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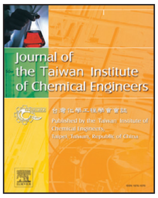

Electrosynthesis of polypyrrole–nanodiamond composite film under ultrasound irradiation: Promotion for methanol electrooxidation by gold and Cu_2O nanostructures

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ABSTRACT

This work presents the preparation of the modified electrode based on polypyrrole which is electrochemically doped by nanodiamond (ND), gold nanoparticles and cuprous oxide and the corresponding electrocatalytic performance for the methanol oxidation reaction was studied. Herein, decorated PPy–nanodiamond composite films on St-12 steel electrodes were electro-synthesized using in situ polymerization process under ultrasonic irradiation. Afterward, the potentiostatic and galvanostatic techniques were used to synthesize the Au nanoparticles and cuprous oxide on the PPy/ND coated electrode, respectively. The results of cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy measurements showed significantly enhanced catalytic performance of the prepared electrode. It was observed that the modified electrodes prepared from PPy(ND) decorated with Au and Cu_2O yielded a slightly higher current and lower onset potential for the oxidation of methanol. Besides, the mechanism based on the electrochemical synthesis of Cu_2O active sites and the effects of nanodiamond along with gold nanoparticles have been discussed.

1. Introduction

In the recent years, the fuel cells especially direct methanol fuel cells, DMFCs, have attracted massive research interest due to their simple structure, high-efficiency, low operating temperature, low cost and high energy density; they can also be used as portable, environmentally friendly devices with liquid fuel [1–6]. Moreover in order to improve the electrocatalytic oxidation of methanol efficiency, great attachment exists in the development of DMFCs, so that to increase the oxidation current density and decrease the over-voltages encountered in its direct oxidation [1,2,7]. The conventional Platinum based catalysts are used as the electrode and have been extensively investigated [8]; but, the major problems with their uses are availability, high costs and deactivation of catalyst properties due to adsorbed carbonyl species [9–11]. Therefore, the composites of platinum with other transition metals or their dispersions in a conducting matrix have been superseded by researchers [12–23]. PtAuCu alloy nanoparticle catalysts for methanol electro-oxidation have been investigated by Wang and co-workers [24]. Their experimental and also density function theory (DFT) theoretical calculation indicates that, the co-function of Pt and Au can alter the major reaction pathway for alcohol oxidation, accelerating the whole alcohol catalytic oxidation reaction. Also, they prepared nanoporous Pd–Au catalyst for methanol electro-oxidation and found that Au enhances the activity and poisoning tolerance of neighboring Pd for MOR [25]. Indeed, the inhomogeneous distribution of zones with bimodal porosities may also be helpful for catalysis applications. Pd-based bi-/ternary catalysts were synthesized with Sn or/and Cu as alloying element by Zhu et al. [26]. The excellent activity of ternary PdCuSn/CNTs may derive from distinct effect by alloying with Cu and Sn. In another different work Li and co-workers [27] found that the introduction of Cu hybrid supporting can greatly improve not only the catalytic activity but also the stability of noble metal catalyst.

On the other hand, nanostructured materials, especially semi conductive transition metal oxides, MO, can be used as suitable replacements for above expensive catalysts [19,28–31]. Among the various semi conductive materials, cuprous oxide, Cu_2O, has attracted intensive attention because of its potential applications in devices such as the photo-electrochemical cells, sensors, catalysts and batteries [32–36]. The uniform dispersion of noble metal nanoparticles through various metal oxide supports has shown specific effects on the improvement of catalytic activity of metal oxides [37,38]. Actually, it was reported that Cu_2O may provide a promotional effect on the electrooxidation of methanol [35,39–41]. Moreover, recent researches have demonstrated that the con-

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ductive polymer films are able to enhance the electrocatalytic behavior of the electrodes [16,42–46].

In the present research, we investigated the electrocatalytic performance of sonoelectrochemically synthesized polypyrrole film modified by noble metal and metal oxide nanoparticles. Accordingly, we selected electrodeposited cuprous oxide (Cu_2O) on PPy film as a base model and compared its performance with same composite modified electrodes containing Au or diamond nanoparticles as extra additives. Therefore, the electro-oxidation of methanol on different modified electrodes namely; PPy/Cu_2O, PPy/Au/Cu_2O, and PPy (ND)/Au/Cu_2O has been investigated. The surface morphology of prepared nanocomposite films was characterized by scanning electron microscope, SEM. Their electrochemical performances were investigated under direct methanol fuel cell conditions, and the highest current density was achieved for PPy (ND)/Au/Cu_2O anodes. We identified that the Au nanoparticles lead to decrease in over voltage value for methanol oxidation. Moreover, ND along with Cu_2O nanostructures represented the synergistic effect and exhibited superior electrocatalytic activity.

2. Experimental

2.1. Materials, apparatus and measurements

Pyrrole monomer (Merck Co.) was purified just prior to use by distillation. The nanodiamond powder with purity of 97.0% and average size of 4.0 nm was supplied from Plasma Chem GmbH Co. Dodecyl benzene sulfonic acid, DBSA, as a surfactant was purchased from Fluka Co. Also, Chloroauric acid, $HAuCl_4\ xH_2O$, (with 48.0% Au, Germany) and $CuSO_4{\cdot}5H_2O$ (Merck Co.) were used during synthesis of Au and Cu_2O nanoparticles respectively. All of the reagents were in analytical grade and used without further purification.

Dr. Hielscher S400UP ultrasound generator with a titanium horn (H2) was used as ultrasound wave source for sonoelectropolymerization. Experiments were conducted under ultrasound irradiation with a constant frequency of 24 kHz using a 150 cm^3 reaction cell.

An Autolab PGSTAT30 Potentiostat/Galvanostat (Netherland Instruments) was employed to the synthesis and electrochemical tests. Cyclic voltammetry, CV, and electrochemical impedance spectroscopy, EIS, tests carried out at 298 K using GPES and FRA softwares, respectively. The EIS results were analyzed by Zview® (II) software and an appropriate equivalent electrochemical circuit was proposed.

2.2. Sonoelectrochemical synthesis of PPy and PPy (ND) films

Based on our recent works [47,48], PPy and PPy (ND) films were deposited sonoelectrochemically by galvanostatic method with current density of 4.0 mA/cm^2 for 600 s; the potential was then measured as a function of time. In all of the synthesis processes, the tip of the ultrasound horn was inserted 1 cm into the electrosynthesis solution. A three-electrode electrochemical cell consisted of saturated calomel electrode, SCE, and Pt plate as reference and counter electrodes, respectively. The working electrodes were prepared from 1 cm × 1 cm sheets of St-12 steel that mounted in a polyester resin. They were polished with SiC papers and were washed with distilled water. The suspensions were composed of 0.1 M pyrrole, 0.1 M oxalic acid, 10^{-4} g/cm^3 DBSA and 5×10^{-5} g/cm^3 ND nanoparticles. Prior to electropolymerization, the NDs were completely dispersed by ultrasound for 1 h. After synthesis, the prepared electrodes were rinsed with distilled water and dried in air.

2.3. Electrochemical deposition of Au and Cu_2O nanoparticles

Electrodeposition of Au nanoparticles on PPy and PPy (ND) coated St-12 steel electrodes was performed using potentiostatic technique. A constant potential of −0.273 V *versus* SCE was applied to the working electrodes for 300 s in an aqueous solution of 3 mM $HAuCl_4$ and 0.1 M KCl as Au ions source and supported electrolyte, respectively. In addition, for synthesis of Cu_2O nanoparticles, a current density of −1.5 mA/cm^2 was applied to the electrodes using the 0.5 M solution of $CuSO_4{\cdot}5H_2O$. A layer of Cu_2O nanoparticles were formed on steel/PPy/Au and steel/PPy (ND)/Au electrodes.

2.4. Physical characterization of electrodes

By using a Bruker, Tensor 27 spectrophotometer in the wave number range of 4000–500 cm^{-1}, the Fourier transform infrared (FT-IR) spectra of PPy (ND) nanocomposite, pure PPy and NDs were recorded. The prepared PPy and PPy (ND) nanocomposite films on St-12 steel were scratched and mixed with KBr to prepare the FT-IR spectra. The surface morphology of nanocomposite coatings was studied using a MIRA3 FEG-SEM, Tescan SEM equipped with an EDX analyzer.

2.5. Electrochemical measurements

Electrocatalytic activity of the prepared PPy and PPy (ND) modified with Au and Cu_2O catalysts for methanol oxidation was estimated by CV, chronoamperometry and EIS techniques. The experiments were conducted in a solution of 0.1 M H_2SO_4 and 0.1 M CH_3OH using a conventional three electrode cell at room temperature. The CV tests were performed in the potential range of −0.5 to 1.2 V *versus* SCE with a scan rate of 0.1 V/s. Chronoamperometry tests were carried out at 0.67 V *versus* SCE for 500 s. The EIS measurements were carried out at open circuit potential, OCP, and also methanol oxidation potential using a ±10 mV amplitude voltage in the frequency range of 10 kHz–10 mHz.

3. Results and discussion

3.1. Characterization

The SEM images of synthesized PPy (ND) revealed that the morphology of the nanocomposite is quite different from the pure PPy (Fig. 1a and b).

It is obvious that the incorporation of ND nanoparticles changes the microstructure of films, so that the PPy (ND) film has finer structure. The PPy formation can be initiated around the nanoparticles, as nucleation centers, leading to higher surface area and finer structure. Fig. 2 shows the FT-IR spectra for the ND, PPy and PPy (ND) nanocomposite. The FT-IR spectrum for ND shows bands at 3427, 2906, 1612 and 1105 cm^{-1}, which indicates the typical characteristics of ND consistent with literature [49].

The peaks at 1552–1465 and 1034 cm^{-1} correspond to the stretching vibration of C=C, C–N and C–H bonds of PPy, respectively [50,51]. One can also see intense absorption peaks around ∼2925 and ∼1612 cm^{-1}, which confirm the supposed intercalation of NDs in PPy matrix [48]. The SEM images of the Cu_2O particles electrodeposited on PPy/Au and PPy (ND)/Au films are shown in Fig. 3(a) and (b) respectively. The micrographs show that the amount of deposited Cu_2O on Au/PPy (ND) nanocomposite is more than PPy/Au films. It is well known that the nucleation and growth of catalysts can be affected by nanodiamond [52].

Subsequently, it is clear from high magnification images in the presence of ND and Au nanoparticles, different crystallographic orientations of Cu_2O structures are formed. While in the absence of ND, the growth of the Cu_2O crystals on PPy/Au film were unripe

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