

# Microwave-assisted functionalization of glassy carbon spheres: electrochemical and mechanistic studies

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**Abstract** Functionalization of glassy carbon spheres have been carried out by microwave irradiation in the presence of modifier molecules through oxidation followed by amidation reaction. The glassy carbon spheres were initially catalyzed by treating with concentrated nitric acid to introduce surface-bound carboxylic groups, and its subsequent amidation reaction in the presence of *p*-nitroaniline yields *p*-nitroanilide-functionalized substrate materials. These derivatized glassy carbon spheres have been electrochemically characterized by immobilizing them on bppg electrode and studying its voltammetric behavior. X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy studies have revealed that the modifying molecules are surface bound and covalently attached on the carbon substrate.

**Keywords** Microwave irradiation · Functionalization · Glassy carbon spheres · Voltammetry · X-ray photoelectron spectroscopy · *p*-Nitroaniline

## Introduction

The surface chemistry of graphite and related conducting forms of carbon is of much interest to electrochemists, surface scientists, synthetic chemists, and material scientists in recent years due to its unique properties like chemical inertness, high mechanical strength, good electrical conductivity, high surface activity, and wide potential window

[1]. In recent years, a lot of emphasis has been laid toward the functionalization of carbon substrate materials, primarily due to their potential applications in separation science, adsorption studies, enhancing catalysis, trace metal ion analysis, electroanalysis, chemical sensors, and other electronic components [2, 3]. A few methods such as electrochemical reduction, thermolysis, photolysis, and chemical reduction of diazonium salts have been developed and used for the surface functionalization of different forms of carbon substrates through the reactive intermediates of aryldiazonium salts [4–8]. The resulting reactive species formed such as aryl radical or cationic species can react with the carbon surface, resulting in covalently bonded species [9]. Most of these reactions are based on the use of conventional chemical techniques like refluxing and/or sonication in organic solvents or mineral acids or reducing agents, often making use of high temperatures/pressures, long reaction times, and highly reactive species [10–12]. Consequently, alternative functionalization approaches are highly desirable to enable new protocols easy to execute and scale up. Microwave-assisted organic synthesis enhances the rate of reactions, improves product yield, has low reaction times, as well as shows energy efficiency [13]. A novel fabrication method for the patterned carbon nanotubes (CNTs) conducting arrays by consecutive condensation reaction and their photolithographic application has been reported [14]. The oxidized nanotubes were treated with long-chain alkylamines via acylation, and the resulting functionalized material is soluble in organic solvents [15]. The lipophilic and hydrophilic dendrimers were covalently attached on oxidized CNT via amidation or esterification reactions [16]. The multiple rapid functionalization of CNTs through 1,3-dipolar cycloaddition of aziridines using microwave energy was reported by Brunetti and coworkers [17].

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Microwave radiation is a well-known noninvasive and clean processing tool that has been widely used to activate or accelerate chemical reactions [18, 19]. Typically, microwave energy decreases the kinetic barrier for reactions by altering bond vibrational and/or configuration energies of specific reactants [20]. Such activation can provide reaction to take place at lower temperatures and/or reduced reaction times which can obviate unwanted side reactions and products due to thermal effects and lead to accrued cost savings [21]. In this direction, functionalization of materials with due consideration to minimize the organic solvent use as well as to achieve the required modification under solvent-free conditions has been adopted using microwave irradiation using nitric acid as an oxidizing agent [22]. However, no attempts have been made until now to use microwave energy to functionalize the glassy carbon spheres through oxidation and subsequent amidation reaction. In this report, we have studied the derivatization of glassy carbon spheres in a two-step process via oxidation and amidation processes under solvent-free conditions. The modified glassy carbon spheres with *p*-nitroanilide groups have been designated as *p*-nitroanilide-modified glassy carbon spheres (NAGCs) and characterized by studying its cyclic voltammetry as well as spectroscopy.

## Experimental section

### Chemicals and instrumentation

All reagents used were Analar grade and used without further purification. The glassy carbon spheres (2–12  $\mu\text{m}$  in diameter) were purchased from Aldrich (purity >99.95%) and used directly, and these consisted of irregularly shaped particles. *p*-Nitroaniline (purity >97%) and potassium bromide for Fourier transform infrared spectroscopy (FTIR grade,  $\geq 99\%$ ) were obtained from Sigma-Aldrich. Solutions of known pH in the range pH 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 N 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  $\text{KH}_2\text{PO}_4$  + 0.01 M  $\text{Na}_2\text{HPO}_4$ ; pH 8, 0.01 M  $\text{KH}_2\text{PO}_4$  + 0.01 M  $\text{Na}_2\text{HPO}_4$ ; pH 9, 0.05 M sodium tetraborate ( $\text{H}_3\text{BO}_3$  + 1 N NaOH); pH 10, 0.1 M sodium tetraborate + 0.1 N 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

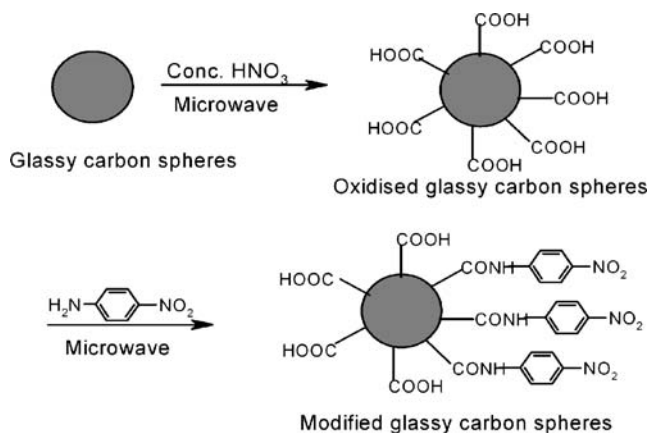
were carried out at room temperature ( $26 \pm 2$  °C) after degassing the solutions using ultrapure nitrogen gas for 15 min in an electrochemical cell of volume 10 mL with a standard three-electrode configuration. A basal plane pyrolytic graphite (bpgg, 0.3  $\text{cm}^2$ , Le Carbone Ltd., Sussex, UK) electrode acted as the working electrode. A Pt (99.99%) wire was used as a counter electrode and Ag/AgCl (3 M KCl; CH Instruments, Texas, USA) as a reference electrode. All pH measurements were carried out using Control Dynamics pH meter. All the Fourier transform infrared spectrophotometer measurements were performed using FTIR-8400S Shimadzu. X-ray photoelectron spectroscopy (XPS) spectra of the samples were recorded in an ESCA-3 Mark II spectrometer (VG Scientific, England) using Al KR radiation (1,486.6 eV). Binding energies were corrected from charge effects by reference to the C (1s) peak of carbon contamination at 285 eV and measured with a precision of 0.2 eV. The experimental data were curve fitted with Gaussian peaks after subtracting a linear background.

### Functionalization of glassy carbon spheres through amidation reaction

One gram of glassy carbon spheres was mixed with 5 mL of 70%  $\text{HNO}_3$  in a glass bowl, and the microwave power was set to about 15% of a total of 900 W, and the reaction was carried out for about 2 min to generate carboxylic groups on the surface of the glassy carbon spheres. Then *p*-nitroaniline (0.138 g, 1 mmol) was added to the reaction mixture, and the reaction was continued for a period of 1-min heating. Then, the reaction mixture was cooled and filtered by washing with water to remove excess acid. Finally, the modified glassy carbon spheres were washed with acetonitrile, acetone, and water to remove any unreacted and physisorbed reactants. The functionalized glassy carbon spheres were then dried by placing inside a fume hood for a period of 12 h and finally stored in an airtight container prior to use (Scheme 1) [9, 10]. The *p*-nitroanilide-functionalized glassy carbon spheres have been designated as NAGCs.

### Electrode modification

The *p*-nitroanilide-modified glassy carbon spheres were electrochemically characterized by immobilizing abrasively onto the surface of the basal plane pyrolytic graphite electrode and studying its voltammetric behavior. The electrode surface was initially polished on glass polishing paper (H00/240) followed by silicon carbide paper (P1000C) for smoothness. The functionalized glassy carbon spheres were immobilized mechanically (Scheme 2) onto the bpgg electrode by gently rubbing the electrode surface



**Scheme 1** Derivatization of glassy carbon spheres with *p*-nitroanilide species

on a fine qualitative filter paper containing the derivatized glassy carbon spheres [7].

## Results and discussion

XPS studies of oxidized and functionalized glassy carbon spheres

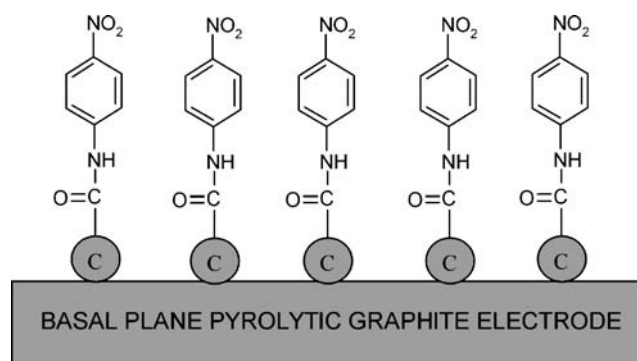
The XPS spectral studies of both oxidized and *p*-nitroanilide-functionalized glassy carbon spheres have been carried out in the range 0 to 1,000 eV (Figs. 1a and 2a). In each case, the observed spectrum was dominated by the peak corresponding to the C1s at ca. 284.7 eV corresponding to graphitic carbon. On closer inspection, it was possible to observe peak corresponding to the O1s at 533.5 eV, which is in agreement with previous studies of carbonaceous surfaces [23]. The presence of different kinds of oxygen on the surface of both samples was confirmed by the corresponding O1s peak of carboxylic acid and nitro groups. The presence of nitrogen on the surface of the modified glassy carbon spheres corresponds to the N1s peak of nitro groups, but the most striking feature is the absence of N1s peak at 402 eV due to the *p*-nitroanilide group on the oxidized glassy carbon surface. This confirms that functionalization has occurred on the surface of the glassy carbon sphere surface through covalent attachment [23].

Next, a series of successive scans was performed on each of the samples (oxidized glassy carbon spheres and NAGCs) over the C1s, N1s, and O1s regions of the spectrum. For C1s emission, it was scanned from 280 to 295 eV. Next, ten scans were performed from 395 to 410 eV corresponding to the N1s region of the spectrum and the cumulative spectrum recorded to improve the signal-to-noise ratio. Similarly, ten scans were recorded over the O1s region from 525 to 540 eV, and its cumulative spectrum was considered.

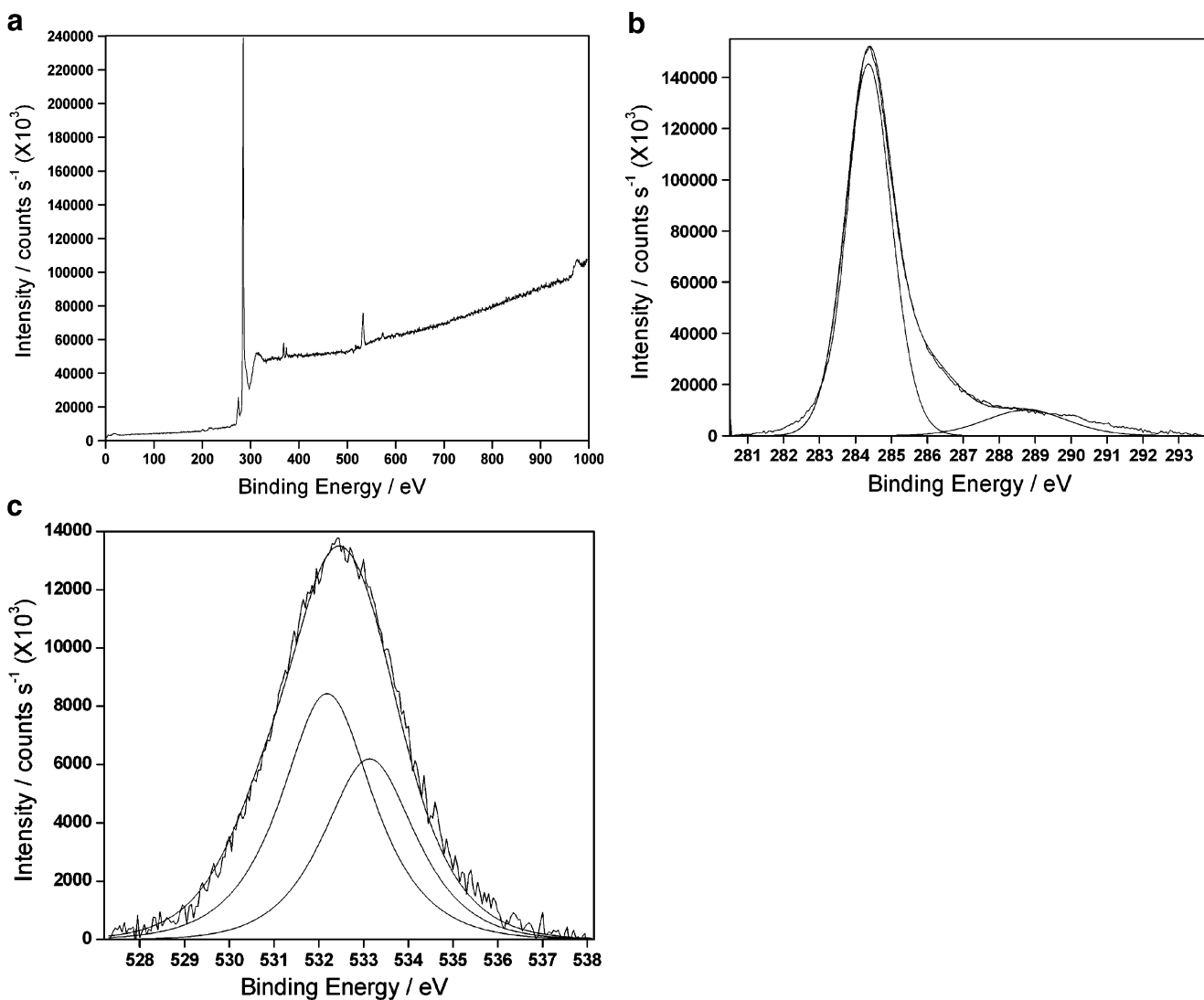
The spectrum was recorded over the C1s region for each of the two samples studied above to identify and distinguish between C1s signals corresponding to the  $-\text{COOH}$ ,  $-\text{CONH}$ , and  $-\text{NO}_2$  groups on the surface of oxidized glassy carbon spheres and functionalized glassy carbon spheres (Figs. 1b and 2b). Oxidized glassy carbon spheres show two peaks pertaining to C1s signals at 284.35 and 288.77 eV in the ratio 13:1 and these peaks correspond to C1s of glassy carbon spheres and C1s of carboxylic groups (Fig. 1b), whereas functionalized material shows four peaks at 284.32, 285.3, 286.4, and 289.64 eV pertaining to C1s, and these peaks are due to C1s of glassy carbon spheres,  $-\text{NO}_2$ , aromatic, and  $-\text{CONH}$  groups, respectively (Fig. 2b).

Next, successive scans were performed on each of the samples pertaining to the O1s region. Figure 1c shows the O1s spectrum of oxidized glassy carbon spheres, while Fig. 2c shows the corresponding spectrum of NAGCs for comparison. Analysis of the resulting spectra reveals that the oxidized glassy carbon spheres shows two peaks at 532.1 and 533.13 eV in the ratio 1.4:1 corresponding to quinonyl and carboxylic acid groups, while NAGC shows three peaks at 531.33, 532.1, and 533.14 eV, respectively. Among these peaks, two peaks correspond to oxygen-containing quinonyl and amide surface groups, while the third corresponds to the oxygen atoms of an aromatic  $-\text{NO}_2$  group [24] (<http://srdata.nist.gov/xps/XPSDetailPage.aspx>).

Similarly, the spectrum was recorded for *p*-nitroanilide-modified glassy carbon spheres in the N1s region. Figure 2d shows two peaks at 400 and 405.7 eV due to the presence of the N1s electrons of  $-\text{CONH}$  group and  $-\text{NO}_2$  groups of the modifying molecule, respectively. Analysis of the resulting spectra for NAGCs showed two peaks. Among these, one peak corresponds to nitrogen-containing amide surface group, while the other belongs to the nitrogen atoms of an aromatic  $-\text{NO}_2$  group. The presence of  $-\text{CONH}$  and  $-\text{NO}_2$  groups are in agreement with the interpretation of the N1s spectral of these materials given above. Comparison with literature values of N1s shifts for different nitrogen-containing moieties allows us to



**Scheme 2** Electrode modification

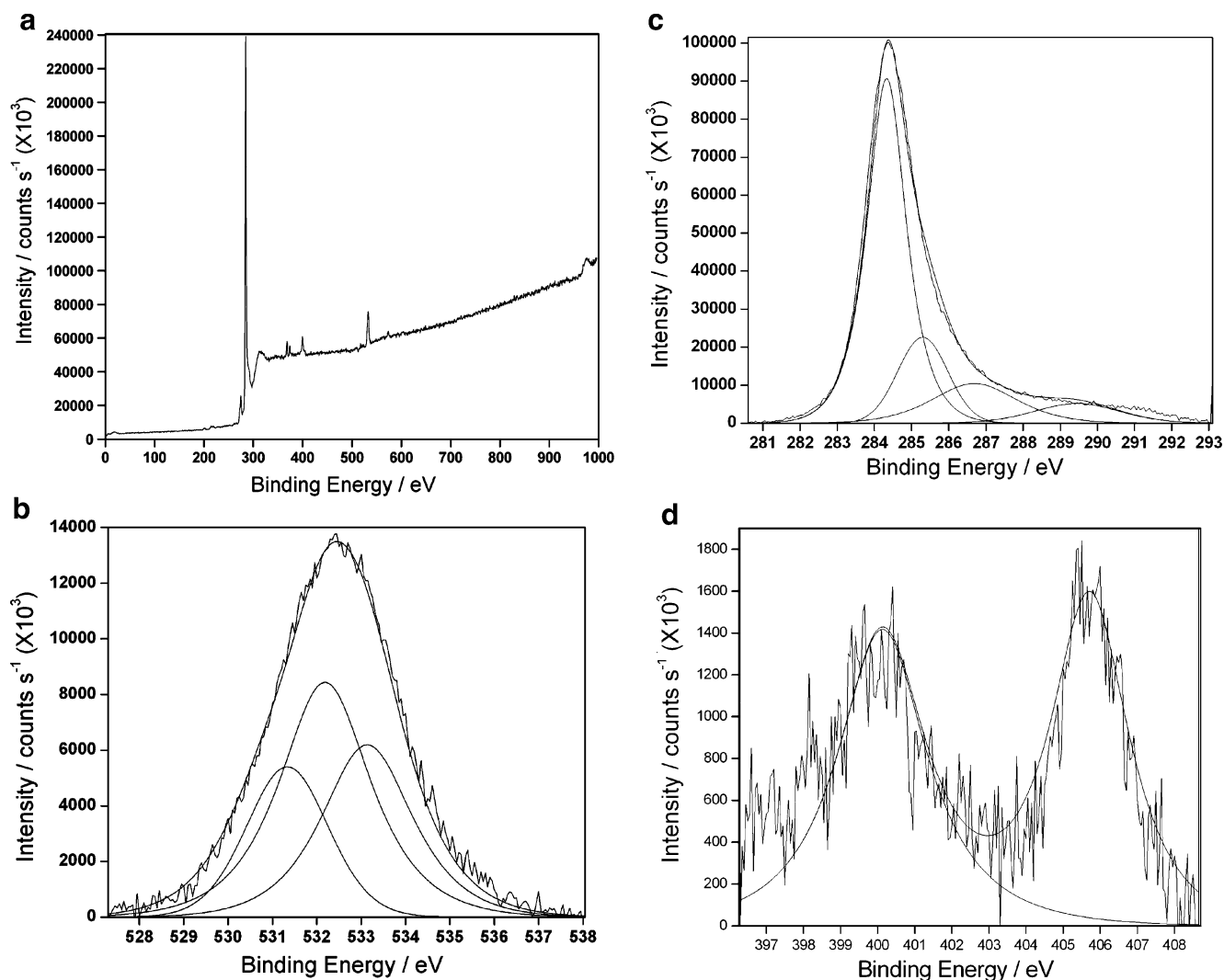


**Fig. 1** The XPS spectra of **a** survey of oxidized glassy carbon spheres; **b** oxidized glassy carbon sphere over the C1s region; **c** oxidized glassy carbon sphere over the O1s region

assign the peaks as arising from an amide and a nitro moiety, respectively. The 1:1 ratio of  $-\text{CONH}$  and  $-\text{NO}_2$  moieties indicates that nitrophenyl is indeed present on the surface of the glassy carbon sphere, and it is in agreement with reported literature [23]. Instead, we identified such oxygen-containing surface groups in addition to the nitrogen-containing moieties by using a simple Gaussian sum function. To minimize the error in measuring peak positions, the C1s peak position for each sample was measured relative to the literature value, and all subsequent peak positions reported for samples were adjusted accordingly. These studies reveal that the surface of the oxidized glassy carbon spheres undergoes functionalization through the carboxylic groups to attach nitrophenyl moieties covalently [23, 24] (<http://srdata.nist.gov/xps/XPSDetailPage.aspx>).

#### Voltammetry of oxidized glassy carbon spheres

The glassy carbon spheres were initially oxidized by acid treatment to introduce carboxylic groups on its surface before amidation reaction. In order to confirm the presence of carboxylic groups on the surface of the oxidized glassy carbon spheres, its cyclic voltammetry has been carried out after immobilizing it on bppg electrode. Initially, voltammetric scans were recorded in the potential range +0.6 to  $-0.6$  V in aqueous buffer of pH 4 (0.1 M acetic acid + 0.1 M sodium acetate) to understand the electrochemical behavior of the oxidized glassy carbon spheres. Upon first scanning in a negative direction, a reductive wave was observed at  $E_{\text{pc}}=0.216$  V vs. Ag/AgCl (3 M KCl), and in its reverse direction its corresponding oxidative wave has been observed at  $E_{\text{pa}}=0.312$  V vs. Ag/AgCl



**Fig. 2** The XPS spectra of **a** survey of functionalized glassy carbon spheres; **b** NAGCs over the C1s region; **c** NAGCs over the O1s region; **d** NAGCs over the N1s region

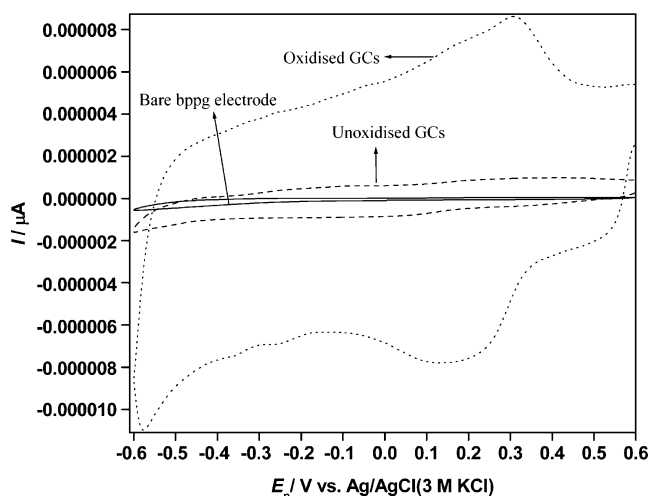
(3 M KCl). The subsequent scans corresponding to reductive/oxidative waves are symmetrical in shape, and the peak current is proportional to the square root of the scan rate. Next, a series of control experiments has been carried out to compare the electrochemical behavior of quinonyl/hydroquinonyl groups with bare bppg electrode and unoxidized glassy carbon spheres. No significant peaks have been observed due to these, indicating the absence of any redox moieties on the surface of unoxidized or native glassy carbon spheres (Fig. 3).

#### Voltammetry of functionalized glassy carbon spheres

The derivatized glassy carbon spheres were examined electrochemically in order to verify whether the modifying molecule has been attached on the glassy carbon spheres or not during microwave-induced derivatization process. The

redox behavior of *p*-nitroanilide-modified glassy carbon spheres were characterized by immobilizing them on bppg electrode and studying its cyclic voltammetry. The potentials due to peaks B, A<sup>1</sup>, and C<sup>1</sup> were found to vary with the pH studied (Scheme 3). Figure 4 shows the initial three scans of modified glassy carbon spheres at pH 4 (0.1 M CH<sub>3</sub>COOH + 0.1 M CH<sub>3</sub>COONa + 0.1 M KCl) with a scan rate of 25 mV s<sup>-1</sup> and in a potential range +0.6 to -0.7 V. the first scan in a reductive sweep from 0.6 V showed a strong irreversible peak at ca.  $E_{pc} = -0.632$  V vs. Ag/AgCl (3 M KCl) electrode (designated as B in Scheme 3). Upon reversing the scan at -0.7 V, two new oxidative peaks were observed at ca.  $E_{pa} = 0.229$  and  $E_{pa} = 0.336$  V vs. Ag/AgCl (3 M KCl; designated as reversible peaks A<sup>1</sup> and C<sup>1</sup> in Scheme 3). Its corresponding reductive peaks at ca.  $E_{pc} = 0.230$  and  $E_{pc} = 0.098$  V vs. Ag/AgCl (3 M KCl; designated as reversible peak A and C in Scheme 3)





**Fig. 3** Overlaid voltammograms of bare electrode, unoxidized and oxidized glassy carbon spheres immobilized on bppg electrode at pH 4 (0.1 M  $\text{CH}_3\text{COOH}$  + 0.1 M  $\text{CH}_3\text{COONa}$  + 0.1 M KCl), bppg electrode  $0.3 \text{ cm}^2$ , scan rate ( $\nu$ )  $25 \text{ mV s}^{-1}$ , potential range + 0.6 to -0.6 V

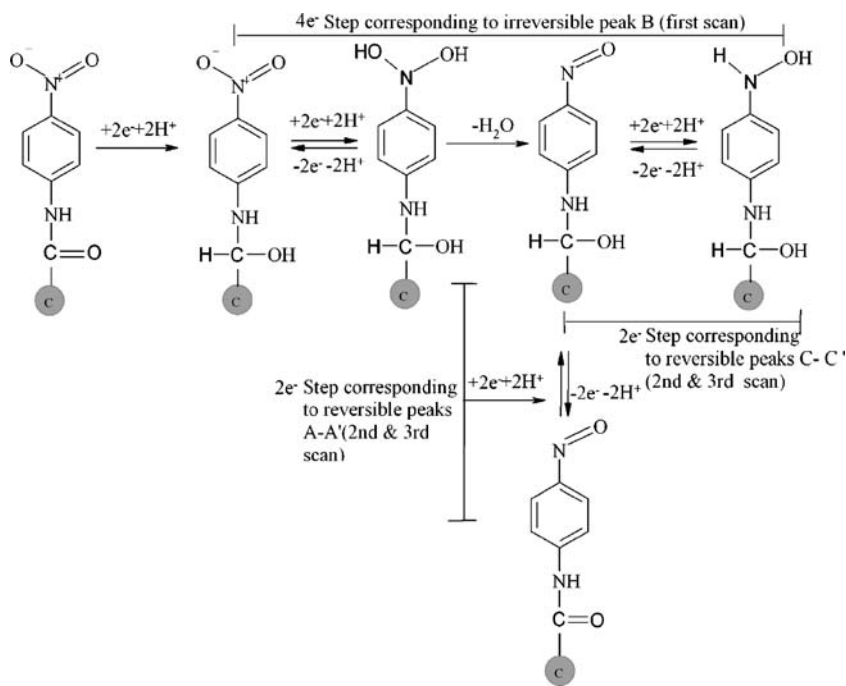
were observed when the scan direction was reversed. These are due to the corresponding reduction of oxidized species at  $E_{\text{pa}}=0.229$  and  $E_{\text{pa}}=0.336$  V vs. Ag/AgCl (3 M KCl); in the subsequent scans, we could not observe any irreversible peak, but the oxidative and reductive peaks were observed in the potential range 0.1 to 0.3 V. These peaks might be due to electrochemically reversible processes, which are designated as  $\text{CC}^1$  and  $\text{AA}^1$ , respectively. The electrochemically irreversible peak designated as B is not observed in subsequent scans, indicating that all the nitro moieties have

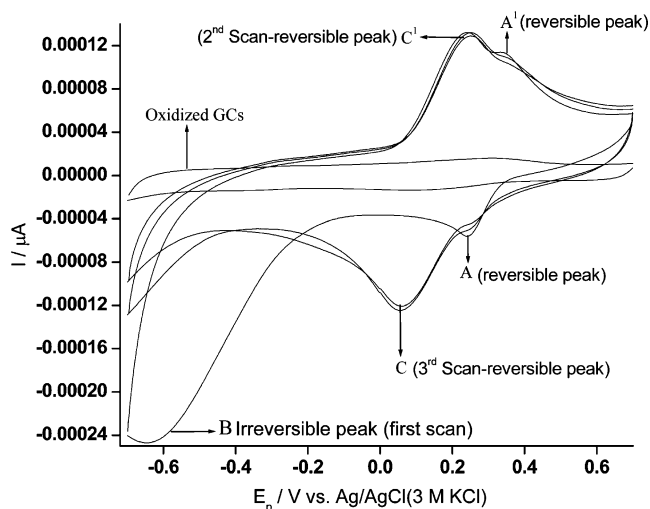
been reduced to phenyl hydroxyl amine group. The observed voltammetric behavior and their wave shapes are consistent with the reported literature studies of *p*-nitrophenyl carbon and correspond to the electrochemical reduction of the surface-bound nitro groups in aqueous media [7]. Peak B corresponds to chemically and electrochemically irreversible reduction of the nitro group in a four-electron, four-proton transfer to form the phenyl hydroxylamine. Then, it undergoes an electrochemically reversible two-electron, two-proton oxidation (peaks  $\text{CC}^1$ ) to form the nitrosophenyl moieties. The peaks  $\text{AA}^1$  corresponds to the electrochemically reversible two-electron, two-proton redox process of  $\text{C}=\text{O}$  moiety of modifying a molecule present on the surface of the glassy carbon spheres. The oxidative/reductive peak potentials of the nitro group present on the modifying molecule are in agreement with the reported literature [6–8].

#### Effect of scan rate

Effect of scan rate ( $\nu$ ) for NAGCs was studied by varying scan rate between 10 and  $100 \text{ mV s}^{-1}$  at pH 4. The scan rate ( $\nu$ ) was increased by an increment of  $10 \text{ mV s}^{-1}$  (figure not shown) at each time the electrochemically reversible peaks  $\text{CC}^1$  (designated as  $\text{C C}^1$  in Fig. 4) have been observed, which rapidly stabilized to give a nearly symmetrical wave shape. The peak current ( $I_p$ ) was found to vary linearly with the scan rate ( $\nu$ ) (figure not shown). However, this is not an indicative of species diffusing into the solution. The *p*-nitroanilide groups are indeed attached to the surface of the glassy carbon spheres. The peak current obtained is

**Scheme 3** The proposed redox mechanism of modifier molecule





**Fig. 4** Overlaid voltammograms of oxidized and functionalized glassy carbon spheres, at pH 4 (0.1 M CH<sub>3</sub>COOH + 0.1 M CH<sub>3</sub>COONa + 0.1 M KCl), bppg electrode 0.3 cm<sup>2</sup>, scan rate (ν) 25 mV s<sup>-1</sup>, potential range + 0.6 to -0.6 V

expected to be 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 glassy carbon spheres with electrons hopping from one *p*-nitroanilide group to another [7, 8].

### Effect of pH

The effect of pH on the peak potentials of NAGCs over the pH range 1–12 has been examined at room temperature. The proton loss/gain occurs on the electrode surface due to the oxidation/reduction of the nitro group of *p*-nitroanilide moieties attached on glassy carbon spheres surface. The shift in the peak potentials may be attributed to the Nernstian behavior, which is described in the following equation [7, 8]:

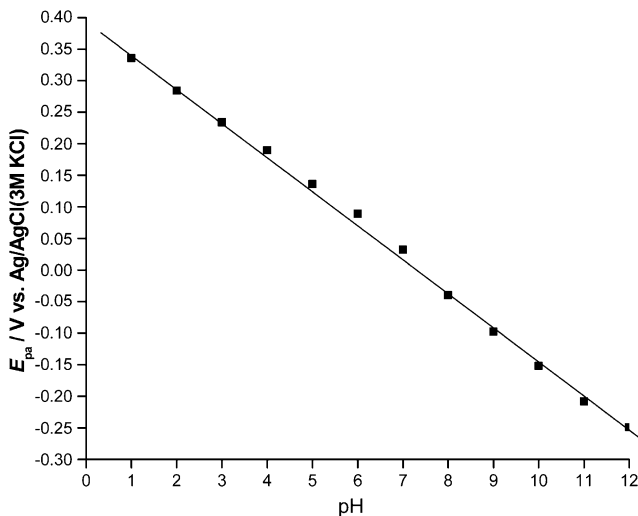
$$E = E^\theta - \frac{2.303RTm}{nF} \text{pH}$$

where  $E$  is the peak potential (V),  $E^\theta$  is the standard potential (V),  $R$  is the universal gas constant (J K<sup>-1</sup> mol<sup>-1</sup>),  $T$  is the temperature (K),  $F$  is the Faraday constant (C mol<sup>-1</sup>), and  $m$  and  $n$  are the number of protons and electrons transferred at the electrode interface, respectively. The  $m$  and  $n$  values are two in the case of *p*-nitroanilide glassy carbon sphere as explained earlier, i.e., the nitrosophenyl/phenylhydroxylamine couple (peaks CC<sup>1</sup> in Fig. 4); the other symbols have their usual meanings. At room temperature, the peak potentials for NAGCs particles were found to shift to more negative potentials with increase in pH. The peak shapes are nearly symmetrical with a slight separation between oxidative and reductive peaks at each pH studied, and also the magnitude of the peak current

decreases corresponding to a decrease in the hydrogen ion concentration at higher pH values. The plot of resulting reductive peak potentials of the functionalized glassy carbon spheres with varying pH values was found to be linear in the pH range (1–12) studied (Fig. 5). The electrochemical studies for modified glassy carbon spheres were repeated five times in each case, and reproducible peak potentials were observed. The SD has been calculated and found to be 0.067. The potential gradient was found to be 58±2 mV per unit pH, which is very close to the theoretical value of 59±2 mV. The electroactive species modified on the glassy carbon sphere surface follows Nernstian behavior, and these studies are comparable to the reported literature values [7, 8].

### Stability of electrode modified by immobilized species

The stability of the modified electrode (bppg) with the immobilized species has been examined by multiscan study. In this study, multiple scans (30 scans) were carried out continuously in order to understand whether the immobilized species would diffuse from the electrode surface into the solution or not. The result pertaining to the multiple scan study has been shown in Fig. 6. These voltammograms are highly symmetrical in shape, and there is a slight decrease in the peak currents which might be due to the diffusion of some particles from the electrode interface into the solution during cycling conditions. We next removed the electrode from the solution and replaced it with a fresh buffer solution of the same pH. The recorded cyclic voltammetry scan was found to overlay the last scan recorded before the solution was replaced. These results confirm that the electroactive material is confined onto the electrode surface and has not detached into the bulk of the solution. The variation of scan rate (ν) in the scan range 10–100 mV s<sup>-1</sup> has resulted into



**Fig. 5** Effect of pH on peak potential

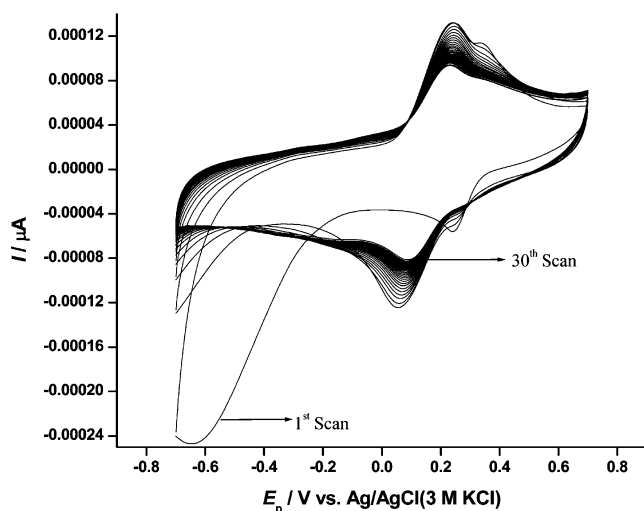


Fig. 6 Stability of the modified electrode

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 (figure not shown), which indicates that they are surface-bound species [7, 8]. Next, the modified material has been subjected to cyclic voltammetric studies over a period of time to understand the stability of the modifier molecule. Even after several months, the electrochemical behavior of the functionalized material remains the same, and the wave shapes are symmetrical with a steady increase in the peak currents with increase in scan rate (not shown). These results revealed that the electroactive material is confined and has not detached from the glassy carbon spheres surface. All these studies indicate that the covalently derivatized glassy carbon spheres with *p*-nitroanilide groups are highly stable and can be used to fabricate electrode after compressing them into pellets. These electrodes can be used in sensor technology [3].

#### FTIR characterization of NAGCs

Infrared spectral studies have been carried out to decipher the presence of modifying molecule and its covalent attachment on the surface of glassy carbon spheres. The functionalized glassy carbon spheres have been mixed with KBr in 1:100 ratio to make the pellet, and it has been exposed to infrared radiation in the range 1,000 to 3,700  $\text{cm}^{-1}$ . The transmission spectrum of the functionalized glassy carbon spheres has revealed the presence of peaks due to nitro ( $\text{NO}_2$ ), amide ( $\text{CONH}$ ), and aryl nitrile ( $\text{C-N}$ ) groups on the modifier molecule (Fig. 7). The presence of two strong bands at 1,385 and 1,560  $\text{cm}^{-1}$  indicates the nitro group on the modifying molecule. These bands are due to the symmetric and asymmetric stretching frequencies of the nitro group. The difference between the symmetric and asymmetric stretching, i.e.,  $\nu_{\text{asymmetric}} -$

$\nu_{\text{symmetric}} = 175 \text{ cm}^{-1}$ , and the expected value for solids is in the range 159 to 177  $\text{cm}^{-1}$  [8]. The peaks at 1,560 and 1,481  $\text{cm}^{-1}$  are due to the asymmetric stretching of the nitro group and the peak at 1,385  $\text{cm}^{-1}$  is due to the symmetric stretching of the nitro group present on the modifier molecule. The band at 1,658  $\text{cm}^{-1}$  is due to the amide stretching substituted on the aromatic ring. The peak at 1,309  $\text{cm}^{-1}$  is due to the presence of aryl nitrile ( $\text{C-N}$ ) on the modifying molecule, while the peaks at 3,320 and 1,525  $\text{cm}^{-1}$  are due to the presence of stretching and bending mode of N-H group on the glassy carbon sphere surface. The relative peak intensities of the modifier molecule has been compared with the relative intensities of the bands due to *p*-nitroaniline, but the intensities of the modifier on glassy carbon spheres is much weaker than the *p*-nitroaniline, which might be due to the substrate presence. All these peaks indicate that the modifying molecule on the glassy carbon sphere surface possesses corresponding functional groups, and it is in agreement with the literature studies [25]. However, the IR spectrum of native glassy carbon powder does not show any significant peaks in this region [8]. Hence, this study brings a strong support to the existence of nitro groups on the modified glassy carbon spheres.

#### Conclusions

Surface modification of glassy carbon spheres could be achieved easily by microwave irradiation of substrate material in the presence of nitric acid, and its subsequent amidation reaction results in *p*-nitroanilide-modified glassy carbon spheres. The surface-functionalized glassy carbon spheres are stable for several months, and these materials

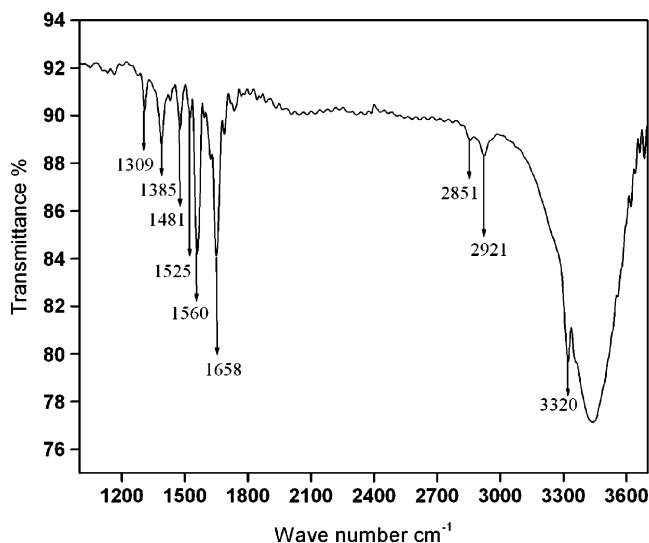


Fig. 7 FTIR spectra of modified glassy carbon spheres



can be used to fabricate bulk-modified electrodes in sensor technology. The electrochemical characterization studies have revealed the redox behavior of the modifier molecules. The spectroscopic characterization studies based on FTIR and XPS have further corroborated the existence of modifier molecule covalently bonded on glassy carbon spheres.

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## References

1. Barriere F, Downard AJ (2008) *J Solid State Electrochem* 12:1231. doi:10.1007/s10008-008-0526-2
2. McCreery RL (2008) *Chem Rev* 108:2646. doi:10.1021/cr068076m
3. Kahlert H (2008) *J Solid State Electrochem* 12:1255. doi:10.1007/s10008-008-0566-7
4. Delamar R, Hitimi R, Pinson J, Saveant JM (1992) *J Am Chem Soc* 114:5883. doi:10.1021/ja00040a074
5. Bahr JL, Tour JM (2001) *Chem Mater* 13:3823. doi:10.1021/cm0109903
6. Pandurangappa M, Lawrence NS, Compton RG (2002) *Analyst (Lond)* 127:1568. doi:10.1039/b209711g
7. Pandurangappa M, Ramakrishnappa T (2006) *Electroanalysis* 18:2290. doi:10.1002/elan.200603658
8. Pandurangappa M, Ramakrishnappa T (2008) *J Solid State Electrochem* 12:1411. doi:10.1007/s10008-007-0470-6
9. Abiman P, Wildgoose GG, Compton RG (2008) *J Phys Org Chem* 21:433. doi:10.1002/poc.1331
10. Pompeo F, Resasco DE (2002) *Nano Lett* 2:369. doi:10.1021/nl015680y
11. Peng H, Alemany LB, Margrave JL, Khabashesku VN (2003) *J Am Chem Soc* 125:15174. doi:10.1021/ja037746s
12. Huang W, Taylor S, Fu K, Lin Y, Zhang D, Hanks TW, Rao AM, Sun YP (2002) *Nano Lett* 2:311. doi:10.1021/nl010095i
13. Lewis DA, Summers JD, Ward TC, McGrath JE (1992) *J Polym Sci A* 30:1647. doi:10.1002/pola.1992.080300817
14. Jung DH, Jung MS, Ko YK, Seo SJ, Jung HT (2004) *Chem Comm* 14:526
15. Chen J, Hamon MA, Hu H, Chen Y, Rao AM, Eklund PC, Haddon RC (1998) *Science* 282:95. doi:10.1126/science.282.5386.95
16. Martin RB, Qu L, Lin Y, Harruff BA, Bunker CE, Gord JR, Allard LF, Sun YP (2004) *J Phys Chem B* 108:11447. doi:10.1021/jp048984s
17. Brunetti FG, Herrero MA, Munoz JM, Ortiz AD, Alfonsi J, Meneghetti M, Prato M, Vazquez E (2008) *J Am Chem Soc* 130:8094. doi:10.1021/ja801971k
18. Fini A, Breccia A (1999) *Pure Appl Chem* 71:573. doi:10.1351/pac199971040573
19. Santagada V, Frecentese F, Perissutti E, Favretto L, Caliendo G (2004) *QSAR Comb Sci* 23:919. doi:10.1002/qsar.200420039
20. Majetich G, Iteks R (1995) *Radiat Phys Chem* 45:567. doi:10.1016/0969-806X(94)00071-Q
21. Hong EH, Lee KH, Oh SH, Park CG (2003) *Adv Funct Mater* 13:961. doi:10.1002/adfm.200304396
22. Wang Y, Iqbal Z, Mitra S (2006) *J Am Chem Soc* 128:95. doi:10.1021/ja053003q
23. Masheter AT, Xiao L, Wildgoose GG, Crossley A, Jonesc JH, Compton RG (2007) *J Mater Chem* 17:3515. doi:10.1039/b705615j
24. Actis P, Caulliez G, Shul G, Opallo M, Mermoux M, Marcus B, Boukherroub R, Szunerits S (2008) *Langmuir* 24:6327. doi:10.1021/la703714a
25. Silverstein RM, Bassler GC, Morrill TC (1991) *Spectrometric identification of organic compounds*, 5th edn. Wiley, New York, p 127