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Hierarchically structured carbon/carbon nanocomposites with adjustable porosity fabricated by twin polymerization

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ABSTRACT

Carbon materials with a complex core-shell structure and adjustable porosity are fabricated by subsequent surface polymerization of twin monomers on carbon black and silica particles. The twin monomers 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (**Spiro**) and tetrafurfuryloxysilane (**TFOS**) are polymerized in one step to an inorganic/organic hybrid material, which contains nanostructured silica and phenolic resin or poly(furfuryl alcohol), respectively, as organic polymer. After carbonization and the removal of silica, a porous carbon shell with defined porosity is obtained. In this process, **Spiro** based materials produce microporous carbon and **TFOS** based materials produce a mesoporous carbon. Quantities of monomer, catalyst and substrate can be varied. This allows to create a library of porous carbon materials with different properties such as controlled porosity, morphology and hierarchically structuring. Thus, mesoporous carbon with a microporous shell can be achieved by using carbon black particles as substrate and **Spiro** as twin monomer. Furthermore, carbon hollow spheres with a double shell with hierarchically structuring can be synthesized by subsequent polymerization of **TFOS** and **Spiro** on silica particles. The porous carbon materials were characterized by quantitative elemental analysis, thermogravimetric measurements, SEM/EDX, TEM, nitrogen sorption isotherms and mercury porosimetry.

1. Introduction

Porous carbon materials are of great interest because of their usage as sorbents for separation processes and gas storage, as substrates in catalytic processes and especially as electrode materials in lithium sulfur batteries [1,2]. The reason for the importance can be seen in the favorable properties, such as thermal and chemical stability, good electric conductivity, high specific surface area, tunable pore size distribution as well as the wide availability and low cost [3,4]. There exist numerous concepts and strategies to produce carbon materials including carbonization and chemical or physical activation of organic precursors [1,5,6].

In this work, a new strategy for the production of hierarchical porous carbon materials is presented. The concept combines the usage of commercially available silica and carbon black particles as substrates with the synthetic methodology of twin polymerization. Twin polymerization is an elegant approach to synthesize inorganic-organic hybrid materials in one step [7]. For this purpose, a specific assembled monomer with two covalently bonded building blocks is polymerized to two structurally different homopolymers in one procedure [8,9]. The formation of these two polymers is mechanistically coupled. This feature is the reason for the resulting nanostructured hybrid materials. The twin monomers used in this work are tetrafurfuryloxysilane (**TFOS**) [8] and 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (**Spiro**) [10]. Both monomers can readily be polymerized to an organic polymer (poly(furfuryl alcohol) (PFA) and phenolic resin, respectively) and silica. The hybrid materials produced by twin polymerization show defined nanostructures making them a promising source for nanoporous carbon or silica preparation. The porous carbon compound can be obtained by thermal treatment under argon atmosphere and subsequent removing of the silica with aqueous hydrofluoric acid or sodium hydroxide solution. The silica can be achieved by oxidation of the hybrid material. The pore size diameter of the resulting counterparts is determined by the dimension of the interpenetrating network and thus indirectly by the molecular structure of the twin monomer which is used for the polymerization. The **Spiro** monomer is suitable for producing

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porous carbon with a high portion of micropores. Furthermore, the twin monomer **TFOS** results in carbon materials with mainly mesopores [11].

The twin polymerization can be applied as surface polymerization on different substrates to create a variety of carbon materials. Structured porous carbon hollow spheres (CHS) with a mesoporous shell were synthesized using SiO_2 particles as templates and **TFOS** as monomer [11]. For this, SiO_2 was initially loaded with an acidic catalyst to catalyze the polymerization of the twin monomer directly onto the surface of the template. After thermal treatment of the coated silica particles and a subsequent washing step with HF solution, the template as well as the silica of the coating can be removed. The carbon hollow spheres, synthesized by this approach, were loaded with sulfur and applied in lithium sulfur batteries [11]. Thereby, sulfur was located inside the porous carbon and on the surface but not inside the hollow spheres.

Furthermore, carbon/graphite nanocomposites can be synthesized using graphite as substrate and **Spiro** as monomer. The surface twin polymerization was catalyzed by a base and the resulting hybrid material was converted into porous carbon. *1,4*-diazabicylco [2.2.2]octane (DABCO) has been found as an effective catalyst for this purpose [12].

The objective of this study is to combine the different polymerization processes of **Spiro** and **TFOS** in modular manner for the production of two different hierarchically structured porous carbon materials. The first target materials are carbon-modified carbon black particles with a mesoporous core and a microporous layer. Therefore, **Spiro** is polymerized on the carbon black substrate, a primarily mesoporous material with application in the battery industry as commercial conducting additive [2,13]. The other targeted hierarchical porous carbon materials are carbon hollow spheres with two layers of different porosity. For this purpose, spherical silica particles have been used as templates for the consecutive surface twin polymerization of two different twin monomers. After polymerization and carbonization, the silica core can be removed and carbon hollow spheres are obtained. Scheme 1 shows the synthetic concept for producing the two target carbon materials with hierarchically structured porosity.

Properties of the carbon materials, such as shape, size, texture and porosity, can be adjusted on demand by variation of the substrate, the choice of twin monomer and the ratio of substrate/monomer. The final materials were investigated by quantitative elemental analysis (EA), thermogravimetric analysis (TGA), SEM/EDX, TEM, ATR-FTIR spectroscopy, nitrogen sorption measurements and mercury porosimetry.

2. Experimental

2.1. Materials

Salicyl alcohol (ABCR), tetramethoxysilane (TMOS, ABCR), tetra-*n*-butylammonium-fluoride (1 M in tetrahydrofuran, ABCR), *1,4*-diazabicyclo[2.2.2]octane (DABCO, Sigma-Aldrich), tetraethoxysilane (TEOS, ABCR), ammonia hydroxide (25%), potassium hydroxide (Merck), sodium hydroxide, methanesulfonic acid (Sigma-Aldrich), aqueous hydrofluoric acid (40%, Prolabo) were commercially available and were used without further purification. Furfuryl alcohol was distilled before usage. Toluene, hexane and dichloromethane were dried with standards methods. Aerosil OX 50 and Nipex 90 were provided from Degussa and di-*iso*-propylnaphthalene (DIPN) was provided by BASF SE. The twin monomers **TFOS** and **Spiro** were synthesized according to literature [8,10].

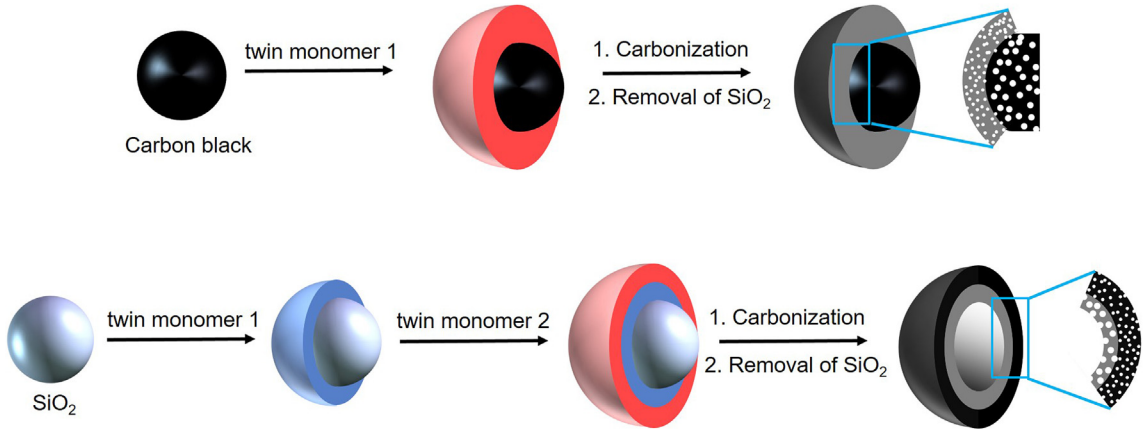
2.2. Synthesis of Stöber particles

Silica particles with a defined diameter were synthesized using the well established Stöber procedure [14]. The reaction was carried out in 300 mL ethanol. First, 40 mL ammonia hydroxide and 3 mL water were added to the solvent and stirred for 10 min. Afterwards, 16 mL of tetraethoxysilane were added dropwise to the solution and stirred for 4 h at room temperature. After addition of TEOS, the clear solution turned gradually from opaque to a white suspension due to the formation of silica particles. The solvent ethanol was removed by distillation and the white solid was washed three times with 30 mL ethanol. The product was dried at 40 °C under reduced pressure. After synthesis, the Stöber particles were calcined for the removal of residual organic species in air atmosphere at 550 °C for 6 h [15].

2.3. Synthesis of porous carbon materials

2.3.1. Porous carbon with mesoporous core and microporous shell (*CB_Spiro_xx-C*)

A mixture of carbon black (NIPEX90), the respective amount of **Spiro** in 25 mL DIPN per gram monomer and the base DABCO (0.05 g base per gram **Spiro**) were heated for 6 h at 160 °C under argon atmosphere. After cooling to room temperature, the suspension was centrifuged and washed three times with 30 mL toluene. The resulting composite materials were dried at 110 °C under reduced pressure. The phenolic resin_SiO_2 hybrid material shell of the coated carbon black particles was converted by heating



Scheme 1. Conceptual work for the synthesis of porous carbon materials with hierarchically structured porosity.