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Research Paper

Synthesis and characterization of solid polymer and carbon spheres derived from an emulsion polymerization reaction of different phenolic compounds with formaldehyde

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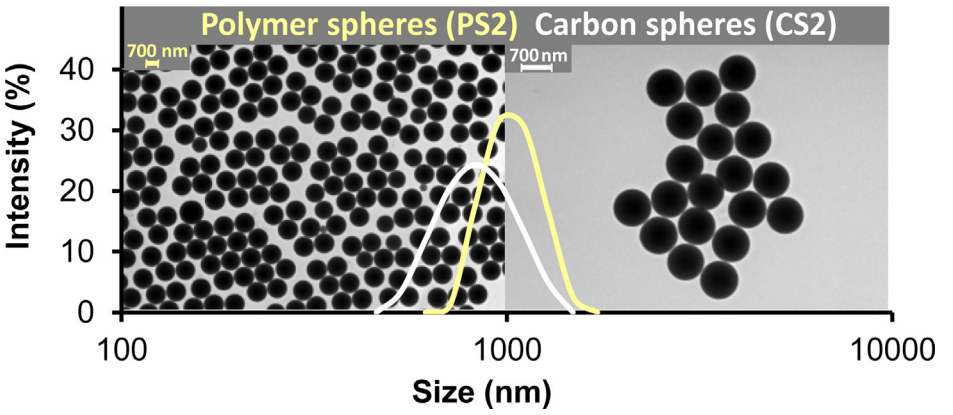
HIGHLIGHTS

- Pyrocatechol yielded CSs with smaller surface area and size than did resorcinol.
- CSs activation augmented their pore texture but had little effect on their size.
- Activation of CSs by O_2 adsorption-desorption cycles yielded wider micropores.
- Physically-activated CSs showed the highest capacitance at 1 A g^{-1}, 17.3 μF cm^{-2}.
- Areal capacitance was higher in N-doped CSs (*ca.* 1.5 at.% N) than in non-doped CSs.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, polymer spheres (PSs) were prepared by an emulsion polymerization of resorcinol, pyrocatechol, or 3-hydroxypyridine with formaldehyde under basic conditions. Carbon spheres (CSs) were obtained by carbonization of PSs at 900 °C, and some of them were activated with KOH and oxygen adsorption-desorption cycles. Resorcinol and pyrocatechol differ in their reactivity during the polycondensation reaction with formaldehyde. The use of 3-hydroxypyridine allowed the introduction of N functionalities in the final CSs obtained. The objective was to examine the effects on the diameter of the carbon spheres, their surface physics and chemistry, and their performance as electrochemical double-layer (EDL) capacitors produced by: i) the replacement of resorcinol with pyrocatechol in the polymerization reaction and the utilization of different carbon sphere activation methods; and ii) the introduction of N functionalities. The size, surface area, micropore volume, total pore volume, and micropore width of the CSs ranged between 159 and 856 nm, 7 and 1156 m^2 g^{-1}, 0.06 and 0.46 cm^3 g^{-1}, 0.15 and 0.58 cm^3 g^{-1}, and 0.50 and 1.23 nm, respectively. The physically-activated sample showed the highest capacitance at 1 A g^{-1}, 200 F g^{-1} or 17.3 μF cm^{-2}. Capacitance was higher in N-doped samples than in the non-doped sample.

1. Introduction

CSs have recently attracted considerable interest due to their new applications, mainly in energy storage and conversion but

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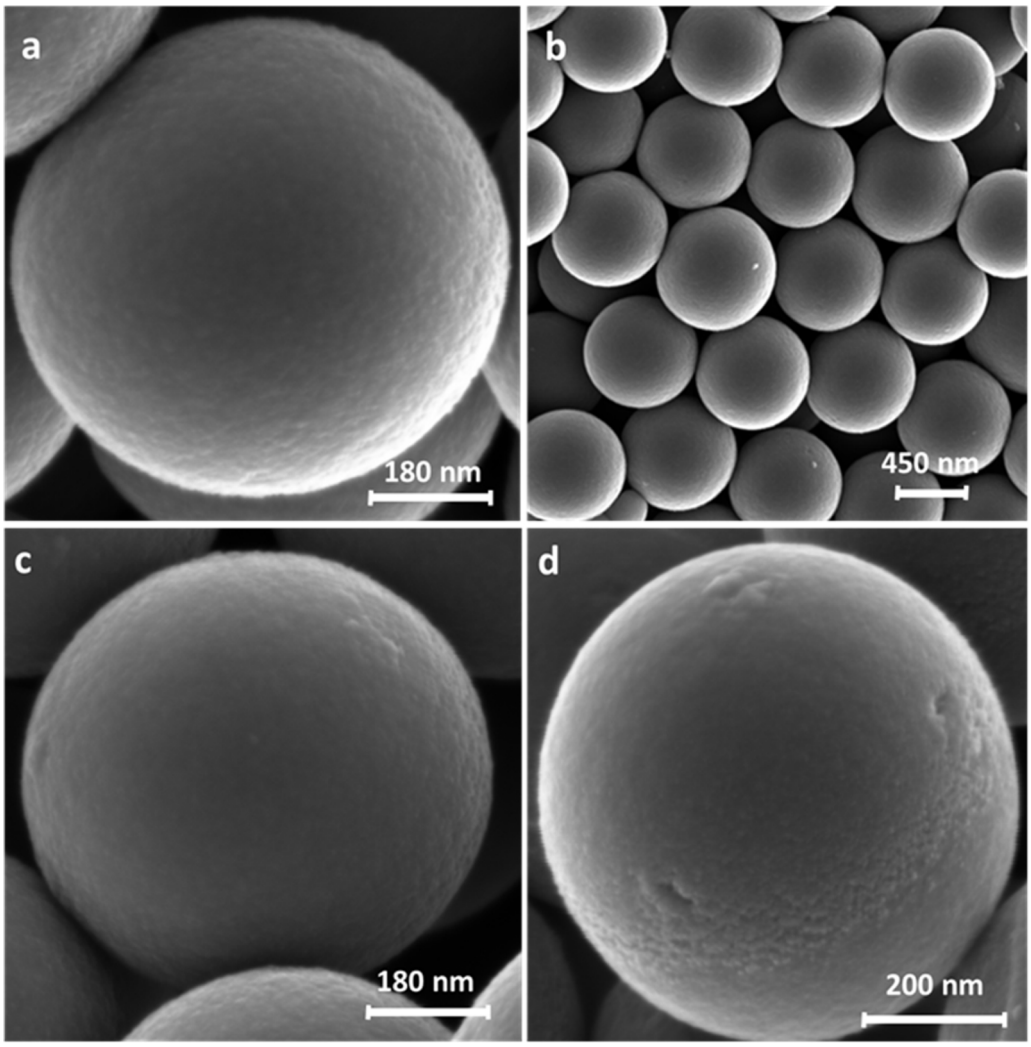

Fig. 1. HRFSEM images of samples: a and b) PS2, c) CS2-O, d) CS2-K.

also in hard-templating, sorption/catalysis processes, and drug delivery systems [1]. This is attributable to their physico-chemical properties, including their tunable morphology (solid, hollow, or core-shell), size, surface area and porosity, good electrical conductivity, high packing density, enhanced mass transport, robust mechanical stability, low cytotoxicity, and excellent biocompatibility. Most of their applications require non-aggregated spheres with strict size control, narrow size distribution, smooth surface, and controlled surface chemistry [1,2].

CSs can be obtained using a wide variety of carbon precursors and methods. One of the most frequent approaches is the carbonization of PSs derived from low-temperature (below 250 °C) polymerization reactions of reactive monomers and oligomers, which is well documented in the literature [1–3]. The different polymerization processes used for this purpose can be classified according to the formation mechanism of the PSs [1] as: emulsion polymerization, and its derivatives seeded emulsion and inverse emulsion polymerizations; precipitation polymerization, and its derivative dispersion polymerization; suspension polymerization; hard-templating; spray-drying; and hydrothermal or solvothermal treatment of carbohydrates and biomass in general.

In this study, PSs were prepared by an emulsion polymerization method [4] based on the Stöber process to prepare silica spheres [5]. The method used the polymerization reaction of resorcinol (R) and formaldehyde (F) in ethanol-water solution and in the presence of ammonia as polymerization and morphological catalyst, heating at 100 °C in an autoclave [4]. Most carbon gels prepared by polymerization reactions use R and F mixtures, either in basic or acid medium, but there are scant data on the utilization of P [6]. The two phenolic compounds differ in their reactivity during the polymerization reaction, with R being much more reactive in comparison to P during polycondensation reaction with F under basic conditions. This is because of the electron donating and *ortho- para*-directing effects of the attached hydroxyl groups [7], leading 2-, 4- and 6-positions of R to be doubly activated for the F addition by the two phenolic groups in *meta*-position, whereas the 3- and 4-positions in P are activated by one of the phenolic groups at the *ortho*-position and by the other at the 5- and 6-positions. Furthermore, the synthesis method employed to prepare the PSs [4] permits their doping with different elements and, in the present study, HP was used to introduce N functionalities in the final spheres obtained. The objective of this study was to examine the effects on the diameter of the CSs, their surface physics and chemistry, and their performance as EDL capacitors produced by: i) the replacement of R with P in the polymerization reaction and the utilization of different CSs activation methods; and ii) the introduction of N functionalities.