

A Review on Polyaniline and Its Noble Metal Composites

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ABSTRACT: Good environmental stability, High degree of processability and interesting redox properties associated with its chain heteroatom, polyaniline (PANI) has been one of the most extensively studied conducting polymers during the past ten years. The present review attempts for the first time to summarize the explicit and quantitative dealings with the various intrinsic oxidation states of PANI and its synthesis, Characterizations, Development and applications of polyaniline derivatives that have been made during the past decade. The paper includes the advantages of some selected studies carried out on polyaniline and polyaniline Nobel metal composites and the superiority of Polyaniline. Details are provided of the different methods used for the synthesis of PANI along with mechanisms, theoretical studies and number of special methods used to obtain a nanostructured PANI. A detailed discussion on the mechanism of electrical conduction in PANI and the factors those influence the conductivity of PANI is also included. Finally, the progress towards technological applications is evaluated.

KEYWORDS: Polyaniline (PANI), Nobel metal, Nanostructure, Graphene/CNT/PANI, Doping

I. INTRODUCTION

Intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity[1]. Everyday polymers, which are more commonly known as plastics, are composed of simple repeating molecule units called monomers. Polymer name derived from the Greek words 'poly' means 'many' and 'mer' means 'part'. Polymers are well known for their insulating properties, indeed it is this characteristic that has led to their wide usage in the packaging and electronics. Conducting polymers (CPs) are differ greatly from these insulating polymers because of they are intrinsically conducting. Developments of conducting polymers are largely due to the work of three scientists namely as A. J. Heeger, A. G. MacDiarmid and H. Shirakawa, who received the Nobel Prize in Chemistry in 2000 for their work on polyacetylene [2]. Polyaniline (PANi, Aniline black) was first described in the mid-19th century by Henry Letheby, who investigated the electrochemical and chemical oxidation products of aniline in acidic media. He noted that reduced form was colorless but the oxidized forms were deep blue.[3]

II. BACKGROUND OR RELATED WORK

MacDiarmid et al. [6]reported significant developments in the conductivity of polyacetylene doped with iodine. Although the first polymerization of acetylene was performed earlier in 1958 by Natta and co-workers [4]. This material had poor processability and attracted little interest, until the work of MacDiarmid and co-workers [4]. Despite the metal-like conductivity of polyacetylene, it has poor thermal stability and accordingly other conducting polymers with better stability and processability have received more attention. Polyaniline (PANI) is a conducting polymer of the semi-flexible rod polymer family. Although the compound itself was discovered over 150 years ago, only since the early 1980s has polyaniline captured the intense attention of the scientific community. This interest is due to the rediscovery of high electrical conductivity. Amongst the family of conducting polymers and organic semiconductors, polyaniline has many attractive processing properties. Because of its rich chemistry, polyaniline is one of the most studied conducting polymers of the past 50 years. [5]Conducting polymers have π -conjugation across the polymer backbone made up of carbon and hydrogen, along with heteroatoms such as nitrogen or sulphur. They include polyaniline (PANi), polypyrrole (PPy), polythiophene and polyacetylene. Polyaniline is a typical phenylene-base polymer having a chemically flexible $-NH-$ group in the polymer chain flanked on either side by a phenylene ring. The

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protonation, de protonation and various physico-chemical properties of Polyaniline can be traced to the presence of the $-NH-$ group [6].

The conjugated polymers in their undoped state are semiconductors or insulators due to energy gap can be > 2 eV, which is too great for thermally activated conduction. Hence, undoped conjugated polymers, such as polythiophene, polyacetylene only have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Even at a very low level of doping less than (1 %), electrical conductivity increases several orders of magnitude up to values of around 10^{-1} S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 100-10000 S/cm for different polymers. Highest values reported up to now are for the conductivity of stretch oriented polyacetylene with confirmed values of around 80000 S/cm [7].

In semiconductor undoped semiconductors are intrinsically conducting, doped semiconductors extrinsically conducting. In reverse, doped polymers are often referred to as “intrinsically conducting polymers”. This to distinguish them from polymers which acquire conductivity by loading with conducting particles such metal flakes, carbon black or fibers of stainless steel. The intrinsically conducting polymers (ICPs), more commonly known as “synthetic metals” are organic polymers which possess the mechanical properties and processability of conventional polymers, as well as unique electrical, electronic, magnetic, and optical properties of metals[8].

The process which converts the neutral polymer backbone to a charged pi-conjugated system is known as “doping”. The doping concept is the most important concept in conducting polymers which distinguishes “intrinsically conducting polymers” (ICPs) from all other types of polymers. Conducting polymers can exist in nonconductive form (non-doped polymer) and conductive form (doped polymer)[8]. The “classical” method of “doping” involves redox doping, i.e., chemical or electrochemical partial oxidation (“p-doping”), or partial reduction (“n-doping”) of the conjugate polymer backbone [9].

Fritzche et al. [10] carried out the tentative analysis of the products obtained by the chemical oxidation of this aromatic amine. Subsequent investigators [11] have verified these results, and similar observations have been made during the oxidation of aqueous hydrochloric acid solutions of aniline.

J.STEJSKAL et al. [12] reported standard deviation of 40% in the conductivity of polyaniline chooses typical for polymerization prepared by oxidation of 0.2 M aniline hydrochloride with 0.25M ammonium peroxydisulphate at room temperature using eight people from five institutions in different country following the same preparation of protocol.

Jianbo Lu et al. [13] were prepared Chemo-resistive sensors from mono disperse polyaniline nanoparticles synthesized via oxidative dispersion polymerization. Polystyrene sulfonic acid was used as the stabilizer and dopant agent. Polyaniline nanoparticles based chemo-resistive transducer was presented high potential for vapor sensing applications. Sharma et al.[14] reported nano conducting Biodegradable nano conducting polymer based composite are useful in aerospace, food packaging, solar cell, automotive, electrical and electronic goods, body moldings, engine cover, catalyst, batteries and biosensors application.

Lau et al.[15] prepared Graphene quantum dot/polyaniline (PANI/GQD) composite films by chemical oxidation process. Au/PANI-GQDs/ITO sandwich device was fabricated in order to investigate the transport properties of the composite. A stable hysteresis loop was observed in response to the applied voltage. The PANI/GQD composite films are applied in photonic devices.

Jin-Woo Choi et al. [16, 17] proposed Conducting Polyaniline Nanowire and Its Sensing Applications of One dimensional nanomaterial-based chemiresistors can achieve high sensitivity and fast response. Qian Cheng et al. [18] fabricated and studied Graphene and single-walled carbon nanotube composites are as the electrodes by coating polyaniline (PANI) for asymmetric supercapacitors. A highest energy density of 188.4 Wh kg^{-1} and maximum power density of 200.5 kW kg^{-1} have been obtained. They suggested increasing the electric conduction and utilization of active material which lead to significant increase of the specific capacitance that is highly desirable for applications in electric vehicles.

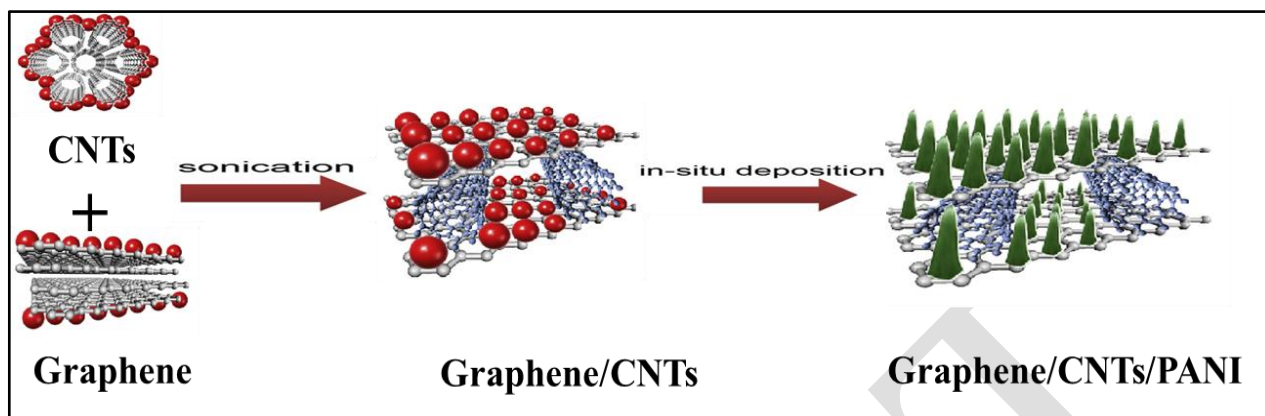


Fig.1. Fabrication of graphene/CNT and graphene/CNT/PANI composites.

Fig.1 shows the chemically modified polyaniline (PANI) nanofiber and graphene composites were prepared by in situ polymerization of aniline monomer in the presence of graphene oxide under acid conditions. The resulting PANI/graphene oxide composites were reduced to graphene using hydrazine followed by reoxidation and reprotonation of the reduced PANI to give the PANI/graphene nanocomposites [19]. The research data revealed that high specific capacitance and good cycling stability can be achieved either by doping chemically modified graphenes with PANI or by doping the bulky PANIs with graphene/graphene oxide. Polymerization is a process of reacting monomer molecules together in a chemical reaction to form polymer chains or three-dimensional networks [20, 21, 22].

III. EXPERIMENTAL PART

1. STRUCTURE

Conducting polyaniline have ordered structure contain regularly alternating phenyl rings and nitrogen-containing groups. This structure of polymer chain forms a zigzag lying in one plane, and π -electron clouds overlap above and below this plane known as polyconjugation.

Hagiwara et al. 1987 suggested that the lone electron pair of nitrogen performs the same function as π -electrons and assures polyconjugation. Polyconjugated system is a transport path providing charge carrier mobility. It is formed as a result of strictly regular assembly of monomer units. The chain of conducting PANI contains more than 95% of para-substituted aniline fragments linked in a “head-to-tail” configuration. During oxidation, i.e., removal of electron, positive polaron is generated in the chain; it deforms chain structure considerably. Nitrogen atoms of PANI serve as oxidation centers. Oxidized nitrogen atoms in the polymer can change from zero to nearly one i.e. leucoemeraldine to pernigraniline. The most stable form of polyaniline is emeraldine, in which every second nitrogen atom is oxidized, and polymer chain contains equal number of oxidized and reduced units. In the absence of external potential, the fully reduced and fully oxidized forms of the polymer simultaneously transform into this oxidation state. In the case of leucoemeraldine, the transformation into emeraldine takes place at the expense of slow oxidation of amino groups by air oxygen. This reaction is reversible. Pernigraniline also tends to lower its oxidation state and turn into emeraldine. When the degree of oxidation of PANI exceeds 0.7, the polymer becomes unstable, and irreversible transformations of macromolecules begin.

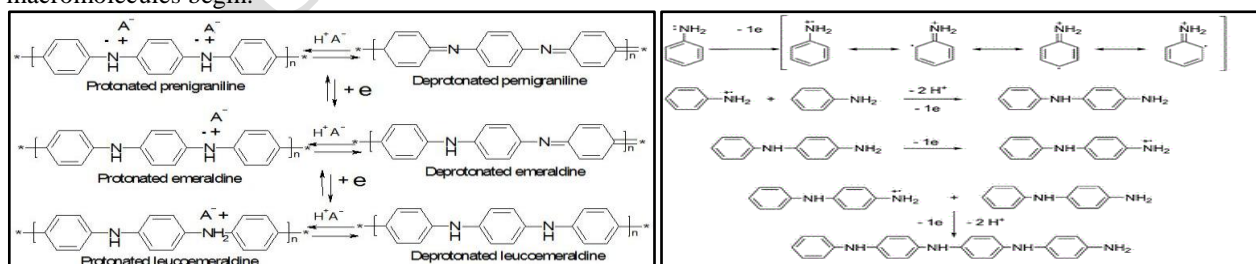


Fig.2. Polyaniline forms

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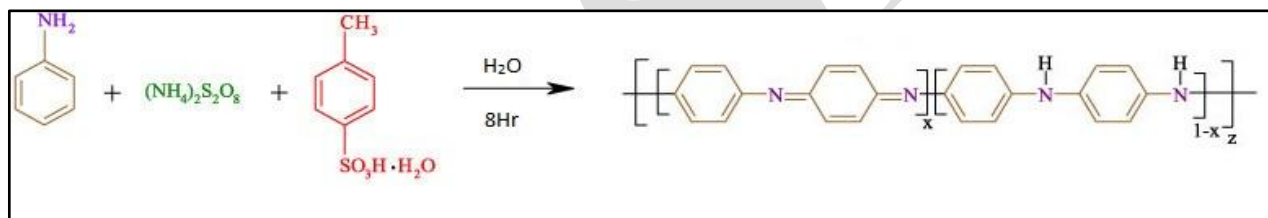
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IV. MATERIALS AND SYNTHESIS METHODS

Oxidative polymerization may be considered as formation of covalent bond between monomer molecules at the expense of abstracting two protons. Oxidative polymerization is used for the synthesis of polymeric (oligomeric) products from various classes of monomers (aromatic amines, phenols, thiophenols, aromatic hydrocarbons and heterocycles (Higashimura& Kobayashi, 2004). Oxidation of monomer takes place under the action of inorganic or organic oxidizing agent as well as the applied potential. During this process, cation or cation radical sites are generated in monomer (polymer) molecule, thus initiating polymer growth.

The formation of chain may proceed in two ways. The first one is recombination of cation radical oxidation sites. In this case, polymer growth process is classed as polycondensation, since fragments of any length may recombine. The second way of chain growth belongs to electrophilic substitution; in the case of aniline, oxidized nitrogen-containing structure attacks phenyl ring of another aniline molecule and substitute's one proton of the ring. The ring and nitrogen-containing structure lose one proton; after that, monomer units bind with each other, and the chain becomes longer. Y.We (Wei, 2001) singled out the polymerization of aniline into a special type of reactivation chain process. The chain growth involves repeated acts of activation/deactivation of the polymeric structure.

Polymerization of aniline and synthesis of its conducting polymer may be performed by electrochemical or chemical methods. 1 mol of aniline was dissolved in 1mol of acid like HCl, H₂SO₄, and p-toluene sulfonic acid etc. solution. The solution was kept at 0 °C under argon atmosphere. A pre-chilled solution of 1 mol of ammonium persulfate act as oxidizing agent in acid solution was slowly added with vigorous stirring. The reaction mixture was continuously agitated for another 8hr. The precipitate was subsequently filtered and washed several times with methanol and dried overnight in vacuum. Scheme1 shows, that typical synthesis method of polyaniline by chemical synthesis route.



Scheme 1. Synthesis of polyaniline

Experimental behavior showed that aniline is also oxidized under the action of weak oxidants with a potential close to +1 V or even lower (Sapurina&Stejskal, 2012). Such agents can oxidize aniline not only in basic and neutral media, but also, strange as it may seem, in acidic media where potential barrier of oxidation is high. However, the use of weak oxidants causes some problems because it does not necessary lead to the formation of conducting products.

V. KINETIC OF POLYMERIZATION

During induction period known slow process, aniline oligomers are formed. The induction period is followed by the rapid exothermic step of polymer chain propagation. The following kinetic dependences were suggested for description of this two-step process (Tzou& Gregory, 1992).

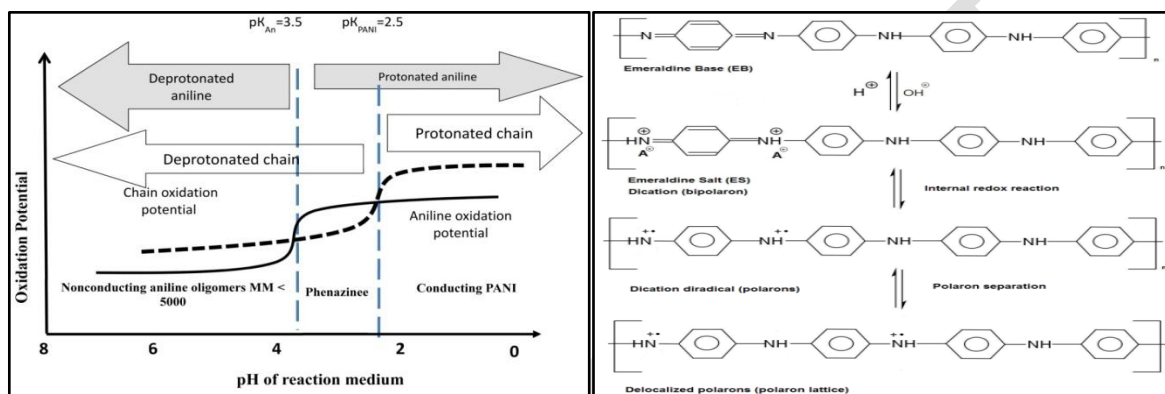
$$-d [An]/dt = k_1 [An] [Ox] + k_2 \sigma [An] P,$$

Where,

[An] is the molar concentration of aniline; [Ox] is the molar concentration of the oxidant; P is the surface of the reaction medium interface; σ is the surface factor; k_1 is the rate constant for the initial step (induction period) of polymerization; k_2 is the rate constant for the polymer chain propagation.

Both the first and second steps are first-order reactions with respect to monomer. For the initial step, the reaction order with respect to the oxidant is also the first one. In the propagation step, monomer is oxidized with pernigraniline form

of polyaniline rather than with the original oxidant. Polyaniline is insoluble, and the reaction is heterogeneous; hence, the P parameter and the σ factor are introduced into the equation in order to characterize the interface on which the reaction proceeds. The rate constant for the chain propagation (k_2) is three orders of magnitude higher than the rate constant for the initial step of polymerization (k_1), so the formation of the polymer leads to impressive acceleration of oxidative polymerization. Similar acceleration was also observed upon the introduction of polyaniline seeds into the reaction medium. This process is called auto acceleration (Tzou & Gregory, 1992). Under high acidity conditions ($\text{pH} < 1$), direct proportionality between molar concentration of the strong acid and k_2 was observed. At the same time, the increased acidity has a little effect on the rate constant of the initial step; however, the induction period shortens substantially with decreasing pH.



Scheme 2. Oxidation of aniline depending on protonation constant of monomer.

Scheme 2 shows that oxidation of aniline depends on the protonation constant of the monomer. The oxidation products obtained in water and acetic acid (Fig. 4 & 5) exhibited characteristics intermediate between those of aniline oligomers and high molecular weight PANI. As compared with polyaniline synthesized in sulfuric acid (Fig. 6), molecular masses of the products were lower and their polydispersities were higher; their conductivities were two orders of magnitude lower and the band corresponding to polaron charge transfer was less intense and shifted to the short wavelength range. (Fig. 7, 8) shows the morphology of Polyaniline synthesized in the intermediate pH range ($1 < \text{pH} < 4.5$) that includes two temperature waves

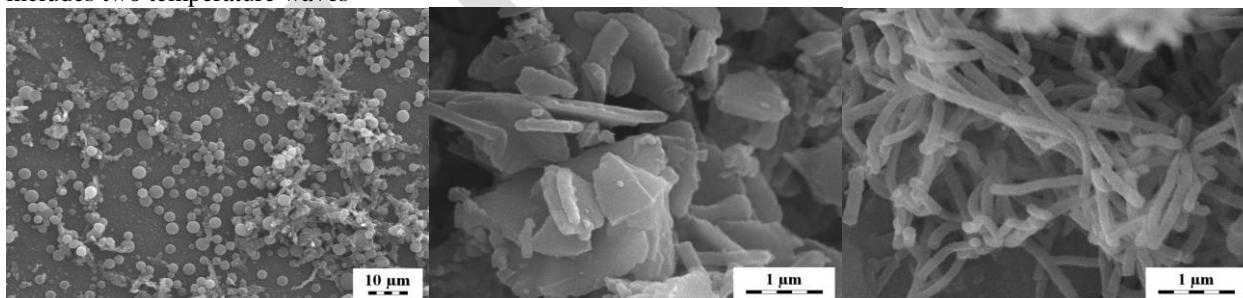


Fig. 3. SEM of PANI using APS in aq. ammonia. Fig. 4. SEM of PANI using APS in water

Fig. 5. SEM of PANI using APS in acetic acid

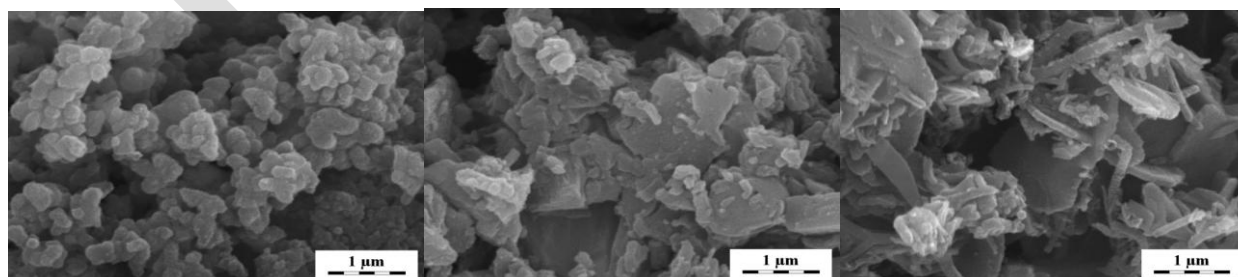


Fig. 6. SEM of PANI using APS in sulfuric acid

Fig. 7. SEM of PANI using APS at $\text{pH} > 3.5$. Fig. 8. SEM of PANI using APS in acetic acid at $\text{pH} \sim 2.5-3$.

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Liu et al. [25] worked out copper nanoparticles were fabricated by electrical explosion of wire (EEW) in solution of polyacrylic acid (PAA) and ethanol. Conductive polyaniline-copper (PANI-Cu) composites have been synthesized by in-situ polymerization of aniline in the fabricated copper suspension. Optical absorption in the UV-visible region of these suspensions was measured in the range of 200-900 nm. The copper selenide (Cu₂Se)/polyaniline (PANI) nanocomposites was successfully synthesized by insitu polymerization. The XRD pattern indicates that PANI/Cu₂Se nanocomposite has an orderly arrangement of the polymer chain; whereas synthesized PANI is slightly crystalline in nature [26]. The catalytic and photocatalytic ability of copper modified polyaniline films towards the reduction of Cr (VI) are compared with those of pure polyaniline and pure copper.

Gupta et al. [27] magnetic susceptibility of the polyaniline and doped polyaniline are measured and from the magnetic susceptibility values anisotropy constants of doped polyaniline.

Varga et al. [28] present a brief overview of the electrical properties of conductive composites containing silver and conducting polyaniline. Composites were produced by oxidation of aniline with silver nitrate in the presence of various acids playing the role of doping agents. A semiconducting behavior was observed under the threshold about 21–27 vol. % of silver in composite.

Smith et al. [29] has been reported synthesis of PANI gold composites using HBF₄ as oxidizing agent by the conductance of the resultant PANI-Au composite doped with HBF₄ was higher when compared to an undoped composite.

Tseng et al. [30] reported a charge transfer effect in the polyaniline nanofiber/gold nanoparticle nanocomposite memory system. The electric-field-induced charge transfer in this device occurs between the conjugated polyaniline and gold nanoparticle and is responsible for the electrical conductance switching. The realization of the charge transfer effect in this polymer-nanoparticle system could benefit applications of memory devices in the field of organic electronics.

VI. CONCLUSION

This review attempts to consider synthesis of PANI from a general viewpoint, starting with structure, molecular reactions and Nano composites with noble metals. Conductivity, magnetic, optical and other properties of PANI may change depending on its oxidation state and degree of protonation. The information is presented succinctly, and we have no opportunity to give experimental proof of different points, but it can be found in the given references. PANI, have high selectivity of synthesis and formation of polyconjugation in other polymers are related to the presence of excess positive charge on the growing chain. Evidently, the formation of aggregates between growing chains of conducting polymers involves electronic and ionic transport. In the recent era polyaniline and its composite are widely used as energy, electronic devices and better in sensor application.

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