

Derivatization and characterization of functionalized carbon powder via diazonium salt reduction

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Abstract Chemical reduction of 4-chloro-2-nitrobenzene-diazonium chloride salt in the presence of hypophosphorous acid and carbon powder results in functionalized carbon powder with chloronitrophenyl groups attached on carbon particle surface. This type of bulk derivatization protocol is very useful and most inexpensive compared to widely used electrochemically assisted derivatization protocol. The derivatized carbon powder has been characterized by studying its Fourier transform infrared spectroscopy (FTIR) and cyclic voltammetric studies. The surface functionalized moieties have been examined electrochemically by immobilizing them onto the surface of basal plane pyrolytic graphite electrode and studying its cyclic voltammetry. The effect of pH, scan rate (ν), and the peak potentials (E_p) as a function of pH has revealed that the species are surface bound in nature and covalently attached on the carbon surface. The FTIR studies of the derivatized carbon powder have revealed that the modifying molecule is covalently attached on the carbon particle surface.

Keywords Functionalization · Diazonium salt · Modified carbon · Immobilization · Cyclic voltammetry

Introduction

Chemically assisted covalent modification of carbon surfaces by the reduction of diazonium salts for sensing a variety of analytes is a recent development in the area of

modified electrodes [1]. The resulting material can be used in “electroanalytical chemistry” due to its selective indicator properties. The functionalization of carbon surfaces has allowed electrochemists to use modified material directly to fabricate electrodes, which offer distinct advantages for catalysis, analysis, combinatorial chemistry, and biological applications over the past few years [2, 3]. The modification procedures reported are mainly based on two major strategies. The first approach in this type is based on the direct electrochemical oxidation of carbon surfaces by applying an oxidizing potential sufficiently high enough to produce oxygenated functional groups on carbon surface, and the second approach is electrochemically induced one which relies upon the formation of a covalent bond between a carbon electrode and the functional group [4]. To carryout electrochemical derivatization, the carbon surface has to be in the form of rigid electrode, which can be undesirable under certain applications. In case of chemical-assisted derivatization procedure, various forms of carbon have been used such as glassy carbon, highly oriented pyrolytic graphite, carbon fibers, glassy carbon spheres, carbon felts, and more recently, carbon in another form, i.e., nanotubes (CNT) [5]. Carbon-based materials are relatively inert in most of the electrolytic solutions, while retaining a high degree of surface activity. They have a wide potential window and easy to derivatize to form bulk-modified carbon electrodes (BMCE) [6]. The bulk-modified carbon powder can be compressed into pellets and used as an electrode material to fabricate BMCE or pencil rod electrodes. Carbon powder can be conveniently derivatized with suitable functional moieties to fabricate carbon electrodes with required properties on its surface which can be used as bulk-modified electrodes to sense analytes [7]. This type of chemically modified electrodes can be potentially applied in sensing environmental pollutants, toxic metal ions in

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industrial effluents at trace level and pH sensors [8]. Bulk modification of carbon powder through diazonium salt reduction facilitates easy and inexpensive methodology to modify different carbon materials in fabrication of ion sensitive and selective electrodes [9]. Herein, we describe the derivatization of carbon powder with chloronitrophenyl groups and its electrochemical characterization by immobilizing them onto the bppg electrode and studying its electrochemical behavior of the functional moieties.

Experimental

All reagents used were Analar grade and used without further purification. The synthetic graphite powder (<20 μm diameter) was purchased from Aldrich (purity > 99%) and used directly, and it consisted of irregularly shaped particles. Hypophosphorous acid (50%) was purchased from Merck grade, Fast Red 3 GL Salt AR Grade (purity 99%), and potassium bromide for IR spectroscopy (FT-IR grade, $\geq 99\%$) was obtained from Sigma-Aldrich. Solutions of known pH in the range 1.0 to 12 were prepared using deionized water from MilliQ water purifier (Millipore, USA) with a resistivity of not less than $18.2 \text{ M}\Omega \text{ cm}$ as follows: pH 1, 0.1 M HCl; pH 2, 0.1 M sodium citrate + 0.1 M HCl; pH 3, 0.1 M glycol + 0.1 M NaCl + 0.1 M HCl; pH 4, 0.1 M acetic acid + 0.1 M Sodium acetate; pH 5, 0.2 M acetic acid + 0.1 M Sodium acetate; pH 6, 0.2 M acetic acid + 0.2 M Sodium acetate; pH 7, 0.01 M KH_2PO_4 + 0.01 M Na_2HPO_4 ; pH 8, 0.01 M KH_2PO_4 + 0.01 M Na_2HPO_4 ; pH 9 0.05 M sodium tetra borate (H_3BO_3 + 1 M NaOH); pH 10, 0.1 M sodium tetraborate + 0.1 M NaOH; pH 11, 0.01 M NaOH, or KOH. The cell contained 4 ml of buffer and 4 ml of 0.1 M KCl as supporting electrolyte.

Voltammetric measurements were performed using a CH Instruments (Texas, USA) Model 619B series computer controlled Potentiostat. All electrochemical measurements were carried out at room temperature ($27 \pm 2 \text{ }^\circ\text{C}$) in an electrochemical cell of volume 10 cm^3 with a standard

three-electrode configuration after degassing the solutions using ultrapure nitrogen gas for 15 min. A basal plane pyrolytic graphite (bpgg, 0.2 cm^2 , Le Carbone Ltd, Sussex, UK.) electrode acted as the working electrode. A moulded Pt (99.99%) wire was used as a counter electrode and CH Instruments (Texas, USA) Ag/AgCl (3 M KCl) as a reference electrode. All pH measurements were carried out using Control Dynamics pH meter. Scanning electron micrograph images were recorded by using JEOL (JSM-840A) scanning electron microscope. All the FTIR spectrophotometer measurements were performed using FTIR-8400S Shimadzu.

Analytical procedure

Derivatization protocol

Two grams of graphitic carbon powder is mixed with a 25-ml of 5 mM solution containing 4-chloro-2-nitrobenzene-diazoniumchloride to which 30 ml of hypophosphorous acid (H_3PO_2 , 50%) is added slowly. The reaction mixture is then left to stand for 30 min with occasional stirring at regular intervals. After this, the resulting 4-chloro-2-nitrophenyl-modified carbon (CNPCarbon) was then filtered under suction and washed with ample quantities of acetonitrile, acetone, and water to remove any unreacted, physisorbed species. The CNPCarbon was then dried by placing inside a fume hood for a period of 12 h and finally stored in an airtight container before use Scheme 1 [2, 10].

Surface morphology of functionalized carbon powder

The surface morphology of functionalized carbon powder has been examined by studying scanning electron microscopy. It was carried out by spreading the carbon particles on fine qualitative filter paper and attaching them onto a small conducting strip by gently tapping the filter paper containing carbon powder and taking SEM images. The corresponding SEM images of derivatized carbon particles

Scheme 1 Homogeneous derivatization of carbon powder with chloronitrophenyl moieties

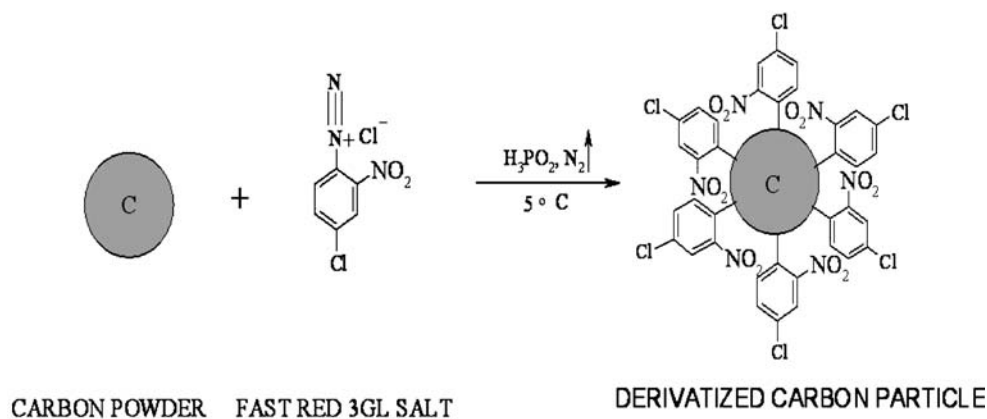
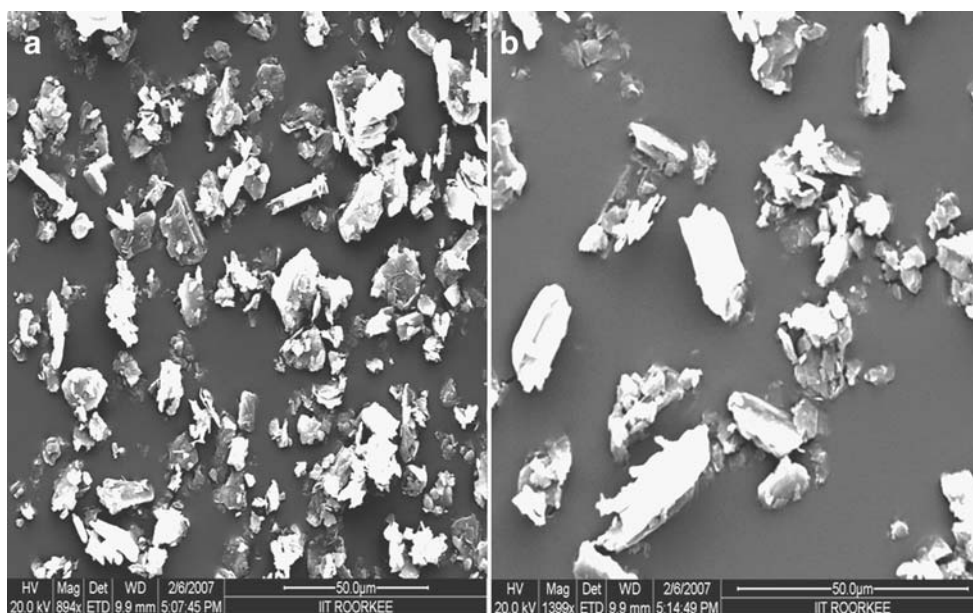


Fig. 1 Scanning electron microscopy images of **a** native carbon powder; **b** functionalized carbon powder

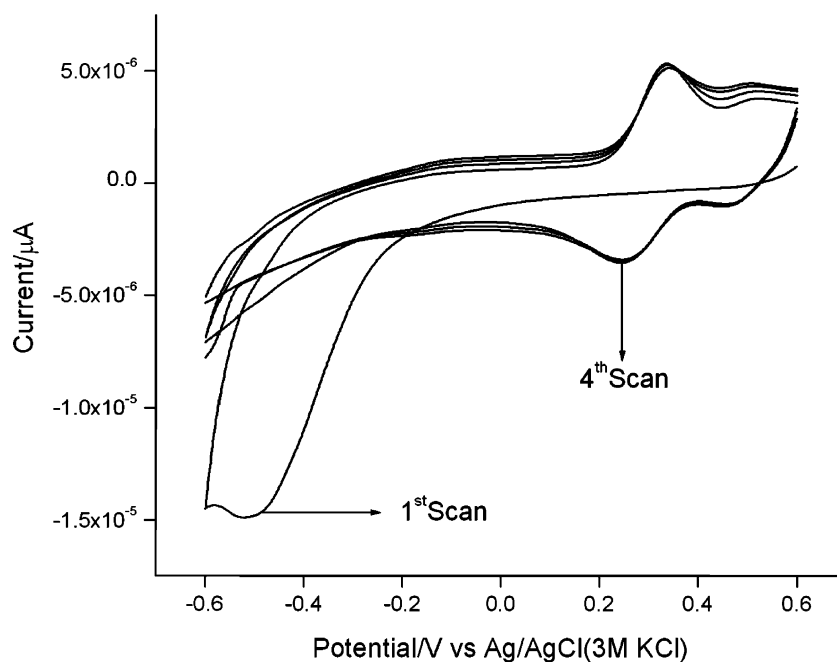


have revealed that the chloronitrophenyl-group-modified carbon particles have broadly similar surface morphology than its underivatized counterparts (Fig. 1 a,b). The surface coverage values have been obtained from the charge of the respective oxidative (E_{pa}) and reductive (E_{pc}) peaks of corresponding voltammograms (Fig. 2) on the charge obtained by the integration of the reductive/oxidative peaks at a scan rate (ν) of 50 mV/s. The relative peaks (E_p) positions at ca -0.521 , 0.244 , and 0.336 V are shown in Fig. 2. The surface concentration was calculated by using the formula $\Gamma = q/nFA$ where q =charge of the peak [C], n =

number of electrons involved in the redox process, F =Faraday constant [C/mol], A =area of the electrode [cm^2], Γ =surface concentration on the electrode [mol/cm^2]. Based on the charge of reductive peaks (Fig. 2), the surface concentration was found to be 3.6×10^{-8} , 3.5×10^{-9} , and 3.5×10^{-9} mol/ cm^2 for oxidative and reductive peaks, respectively [11].

Next, we have measured the specific surface area (SSA) of commercially procured graphitic carbon powder and functionalized carbon powders by studying adsorption/disorption isotherms using nitrogen as an adsorbate. The

Fig. 2 The initial four scans of voltammetric behavior of 4-chloro-2-nitrophenyl-derivatized carbon immobilized on bppg electrode at pH 1 (0.1 M HCl+0.1MKCl) scan rate (100 mV/s)



commercially procured graphitic carbon powder has showed specific surface area of 34 m²/g, functionalized carbon powder with a value of 13 m²/g. The specific surface area decreased upon functionalization, which might be due to the agglomeration during the derivatization protocol. The surface area in functionalized carbon has decreased by 61% after functionalization. These results proffer that the functionalization may result in partial intercalation along with the bundling or agglomeration of the carbon particles [9, 12–15]. However, the SEM images of the modified carbon particles looks like uneven in size and irregularly shaped which might be due to the agglomeration of carbon particles during chemical derivatization process. Based on the above facts, we conclude that the surface morphology of functionalized carbon particles has altered when compared to native carbon particles.

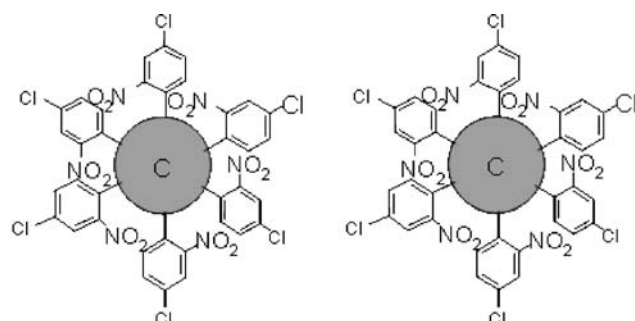
Electrode modification

The chloronitrophenyl derivatized carbon particles have been electrochemically characterized by abrasively immobilizing them onto the surface of the basal plane pyrolytic graphite electrode. This is done by initially polishing the electrode on glass polishing paper (H00/240) after which it is again polished on silicon carbide paper (P1000C) for smoothness. The derivatized carbon powder is mechanically immobilized onto the bppg electrode by gently rubbing the electrode surface on a fine qualitative filter paper (Whatman) containing the functionalized carbon (Scheme 2).

Results and discussion

Voltammetric behavior of modified carbon powder

The derivatized carbon was examined electrochemically to verify whether the modifying molecule has been attached



Scheme 2 Schematic diagram of the 4-chloro-2-nitrophenyl-derivatized carbon powder immobilized on bppg electrode

on the carbon particle or not during chemical derivatization process. The electrochemical behavior of chloronitrophenyl carbon powder was characterized by immobilizing it on basal plane pyrolytic graphite (bppg) electrode and studying its cyclic voltammetry. Figure 2 shows the initial four scans of modifying carbon powder at pH1 with a scan rate of 100 mV/s in a solution(0.1 M HCl + 0.1 M KCl) at potential range 0.6 to –0.6 V. The first scan in a reductive sweep from 0.6 V with a scan rate (ν) of 100 mV/s showed a strong irreversible peak (E_{pc}) at ca –0.521 V (vs Ag/AgCl) electrode. The scan reversed at –0.6 V has showed a new peak at more positive potential than the irreversible peak (E_{pa}) at ca 0.336 V (vs Ag/AgCl). The scan was again reversed in a reductive direction to observe peak (E_{pc}) at ca 0.244 V (vs Ag/AgCl). This is corresponded to oxidized peak (E_{pa}) at ca 0.336 V (vs Ag/AgCl), and in the subsequent, scans we could not observe any irreversible peak, but oxidative and reductive peaks have been observed between 0.2 and 0.4 V. The oxidative/reductive peaks due to nitro group present on modifying molecule are in good agreement with literature [10].

An examination of the voltammetric response of 10 μ l of 5 mM nitrobenzene in solution phase at pH 1 was recorded in the potential range +0.9 to –0.6 V. Redox couple of nitrobenzene group shows that they have a symmetrical wave shape, which is a characteristic of a nitro group present in solution. First scan in a reductive direction from 0.9 V with a scan rate (ν) of 25 mV/s showed a strong irreversible peak (E_{pc}) at ca –0.485 V (vs Ag/AgCl), and when the scan range is reversed at –0.6 V, an oxidative (E_{pa}) peak at 0.637 V (vs Ag/AgCl) has been observed. The scan was once again reversed in a reductive direction, and the reductive peak (E_{pc}) was observed at ca 0.12 V (vs Ag/AgCl). These studies confirm that the chloronitrophenyl groups are strongly attached to the carbon particle surface suggesting that the derivatization process has occurred.

To understand the electrochemical behavior of chloronitrophenyl-modified carbon, the carbon particles were physisorbed with nitrobenzene molecules, and it has been immobilized abrasively onto the surface of the basal plane pyrolytic graphite electrode and studying the cyclic voltammograms. The nitrobenzene physisorbed carbon particles showed similar behavior as that of derivatized carbon powder with a slight shift in its peak potentials. This shift may be due to the physical stacking of nitrobenzene molecules on the carbon surface than the derivatized carbon powder, where the nitrophenyl group is covalently attached on the carbon surface [10].

Control experiment

Physisorbed nitrobenzene carbon powder was mixed with 10 ml of distilled ethanol, and the reaction mixture was

stirred continuously for 1 h in a round bottom flask and then filtered by water suction. Furthermore, it was washed with deionized water followed by excess distilled ethanol to remove the physisorbed nitrobenzene from the carbon surface. This procedure was repeated several times to remove all physisorbed nitrobenzene from the carbon surface. It was dried, and then, its voltammetric behavior was examined. This study has revealed that no significant peaks corresponding to the presence of nitro group on the surface of carbon powder was observed [10]. Hence, the modifier on the surface of the physisorbed carbon can be easily removed by solvent washing, but the functional groups incorporated by the chemical derivatization method on the surface of carbon cannot be removed either by solvent washing or physical abrasion methods. Based on these facts, we can conclude that the chemical derivatization method has yielded highly stable functionalized carbon powder with the covalent attachment of the functional groups on the surface of carbon powder.

Electrochemical pathway of 4-chloro-2-nitrophenyl-derivatized carbon powder

Electrochemical path way of the 4-chloro-2-nitrophenyl carbon is carried out by examining the cyclic voltammetry of the derivatized carbon after immobilizing onto a bppg electrode. The initial four cyclic voltammograms [scan rate (v) 50 mV/s] of the CNPcarbon in a solution containing 0.1 M acetic acid + 0.1 M Sodium acetate (0.1 M KCl is used as a supporting electrolyte) are detailed in Fig. 3. The peak potentials of system I and system II was found to vary

with the pH studied. After electrode modification, first, we scan in a reductive direction from 0.6 to -0.8 V (vs Ag/AgCl); at pH 4, a large reductive peak (E_{pc}) was observed at -0.713 V (vs Ag/AgCl; labeled as I in Fig. 3). Reverse of the scan direction at -0.8 V has not showed the corresponding oxidation peak for system I indicating that it is an electrochemically irreversible process. But the oxidative peak (E_{pa}) was observed at ca 0.190 V (vs Ag/AgCl), and the subsequent reduction sweep shows a new reductive peak (E_{pc}) at ca 0.164 V (vs Ag/AgCl) corresponding to the reduction of oxidized species at ca 0.190 V (vs Ag/AgCl). This peak may be due to an electrochemically almost reversible process, labeled as “system II”. The electrochemically irreversible “system I” is not present in subsequent scans indicating that all the chloronitrophenyl moieties have been reduced to chlorophenyl hydroxyl amine group. The observed voltammetric behavior and their wave shapes are consistent with the reported literature studies of nitrophenyl carbon and correspond to the electrochemical reduction of the surface-bound nitro groups in aqueous media [10]. Figure 3 illustrates the electrochemical reduction behavior of nitro group present in chloronitrophenyl derivatized carbon. In this mechanism, “system I” corresponds to the chemically and electrochemically irreversible reduction of the nitro group in a four-electron, four-proton transfer to form the chlorophenyl hydroxylamine. Then, it undergoes an electrochemically reversible two-electron, two-proton oxidation (system II) to form the chloro-nitroso-phenyl species. Therefore, it is a chemically and electrochemically reversible process, which leads to a chemically irreversible process followed by

Fig. 3 The initial four voltammograms of 4-chloro-2-nitrophenyl-derivatized carbon immobilized on bppg electrode at pH 4, scan rate (100 mV/s); inset: mechanism of electrochemical reduction of nitro group of modified carbon

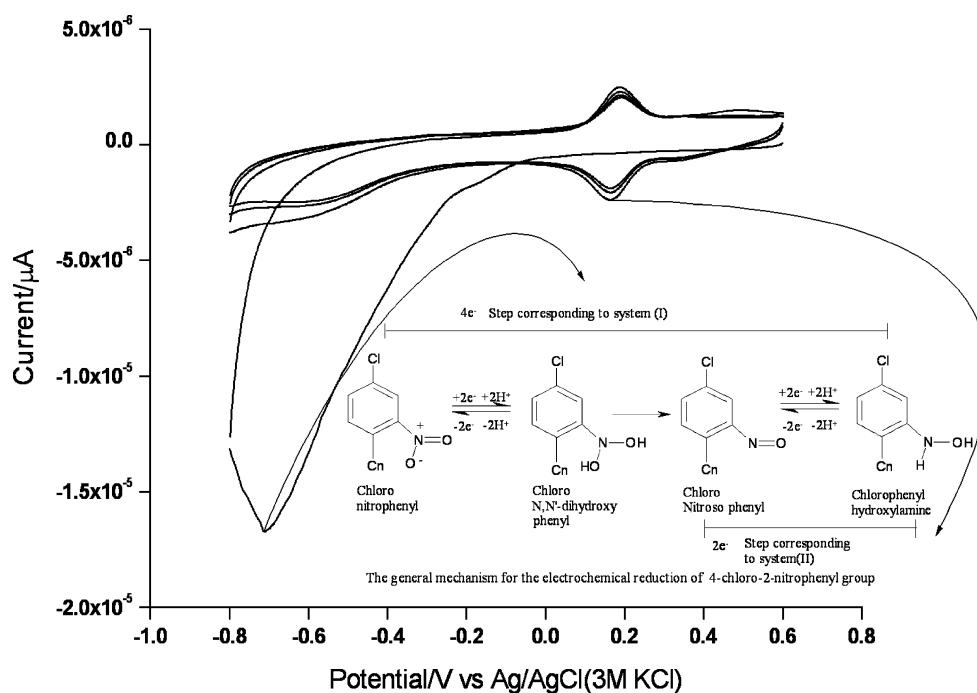
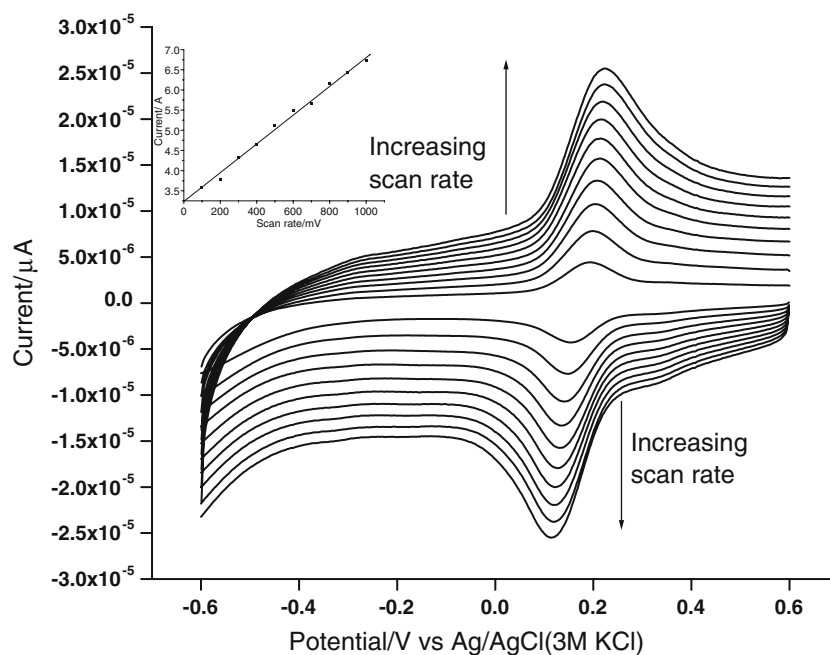


Fig. 4 The effect of varying scan rate at pH 4, *inset*: current vs scan rate



chemically and electrochemically reversible mechanisms. These results are in agreement with reported literature for the electrochemical reduction of the nitro group on derivatized carbon [6, 10].

Effect of scan rate

Effect of scan rate for CNPcarbon was studied by varying scan rate (ν) between 100 and 1,000 mV/s at pH 4. The scan rate

(ν) was increased by the increment of 100 mV/s (Fig. 4) at each time the electrochemically reversible “system II” could be observed, which rapidly stabilized to give a nearly symmetrical wave shape, and the peak current (I_p) was found to vary linearly with the scan rate (ν) (Fig. 4, inset). However, this is not an indicative of species diffusing into solution. The chloronitrophenyl groups are indeed attached to the surface of the carbon powder. The peak current (I_p) obtained is expected to be a surface-bound species.

Fig. 5 The overlaid voltammograms of modified carbon powder at different pH values (pH 1, 4, 5, 6, 7, 8, 9, 10, and 12; step potential 5 mV, scan rate 100 mV/s)

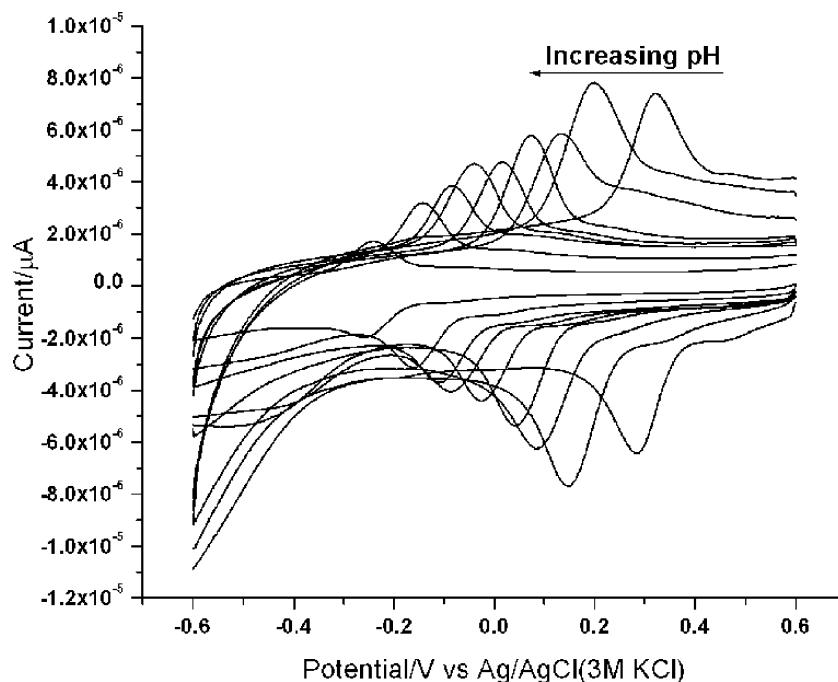


Table 1 The effect of pH on oxidative and reductive peak potentials

pH	Oxidative potential (E_{pa})/V vs Ag/AgCl (3 M KCl)	Reductive potential (E_{pc})/V vs Ag/AgCl (3 M KCl)
1	0.336	0.244
2	0.284	0.213
3	0.234	0.156
4	0.19	0.124
5	0.136	0.085
6	0.089	-0.003
7	0.032	-0.039
8	-0.04	-0.086
9	-0.098	-0.113
10	-0.152	-0.168
11	-0.208	-0.248
12	-0.249	-0.311

Effect of pH

Next, we studied the effect of pH on the peak potentials of CNPcarbon over the pH range 1–12 at room temperature. The proton loss/gain occurs on the electrode surface due to the oxidation/reduction of nitro group of chloronitrophenyl moieties attached on carbon powder surface (Fig. 3). The shift in the peak potentials (E_p) may be attributed due to the Nernstian behavior, which is described in the following equation [6, 10]:

$$E_{peak} = E_{formal}^{\circ} - \frac{2.303 RTm}{nF} pH$$

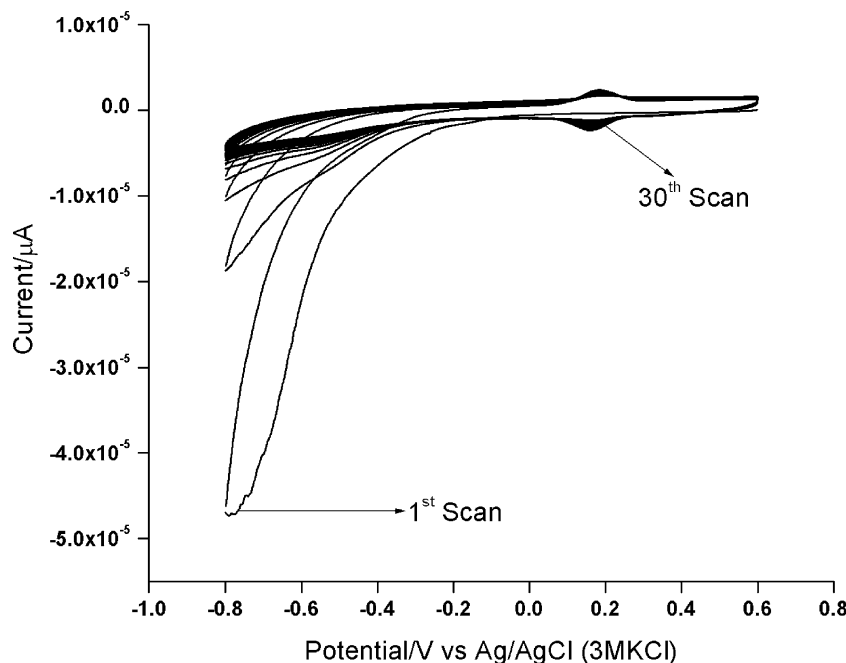
Where E_p [V] is the peak potential, E^0 [V] is the formal potential of the redox couple, R [JK^{-1}] is the universal gas

constant, T [K] is the temperature, and m and n are the number of protons and electrons involved in the redox process, respectively, where $n=m$ and is likely to be equal to two in the case of 4-chloro-2-nitrophenyl carbon particles as explained earlier, i.e., the 4-chloro-2-nitrosophenyl/4-chlorophenylhydroxylamine couple (system II in Fig. 3); the other symbols have their usual meanings. At room temperature, the peak potentials for CNPcarbon particles were found to shift to more negative potentials with increase in pH which have been shown as overlaid voltammograms in Fig. 5. The peak shapes are nearly symmetrical with a slight separation between oxidative and reductive peaks (E_p) at each pH studied. The resulting oxidative and reductive peak potentials of the nitrophenyl-derivatized carbon powder with varying pH values are given in Table 1. The plot of peak potentials against pH was found to be linear in the pH range (1–12) studied (not shown). The potential gradient was found to be 58 ± 2 mV/pH unit, which is very close to the theoretical value. The electroactive species derivatized on the carbon surface follows Nernstian behavior, and these studies are in agreement with reported literature [10].

Stability of modified electrode

To understand the stability of the immobilized species on bpgg electrode, multiple scans (30 scans) were examined after immobilizing the modified carbon as discussed above (Fig. 6). We next removed the electrode from the solution and replaced it with a fresh buffer solution of the same pH. The recorded CV scan was found to overlay the last scan

Fig. 6 Stability of the immobilized carbon species at pH₄ (0.1 M acetic acid + 0.1 M sodium acetate) scan rate (100 mV/s)



recorded before the solution was replaced. These results confirm that the electroactive material is confined on to the electrode surface and has not detached into bulk of the solution. The variation of scan rate in the scan range 100–1,000 mV/s has resulted in symmetrical wave shapes with a steady increase in the peak currents. The plot of peak current (I_p) vs scan rate resulted in a linear relationship (Fig. 4, inset), which indicates that they are surface-bound species. The functionalized carbon particles also showed a similar behavior when multiple scan study was examined.

Stability of functionalized carbon powder

To understand the stability of the functionalized carbon, the modified carbon powder was subjected to cyclic voltammetric studies over a period of time. Even after several months, the electrochemical behavior of the modified carbon remained the same, and the wave shapes are symmetrical with a steady increase in the peak currents (I_p) with increase in scan rate (ν) (not shown). These results revealed that the electroactive material is confined and has not detached from the carbon powder surface. All these studies indicate that the function-

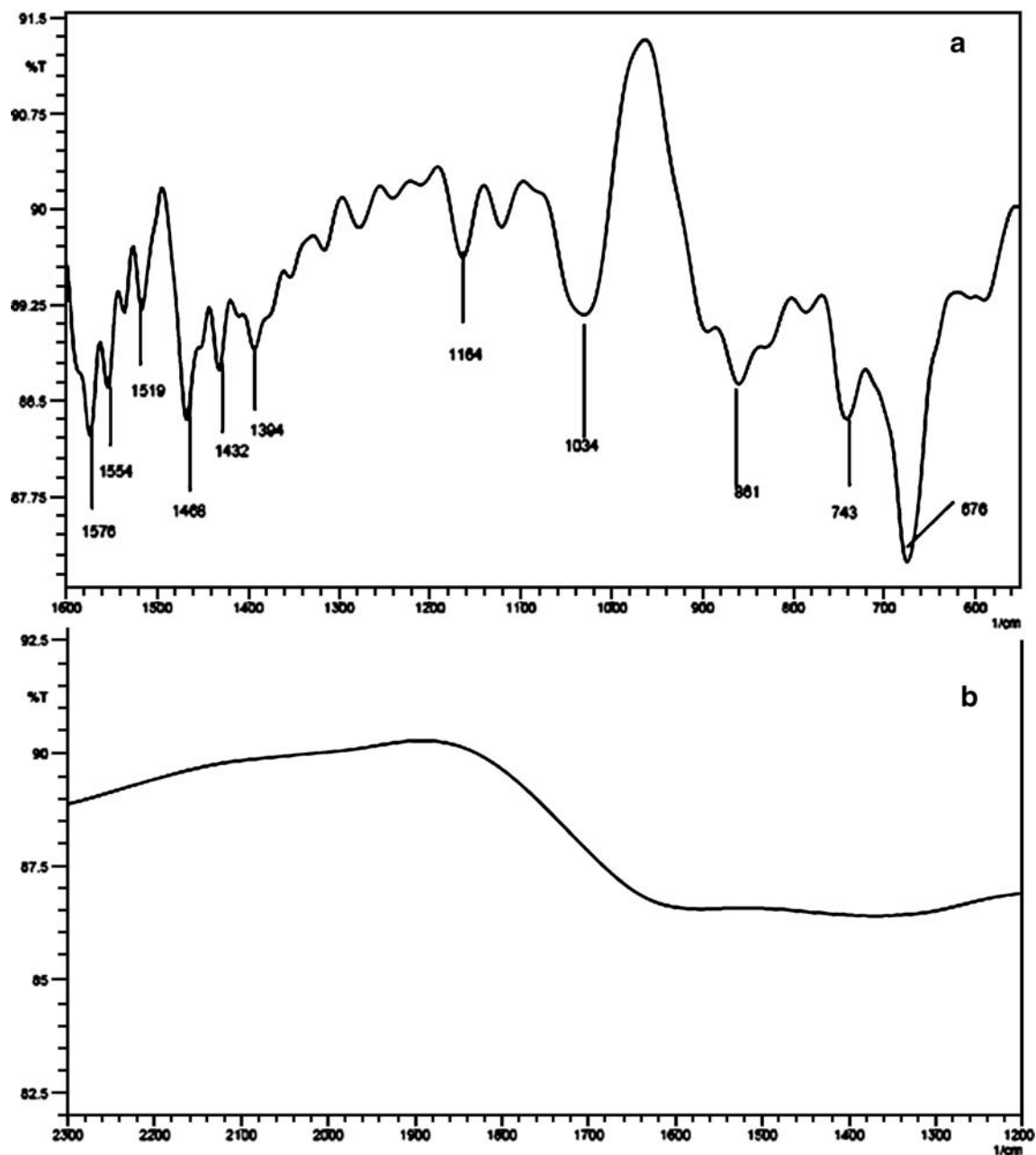


Fig. 7 The Fourier transform infrared spectroscopy (FTIR) spectra of **a** Chloronitrophenyl-functionalized carbon powder. **b** Control carbon powder

alized carbon powder is stable, and this type of stability for the functionalized carbon can be made into use to fabricate bulk-modified electrodes. This derivatization protocol is inexpensive and can be applied to synthesize carbon powder or any other substrate material with the required properties in bulk scale. The modified carbon can be used to fabricate electrodes in ion-sensing applications.

FTIR spectroscopy of functionalized carbon powder

Infrared spectral studies have been carried out to decipher the presence of functional groups on the modifier and its covalent attachment on the surface of carbon particle. Reduction of diazonium salt in the presence of carbon powder through hypophorous acid generates aryl radicals and its covalent attachment on the carbon surface [2]. The modified carbon powder has been mixed with potassium bromide in 1:100 ratio to make the pellet, and the pellet has been exposed to IR light in the range 550 to 1,600 cm^{-1} . The transmission spectrum of the modified carbon powder has revealed the presence of peaks due to nitro, azo, and methoxy functional groups on the modifying molecule on the surface of carbon particle. The presence of nitro group on the modifier molecule was indicated by strong bands between 1,576 and 1,519 cm^{-1} . These bands are due to the asymmetric stretching of the nitro group and the bands at 1,488 and 1,394 cm^{-1} are due to the symmetric stretching of the nitro group [16]. The peaks at 676 and 1,164 cm^{-1} are due to the C–Cl in-plane and out-of-plane vibrations of the chloro group. These peaks indicate the presence of chlorine on the modifying molecule. The peak at 1,034 cm^{-1} indicates the phenyl ring vibration of the modifier. The two peaks at 743 and 861 cm^{-1} correspond to the C–H out-of-plane bending vibrations of phenyl ring. All of the above peaks indicate that the modifying molecule on carbon surface possesses corresponding functional groups and are in good agreement with reported literature ([17]; Fig. 7a). However, the IR spectrum of native carbon powder did not reveal any significant peaks in this region (Fig. 7b). Hence, based on all of these studies, we conclude that the carbon powder surface has been functionalized with the modifier molecule during derivatization process (Scheme 1).

Conclusions

Surface modification of carbon powder could be achieved easily by the chemical reduction of aryl diazonium salts in the presence of hypophosphorous acid as a reducing agent using

an established protocol. The surface-derivatized carbon powder is quite stable for several months, and its cyclic voltammetry studies have revealed that it produces stable symmetric wave-shaped voltammograms with the same peak currents and potentials. A linear relationship between peak current and scan rate is as expected for a surface-bound species. This confirms that there is no desorption of functional groups from the surface of carbon particle while storing for several months. The effect of varying pH (1–12) on the voltammetric behavior of CNPcarbon is studied, and it shows a Nernstian behavior over the pH range studied.

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