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Original Research Paper

Fabrication and Characterization of Graphene/ Poly (P-Chloroaniline) Nanocomposite for Electrical Properties

Physics

KEYWORDS : electrochemical energy storage; cycling stability; nanocomposite; crosslinked F-GE; poly Chloroaniline (PCA)

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ABSTRACT

The poor cycling stability of Poly (p Chloroaniline) PCA limits its practical application as a pseudo capacitive material due to the volume change during the charge-discharge procedure. Herein, cross linked GE-CS-PCA, GE-CS-AuNPS-PCA composites have been designed by the in situ chemical oxidative polymerization of PCA in the presence of crosslinked GE-CS-AuNPs, which were obtained by coupling of the functionalized GE. The prepared nanocomposites are characterized by UV-visible spectroscopy. The structural and electrical behaviour of composites were characterized by X- ray diffractometer (XRD) and electrical conductivity (four probe method).

Introduction

Human activity and energy supplies mainly rely on the consumption of non-regenerative fossil fuels. With the gradual decrease of these carbon-based energy sources and the increase in environmental pollution, finding alternative green and sustainable energies has become necessary. Therefore, innovative and renewable energy technologies must be developed to combat global warming and climate change.[1-6] Extensive research has been performed on the development of solar cells,[7] fuel cells,[8] and supercapacitors [9] to replace carbon-based energy.

Graphene has been considered a promising electrode material for energy storage applications due to its ultrahigh surface area (2600 m^2 g−1),[10] excellent electric conductivity,[11] and one-atom thick two-dimensional sp^2 carbon arrangement.[12] Many approaches have been developed to solve this problem such as using surfactant to stabilize graphene nanosheets, grafting polymer chains to change the polarity of graphene surface, and decorating graphene surface with nanoparticles to decrease the π-stacking interactions between graphene sheets [13-17]. Recently, the decoration of graphene with nanoparticles could provide larger electrochemically active surface areas for the adsorption of biomolecules and effectively accelerate the electron transfer between electrode and detection molecules, which could lead to a more rapid and sensitive current response [18].

Deposition of nanoparticles, such as MnO_2 [19], TiO_2 [20], Mn_3O_4 [21], NiO [22] $Co(OH)_2$ [23], ZnO [24], Pt [25,26], Ag [27,28], Au [29,30],etc., onto GNS has been demonstrated to reveal special features in new hybrids that can be widely utilized in supercapacitors, Li-ion batteries, catalysts, photocatalysts, etc. However, assembling Au nanoparticles in nanostructured materials with electronic and ionic conduction pathways for electrochemical applications still remains a challenge [31, 32].

Herein, we report Photocatalytic and electrical conductivity of AuNPs on the surface of GE-CS via employing poly Chloroalanine (PCA). The microstructures and electrochemical activity of GE, AuNPs/GE-CS and AuNPs/GE-CS-PCA were investigated by UV-visible spectrophotometer, XRD and electrochemical measurements. The AuNPs/GE hybrids exhibited excellent electrochemical and highly electro catalytic activity notably, the simple and straightforward synthesis of this procedure is expected to be a widely accepted approach with potential applications in the future.

Experimental

Materials

Poly (chloroanaline) was purchased from sigma Aldrich. Graphene and chitosan used in this work was purchased from Sigma-Aldrich. AuNPs (60nm) were purchased from AC Dignostics, USA, and other reagents like ammonium persulfate (APS), hydrochloric, sulfuric and nitric acid (Sigma Chemicals) were of analytical grade.

Synthesis of Functionalized Graphene

Synthesis of Graphene was described earlier in our previous research work [33]. Typically, GE were reacted with H_2SO_4:HNO_3 (3:1), then tip sonicated for 30 minutes using an ultrasonic processor with amplitude at 30% and 7s pulse to yield carboxylic acid functionalized GE (GE-COOH). The carboxylic acid group was converted to formyl chloride via reaction with thionyl chloride for 24 h at 75 °C while refluxing; hereafter product is referred to as GE-COCl. After the reaction was stopped, reaction mixture was cooled before centrifuging and washing to remove excess reactants. Samples were dried overnight at 90 °C and 30 in Hg.

Synthesis of GE-chitosan Derivative

GE-COCl (400 mg) was reacted with chitosan (2 g) in 100 mL 2% acetic acid with AuNPs 2ml (60 nm) at 75 °C for 24 hours while stirring. After the reaction was stopped, the product was washed three times with 2% acetic acid to remove unreacted chitosan.

Synthesis of GE-CS-AuNPs-PCA

The GE-CS-AuNPs /PCA composites were prepared via the in situ chemical oxidative polymerization of aniline in the presence of the GE-CS-AuNPs: 5.0 ml PCA and a certain amount of GE-CS-AuNPs (feeding ratio to aniline of 0.05:1, 0.1:1, 0.15:1, or 0.2:1) were added into 26.3 mL 1.0 mol/l hydrochloric acid, respectively. Then 5 ml ethanol was added and ultrasonicated for 30 min to disperse the GE-CS-AuNPs. Five milliliters of aqueous solution containing APS (molar ratio to aniline of 1:1) were added drop by drop to the above mixture over 20 min. The reaction vessel was maintained at room temperature for 6 h. The products were filtered and washed with a large amount of distilled water and then ethanol, followed by vacuum drying at 45 °C overnight.

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Result and discussion

UV-visible spectrophotometer

Figure 1 shows the UV–visible absorption spectrum of the AuNPs, CS, GE, PCA, GE-CS, GE-CS-AuNPs and GE-CS-AuNPs-PCA solution. The characteristic absorbance peak at 279 and 277 nm is clearly observed in GE and GE-CS-AuNPs-PCA [34-37]. Besides electronic properties, graphene is a very good optical material due to its π -electron cloud (puddle) formation, very low optical reflectivity and high optical transmittance. Due to its unique electronic structure, single-layer GE has 97.4% optical transmittance and it decreases linearly with the number of layers. The stability of compound was determined by measuring the absorption spectrum at 24-h intervals for 90 days. No significant changes in absorbance were noted during storage, indicating that the compound were very stable during this period.

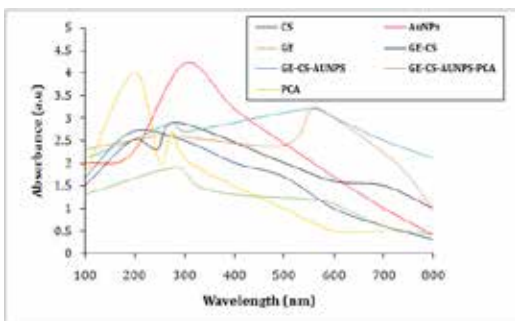
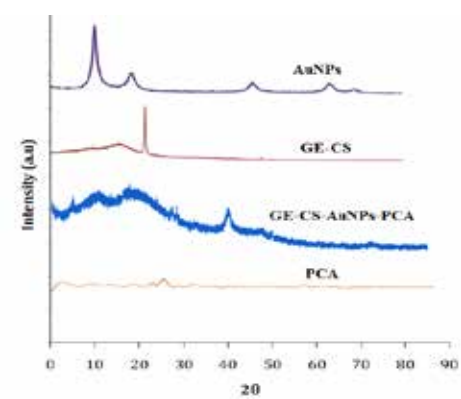


Figure 1. UV–Vis spectra of AuNPs, CS, GE, GE-CS, GE-CS-AuNPs and GE-CS-AuNPs-PCA.

X-ray diffraction

Figure 2 shows the PCA diffraction peaks (broad) around $2\theta = 4^0$ and 24^0 due to the characteristic peaks of emeraldine salt structure. This also substantiates the absorption in the IRspectrum at 1124 cm^{-1} which is the electrical conductivity peak due to the emeraldine salt structure [33]. The XRD pattern of GE-CS-PCA hybrid carbon assemblage composite shows highly crystalline nature of composite due to the incorporation of GE into PCA. The peaks at 2θ=27°, 42° and 56° correspond to the graphitic peaks of grapheme (FIG-3B). PCA gives a sharp peak at around $2\theta = 24°$.The GE-CS-AuNPS-PCA nanoparticles show two sharp peaks between $2\theta = 21^0$ and 40^0 due to highly crystalline nature of AuNPs nanoparticles. In the composites, the high intensity peaks of AuNPs were masked by the presence of poly (chloroaniline). The peak at $2\theta = 24^0$ seem to shift to higher diffraction angle with addition of AuNPs. This observation from the XRD data endorses the uniform molecular level dispersion of AuNPs nanoparticles into the poly (chloroaniline) chain.



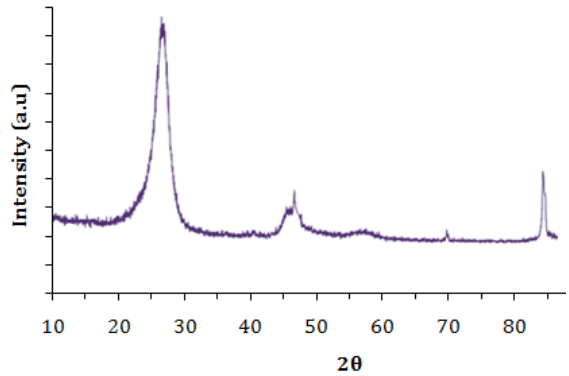


Fig-2. XRD of PCA, GE-CS-PCA, GE-CS-AuNPS-PCA

Electrical conductivity

Figure 5 shows the electrical conductivity of the GE-CS-PCA, GE-CS-AuNPS-PCA composites with different feeding ratios of GE, measured with the standard four probes method at room temperature. The electrical conductivity has a significant influence on the C-rate performance, not only decreasing the impedance of the electrode, but also helping the electron transfer inside the material [33]. It is noteworthy that all the electrical conductivity values of the GE-CS-PCA, GE-CS-AuNPS-PCA composites were higher than for pure PCA, GE, CS and GE-CS. When the feeding ratio of the GE was lower than 8 wt%, the conductivity of the composites gradually increased, reaching the highest electrical conductivity of 12.12 S/cm for the composite, because the electrons could transport through the overlapped PCA-PCA contact between the GE/PCA bundles [38]. However, when the feeding ratio of the GE increased further, the conductivity of the composites showed a downward trend; this was mainly due to the diameter of PCA-coated GE-CS-AuNPs decreasing and the contact areas between GE-CS-AuNPs-PCA bundles decreasing. The relatively high electrical conductivity of the GE-CS-PCA, GE-CS-AuNPS-PCA composites in the present work might be mainly due to the fact that the GE-CS-PCA, GE-CS-AuNPS-PCA may serve as a "conducting bridge" between the PCA-conducting domains, thus increasing the effective path .

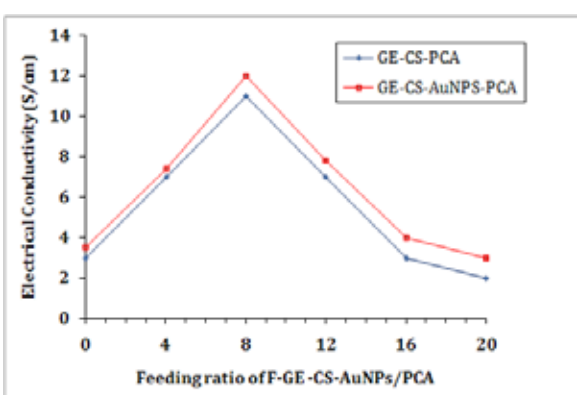


Figure3. Electrical conductivity of the pure GE-CS-PCA, GE-CS-AuNPS-PCA composites.

Conclusions

In summary, pristine commercial grapheme and chitosan were covalently crosslinked with PCA, which was grafted and coated via facile *in situ* chemical oxidative polymerization. Due to the highly conductive of the crosslinked graphene (F-GE) and the covalent linkage between the GE-CS-

PCA and GE-CS-AuNPS-PCA composites possessed higher electrical conductivity.

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