Covalent Grafting of Organic Molecules onto Activated Carbon by a Single Step

Tao Li,[a,b] Biao Huang,[a] Siqun Wang,[c] Cuixia Chen,[a] Lirong Tang,[a] Qilin Lu,[a] and Wenyi Lin [a]

Activated carbon appended with organic groups was obtained by a grafting technique using a one-step reaction with diazonium salts. Using the organic aryl amines of 4-bromo aniline and 4-aminoantipyrine as precursors for the corresponding functional diazonium reagents, the bromobenzene and antipyrine molecules were bonded to the surface of carbon. The modified activated carbon was characterized by Fourier transform infrared spectroscopy, X-ray and photoelectron spectroscopy, and BET methods. The results provided evidence of covalent grafting of the organic groups onto the activated carbon by aryldiazonium cations. The present method may provide a convenient and efficient procedure for the preparation of various functionalized activated carbons by means of a single step process.

Keywords: Activated carbon; Diazonium salt; Graft; Organic molecules

*Contact information: a: College of Material and Engineering, Fujian Agriculture and Forestry University, FuZhou, Fujian 350002, China; b: School of Life Sciences, Fujian Agriculture and Forestry University, FuZhou, Fujian 350002, China; c: Center for Renewable Carbon, The University of Tennessee, Knoxville, TN 37996-4570, USA; *Corresponding author: fjhuangbiao@hotmail.com*

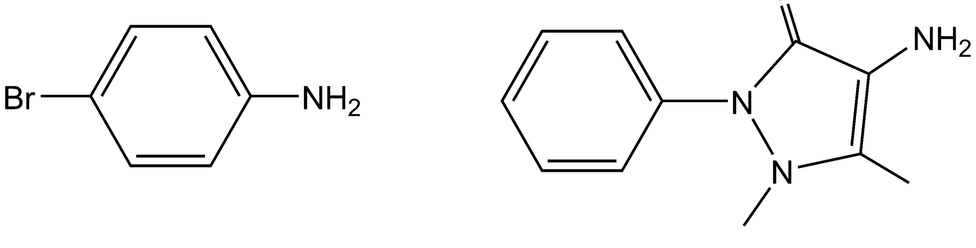
INTRODUCTION

Recently, activated carbons (ACs) have aroused great interest not only because of their physical surface properties, but also the chemical surface properties of specific modification on the carbon materials (Figueiredo *et al.* 1999; Pradhan and Sandle 1999; Julien *et al.* 1998; Li *et al.* 2011; Chowdhury *et al.* 2012; Derylo-Marczewska *et al.* 2008). Research in this rapidly growing area of surface modification has been significant in many fields (Ellison and Gasda 2008). Among the modification techniques developed to date, surface grafting has emerged as a simple, useful, and versatile approach to improving surface properties of ACs for a wide variety of applications (Pal *et al.* 2006; Figueiredo *et al.* 2007; Sharma *et al.* 2009; He *et al.* 2011; Bansode *et al.* 2004; Rivera-Utrilla *et al.* 2011; Thirumalisamy and Subbian 2010).

Many different grafting routes can be employed to introduce compounds onto the surface of AC. The grafting methods can be generally divided into two classifications, *i.e.*, grafting-on and grafting-to processes. The grafting-on method utilizes active species existing on the AC surface to change the chemical properties of treated carbon materials (Nguyen-Thanh and Bandosz 2005; Choi *et al*. 2009; Shi *et al*. 2011; Ma et al. 2011). In the case of the grafting-to method, selected organic molecules carrying reactive groups are covalently coupled to the functional groups of the AC surface (Mahata *et al*. 2007; Silva *et al*. 2001, 2007; Toumi *et al*. 2006). In most cases ACs are pretreated to improve the surface reaction activity before modification. The most common grafting-to method is to form amides, esters, or ethers that will connect organic molecules with amide groups or hydroxy groups to the AC surface. Before grafting it is necessary to increase the quantity of carboxyl and hydroxy groups on the ACs (Zhu *et al.* 2009; Silva *et al*. 2002; Alves *et al*. 2001). Such functionalizations have been most extensively explored through oxidation and reduction processes. The former generates carboxylic acids, which have been further derivatized by reactions with thionyl chloride and amines or by esterification (Tamai *et al*. 2006; Zhu *et al*. 2009; Wang *et al*. 2009), while the latter often involves hazardous reducing reagents (*e.g.*, $AlLiH_4$ and $NaBH_4$) for the reaction (Alves *et al*. 2001; Cosnier *et al*. 2005). The technology behind these modes of connection onto the surface by these bonds is mature, but the bonds tend to be fairly unstable and restrictive. A severe drawback of all processes thus far established has been the extraordinary amounts of noxious chemical reagents (thionyl chloride and sodiumborohydride) required for the activation process of the carbon. Moreover, some corrosive oxidants tend to destroy the framework of the AC, which affects its adsorption ability.

To overcome the above limitations for the functionalization of ACs, one of the most challenging tasks is to develop novel selective and highly efficient reaction systems containing diazonium salts. In the literature, diazonium compounds have been covalently grafted to the surface of carbon materials, such as grafting through electrochemical (Bahr *et al*. 2001) or chemical reduction of aryl diazoniums (Pandurangappa *et al*. 2002). However, the instances of ACs modified by diazonium compounds are limited.

The main focus of this work is to graft organic molecules onto the surface of ACs with diazonium salts supplied by aryl amines. To accomplish this, a one-step but effective and eco-friendly functionalization of AC without oxidation or reduction processes is presented. Compared to other grafting sources, diazonium salts can offer (1) easy availability and low cost of the starting materials, (2) mild modifying conditions (low temperature and ambient pressure), (3) no activation process, (4) reaction in aqueous solutions, and (5) using only small amounts of solvents. The present functionalization is based on the substitution of aryl groups, which uses the organic aryl amines of 4-bromoaniline and 4-aminoantipyrine (Fig. 1) as precursors for the corresponding functional diazonium salts. These precursors were chosen on the basis of the aryl primary amine. Precursors of the form $R\text{-}Y\text{-}NH_2$, where Y can be any aryl group and R is an organic group or inorganic anion such as a halogen, readily decompose to form the diazonium cation $R\text{-}Y\text{-}N_2^+$ at a low temperature (about 273 K). The reagent 4-bromoaniline ($Br\text{-}Ph\text{-}NH_2$**)** decomposes to form bromobenzene diazonium salt, and then they can subsequently release nitrogen in the process of being coupled to the carbon. 4-aminoantipyrine ($APy\text{-}NH_2$**)** would be expected to be attached to the carbon by a similar route (Fig. 2). The diazonium salts from precursors can form covalent single bonds onto the ACs to generate samples of AC1 and AC2.



(a) (b)

Fig. 1. Structure of the precursors for the corresponding functional diazonium salts. (a) 4-bromoaniline, (b) 4-aminoantypirine

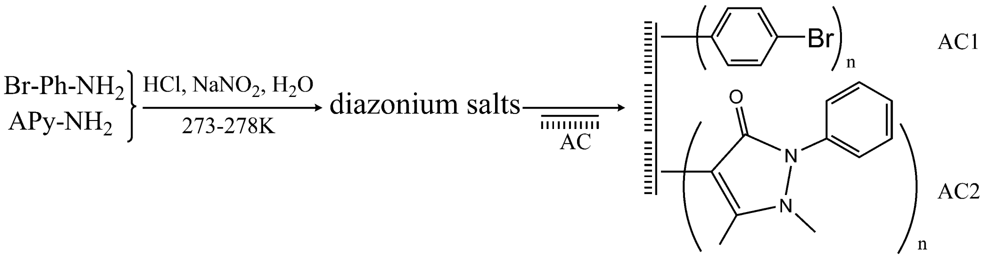


Fig. 2. Functionalization performed with organic molecules onto AC by diazonium salts

EXPERIMENTAL

Materials

All reagents (Sinopharm Chemicals Reagent Co.) were commercial products of the highest purity available (>98%) and used for the reactions without further purification. The AC used in this study was FuJian Yuanli 200 mesh.

Preparation of AC1 and AC2

AC1

To prepare AC1 (Dyke and Tour 2003), 1.72 g 4-bromoaniline was dissolved in 25 mL of deionized water and mixed with 2.5 mL of concentrated HCl. Next, a 10% solution of 7 g sodium nitrite was dropped into the mixture at 273 to 278 K for 0.5 h, after which the diazonium solution was mixed with 0.24 g AC and stirred for 1.5 h. The mixture was filtered, and the purified AC was washed with deionized water and ethanol through soxlet extraction for 12 h to ensure the removal of all free chemicals from the carbon. Finally, it was dried under vacuum at 80 °C for 12 h.

AC2

To bond the antipyrine, 8 g of 4-aminoantipyrine was dissolved in 50 mL of deionized water and mixed with 8 mL of concentrated HCl. Then, a 16% solution of 18 g sodium nitrite was dropped into the mixture at 273 to 278 K for 0.5 h. After that, the general procedure was similar to the preparation of AC1.

Characterization

Fourier transform infrared spectroscopy (FT-IR) was performed with a Nicolet 380 FT-IR Spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific Escalab 250 equipped with an Al Kα X-ray source. The binding energies were corrected for specimen charging by referencing the C1s peak to 284.6 eV and analyzed with the Peakfit software (version 4.12). The values of atomic sensitivity factors for C, N, O, and Br are 0.25, 0.42, 0.66, and 0.83, respectively. The Shirley method was used for the background subtraction in XPS. The porous texture was characterized by the adsorption of N_2 in a semiautomatic adsorption SSA-4000 apparatus. Prior to measuring the adsorption isotherm, the activated carbon was heated at 573 K for 4 h in vacuum to clean its surface. The specific surface area of the AC was calculated based on the adsorption isotherm data of N_2 by the Brunauer-Emmett-Teller (BET) method. The mesopore volume was calculated based on the amount of N_2 adsorbed within a relative pressure range of 0.01 to 0.99 by the Barrett-Joyner-Halenda (BJH) method.

RESULTS AND DISCUSSION

The functionalization procedure was based directly on diazonium reactions. Considering that radical grafting has been widely demonstrated, it can be suggested that the use of mediated diazonium salts is an alternative way to generate aryl radicals at a potential where these intermediates cannot be oxidized to their corresponding carbocations. In this way the grafting of a carbon surface with aryl groups could be achieved starting from aryl amines. The procedure of the grafting is shown in Fig. 3.The results showed that it is possible to anchor the benzene rings with para bromo groups and antipyrine onto the ACs. It is notable that bromobenzene molecules can be further connected with other functional groups, using the convenient Grignard reagent. As a support, the carbon with bromo-benzene may be a better-stabilized intermediate for linking other functional groups. Alternatively, anti-inflammatory antipyrine molecules may act as a sustained-release drug, supported by the carbon.

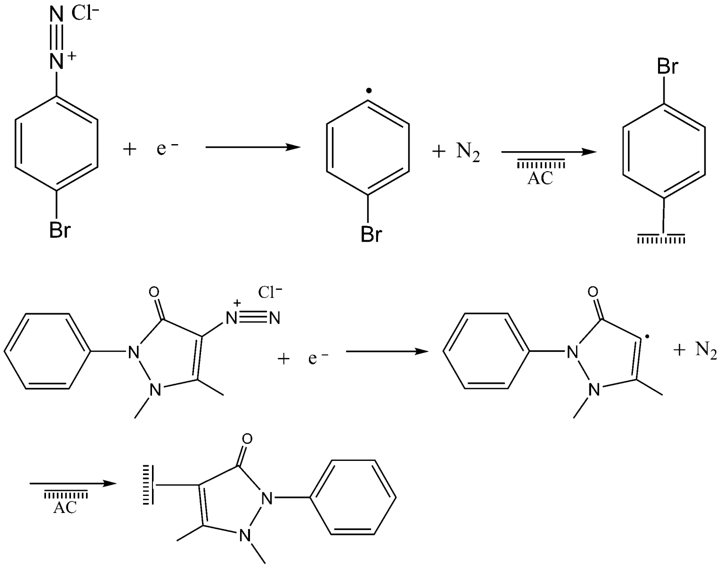


Fig. 3. The aryl diazonium salts covalently attached to carbon surface by giving reactive radicals

Identification of Surface Functional Groups by FT-IR

Figure 4 shows the spectra of the different samples. In the case of AC, the peak at 3424 cm^{-1} arises from the O–H stretch. The carbonyl stretch of AC occurred at 1686 cm^{-1}. The peak near 1600 cm^{-1} corresponds to polyaromatic C–C stretching. The peak at 1172 cm^{-1} indicates C–O stretching. The FT-IR spectrum of the functionalized AC1 was dominated by a peak at 3454 cm^{-1}, arising from O–H stretching vibrations. The carboxylic C=O stretch was evident at 1707 cm^{-1}, whereas the C–O–H in-plane bend and the C–O stretch were identified at 1484 and 1248 cm^{-1}, respectively (Pradhan *et al.* 1999). Notably, the strong band at 822 cm^{-1} in the molecule appeared in the spectrum of the AC1, which indicates a 1,4-disubstituted mode. In addition, a C–Br band at 518 cm^{-1} was observed (Silverstein *et al.* 2005). The results are consistent with the product of the reaction of 4-bromoaniline, indicating that the bromobenzene groups were indeed available to para-graft onto the AC. The IR peaks of AC2 at 1697, 3407, and 1400-1600 cm^{-1} are due to C=O, O–H, and aromatic rings (Zawadzki 1980), respectively. The appearance of a weaker peak at 1385 cm^{-1} is attributed to the C–H symmetrical bending vibration of the methyl groups, and the asymmetrical bending vibration is at 1418 cm^{-1}

(Silverstein *et al.* 2005). The existence of methyl stretching provides good evidence that the molecules were bound to the AC. The weaker peak observed at 1104 cm^{-1} arises from C–N vibrations. In the 680-850 cm^{-1} region, several peaks were observed at 682, 707, and 682 cm^{-1} that arise from the phenyl-like C–H vibrations. The results showed that although a few of the peak positions remained unchanged, there were very significant changes in the absorption bands. The evidence presented in the IR spectra of the AC1 and AC2 confirms the covalent grafting of organic molecules onto the surface.

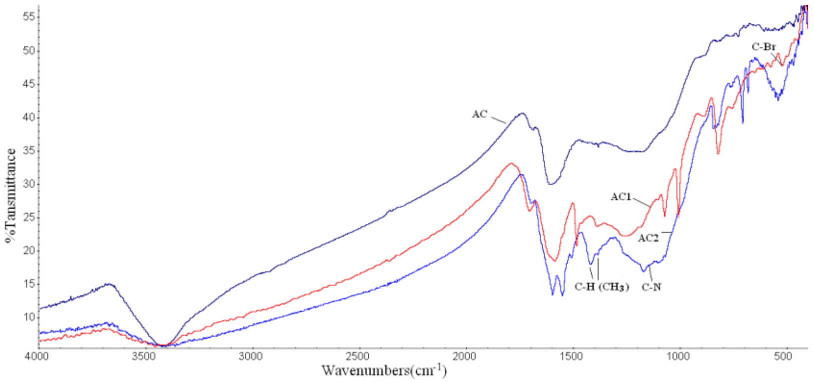
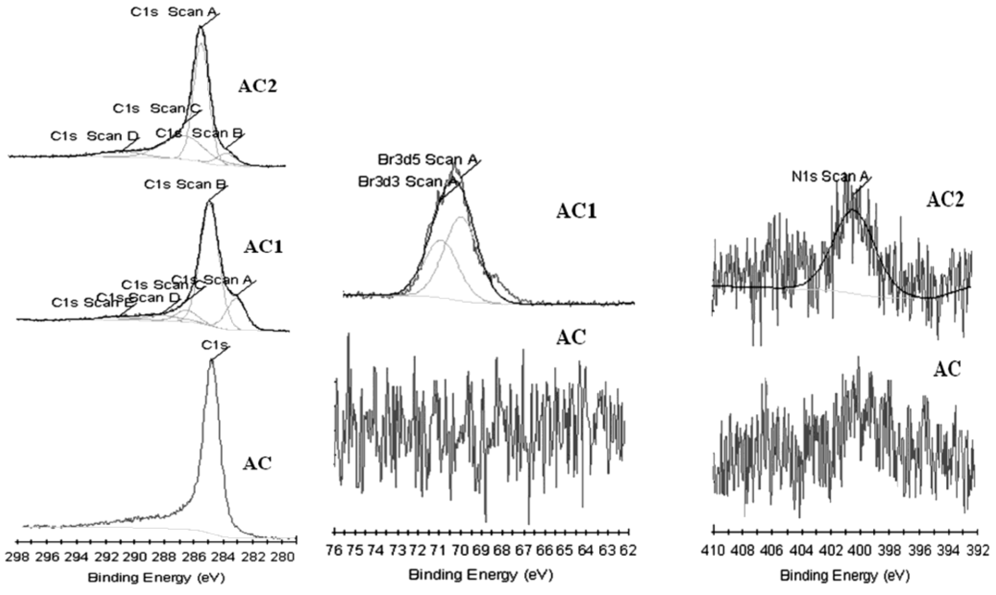


Fig. 4. FT-IR spectra of AC, AC1, and AC2

X-ray Photoelectron Spectroscopy

The XPS spectra of AC1 and AC2 are shown in Fig. 5. All samples showed an intense peak in the C1s region (Fig. 5a) centered at about 284.7 eV, due to the graphitic structure (Figueiredo *et al.* 1999). In the XPS spectra of ACs, there were new peaks due to bromine in AC1 and nitrogen in AC2. The calculated Br/C, N/C, and O/C atomic ratios are presented in Table 1. Figure 5b shows the corresponding Br(3d) spectra. The Br(3d) spectra clearly show two Br peaks at 70.28 and 71.23 eV (Wagner *et al.* 1979). The observed Br/C atomic ratio of 0.069 indicates that some of the surface atoms in AC had



(a) (b) (c)

Fig. 5. XPS spectra of samples: (a) C(1s), (b) Br(3d), (c) N(1s)

been displaced. The new peaks were attributed to anchored bromobenzene formation. The N(1s) spectrum (Fig. 5c) shows a single peak with binding energy 400.1 eV and a full width at half-maximum (fwhm) of 3.34 eV, suggesting that there was only one chemically distinguishable form of nitrogen on the surface'. The observed N/C and O/C atomic ratios of 0.011 and 0.15 indicate that some of the surface atoms in AC had been displaced. The results are in agreement with N(1s) spectra for antipyrine bonded onto AC.

Table 1. XPS Elemental Atomic Ratios and Atomic Percentage for ACs

Sample	C (%)	N (%)	O (%)	Br (%)	Br/C	N/C	O/C
AC	90.01	<0.1	9.98	-	-	-	0.11
AC1	85.64	-	8.41	5.94	0.069	-	0.098
AC2	86.41	0.98	12.61	-	-	0.011	0.15

Porous Texture of ACs

Figure 6 shows the N_2 adsorption isotherms of samples at 77 K; all of them were type II. The adsorption volume presented a quick increase at relatively low pressure, indicative of the developed microporosity of ACs. The results in Fig. 6 also imply that the adsorbed nitrogen volumes of AC1 and AC2 were lower compared with the AC, indicating that the grafting process had an effect on the adsorption capacity of the AC.

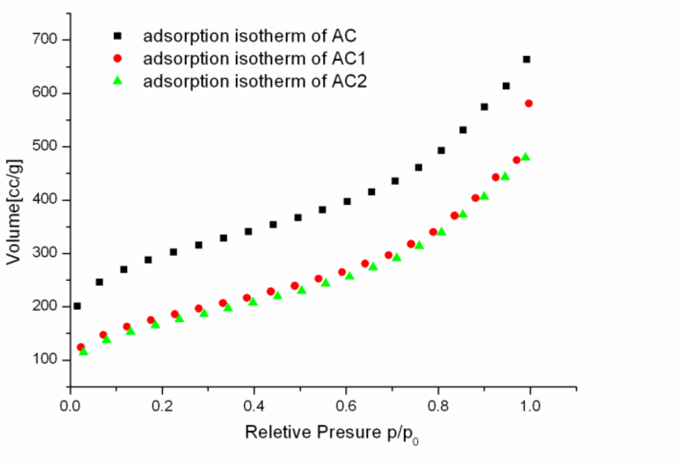
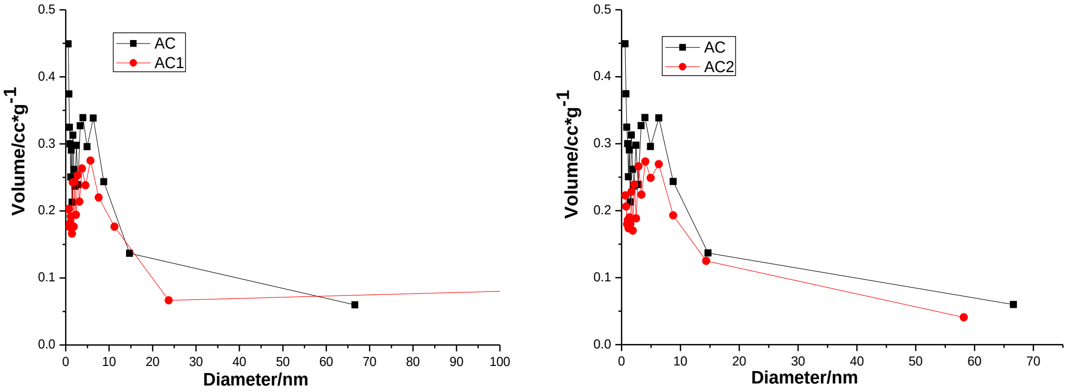


Fig. 6. Adsorption isotherm of N2 at 77 K

Table 2. Porous Parameters of ACs*

Sample	S_{BET} [m^2/g]	V_t [ml/g]	D_{avg} [nm]	V_{mi} [ml/g]	BJH S_{me} [ml/g]	 V_{me} [ml/g]	 D_{me} [nm]
AC	1052	1.032	1.96	0.471	606	0.814	2.68
AC1	631	0.903	2.86	0.289	406	0.623	3.07
AC2	593	0.746	2.50	0.274	495	0.679	2.75

* S_{BET} is the specific surface area of activated carbon, V_t is the total adsorption volume of activated carbon, V_{mi} is the microporous adsorption volume of activated carbon, S_{me} is the mesopore specific surface area, V_{me} is the mesopore volume, and D_{me} is the average mesopore diameter



(a) (b)

Fig. 7. Pore size distributions of (a) AC and AC1, (b) AC and AC2

Some physical properties of the tested ACs are tabulated in Table 2. The values of V_t and V_{mic} decreased from the treatment with diazonium salts. When the reaction occurred, the process enlarged the existing micropores of AC1 and AC2. The micropores constituted *ca.* 50% of the total volume. Moreover, inspection of Fig. 7 also suggests micropore size large distribution of ACs. However, compared with the results in Table 2 it is clear that the grafting of organic groups resulted in a decrease of the BET surface areas of AC1 and AC2. It is well known that these grafting molecules can cause some hindrance to the pores' entrance (Figueiredo *et al.* 1999), which might have restricted the accessibility of the porous surface to nitrogen at 77 K. In addition, the relative micropore ratio decreased slightly and the relative mesopore ratio increased. The pore volume decreased in the macropore range (>50 nm), which indicates that the chemical treatment of AC resulted in the development of mesopores and the reduction of macropores.

CONCLUSIONS

1. A single-step process was used to graft the bromobenzene and antipyrine onto activated carbon (AC) through functional diazonium salts.
2. The grafted molecules bonded to the surface of carbon could not be removed by protracted treatment with reagents.
3. This functional process directly attaches groups by diazonium salts and can be regarded as a potentially valuable tool for simplifying the attachment of further functionalities to ACs.

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