

Brominated nanostructured carbons: Surface properties and preparation of N-, S- and O-containing sorbents and catalysts

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Carbon nanomaterials are used to create sensors and electronic devices and are traditionally used as sorbents, carriers, and catalysts. Bromination and the subsequent substitution of bromine are composed in a universal approach for surface functionalization. The purpose of this work is to brominate carbon granular and fibrous nanostructured materials and to study their functional properties.

KAU, SKN1, and SKN2 activated carbons and carbon fibers (CFs) of Belarusian trademarks (CFPAN and CFBus), which were used as initial CMs. KAU was an activated carbon obtained from peach stones. SKN was a spherical nitrogen-containing activated carbon obtained by standard method for carbonization and vapor activation of vinyl pyridine rubber. SKN2 was obtained from the same raw material as SKN1, but, at the carbonization stage, the level of carbon burnoff was maintained greater than 80%. The CFPAN was a carbon fiber made on the basis of polyacrylonitrile (PAN). A technical viscose thread was used to make CFBus.

CMs were bromated with liquid bromine or Br₂-KBr solution at room temperature. Also, we treated CMs with Br₂-KBr solution, bromine water, or KBrO₃ solution at different pH (0, 1, 3, 4, 7, 8, and 12).

Table 1. Surface chemistry of brominated CMs from DTG and TPD IR data

Sample	C.A. C(Br) (mmol/g)	^a DTG		T ₁ (°C)	Surface groups (mmol/g)		
		Weight loss (g/g) Δm _{FG}	Δm ₁		Δn(Br) (DTG)	C _{FG} (TPD IR)	
						ΔC(CO ₂)	ΔC(CO)
KAU-KBr ₃	0.62	0.104	0.032	293	0.29	0.25	1.41
KAU-Br ₂	0.52	0.096	0.034	283	0.24	0.29	1.44
SCN1-KBr ₃	0.41	0.095	0.040	302	0.17	0.16	1.89
SCN1-Br ₂	0.44	0.112	0.019	298	0.19	0.17	1.62
SCN2-KBr ₃	0.44	0.091	0.023	280	0.22	0.12	1.27
SCN2-Br ₂	0.45	0.094	0.038	287	0.23	0.18	1.13
CFBus-KBr ₃	0.51	0.124	0.027	262	0.25	0.31	1.71
CFBus-Br ₂	1.02	0.158	0.067	231	0.46	0.34	1.26
CFPAN-KBr ₃	0.43	0.159	0.037	220	0.20	0.52	3.22
CFPAN-Br ₂	0.49	0.161	0.050	230	0.25	0.59	2.92

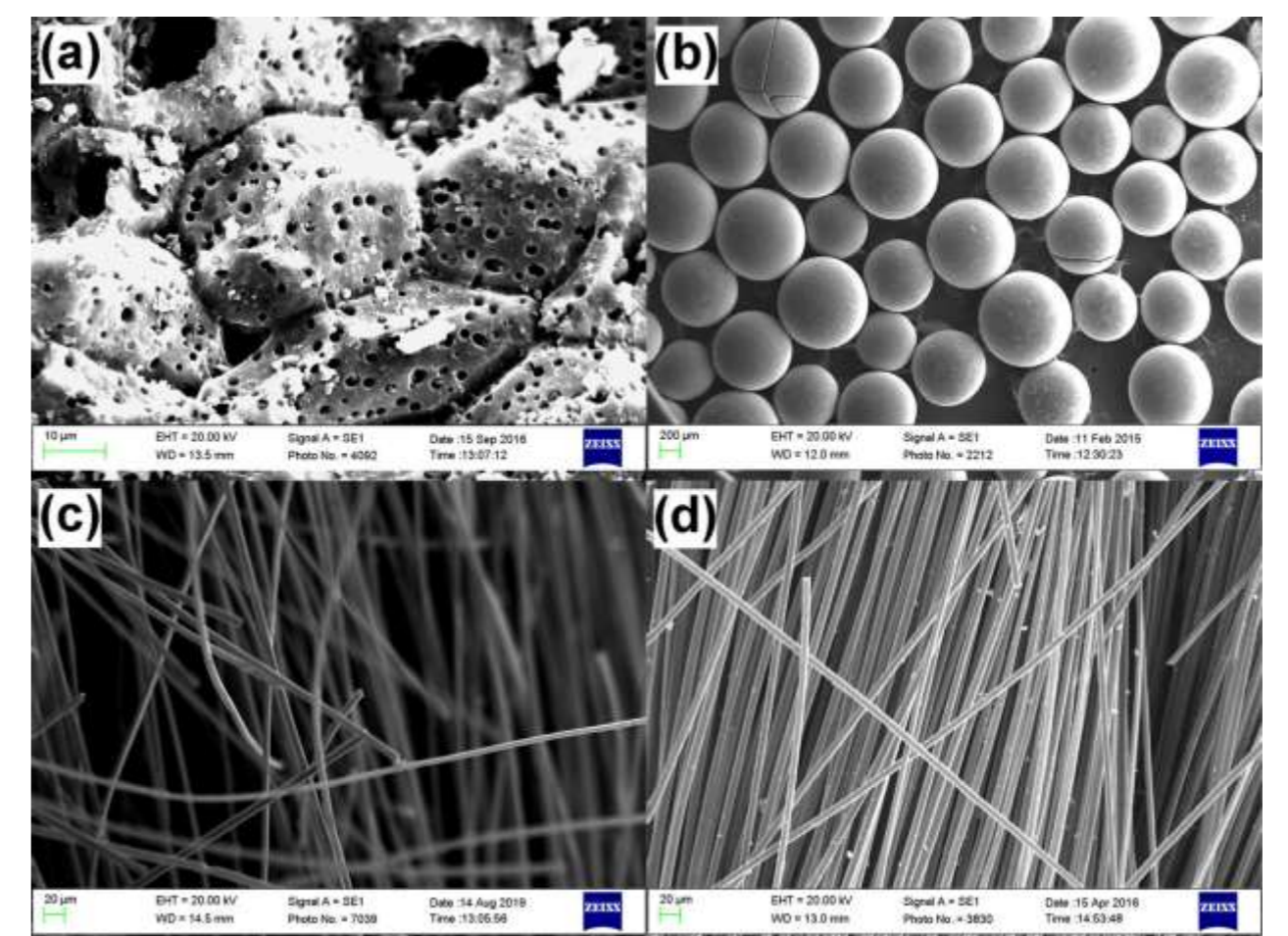


Fig. 1. SEM images of the initial CM: (a)–KAU, (b)–SCN1, (c)–CFBus, (d)–CFPAN.

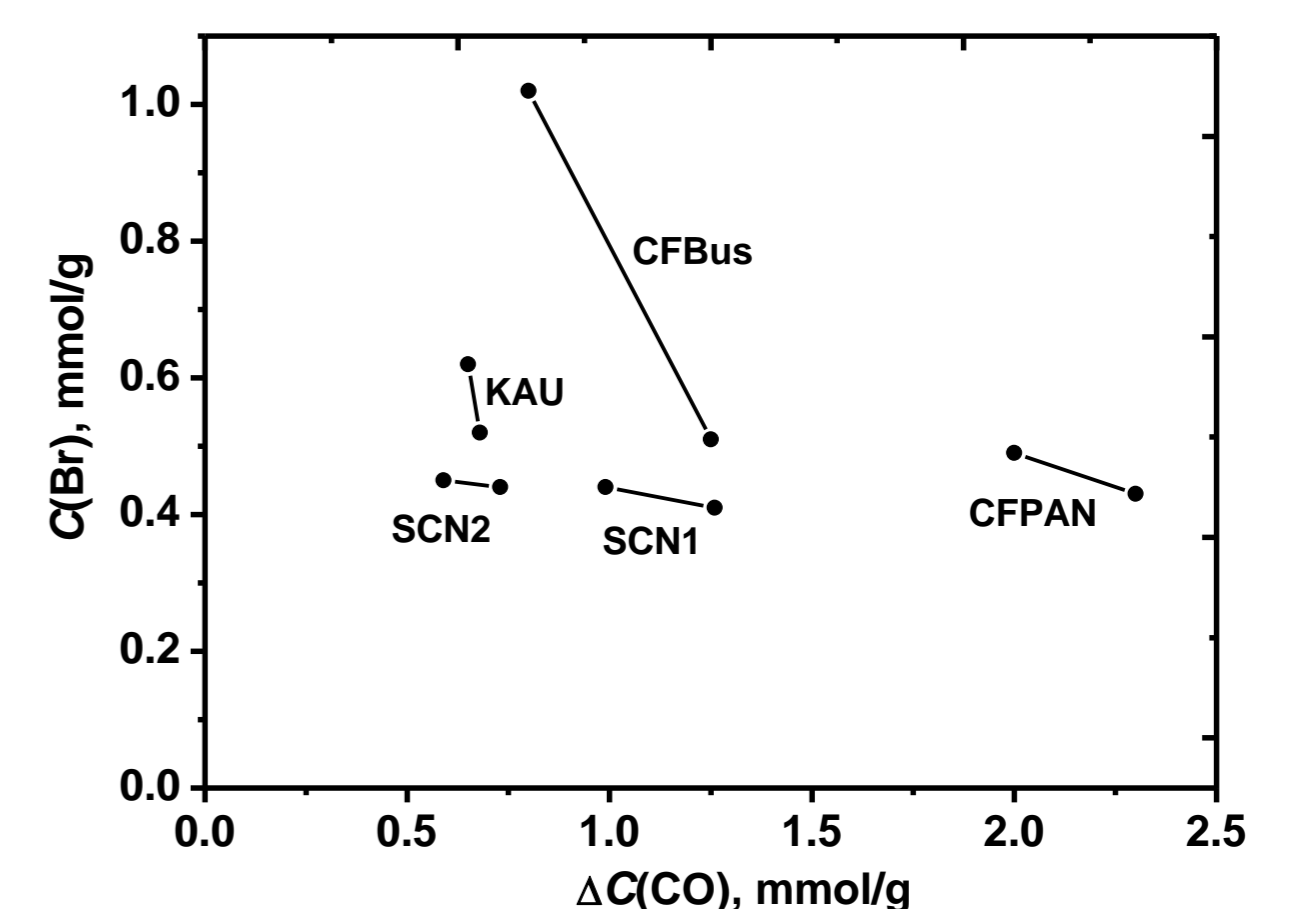


Fig. 2. Negative correlations between C(Br) and ΔC(CO).

By C.A., TG/DTG, and TPD IR methods, it was shown that the proposed bromination methods provide the formation of up to 1 mmol/g of chemisorbed bromine. The grafted bromine is desorbed in the form of HBr in two stages: in the temperature range of 200-500 °C and 400-600 °C. Bromination is accompanied by partial oxidation of the CMs surface, resulting in the formation of high-temperature CO centers (phenolic groups). High oxidative capacity of molecular bromine and the formation of HBr as the primary product of bromine disproportionation (in the aqueous medium) are likely reasons for the intense surface oxidation during bromination. Possible transformations in bromine solution at different pH can be described by the following scheme:

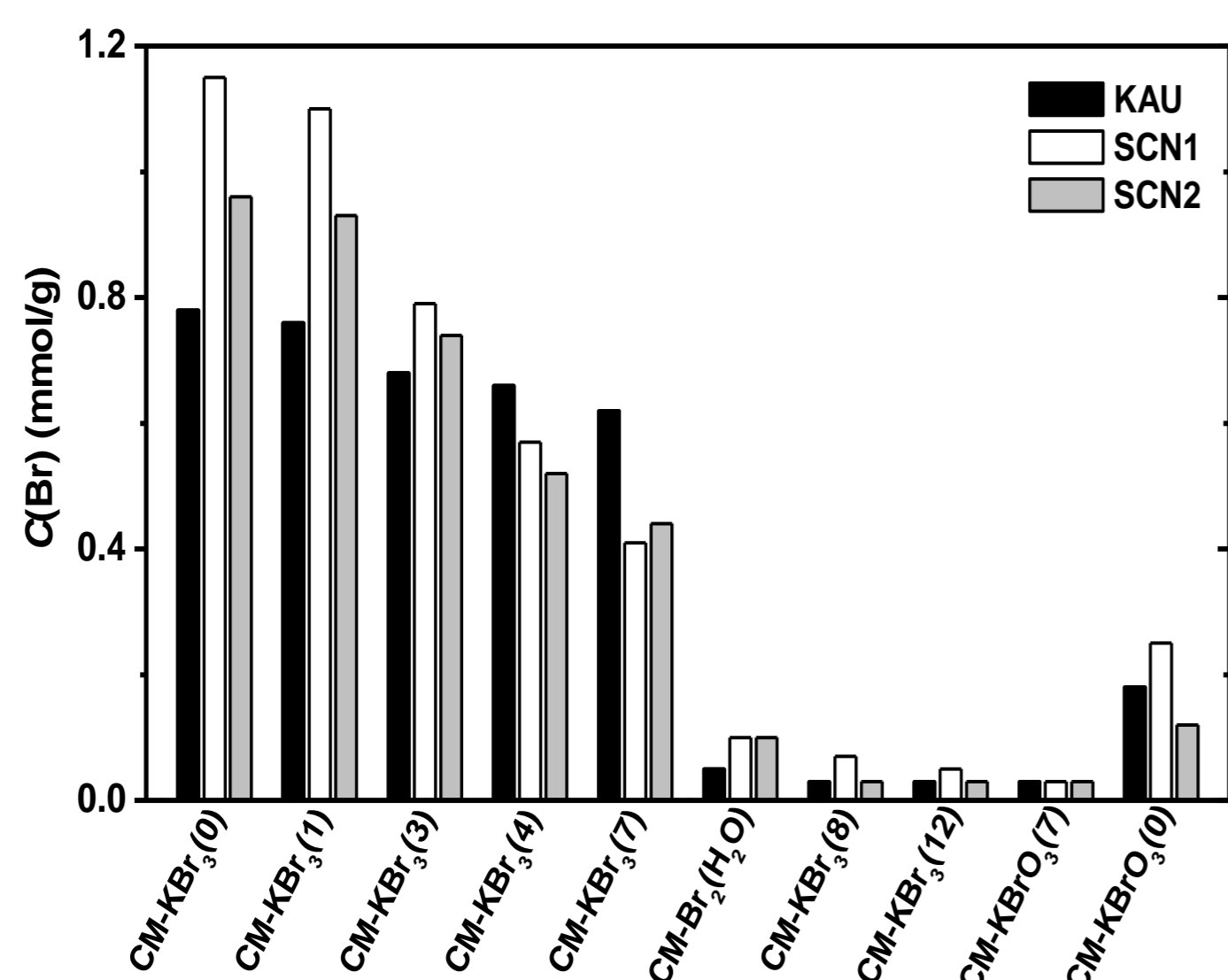
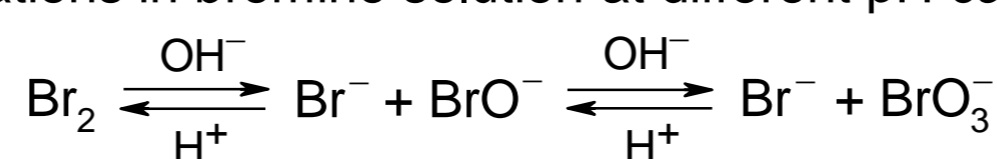


Fig. 3. The dependence of C(Br) on the pH and bromination method.

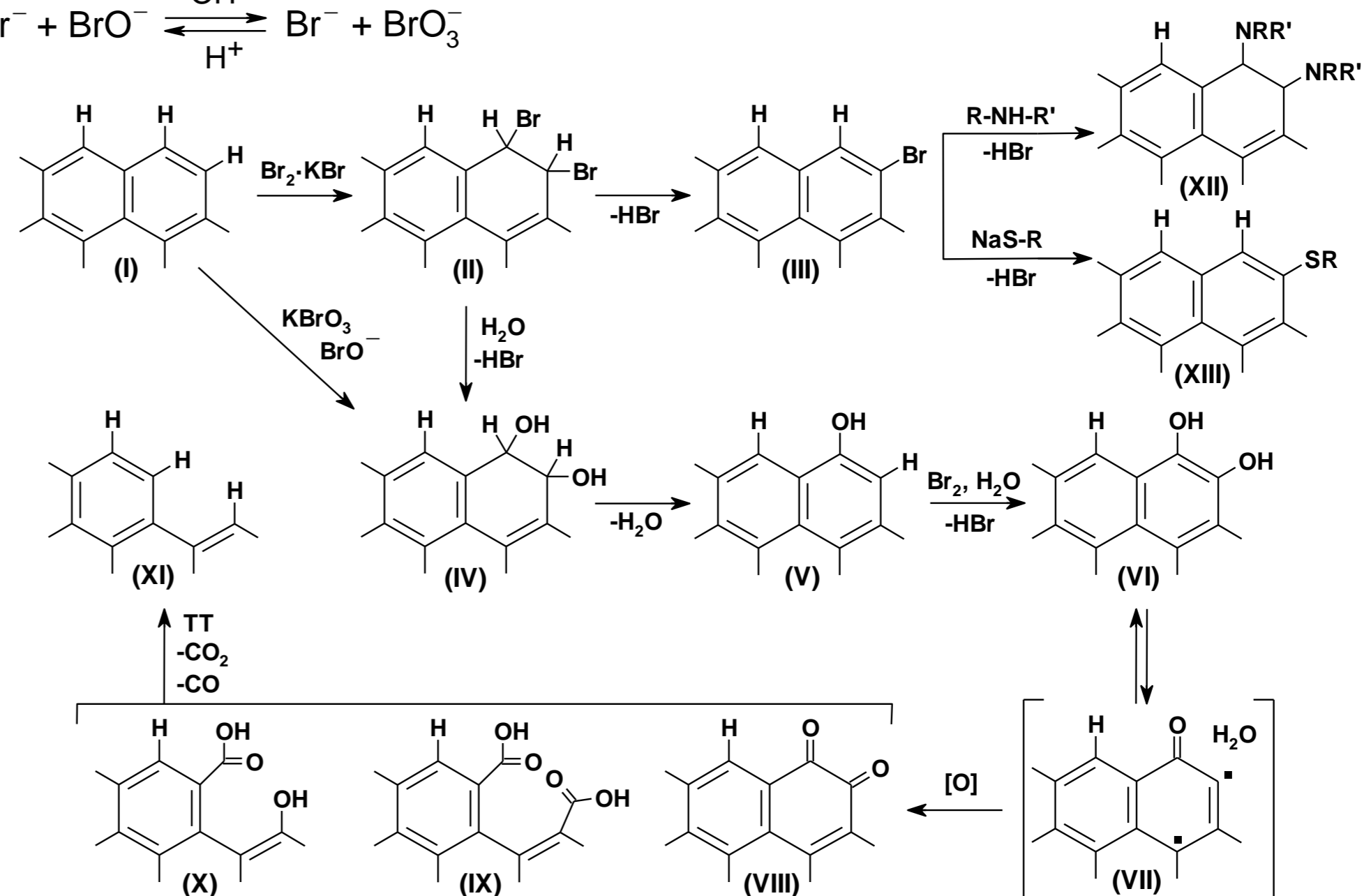


Fig. 4. Schematic diagram showing CMs surface chemistry changes after bromination, oxidation, thermal treatment, and modification with N- and S-containing compounds.

Conclusions. The proposed bromination techniques are effective in creating a chemically-active bromine-containing carbon surface layer. Combining different brominating agents at different pH allows directional introduction into the surface layer of Br- and O-containing functional groups. Increasing the acidity at bromination with Br₂-KBr mixture introduces more bromine, of about 1 mmol/g of Br groups at pH = 0. Bromination in neutral or alkaline media results in the monolayer coverage completed below a specific amount ~2 mmol/g of mainly Ph groups. Oxidation of the carbon surface almost completely prevents the following bromination. By removal of oxygen-containing functional groups during thermal treatment, the reactivity of the oxidized carbon surface can be partially or completely renewed. Despite the nature of oxygen-containing functional groups, only the number of removed groups determines an increase in the surface reactivity. Overall, these experimental results demonstrate that the brominated surface derivatives serve as effective centers for chemical functionalization. They can facilitate the production of nitrogen- and sulfur-containing surface coverage on the voluminous nanoporous carbons.