Polyaniline doping with nanoparticles: A review on the potential of electrical properties

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Abstract. During this decade, there is a growing interest of the conducting polymers owing to their exceptional and outstanding electrical properties which makes them potentially applicable in a wide range such as electrochromic displays electronic devices, modified electrodes, chemical and biosensors. Here we aimed to examine the reported polyaniline doping (PANI) with graphene oxide (GO) and carbon nanotubes (CNT) by in situ polymerization. The molecular structure of PANI and its composites was characterized using FTIR, X-ray diffraction and their morphologies described by scanning electron microscopy (SEM). Previous results showed that the strength of composite peaks was higher than pure PANI due to charge transfer between PANI and graphic allotropes, and the aniline molecules have been physically adsorbed and polymerized on the surface of GO and CNT due to the interaction of p – p * electron. PANI describes a multi-diameter external layer of composites depending on the PANI degree of deposition, where the core GO and CNT participate. The conductivity calculation explained that 0.1 wt % of PANI with CO matrix has conductivity 17 folds higher than that without GO.

Keywords: Polyaniline PANI, Doping, Nanoparticles, graphene oxide GO, carbon nanotube CNT

1. Introduction

Inherently conductive polymers (ICPs) [1] are polymers with electric conduction. More generally referred to as plastics, everyday polymers are made up of simple units of repeating molecules called monomers. The name of polymer derived from the Greek words "poly means "many and "mer" means "art," Polymers are well known for their insulating properties that have resulted in a wide range of packaging and electronics applications. Conductive polymers (CPs) are separate from the insulating compounds obtained by H. Shirakawa, A. G. MacDiarmid and A. J. Heeger who received the Nobel Prize in Chemistry in 2000 for their work on polyacetylene [2] In the mid-19th century, Henry Letheby, who researched the electrochemical and chemical oxidation products of aniline in acidic media, first described polyaniline (PANI, Aniline black). The reduced form was colorless, Letheby noticed, but the oxidized forms were dark blue [3]. Polymer nanocomposite materials have recently been extensively studied in a wide variety of applications for advanced technologies, such as super condensers, solar cells, electronic devices and sensors [4-6]. Poly (acetylene), poly (aniline), poly (pyrrole), and poly (thiophene) are conductive polymers that are widely studied for their high electrical conductivity, catalytic, and environmental stability benefits. In this context, because of rapid and cost-effective synthesis, reversible redox activity, excellent environmental
stability and bio-compatibility [7], electro-active material-conductive polymer (PANI) nanostructures are an exceptional variety. The electrical conductivity of polyaniline depends primarily on the internal imino group and the backbone charging carriers of (PANI)[8]. In addition, nitrogen atoms are present in (PANI) structures that indicate potential interaction sites of metal oxide (PANI) that are responsible for the functional properties of PANI-V2O5 nanocomposites. It is clear that π-conjugated polyaniline can be reduced or oxidized to be either negatively or positively charged and doped into the conjugated chain by charged polarons and bipolarons [9]. To shed light on the above growth, this review article discusses morphological and electrical conductivity of effect doping, polyaniline with nanoparticle, carbon nanotubes.

2. Polyaniline

Polymer structures with particular properties are recent fields of increasing scientific and technological interest, providing the opportunity to synthesize a wide variety of exciting new materials with a wide range of magnetic, optical and electrical properties. A reproducible control of the macromolecular and supramolecular architecture is crucially dependent on technical applications. Among conductive polymers, PANI does not require any special equipment or precautions. Usually, conducting polymers with visible chemical memory demonstrate extremely reversible redox activity and are therefore considered to be popular new materials for the manufacture of devices such as industrial sensors. The properties of conducting polymers are highly dependent on the degree of doping, the degree of protonation, the size of the dopant ion and the content of water. PANI is either prepared by electrochemical oxidative polymerization or by a chemical oxidative polymerization method. Two distinct mechanisms of doping

Emeraldine base can be converted into a conducting form by two different doping processes: protonic acid doping and oxidative doping. Emeraldine base doping of protonic acid refers to the protonation of atoms of imine nitrogen, in which no electron exchange takes place. Leucoemeraldine removes emerald salt by the exchange of electrons through oxidative doping. The process causes such structural changes primarily due to the presence of the -NH group in the polymer backbone, enabling the events of protonation and deprotonation in the color of electrical and polymer conductivity. Major work is underway to develop nanomaterial-based sensors and artificial noses for the best detection of chemical vapors and gases. The emeraldine base layer of PANI is an electrical insulator consisting of two atoms of amine nitrogen followed by two atoms of imine nitrogen, Figure 1. PANI [10-12]

![Figure 1. Homo polymerization of PANI](image)

Figure 1. Homo polymerization of PANI
3. Doping

PANI doping with graphene oxide (GO) and carbon nanotube (CNT) used in specific applications because of its useful environmental stability, electrical conductivity and high mechanical strength if compared to pure PANI. The PANI's associated with graphic allotropes is very attractive, not only because of strengthening conductive polymer but also for introducing developed electronic properties. Modification of morphology or electronic interaction between the two components produce new electronic proprieties [13–16]. The method in situ polymerization is commonly used to produce composite have noncovalent bonds.

The PANI matrix and graphic filler interact by relatively weak p-p interactions between the PANI quinoid rings and p-bond of the graphic material lattice [17–19].

4. Synthesis of PANI composites

4.1. Synthesis of PANI-GO as Nanocomposite

A previous method showed that the synthesis of polyaniline-graphene oxide (PANI-GO) was successfully achieved when 1 g of graphene oxide was ultra-sonicated with distilled aniline for 20 minutes and filtered and then submerged in an ice bath. A volume of 20 ml of 1 M HCl was wisely added to the drop and 10 ml of 1 g ammonium persulfate APS (dissolved in 10 ml of 1 M HCl) was wisely added to preserve the mixture temperature at 0 ° C. The solution was then stirred for 2 hours in an ice bath and kept overnight in the refrigerator. The resulting precipitate was filtered and washed 5 times with distilled water and 1 M with 20 ml of ammonium hydroxide and stirred for 30 minutes, then collected and washed with distilled water until the pH was neutralized. Finally, the precipitate was washed by 15 ml of benzene with stirring for 15 min and dried at 80 ° C for 6 hours. The produced GO was then functionalized with PANI [20].

4.2. Synthesis of PANI-CNT as Nanocomposite

To synthesize the PANI-CNT composites, an earlier study used a technique described elsewhere [14]. In general, 0.5 g of aniline was dissolved in 10 mL of deionized water and 50 mg of CNT-COOH was dissolved in 10 mL of deionized water, followed by 0.5 mL of hydrochloric acid (1 M HCl) or nitric acid (1 M HNO3) and 2.9 g of potassium persulfate KPS. The KPS to molar aniline ratio was 2:1. Green polyaniline was then slowly diffused at the interface into the aqueous phase that emerged. After three hours, the entire water flow was homogeneously filled with a dark-green CNT/PANI nanocomposite. To remove the aniline oligomers and non-reacted chemicals, the aqueous phase was then collected and washed with ethanol and water. The resulting PANI-CNT composite was dried in a vacuum oven at a temperature of 40 ° C, for 24 hours [21].

5. Characterization of PANI composites

5.1. PANI-GO as Nanocomposite

In 2012, M. Hakimi and P. Alimard demonstrated the FTIR spectrum of PANI-GO composite and suggested a good functionalization of GO with PANI [22]. Figure 2 shows that spectra of PANI chains were allocated, but a slight change to a lower frequency, indicating the stacking and (H:B) between GO nano sheets and the backbone of PANI. Peaks assigned to 1574 and 1488 cm\(^{-1}\) refer to stretching vibrations of C=C quinonoid and benzenoid, respectively. Aromatic amine stretching deformation peaks at 1297 and 1135 cm\(^{-1}\) assigned to C-N and C=N stretching of (-N=quinoid=N-), respectively. A broad peak at 3196 cm\(^{-1}\) corresponded to
the N-H stretch vibration, and a peak at 823 cm\(^{-1}\) corresponded to the C-H aromatic ring vibration. The presence of PANI-GO has been clearly demonstrated by these bands [22].

![Figure 2. FTIR Spectrum PANI-GO, reused from [22].](image1)

In a previous article in 2006, to demonstrate the PANI-GO structure, Z. F. Liu and his co-authors used X-ray diffraction analysis (XRD) [23]. Three new wide peaks of GO with PANI centered at \(2 = 8.3^\circ\) and wide intensive peak at \(25.6^\circ\) and about \(43.1^\circ\) corresponds to (001), (002) and (100) were identified, Figure 3. Crystal planes are approximately the same as those of pure polyaniline as implied by Kumar, which were also the characteristic Bragg diffraction peaks of the polymer. Interestingly, a weak and wide peak, appeared almost at \(2\theta = 8.3\), which was lower than that of graphene oxide, was observed for the GO-functionalized with PANI. It may be due to the inter-planar spacing of the GO with PANI, which was widened due to possible intercalation of PANI, and that the GO was completely exfoliated by treatment with PANI. Therefore, the production of PANI grafting on GO surfaces also supported the X-RD trends, which all provided more insight and strong evidence for the creation of the functionalized PANI-GO

![Figure 3. A pattern of X-RD for graphene oxide with polyaniline, reused from [23].](image2)
Results of scanning electron microscopy (SEM) showed that the graphene nano sheets morphology before doping were more complicated and obvious small and irregular holes observed inside sheets (Figure 4A). However, after doping, these holes were filled and the surface of the sheets appeared smoother due to the effect of the functionalization with PANI, Figure 4B.

A- SEM of GO                                                B- SEM of GO with PANI

Figure 4. SEM of PANI and GO with PANI. A) morphology of GO and B) morphology of PANI-GO

5.2. PANI-CNT as Nanocomposite

In 2006, Tzong-Ming Wu, Yen-Wen Lin demonstrated FTIR spectra of PANI before and after doping with CNT (Figure 5) [24]. The band at 3410 cm\(^{-1}\) showed stretching in the N-H band of aromatic ring of PANI and composite. A peak at 837 cm\(^{-1}\) attributed to N – H out-of-plane bending absorption, a band at ~ 1474 cm\(^{-1}\) of benzoid and that at ~1582 cm\(^{-1}\) of quinoid vibration suggested that the PANI and PANI-CNT composite were generated form of the emeraldine salt. The peak at ~1592 cm\(^{-1}\) corresponded to the CNT active mode and that at ~ 1730 cm\(^{-1}\) corresponded to the stretching mode of the COOH groups were indicated that the formation of COOH groups was at both ends and on the CNT sidewalls responsible on mixing CNT with PANI. PANI-CNT composite showed a reduction in the intensity of the ratio of benzoid to quinoid, which means a stable and conductive form of nanocomposite compared to that of pure PANI [24].
Later in 2012, Liang Ding et al have shown the XRD pattern of pure PANI before and after doping with CNT (Figure 6) [25]. The characteristic peaks for PANI appeared in PANI at 15.4°, 20.5° and 26.29°. Once CNT was integrated into the PANI matrix, a sharp CNT peak of diffraction overlapped at 26.28° with the PANI peak and showed a large and intense composite peak. As compared to functionalized CNT, the data showed no additional crystalline order was added to the composite. In PANI-CNT, noticeable characteristic peaks may be due to the crystallization of the outer layers of nanotubes. This finding confirms that PANI is capable of homogeneously coating the CNT[25].

Figure 5. FTIR spectra of PANI-carbon nanotube and pure PANI. Reused from [24].

Figure 6. A pattern of X-RD for PANI-CNT and pure PANI. Reused from [25].
The same study has also showed the SEM images of PANI before and after functionalized with CNT, Figure 7 [25]. Figure 7 indicated thin and long fibrous structures of PANI and (CNT) before doping (A) and (B), respectively. Nevertheless, the PANI-CNT composite displayed homogeneous PANI coating on CNT suggesting that carbon CNT was well dispersed in the polymer matrix (Figure 7C). The CNT diameter (30-40 nm) increased after coating with PANI and a rough surface area of the composite indicated by scanning electron microscopy (SEM) suggested that PANI was successfully doped over CNT. Nanocomposite has shown new fibrous structures that act as good conductive fibrous compared to that of pure PANI [25].

![Figure 7. SEM images of pure PANI and pure CNT before and after doping. A) PANI before doping, B) CNT before doping and C) PANI-CNT after doping. Reused from [25].](image)

6. Electrical properties

During 2013, Devi, D.P. and co-authors managed to measure the conductivity of PANI and its composites PANI-GO and PANI-CNT according to two-probe method [26]. The findings explained that the PANI-CNT composite’s electrical conductivity value improved from 0.1% to 1% relative to CNT. According to a previous report, CNT could serve as a "conductive bridge" between the PANI conductive domains to boost the electrical conductivity of PANI nanoparticles [27]. Given the increased electrical conductivity of PANI-GO composite compared with pure PANI, where GO can act as a PANI dopant [28], Posudievsky, O.Y. et al showed that conductivity of PANI –GO composite was reduced as the GO ratio increased [29]. Disruption in the conjunction system of GO plates caused electrically insulating material [30]. The oxidized layers serve as an insulating region between PANI electrical conducting domains and result in a decrease in the conductivity value of PANI-GO composite. On the other hand, the conductivity of PANI-GO composite is higher than that of PANI-CNT composite because of higher surface area of GO sheets than that of CNT composites [31].

7. Conclusion

This review studied the methods of preparation and characterization of the PANI-GO and PANI-CNT composites to gain near insight into the best electrical composite. Polymerization In-situ. FTIR, XRD and SEM showed that all allotropic composites had identical behaviors, but they did have different measurements of morphologies and conductivity. The PANI-GO composite is plated in shape, the PANI-CNT composite is tubular and thus shows that PANI was shaped in graphic allotropic format. The
conductivity indicates a contrary behavior of PANI-GO’s to PANI / CNT due to the difference in the form and sensitivity between graphic allotropes and polymerization of oxidizing agent.

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