Abstract— Polyaniline-Pt-Ru nanocomposite is prepared by in situ oxidative polymerization of aniline and reduction of Pt\textsuperscript{4+} and Ru\textsuperscript{3+} ions into Pt and Ru nanoparticles. The polymerization of aniline was carried out in the presence of K\textsubscript{2}PtCN\textsubscript{6} [Potassium Hexa Cyano Platinate (IV)] and Ruthenium (III) nitrosyl nitrate (Ru(NO)(NO\textsubscript{3})\textsubscript{3}) as oxidizing agents. During the reaction aniline monomers undergo oxidation and form polyaniline (PANI) whereas the reduction of cations, result the formation of Pt and Ru nanoparticles. Nano-sized Pt and Ru particles were prepared by controlled reduction of precursors in micro emulsion medium, stabilized with the anionic surfactant (SDS). Micro emulsion solution acts as both emulsifier and dopant to obtain stable nanocomposite. PANI-SDS-Pt/Ru nanocomposite is characterized by FT-IR spectroscopy, scanning microelectronic microscopy (SEM) and cyclic voltammetry (CV) for sensing trace amounts of methanol.

Keywords— Polyaniline; nanocomposite; Pt-Ru Nanoparticles; Micro emulsion; Sensor electrode.

Introduction

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, particularly in nanoscale [1-3]. Most 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 [4-8]. Nanomaterials with high surface area and porosities are known to show better performance electrodes as materials for direct methanol fuel cell applications[9]. 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 nanofibiral morphology, 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 in organic systems[10-11]. 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. Microemulsion processing technique has been employed to fabricate various nanocomposite materials. In this paper we introduce a simple in situ synthesis of polyaniline-platinum and Ruthenium nanocomposite by utilizing the microemulsion processing technique and the nanocomposite is used as an effective sensor electrode.

2. Experimental

2. 1. Materials

Aniline (99%, monomer) from merk, potassium hexacyanoplaitate(IV), Ruthenium (III) nitrosyl nitrate (Ru(NO)(NO\textsubscript{3})\textsubscript{3}) and SDS were purchased from Aldrich chem. Co. All chemicals solvents and reagents were used as received, except for aniline, which was distilled before use.

2. 2. Synthesis of polyaniline-Pt/Ru nanocomposite

The reaction was performed in 100 mL of 0.1M SDS solution, in which the aniline monomers were added drop-wise and stirred for one hour to yield homogeneous transparent solution. 50 mL of a solution containing 0.05M K\textsubscript{2}PtCN\textsubscript{6} and Ru(NO)(NO\textsubscript{3})\textsubscript{3} was added drop-wise to the previous solution to form nanocomposite. Nano-sized Pt-Ru particles were prepared by controlled reduction of cationic precursors in micro emulsion medium, stabilized with the anionic surfactant (SDS). Micro emulsion solution acts as both emulsifier and dopant to obtain stable nanocomposite. In this method of synthesis, the complete synthesis and purification procedure is
carried out in an aqueous solution, which is environmentally benign.

2. 3. Characterization

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. All electrochemical experiments were carried out in a conventional three-electrode electrochemical cell by means of CHI660B electrochemical analyzer. The working electrode was a platinum disk encapsulated in epoxy resin (electrode geometric area: 0.0366 cm\(^2\)), a platinum wire and a saturated calomel (SCE) electrode were used as counter electrode and reference electrode, respectively.

3. 2. FT-IR spectroscopy of nanocomposite

The FT-IR spectra for the PANI-SDS-Pt/Ru nanocomposite is depicted 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.

3. 3. Morphlogy

The SEM images of the inner layer surface morphology of the PANI-SDS nanocomposite is shown in Fig. 2. As can be seen, the polyaniline layer of the PANI-SDS-Pt/Ru has a porous structure with different pore diameters, while on the outer surface of the composite film there are a lot of small pores. The porous structures of the inner and outer layers are asymmetrical. From Fig. we find that the Pt-Ru particles disperse uniformly in the polyaniline layer. Part of the Pt-Ru particles is dispersed on the framework of the porous structure, while the other part of Pt-Ru particles is held in the holes of the polyaniline layer.
3.4. Electrochemical characterization
Electroactivities towards methanol oxidation of PANI-SDS-Pt/Ru electrodes were measured by CV, and a three-electrode test cell at room temperature. The working electrode was a thin layer of Nafion impregnated PANI-SDS-Pt/Ru composite cast on a vitreous carbon disk electrode. A 5.0 mg catalyst sample were suspended in 1.0mL of ethanol, and 10.0 wt.% Nafion was added as adhesive and proton conductor. The mixture were ultrasonically scattered for 10 min to form homogeneous ink. Then 25 µL of ink was pipetted on a vitreous electrode with 4mm diameter to act as the working electrode. The supporting electrolyte was 0.5M H$_2$SO$_4$. The counter electrode was a Pt wire. The reference electrode was a saturated calomel electrode (SCE). For all experiments the sweep rate is 50mVs$^{-1}$ and the concentration of methanol was 0.5 M. while holding the PANI-SDS-Pt/Ru catalyst electrode potential.

![Cyclic voltammograms](image)

Fig. 3 Cyclic voltammograms of PANI-SDS-Pt/Ru catalysts in 0.5M H$_2$SO$_4$ and ethanol electrolyte

4. Conclusion
PANI-SDS-Pt/Ru nanocomposites have been synthesized employing the microemulsion processing technique. The lower intensity polaron absorption for PANI-SDS-Pt/Ru nanocomposites in the spectrum indicates that the doping state of the polymer has been improved. The corresponding results show that the PANI-SDS-Pt/Ru electrode exhibits a better catalytical activity than Pt graphite electrode and can be used as an effective sensor electrode for trace amounts of methanol in fuel cells.

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