of carbon based materials, these conditions are expected to be satisfied in a range of temperature from about 500 to 1000 °C [2,10,13]. The two temperatures used here have been chosen as limit points of this range.

3.3. Analysis by Scanning Electron Microscopy (SEM)

The morphology of the solid foams obtained with the different compositions of the precursor as well as the corresponding green bodies before the high temperature treatment were investigated