

Synthesis of some azacrown derivatives and fabrication of their nanofilms on the glassy carbon surface

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Abstract The modification of *N*-phenyl-aza-15-crown-5 (PA15C5) and *N*-(4-aminophenyl)-aza-15-crown-5 (4APA15C5) on glassy carbon (GC) electrode was performed by the electrochemical oxidation of the corresponding azacrown derivatives in anhydrous acetonitrile media. The electrochemical behavior of the resulting modified GC electrode was investigated in the presence of electroactive redox probes and these results, together with the X-ray photoelectron spectroscopy (XPS) and reflection-absorption infrared spectroscopy were used to confirm the attachment of these molecules onto the GC surface. The ellipsometric thicknesses of PA15C5 and 4APA15C5 films at the GC surface was obtained around 9.28 ± 0.40 and 10.50 ± 1.10 nm, respectively. Azacrown modified nanoscale surfaces serve as alkali metal sensor specific for their cavity in the crown ring.

Keywords Azacrown ethers · Nanofilms · Surface characterization · X-ray photoelectron spectroscopy

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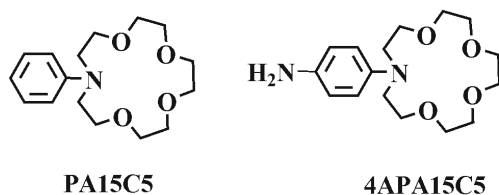
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Introduction

Synthesis of azacrown ethers is one of the challenging areas in the field of supramolecular chemistry. To date, the fascinating behavior of azacrown derivatives has been exploited in a wide range of applications, including selective polydentate ligands for metal cations [1], fluorescent and photochromic ligands [2] for extraction and separation of alkaline, and alkaline earth metal cations [3, 4] in ion transport through membranes, in ion-selective electrodes as phase transfer catalysts [5] for instance. Although most works in this area have involved synthesis, characterization, and chemical properties of these compounds, electrochemical grafting of azacrown ether derivatives and their binding properties on the GC surfaces has not been thoroughly investigated [6–8]. Due to the broad analytical interest in azacrown derivatives and their great potential for important applications, electrografting of azacrown moieties on a GC surface can be important and can lead to new chemically modified electrodes (CMEs) with unique electroanalytical properties. Derivatization of surfaces is often required to improve the performance of many materials, may change their surface properties, and is also often critical for particular applications [9–11]. For these reasons, the field of CMEs in electrochemistry has been a topic of great interest to many researchers for decades [12]. The goal of this research is to prepare novel GC surfaces modified with PA15C5 and 4APA15C5 compounds, as shown in Scheme 1, to gain new insight into the modification area. To this end, firstly, PA15C5 and 4APA15C5 compounds were synthesized and characterized with spectral analysis.

GC surfaces were modified by the electrochemical oxidation of PA15C5 and 4APA15C5 to yield a covalently attached and compact multilayer. The mechanism of modification and surface characterization are carefully



Scheme 1 The formulae of PA15C5 and 4APA15C5

studied by various characterization techniques including CV, XPS, and RAIRS. The ellipsometry technique was also used to determine the thicknesses of the PA15C5 and 4APA15C5 nanofilms on a GC surface.

Experimental section

Chemicals

Silver nitrate (Fluka), activated carbon (Sigma-Aldrich), tetrabutylammoniumtetrafluoroborate (TBATFB) (Fluka), potassium ferricyanide (Sigma-Aldrich), potassium ferrocyanide (Merck), potassium chloride (Merck), ferrocene (Sigma), acetonitrile (MeCN) (Sigma), isopropyl alcohol (IPA) (Sigma), and other chemicals were reagent grade quality and used as received from the supplier. All the processes performed in aqueous media and the preparation of the aqueous solutions were carried out using ultra pure quality of water with a resistivity of $\sim 18.3 \text{ M}\Omega \text{ cm}$ (Human Power 1⁺ Scholar purification system). Before electrochemical experiments, solutions were purged with pure argon gas (99.999%) at least for 10 min, and an argon atmosphere was maintained over the solution during experiments.

Apparatus

The ^1H and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer (UK) in CDCl_3 with tetramethylsilane as internal standard. Infrared spectra were recorded as KBr pellets and from the film deposited on GC electrode directly in a FTIR spectrometer Bruker-Tensor 27 (Bruker Optics Inc., Ettlingen, Germany). All the electrochemical experiments were performed using a Gamry Reference 300 workstation (Gamry, USA). Working electrode was a bare or modified GC disk (BAS) with a geometric area of 0.027 cm^2 . The reference electrode was either a $\text{Ag}/\text{AgCl}/\text{KCl}_{(\text{sat.})}$ used in aqueous media or a Ag/Ag^+ (0.01 M) used in MeCN. The auxiliary electrode was a Pt wire. GC electrodes were prepared by polishing first with fine wet emery papers with grain size of 4000 (Buehler, Lake Bluff, IL, USA) followed by 0.1 and $0.05 \mu\text{m}$ alumina slurry on a polishing pad (Buehler, Lake Bluff, IL, USA) to gain a mirror-like appearance. The electrodes were sonicated for

15 min in water and in 50:50 (v/v) IPA and MeCN solution purified over activated carbon. Before derivatization, the electrodes were dried with an argon gas stream. The surface of the samples was analyzed using a SPECS X-ray photoelectron spectrometer (Berlin, GERMANY) system with unmonochromatized $\text{AlK}\alpha$ radiation (1486.6 eV) as an X-ray anode. Survey and high-resolution spectra were collected using 144 and 48 eV pass energy, respectively. The X-ray gun was operated at 10 kV voltage and 20 mA current. The pressure inside the analyzer was maintained at 10^{-9} Torr. The binding energy scale was referenced by setting the C–H peak maximum in the C_{1s} spectrum to 285.0 eV and the atomic composition estimated using SpecsLab software. Concerning data manipulation, a linear background subtraction was performed prior to any peak-fitting procedure. A Gaussian–Lorentzian sum function in 70:30 ratios was used to fit the individual peak. Ellipsometric thickness measurements of PA15C5 and 4APA15C5 nanofilms were made with an ELX-02C/01R Model (GERMANY) high precision discrete wavelength ellipsometer. The wavelength was 532 nm for all experiments. The thickness values of the films at the GC-20 (Tokai, Japan) surface were determined from the average of the measurements using incidence angle of 70° . Theoretical thickness of the nanofilm was determined using Chemoffice Ultra v.10 software [13, 14].

Synthesis of the azacrown ethers

N-phenylaza-15-crown-5 [PA15C5]

This compound was prepared by the modification of the procedure reported in the literature [15]. *N*-phenylaza-15-crown-5 sodium perchlorate monohydrate (14 g) was decomposed by treatment with a mixture of $\text{CH}_2\text{Cl}_2:\text{H}_2\text{O}$ (1:1), the organic layer was separated, dried, and evaporated to give *N*-phenylaza-15-crown-5, 7 g of (73%), mp. 45°C (mp. $44\text{--}45^\circ\text{C}$ [15]).

IR (cm^{-1}), 3070, 3040, 2947, 2940, 2890, 2869, 1680, 1599, 1505, 1465, 1370, 1250, 1100, 982, 843, 729. ^1H NMR (CDCl_3 , 400 MHz, 25°C): 3.48 (*t*, 4H, $\text{NCH}_2\text{CH}_2\text{O}$) 3.65–3.72 (*m*, 16H, $\text{CH}_2\text{CH}_2\text{O}$), 6.66–6.70 (*m*, 3H, ArH), 7.18–7.25 ppm (*m*, 2H, ArH). ^{13}C NMR: $\delta=52.68, 68.83, 70.41, 71.57, 71.59, 111.61, 115.93, 129.49, 147.77$ ppm. $\text{C}_{16}\text{H}_{25}\text{NO}_4$: calcd. C 65.06, H 8.53, N 4.74; found C 65.15, H 8.48, N 4.90.

Synthesis of the *N*-(4-aminophenyl)aza-15-crown-5 [4APA15C5]

This compound was prepared according to the literature procedure [16]. *N*-(4-nitrosophenyl)aza-15-crown-5 (1.60 g, 4.90 mmol) was dissolved in 3 mL hydrochloric acid (37%)

and 1.6 mL water. SnCl_2 (2.60 g, 14.00 mmol) was then added in portions under stirring at 40°C. Water (20 mL) was added to dilute the solution after 20 min and the mixture was allowed to continue stirring for another 30 min. After addition of NaOH (40%), the crude product appeared as a brown oil. The mixture was extracted with dichloromethane several times, and the combined dichloromethane extracts were dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to dryness leaving brown oils. Subsequent recrystallization from MeCN gave the product as brown crystals. Yield 1.2 g, 78%. (Scheme 1) mp 53°C (mp 53°C [17]).

IR (cm^{-1}), 3338, 3040, 3020, 2900, 2878, 2873, 2860, 1647, 1514, 1472, 1351, 1274, 1113, 943, 834, 759, 693. ^1H NMR (CDCl_3 , 400 MHz, 25°C): 3.22(*s*, 2H, NH_2), 3.48(*t*, 4H, $\text{NCH}_2\text{CH}_2\text{O}$) 3.62–3.72(*m*, 16H, $\text{CH}_2\text{CH}_2\text{O}$) 6.54–6.62(*m*, 4H, ArH). ^{13}C NMR: δ =52.95, 69.23, 70.38, 70.45, 71.47, 113.65, 117.25, 136.77, 141.74 ppm. $\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_4$: calcd. C 61.91, H 8.44, N 9.03; found C 61.15, H 8.48, N 9.39.

Preparation of PA15C5 and 4APA15C5 nanofilms on GC

Modification of GC electrodes was performed in a solution of 1 mM PA15C5 and 4APA15C5 in 0.1 M TBATFB in MeCN vs. Ag^+/Ag (0.01 M) reference electrode using CV with a scan rate of 100 mV s^{-1} for ten cycles between 0 and 2.6 V. The PA15C5 and 4APA15C5 solutions were deaerated with argon for at least 10 min prior to grafting, and a fresh sample of these solutions were used for each modification process. Following the modification, electrodes were rinsed with MeCN and kept in dust-free argon atmosphere until use.

Results and discussion

Synthesis of the azacrown derivatives PA15C5 and 4APA15C5 was carried out according to literature [15–17]. To confirm their proposed structure, detailed characterization techniques such as FT-IR, ^1H NMR, ^{13}C NMR, and DEPT were used. Due to the importance of azacrown compounds in the field of analytical chemistry [6], chemical sensors [7, 8] and ionic extraction [18] as molecular receptors [19], we also investigated the grafting of PA15C5 and 4APA15C5 on a GC surface to get a new insight into the modification area. The modifications of these molecules onto GC surfaces were verified by CV, XPS, and RAIRS.

Spectroscopic characterization of PA15C5 and 4APA15C5 compounds

In the FT-IR spectra of PA15C5 and 4APA15C5 compounds, asymmetric and symmetric stretching vibrations of

$\nu_{\text{Ar-H}}$ are observed at 3070–3050 cm^{-1} and 3030–3020 cm^{-1} , respectively. The observation of asymmetric and symmetric C–O–C signals at 1100 and 982 cm^{-1} for PA15C5, and 1113 and 943 cm^{-1} for 4APA15C5 indicates that the proposed reaction has occurred. In the ^1H NMR spectra of PA15C5 in CDCl_3 , the signals of the crown ether moiety are in the range of ca. 3.64–3.72 ppm as a multiplet for 16H ($-\text{CH}_2\text{OCH}_2-$) and 3.45–3.50 ppm as a triplet for 4H ($-\text{CH}_2\text{NCH}_2-$), and the signals of the aromatic protons are in the expected range. In the ^{13}C NMR spectra of the PA15C5 compound, nine different carbon atoms are expected to be observed, which is consistent with the structure of the compound. The total assignments of ^1H and ^{13}C NMR spectra for the structure 4APA15C5 are made with the help of the DEPT technique. In the ^1H NMR spectrum, aromatic protons in the benzene ring are observed at 6.54 ppm for H_6 and 6.62 ppm for H_7 as two doublets of doublets ($^3J_{\text{HH}}=8.8$ Hz, $^4J_{\text{HH}}=1.69$ Hz). The signals of the crown ether moiety are in the range of 3.62–3.72 ppm as a multiplet for 16H (CH_2OCH_2) and 3.47–3.50 ppm as a triplet for 4H (CH_2NCH_2). The broad singlet of the NH_2 proton is observed at 3.22 ppm. In the ^{13}C NMR spectrum of 4APA15C5, nine different carbon signals are observed, consistent with the structure of 4APA15C5 on the basis of molecular symmetry. The DEPT spectra is used in order to better discriminate the different types of carbons present in the azacrown derivative 4APA15C5. The DEPT spectrum of 4APA15C5 gives the CH_2 peaks at 52.95, 69.23, 70.38, 70.45, 71.47 ppm and CH peaks at 113.65 and 117.25 ppm. The other peaks of ^{13}C NMR, except for the peaks in DEPT spectrum, are non-protonated carbons.

Electrochemical preparation and characterization of PA15C5 and 4APA15C5 nanofilms

Electrografting processes were performed in a solution of 1 mM PA15C5 and 4APA15C5 in 0.1 M TBATFB in MeCN vs. Ag^+/Ag (0.01 M) reference electrode using CV with a scan rate of 100 mV s^{-1} for ten cycles between 0 and 2.6 V (Fig. 1). The modified GC electrodes were then thoroughly rinsed under ultrasonication in MeCN for 5 min to remove any species loosely attached or adsorbed to the surfaces. Approximately ten CV scans were required to obtain a steady-state response, at which a single, broad, and irreversible oxidation peak appeared at about 2.01 V, and a reversible peak appeared at about 0.52 V. The less positive peak is characteristic for the oxidation of redox active N atom in the azacrown ring and gives the resonance-stabilized radical cation. This behavior is also observed for the *N*-phenylaza-15 crown-5 compound on a Pt surface [6–8]. The irreversible peak around –2.01 V can be attributed to the resonance-stabilized radical cation in PA15C5 (Scheme 2a) and oxidation of the amine group in

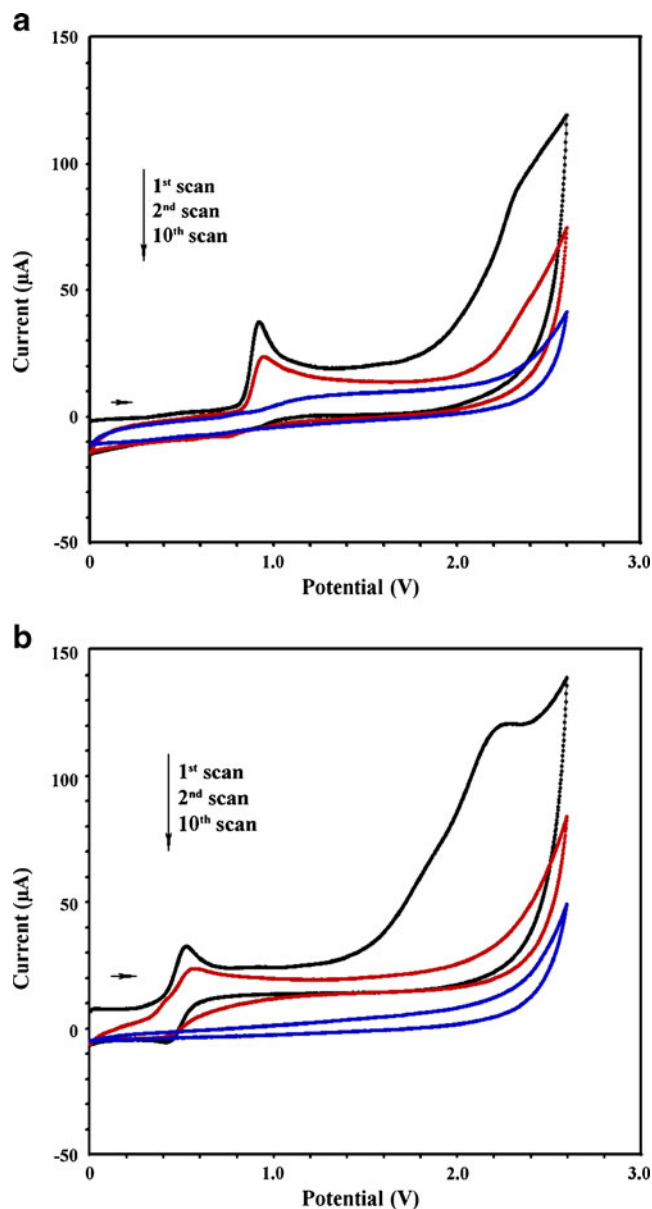


Fig. 1 Cyclic voltammogram for electrografting of **a** PA15C5 and **b** 4APA15C5 on GC vs. Ag/Ag^+ (0.01 M) in 0.1 M TBATFB in MeCN. Scan rate is 100 mV s^{-1}

the 4APA15C5 molecule (Scheme 2b). When the potential is repeatedly scanned over the same range, this peak rapidly diminishes in size. These observations are indicative of formation of a film on the electrode surface, which blocks further oxidation of the PA15C5 and 4APA15C5 compounds in the solution [13, 20, 21]. It is a well-known fact that the anodic switching potential has a strong impact on the immobilization of aromatic organic molecules. When the switching potential is extended to the oxygen-evolution potential range, the GC surface is oxidized, giving rise to the formation of carboxylic and alcoholic functionalities [22]. These oxygen-containing functionalities probably

come from the residual water present in MeCN, which has been reported as approximately in the range of 10^{-3} to 10^{-2} M [23], almost at the same level with or more than the PA15C5 species. Therefore, PA15C5 modification on the GC surface can be realized as a reaction of the surface hydroxyl functionalities with the oxidation product of the PA15C5 compound through the aromatic *p*-carbon, resulting in the etheric (GC)C–O–C C–(PA15C5) bond, as is shown in Scheme 2a.

Considering our results and other works in literature on the oxidation of amines at carbon-based electrodes [24], the reaction process is attributed possibly to a one-electron oxidation of the amino groups with its corresponding cation radicals that attack the GC surface immediately (Scheme 2b).

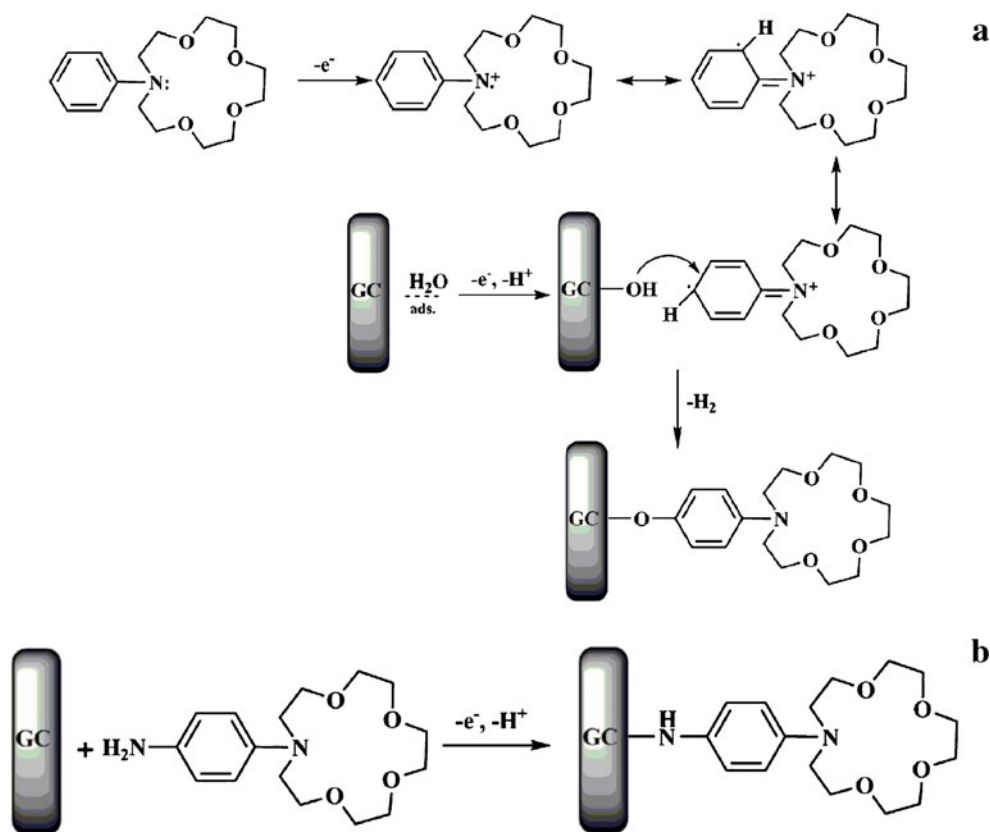
The modified electrodes were characterized electrochemically using various redox probes, such as potassium ferricyanide and ferrocene by the CV technique. The cyclic voltammograms were recorded for 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ (in 0.1 M KCl) and 1 mM ferrocene (in 0.1 M TBATFB in MeCN) at the PA15C5 and 4APA15C5-modified GC as well as on the bare GC surfaces (Fig. 2). The reversible waves for potassium ferricyanide and ferrocene on the bare GC surface were almost completely obscured on the modified surface, suggesting that electrografting was successfully performed [25, 26].

Characterization of PA15C5 and 4APA15C5 nanofilms by XPS

To verify that PA15C5 and 4APA15C5 have been grafted on the GC surface, XPS experiments were performed, and the results were shown in Figs. 3 and 4. Figure 3 presents the survey spectra of GC electrodes before and after modification with thin PA15C5 and 4APA15C5 layers. The spectrum of the GC surface presents only the expected peaks and is devoid of any N_{1s} and F_{1s} component. In the XPS spectrum of the modified GC surfaces, C, N, O and F peaks are observed, showing evidence that PA15C5 and 4APA15C5 have been immobilized onto the surface. A more detailed analysis of the surface composition of the modified electrodes can be obtained from the core-level spectra (Fig. 4).

Figure 4 shows the expected C_{1s} , N_{1s} , and O_{1s} XPS spectrums of PA15C5 and 4APA15C5 on the GC surface. After the chemical attachment of these organic moieties, the single peak at 284.5 eV, which is due to the sp^2 hybridized C atoms [27, 28], is transformed into a broad envelope, and deconvolution reveals that it consists of two components for each surface: the peaks at 287.20 and 286.37 eV (assigned to C–N and C–O) [29] and the peak at 285.09 and 284.64 eV (assigned to C–C and C–H) [30] for PA15C5-GC and 4APA15C5-GC surfaces, respectively.

Scheme 2 Possible grafting mechanism for **a** PA15C5 and **b** 4APA15C5 on the GC



The XPS N_{1s} core-level spectra of the modified GC electrodes were curve-fitted with two components at 402.07 and 400.23 eV and three components at 399.38, 400.30, and 402.12 eV for PA15C5-GC and 4APA15C5-GC surfaces, respectively. The peaks located at 400.23 and 399.38 eV are attributable to the presence of C–N groups in the organic film, already highlighted in previous studies [29]. The peak at 400.30 eV is assigned to the amine nitrogen of compound

4APA15C5, covalently bonded to the GC surface [31–33]. The other peak located at 402.07 and 402.12 eV is due to the tetrabutylammonium cations of the supporting electrolyte, trapped inside the film during its formation and not totally removed by the rinsing of the deposit in acetonitril [34]. Examination of the O_{1s} spectra supports the analysis by the C_{1s} and N_{1s} spectra and provides evidence for successful modification with PA15C5 and 4APA15C5. The

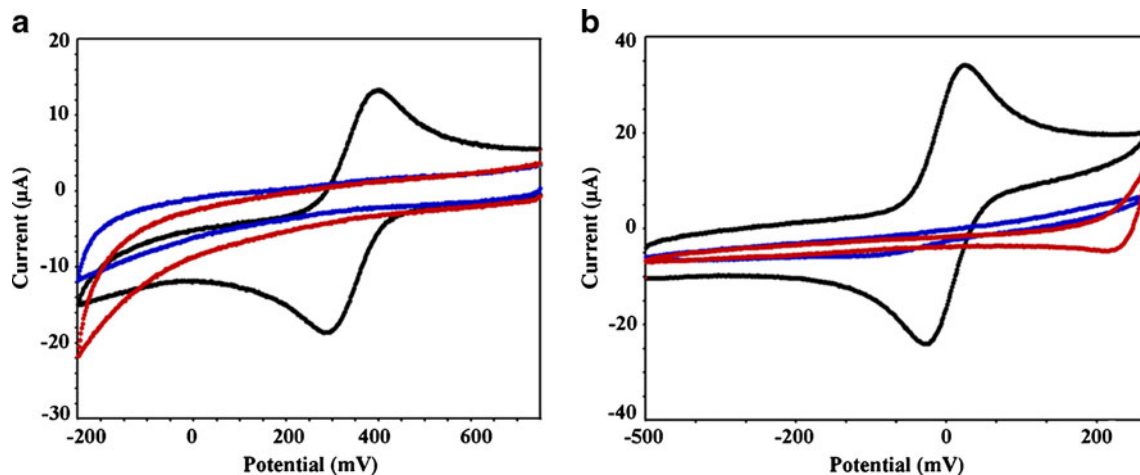


Fig. 2 Cyclic voltammograms of **a** 1 mM potassium ferricyanide (in 0.1 M KCl) vs. Ag/AgCl/KCl_{sat} reference electrode and **b** 1 mM ferrocene (in 0.1 MTBATFB in MeCN) vs. Ag/Ag⁺ reference

electrode on bare GC (black curve) and on PA15C5-GC (red curve) and 4APA15C5-GC (blue curve) electrodes. Scan rate is 100 mV s⁻¹

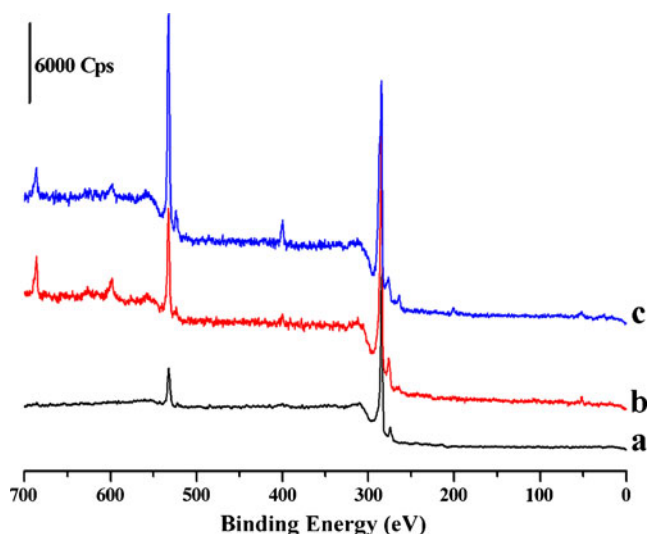


Fig. 3 XPS survey spectra for the **a** bare GC, **b** 4APA15C5, and **c** PA15C5 modified GC surfaces

peak centered about 532 eV is assigned to the azacrown ether C–O–C groups. The observation of the F_{1s} peak at around 690 eV for all modified surfaces is anticipated as some surface contamination by the BF_4^- ions of the supporting electrolyte during modification [35]. A small O_{1s} peak observed in the bare GC spectrum at about 530 eV is attributed to the surface oxides that form spontaneously on most carbon surfaces due to atmospheric attacks, as has been reported in literature [28, 36, 37].

Characterization of PA15C5 and 4APA15C5 nanofilms by RAIRS

In addition to CV and XPS techniques, RAIRS measurements were carried out to further characterize the deposited species after modification of the GC surface (Fig. 5).

RAIRS spectrums were acquired at a range of 4000 to 600 cm^{-1} and shown in Fig. 5. Saturated C–H-stretching vibration modes and aromatic ring modes (C=C stretch) appeared at a range of 2959–2865 cm^{-1} and 1588–1404 cm^{-1} , respectively. Observation of asymmetric and symmetric C–O–C signals at about 1049 and 871 cm^{-1} for the PA15C5-GC surface and 1016 and 836 cm^{-1} for the 4APA15C5-GC surface, respectively, indicates that the proposed grafting has occurred. Although the peak at 3400 cm^{-1} for the N–H vibration [38] is not noticeable in the RAIRS spectrum of the 4APA15C5-GC surface, the weak N–H in plane vibration mode at 1675 cm^{-1} implies the existence of N–H stretching vibration bonds for the immobilized 4APA15C5 moieties [32]. A possible reason for the absence of N–H bonds may be the orientation of the molecules with respect to the surface. Since RAIRS offers a means of probing vibrations at the surface, which have a dipole perpendicular to the surface [39], it is possible that some of the N–H bonds are positioned parallel to the surface. Therefore, absence of the main vibration of N–H does not necessarily imply the lack of N–H bonds in the final structure.

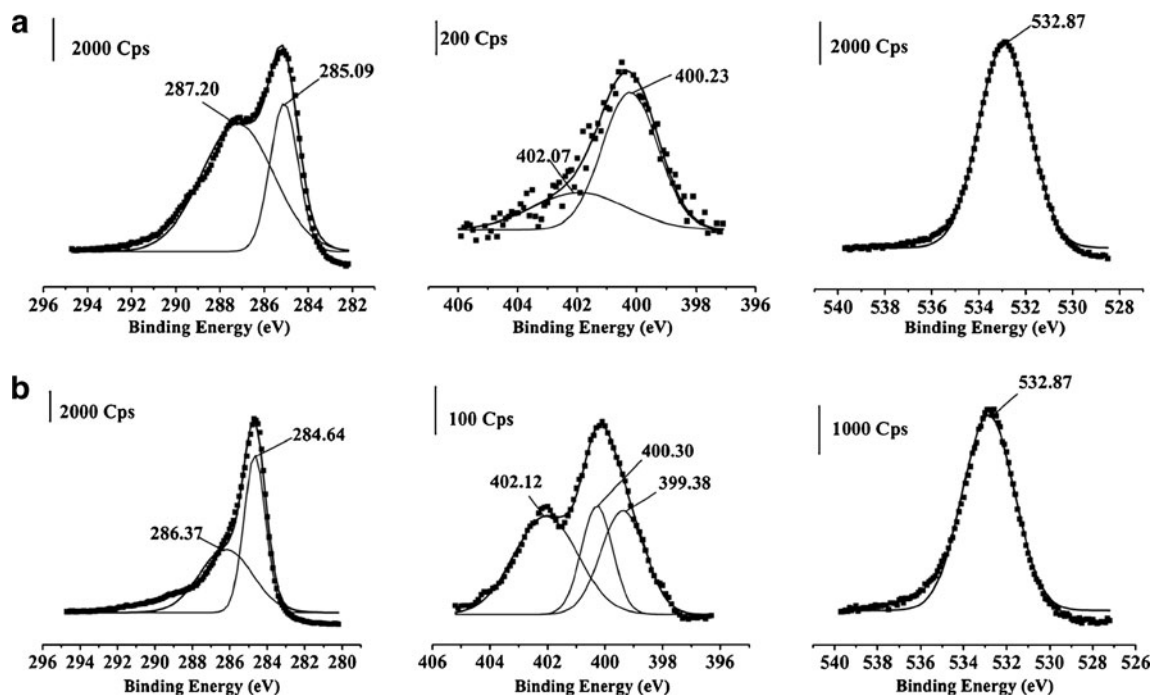
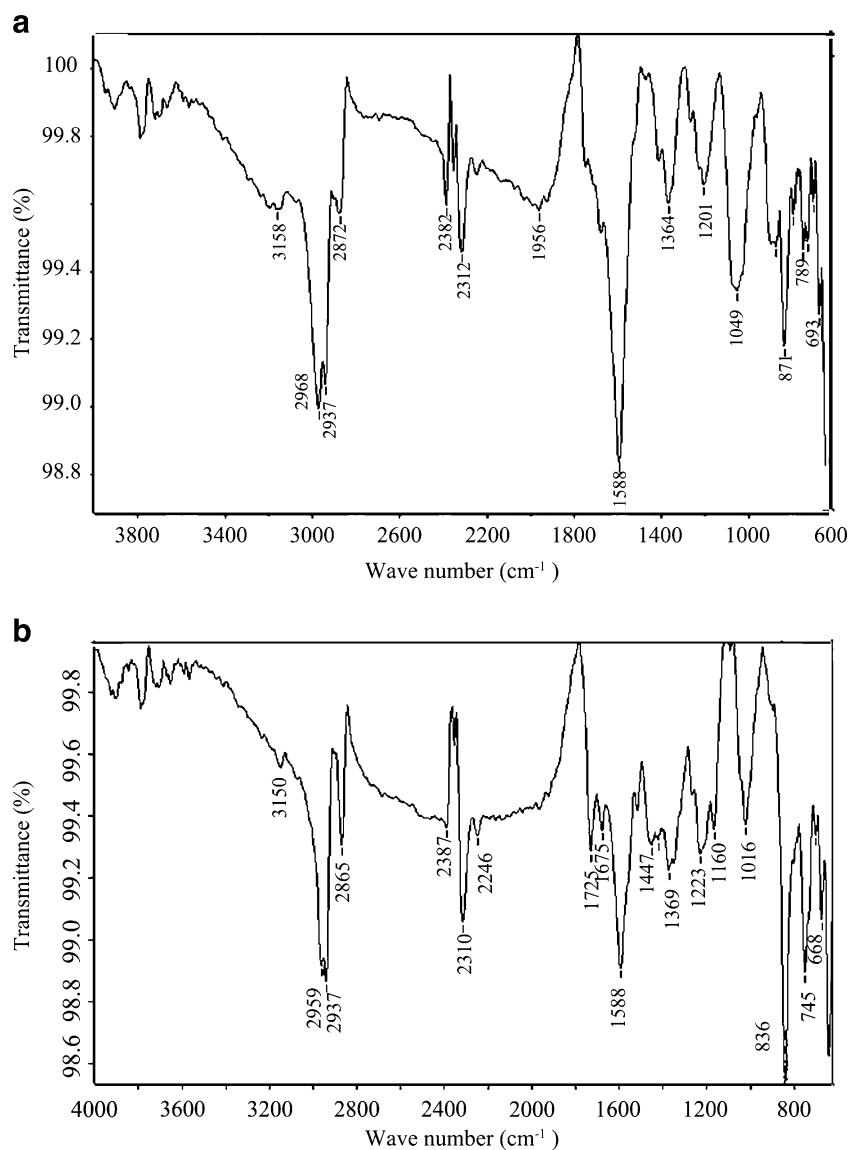


Fig. 4 The narrow region XPS spectra of **a** PA15C5 and **b** 4APA15C5 modified GC surface for the deconvolution spectra of the C_{1s} , N_{1s} , and O_{1s}

Fig. 5 RAIRS spectrum of **a** PA15C5 and **b** 4APA15C5 modified GC surface



Thickness measurements of PA15C5 and 4APA15C5 nanofilms by ellipsometry

Ellipsometric thicknesses of the PA15C5 and 4APA15C5 films at the GC surface were measured as 9.28 ± 0.40 and 10.50 ± 1.10 nm, respectively, by modeling the system using the software of the instrument [40]. The four-layer model was used as a graphite/GC substrate PA15C5 and 4APA15C5 film/air to fit experimental data. Refractive indices of 3.0841 for graphite, 1.9000 for GC, 1.0000 for organic layer, 1.0000 for air and extinction coefficients of -1.7820 for graphite, -0.8100 for GC, 0.0000 for organic layer, and 0.0000 for air are assigned, supposing that thickness, refractive indices, and extinction coefficients are reasonably correlated for all films [20, 28, 41]. The thickness of the 4APA15C5 film is 10.50 ± 1.10 nm,

which corresponds approximately to 9–10 layers by comparing to the theoretical thickness of 1.18 nm [13, 14].

Conclusion

In this study, azacrown derivatives PA15C5 and 4APA15C5 were synthesized, and their structures were characterized by using elemental analysis, RAIRS, ¹H NMR, and ¹³C NMR spectra. It has been demonstrated that a new kind of multilayer thin film containing PA15C5 can be fabricated on GC by oxidation, and a new kind of multilayer thin film containing 4APA15C5 can be fabricated on GC by the amine oxidation technique. The formations, structures, and properties of the multilayer films were carefully characterized by using XPS, RAIRS, and electrochemical methods.

The films on the GC surface were formed by the direct electrochemical grafting, and the ellipsometric thickness of PA15C5 and 4APA15C5 films at the GC surface was obtained around 9.28 ± 0.40 and 10.50 ± 1.10 nm, respectively.

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