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ELECTROCATALITYC APPLICATION OF GOLD–POLYANILINE NANOCOMPOSITE

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ABSTRACT

Gold–polyaniline (Au–PANI) nanocomposite, with granular morphology of PANI and rod–like Au nanoparticles (NPs) as dominate structure distributed in it, was prepared by interfacial polymerization method in an immiscible water/toluene biphasic system. Simultaneously with the aniline polymerization to polyaniline (PANI) by $HAuCl_4$, as an oxidant, AuNPs are formed. Au–PANI composite as green precipitate is collected from aqueous phase. Polyaniline in the composite is in the conductive emeraldine salt form (PANI–ES), with high amount of Au (28.85 wt %). Nanocomposite showed great electrocatalytic activity towards the electrochemical O_2 reduction reaction (ORR), with high ORR onset potential and high selectivity for O_2 reduction to water. This makes it a good candidate for a new class of Pt–free ORR catalyst.

INTRODUCTION

In order to obtain new functional materials, nanocomposites, conductive polymer PANI with excellent optical, electrical and morphological properties, has been combined with metal nanoparticles, such as AuNPs [1-3]. By combining these two components, nanocomposite materials were created, which possess the merits of their organic and inorganic components, and may also exhibit new properties that one component does not have. The interaction between them is important from an applications point of view in various electronic devices with regard to the charge transfer at their regions of contact. In this paper we present Au–PANI nanocomposite prepared by simple method based on the oxidizing properties of $HAuCl_4$, which initiates the polymerization process of aniline, but at the interface of water/toluene biphasic system [1]. This approach is

based on the fact that Au^{3+} ions in water phase can oxidize aniline due to their standard reduction potential (+1.498 V), and simultaneously aniline in toluene phase is used as reductant to prepare AuNPs. The aim of this work was to synthesize Au–PANI nanocomposite with PANI chains in its doped, ES form, with high amount of AuNPs in it, in order to improve its electrical conductivity and develop highly active Pt-free ORR catalyst with appreciable catalytic performance.

EXPERIMENTAL

10 ml of 100 mM aniline in toluene was placed into a round bottom flask containing 10 ml of 50 mM $HAuCl_4$ in water. The system was stirred for 20 h. As the reaction proceeds, the color of the lower water phase changes to deep green, indicating the formation of conductive PANI–ES, while due to formation of aniline oligomers as byproducts, the color of the upper toluene phase turns to orange. In order to collect the green powder of composite, the water phase was first filtered, and then the collected precipitate was rinsed with 5 mM aqueous solution of sulphuric acid and dried under vacuum at 60 °C for 3 h. The content of gold in Au–PANI nanocomposite determined by inductively coupled plasma atomic emission spectrometer was 28.85 wt %. Electrochemical activity of the nanocomposite toward the electrochemical ORR was examined by rotating disk electrode (RDE) voltammetry in O_2 saturated 0.1 M KOH, in a one-compartment three-electrode electrochemical cell with wide Pt foil as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode [see details in ref 1].

RESULTS AND DISCUSSION

Molar ratio of Au^{3+} to aniline plays a significant role in controlling the reaction products. It was found that optimal molar concentration ratio of reactants Au^{3+} and aniline for the formation of conductive nanocomposite with dispersed AuNPs is 1:2, which is indicated by the absorption spectrum of Au-PANI nanocomposite water dispersion, obtained after isolation process (Fig. 1a Inset). Wide band consisting of two superimposed peaks at 350 nm (π–π* electron transition within benzenoid rings) and 440 nm (polaron–π* transition of PANI) and second band at 750 nm (π–polaron transition of PANI) confirm the formation of PANI□ES form [1,3]. It can also be seen that absorption band of AuNPs is not observed (Fig. 1a Inset), similar to our previous report [2], due to AuNPs interaction with PANI chains, through the charge transfer. In the polymerization process, H^+ ions from chloroauric acid first protonates the aniline monomers to radical cations, while $AuCl_4^-$ act as oxidizing agent that oxidize these cations. Each

polymerization step is accompanied by the release of electrons that can reduce the Au^{3+} ions to Au atoms. As the reaction proceeds, PANI forms in its doped, hydrophilic emeraldine salt form, and rapidly move away from the interface diffusing into the water layer. PANI chains in nanocomposite are organized in granular structures (Fig 1a), due to polymerization conditions. Namely, initial reactants concentrations are high, and $HAuCl_4$ is a strong oxidizing agent (high electrode potential) which provides short induction period of reaction and fast polymerization process, causing agglomeration of aniline phenazine segments nuclei to granules. These quasi-spherical formations are found in the range of 64-400 nm. TEM measurements indicated that Au nanorods with 10 nm in diameter are dominated nanostructures in composite (Fig 1b).

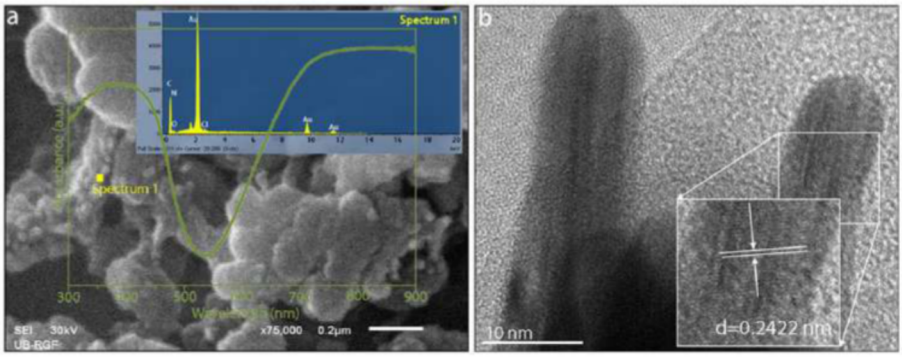

Figure 1. a) SEM image of Au–PANI nanocomposite with EDX and absorption spectrum; b) TEM image of nanocomposite

It was found that electrical conductivity of the nanocomposite (1.19 S/cm) is four–fold higher than that of the PANI itself (0.29 S/cm) [3]. More conductive Au nanorods – conductive nodes, dispersed in less conductive PANI matrix – conductive cables, enables formation of infinitely long conductive pathways and consequently drastically increase the conductivity.

The results of electrocatalytic activity of the Au–PANI, showed that nanocomposite, as electrocatalyst, had much higher ORR onset potential (Fig. 2a) due to fast charge transfer kinetics compared to similar nanocomposite reported so far [2], which contained exceedingly high Au content of 97 wt %. Furthermore, based on K–L analysis (Fig. 2b), evaluated number of electrons consumed per O_2 molecule was found to be 2.25 3.2, which indicated that Au PANI nanocomposite provided high selectivity for O_2 reduction to water (OH^-). This led us to conclude that the presence of PANI in this composite enhances Au surface oxophilicity, facilitating charge transfer kinetics and ORR selectivity to OH^-.

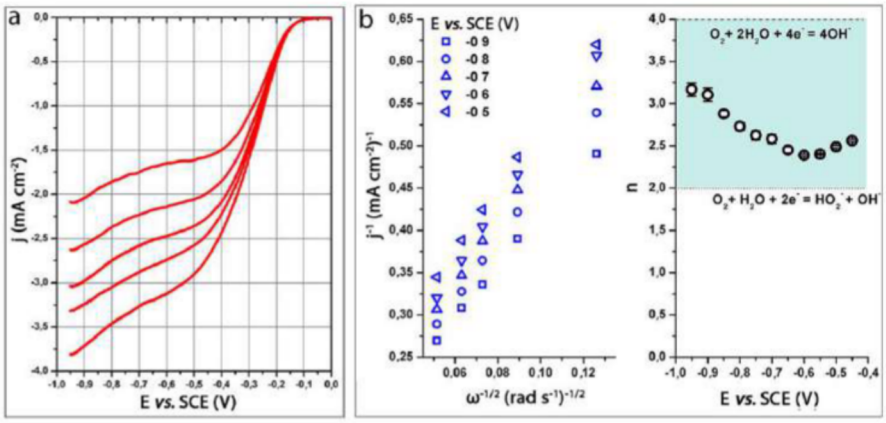

Figure 2. a) ORR RDE polarization curves recorded at different electrode rotation rates (600, 1200, 1800, 2400 and 3600 rpm); b) Koutecky–Levich (K–L) plots (left) and evaluated number of electrons consumed *per* O_2 molecule in the potential range −0.95 to −0.45 V *vs*. SCE (right).

CONCLUSION

A novel nanomaterial presented in this paper, Au–PANI nanocomposite, with granular morphology and incorporated Au nanorods, shows relatively high electrical conductivity due to formation of long "infinite" conductive pathways of PANI chains. Moreover, compared to other Au−based ORR catalysts reported so far, Au−PANI composite provided excellent electrocatalytic activity towards electrochemical O_2 reduction to water (OH^-), which makes it a promising candidate for a new class of Pt–free ORR catalyst.

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