Electrochemical deposition and characterization of polyaniline-grafted graphene oxide on a glassy carbon electrode

Ahmed Abdi Hassan¹ · Ismail Abdulazeed¹ · Omobayo Adio Salawu¹ · Abdul Rahman Al-Betar¹

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Abstract

The synthesis and characterization of electrochemically deposited polyaniline-grafted graphene oxide was successfully carried out. Excellent electrochemical stability, thermal consistency, reversibility and lower internal resistance were noted at various current densities when graphene oxide was electrochemically deposited on the surface of conducting polyaniline at +0.75 V. Electrochemical deposition of graphene oxide on the polyaniline was confirmed by scanning electron microscopy, Fourier transformed infrared spectroscopy, Raman scattering and UV/Vis spectroscopy measurements. The electrochemically deposited polyaniline-grafted graphene oxide is confirmed in various characterization techniques employed and has promising electrochemical features due to its good transparency and stability and hence can find various applications in the manufacture of electronic materials and in the construction of electrochemical sensors that are cheap, simple and environmental friendly.

Keywords Conducting polymer · Graphene oxide · Polyaniline · Electrochemical deposition · Polymerization

1 Introduction

Conducting polymers are organic in nature and obviously, insulators and their conductivity have attracted the attention of many researchers particularly on how to enhance the stability of materials like polyanilines, polythiophenes, polypyrroles, polyfuran, polyindole and polyazulene. conducting polymers have of late got more consideration due to low cost, ready availability, low density, easier and better processability, their mechanical flexibility and furthermore, broader chemical functionalization abilities compared to inorganic materials [1]. Water-soluble conducting polymers has also been studied focusing mostly on solubility in a mixture of arsenic trifluoride/pentafluoride [2]. In addition, two states of conducting polymer, doped and undoped has been reported [2]. Several reviews and journal papers have been published on various properties of conducting polymers. Another special area of possible

essential application of the polymers getting popularity is the electrochemical capacitors and electrode-active material that have demonstrated excellent power and energy storage that is now receiving more growing attention [3].

A lot of research work has been dedicated particularly to the synthesis and characterization of new organic conducting and semiconducting polymers and materials. Subsequently, the chemical structure and physical properties can be totally different. Hence a comprehensive understanding of the conduction mechanisms is always important. In addition, these organic compounds have wide and various applications, such as microelectronic, display, photovoltaic devices and many more [4]. Furthermore, the conducting inks for direct printing of conducting patterns in inkjets made from nanoparticles of silver and copper have been a novel area that scientists have ventured on and recently it has expanded to biological applications as they are more preferred than metallic inks. Due to the stiff

✉ Ahmed Abdi Hassan, ahmedabdi@kfupm.edu.sa | ¹Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia.

and rigid structure and conjugated backbones, the conducting polymers are insoluble and infusible in general and to make them useful and easily processable is to prepare colloidal dispersions of the polymers. Most scientists, therefore, prefer polyaniline, polypyrroles and polythiophene because of their environmental stability [5, 6].

One of the simplest well-known organic conducting polymers are polyacetylenes, $(CH)_x$, which can be chemically or electrochemically reversibly doped using a partial oxidation or reduction approach to the metallic regime. Also doping of polyaniline to the metallic regime can be easy and simple acid–base protonation reaction. Now, many electronic conductive polymers are well known and several applications and technological advancement in the field have been noted in the last decades and essential projections made [7].

Several techniques have been used to synthesize and characterize conducting polymers for various applications such as supercapacitors, light emitting diodes (LEDs), solar cells, sensors, transistors and storage of data, photographic film, smart windows electromagnetic shielding, mobile displays, batteries, electrochromic devices and corrosion inhibition studies [8]. Moreover, conducting polymers have unlimited characteristics such as excellent electrical conductivity, outstanding magnetic features, better optical and mechanical properties efficient microwave absorbing feature and, they have manageable light weight. Among the various scientific methods used to synthesize conducting polymers are; chemical synthesis, electrochemical synthesis, photochemical method, metathesis method, concentrated emulsion method, inclusion method, solid-state method, plasma polymerization and pyrolysis method [8].

There are several techniques used to characterize conducting polymers: surface characterization such as scanning electron microscopy (SEM), transmission electron microscope (TEM) X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) etc. Others are molecular spectroscopic characterization methods such as UV–Vis, Raman, Fourier-transform infrared spectroscopy (FTIR), and Nuclear magnetic resonance spectroscopy (NMR).

There are several instances where activated carbon has been used for adsorption and it was found to be the most efficient, but not many literature have shown its conductivity enhancement mechanism. However, the utilization of silver impregnated carbon and of carbon nanotubes to boost the electrosorption capacity and desalination kinetics of electrodes for applications in capacitive deionization technology has been described in detail [9]. It was found that silver impregnated activated carbon has higher electrosorption capacity of electrodes from 2 to 5.3 mg/g compared to activated carbon alone. Furthermore, it was recorded that functionalized

multi-walled carbon nanotubes significantly improved the hydrophilicity of the electrodes and therefore, enhancing desalination kinetics process. In addition, when (modified electrodes) were tested for deionization characteristics it was noted that salt removal rose from 42 to 67% which is a remarkable improvement [9].

Lithium-ion capacitor (LIC) is best known to act as a bridge between lithium ion battery and the supercapacitors because of its high-performance energy storage. The major challenge with this device is how to enhance the energy density without interfering with its high rate of power output performance. Lately, a conventional and green approach has been designed consisting of a three-dimensional (3D) hierarchical porous nanostructure of hydrogen-treated TiO_2 nanoparticles covered with conducting polypyrroles polymer (PPy) framework with only single-walled carbon nanotubes that acts as hybrid anode material for Lithium Ion Capacitor (LIC) and such novel technique that has given unique network that continuously transport electrons and decrease the extent of lithium ions diffusion.

It was further recorded that reversible release limit $\sim 213 \text{ mA h g}^{-1}$ which depended on the mass of TiO_2 more than 50 cycles at 0.1 A g^{-1} , which is nearly three times more compared to raw TiO_2 directly obtained as nanoparticles powder from the market [10]. Furthermore, Nitrogen-doped activated carbons (NACs) indicate high surface regions of up to $2900 \text{ m}^2 \text{ g}^{-1}$ with a direct N substance of up to 4 wt%. Electrochemical assessment of the NACs demonstrates a high limit of 129 mA h g^{-1} (185 F g^{-1}) in an organic electrolyte at a current density of 0.4 A g^{-1} , and in addition, outstanding rate capacity and cycling stability were also achieved. The hybrid form supercapacitor amassed utilizing the NACs and a Si/C cathode has been demonstrated that displays a high material level energy density of 230 W h kg^{-1} at 1747 W kg^{-1} and the hybrid device accomplished 76.3% limit maintenance after 8000 cycles tried at 1.6 A g^{-1} [11].

Therefore, no doubt polyaniline has excellent electrochemical activity, its cheap, highly conductive and ease in preparation but the main challenge is poor stability during charge and discharge process and to overcome that graphene-based compounds increase stability due to high surface area of $2630 \text{ m}^2/\text{g}$ [12, 13].

Graphene has an outstanding physical, electrical, optical and thermal properties and it is considered one of the greatest essential materials in the scientific world today. As a result of its excellent properties it has attracted great research interest from the fundamental study to several applications [14]. Structurally graphene oxide (shown in Fig. 1), is also termed as graphitic oxide or graphitic acid, comprises of carbon, oxygen, and

Fig. 1 Structure of graphene oxide [16]

hydrogen in different ratios, achieved by oxidation of graphite and turns yellow when fully oxidized [15].

Recently, most reported electrochemical polymerization of aniline have used carbon nano tubes which makes the material more expensive in terms of feasibility and furthermore, high heat loss, pick up by steel, increases load reducing conductivity and generation of CO_x at high carbon concentration is an added disadvantage [17]. However, carbon contributes to mechanical strength the drawbacks outweigh the benefits. When also binary based composites of polyaniline like metals are used toxicity plays major problem [18]. All these methods have weakness like preparation complication, cost and long run [19, 20].

In this study we report for the first time successful electrochemical synthesis of polyaniline grafted graphene oxide on a glassy working electrode and various spectroscopic and surface characterizations performed to prove the effective electrochemical deposition. It is a simple, cheap and environmentally friendly process that causes polymerization in both the aniline and the graphene oxide which has important electrochemical applications.

2 Experimental

2.1 Materials and chemicals

All the chemicals used were of analytical grade from Sigma Aldrich and they include acetone, graphene oxide, and aniline. The distilled water was from Siemens ultra clean, the electrochemical potential was measured using CH1760E from CH Instruments, Inc. (USA). FTIR measurements was carried out using NICOLET 6700 FT-IR to determine the functional group present. The sample was solid thin film and transmission spectra were recorded between 700 and 4000 cm⁻¹.

2.2 Synthesis procedure

Graphene oxide (3 mg) was accurately weighed out and mixed with 3 mL of acetone. The mixture was sonicated for about 25 min until all the graphene oxide was dispersed giving a complete homogenous dispersion which was darkish brown in color and carefully dropped on the glass working electrode using a dropper after electrochemical polymerization of the polyaniline. Collection of samples were done directly from the working electrode after cyclic voltammetry of polyaniline deposited graphene oxide scanned for 30 and 50 cycles in the potential range of from - 0.2 to + 1.0 V, scan rate of 0.1 V/s and sample interval (V) of 0.001 after the working electrode was air dried.

2.3 Electrochemical measurements

Before the deposition of the graphene oxide, the glass substrate was cleaned very well and afterwards rinsed with acetone and distilled water. Solutions were prepared using distilled water although, the graphene oxide was well dispersed in acetone solvent. Prior to deposition, the electrochemical behavior of only the polyaniline was examined to study its polymerization potential using cyclic voltammetry of 30 cycles (Fig. 6). Using constant potential, the graphene oxide was deposited carefully on the working electrode on top of the polyaniline and air dried for 10–15 min until all the acetone evaporated. The electrochemical cell consisted of three electrodes the working, counter and reference electrodes, the three electrodes system comprising of Ag/AgCl (reference) and platinum (counter) electrodes respectively were well maintained and kept before and after use.

3 Results and discussion

To ensure that the graphene oxide and the polyaniline were successfully prepared, several spectroscopic and surface characterization methods were employed. In Figs. 2 and 3 the cyclic voltammograms of polyaniline and polyaniline deposited graphene oxide scanned for 30 and 50 cycles respectively are shown with potential range of - 0.2 V to + 1.0 V and a scan rate of 0.1 V/s. It was noted that polyaniline deposited graphene oxide polymerization potential started on the surface at around + 0.70 V when the upper limit of the cyclic voltammetry was set at + 1.0 V, similar procedure was adapted in literatures [21–23]. This is a clear indication of nucleation process of graphene oxide on the substrate. The amount of graphene oxide deposited increased as the scanning potential approaches + 1.0 V. Only small reduction peaks are observed at + 0.4 V and - 0.1 V way back to - 0.2 V, which conforms to fully

Fig. 2 Cyclic voltammograms of polyaniline scanned for 30 cycles in the potential range of from -0.2 to $+1.0$ V; scan rate of 0.1 V/s, sample interval (V) of 0.001 . Red polynomial line indicates the trend of the scanning

Fig. 3 Cyclic voltammograms of polyaniline deposited graphene oxide scanned for 50 cycles in the potential range of from -0.2 to $+1.0$ V; scan rate of 0.1 V/s, sample Interval (V) of 0.001 . Red polynomial line indicates the trend of the scanning

oxidized graphene oxide deposited polyaniline at around $+0.26$ V peak on positive scan followed by subsequent oxidation at $+0.985$ V approaching $+1.0$ V and this is in agreement with work done by Suleiman and his group [24]. The polymerization growth of the polyaniline recorded occurred at the same time as the oxidation of graphene oxide deposited polyaniline and this was ascertained by the reduction peaks on the current density of the successive cycles. Due to the presence of more graphene oxide deposited on the polyaniline oxidation peaks tend to shift to more positive potentials with respect to several cycles and similar results were also observed for the reduction processes. A peak responding to the reduction potential appeared at approximately $+0.27$ V along the cathodic scan. The results observed exhibits the rate of polyaniline deposited graphene oxide polymerization that was rampant on the upper limit of the cyclic voltammetry and

similar result has been reported [23]. Also, current density increases as number of cycles increases as seen in Fig. 2 when only 30 cycles were used and when 50 cycles were used in the case of Fig. 3, that behavior can be attributed to polyaniline growth which is in consistent with increasing the number of cycles similar observation has been reported in literature [25].

Scanning electron microscope (SEM) was further used to examine the surface of graphene oxide, polyaniline and electrochemically deposited graphene oxide on the surface of the polymer. As shown in Fig. 4 the graphene oxide exhibited numerous layers of wrinkled sheets which are closely packed and in square shapes forming conducting network that is continuous same observation has been reported [26–28]. The elemental composition was checked using energy-dispersive x-ray spectroscopy (EDS) to comprise of carbon (C) and oxygen (O) as shown in Fig. 4 (right), no extra elements observed and that indicates no impurities.

The method used for synthesis dictates structural arrangement and morphology of the polyaniline. Figure 5 shows SEM of electrochemically synthesized polyaniline. From the figure it was observed that the synthesized polyaniline has a spherical shape and the particles are bigger in size due to the ability of combination of smaller monomer particles (aniline) to form bigger polymer particles (polyaniline). This behavior is attributed to deposition of polyaniline on the electrode as more cycles form multiple layers and every layer that is created reduces the discharging efficiency of the cathode [29].

Figure 6 shows the SEM of graphene oxide electrochemically deposited on the polyaniline and it can be observed that the polyaniline is distributed on and in between the graphene oxide after protonation, reduction and oxidation processes, although no much morphological difference recorded [30]. It is noted that in overall the polyaniline alone or graphene oxide alone as shown in Figs. 4

Fig. 4 SEM and EDS graphene oxide

Fig. 5 SEM of electrochemically synthesized polyaniline

Fig. 6 SEM Polyaniline grafted graphene oxide showing. **a** 5 μm , **b** 10 μm and **c** 20 μm magnification

and **5** are totally different from the morphology obtained when graphene oxide is electrochemically deposited on the surface of the polyaniline. Such morphology variation can be linked to better stability, improved conductance and longer cycling life as previous reported [31].

FTIR characterization of graphene oxide (Fig. 7) and electrodeposited polyaniline on a thin film before depositing the graphene oxide was carried out (Fig. 8). Broad peak in the spectrum at around 3300 cm^{-1} was observed in the spectrum of polyaniline which indicates the presence of N–H amine stretching [23]. C–N stretching of secondary aromatic amine presence was also noted which appeared at peaks 1355 cm^{-1} and 1221 cm^{-1} . The more peaks recorded in the spectrum at 1558 cm^{-1} and 1446 cm^{-1} are due to the vibration stretching of benzenoid (N–B–N) rings

Fig. 7 FTIR spectrum of graphene oxide

Fig. 8 FTIR of electrochemically synthesized polyaniline

and quinoid ($\text{N}=\text{Q}=\text{N}$) [32, 33]. In addition, more absorption peaks were seen at 1086 cm^{-1} and 978 cm^{-1} which are attributed to a protonated band of the polyaniline [32]. Furthermore, strong sharp peaks were observed at 1716 cm^{-1} and 1662 cm^{-1} which illustrates characteristic absorption of aromatic C=C bending. All these peaks clearly confirm the formation of polyaniline and similar observation has been reported [23].

Figure 9 shows the FT-IR spectra of electrochemically deposited graphene oxide on polyaniline. The broad spectrum at around 1500 cm^{-1} is indicative of OH functional groups of the graphene oxide bending. Sharp intense peak is observed at 1719 cm^{-1} which shows presence of C=O stretch of the graphene oxide and $1451\text{--}972\text{ cm}^{-1}$ are associated with the COOH and C–O in COH/COC (epoxy) functional groups respectively of the graphene oxide [34]. If the result is compared with the peaks of polyaniline alone (Fig. 8) it is observed that C=O peak slightly downshifted to 1719 cm^{-1} . More so, the C–O peaks of the epoxy group red shifted clearly [35]. These are indications of backbone linkage between the carboxyl groups of the graphene oxide

Fig. 9 FTIR of graphene oxide electrochemically deposited on polyaniline

Fig. 10 Raman spectrum of graphene oxide before reduction

and the nitrogen of polyaniline [34]. The hydrogen bonding and π - π interaction between the graphene oxide and the polyaniline backbone are shown by the spectral red-shift. The quinoids of the pure polyaniline C-N stretching band at 1558 cm^{-1} is blue-shifted to 1597 cm^{-1} and this can be attributed to the CO group which has withdrawing induction effects. However, the conjugative effect remains [35]. In addition, graphene oxide contains an enormous number of oxygenating groups which can freely interact with the nitrogen atoms of the polyaniline backbone through the hydrogen bonds [34].

Further spectroscopic characterization was performed using Raman before and after electrochemically depositing the graphene oxide on the surface of the polymer. The Raman spectrum of the graphene oxide before reduction (Fig. 10) showed two sharp peaks at 1347 and 1594 cm^{-1} respectively indicative of the D and G bands.

Fig. 11 Raman spectra of polyaniline

Fig. 12 Raman spectrum of graphene oxide electrochemically deposited on polyaniline

Furthermore, two broad peaks are observed at 1309 cm^{-1} and at 4757 cm^{-1} . This implies that the graphene oxide compose of graphite surrounded by carbon atoms which have a similar arrangement as already shown in the SEM image Figs. 4, 5 and 6 and finding is in agreement with literature [36].

In both Figs. 11 and 12 broad Raman spectrum is observed with no proper separation of the peaks. However, peaks are seen at around 1290 and in 1509 cm^{-1} that corresponds to D and G band respectively where the G band is associated to bond stretching and D is the breathing mode and it is higher than the D band. In Fig. 12 when graphene oxide is deposited on the polyaniline, it is

Fig. 13 Overlays of 1st and 50th cycles of cyclic voltammograms of polyaniline deposited graphene oxide

Fig. 14 UV-Vis spectrum of graphene oxide electrochemically deposited on polyaniline, graphene oxide and polyaniline

observed that the D and G bands shifted to lower values at around 1009 and 1307 cm^{-1} respectively confirming the deposition of graphene oxide on polyaniline.

Figure 13 indicates a cyclic voltammogram overlay of 1st and 50th cycle of polyaniline graphene oxide which illustrates clearly reduction peaks at 50th cycle and negligible change in oxidation peak. This shows excellent stability and reversibility from oxidized to reduced states after running for 50 cycles [37].

UV-Vis spectra of graphene, polyaniline and graphene oxide electrochemically deposited on polyaniline are shown in Fig. 14. The broad peak observed at around 230 nm is characteristic of graphene oxide while the sharp intense peak at 203 nm is associated to the molecule; lastly the very weak peak at around 236 nm is due to polarons charged cationic species [38]. The electrochemical

reduction process has removed oxygen functionalities and hence no graphene adsorption [35]. The polyaniline as p doped state is confirmed by the characteristic broad peak at 240 nm due to π - π^* transition of benzene ring which is essential for its application in supercapacitors; the slight shift from 220 to 230 nm and around 240 nm in the polyaniline is a clear indication that there is conjugation formed in the molecule between polymer and the graphene oxide [39].

4 Conclusion

In this study, we reported the electrochemical deposition of polyaniline-grafted graphene oxide using cyclic volumetric technique. The study was further supported by findings from surface and spectroscopic characterizations and the results showed that polyaniline was successfully grafted to graphene oxide. The polyaniline deposited graphene oxide has promising electrochemical features which could find various applications due to its good transparency and high stability.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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