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COMMUNICATION

Modification of activated carbons based on diazonium ions *in situ* produced from aminobenzene organic acid without addition of other acid†

Estelle Lebègue,[abc] Lenaic Madec,[b] Thierry Brousse,[c] Joël Gaubicher,[b] Eric Levillain[a] and Charles Cougnon*[a]

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Activated carbon products modified with a benzene sulfonic acid group were prepared based on the spontaneous reduction of diazonium salts *in situ* generated in water without addition of an external acid. The diazotization reaction assisted by the organic acid substituent, produced at once amine, diazonium and triazene functionalities that maximize the grafting yield by a chemical cooperation effect.

Diazonium chemistry offers great potentialities for the preparation of functionalized carbons which can be used in many applications including materials for energy storage. This chemical grafting procedure has been recently used by our group for preparing silicon/graphite[1] and silicon/CNTS nanocomposites acting as negative electrodes in lithium ion batteries.[1,2] The performances of pseudo-capacitive materials applied to the energy storage have also been maximized by chemical grafting of redox functionalities. Resultant supercapacitors are promising for the improvement of the capacitance gain, since electrochemical double layer and faradaic reaction occur in tandem.[3–6] Nevertheless, the additional redox pseudo-capacitance is directly related to the grafting yield at surfaces. Since then, many efforts have been made to increase the faradaic charge without damaging the purely capacitive storage.[7,8] In this context, Bélanger and coworkers have recently concluded that "other approaches need to be developed to increase the grafting yield at the carbon powder substrate",[7] whereas Pickup and coworkers claim that "the presence of HCl clearly inhibits the coupling of the diazonium ion to the carbon, while H_3PO_2 has an even greater inhibiting effect".[8] Subsequently, improving the yield of chemical grafting at surface is the bottleneck for increasing electrochemical performance of surface modified carbons in energy storage applications.

In general, two equivalents of protons are required for the Griess reaction, but diazotization was already performed with less than two protons per amine and even, when the aromatic amine contains a strong acidic substituent, the Cabot Corporation report that the diazotization occurs with no additional acid.[9] Nevertheless, the diazotization assisted by the acidity of the amine-containing compound is not well understood and the process by which the grafting occurs was not studied.

Here, we report on the preparation of activated carbon products based on the spontaneous reduction of diazonium salts *in situ* generated in water without addition of other acidic species than those already present onto the molecule as substituents. Comparison with *in situ* diazotization in HCl solution, chemical composition analyses and X-ray photoelectron spectroscopy allow the conclusion to be drawn that the substituent-assisted diazotization route is efficient for spontaneous derivatization of activated carbon (Norit-S50) and glassy carbon (GC) electrodes. The procedure is illustrated by the use of 4-aminobenzene sulfonic acid (4-ABSA) in pure water with the addition of sodium nitrite.

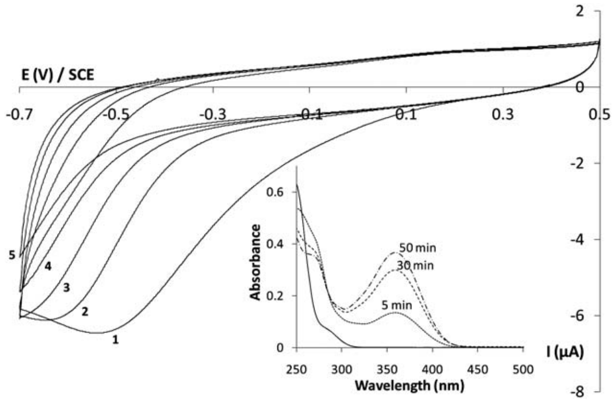

Fig. 1 CVs recorded at a GC electrode in deaerated water + 0.1 M $LiClO_4$ containing 5 mM 4-ABSA and 3 eq. $NaNO_2$. The scan rate was 50 mV s^{-1}. Inserts show UV-visible spectra recorded 5, 30 and 50 min after addition of $NaNO_2$. Solid curve in UV-visible spectra correspond to 4-ABSA in a $NaNO_2$-free solution (see ESI† for more experimental details).

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[a] *Laboratoire MOLTECH Anjou, UMR-CNRS 6200, Université d'Angers, 2 boulevard Lavoisier, 49045 Angers, France. E-mail: charles.cougnon@univ-angers.fr; Fax: +33 (0)2 41 73 54 05; Tel: +33 (0)2 41 73 52 66*
[b] *Laboratoire de Génie des Matériaux et Procédés Associés EA 2664, Polytech Nantes, Université de Nantes, BP50609, 44 306 Nantes, France*
[c] *Institut des Matériaux Jean Rouxel, 2 rue de la Houssinière, BP32229, 44322 Nantes, France*

† Electronic Supplementary Information (ESI) available: Synthesis of 4-diazobenzene sulfonic acid, GC electrode modification, preparation of NS1, NS2, NS3 and NS4, CVs (Figure S1) and UV-Visible spectra (Figure S2) for diazotization of 4-ABSA in 0.5 M HCl, NMR spectrum (Figure S3) for self-diazotization of 4-ABSA in D_2O and CVs (Figure S4) of modified GC electrode in 5 mM $Fe(CN)^{3-/4-}$ redox solution in water. See DOI: 10.1039/c1jm11538c/

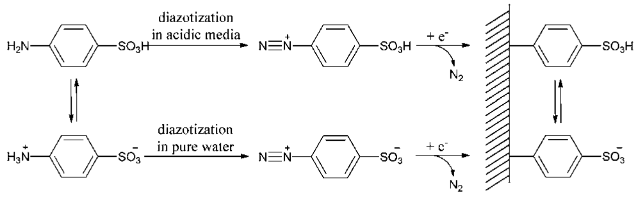
Fig. 1 shows typical cyclic voltammogram (CV) responses and UV-visible spectra for the *in situ* substituent-assisted diazotization of 4-ABSA. CVs recorded in HCl-free solution, 30 min after $NaNO_2$ addition, show typical *I–E* patterns as for the *in situ* diazotization in strong acidic conditions (Fig. S1†), except a lower intensity in current. The first CV recorded at a GC electrode shows an irreversible wave located at −0.54 V that corresponds to the reduction of the *in situ* produced diazonium salt to form the substituted phenyl radical, which passivates the carbon surface. Concomitantly, after $NaNO_2$ addition, a peak at 270 nm emerges on the UV spectrum that can be attributed to the diazonium ion, which rapidly reacts with the initial primary amine to provide a triazene (λ_{max} = 358 nm). These assignments were confirmed by UV performed in 0.5 M HCl (Fig. S2†) and by NMR experiments in D_2O (Fig. S3†).

In pure water, it is assumed that the sulfonic acid protonates the amino group,[10] after which the diazonium ion can be generated (Scheme 1).

Because only one proton per arylamine compound can be provided, the incomplete diazotization reaction can be combined with the subsequent N-azo coupling due to the nucleophilicity of primary arylamines, to form the symmetric 1,3-diaryltriazene product (Fig. S3†). During the first 30 min, the pH of the solution changes from 2.8 to 5.3 and remains constant beyond. So, the pH is low enough to avoid C-coupling, but not too low for limiting the decomposition of the triazene that would regenerate the starting products.[11] As indicated by NMR experiments in D_2O (Fig. S3†), after a few minutes at room temperature, the self-diazotization reaction was optimal and the solution becomes slightly reddish one hour after sodium nitrite was added. It must be noted that, in our conditions, three days after the diazotization started, the UV-visible spectrum shows an absorption peak assigned to the diazonium salt. So the solution obtained in pure water contains at once amine, azo and triazene functionalities, being suitable for surface derivatization in mild conditions.

Cyclic voltammetry was used to investigate the blocking properties of modified GC electrodes in the presence of ferri-ferrocyanide in water (Fig. S4†). For electrografting, strong blocking effects against redox reaction were obtained whatever the conditions in which the diazonium salts were produced (in acidic condition or in water). Intriguingly, for electroless grafting, the redox reaction of $Fe(CN)^{3-/4-}$ was more suppressed at a surface modified from 4-ABSA diazotized in acid-free solution. These changes in blocking properties are evidence that electrografting and grafting occur through different mechanisms.

For electrografting, the carbon electrode serves as the cathode and it is well assumed that the neutral aryl radical formed by homolytic dediazoniation is responsible for the arylation of the substrate. For chemical grafting, the mechanism remains elusive. Mono- or multilayers can be obtained, depending on the substrate and to the conditions used. Downard and co-workers[12] have recently claimed that two distinct mechanisms are responsible for the grafting at a glassy carbon surface: a first potential-dependent process gives the radical aryl and a second potential-independent step extends the film growth by chemical grafting onto a primer layer. For the grafting at activated carbon substrates, the mechanism is less clear and no evidence for radical arylation at the surface has been reported.[13] In all cases, less than a monolayer was obtained and, as Bélanger suggests, the grafting is blocked as soon as the available reactive sites at surface are saturated.[7] In the latter study, surface reactions, implying oxygenated functionalities, are suspected. So the chemical grafting is probably the result of complex surface chemistry processes, implying dediazoniation products (phenyl cations or aryl radical), azo-coupling reactions and surface functionalities.



Scheme 1 Reaction systems for the diazotization of sulfanilic acid in acidic solution and in water.

Assuming the inclination of amine-containing compounds to react with carbon,[14] we postulate that the higher blocking effect for GC spontaneously modified in HCl-free solution results in a chemical cooperation of the starting amine and diazo functionalities, which implies different active sites at the carbon surface. To validate our assumptions, activated carbon (Norit-S50) was spontaneously functionalized in various conditions either from *in situ* produced 4-diazobenzene sulfonic acid (4-DBSA) or from previously synthesized 4-DBSA (Table 1).

Highest values of the percentage of sulphur were obtained when the diazotization was promoted by the acidic substituent in pure water (NS1) and when the carbon product was prepared from the synthesized diazonium salt (NS4). On the other hand, the nitrogen content was higher for NS1 compared to all other carbon products. First, these results show that for different conditions in solution, the surface concentration of benzene sulfonic acid groups tends to the same value, suggesting that the grafting mechanism is governed by heterogeneous factors. Second, the highest nitrogen percentage for NS1 is evidence for the concomitant participation of amine and diazo compounds in the grafting process based on the substituent-assisted diazotization procedure. It is noteworthy that the simpler diazotization strategy reported is more efficient for the grafting onto activated carbon than the conventional *in situ* diazotization reaction in HCl solution and as much as with synthesized diazonium salt. In the latter case, only the nitrogen content changes, indicating that the grafting occurs through the amine and the diazonium ion when the diazotization is substituent-assisted.

NS1 and NS2 carbon powders were studied by X-ray photoelectron spectroscopy (Fig. 2). Both carbons show a N 1s peak in the vicinity of 405–406 eV, due to NO_2 groups that stem from the use of sodium nitrite. An additional nitrogen peak, located at 401.4 eV, was observed in NS1 and NS2 carbons with an atomic ratio depending on the *in situ* procedure. This N1s peak, characteristic of ammonium cations, is more intense for the NS1 carbon because the amino group was fully protonated in strong acidic conditions.[15]

Moreover, for NS1 a nitrogen peak at 400 eV mainly contributes to the N1s core level spectrum, unlike NS2 for which the major contribution is located at 399.4 eV. The two latter peaks are evidence that the grafting occurs through different routes depending on the procedure. In the presence of HCl, an azo bond can be suspected,[16] whereas in water, it could be assumed that the unprotonated amine contributes to the grafting. So, in the absence of strong acidic conditions, the grafting at the surface seems to take advantage of the incomplete diazotization reaction by combining amine and diazonium salts for optimal grafting at the surface.

Table 1 Chemical compositions of modified carbon powders

	Grafting conditions				Chemical composition	
Carbons	Eq. $NaNO_2$	V_{HCl} (ml)	Eq. 4-DBSA	Eq. 4-DBSA	%N	%S
NS	—	—	—	—	0	0
NS1	0.6	—	0.2	—	1.39	5.64
NS2	0.6	2	0.2	—	0.83	4.05
NS3	—	—	—	0.2	0.53	4.92
Ns4	—	2	—	0.2	0.66	5.63

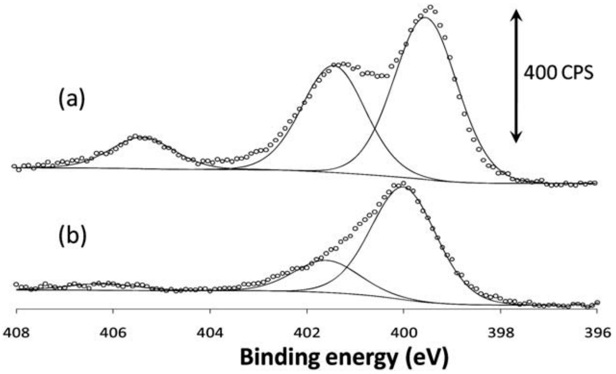


Fig. 2 N1s core level spectra for NS2 (a) and NS1 (b) carbon powders.

Conclusions

To benefit from recent advances in surface chemistry, specific substrates, which are difficult to manipulate as electrodes, require new procedures to increase the grafting yield at surfaces. Herein, a new step in the grafting of activated carbon substrates was reported. Activated carbon products were prepared by electroless grafting based on *in situ* generated diazonium salts. Diazotization of 4-aminobenzene sulfonic acid was promoted by the acidity of the organic acid substituent, without addition of other acid. In such conditions, the grafting at activated carbon substrates is beneficial for the incomplete diazotization reaction and comes from both the amine and the diazonium salt through a chemical cooperation effect. This procedure could be advantageously extended to other aminobenzene organic acids such as aminobenzoic acid or aminobenzene phosphonic acid and is suitable for the preparation of surface-tethered organic acids that can be easily post-derivatized for appropriate applications.

Acknowledgements

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