SCALABLE PRODUCTION OF NITROGEN-DOPED CARBONS BY PYROLYSIS OF BIOMASS-DERIVED CARBONS IN NH_3 GAS

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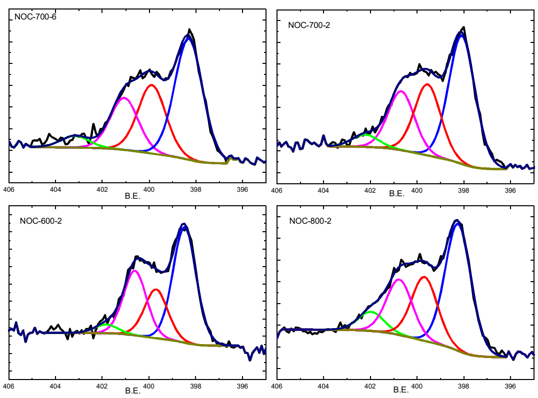
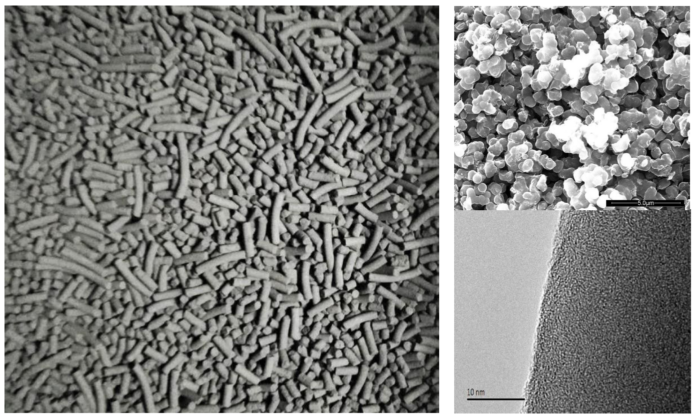
Nitrogen-doped carbons (NCs) possess superior characteristics and attract interests in many fields, e.g. energy storage, catalysis, separations etc., yet the costly preparation process mainly due to expensive N-containing precursors limits its large-scale application. Furthermore, the low nitrogen content and the poor control of nitrogen species (i.e. pyrrolic, pyridinic, graphitic, and oxide of nitrogen) challenge its industrialization. We hereby report a facile method to prepare NCs, of which the nitrogen content can be achieved up to 8% w/w by XPS with a better control of nitrogen species.

Inexpensive production of NCs normally uses low-cost carbon and nitrogen precursors such as biomass and ammonia. Luo et al. reported a simple preparation of NCs by means of pyrolyzing cellulose in NH_3 gas [1]. This method enables large-scale production of NCs. They proposed a preliminary mechanism of NCs formation at very high temperature. However, the content and species of nitrogen were still unsatisfactory to various of applications. We use an alternative route starting with synthesizing oxygen-containing carbons (OCs) by hydrothermal treatment of biomass [2], and then pyrolyzing OCs in NH_3 gas with lower temperatures. The content and species of oxygen are correlated to those of nitrogen with appropriate conversions [3]. Therefore, by altering the idea of modulating nitrogen species into that of modulating oxygen species followed with confined conversions of OCs to NCs, we widen the window of the synthesis process and obtain controllable, cost-friendly NCs.



XPS of N1s (pyridinic, pyrrolic, quarternary and pyridinic N^+-O^-)



NCs pellets and micrographs

Samples	Pretreatment in Ar	Pyrolysis in NH_3	BET SSA (m^2/g)	N % *	H % *	O % *
OC-700-6	700°C for 6 h	none	669	0	1.1	3.5
NC-700N-6	none	700°C for 6 h	681	13.5	1.2	6.5
NC-700-2	350°C for 0.2 h	700°C for 3 h	623	11.1	1.0	5.0
NC-700-6	350°C for 0.2 h	700°C for 6 h	698	12.3	1.1	4.6
NC-600-2	350°C for 0.2 h	800°C for 2 h	506	5.9	2.5	7.5
NC-600-6	350°C for 0.2 h	600°C for 6 h	584	7.0	2.2	6.9
NC-800-2	350°C for 0.2 h	800°C for 2 h	720	10.9	0.9	4.9
NC-800-6	350°C for 0.2 h	800°C for 6 h	803	10.5	0.8	2.8

Properties of NCs with different pyrolysis

* wt% from combustion analysis

References
[1] W. Luo, B. Wang, C. Heron, et al., Nano Lett. 14, pp. 2225-2229, 2014.
[2] A. Romero-Anaya, M. Ouzzine, et al., Carbon 68, pp. 296-307, 2014.
[3] D. Wang, D. Su, Energy Environ. Sci. 7, pp. 576-591, 2013