

## Nitroazobenzene Functionalized Carbon Powder: Spectroscopic Evidence for Molecular Cleavage

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Carbon powder has been functionalized with nitroazobenzene groups by the reduction of 3-methoxy-6-methyl-4- [(2-nitro-4-methylphenyl) azo] benzene diazonium zinc chloride double salt (“Fast Corinth V zinc chloride double salt”) in the presence of hypophosphorous acid as a chemical reducing agent. This provides an easy and inexpensive methodology to modify the carbon particle surface. The derivatized carbon powder has been spectroscopically characterized in order to confirm the functionalization of the carbon by studying its diffuse reflectance spectroscopy (DRS) and with FTIR. The electrochemical characterization of a novel carbon powder derivatized with nitroazobenzene moieties has been studied by immobilizing onto a bppg (Basal plane pyrolytic graphite) electrode for cyclic voltammetry. The voltammetric behaviour of the azo/hydrazo groups of modified carbon at low potentials is a two-electron, two-proton redox process and is a chemically reversible reaction. The peaks observed from the voltammograms of modified carbon at higher (more negative) potentials indicated that the functionalized carbon powder undergoes reductive cleavage.

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**Keywords:** Derivatization, Diazonium salt, Modified carbon powder, Nitroazobenzene, Cyclic voltammetry

### 1. INTRODUCTION

Carbon based materials have been extensively used in a wide range of practical applications in many fields over the past decade due to their properties such as chemical inertness, high mechanical strength and good electrical conductivity [1,2]. The main conducting forms of carbon in common use are glassy carbon, carbon fibres, carbon black, various forms of graphite, carbon paste and carbon-epoxy, which have all been used as materials to fabricate electrodes [3]. Graphitic carbon is widely

used as an electrode material due to its low cost, good conductivity, high surface activity and wide potential window. In recent years carbon nanotubes (CNTs) have seen a large expansion in their utilization especially in the field of electrochemistry since the landmark paper in 1991 by Iijima [4]. These carbon nanotubes in modified form have been extensively used in a variety of applications such as electroanalysis, catalysis, membrane technology and sensor technology [5]. Several modification protocols exist for the surface functionalisation of carbon based materials [6]. One such method involves oxidation of carbon surfaces with nitric acid or ozone, which produces oxygenated functionalities such as carboxylic acid, esters, quinones and anhydrides followed by the reaction of thionyl chloride with the carboxylic group which makes it possible to graft and further elaborate the surface modification with different properties [7]. The drawbacks of this method include low surface reactivity and possible damage to the carbon materials during the oxidation treatment [8]. In recent years, intensive studies on the modification and dispersion of carbon nanotubes in solution or polymer matrices have led to several novel and efficient methodologies to modify the carbon surface with covalent attachment including fluorination, grafting of moieties using diazonium salts, modification with carbenes/nitrenes and the reduction of the carbon surface with lithium compounds [9-12]. The electrochemically assisted reduction of diazonium salts has proved to be a very useful approach for the derivatisation of electrode surfaces in recent years [13]. However this method of surface functionalisation requires the carbon to take the form of an electrode surface [11]. The modification of the electrode surfaces through the *chemical* reduction of diazonium salts has been proved to be very useful and efficient approach of grafting functional moieties on carbon [14]. This type of surface modification can be efficiently adopted to derivatize carbon powder which can subsequently be used as an electrode material. The modified carbon powder can be compressed into pellets or rods which can be fabricated as bulk modified electrodes for sensing purposes. The surface renewal of these electrodes can be done very easily by polishing the electrode on sand paper. Subsequently they can be polished on silicon carbide paper for greater smoothness before its use. We have recently reported the chemical functionalization of graphitic carbon powder templated with methoxy nitrophenyl groups, using a technique in which the diazonium compound is reduced by hypophosphorous acid to generate aryl diazonium radicals in situ and attaching the same moieties covalently on the carbon powder surface [14, 15]. Recently Compton et al have reported the mechanistic aspects of covalent attachment of electroactive moieties based on the reduction of aryl diazonium salts on carbon surfaces [16, 17]. The resulting interfaces can exhibit desirable qualities depending on the type of chemical modifier that is covalently attached to the carbon powder surface [18, 19]. Azobenzene and its derivatives have been studied previously as Langmuir–Blodgett films on the surface of electrodes for potential use as photoelectrochemical switching devices, memory storage materials and photoelectrochemically driven machines [20, 21]. Azobenzene modified carbon powder can undergo reduction to hydrazobenzene under suitable conditions at different potentials. The attached molecule can exist as cis and trans isomers. The interconversion from one isomeric form to another isomeric form can be easily achieved under photochemical and/or thermal conditions [22, 23]. Compton et al have covalently derivatized the carbon nanotube surfaces with functional moieties containing azobenzene groups to synthesize a novel material using Fast Black K salt and the modified carbon exists in cis-trans isomeric forms of the modifier [24, 25]. The existence of cis-trans isomeric forms have been examined based on the

chemical cleavage during electrochemical studies. Herein we report the chemical derivatization of graphitic carbon powder (FCVcarbon) with Fast Corinth V salt based on chemical activation method and its characterization by examining cyclic voltammetry, FTIR and DRS techniques. In this study a spectroscopic evidence for the cleavage of the cis-trans isomeric forms of modifying molecule and its fragmentation has been emulated. This gives an additional evidence for the existence of modifying molecule in isomeric forms on the surface of carbon powder. The FTIR study of fragmented molecules clearly indicates that the modifier on the carbon particle surface undergoes molecular cleavage through N=N bond during electrochemical study.

## 2. EXPERIMENTAL PART

### 2.1. Chemicals and Instrumentation

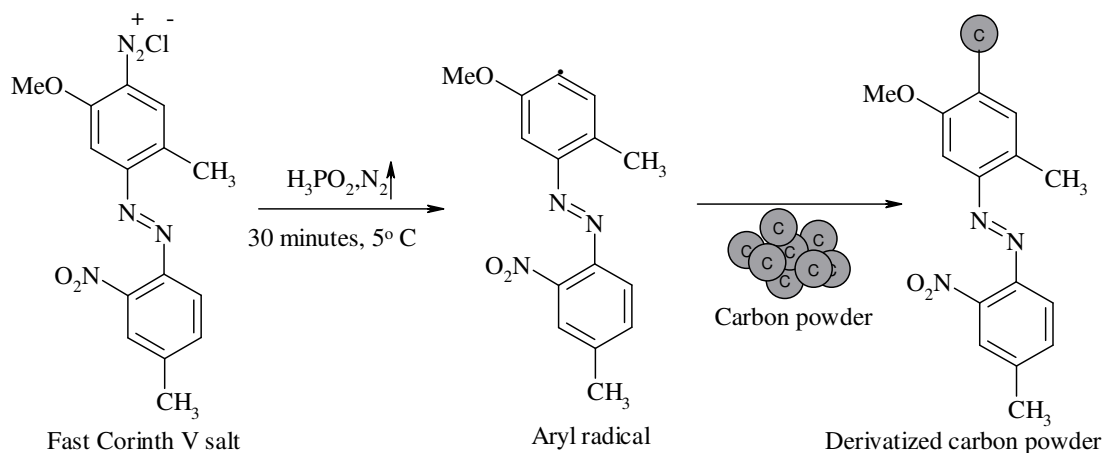
All reagents used were AnalaR grade and used without further purification. The synthetic graphite powder (< 20  $\mu\text{m}$  diameter) was purchased from Sigma-Aldrich (purity > 99%) and used directly and it consisted of irregularly shaped particles. Hypophosphorous acid (50%) was purchased from Merck grade and Fast Corinth V zinc chloride double salt AR Grade (purity 90%) and potassium bromide for IR spectroscopy (FT-IR grade,  $\geq 99\%$ ) was obtained from Sigma-Aldrich. Solutions of known pH in the range pH 1 to 12 were prepared using deionised water from milliQ water purifier (Millipore, USA) with a resistivity of not less than 18.2 M $\Omega$  cm (25 °C) as follows: pH 1, 0.1M HCl; pH 2, 0.1M sodium citrate + 0.1M HCl; pH 3, 0.1M glycol+0.1M NaCl+0.1 M HCl; pH 4, 0.1M acetic acid + 0.1M sodium acetate; pH 5, 0.2M acetic acid + 0.1M sodium acetate; pH 6, 0.2M acetic acid + 0.2M sodium acetate; pH 7, 0.01M KH<sub>2</sub>PO<sub>4</sub> + 0.01 M Na<sub>2</sub>HPO<sub>4</sub>; pH 8, 0.01M KH<sub>2</sub>PO<sub>4</sub> + 0.01 M Na<sub>2</sub>HPO<sub>4</sub>; pH 9 0.05M sodium tetra borate (H<sub>3</sub>BO<sub>3</sub> +1M NaOH); pH 10, 0.1M sodium tetraborate + 0.1N NaOH; pH 11, 0.01M NaOH or KOH. The cell contained 4cm<sup>3</sup> of buffer and 4cm<sup>3</sup> of 0.1M 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 (26  $\pm$  2 °C) after degassing the solutions using ultra pure nitrogen gas for 15 min in an electrochemical cell of volume 10 cm<sup>3</sup> with a standard three-electrode configuration. A basal plane pyrolytic graphite (bppg, 3mm, Le Carbone Ltd, Sussex, UK.) electrode acted as the working electrode. A Pt (99.99%) wire was used as a counter electrode and Ag/AgCl (3M KCl) CH Instruments (Texas, USA) 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. Surface area measurements were carried out using NOVA-1000 Ver.3.70. All the Fourier transform infrared spectrophotometer measurements were performed using FTIR-8400S Shimadzu, All the Diffuse Reflectance spectra were recorded using a UV-3101PC, UV-VIS-NIR Scanning Spectrophotometer Shimadzu, and all of the Diffuse Reflectance spectra were recorded using a fine BaSO<sub>4</sub> powder as background.

## 2.2. Homogeneous derivatization of carbon powder

The chemically activated derivatization of carbon powder forming 3-methoxy-6-methyl-4- [(2-nitro-4-methylphenyl) azo] benzene derivatized carbon powder (FCVcarbon, as shown in Scheme 1) was achieved using the following protocol:

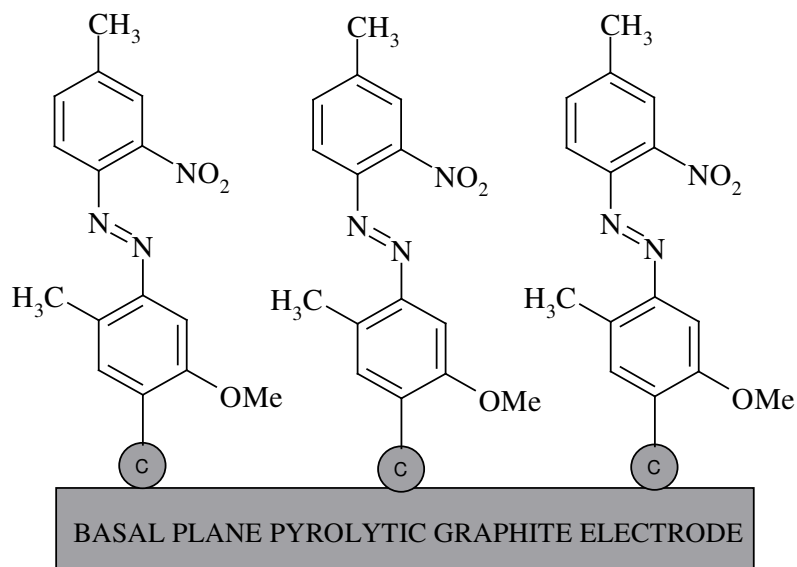
Two grams of carbon powder is mixed with a 15 cm<sup>3</sup> of solution (acetonitrile as solvent) containing 10mM Fast Corinth V salt to which 50cm<sup>3</sup> of hypophosphorous acid is added slowly. The reaction mixture is then left to stand at 5°C for 30 min. with occasional stirring at regular intervals and after this the resulting modified carbon was then filtered under suction and washed with ample quantities of acetonitrile followed by acetone and water to remove any unreacted and reduced diazonium salt. This washing facilitates the removal of any physisorbed diazonium salt on the surface of carbon particle. The FCVcarbon was then dried by placing inside a fume hood for a period of 12h and finally stored in an airtight container [14].



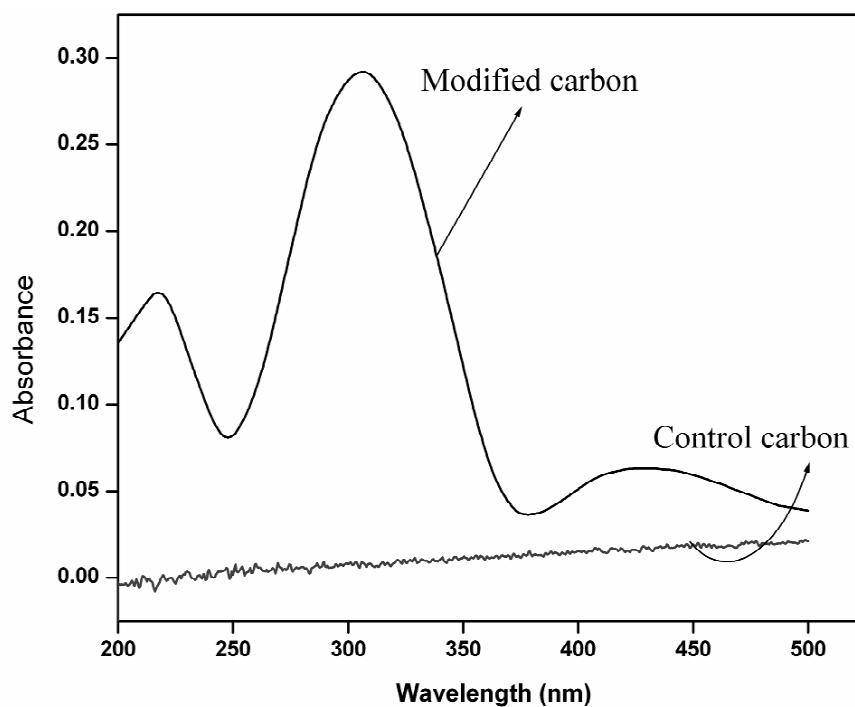
**Scheme 1.** Derivatization scheme

## 2.3. Electrode modification

The derivatized 3-methoxy-6-methyl-4- [(2-nitro-4-methylphenyl) azo] benzene carbon particles were electrochemically characterized by immobilizing abrasively onto the surface of the basal plane pyrolytic graphite electrode and studying its voltammetric behaviour. The electrode surface was initially polished on glass polishing paper (H00/240) followed by silicon carbide paper (P1000C) for smoothness. The functionalized carbon powder was immobilized mechanically (as shown in Scheme 2) onto the bppg electrode by gently rubbing the electrode surface on a fine qualitative filter paper containing the derivatized carbon powder [14].



**Scheme 2.** Electrode modification scheme



**Figure 1.** The Diffuse reflectance spectra of modified carbon powder.

#### 2.4. Diffuse reflectance spectroscopy of modified carbon

The nitroazobenzene modified carbon powder was examined to identify the cis-trans isomers of azobenzene groups on the carbon surface by studying diffuse reflectance spectroscopy (DRS) in the

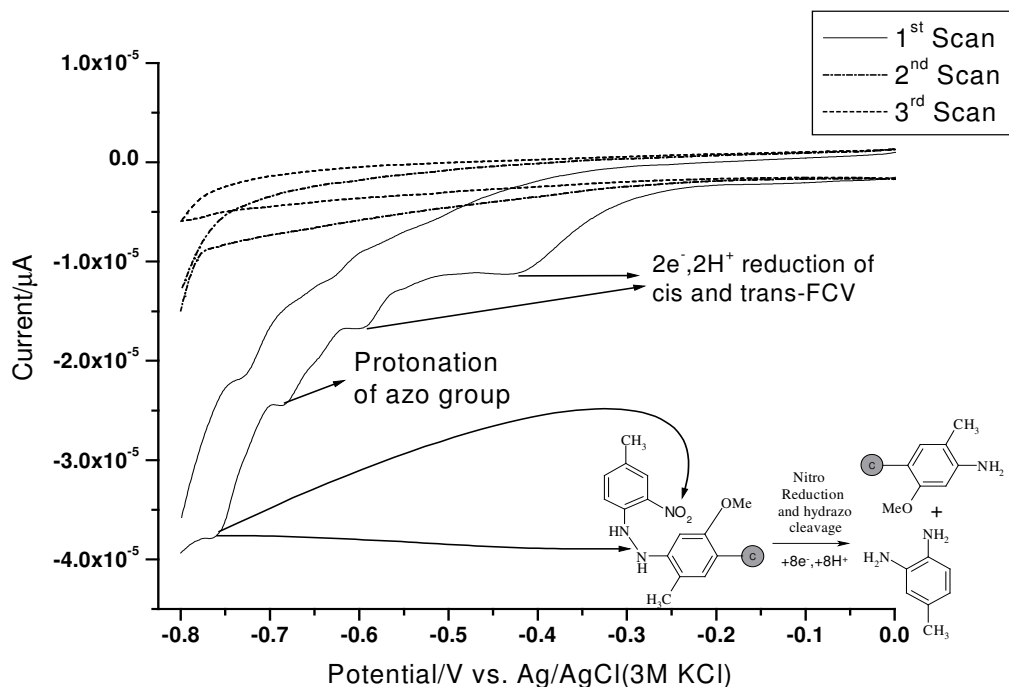
UV-Vis range between 500 to 200 nm (Figure 1) These studies were carried out by mixing a small amount of functionalized carbon powder with BaSO<sub>4</sub> in 1:100 ratio and the resulting mixture was used for pellet making. The electronic absorption spectra showed a strong band at 307 nm and a weak band at 428 nm. The strong band at 307 nm is attributed due to  $\pi \rightarrow \pi^*$  transition corresponding to trans azobenzene while the weak band at 428 nm is due to  $n \rightarrow \pi^*$  transition. The band at 217 nm is due to  $n \rightarrow \pi^*$  transition of nitro group on modifying molecule. The trans component of azobenzene modified carbon is characterized by a more pronounced band at 307 nm. If the cis component of modifying molecule is present then the band at 428 nm could have been a predominant one. The bands at 307 nm and 428 nm are in good agreement with the reported literature [26]. These studies have revealed that the carbon particle surface has been successfully functionalized with nitroazobenzene groups.

### 3. RESULTS AND DISCUSSION

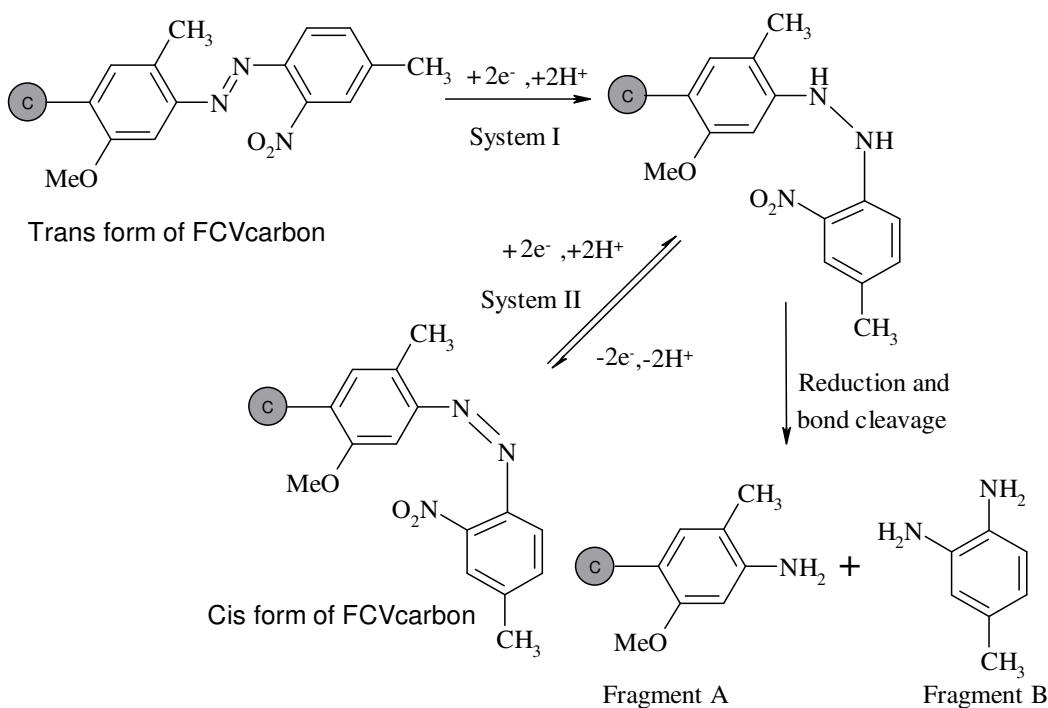
#### 3.1. Voltammetry of 3-methoxy-6-methyl-4- [(2-nitro-4-methylphenyl) azo] benzene derivatized carbon powder

The derivatized carbon powder was electrochemically characterized after immobilizing it onto the surface of basal plane pyrolytic graphite (bppg) electrode and studying its cyclic voltammetry [14, 15]. The initial three scans of voltammetric responses of FCV modified carbon powder are shown in Figure 2. These scans were recorded in the potential range 0.0 V to -0.8 V in aqueous solution (0.1M HCl + 0.1M KCl) to understand the electrochemical behaviour of the derivatized carbon powder. The initial scan in a reductive sweep from 0.0 V with a scan rate of 50 mV/s showed four peaks, in which cathodic waves are  $E_{pc}$  at -0.427 V,  $E_{pc}$  -0.597,  $E_{pc}$  -0.687 V and  $E_{pc}$  -0.764 V as shown in Figure 2. The reverse of the scan from -0.8V does not show any oxidative peaks for the corresponding reductive peaks. The peak potentials due to the reduction of the immobilized species on the electrode surface were found to vary with the pH studied. The peak potentials of this modified carbon immobilized on bppg electrode compares with the literature values [24].

The cathodic peaks  $E_{pc}$  at -0.427 V and  $E_{pc}$  -0.597 V (Figure 2) correspond to an electrochemically reversible system comprising the two electron, two proton reduction of the azo-linkage to the hydrazo form for cis-FCV and trans-FCV species respectively. The small peak at ca. -0.687 V is due to the protonation of the azo group of the modifier molecule. However a large reductive peak was observed at -0.764 V as shown in Figure 2, which is due to an electrochemically irreversible in nature which corresponds to the six-electron, six-proton reduction of the nitro group present in the FCV molecule, followed by simultaneous cleavage of the hydrazo linkage in a further two electron, two proton step at a similar potential. Cleavage of the hydrazo linkage is mainly responsible for the fragmentation of the modifier molecule present on the carbon particle surface into two fragments namely, 2-methoxy-5-methylaniline(fragment A, Figure 3) and the other fragment i.e 4-methyl-1,2-phenylenediamine (fragment B, Figure 3) which diffuses into electrolytic bath while the fragment A remains on the carbon particle surface. No further voltammetric peaks were observed corresponding to either nitro group or azo group after the fragmentation of the modifying molecule [23, 24].



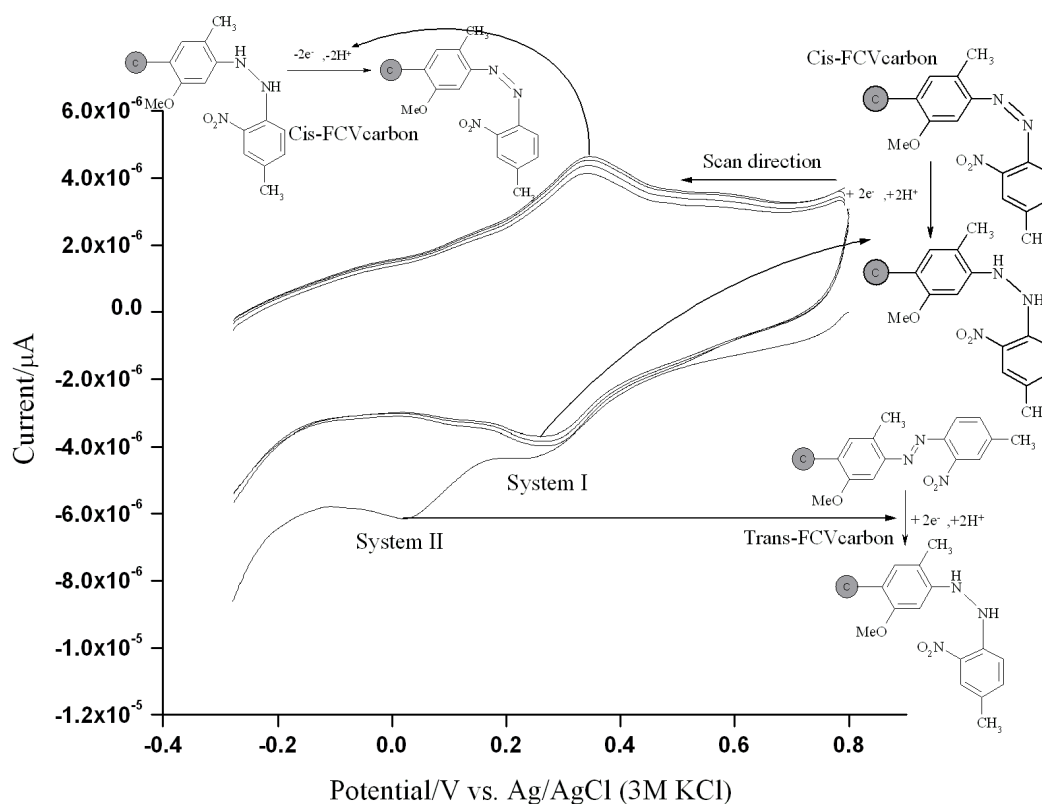
**Figure 2.** The voltammetric behaviour of FCV derivatized carbon at pH 1 (potential range: 0.0 to -0.8V, scan rate: 50mVs<sup>-1</sup>).



**Figure 3.** Mechanism of cis-trans azobenzene isomeric forms of carbon .

### 3.2. Reversibility of azobenzene-hydrazobenzene system

The FCV modified carbon powder was characterized electrochemically by studying its cyclic voltammetry in order to understand the structural changes of the azo group present in the FCV molecule which is covalently attached to the carbon surface. Figure 4 shows the four successive voltammetric scans of FCV derivatized carbon immobilized on bppg electrode at pH 4 (0.1M acetic acid + 0.1M Sodium acetate, potential range between 0.8 to  $-0.3$  V, scan rate  $50 \text{ mVs}^{-1}$ ) was showing the different potential zones that are responsible for irreversible electrochemical conversion of trans form to cis form. The reduction peak potential of cis-azobenzene to hydrazobenzene of modifier was observed at more positive potential than that of the trans form at the basal plane pyrolytic graphite electrode. Further the reduced hydrazobenzene undergoes oxidation to cis form. In the second scan, the peak due to oxidation of the reduced hydrazobenzene disappears which indicates that only cis form exists after the first sweep. The charge passed in these peaks has been considered to establish the number of electrons involved in the redox process of azobenzene to hydrazobenzene. These studies have revealed that the conversion of azo to hydrazo group is a two electron process and these results are in agreement with the reported literature [22-24].



**Figure 4.** The Voltammetric behaviour of modified carbon for cis-trans azobenzene isomers at pH4 (potential range: 0.8 to  $-0.3$  V, scan rate:  $50 \text{ mVs}^{-1}$ )

The azobenzene-hydrazobenzene system has been repeatedly studied at the bppg electrode, but the widely discordant results obtained indicated that it would be of interest to investigate the



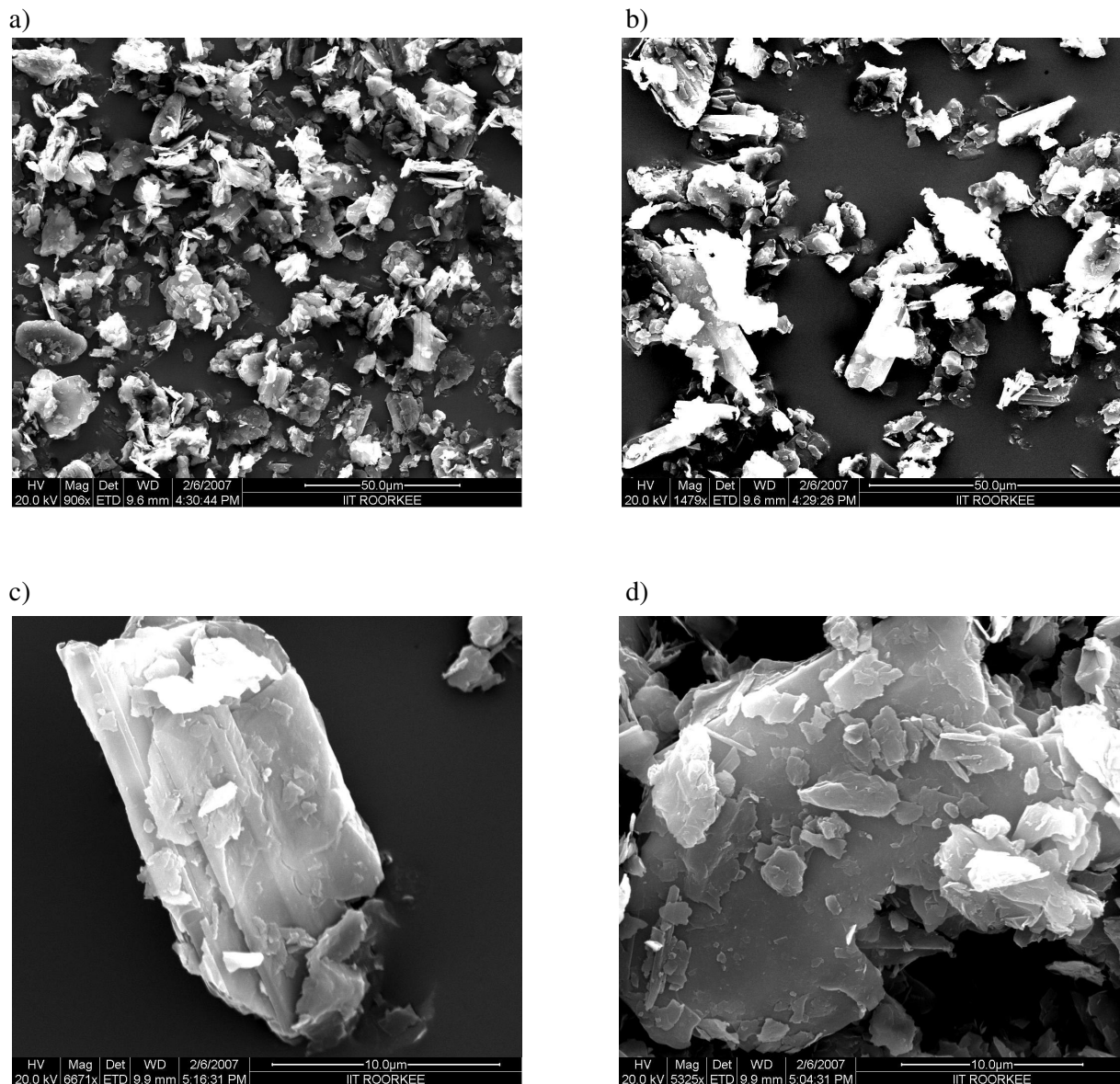
voltammetric behavior of this system at the basal plane pyrolytic graphite electrode. So we have used cyclic voltammetry to briefly describe the voltammetric behaviour of FCV functionalized carbon in aqueous solution by abrasively immobilization onto a bppg electrode. The first cycle in a reductive direction within the potential window 0.8 to  $-0.3$  V FCVcarbon showed two principal voltammetric features. The first scan consists of two cathodic waves which have been observed  $E_{pc}$  at 0.244 V and  $E_{pc}$  at 0.021 V labelled as system I and II in Figure 4. The exact peak potentials of these waves depend on the solution pH with peak separation of 0.223 V. However if the scan is reversed at a potential slightly more negative than system II, only one oxidative wave is observed  $E_{pa}$  at 0.338 V corresponding to system I. But there is no corresponding oxidation peak for system II that disappears after the first scan, thus we conclude that system I is chemically reversible and system II is electrochemically irreversible. Thus we conclude that, the voltammetry of FCVcarbon can be explained by the mechanism shown in Figure 3 as well as in Figure 4. According to the proposed mechanism for azobenzene species as the potential is swept in a reductive direction, the azo-linkage is reduced in a two-proton, two electron step corresponding to system I. If the scan is reversed the hydrazo-linkage is reoxidised back to the azo form and the system appears to be chemically reversible.

The splitting of the reduction peak into two peaks labelled as systems I and II can be attributed due to the different reduction potentials of cis and trans isomers of the azo moiety within the FCV molecule. Over the pH range studied both cis and trans isomers of azobenzene itself are reduced at the same potential [23-25]. The study of azobenzene in ethanolic solution and the physisorbed azobenzene carbon in aqueous solution have revealed that the trans isomer was found to be reduced at a more negative potential than the cis isomer [18]. Upon reoxidation of the hydrazo linkage only one oxidative peak is observed as the mixture of the two isomers which is electrochemically converted to the most stable form and these results are comparable with the reported literature [22, 24]. The peak potentials of FCV modified carbon powder for the system (II) at varying pH compares with the voltammetric behaviour of azobenzene in ethanol solution (not shown). On the basis of these results, we can conclude that the redox peaks observed only in the first scan between 0.8 to  $-0.3$  V are due to the reduction of the cis-azobenzene to hydrazobenzene and the oxidation of reduced hydrazobenzene to the cis form as shown in Figure 4.

### 3.3. Effect of scan rate

The effect of scan rate on FCV derivatized carbon was studied by varying the scan rate between  $100 - 1000 \text{ mVs}^{-1}$  at pH 4. Scan rate was increased in increments of  $100 \text{ mVs}^{-1}$  (not shown) at each increase in scan rate, the electrochemically reversible "system I" (Figure 4) could be observed which rapidly stabilized to give a symmetrical wave shape and the peak current was found to vary linearly with the scan rate. These studies revealed that the electrode surface modified with the functionalized carbon particles does not diffuse into the solution. The (3-methoxy-6-methyl-4- [(2-nitro-4-methylphenyl) azo] benzene groups are indeed attached to the surface of the carbon powder. The peak current Vs scan rate behaviour obtained is expected from a surface bound species. This dependence of  $i_p$  on scan rate has been observed and is attributed to the diffusion of charge on the

surface of the solid carbon powder with electrons hopping from one azonitrophenyl group to another. This characterization protocol was repeated in the pH range 1-12 and the results were similar. Hence we conclude that azonitrophenyl groups are present on the carbon powder surface [15].



**Figure 5.** SEM images of a) Native carbon powder. b) Functionalized carbon powder. c) Magnified image of native carbon particle. d) Magnified image of functionalized carbon particle.

### 3.4. Effect of pH

In order to understand the effect of pH, the FCV derivatized carbon powder has been examined over the pH range 1-12 (not shown) using different buffers after immobilizing it onto the surface of

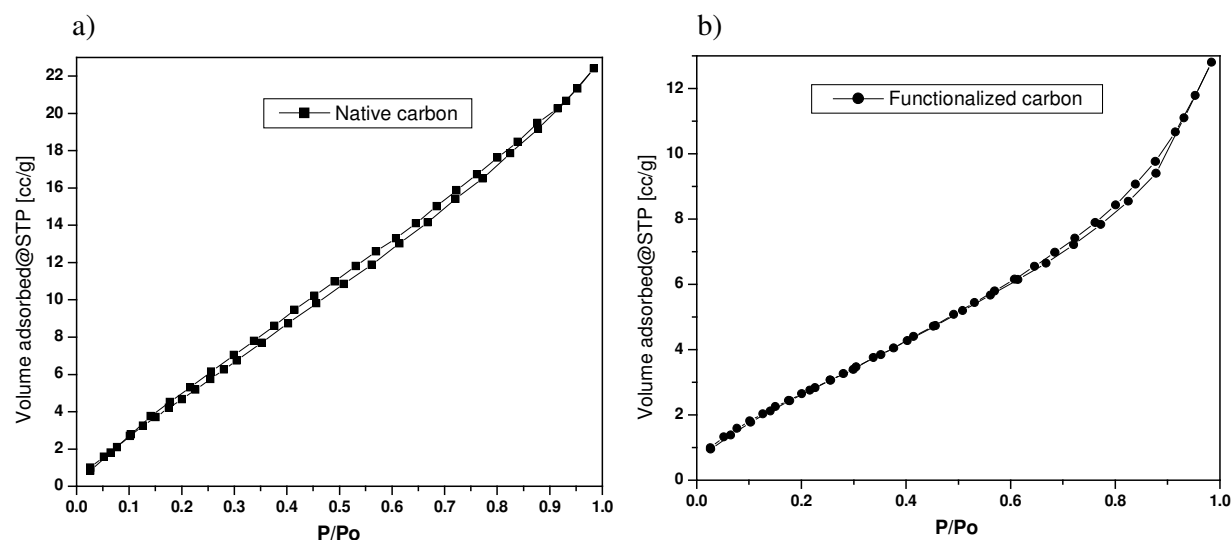
basal plane pyrolytic graphitic electrode and studying its cyclic voltammetric behaviour. The FCVcarbon is found to produce a stable well defined reversible voltammetric peaks over the entire pH range studied at room temperature ( $26 \pm 2^\circ \text{C}$ ). As the pH increases the peak potential shifts towards more negative values and the effect of peak potentials on pH is linear which suggests Nernstian behaviour with a gradient of 0.054V per unit pH. These results are in consistent with the reported literature [15].

### 3.5. Surface morphology of functionalized carbon powder

The surface morphology of functionalized carbon powder has been examined by scanning electron microscopy. It was carried out by spreading the carbon particles on a fine qualitative filter paper and attaching them onto a small conducting strip by gently tapping the filter paper containing carbon particles and taking SEM images. The corresponding SEM images of derivatized carbon particles revealed that the 3-methoxy-6-methyl-4- [(2-nitro-4-methylphenyl) azo] group modified carbon particles have broadly similar surface morphology than its underivatized counterparts (Figure 5a-d). The surface coverage values have been obtained from the charge of the respective oxidative and reductive peaks of corresponding voltammograms as shown in Figure 2 and 4. Based on the charge obtained by the integration of the reductive/oxidative peaks at a scan rate of  $50 \text{ mVs}^{-1}$  the relative peaks positions at  $E_{pc} 0.427 \text{ V}$ ,  $E_{pc} -0.764 \text{ V}$ ,  $E_{pc} 0.244 \text{ V}$  and  $E_{pa} 0.338 \text{ V}$  are shown in the Figure 2 and 4. The surface coverage concentration of the electrode (not of the carbon powder) was calculated by using the formula  $\Gamma = Q/nFA$  where  $Q$  = charge involved in the reaction,  $n$  = number of electrons involved in the redox process,  $F$  = Faraday constant,  $A$  = Area of the electrode,  $\Gamma$  = Surface concentration on the electrode [27]. The surface concentration of the modified working electrode has been calculated based on the charge of corresponding reductive peaks which have been found to be  $3.6 \times 10^{-8} \text{ mol/cm}^2$ ,  $3.5 \times 10^{-9} \text{ mol/cm}^2$  respectively (Figure 2). Similar measurements have revealed that the surface concentration of  $3.8 \times 10^{-10} \text{ mol/cm}^2$  and  $2.3 \times 10^{-10} \text{ mol/cm}^2$  respectively for oxidative and reductive peaks are as shown in figure 4 [23].

Next we have measured the specific surface area (SSA) of commercially procured graphitic carbon powder and functionalized carbon powders by studying adsorption/desorption isotherms using liquid nitrogen as an adsorbate. Figure 6a & b shows the adsorption isotherms obtained for both chemically modified and native carbon powder samples. Applying the BET model, the specific surface area of a solid sample in contact with the gas phase was calculated. The relative adsorption is obtained by dividing the amount of adsorbed nitrogen at a given pressure by the BET monolayer capacity for the sample. These studies reveal that the native carbon powder exhibit higher adsorption behaviour than functionalized carbon powder. Due to the surface modification, the surface area and the total pore volume of the sample decreased with the increase in coverage of organic moieties on the substrate material. However, the shape of the adsorption-desorption isotherms and its hysteresis loop is slightly altered when compared to native carbon powder. This indicates that the porous structure of the graphitic carbon powder has not appreciably altered [28] (Figure 6a & b). The adsorption-desorption curves for the chemically modified carbon is almost identical, however the native carbon powder

exhibits much higher adsorption than that of the chemically modified sample. Based on these studies we can conclude that the pore size distribution in the chemically modified carbon powder has been increased. These results indicate in the disappearance of the smallest pores as can be noticed in adsorption-desorption isotherms of the modified carbon powder with increase in the average pore diameter. The BET specific surface area, total pore volume and average pore diameter were significantly altered and the results are shown in Table 1. These results also indicate that the functionalization may result in partial intercalation along with the bundling or agglomeration of the carbon particles [29-32]. However the SEM images of the modified carbon particles shows it is uneven in size and their irregular shape might be due to the agglomeration of carbon particles during derivatization process. Based on these facts we conclude that the surface morphology of functionalized carbon particles has altered when compared to native carbon particles [31, 32].



**Figure 6.** Relative adsorption-desorption isotherms of a) Native carbon powder b) Functionalized carbon powder

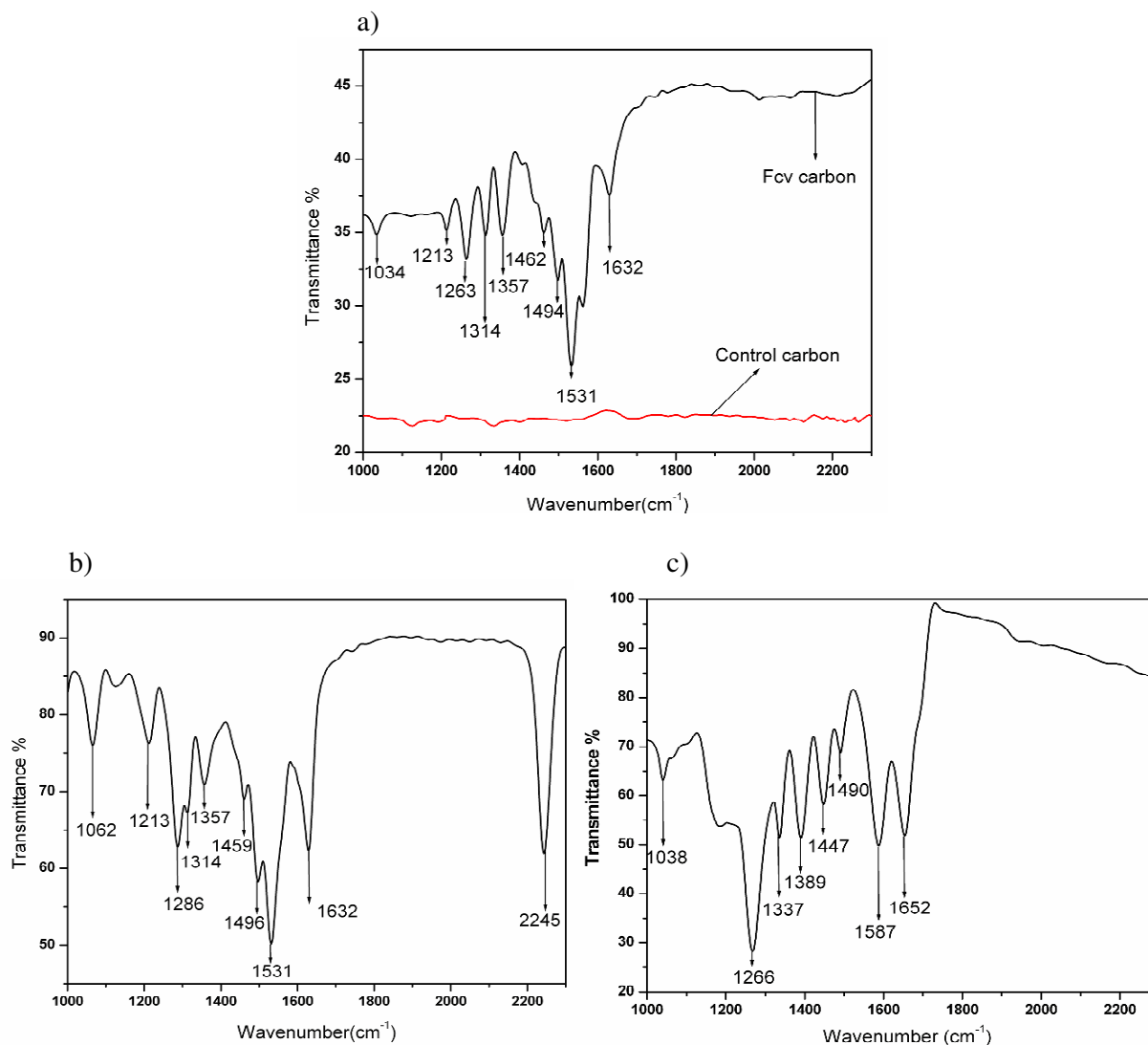
**Table 1.** Surface area parameters of the functionalized carbon powder

Sample	BET specific surface area ( $\text{m}^2/\text{g}$ )	Total pore volume ( $\text{cm}^3/\text{g}$ )	Average pore diameter (nm)
Native carbon powder	34	0.042	4.85
Modified carbon powder	16	0.028	6.93

### 3.6. FTIR spectroscopy of functionalized carbon powder

Infrared spectral studies have been carried out to decipher the presence of modifying molecule and its covalent attachment on the surface of carbon particle. The derivatized carbon powder was

mixed with KBr in 1:100 ratio to make the pellet and it has been exposed to infrared radiation in the range 1000 to 2300  $\text{cm}^{-1}$ . The transmission spectrum of the derivatized carbon powder has revealed that the presence of peaks due to azo ( $\text{N}=\text{N}$ ), nitro ( $\text{NO}_2$ ), aryl nitrile ( $\text{C}-\text{N}$ ) and methoxy ( $\text{OCH}_3$ ) groups on the modifier molecule (Figure 7a). The band at 1632  $\text{cm}^{-1}$  indicates the presence of azo group. But two strong peaks at 1357  $\text{cm}^{-1}$  and 1531  $\text{cm}^{-1}$  signify the presence of nitro group on the modifier molecule. The peaks at 1531  $\text{cm}^{-1}$  and 1494  $\text{cm}^{-1}$  are due to the asymmetric stretching of the



**Figure 7.** The FTIR spectra of a) Modified carbon powder. b) Commercially procured FCV diazonium salt. c) Reduced diazonium salt after functionalization

nitro group and the peaks at 1462  $\text{cm}^{-1}$  & 1357  $\text{cm}^{-1}$  are due to the symmetric stretching of the nitro groups present on the modifier molecule [33]. The difference between the symmetric and asymmetric

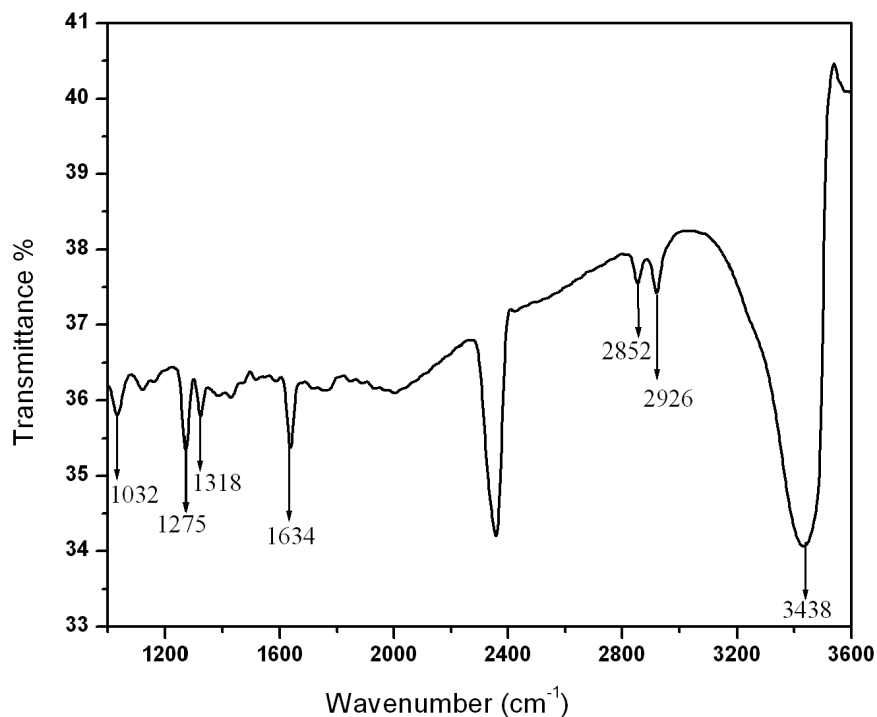
stretching frequencies i.e.  $\nu_{\text{asymmetric}} - \nu_{\text{symmetric}} = 174 \text{ cm}^{-1}$ . The expected value for solids is in the range  $159 - 177 \text{ cm}^{-1}$  [34, 35]. The peak at  $1314 \text{ cm}^{-1}$  indicates the presence of aryl nitrile (C–N) on the modifying molecule while the peaks at  $1263 \text{ cm}^{-1}$  and  $1034 \text{ cm}^{-1}$  signifies the presence of aromatic methoxy group on the modifier. The spectra of aryl alkyl ether display an asymmetrical C–O–C stretching peak between  $1275\text{--}1200 \text{ cm}^{-1}$  and symmetrical stretching peak in the range  $1075\text{--}1020 \text{ cm}^{-1}$ . The peak at  $1263 \text{ cm}^{-1}$  and  $1034 \text{ cm}^{-1}$  is due the asymmetric and symmetric stretching frequencies of the aromatic methoxy group (C–O–C). The relative peak intensities of various groups of the modifying molecule on carbon powder was compared with the peaks of commercially procured corresponding diazonium salt (Figure 7b), and this decrease might be due to the presence of substrate (carbon) on which the modifier is covalently attached.

The most striking feature is the absence of the stretching frequency of ( $\text{N}\equiv\text{N}$ ) group near  $2245 \text{ cm}^{-1}$  on the grafted carbon surface. To confirm the absence of diazonium group in the modifier after derivatization process by diazonium salt reduction method, the filtrate is collected from the reaction mixture and extracted into organic solvent. The extracted compound has been examined for IR spectral studies, which has not showed any peak due to the presence of diazonium group (Figure 7c). This confirms that the diazonium salt undergoes complete nitrogen loss in presence of hypophorous acid during functionalization process and the results are in comparison with the commercially procured salt IR spectra (Figure 7b). This suggests that the surface of the carbon particle has been modified by chemically induced derivatization method with the loss of nitrogen. All these peaks indicate that the modifying molecule on the carbon surface possesses corresponding functional groups and are in comparison with reported literature [33, 34] (Figure 7a). However the IR spectrum of control carbon powder does not show any significant peaks in this region (Figure 7a). The present study brings a strong support to the existence of nitroazo groups and the absence of diazonium group on the modifier which is covalently attached on carbon particle surface.

### 3.7. Spectroscopic evidence for chemical cleavage of modifier

The derivatized carbon powder has been examined to understand whether the modifier molecule on the carbon particle surface undergoes chemical cleavage during electrochemical studies or not. The modified carbon powder was immobilized on basal plane pyrolytic graphite electrode and its cyclic voltammetric behaviour was recorded in the potential range  $0.0 \text{ V}$  to  $-0.8 \text{ V}$ . The CV studies revealed that, at this potential both nitro and azo groups on the modifier molecule simultaneously reduce followed by cleavage at hydrazo group to give two fragments as shown in figure 3. Thus the cleavage of the hydrazo linkage is responsible for the chemical release of a 4-methyl-1, 2-phenylenediamine fragment (fragment B, Figure 3) while the 2-methoxy-5-methylaniline moiety (fragment A, Figure 3) remains on the carbon particle surface which is immobilized on basal plane pyrolytic graphitic electrode. No further voltammetric peaks were observed corresponding to either nitro group or azo group after the fragmentation of FCV molecule attached covalently on the carbon particle surface and these studies confirms with the reported literature [15]. The above experiment was

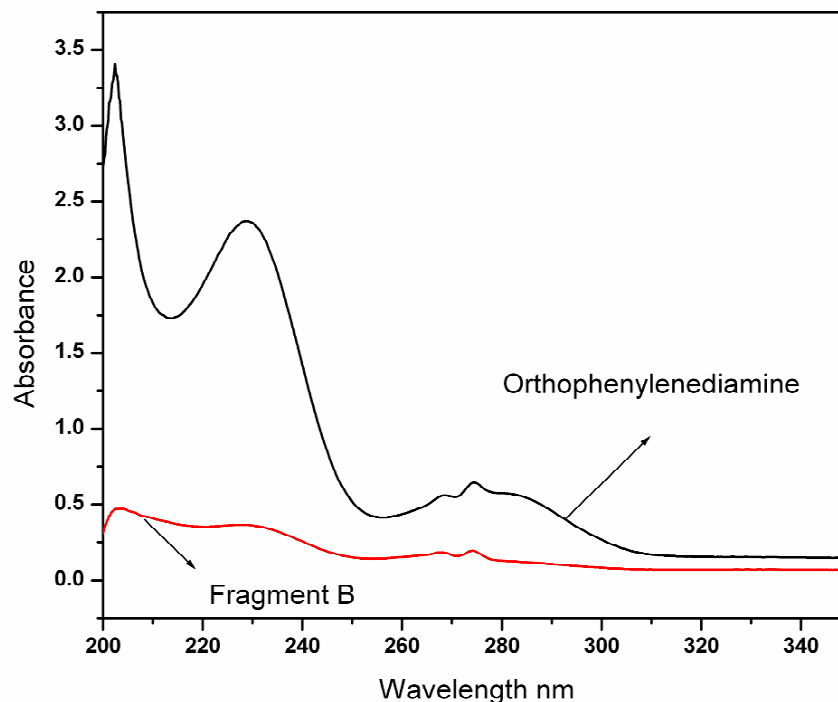
repeated 15 times and all the reduced carbon present on the electrode surface was collected for further studies.



**Figure 8.** FTIR spectra of fragment A retained by the carbon particle after molecular cleavage during electrochemical study

FTIR technique has been used to confirm the presence of surface bound species after CV studies. The surface bound fragment A was collected separately and dried in an oven at 100°C for about 30min. It was mixed with KBr in the ratio 1:100 to make a pellet and the pellet has been exposed to IR light in the range 1000 to 3500  $\text{cm}^{-1}$ . The transmission spectrum of the fragment A (Figure 8) has revealed the presence of peaks due methyl, methoxy and amine groups. The peaks at 2926  $\text{cm}^{-1}$  and 2852  $\text{cm}^{-1}$  are due to the methyl C-H stretching which confirms the presence of aromatic methyl group. The peak at 3438  $\text{cm}^{-1}$  is due to the N-H stretching and the peak at 1634  $\text{cm}^{-1}$  is due to the N-H bending stretching. These stretching frequencies indicate the presence of primary amine group on the modifier molecule. The peak at 1379  $\text{cm}^{-1}$  signifies presence of aryl nitrile group (C-N) but the peaks at 1275  $\text{cm}^{-1}$  and 1032  $\text{cm}^{-1}$  indicate the presence of aromatic methoxy groups on the carbon particle surface. The spectra of aryl alkyl ether display an asymmetrical C-O-C stretching band at 1275-1200  $\text{cm}^{-1}$  with symmetrical stretching near 1075-1020  $\text{cm}^{-1}$ . The peak at 1275  $\text{cm}^{-1}$  is due to the C-O-C asymmetric stretching and the peak at 1032  $\text{cm}^{-1}$  is due to the C-O-C symmetric stretching of the aromatic methoxy group. The peaks at 1275  $\text{cm}^{-1}$  and 1032  $\text{cm}^{-1}$  indicate the presence of aromatic methoxy group on the modifying molecule. But there is no peak corresponding to nitro ( $\text{NO}_2$ ) or azo ( $\text{N}=\text{N}$ ) groups. All these peaks indicate that the modifier molecule on the carbon surface undergoes chemical cleavage under controlled potential conditions and possesses corresponding functional groups and are in comparison with reported literature [33, 34]. The present study brings a strong

support to the existence of aryl methyl, aryl methoxy and aryl amine groups and the absence of nitro and azo groups on the modified carbon surface. Hence, FTIR studies clearly indicate that the nitroazo compounds undergoes complete reduction and cleavage during electrochemical study.



**Figure 9.** The UV absorption spectra of diffused fragment B.

Further we have examined UV Spectroscopy to understand the release of fragment B after cleavage into bulk of the solution during electrochemical studies. Similar to the above studies, the bulk of the solution in the electrochemical cell was concentrated and studied for its absorption in the UV region. The UV absorption spectra of the fragment B has been shown in figure 9. The released chemical fragment contains two amine and a methyl groups on the benzene ring. The UV-VIS absorption spectra of fragment B (Figure 3) shows four absorption bands at 204 nm, 229 nm, 267 nm and 275 nm. Usually absorption spectra of substituted benzene ring give three bands, the band at around 204 and 229 nm are due to primary bands and the band at around 268 nm or 275 nm is due to secondary band, these bands shifts depending on the substituents present on benzene ring [35]. Substituents have differing effects on the positions of absorption maxima, depending upon whether they are electron releasing or withdrawing. The electron releasing groups shifts both primary and secondary bands to longer wavelength and also increases the intensity of these bands. The bands at 204 nm and 267 nm are due to primary and secondary bands of aromatic methyl group. This confirms the presence of methyl group on the “fragment B” (Figure 3) and the bands at 229 nm and 275 nm are due to primary and secondary bands of aromatic primary amine group. This confirms the presence of primary amine group on the fragment B (Figure 3). Since the fragment B contains two amine groups



on benzene which are ortho to each other so we compared the absorption spectra of the fragment B with o-phenylenediamine as a standard [35]. These values are good comparison with the absorption spectra of o-phenylenediamine as shown in figure 9. It was found that all spectra of both o-phenylenediamine and “fragment B” have the similar shape, and almost at the same position but there is a tremendous decrease in the peaks intensity due to very low concentration of the “fragment B” produced during electrochemical study. Hence, UV-VIS spectroscopic studies clearly indicate that the nitroazo compounds undergoes complete reduction under controlled potential by releasing chemical into bulk solution.

#### 4. CONCLUSIONS

Carbon powder has been chemically modified with nitroazobenzene groups by the reduction of corresponding diazonium salt in presence of hypophosphorous acid as a reducing agent. The derivatized carbon powder has been electrochemically characterized after immobilizing it on basal plane pyrolytic graphitic electrode and studying its cyclic voltammetric behaviour. The spectroscopic studies of modified carbon powder based on FTIR, DRS and UV-VIS techniques confirm the surface modification of the carbon particle by the modifying molecule. These studies further revealed that the modifier molecule undergoes cis-trans isomeric conversion of modifier in addition to molecular cleavage during electrochemical studies.

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#### References

1. R.N. Adams, *Electrochemistry at solid electrodes*, Marcel Dekker, New York, (1969).
2. M. Delamar, R. Hitmi, J. Pinson and J.M. Saveant, *J. Am. Chem. Soc.* 114 (1992) 5883.
3. A.J. Downard, *Electroanalysis* 12 (2000) 1085.
4. S. Iijima, *Nature* 354 (1991) 56.
5. B. Barbier, J. Pinson, G. Desarmot and M. Sanchez, *J. Electrochem. Soc.* 137 (1990) 1757.
6. C. P. Andrieux, F. Gonzalez and J. M. Saveant, *J. Am. Chem. Soc.* 119 (1997) 4292.
7. T. A. Zwier and M. F. Burke, *Anal. Chem.* 53 (1981) 812.
8. J. L. Bahr and J. M. Tour, *J. Mater. Chem.* 12 (2002) 1952.
9. E. T. Mickelson, I. W. Chiang, J. L. Zimmerman, P. J. Boul, J. Lozano, J. Liu, R. E. Smalley, R. H. Hauge and J. L. Margrave, *J. Phys. Chem. B* 103 (1999) 4318.
10. J. L. Bahr, J. P. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley and J. M. Tour, *J. Am. Chem. Soc.* 123 (2001) 6536.
11. C. A. Dyke and J.M. Tour, *J. Am. Chem. Soc.* 125 (2003) 1156.
12. V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger and A. Hirsch, *J. Am. Chem. Soc.* 124 (2002) 760.

13. P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson and J.M. Saveant, *J. Am. Chem. Soc.* 119 (1997) 201.
14. M. Pandurangappa, N.S. Lawrence and R.G. Compton, *Analyst* 127 (2002) 1568.
15. M. Pandurangappa and T. Ramakrishna, *Electroanalysis* 18 (2006) 2290.
16. P. Abiman, G. G. Wildgoose and R.G. Compton, *Int. J. Electrochem. Sci.* 3 (2008) 104.
17. P. Abiman, G.G. Wildgoose and R. G. Compton, *J. Phys. Org. Chem.* 21 (2008) 433.
18. R. G. Compton, G. Wellington, D. Bethell, P. Lederer and D.M. O'Hare, *J. Electroanal. Chem.* 322 (1992) 183.
19. Z. F. Liu, K. Hashimoto and A. Fujishima, *Nature* 347 (1990) 658.
20. C. Wang and R. G. Weiss, *Macromolecules* 36 (2003) 3833.
21. I. Willner, V. Pardo-Yissar, E. Katz and K.T. Ranjit, *J. Electroanal. Chem.* 497 (2001) 72.
22. H.Z. Yu, Y.Q. Wang, J.Z. Cheng, J.W. Zhao, S.M. Cai, H. Inokuchi, A. Fujishima and Z.F. Liu, *Langmuir* 12 (1996) 2843.
23. T. Kondo, T. Kanai and K. Uosaki, *Langmuir* 17 (2001) 6317.
24. G. G. Wildgoose, N. S. Lawrence, H. C. Leventis, L. Jiang, T. G. J. Jones, and R.G. Compton, *J. Mater. Chem.* 15 (2005) 953.
25. S. Wawzonek and J. D. Fredrickson, *J. Am. Chem. Soc.* 77 (1955) 3985.
26. Y. Osada and D. E. D. Rossi, *Polymer Sensors and Actuators*, Springer, Technology & Industrial Arts, (2000)
27. S. F. Wang, T. Chen, Z.L. Zhang, X. C. Shen, Z. X. Lu, D. W. Pang and K.Y. Wong, *Langmuir* 21 (2005) 9260.
28. M. Kruk, M. Jaroniec, R. K. Gilpin and Y. W. Zhou, *Langmuir* 13 (1997) 545.
29. S. Chakraborty, J. Chattopadhyay, H. Peng, Z. Chen, A. Mukherjee, R. S. Arvidson, R. H. Hauge and W. E. Billups, *J. Phys. Chem. B* 110 (2006) 24812.
30. P. Barbara, H. Michael and R. Siegmund, *Carbon* 43 (2005) 2209.
31. G. G. Wildgoose, M. E. Hyde, N. S. Lawrence, H. C. Leventis, L. Jiang, T. G. J. Jones and R. G. Compton, *Langmuir* 21 (2005) 4584.
32. Y. Ye, C. C. Ahn, C. Witham, B. Fultz, J. Liu, A. G. Rinzler, D. Colbert, K. A. Smith and R. E. Smalley, *Appl. Phys. Lett.* 74 (1999) 2307.
33. R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 5<sup>th</sup> edition, John Wiley & Sons, New York, (1991).
34. E. Coulon, J. Pinson, J. D. Bourzat, A. Commercon and J. P. Pulicani, *J. Org. Chem.* 67 (2002) 8513.
35. D. L. Pavia, G. M. Lampman and G. S. Kriz, *Introduction to Spectroscopy*, 3<sup>rd</sup> edition, Thomson, New Delhi, (2007).