Platinium-Ruthenium electrocatalyst as sensor electrode for methanol oxidation

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ABSTRACT

Hybrid nanocomposites of binary Pt-Ru/Polyaniline were prepared by oxidative polymerization of aniline and formation Pt and Ru nanoparticles. The polymerization of aniline was carried out in the presence of Potassium hexa cyano Platinate (IV) and Ruthenium (III) nitrosyl nitrate 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 Sodium Dodecyl Sulfate. Micro emulsion solution acts as both emulsifier and dopant to obtain stable nanocomposite. Pt-Ru/PAn nanocomposites are characterized by cyclic voltammetry (CV), FT-IR spectroscopy and scanning microelectronic microscopy (SEM).

INTRODUCTION

Nanoparticles technology is of great interest for a large number of practical applications because material properties become different on the nanoscale,. Polymeric nanocomposites, consisting of organic polymers introduce an interesting class of materials with good efficiency. There has been recent surge and interest in the synthesis and application of electroactive polymers with incorporated metal particles, practically in nanoscale [1-3].

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, 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. Most studies in the field were devoted to the preparation of PANi/noble metal composites.

Conducting polymers find applications in fields like: sensors, electrocatalysts, microelectronics, electromagnetic shielding, rechargeable batteries and controlling systems [4-11]. Nanomaterials with ahigh surface area and porosities are known to show better performanceelectrode as materials for direct methanol fuel cell applications [9]. Methanol is so far the most advanced alternative to traditional hydrogen fuel cells, at least for portable applications [12]. In the so-called direct methanol fuel cells (DMFCs) methanol is fed directly into the anode side of the fuel cell, where it is oxidized and electrons are released .Ideally, besides water, CO_2 is the only by-product of the reaction [13, 14].

Pt/C and Pt-Ru/C catalysts have been prepared from several methods, utilizing colloidal techniques, organometallic or coordination complexes, salt precursors and metallic deposition by electrochemical techniques [15-17].

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Recently, increasing interest in low temperature fuel cells has driven attention to alloyed Pt–Ru nanoparticles as anode catalysts for hydrogen or methanol electrooxidation [18-20]. Pt–Ru alloys display superior activity as fuel cells anode catalyst in comparison to Pt without Ru because of their markedly improved resistance to carbon monoxide (CO) [21, 22].

Platinum-group metal nanoparticles were synthesized in a water-in-oil microemulsion [23]. The microemulsion technique has been used to prepare a great number of nanomaterials such as pure metals [24], alloys [25, 26], metal borides[27], metal oxides and hydroxides [28-33], organic polymers [34] and etc .

In this paper microemulsion processing technique has been employed to fabricate hybrid nanocomposite and due to the synergistic effect of the organic and inorganic components we introduce a simple in-situ synthesis of polyaniline-Platinium and Ruthenium nanocomposite by utilizing this technique. The nanocomposite is used as an effective electrocatalyst for methanol oxidation.

EXPERIMENTAL
Reagents and apparatus
Aniline (99%, monomer) from merk, potassium hexacyanoplatinte(IV), Ruthenium (III) nitrosyl nitrate $(Ru(NO)(NO_3)_3)$ and SDS were purchased from Aldrich chem. Co. Nafion solution (5 w/w %) from Alfa Aesar , sulfuric acid and methanol were analytical grade of Merck origin and were used without further purification. All chemicals solvents and reagents were used as received, except for aniline, which was distilled before use. For preparing the solutions high-purity water (Millipore, 18 MΩ cm resistivity) is used. 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. A Perkin-Elmer model Spectrum GX Fourier Transform Infrared (FT-IR) spectrophotometer was used to determine the

infrared (IR) absorption spectra, in the wavelength range 4000–370 cm^{-1}. Scanning electron microscope (SEM) images were taken with a Hitachi S-4700 (New Jersey USA) operating at an acceleration voltage of 15 kV.

Synthesis of Pt-Ru/PAn 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_2PtCN_6 and $Ru(NO)(NO_3)_3$ 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. The solid sample is recovered, further separated by centrifugation and washed with ethanol several times .In order to remove the remaining traces of surfactant, the sample is calcined under a N_2 atmosphere at 673 K for 3 h.

RESULTS AND DISCUSSIONS
FT-IR spectroscopy of nanocomposite
The FT-IR spectra for the Pt-Ru/PAn nanocomposite is depicted in Fig. 1. The appearance of characteristic absorption band around 1240 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 near 1466 cm^{-1} corresponds to C–N stretching of secondary amine in polymer main chain and can be clearly seen for the samples. The broad absorption band ranges from 3200 to 3410 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 2920 cm^{-1} is assigned to aliphatic C–H stretching of the polymer. 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

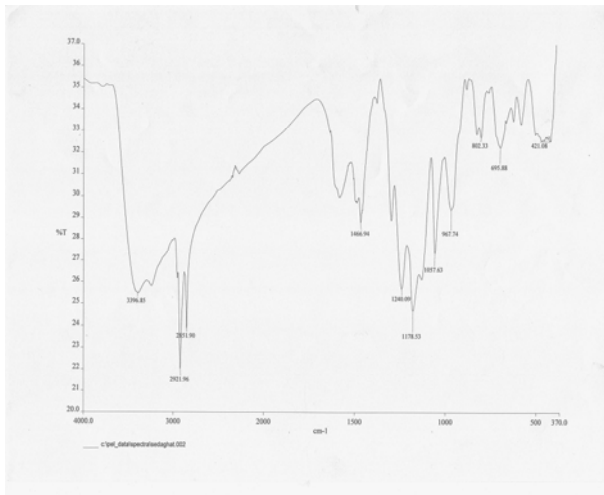and absorbed as an outer layer surrounding the PANi particles.

Fig. 1. FT-IR spectra of Pt-Ru/PAn nanocomposite.

Morphology

The SEM images of the surface morphology of the Pt-Ru/PAn 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.2 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.
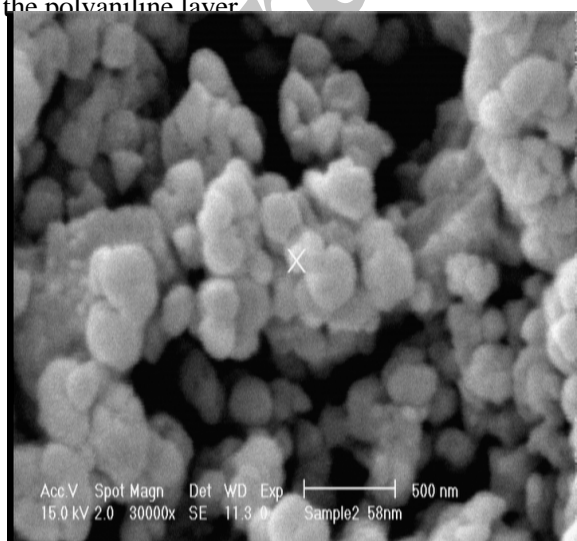

Fig. 2. SEM images of the Pt-Ru/PAn nanocomposite.

Modified electrode preparation

Prior to each experiment,glassy carbon (GC) electrode surface was polished with slurry of 0.05 μm alumina powder until a mirror-like surface obtained. Then the electrode was washed thoroughly with acetone and distilled water. The polished electrode was activated electrochemically in a 0.50 M sulfuric acid solution by a potential sweep between -1100 and 1600 mV vs. SCE for about 9 min. and with a scan rate of 100 mVs^{-1}. A 0.5 mg of Pt-Ru/PAn nanocomposite powder with 20 μL of Nafion solution (5 % w/w) [35] was added in 1 mL   of deionized water and   the suspension was agitated in an ultrasonic bath for 50 min at   a power of 20 watt. 10 μL of this suspension solution containing desired amount of Pt-Ru/Pan loading was transferred on the activated electrode surface by a micropipette in the form of a thin film and then it was allowed to dry in an air oven at 60 ^{o}C for 2 hours to produce a Pt-Ru/PAn modified glassy carbon electrode.

Electrochemical characterization

Electroactivities towards methanol oxidation of Pt-Ru/PAn modified glassy carbon electrodes as prepared in previous section. In fig. 3 insert A (Pt-Ru/PAn), the increase for methanol oxidation current rather than insert B (Pt-Ru/C) is due to the synergic effect in nanocomposite.
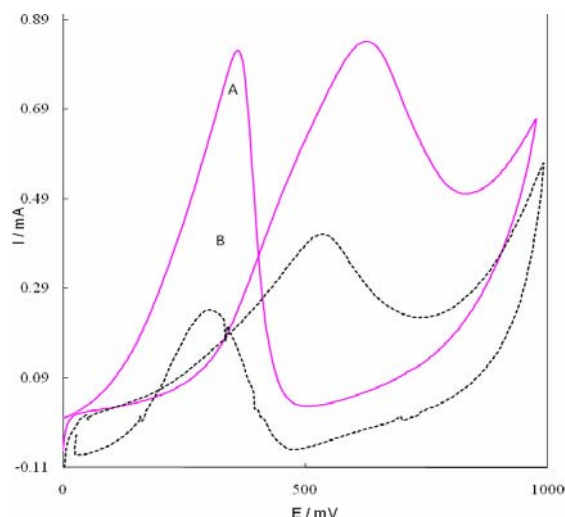

Fig. 3. Cyclic voltammograms of prepared Pt-Ru/PAn nanocomposite catalysts (insert A) and Pt-Ru/C catalysts (insert B) in 0.5 M H$_2$SO$_4$ and 0.5 M of methanol.

211

CONCLUSION

Pt-Ru/PAn nanocomposite 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 nano size of the nanocomposites is observed in the SEM micrograph and the corresponding results show that the Pt-Ru/PAnnanocomposite electrocatalyst exhibits a better catalytic activity than Pt-Ru/C.and can be used as an effective catalyst for methanol oxidation in fuel cells.

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