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Copolycondensation of heterocyclic aldehydes: A general approach to sulfur and nitrogen dually-doped carbon gels

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ABSTRACT

Recent research concerning heteroatom-doped carbon materials reveals strong evidence of the superior electrochemical performance of S, N-dually doped carbons over their mono- or multidoped counterparts enriched with different elements. Herein sulfur and nitrogen co-doped carbon gels produced *via* sol–gel copolycondensation of a mixture of S- and N-containing heterocyclic aldehydes with resorcinol are presented and examined for the first time. The characteristics of the carbonaceous materials can be tuned by means of the initial ratio of the aldehydes (control of the S and N content, control of the texture), sol–gel synthesis conditions (control of morphology) and carbonization conditions (control of texture, amount of doped heteroatoms, their chemical state and the structure of the carbon framework). The S, N-co-doped carbon gels obtained are characterized by specific surface areas of up to 570 m^2/g, maximal S and N content of up to 14 and 9 wt%, respectively, and a peculiar correlation between the amount of S- and N-doping, carbonization temperature and the development of micro- and ultramicroporosity.

1. Introduction

For decades graphenic nanocarbons have remained at the frontier of materials chemistry as promising functional materials [1–4]. Great expectations concerning carbon-based technology have been raised after the discovery of fullerenes and nanotubes, and the isolation and characterization of graphene. However, the potential of carbon nanomaterials is far greater than “carbon-only” graphenic nanostructures. The basic properties of sp^2-carbons, by analogy to silicon, can be altered by substitutional elemental doping, especially with the p-block elements of the periodic table (not only the most popular B, N, P or S, but also Al, As, Ga, Se or Si) [5,6]. Since carbon is chemically similar to silicon, the ground rules of traditional Si-based electronics should also apply to carbon-based electronics. Group-IV silicon can be turned into a p or n type semiconductor if doped with group-III or -V elements [5]. A similar property was observed for graphene when it is doped with B or N [6,7].

Rapid progress in research of heteroatom-doped carbons has delivered convincing evidence that multi-doping yields carbons superior to mono-doped ones. It is speculated that some effects caused by one heteroatom can be significantly amplified by additional co-doping. For instance additional B or P doping of N-doped graphene allows controlling the semiconductivity type (n or p) [8]. Even though the origin of the (electro)catalytic activity and improved electrochemical performance of heteroatom-doped graphenic carbons has not yet been fully understood, and sometimes even questioned [9,10], new evidence shows that S, N-co-doped carbons in particular are indeed active metal-free catalysts. Furthermore, new experimental results complemented by theoretical calculations show that S, N-dually doped carbons exhibit superior electrochemical performance in comparison to single doped carbons and possibly other multidoped carbons [11,12]. Simultaneous insertion of 2p and 3p dopants significantly increases the reactivity of graphene in respect to monodoped or bare graphenes [13]. In addition, the presence of sulfur facilitates doping of nitrogen and *vice versa* [11]. Are S, N-co-doped carbons indeed better than other N/B, N/P or N/B/P heterogeneous carbons? Some results show this might be the case [14,15]. Many papers presented evidence that dually S, N-doped graphenic carbons can indeed outperform single N- or single S-doped carbons in a variety of

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electrochemical applications including the oxygen reduction reaction (for fuel cells and metal–air batteries) [14–24], the hydrogen evolution reaction (production of H_2 through the process of water electrolysis) [25,26], when utilized in electrodes for Li-ion batteries [27–29] and lithium–sulfur batteries [30], in supercapacitors [31–34], for electrochemical sensing [35–37], oxidation/degradation of organic molecules [15,38] and for dye-sensitized solar cells [39,40].

Interestingly, the enhanced reactivity of dual S, N-doped graphenic carbons does not necessarily correlate with high dopant concentration but rather originates from the particular arrangement of the dopants within the graphene sheet (especially the chemical position of the heteroatoms with respect to each other) [13,14,16]. In fact, the synergetic effect can be weakened when superabundant S is introduced into the N-doped graphene [15]. Further pursuit of the full potential of S, N-co-doped carbons as promising advanced functional materials calls for new synthesis strategies where the amount and chemical state of the heteroatoms can be precisely controlled. Multistage processes such as nanocasting are disadvantageous not only due to high cost but also due to the possibility of unintended contamination of the final S, N-doped carbons. A variety of S and N-co-doped graphenic carbons has been obtained from natural feedstock [25,28,31]. This approach is appealing, however, even though abundant and renewable, biomass has many disadvantages as a source of heterogeneous carbons for advanced applications. The chemical composition of natural materials is complex, the content of heteroatoms cannot be easily tailored (it can be high in nitrogen, yet usually low in other foreign atoms) and the final carbon material is incidentally contaminated by inorganic residues (i.e. transition metals).

Synthetic polymers (phenolic resins or polyacrylonitrile, for instance) constitute an important source of nanoporous carbons [41,42]. Utilization of synthetic polymers allows better control of the heteroatom content and type, microstructure and purity of the resultant carbon materials. By that reason, porous polymers which can be directly carbonized into porous carbons would be of special interest. Over a quarter century ago Pekala introduced resorcinol–formaldehyde sol–gel polycondensation to organic and carbon gels [43]. Consequently, he became the father of the new carbon materials family, that is carbon gels, which include aero-, xero- and cryogels. While the old fashioned resorcinol–formaldehyde-based carbon gels and their modifications remain materials of significant interest [44,45], recently we proposed yet another approach to carbon gels synthesis. As we showed, phenols undergo acid catalyzed sol–gel polycondensation with a range of heteroaromatic aldehydes (2-thiophenecarboxaldehyde, 2-pyrrolecarboxaldehyde and their derivatives) yielding nitrogen or sulfur rich phenolic resins [46,47]. Such thermosetting polymers can be carbonized with high yield giving rise to heterogeneous, nanoporous carbons. A new family of organic and carbon gels structurally doped with aromatic S or N has been introduced. Heteroaromatic aldehydes contain foreign atoms in the aromatic –C–S–C– and –C–N–C– states; such arrangements have been shown to be responsible for the electrochemical activity of doped graphenic carbons [16,26]. Here we explore the full potential and versatility of the copolycondensation approach to produce dually S, N-doped carbons. Sol–gel polycondensation of resorcinol and a mixture of various heterocyclic aldehydes is an efficient way to produce nanoporous S, N-co-doped carbon gels with properties that can be tuned depending on the synthesis conditions. The co-gelation allows easy control of the amount of –C–S–C– and –C–N–C– moieties introduced into the produced gels. This manuscript presents detailed characteristics of S, N-co-doped carbon xerogels. The possibility of additional doping with phosphorus to obtain S, N, P-ternary doped carbon gels is also explored.

2. Experimental

2.1. Synthesis of the heteroatom-doped organic and carbon xerogels

The general idea for S, N-dually doped carbon gels synthesis in presented in Fig. 1. In order to get a better understanding of the basic physicochemical properties of the S, N-co-doped gels, solely S-doped and solely N-doped gels were first prepared and characterized. Two different types of heteroaromatic aldehydes were used to synthesize S-doped gels (2-thiophenecarboxaldehyde or 5-bromo-2-thiophenecarboxaldehyde) and N-doped gels (pyrrole-2-carboxaldehyde or N-methyl-2-pyrrolecarboxaldehyde). Furan-2-carboxaldehyde (furfural) was also utilized to obtain organic and carbon gels consisting only of C, H and O (here referred to as undoped gel). Regardless of the gel type, all materials were obtained from resorcinol (R) and chosen heteroaromatic aldehyde or aldehydes mixture (for dual doping of S and N). Sol–gel polycondensation was initiated using an aqueous HCl solution and the molar ratio of resorcinol/aldehyde (or aldehydes mixture) was always equal to 1:2. A methanol or methanol/water mixture was used as a solvent. Water was added to methanol in order to modulate the separation of the polymer phase from the solvent, as described elsewhere [48]. All ingredients were simultaneously dissolved in the solvent at room temperature using magnetic stirring. Then the mixture was acidified with concentrated hydrochloric acid and vigorously stirred for several seconds. The liquid mixture was placed in an oven set at 60 °C. Once obtained, the wet gels were aged for 24 h at 60 °C and then dried at atmospheric pressure at 70 °C to a constant mass (ca. 24 h). Eventually black monoliths were obtained (Fig. S1, Supplementary data). The dry organic xerogels were subsequently carbonized at 600, 800 or 1000 °C for 1 h under a stream of N_2 at a heating rate of 5 °C min^{-1}. For brevity, the chemicals used and materials obtained are labeled by symbols as follows: the monodoped organic gel referred to as RT gel was obtained from resorcinol (R) and 2-thiophenecarboxaldehyde (T), RT-Br gel was obtained from 5-bromo-2-thiophenecarboxaldehyde (T-Br), RP gel from pyrrole-2-carboxaldehyde (P), RMP gel from N-methyl-2-pyrrolecarboxaldehyde (MP) and finally, the undoped RF

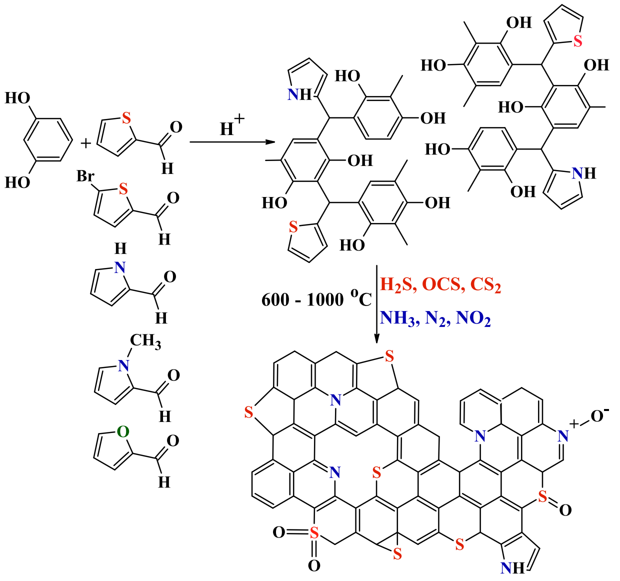

Fig. 1. Scheme of resorcinol/heteroaromatic aldehydes mixture polycondensation followed by carbonization to produce S, N-co-doped carbon gels. A mixture of various aldehydes can be polymerized simultaneously allowing control of the final content of heteroatoms.