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Beyond Adsorption: The Effect of Sulfur Doping on Emerging Applications of Nanoporous Carbons

Teresa J. Bandosz

Department of Chemistry, The City College of York, New York, NY 10031, USA

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Abstract

Recently we have directed our attention to new applications of "old" materials, nanoporous carbons, as photocatalysts for oxidation of dibenzothiophenes, as water splitting catalysts, as gas sensors and as photosensitizers. Our inspiration was in graphene science. We found that both surface chemistry and porosity are crucial factors determining the specific performance. Since the effects are synergistic, it is not possible to totally separate the influence of these two factors. In terms of photoactivity and photosensitivity, surface chemistry was found as having the predominant effect on the catalytic performance. Sulfur containing groups were indicated as playing a major role in these processes. Of course physical adsorption was necessary to take place on the surface before further reactions promoted by absorption of photons occurred. Since some level of conductivity of the carbon matrix is important for an electron transfer, formation of radicals, and active oxygen species, the presence of sp^2 graphitic dots of 10 nm in size in the carbon matrix enhanced the photoactive performance. In the case of gas sensing where the reversibility of the signal is important, physical adsorption was a predominant factor. Here the specific polar or electrostatic interactions enhance the sensitivity and affect markedly the selectivity. A minireview of our recent work on these two emerging topics, photoactivity of carbon and their sensing application, is presented in this paper. The emphasis is on the importance of both, specific surface chemistry and developed porosity. The latter is a unique factor, which differentiates the performance of porous carbons from that of nanoforms of carbons such as graphene or carbon nanotubes.

1. Introduction

Discovery of fullerenes [1], carbon nanotubes [2] and graphene [3] directed the attention of scientists to the new applications of this group of materials, often referred to as nanocarbons. Applications, which has been explored so far include electronic devices, sensors, components of metal-oxide semiconductor field effect transistors (MOSFET), radio frequency electronics, novel field effect transistors (NFET), nanoelectromechanical systems (NRMS), free standing membranes, and others [4, 5]. This broad range of technology is related to their physical properties including a high electrical and thermal conductivity, flexibility, strength, and transparency.

The graphene discovery met us at a developed stage of understanding surface chemistry of porous carbons and of exploring the most efficient and controllable ways of its modifications [7–9]. We have been also reaching deeply into the complexity of surface processes, especially those involving reactive adsorption of toxic reactive gases such as hydrogen sulfide or ammonia [10]. To find the most efficient adsorbent of the latter gas, we found graphite oxide geometry and surface chemistry very advantageous to adsorb ammonia by itself or to build composites with Metal Organic Frameworks (MOFs) [11, 12]. At that time we have also noticed a very high adsorption capability of S – containing carbon towards oxidation of arsine [13]. This directed our research to an extensive study of sulfur doped carbons [14, 15]. The objective of this minireview is to introduce the visible light-driven oxidative capabilities of sulfur containing carbons and their gas sensing potential. All of this expands the usage of nanoporous carbons "*beyond adsorption*" although adsorption in a carbon pore system is still a crucial step governing this new and emerging "journey" of these old adsorbents.

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*Corresponding author. E-mail: tbandosz@ccny.cuny.edu

2. Desulfurization of liquid fuel/oxidation of dibenzothiophenes

One of our research topics at the time of S-doped carbons synthesis and their initial exploration was desulfurization of liquid fuels. Refractory thiophenic compounds were our targets. Since their removal from liquid fuel is an important environmental task and their oxidation might help in an adsorptive removal, sulfur-containing carbons became our adsorbents of choice to test the hypothesis on their visible light enhanced reactive adsorption capability. Dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) of low concentration (20 ppb each) dissolved in simulated diesel fuel were used as model compounds. The carbon was synthesized from poly(4-styrenesulfonic acid co-maleic acid) sodium salts with 2% graphene phase [16]. The latter was added to increase a conductivity.

The carbons with adsorbed DBT and DMDBT were exposed to visible light as dry (filtered) samples with the adsorbates deposited in the pore system [14–16]. Control experiments were run in the dark conditions.

The surface features of the carbon and the composites are collected in Table 1. The addition of only 2% graphene markedly decreased the surface area and porosity of the final composite. On the other hand, an increase in DC conductivity and in the sulfur content was recorded. Apparently some reduction of surface functional groups took place since the content of oxygen and the amount acidic groups on the surface decreased. This suggests that sulfur in the composite is mainly in the thiophenic compounds and in biosulfides.

The results of the MS analysis of the extracts from the carbon surfaces showed the presence sulfoxides, sulfones, sulfonic acids, diones, aldehydes, and even alcohols (Fig. 1). The cleavage of the C-C bonds in aromatic rings was observed. Table 2 and Fig. 1 list the species detected in the extracts from the particular samples either under exposure to UV or visible light. The results in control experiments in dark are also included.

Apparently the graphene phase addition to the polymeric precursor of the sulfur-doped carbon has a positive effect on the photoactivity of the composite towards oxidative degradation of refractory sulfur organic compounds, DBT and DMDBT.

Table 1

The parameters of porous structure calculated from nitrogen adsorption isotherms and DC conductivity values, content of carbon, oxygen in sulfur (in at.%; from EDS) and the numbers of strongly acidic ($pK_a < 7$) and weakly acidic ($pK_a < 7$) groups (in mmol/g). Adapted with permission from Ref. [16]. Copyright 2014, Elsevier

Sample	S_{BET} [m^2/g]	V_t [cm^3/g]	V_{meso} [cm^3/g]	$V_{<1\ nm}$ [m^3/g]	σ [S/m]	C	O	S	$pK_a < 7$	$pK_a > 7$
CPS	1416	1.019	0.582	0.226	16.3	84.3	15.3	0.4	0.340	0.354
CPSGr	1056	0.634	0.306	0.182	68.5	87.6	10.8	1.6	0.271	0.288

Table 2

Speciation of the products detected in the extract from the samples' surface using Mass Spectrometer.
Letters refer to the detected species listed in Fig. 1.
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	CPS-D	CPS-UV	CPS-VL	CPSGr-D	CPSGr-UV	CPSGr-VL
A	+	+	+	+	+	+
B	+	+	+	+	+	+
C	+	+	+	+	+	+
D		+	+	+	+	+
E		+	+		+	+
F		+	+			+
G			+			
H					+	+
I			+			
J		+	+		+	+

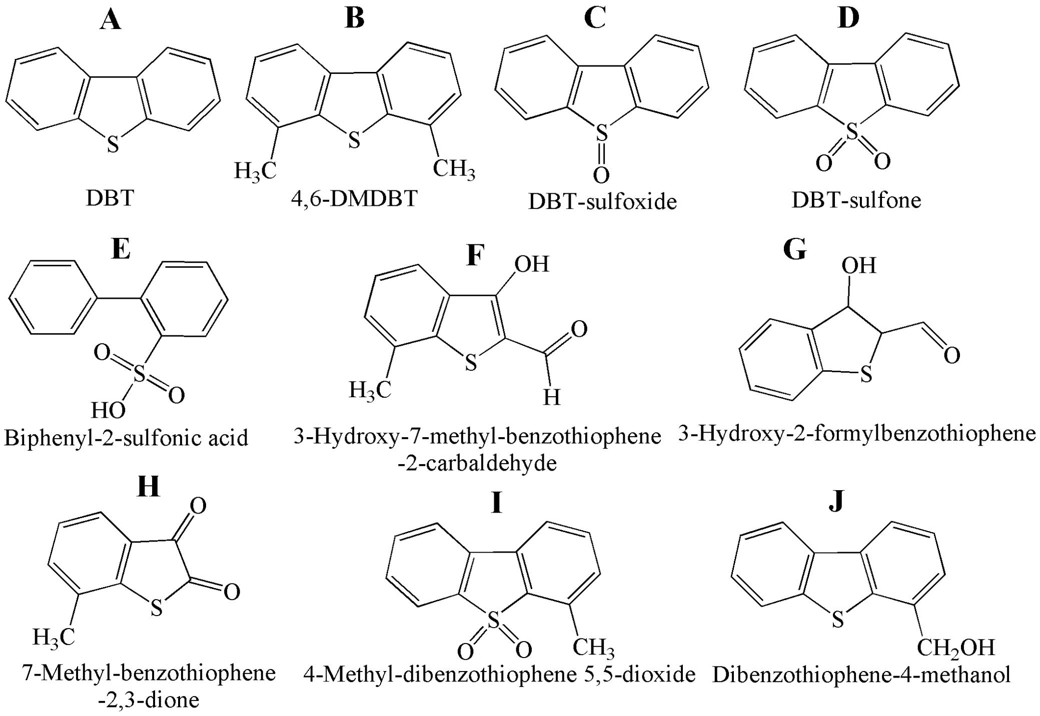

Fig. 1. Compounds detected in the extract from the surface of carbons exposed to DBT and DMDBT. Adapted with permission from Ref. [16]. Copyright 2014, Elsevier.

This was linked to its scaffolding effect limiting the release of sulfur-containing gases, which resulted in more sulfur doped into the composite/carbon phase. That graphene phase might also contribute to the reduction of surface leading to more sulfur in photoactive thiophenic configurations. Owing to higher electronegativity of sulfur than that of carbons these species result in a positive charge on the neighboring carbon atoms [17]. These catalytic centers were suggested as attracting of more superoxide ions to the carbon surface in small pores. At that time when these results were published we did not go deeply into understanding the mechanism of photoactivity. Nevertheless, since the extent of oxidation was much more pronounced upon irradiation than in dark holes were considered as contributing to the formation of OH radicals (the carbons were exposed to radiation in ambient air containing moisture). Thus the graphene phase could enhance the transport of photogenerated electrons and helped in their separation from holes, increasing the efficiency of surface reactions and delaying the recombination of both. Not without importance was the high volume of small pores promoting the physical adsorption of DBT and DMDBT in the pore system. Therefore the results obtained were very encouraging and they suggested that the high adsorption capacity of the composite combined with its photoactivity could open a new route for reactive adsorption-based separation processes. Oxidation of DBT and DMDBT markedly changed the polarity of these species and could increase the selectivity of their adsorption from the liquid fuels. That selectivity is an important issue in liquid fuel desulfurization.

3. Photoelectrochemical water splitting

One of important contemporary research needs to be addressed by scientists is a development of inexpensive catalysts being able to use solar energy for water splitting. This, and the photosensitivity of our sulfur containing carbons directed our attention to test these materials as photoelectrocatalysts [18]. The carbons obtained from poly(4-ammonium styrene-sulfonic acid) polymers were used. The choice to use this polymer was motivated by the particular chemistry of this compound and the possibility to incorporate both, sulfur and nitrogen to the carbon matrix. The latter is an important heteroatom affecting the charge distribution on the carbon surface and bringing the catalytic properties related to activation of oxygen [17]. To further modify the surface, the initial carbon, obtained without any pore former and referred to as CONS, was oxidized at 350 °C for three hours to further develop the porosity. This treatment resulted in the sample referred to as CONS-I. The basic information about surface chemistry and porosity of carbons tested is summarized in Table 3.

Table 3
The parameters of porous structure calculated from nitrogen adsorption isotherms, and the samples' conductivity (σ). Adapted with permission from Ref. [18]. Copyright 2014, Elsevier.

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{meso} (cm^3/g)	$V_{<1\ nm}$ (cm^3/g)	σ (S/m)
CONS	38	0.022	0.021	0.000	0.5
CONS-I	727	0.363	0.103	0.184	0.6
BAX	2010	1.463	0.991	0.112	4.1×10^{-4}

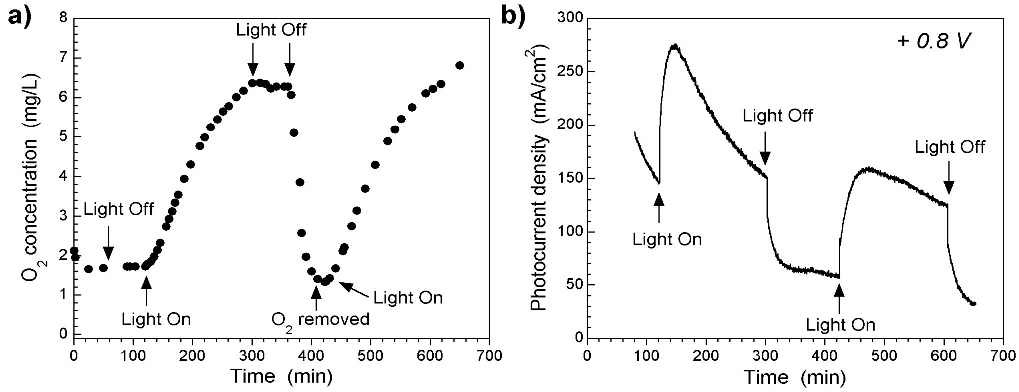

Fig. 2. (a) O_2 evolution during chronoamperometry run; (b) Chronoamperometric response of the carbon (CONS-I) photoanode upon on/off illumination at +0.8 V vs Ag/AgCl. Reprinted with permission form Ref. [18]. Copyright 2014, Elsevier.

To differentiate the effects of surface chemistry, the photoelectrochemical experiments were also carried out on a commercial wood-based carbon, referred to as BAX. This carbon did not show the enhanced activity in oxidation of DBT and DMDBT upon VL or UV exposure [14]. Under simulated solar light irradiation (irradiation density of 75 W/cm^2) in 0.5 M Na_2SO_4 at pH 2 the marked photocurrent was measured on only one carbon catalyst, CONS-I, and it was linked to the evolution of oxygen at low over potential of 0.8 V vs. Ag/AgCl (Fig. 2) [18]. As seen in Fig. 2 generated photocurrent reached 100 mA/cm^2.

Table 3 summarizes porosity and conductivity of carbons tested. XPS analysis showed that both polymer-derived carbons had a marked content of nitrogen, sulfur and oxygen on the surfaces (CONS: 1.3 at.% N, 1.7 at.% S and 8.6 at.% O; in CONS-I: 1.2 at.% N, 0.7 at.% S and 16.6 at.% O). Sulfur was predominantly in bisulfides and thiophenic species and nitrogen- as pyrroles and in quaternary configurations. Oxygen had almost equal contributions in O=C and O-C bonds. An interesting and very unique feature in both samples was the presence graphitic "dots" of 10 nm embedded to carbon matrix (Fig. 3). CONS-I showed also the hierarchical pore structure, which was not detected in CONS. The BAX carbon on the other hand, was a totally amorphous material of the highest surface area. These results suggested that surface area alone is not a critical factor governing the catalytic performance and surface chemistry might play a marked role in this process. Since Both CONS and CONS-I contain S, N and O heteroatoms and graphitic units, and still they behave differently, apparently these features are not sufficient to provide catalytic activity for water oxidations. Therefore, based on the results collected, it was suggested that for photoelectrochemical water splitting the combination of both specific surface chemistry and porosity is needed. The conductivity of the carbon electrode is also an important factor.

A search of the literature indicated that photoactivity of carbonaceous materials is influenced by the density of electronic states (DOS) formed by σ and π bands, and the band gap energy depends upon the sp^2/sp^3 content and configurations [19-20]. The size and ordering of the sp^2 clusters, their population in the carbon matrix, and the distortions of π states were also suggested as important. In our polymer derived porous carbon of photocatalytic activity these two features (sp^2 configurations and distortion of π states) are present. Nevertheless, nothing about the porosity effect has been mentioned in the papers analyzing the photoactivity of carbon materials. The reason for this might be in the scarcity of studies involving the application of activated carbons as photocatalysts. In analyzing the role of pores and the effect of their sizes and volumes the S, N, and O

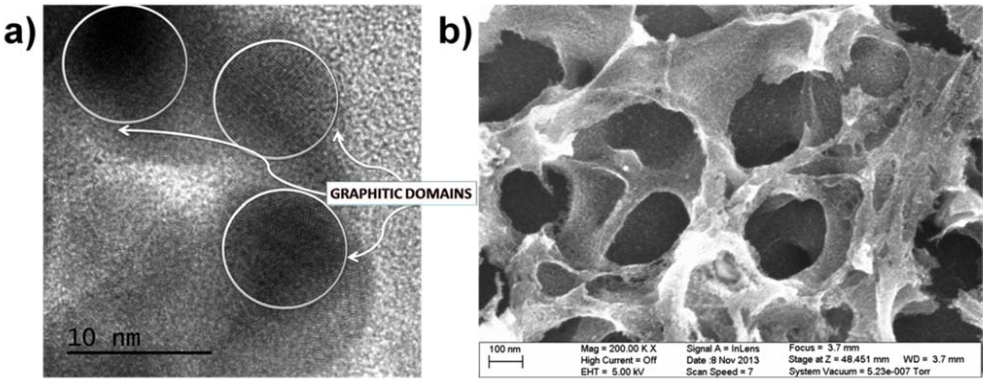

Fig. 3. HRTEM (a) and SEM (b) images of CONS-I carbon. Adapted with permission form Ref. [18]. Copyright 2014, Elsevier.

containing functional groups, which decorate their surface, should not be neglected. In dyes [21] and proteins [22] the arrangements of S, N and O heteroatoms were found as critical for photoactivity. In our case they form the specific light active chromophores. Electron in these chromophores located in the pore system are excited by the energy of photons and instead of coming back to the ground state they likely migrate to the cathode through the sp^2 graphitic dots present in the texture of our polymer derived carbons. This results in the formation of holes on these functional groups. Simultaneously water adsorbs in the pore system, owing to surface hydrophilicity. Then the electrons from water oxygen fill the holes, which results in splitting H_2O molecules and in the evolution of that oxygen. The dipol moment of water and negative charge of oxygen cause that H_2O molecules are attracted in a specific spatial direction, via oxygen, to these vacancies. Moreover, this process can be even more efficient in confined pore space where, owing to the overlapping of the adsorption potential, strong adsorption of water takes place. Unfortunately, during this complex water splitting process the formed molecular oxygen oxidized the carbon surface. As a result of this chemistry changed, and thus the performance of the catalyst decreased.

4. Nanoporous carbons as gas sensors

Carbon derived from polystyrene based polymers had such interesting properties that we decided to check their performance in gas sensing [23, 24]. For this purpose chips coated with a carbon active phase were needed. Their preparation with a sufficient integrity of the film providing measureable resistance was a challenging task. Nevertheless, our efforts led to the rewarding results. Synthetic carbons were obtained from either polystyrene sulfonic acid ammonium salt or from a 1:1 mixture of polystyrene sulfonic acid ammonium salts and poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (C-A and C-B, respectively). Carbonization was followed by air oxidation at 350 °C and the samples were referred to as C-AO and C-BO [24]. They differed in surface chemistry and porosity (XPS results: C-A: O-8.6 at.%; N-1.3 at.%; S-1.7 at.%; C-B: O-9.3 at.%; N-2.4 at.%; S-2.4 at.%; C-AO: O-16.6 at.%; N-1.2 at.%; S-0.7 at.%; C-BO: O-9.3 at.%; N-2.63 at.%; S-0.9 at.%; S_{BET}: C-A: 38 m^2/g; C-B: 290 m^2/g; C-AO: 727 m^2/g; C-BO: 847 m^2/g) and these differences reflected in both, the initial resistance of the chips and in the extent of the signal change upon exposure to ammonia (Fig. 4). The concentration range was from 10–500 ppm. The performance of C-A was found as not adequate and all other chips showed linear response, which is an important feature of a gas sensor (Fig. 4). The change of the resistance reached 15%, similar to the results addressed in the literatures on modified graphene [25]. Important for ammonia sensing is a p type conductivity of the carbon samples where holes are the charge carriers [26]. Ammonia is an electron donor and when adsorbed on the surface it decreases the number of holes causing an increase in the resistance. Since p-type conductivity is also specific for graphene sensors we decided to look deeper into the effects of porosity and surface chemistry on the sensing mechanism. We had extensive experience with reactive adsorption of ammonia governed by the latter features [10]. Obviously, the presence of acidic groups such as carboxylic or sulfonic (for S – doped carbons) resulted in formation of ammonium ions which contributed to charge transfer. Physical adsorption of ammonia in the pore system (especially in pores smaller than 0.7 nm) was found as a very important feature promoting sensing. It was proposed that charge could hop through the more conductive liquid ammonia than air. More ammonia with stronger forces was adsorbed in pores similar to the size of NH_3 molecule (Fig. 5) enhancing the sensing signal. That ammonia could be also retained in the larger pore through hydrogen bonding. The mentioned above ability of polymer derived carbon to activate oxygen and to form superoxide ions [16, 27] led to ammonia oxidation. Formed NO_2, which is an electron withdrawing molecule, caused an increase in the hole carriers in the matrix resulting in an increase in the chip conductivity when exposed to ammonia [24].

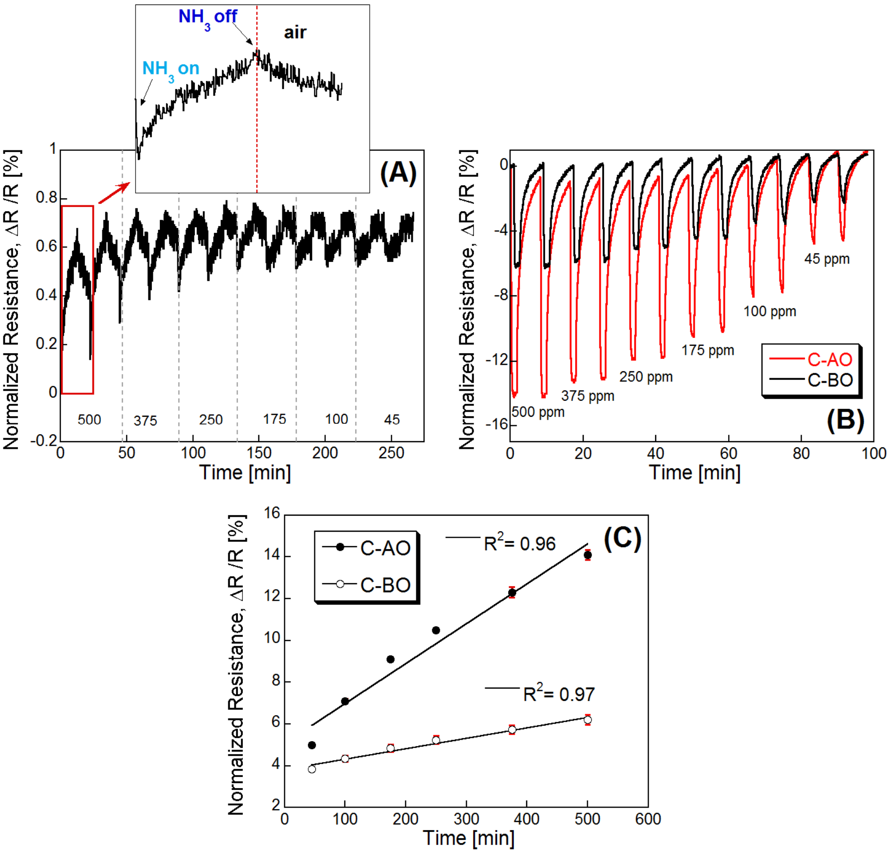

Fig. 4. Response curves for C-B (A), C-AO and C-BO (B) exposed to various ammonia concentrations. (C) Dependence of $\Delta R/R_o$ of the oxidized samples on NH_3 concentration. The error bars are similar or smaller than the size of the data points used. Reprinted with permission from Ref. [24]. Copyright 2016, Elsevier.

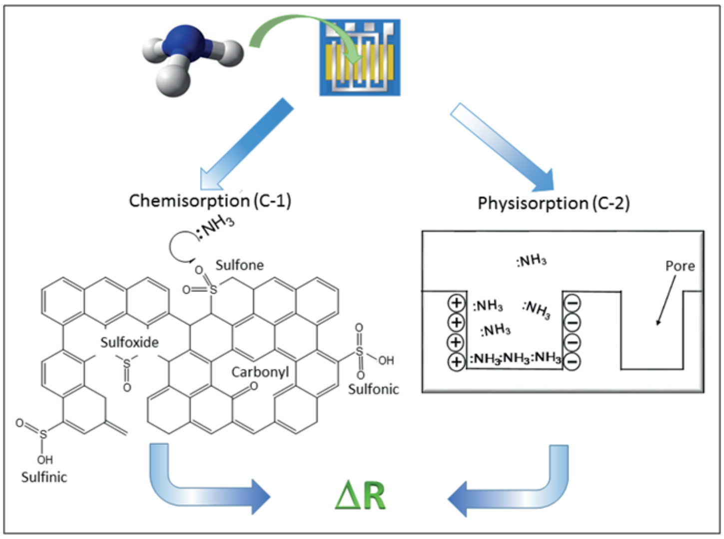

Fig. 5. Visualization of the working principles of the nanoporous-carbon based sensor (only sulfur-containing groups active in adsorption of NH_3 are presented on the surface of the C1-carbon). Reprinted with permission from Ref. [23]. Copyright 2015, Elsevier.

The application of carbons as gas sensors is a very exciting field of research. Ammonia is considered as a toxic industrial compound (TIC) and carbon-based sensors, when incorporated to garment can not only detect ammonia but also protect against it. The challenge would be in sensitivity of the chip and their stability at ambient conditions. For the former, an extensive study on the effects of surface chemistry is needed.

5. Conclusions

This minireview provides the examples of our recent research approach leading to applications of nanoporous (microporous) carbons beyond adsorption phenomenon. We want to show and explore the photoactivity of carbons in visible light and their electronic properties. Those features might open new routes for the applications of nanoporous carbons in energy harvesting and other cutting-edge applications. We also consider gas sensing ability as an important feature since the signals measured are comparable to those on graphene and porous carbons provide something very unique, which so far could not been achieved with graphene without its significant alterations – a developed surface area. A significant challenge is in explaining the complex phenomena on nanoporous carbons. This is due to the fact that both chemistry and porosity contribute to the observed/measured behavior and it is practically impossible to separate these two contributions. A confined space in small nanopores can also affect the thermodynamic of the processes. Nevertheless, we hope that our results will inspire other carbon scientists to go deeper and immerse into the phenomena addressed in this minireview. So far we have consider that only a surface has been scratched…..

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