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New ferromagnetic mesh electrode material for electroanalytical applications

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ABSTRACT

A new, advanced, ferromagnetic carbon material (Fe@C NPs–GC 3D porous mesh) has been developed. The application of this electrode material has led to an increase in the voltammetric current density of paramagnetic species, such as $FcTMA^+$, $Fc\text{-}FcTMA^+$, on the application of a 140 mT magnetic field, compared with a glassy carbon electrode modified with a layer of Fe@C NPs alone. The functionality of the developed material was tested with two biologically important paramagnetic species: hemoglobin and dioxygen.

1. Introduction

Carbon materials are widely used in analytical, biological, medical, industrial and electrochemical applications [1,2,3]. Recently, in addition to graphite and glassy carbon, several other forms of carbon (e.g. boron-doped diamond, fullerenes, nanotubes and graphene) have been employed [4–6]. All these forms of carbon differ in their electrochemical performance [7,8].

The appropriate orientation of molecules that reach or become attached to the electrode surface is a condition sine qua non for getting well-defined current signals. This effect is especially important in the case of biologically important compounds such as nucleic acids and electroactive proteins. To attach an analyte in its desired orientation on the surface of a carbon electrode, the surface should first be appropriately modified to ensure stable anchoring. A set of typical carbon-surface modifiers includes: polyaromatic hydrocarbons [9], phenyl layers formed by electroreduction of diazonium salts [10,11], layers of aliphatic amines obtained by electrochemical oxidation [12,13], and layers formed by "click" cycloaddition chemistry via azide groups [14]. It should be stressed here that modification of the layer should not affect electron transfer between the electrode surface and the analytes. Additionally, the modifying layer should be thin (ideally a monolayer), tight, and uniform. Efficient electron transfer between the electroactive analyte and the electrode surface requires the presence of a dense mesh of electrical connections in the modifying layer. Carbon nanoparticles with a magnetic core (such as carbon-encapsulated iron nanoparticles) are conductive nanomaterials that satisfy the above requirements. They have been successfully used in the construction of biosensors, biomolecular electronic devices, and biofuel cells [15,16]. The combination of magnetic nanoparticles (e.g. iron encapsulated in carbon or iron oxide) and the presence of an external magnetic field may compel an electroactive paramagnetic molecule to adopt an appropriate spatial position with respect to the electrode surface [17,18]. This leads to more effective exchange of electrons between the electroactive molecule and the electrode surface through the layer of magnetic nanoparticles. The presence of a magnetic field may also affect the rate of electrochemical reactions due to the magnetohydrodynamic effect [19].

Generally, physical adsorption is used to graft the electrode surface with magnetic nanoparticles [17]. However, magnetic nanoparticles tend to aggregate together and this hampers the formation of a thin, stable and homogenous layer [20]. Furthermore, layers formed by physical adsorption can easily be destroyed mechanically, and the position of magnetic nanoparticles can easily change in the presence of a magnetic field. These problems would be avoided if the magnetic nanoparticles were tightly embedded in the electrode material.

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In this paper we present a new, advanced carbon electrode material: a composite of carbon-encapsulated magnetic nanoparticles (NPs) with a glassy carbon (GC) 3D porous mesh matrix. The resulting electrodes were characterized by cyclic voltammetry (CV) using various types of electroactive species. The morphology of the electrode surface was examined using scanning electron microscopy (SEM).

2. Materials and methods

2.1. Chemicals

All chemicals were of the highest purity available. Ferrocenylmethyltrimethyl-ammonium iodide ($FcTMA^+$) and (diferrocenyl)methyltrimethylammonium iodide ($Fc\text{-}FcTMA^+$) were synthesized according to the procedure described in the literature [21, 22]. Human hemoglobin (Hb) was purchased from Sigma-Aldrich. All solutions used for measurements were prepared from ultrapure water (Hydrolab, conductivity of ca. 0.060 $\mu S \cdot cm^{-1}$). Carbon-encapsulated iron nanoparticles (Fe@C NPs) were synthesized according to the procedure described elsewhere [23]. The diameter of the carbon-encapsulated iron nanoparticles ranged from 5 to 65 nm; however, ca. 70% of the nanoparticles had a diameter in the range 5–30 nm. Carbon-encapsulated iron nanoparticles have ferromagnetic properties with a saturation magnetization (298 K) of 70 emu/g.

2.2. Electrochemical measurements

Cyclic voltammetry was performed using an Autolab PGSTAT 12 potentiostat. The measurements were carried out with a three-electrode system. A glassy carbon (GC) disc electrode (A_{geom} = 0.0706 cm^2, BAS, UK) and a Fe@C NPs–glassy carbon 3D porous mesh (homemade electrode, A_{real} = 1.15 cm^2) served as the working electrodes. An Ag/AgCl/3 M KCl electrode and a platinum plate (of 1 cm^2 area) were used as the reference and auxiliary electrodes, respectively. The real surface area of the Fe@C NPs–glassy carbon 3D porous mesh electrode was determined voltammetrically using 0.5 mM $Fe(CN)_6^{3-/4-}$ solution in aqueous 1 M KCl. The contribution of spherical transport to the electrode surface was smaller than 3.4%. The magnetic field (140 mT) was applied to the working electrode using a $Fe_{14}Nd_2B$ ring permanent magnet. The position of the magnet relative to the electrochemical cell was the same in all tests.

2.3. SEM measurements

The images obtained by scanning electron microscopy (Merlin, Zeiss, Germany) were used to elucidate the morphology of the Fe@C NPs–glassy carbon 3D porous mesh electrode. The SEM images were obtained with a relatively low EHT (10 kV) using a secondary electron detector.

3. Results and discussion

3.1. Preparation of Fe@C NPs–glassy carbon 3D porous mesh electrode

A two-step process (illustrated in Fig. 1) was used to obtain the Fe@C NPs–GC 3D mesh electrode. In the first step, the starting polyurethane foam (ca. 280 mg, 40 × 35 × 6 mm in size, containing 10 pores per inch) was impregnated with a suspension containing Fe@C NPs and phenol formaldehyde resin (the Novolac type with 2 wt% addition of a hardener, urotropine) in ethanol. The mass ratio of the ingredients (ethanol:resin:Fe@C NPs) was 25:50:1. After the impregnation stage, the mass doubled. In the second step, the impregnated foam was placed in a tubular furnace of volume 350 cm^3. The foam was carbonized under argon. The carbonization process consisted of three steps with different heating rates. The first step involved annealing up to 400 °C at a heating rate of 0.1 $°C \cdot min^{-1}$, whilst the second one involved annealing up to 1000 °C at a heating rate of 1 $°C \cdot min^{-1}$. Finally, the sample was isothermally heated at 1000 °C for 60 min. The whole process took 75 h. The mass of the carbonized foam was ca. 260 mg. Finally, the mesh electrode was annealed under air at 300 °C for 1 h in order to remove possible surface organic contaminants.

The morphology of the prepared Fe@C NPs–glassy carbon 3D porous mesh electrode was analyzed both optically and using electron microscopy. Fig. 1A shows a representative image of the electrode. The pores are clearly visible and their mean size is between 2 and 3 mm. Fig. 1B–E present the electrode surface and its cross-section. The images reveal that the external part of the electrode is glassy and continuous and its thickness is ca. 5 μm. The internal part is less compact and exhibits some porosity. The distribution of Fe nanoparticles in the material was determined using EDS (see Fig. 1F). It is evident that the distribution is homogeneous and no substantial aggregation was observed except in rare individual cases. It can be concluded that the Fe@C nanoparticles are primarily present in the porous bulk of the electrode.

The hysteresis loop of the Fe@C NPs–glassy carbon 3D porous mesh electrode is shown in Fig. 1G. The electrode material is ferromagnetic

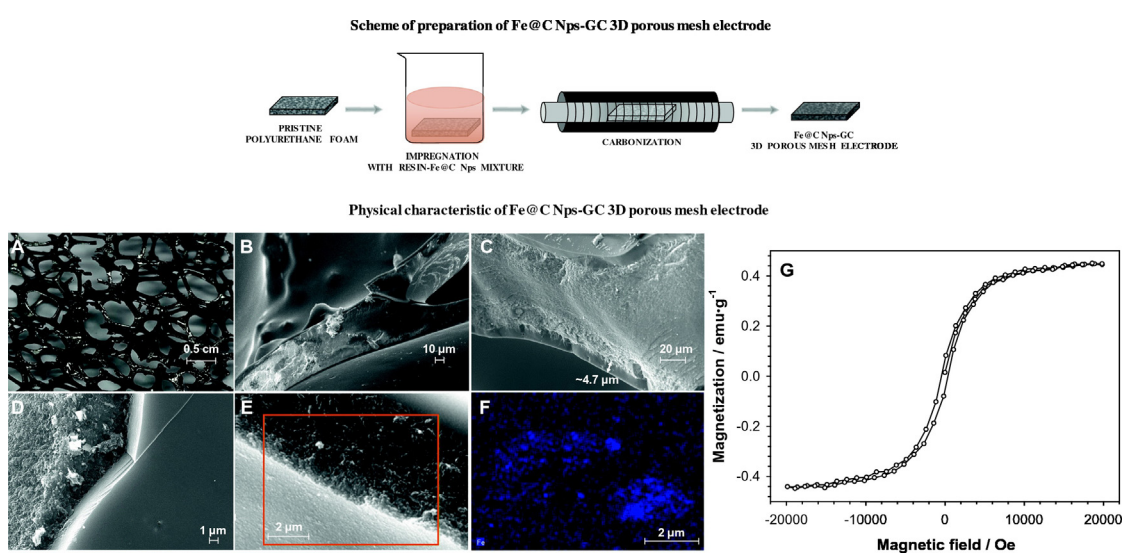

Fig. 1. Scheme of preparation of Fe@C NPs–glassy carbon 3D porous mesh electrode and its visual image (A), SEM images (B, C, D and E), EDS map of distribution of Fe (F) and magnetic hysteresis loop (measured at 25 °C) for Fe@C NPs–GC 3D porous mesh.