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Coupled polaron-electron charge transport in graphite functionalized polyaniline on cellulose: Metal free flexible p-type semiconductor

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ABSTRACT

Electron-polaron coupling and long-range carrier translation has been achieved in engineered macro molecule of polyaniline, incorporated with graphite, prepared on flexible paper substrate. For this a metal free flexible p-type semiconductor in a hybrid structure of paper/graphite/polyaniline has been prepared in a facile technique of vapor phase oxidation of aniline on graphite incorporated paper. The interaction of graphite with organic polymer (polyaniline) having conjugated π electrons have been studied for its structural, optical and electrical properties. Charge transport in graphite functionalized polyaniline has been explored owing to the formation of charged defect states of polaron and bipolaron and their coupling with delocalized electron in graphitic framework. As a result, a significant two order increase in electrical conductivity has been observed in the polyaniline loaded paper, functionalized with graphite. Raman spectroscopic studies reveal the increased interchain interaction and coupling of the π-conjugated polyaniline towards more planner charge transfer.

1. Introduction

Charged defect states of polaron and bipolaron in conjugated polymer has opened up a new and outstanding area in the field of polymer-based electronics [1,2], and consequently polymer based electronic materials are emerging out with a greater scientific interest in fundamental as well as applied research in the recent years [3]. The π-conjugated polymer like polyacetylene [4,5], polypyrrole [6], polyaniline [7,8], poly (p phenylene-vinylene) (PPV) [9], poly(3,4-ethylene dioxythiophene) (PEDOT) [10], and their composites in nanoscale dimensions attracts for new scientific perceptions [11,12], and these recent literatures are also indicative that there are ample scope of further developments. Polyaniline is an outstanding conductive polymer and attractive hole transport layer [13,14] and it can achieve electrical conductivity through chemical doping by changing its oxidation state through protonation with acids.

Owing to recent advances in organic electronic materials, in this present work we have approached for a fascinating paper-based semiconductor material of polyaniline, functionalized with graphite, which has sp^2-hybridized carbon atoms. With best of our knowledge paper-based metal free semiconductors are not explored so far. This work thus attracts more significance as it has been prepared on the amorphous matrix of paper owing to its flexibility, metal free composition, low cost and environmental significance of being decomposable electronic garbage. The synthesis of polyaniline is reported through different processes such as electrochemical synthesis [15], interfacial polymerization [16], seeding polymerization [17], vapor phase self-assembling polymerization [18], photoinduced polymerization [19], plasma polymerization [20], solution polymerization [21], and sonochemical synthesis [22] process. In this work, we present a facile method to prepare a new type of sandwich-patterned paper/graphite/polyaniline hybrid structure with anticipated properties of high electrical conductivity, good chemical stability and excellent flexibility. The synthesis process was conducted through vapor phase polymerization of aniline in a reaction chamber at a temperature of 60 °C. The prepared hybrid structure has been characterized for its structural, compositional, optical and electrical properties. The polyaniline acts as a hole transport media in its partially oxidized state of emeraldine salt form, and its electrical conductivity has been increased with two degree, when functionalized with graphite in paper/graphite/polyaniline hybrid structure. The coupling of polaron and electron plays the vital role in stimulating the electronic behavior and long-range charge transport properties of this hybrid structure.

2. Synthesis of graphite incorporated polyaniline paper

Vapor phase polymerization technique has been employed for the deposition of polyaniline onto the paper cut into pieces of (4.0 cm ×

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2.0 cm) in size. A uniform graphite layer has been introduced on the paper by rubbing a graphite pencil. On the other hand, by mixing 9.72 gm of solid ferric chloride anhydrous powder with appropriate amount of methanol, a 3 M solution of $FeCl_3$ was prepared. The graphite loaded paper cut was dipped into the solution and then taken out gently, kept in ambient temperature for few minutes to evaporate the solvent. Double distilled aniline monomer was kept at 60 °C to produce aniline vapor in a reaction chamber. $FeCl_3$ soaked graphite loaded paper was then introduced inside the chamber, where aniline monomer comes in contact with the $FeCl_3$ coated paper and allowed there for 30 min for polymerization of aniline vapor. A green colored layer was formed on the graphite loaded paper due to the polymerization of aniline into polyaniline. The polyaniline coated paper was then taken out from the chamber, and washed several times with methanol to remove unreacted ferric chloride. Finally the films were dried in open air for 30 min at 50 °C

3. Result and discussion

3.1. Crystal structure analysis

To check the influence of graphite on the crystallinity of polyaniline framework on paper, the X-ray diffraction measurement was conducted using XRD (Bruker, D-8 Advance). The X-ray diffraction patterns are shown in Fig. 1a. The characteristic peak of polyaniline appeared at 2θ = 22.77° corresponding to the reflections occurred from (020) Miller plane of emeraldine salt form. Along with the above peaks there is an intense and sharp peak which is a characteristic peak of graphite appeared at 2θ = 26.6°, is due the reflection from crystalline graphite corresponding to C-axis and reflections from (0 0 2) plane with interlayer spacing of 0.34 nm. Thus, X-ray diffraction pattern reflects the successful deposition of polyaniline upon crystalline graphite layer. The crystallite size (T) of the prepared polyaniline sample is found 5.0 nm

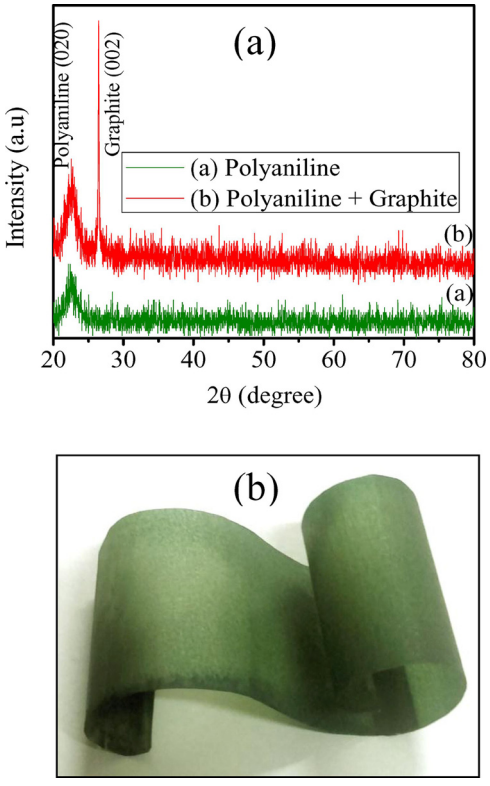

Fig. 1. (a) X-ray diffraction pattern of polyaniline and graphite implanted polyaniline, (b) Photographic view of the flexible graphite implanted polyaniline loaded paper.

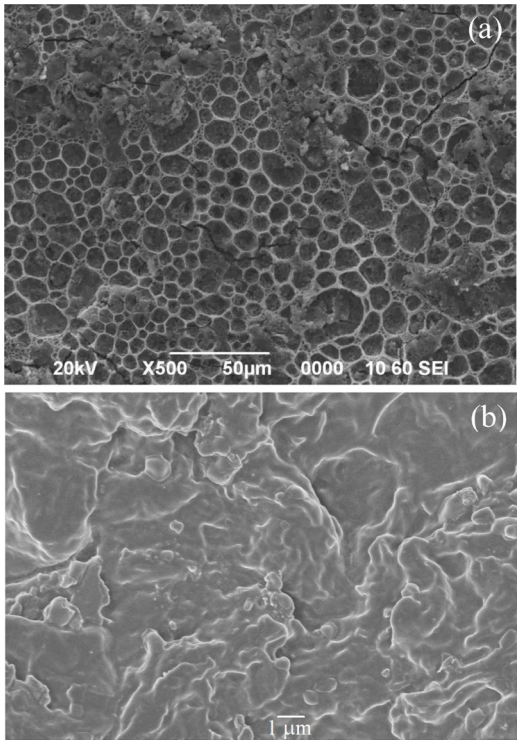

Fig. 2. (a) SEM image of graphite implanted polyaniline, and (b) SEM image of only polyaniline loaded paper.

and that of graphite is 45.3 nm by employing Scherrer relation

$$T = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where k is the shape factor for the average crystallite (~0.9), λ is the wavelength of the incident X-ray, and β is the full width at half-maxima of the crystalline peak in radian and θ is the Bragg angle. The interplanar separation of polyaniline (d_{020}) is 0.3 nm and that of graphite (d_{002}) is 0.33 nm as calculated from the above diffraction peaks using the Bragg relation. The photographic view of the prepared flexible hybrid structure of paper/graphite/polyaniline is depicted in Fig. 1b.

3.2. Surface morphology

The scanning electron microscopic (SEM) studies obtained from SEM (JEOL, JAPAN, model JSM 6390 L V) shows the morphological pattern of polyaniline prepared on graphite loaded paper as shown in Fig. 2a. The SEM image demonstrates a two dimensional planner arrangement of polyaniline over the paper substrate. Furthermore the distribution of polyaniline nanoparticles on graphite layer having good uniformity can be observed from this image. The SEM image of polyaniline deposited on paper without graphite is also depicted in Fig. 2b. Thus, retention of crystallinity as well as morphology indeed suggested an effective utilization of the void space in graphite polyaniline hybrid structure.

3.3. Analysis of chemical bondings

The Fourier transform infrared spectroscopy (FTIR) measurements were performed for the sample to investigate the chemical bonding configurations of polyaniline using FTIR instrument (NICOLET, USA model IMPACT 410). The FTIR spectra as shown in Fig. 3 indicates an intense and sharp peak at 3435 cm^{-1}, which is due to the trace of water in the sample [23]. The characteristic band of polyaniline at 2923 cm^{-1} is attributed to C—H stretching [24]. The presence of characteristic