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Modification of glassy carbon electrode with iron-terpyridine complex and iron-terpyridine complex covalently bonded to ordered mesoporous carbon substrate: Preparation, electrochemistry and application to H_2O_2 determination

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ABSTRACT

In this paper, simple strategies for the modification of glassy carbon electrode (GCE) with iron-4″(phenyl)-2, 2″:6″, 2"-terpyridine complex (Fe-PTPY) and Fe-PTPY covalently bonded to ordered mesoporous carbon (OMC) are described. The Fe-PTPY/OMC modified GCE (Fe-PTPY/OMC/GCE) was prepared in a three steps strategy. In the first step, OMC modified GCE was prepared by simple casting. Then, PTPY ligand was attached directly to the electrode surface through electrochemical reduction of 4'(4aminophenyl)-2, 2':6', 2"-terpyridine (APTPY) diazonium salt. The modification was completed by iron attachment to the electrode surface through complex formation reaction with surface PTPY groups. The Fe-PTPY modified GCE (Fe-PTPY/GCE) was prepared in similar manner by omitting the first step of the above strategy. The reactions progress and the electrochemical behavior of the modified electrodes were studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The modified electrodes showed good electrocatalytic activity for reduction of H_2O_2. Using hydrodynamic amperometry, under optimum conditions, calibration plots for H_2O_2 were linear in the ranges of 0.15–0.4 and 0.4–5.0 mM with slopes of 0.2743 and 0.2112 μA/mM on Fe-PTPY/GCE and 0.01–0.1 and 0.1–13.0 mM with slopes of 4.91 and 0.91 μA/mM on Fe-PTPY/OMC/GCE, respectively.

Introduction

In recent years, considerable attention has been focused on surface modification by forming highly ordered films of few nanometers to several hundred nanometers thickness [1–5]. In particular, those incorporating metallic complexes such as metal-terpyridine complexes offering multiple redox or spin states have attracted much attention due to their excellent properties such as electronic [6], photochemical [7–9], electrochemical [9–11] and magnetic characteristics [12,13]. These properties have led to many applications of these compounds in sensors [14–17], solar cells [18–21], energy storage [22,23] and molecular electronics [24,25].

Various techniques including electropolymerization [26], adsorption [27], supporting on the carbon nanotubes [28] and self-assembling method [29,30] were used for the preparation of metal complex-modified surfaces. However, development of new simple and reliable procedures for the preparation of robust and stable metal complex-modified surfaces is still desirable. Chemical or electrochemical reduction of aryldiazonium salts leads to the strong covalent bonding between the substrate and the aryl functional groups. This immobilization method can be used for the modification of both conductive and nonconductive substrates [31,32]. There are some papers in which the electrochemical reduction of diazonium salts is used for the covalent modification of the electrode surface by metal complexes [33–38].

Nanomaterials have been shown to exhibit excellent characteristics in many electrochemical devices, especially in energy storage and conversion devices such as lithium ion batteries, solar cells, supercapacitors [39–42] and biosensors [43–45]. Among the various nanomaterials, ordered mesoporous carbons (OMCs) offer numerous remarkable properties such as high specific surface area, ordered mesostructure, high conductivity, chemical stability and tunable surface chemistry [45] that allows the development of a range of strategies for the introduction of functional groups, and consequently, for the anchoring of metal and metal complexes.

In this article a new method is proposed for preparation and characterization of transition metal based structures by applying 4″(phenyl)-2, 2″:6″, 2″-terpyridine (PTPY) (Fig. 1) in order to modify glassy carbon electrode (GCE) and OMC/GCE. The comparison of the findings in this new method indicate that presence of OMC at GCE improves the

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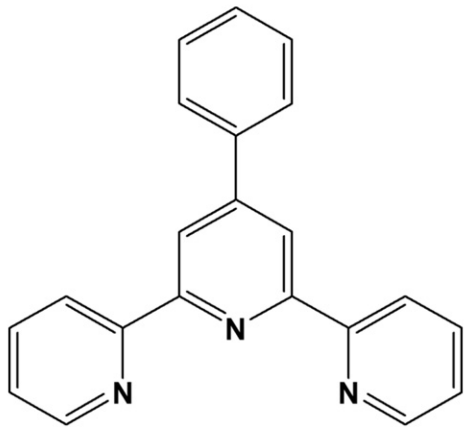


Fig. 1. 4″(phenyl)-2, 2″:6″, 2″-terpyridine (PTPY).

analytical performance of nanostructure. Furthermore, data for interfacial structures prepared by sequential reactions such as depicted in Scheme 1 have been presented.

Experimental

Apparatus.

All electrochemical measurements were carried out in a three-electrode cell including GCE or GCEs modified with PTPY or (Fe-PTPY) complex as working electrodes, together with an Ag/AgCl (saturated KCl) as reference electrode and a platinum wire as counter electrode. A computer-controlled potentiostat, Autolab electrochemical analyzer model PGSTAT30 (EcoChemie, Utrecht, The Netherlands) was used for these measurements. For amperometric measurements a magnetic stirrer and a stirring bar provided the convective environment. A Bruker D8-Advance powder diffractometer using Cu-K_α radiation (λ = 1.54056 Å) was used for recording the XRD pattern of the synthesized OMC. The morphologies of the synthesized OMC were characterized by a Philips CM120 transmission electron microscope (TEM) instrument operating at 120 kV.

A Nicolet Impact 410 FT-IR spectrophotometer was used for recording the FT-IR spectrums. The UV–Visible absorption spectrum were recorded using a Carry 2501-pc spectrophotometer. pH measurements were done with a Metrohm 827 pH meter. Scanning electron microscopy (SEM, MIRA3 TESCAN) was employed to observe the surface morphology of various modified electrodes.

Materials and reagents.

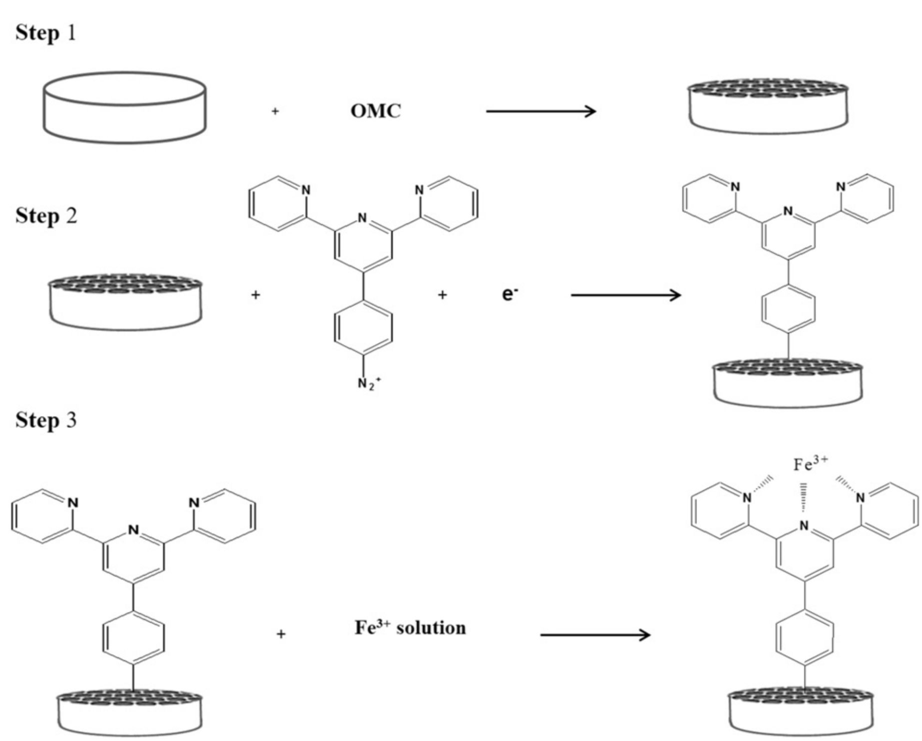
Hydrochloric acid, sulfuric acid, sodium hydroxide, tetraethyl orthosilicate (TEOS), sucrose, non-ionic triblock copolymer poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) surfactant (pluronic P123, MW = 5800), iron(III) chloride hexahydrate salt ($FeCl_3.6H_2O$), tin(II) chloride dihydrate, acetonitrile, tetrabutylammonium tetrafluoroborate (TBATFB), acetyl pyridine, 4-nitrobenzaldehyde, styrene and other chemicals were of analytical grade from Merck, Fluka, and Aldrich and used without further purification. The phosphate buffer solutions (PBSs) were prepared from 0.02 M Na_2HPO_4/NaH_2PO_4 in 0.1 M KCl. The pHs were adjusted using 0.1 M H_3PO_4 or 0.1 M NaOH solutions. Deoxygenating of solutions were carried out by bubbling high purity N_2 prior to electrochemical experiments.

The OMC [46,47] and 4″(4aminophenyl)-2, 2″:6″, 2″-terpyridine (APTPY) [48] have been synthesized and characterized according to the procedures already used in our laboratories. The details of these procedures are presented in the supporting information.

Modification of GCE surface.

Prior to electrode modification, the electrode surface was polished successively in 1.0, 0.3 and 0.05 μm alumina slurries on micro cloth pads. After polishing, the electrode was thoroughly rinsed with water and sonicated in ethanol and distilled water, successively.

The PTPY/OMC/GCE was prepared according to the following methodology. In the first step, 2 μl of a mixture containing 5 mg OMC in 1 mL *N*, *N*′-dimethyl formamide was transferred onto the GCE surface, and the solvent was evaporated under an infrared lamp. Then, PTPY was electrochemically grafted on the OMC/GCE using the previously methodology for the in situ generation of aryldiazonium salts and their



Scheme 1. Illustration of different steps in preparation of iron(III)-modified GCE.