Thesis Review. Sustainable approaches towards novel nitrogen-doped carbonaceous structures

Li Zhao[1]
[1] *National Center for Nanoscience and Technology, 100190 Beijing, China*
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Supervisors: Prof. Markus Antonietti (Max-Planck Institute of Colloids and Interfaces, Germany), and Dr. Maria-Magdalena Titirici (Max-Planck Institute of Colloids and Interfaces, Germany).

Objectives and novelty

Nowadays, functionalized carbonaceous materials have attracted particular interest due to their remarkable performance in industrially and environmentally important applications such as CO_2 sequestration, separation, absorption, catalysts, or in electrochemistry, etc.. However, the production methods normally rely on chemically harsh and multistep processes, typically involving high temperature treatment and often leading to the generation of significant quantities of waste, whilst in some cases the overall carbon yield of the process is rather limited. Furthermore, conventional precursors are not necessarily sustainable and relatively expensive as compared to abundant biomass-derived precursors such as the carbohydrates. Thus, this thesis will focus on novel carbonaceous materials which were produced in a sustainable fashion, using cheap starting precursors and uncomplicated synthetic approaches.

Results

The first part of this thesis presents nitrogen-doped carbons synthesized via "*in-situ*" and "*post-functionalization*" approaches. Firstly, nitrogen-doped carbons were synthesized by a one-step hydrothermal carbonization of cheap nitrogen-containing carbohydrates (e.g. chitosan and glucosamine) at a mild temperature (180 ºC). These nitrogen-doped HTC materials (HC-CH and HC-GA) presented very different particle texture as compared to a reference sample prepared from pure glucose (HC-G) under the same conditions (Figure 1 a, b, c). While the resulting materials contained significant amounts of nitrogen and displayed a high degree of aromatization (Figure 1e). What's more, these N-doped carbons showed very good performance as heterogeneous base catalysts in the Knoevenagel reaction of bezaldehyde with malononitrile as well as in the cycloaddition reaction of CO_2 with propylene oxide. Furthermore, the level of structural order of these N-doped hydrothermal carbons can be improved by further carbonization at higher temperatures, importantly, further carbonization did not result in the lose of nitrogen or the change of morphology (Figure 1 d, e). The beneficial properties of these samples were exemplified by the conductivity measurements where an increase of the conductivity was found. Since the carbonaceous materials directly synthesized *via* hydrothermal carbonization do not present high specific surface areas or porosity, methods were developed to increase these textural properties (e.g. chemical activation & carbonization of carbohydrate aerogels). After the chemical activation of hydrothermally treated glucosamine with KOH, the carbon particles of HC-GA were oxidized and reduced to smaller aggregated particles porous N-doped carbon materials (Figure 2), while these microporous N-doped carbons showed promising application as supercapacitors both in acid and basic electrolytes (Figure 2).

Besides the "*in situ*" synthesis approach, amine-rich carbonaceous materials were synthesized via a simple two step "*post-functionalization*"procedure at room temperature, by grafting amine groups onto acidic hydrothermal carbons. The resulting materials showed a very high CO_2 uptake (up to 4.3 mmol g^{-1}) (Figure 3), and even more importantly indications for very high CO_2 which can reach as high as 110. selectivity at both low and high temperatures, The second part of this work describes a novel type of carbon/ titanium dioxide nanocomposites structure synthesized at low temperature under one-step solvothermal conditions. Our results demonstrated that the surface of these nanosized carbon materials showed collective polarization modes and therefore these optical absorption transitions were feasible to sensitize TiO_2 acting as a novel "*dyade*" type structure, with an improved TiO_2 hole reactivity while the electron was taken up by the carbon component.

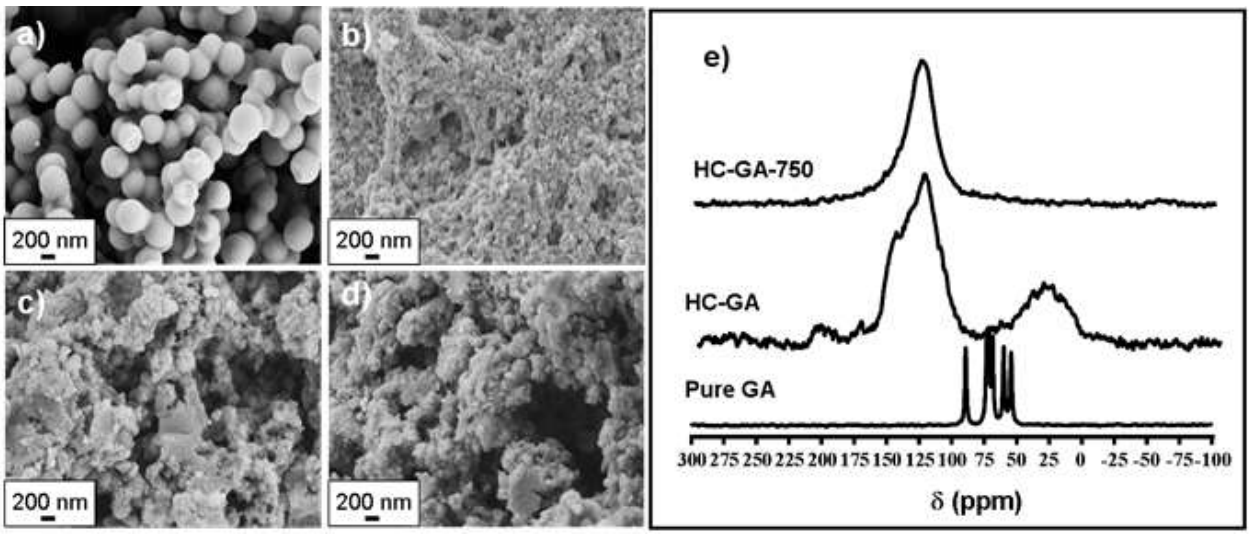

Figure 1. SEM image of the carbons obtained upon hydrothermal carbonization of a) glucose (HC-G); b) chitosan (HC-CH); c) glucosamine (HC-GA) and the sample after treatment at higher temperature (HC-GA-750). e) 13C CP-MAS NMR of pure glucosamine, the hydrothermally treated and further carbonized sample.

Such behavior resulted in an improved photocatalytic activity over the complete spectral range. On the basis of the C@TiO_2 "*dyade*" structure, nitrogen was introduced to form a novel N/C@TiO_2 structure, which has great potential applications in photocatalysis.

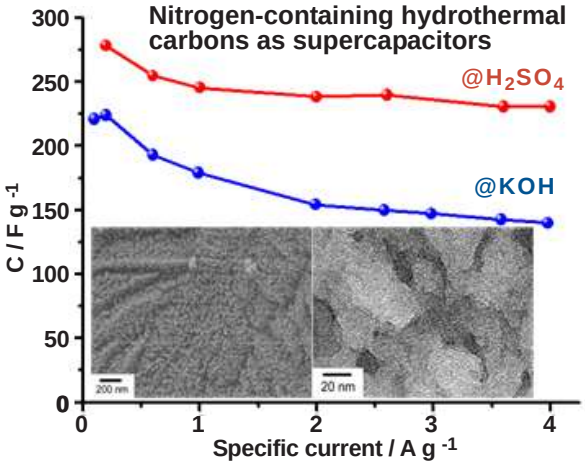

Figure 2. SEM images of microporous Nitrogen-doped materials (chemical activated HC-GA) and the specific capacitance of the resulting materials both in acid and basic electrolytes.

Conclusions

In summary, this thesis has demonstrated the application of sustainable hydrothermal carbonization material synthesis approaches for the production of novel carbonaceous structures possessing different morphologies, structures, functions as well as applications in various domains. We believe that such class of materials will play a very important role in the future, especially in fields related to energy storage or CO_2 sequestration.

Related Publications

[1]L. Zhao, X. F. Chen, X. C. Wang, Y. J. Zhang, W. Wei, Y. H. Sun, M. Antonietti, M.-M. Titirici, "One-Step Solvothermal Synthesis of a Carbon@TiO_2 Dyade Structure Effectively Promoting Visible Light Photocatalysis", Adv. Mater., 2010, 22(30), 3317-3321.

[2]L. Zhao, L.-Z. Fan, M.-Q. Zhou, H. Guan, S. Qiao, M. Antonietti, M.-M. Titirici, "Nitrogen-Containing Hydrothermal Carbons with Superior Performance in Supercapacitors", Adv. Mater., 2010, 22(45), 5202-5206.

[3]L. Zhao, Z. Bacsik, N. Hedin, W. Wei, Y. H. Sun, M. Antonietti, M.-M. Titirici, "Carbon dioxide Capture on Amine-rich Carbonaceous Materials Derived from Glucose", ChemSusChem, 2010, 3(7), 840-845.

[4]L. Zhao, N. Baccile, S. Gross, W. Wei, Y. H. Sun, M. Antonietti, M.-M. Titirici, "Sustainable Nitrogen Doped Carbonaceous Materials from biomass derivatives", Carbon, 2010, 48(13), 3778-3787.

[5]L. Zhao, R. Crombez, F. Pérez Caballero, M. Antonietti, J. Texter, M.-M. Titirici, "Sustainable Nitrogen-Doped Carbon Latexes with High Electrical and Thermal Conductivity", Polymer, 2010, 51, 4540-4546.

[6]S. Kubo, R. Demir-Cakan, L. Zhao, R. J. White, M.-M. Titirici, "Porous Carbohydrate-Based Materials via Hard Templating", ChemSusChem, 2010, 3(2), 188-194.

[7]J. Matos, A. García, L. Zhao, M.-M. Titirici, "Solvothermal Carbon-Doped TiO2 Photocatalyst for the Enhanced Methylene Blue Degradation under Visible Light", Appl. Catal. A: Gen., 2010, 390(1-2),175-182.

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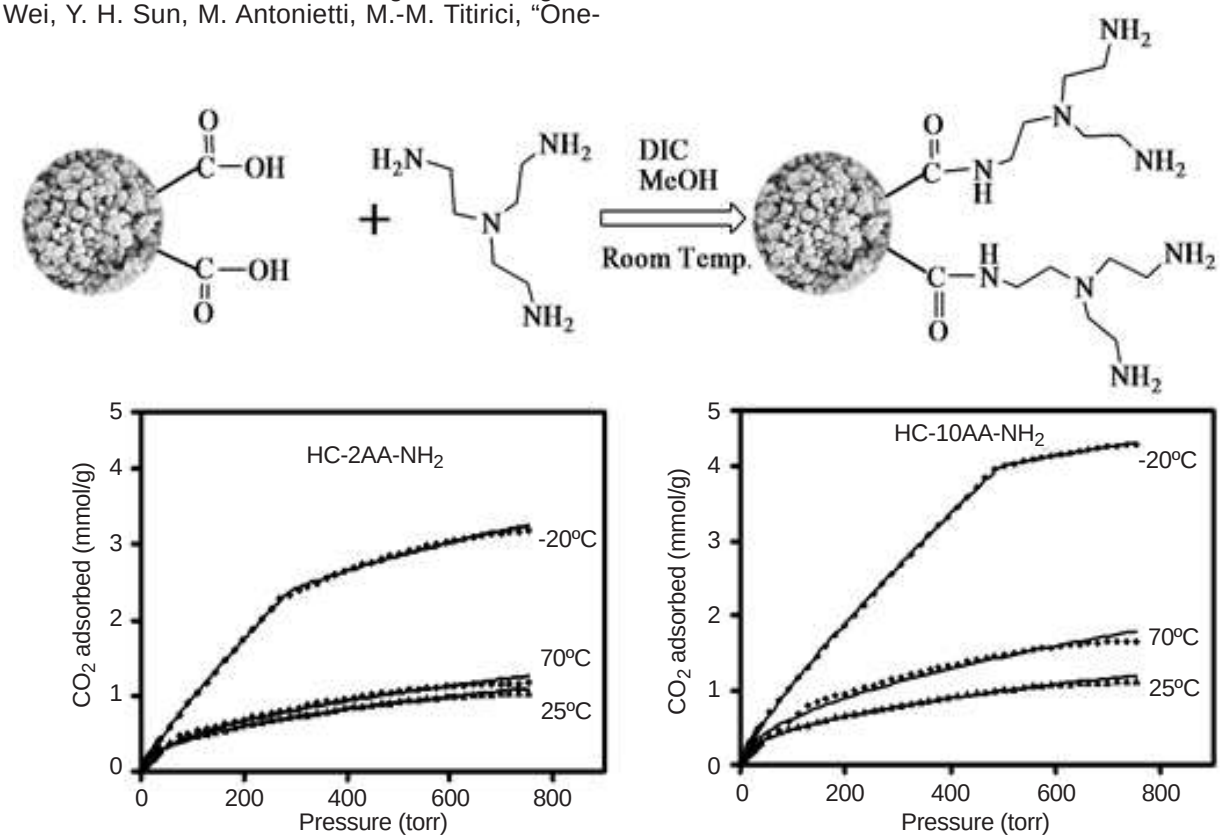

Figure 3. Synthesis scheme of amine-rich material formation from hydrothermal carbon spheres (up); and the temperature and pressure dependent uptake of CO_2 (mmol g^{-1}) on the sorbents (down).