

In-situ synthesis and characterization of conducting metal – polyaniline nanocomposites

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ABSTRACT

Metal-Polyaniline nanocomposites such as Platinum-Polyaniline nanocomposite is prepared by in situ oxidative polymerization of aniline and reduction of Pt^{+4} ions into Pt nanoparticles. The polymerization of aniline was carried out in the presence of K_2PtCN_6 [Potassium Hexa Cyano Platinate (IV)] as oxidizing agent. During the reaction aniline monomers undergo oxidation and form polyaniline (PANI) whereas the reduction of $[PtCN_6]^{-2}$ ions result the formation of Pt nanoparticles. Nano-sized Pt particles were prepared by controlled reduction of Platinum precursor in micro emulsion medium, stabilized with the anionic surfactant (AOT). Micro emulsion solution acts as both emulsifier and dopant to obtain stable nanocomposite. PANI-AOT-Pt nanocomposite is characterized by FT-IR spectroscopy and scanning microelectronic microscopy (SEM).

Keywords: Polyaniline; Nanocomposite; Pt Nanoparticles

INTRODUCTION

Among the conducting polymers, polyaniline (PANI) is under extensive study even today because of its high environmental stability, low cost, and relatively simple polymerization process [1-3]. In spite of various advantages, PANI has received limit of application until several years ago, because PANI is neither soluble nor fusible in organic solvents as well as water. Cao has first achieved the development of PANI with better solubility in common solvents [4-6].

Nanomaterials, which are materials with structural units on a nanometer scale in at least one direction, are the fastest growing area in materials science and engineering. Material properties become different on the nanoscale: for example, the theoretical strength of materials can be reached or quantum effects may appear. Nanoparticles technology is of substantial interest for a large number of practical applications. Polymeric nanocomposites,

consisting of organic polymers introduce an interesting class of materials with good efficiency. There has been recent surge in interest in the synthesis and application of electroactive polymers with incorporated metal particles, practically in nanoscale [7-9].

Studies in the field were devoted to the preparation of PANI/noble metal composites and ease of preparation. Conducting polymers find applications in fields like: sensors, electrocatalysts, microelectronics, electromagnetic shielding, rechargeable batteries and controlling systems [10-14]. Nanomaterials with a high surface area and porosities are known to show better performance electrode as materials for direct methanol fuel cell applications [15]. The electroactive polymers may be particularly suitable as a matrix for hosting the metallic particles for catalytic applications, since these media provide an effective route for the flow of electronic charges. The nanofibilar morphology,

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significantly improves the performance of polyaniline in many conventional applications involving polymer interactions with its environment. The high conjugated polymeric structure of polyaniline produces new nanoscale phenomena that are not accessible with current inorganic systems [16]. Polyaniline (PANI) is an intrinsically conductive polymer (ICP) which is able to conduct electric currents without the addition of any conductive (inorganic) substances. The unique properties of PANI have attracted great attention in order to exploit the feature in various applications such as inhibition of corrosion for metals [17], gas sensing devices [18], biosensors [19], capacitive electrodes [20] and optical recording materials [21]. The preparation of PANI/inorganic nanocomposites has been the subject of considerable interest recently [22]. It has been found that the novel materials exhibit improved mechanical, electrical and thermal properties due to the synergistic effect of the organic and inorganic components. Micro emulsion, which consisted of oil, surfactant and water molecules, is a thermodynamically stable and isotropic transparent solution. In the case of w/o micro emulsion system (oil continuous), it contains a dynamic structure of water nanodroplets that become the medium for the chemical reaction to occur when desirable reactants collide with each other. The surfactant-stabilized nanoreactors provide a cage-like effect that inhibits excess particle growth and agglomeration when the particles size approach to that of water nanodroplets. Micro emulsion processing technique has been employed to fabricate various nanocomposite materials. Leo prepared BDA-PPV/CdS nanocomposites in reverse micro emulsion that consisted of CTAB/n-pentanol/n-hexane/water [23]. Besides, Liu also reported that PbS-polymer nanocomposites with third order nonlinear optical response have been successfully synthesized using the same approach [24].

In-situ synthesis was achieved either through reaction of metal ions that are dispersed in polymer matrices or polymerization of a solution containing monomer and the metal nanoparticles. In this paper, in-situ synthesis of platinum loaded polyaniline in anionic surfactant

(AOT) is prepared using oxidative polymerization technique. Polyaniline as a conducting polymer is a desirable system to support the metal nanoparticles such as platinum, which can be dispersed on the dense surface of these supporting materials.

EXPERIMENTAL

Materials

Aniline, potassium hexacyanoplatinate (IV) and AOT were purchased from Merck. All chemicals solvents and reagents were used as received, except for aniline, which was distilled before use.

Synthesis of Nano composite

The synthesis reaction was performed in 100 ml of 0.1M AOT solution, in which the aniline monomers was added drop-wise and stirred for one hour to yield homogeneous transparent solution. 50 ml of a solution containing 0.05M K_2PtCN_6 was added drop-wise to the previous solution to form Nano composite. Nano-sized Pt particles were prepared by controlled reduction of Platinum precursor in micro emulsion medium, stabilized with the anionic surfactant (AOT). Micro emulsion solution acts as both emulsifier and dopant to obtain stable nanocomposite. The appropriate content of polyaniline in the composite film is a key factor for preparing the PANI-AOT-Pt electrode with better performance. In this method is a simple and facile route for polyaniline nanocomposite synthesis is proposed, which is confirmed and optimized.

RESULT AND DISCUSSION

The UV-Vis absorption spectra of the solutions were recorded on a Perkin-Elmer Lambda 35 spectrophotometer in the wavelength range 300–900 nm. A Perkin-Elmer model Spectrum GX Fourier Transform Infrared (FTIR) spectrophotometer was used to determine the infrared (IR) absorption spectra, in the wavelength range 4000–370 cm^{-1} . The samples were dispersed in potassium bromide (KBr) and compressed into pellets. The electrochemical measurements were carried out using a three-electrode cell including, a glassy carbon electrode as a working electrode (with 2 mm in

diameter), auxiliary electrode was a platinum wire and reference electrode was a saturated calomel electrode (SCE). A Radiometer Model DEA 332 digital electrochemical analyzer equipped with an IMT 102 electrochemical interface and a personal computer was used for data storage.

FTIR Spectroscopy of Nanocomposite

The FTIR spectra for the PANI-AOT-Pt nanocomposite are shown in Fig. 1. The appearance of characteristic absorption band around 1250 cm^{-1} , which is related to the C-N stretching in bipolaron structure, can be observed for the sample. These results indicate that polymer is highly doped and existed in conducting emeraldine salt form. The peak at 1298 cm^{-1} corresponds to C-N stretching of secondary amine in polymer main chain and can be clearly seen for both samples. The broad absorption band ranges from 3430 to 3440 cm^{-1} , which is attributed to the protonation of amine functional group at polymer backbone and is observed for the highly doped PANI emeraldine salt. The absorption band near 2900 cm^{-1} is assigned to aliphatic C-H stretching of the polymer. The appearance of the absorption peak in the spectra is beyond our expectation as it indicates the existence of aliphatic alkyl functional group in the polymers, although none of such substances has been introduced in the system during the polymerization process. Hence, the appearance of the absorption peak may be corresponding to the long alkyl tail of the surfactant. It is well known that the surfactants can become the secondary dopants and absorbed as an outer layer surrounding the PANI particles

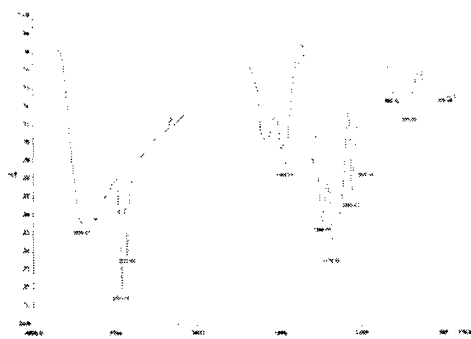


Fig.1. FTIR spectra of PANI-AOT-Pt nanocomposite.

UV-Vis Spectroscopy of Nanocomposite

The UV-Vis absorption spectra of the pure PANI-AOT-Pt nanocomposites prepared by the in-situ technique are shown in Fig. 2. The existence of characteristic absorption band around 420 nm , confirms the formation of doped PANI. The absorption band at 420 nm is attributed to the doping level of PANI.

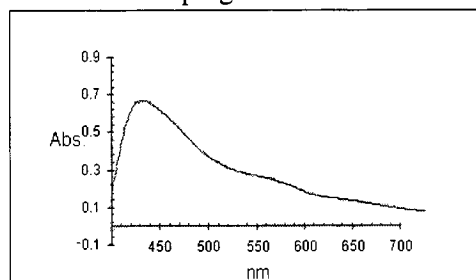


Fig.2. UV-Vis spectra of of PANI-AOT-Pt nanocomposite.

CVs for Methanol Electrooxidation

In Fig. 3, a cyclic voltammogram of modified PANI-AOT-Pt electrode, which is prepared by 0.2 mgcm^{-2} of catalyst loading, in absence of methanol, scan rate of 50 mVs^{-1} and sulfuric acid concentration of 0.50 M , is shown. Fig. 4. shows the cyclic voltammogram curves for methanol electrooxidation. The methanol oxidation was performed on the Pt modified PANI-AOT-Pt nanocomposite electrode in $0.5\text{ M CH}_3\text{OH} + 0.5\text{ M H}_2\text{SO}_4$ solutions at a scan rate of 50 mVs^{-1} . Due to the dispersion of platinum particles in the polyaniline layer matrix of the composite film and the synergistic effects between the dispersed Pt particles and the polyaniline layer, the modified composite electrode has excellent electrocatalytic activity for methanol oxidation. This implies that the Pt substrate only plays a conductor role in the resultant electrode.

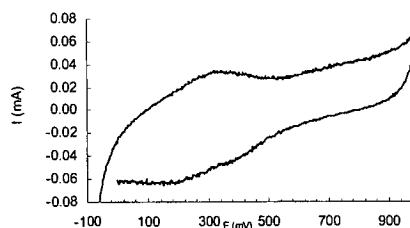


Fig.3. A typical cyclic voltammogram of PANI-AOT-Pt electrode in 0.30 M .

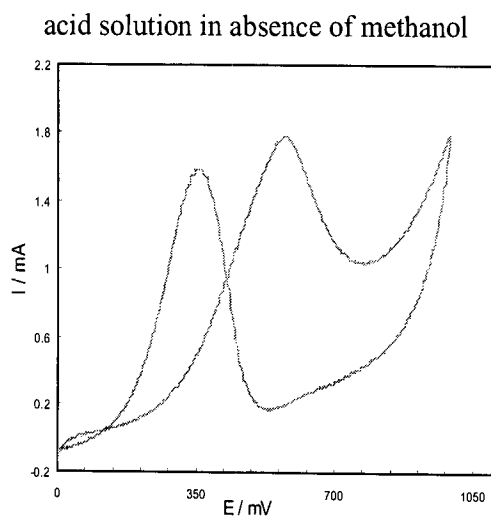


Fig.4.A typical cyclic voltammogram of PANI-AOT-Pt electrode in 0.30 M acid solution and in the presence of 0.20 M methanol.

Morphology

The SEM images of the PANI-AOT and PANI-AOT-Pt is shown in Fig. 5. As can be seen, the polyaniline layer of the PANI-AOT-Pt has a porous structure with different pore diameters, while on the outer surface of the composite film there are a lot of small pores. From Fig. 5b. Which shows the PANI-AOT-Pt nanocomposite, we find that the Pt particles disperse uniformly in the polyaniline layer. Part of the Pt particles is dispersed on the framework of the porous structure, while the other part of Pt particles is held in the holes of the polyaniline layer.

CONCLUSION

Polyaniline-platinum nanocomposites is synthesized in-situ technique. The appearance of characteristic absorption band around 420 nm in the UV-Vis spectra confirms the formation of conducting emeraldine salt. The lower intensity polaron absorption for PANI-AOT-Pt nanocomposites in the spectrum indicates that the doping state of the polymer has been improved. The data and analysis of the FTIR and SEM show that PANI-AOT composite film has a porous asymmetrical structure with a bi-layer where the inner layer comprises polyaniline and the outer layer is composed of AOT.

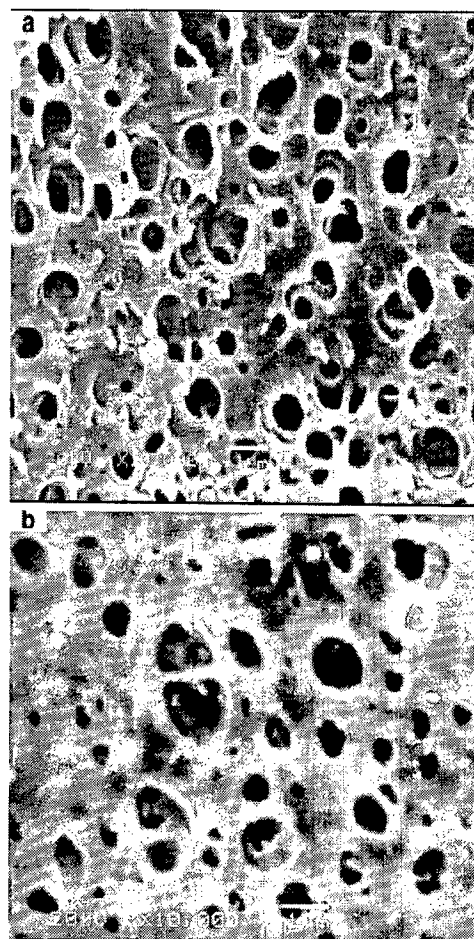


Fig. 5. SEM images of the inner face of the PANI-AOT (a) PANI-AOT-Pt (b).

Its porous bi-layer structure can load platinum particles separately and firmly, which provide a large surface area for electrochemical reaction, prevent the catalysts from agglomerating and consuming in working and lead to the synergistic effects, which promote its electrocatalysis. The appropriate content of polyaniline in the composite film is a key factor for preparing the PANI-AOT-Pt electrode with better performance. The resultant PANI-AOT-Pt electrodes have excellent electrocatalytic activity for methanol oxidation.

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