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Carbon ceramic nanoparticulate film electrode prepared from oppositely charged particles by layer by layer approach

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Abstract

Carbon ceramic nanoparticulate film electrode was prepared of negatively charged sulfonated carbon nanoparticles and positively charged silicate submicrometre particles with appended imidazolium groups. They were immobilised on indium tin oxide surface by layer by layer method: alternative immersion into suspension of positive and negative particles. Film formation is confirmed by scanning electron microscopy – after larger number of immersion and withdrawal steps more material is deposited on the electrode substrate. The nanoparticulate film is stable and the obtained electrode exhibits significant increase of capacitive current and faradaic current corresponding to hydrogen peroxide electroreduction. The effect of the number of immersion and withdrawal steps is strikingly visible on dioxygen bioelectrocatalytic reduction current after adsorption of enzyme: laccase.

Keywords:

Carbon ceramic electrode; Layer by layer; Carbon nanoparticles; Silicate particles; laccase.

1. Introduction

Carbon ceramic electrodes (CCE) were developed in 1992 and become popular electrode support [1,2]. The typical design is based on carbon microparticles encapsulated in sol-gel processed silicate. Typically they are prepared in a form of bulk electrodes: the electrode material is embedded into the glass tube. However, for most applications film electrodes are preferred, because of many reasons like decrease of the volume of electrode material or development of interfacial area. Although successful preparation of film CCE by the same procedure was already mentioned in original paper [1] and their application to lithium batteries was proposed [3,4] they never become popular. This indicates difficulty in preparation process experienced also in our attempts to prepare such electrode using graphite microparticles. More recently the successful preparation sol-gel processed silicate film with encapsulated smaller

carbon based conductive objects like carbon nanotubes [5,6], carbon nanofibers [7] or carbon nanoparticles [8] was proposed.

Here we would like to propose different approach to preparation of CCE film. It is based on the layer-by-layer (LbL) approach [9,10] employing particles of opposite charges.

LbL is a powerful technique for fabricating multilayer nanoparticulate films of controlled architecture and composition [11]. The most conventional LbL approach for film electrode preparation is based on electrostatic interactions between the polyelectrolyte and conductive charged nanoparticles and such approach was combined recently with sol-gel process [12].

However, few attempts of LbL film preparation from nanoparticles of opposite charges were reported [13-19]. Moreover, only recently such procedure involving conducting nanoparticles was applied for film electrode preparation [19].

Here silicate submicroparticles with covalently attached cationic groups and carbon nanoparticles (CNP) with appended sulfonate groups are used as components of the film. The first component was obtained from ionic liquid precursor. These particles adsorb on indium tin oxide (ITO) electrode from methanol and act as sponge for redox active anions in aqueous solution [20]. CNPs were earlier used for LbL film electrode preparation with the use of cationic polymer as a linker [12,21-23].

2. Experimental

2.1. Chemicals and materials

Tetramethoxysilane (TMOS) (99%) and cetyltrimethylammonium bromide (99%) K_2HPO_4 , KH_2PO_4 and citric acid were from Sigma-Aldrich. Methanol, ethanol, $NH_3(aq)$, HCl were from Chempur. Formic acid, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ were from POCh. $NaClO_4$ was from Fluka. Laccase was obtained from the *Cerrena unicolor* fungus and purified as earlier described [12].

Ionic liquid precursor 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium bis(trifluoromethyl sulfonyl)imide was synthesized as described earlier [24]. It was used together with TMOS for cationic silicate submicrometre particles preparation [20]. Their suspension was prepared by mixing 5 mg of particles with 1 ml of methanol and the mixture was sonicated for 30 min. Carbon nanoparticles with phenylsulfonic acid surface functionalities (ca. 7.8 nm mean diameter, with a typical bulk density of 320 g dm^{-3} , Emperor 2000) were obtained from Cabot Corporation (Dukinfield, United Kingdom). Their suspension was obtained by mixing 5 mg of particles with 1 ml of water and the mixture was sonicated for 30 min.

ITO coated glass (resistivity $15\text{-}30 \text{ }\Omega\text{-cm}^{-1}$) was obtained from Image Optics Components Ltd., Basildon, Essex, UK. Water was filtered and demineralized with an ELIX system (Millipore).

2.3. Film electrode modification

ITO substrates were cleaned subsequently with ethanol and deionized water. Then they were heated for 30 min. in tube furnace (Barnstead International) at $500 \text{ }^\circ\text{C}$ in air to remove any remaining contamination. They were immersed for 2 s in suspension of cationic and anionic particles subsequently. Each immersion step was followed by electrode immersion into the clean water to remove weakly immobilized particles. This procedure was repeated desirable number of times. Enzyme adsorption was performed by immersion of nanoparticulate film electrode into 0.7 mg cm^{-3} laccase solution in 0.1 mol dm^{-3} McIlvaine buffer (pH 4.8) buffer solution for 2 hours in ca. $5 \text{ }^\circ\text{C}$.

The electrode surface (0.2 cm²) was defined by masking the electrode with the scotch tape. Electric contact was assured by a piece of copper tape.

2.4. Instrumentation and cell

Scanning electron microscopy was done with a Leo 1530 Field Emission microscope. Cyclic voltammetry was performed with an Autolab (Eco Chemie) electrochemical system in a conventional three electrode cell with dedicated software. Modified ITO, platinum wire (d = 0.5 mm) and Ag|AgCl|KCl_{sat.} were used as the working, counter and reference electrode respectively. All experiments were carried out at 22 ± 2 C.

3. Results and discussion

3.1. Electrode characterization

SEM image of the hybrid particles modified ITO surface (Fig. 1) reveals that after single immersion and withdrawal step electrode is only partially covered by the deposit. However the repeated procedure leads to complete coverage and three dimensional structure is build. The closes inspection reveals the presence of some features on the surface of submicroparticles and their agglomerates. These features are not visible in the absence of CNPs [20] and can be ascribed to CNPs and their small aggregates. This may indicate coverage of positively charged submicroparticles by negatively charged CNPs.

3.2. Electrochemical experiments

The voltammetric experiments reveal that capacitive current is proportional to the number of immersion and withdrawal steps. This indicates increase of the electrochemically active surface and good contact with the ITO electrode substrate. Probably percolation paths are formed by CNPs covering cationic silicate submicroparticles (see above). The voltammetric peak currents obtained in milimolar solution of K₃[Fe(CN)₆] are almost not affected by extension of nanoparticulate film. This is because fast electrode reaction occurs only at outmost plane of the film [12,25-28]. However voltammetry performed in micromolar solution of the same redox species shows some increase of the faradaic current in comparison to bare ITO. This results from minor accumulation of Fe(CN)₆³⁻ anions on cationic submicrometre particles [20], because not all cationic functional groups participate in electrostatic attraction of CNPs.

In order to observe the effect of increase of the amount of nanoparticulate material on film surface on electrode reaction the experiments with slow electrode reaction [12,25-28], namely H₂O₂ electroreduction were done. Although minor increase of the current is observed for one immersion and withdrawal step the application of six steps results in c.a. 10 times increase of the current (Fig. 2). Further deposition of nanoparticulate material (12, 18 and 24 steps) results in 10 – 20% decrease of the current as compared to 6 steps electrode and may be ascribed to depletion of the substrate within more dense porous film.

The most striking effect of the number of immersion and withdrawal steps is observed for bioelectrocatalytic reaction. After laccase adsorption the electrode was transferred to dioxygen saturated 0.1 mol dm⁻³ McIlvaine buffer (pH 4.8) buffer solution. The voltammetry reveals sigmoidal curve characteristic for electrocatalysis of dioxygen reduction (Fig. 3). Such mediatorless process is provided by laccase adsorbed on carbon nanoparticulate film [29,30]. This signal is absent where electrode was not modified by laccase or in nitrogen saturated solution. Moreover the magnitude of plateau current is proportional to the number of immersion and withdrawal steps up to 36 steps. Further electrode modification results in fragile film peeling off the surface. Interestingly no such activity is observed for layer by

layer electrode obtained by sol-gel processing of the same mixture of precursors together with the same enzyme and CNPs [12]. This indicates that proposed approach provide more favorable conditions for the laccase adsorbed on CNPs than imidazolium appended polymer. It has to be mentioned that LbL approach with polymer as a linker technique for mediatorless dioxygen bioelectrocatalysis with laccase or bilirubin oxidase was already reported [31,32], but no clear relationship between number of layers and bioelectrocatalytic current was shown.

4. Conclusions

The simple procedure based on layer by layer approach was proposed to obtain stable carbon nanoparticulate film. It allows for the preparation of carbon ceramic film without solgel process involved in deposition procedure. The stability of the obtained films results entirely from the electrostatic interactions and no new covalent bonds are formed. The film architecture can be controlled by the number of immersion and withdrawal steps to suspension of particles of opposite charges, what in turn affect efficiency of slow electrode reaction or mediatorless bioelectrocatalysis with adsorbed enzyme. The proposed procedure can be easily extended on different types of silicate particles and conductive nanoobjects.

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Caption to Figures

Fig. 1

SEM image of ITO electrode coated by one (A) and three (B) immersion and withdrawal steps to cationic silicate particles and carbon nanoparticles suspension alternatively.

Fig. 2

Cyclic voltammograms obtained in 0.05 mol dm⁻³ H₂O₂ solution in 0.1 mol dm⁻³ H₂SO₄ aq. at a bare ITO electrode (i) or an electrode coated by one (ii) and six (iii) immersion and withdrawal steps to cationic silicate particles and carbon nanoparticles suspension alternatively. Geometric surface area 0.2 cm², scan rate 0.01 V s⁻¹.

Fig. 3.

Cyclic voltammograms obtained in dioxygen saturated 0.1 mol dm⁻³ McIlvaine buffer (pH 4.8) at ITO electrode coated by one (i), twelve (iii), twenty four (iii) and (iv) thirty six immersion and withdrawal steps to cationic silicate particles and carbon nanoparticles suspension alternatively followed by laccase adsorption. Geometric surface area 0.2 cm², scan rate 0.001 V s⁻¹.

Fig. 1.

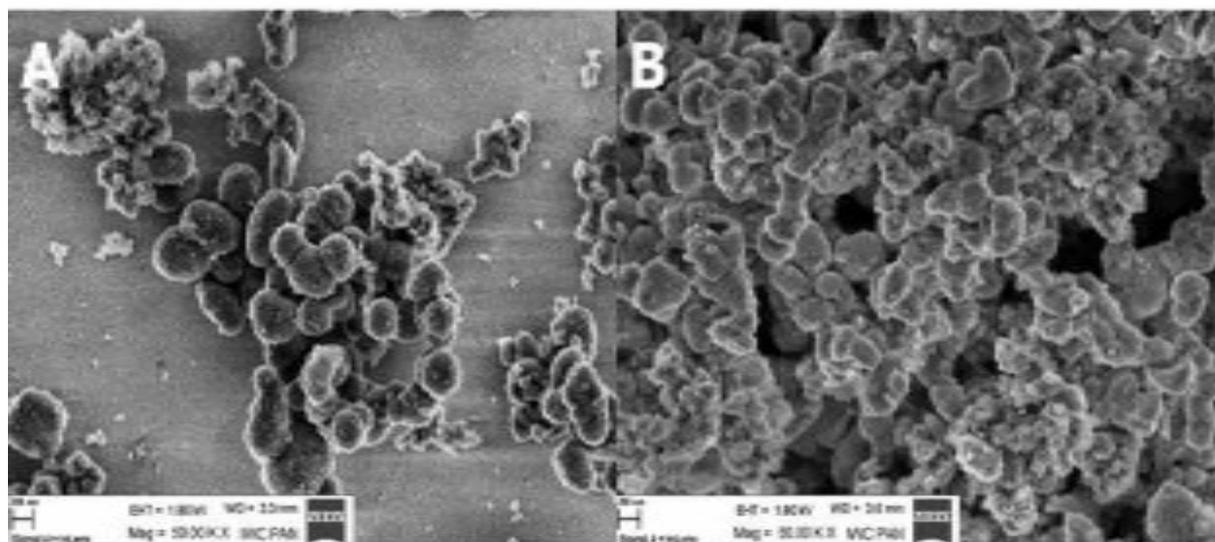


Fig. 2.

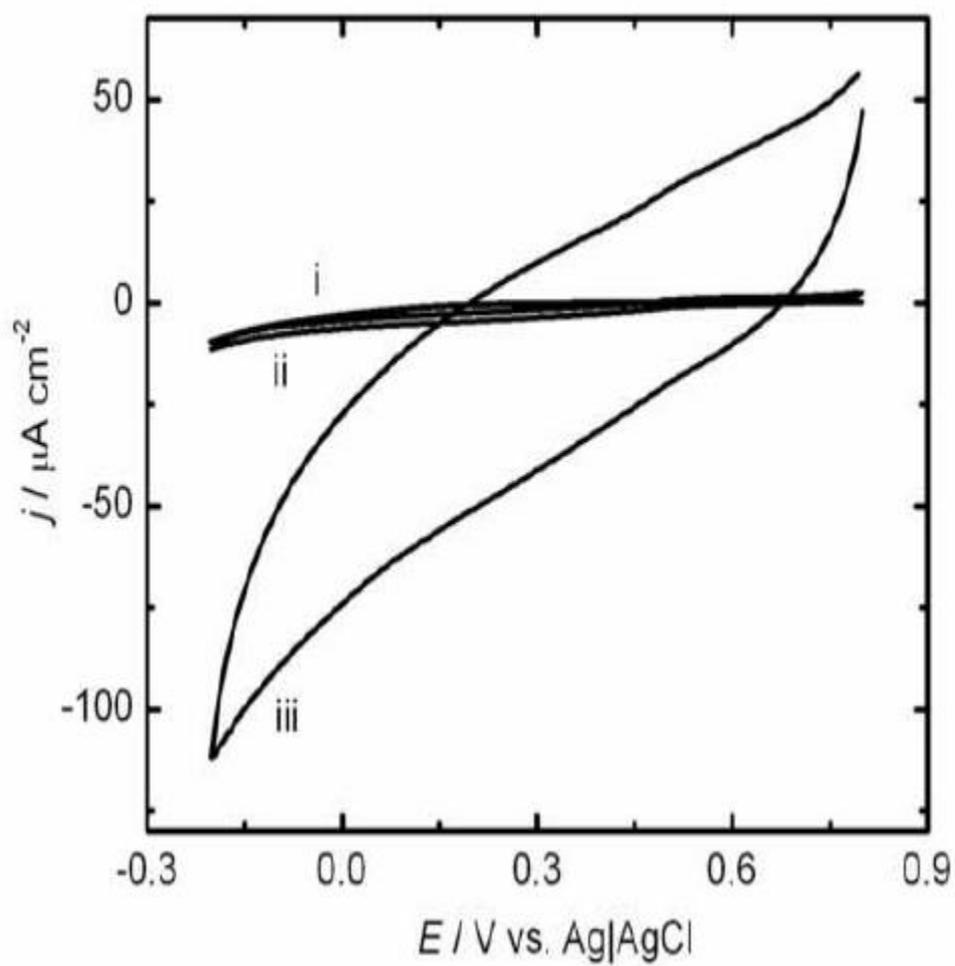


Fig. 3.

