Synthesis and characterization of Si-coated superparamagnetic nanoparticles for bioelectrochemical applications

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In this study, silica coated iron oxide nanoparticles were loaded on carbon felt by means of two different techniques - impregnation of carbon felt samples in suspension of silica coated Fe_3O_4 nanoparticles (Method 1) and attachment of silica coated Fe_3O_4 nanoparticles to carbon felts samples with covalent bonding through amine functional groups (Method 2). The surface morphology of the newly prepared nanomodified carbon materials was studied by scanning electron microscopy (SEM). The Si-coating efficiency was monitored by High-resolution transmission electron microscopy (HR-TEM) in combination with X-ray EDS Microanalysis. The performed physicochemical characterization analysis showed that Method 2 is superior for the deposition of the magnetite nanoparticles than Method 1. Based on this, the electrochemical performance of the samples prepared by Method 2 in neutral phosphate buffer solution was investigated in respect to their potential application as electrodes in microbial fuel cells (MFCs) and/or microbial electrolysis cells (MECs).

Key words: silica coated iron oxide nanoparticles; nanomodified carbon felt; modified electrode materials; microbial fuel cells; microbial electrolysis cells.

INTRODUCTION

Bioelectrochemical systems (BESs) based on utilization of whole microorganisms as biocatalysts such as Microbial Fuel Cells (MFCs) and Microbial Electrolysis Cells (MECs) are intensively studied during the last decade as promising technologies for simultaneous wastewater purification and electricity generation or bio-hydrogen production [1-6]. Mimicking the ability of some microorganisms, known as exoelectrogens, to use an exogenous final electron acceptor, both technologies are based on an extracellular electron transfer from the living cells to a solid conductor serving as a BES anode. The most studied are the so-called "metal respiring" bacteria from *Geobacter* and *Shewanella* families, which naturally use iron or manganese (hydr)oxides as final electron acceptors for their respiration processes [7].

Carbon-based materials such as graphite, carbon cloth, carbon felt, etc., are most commonly used as electrodes in BESs due to their biocompatibility, good conductivity, corrosion stability and low price.

In previous studies [8, 9], it has been found that modified with nickel and iron carbon felt materials used as anodes improve significantly the electric outputs of mediatorless yeast-biofuel cell. In another study [10], it has been demonstrated that the same materials possess high corrosion resistance and electrocatalytic activity towards hydrogen evolution reaction (HER) in neutral and weak acidic solutions, which makes them proper cathodes for MECs in respect to bio-hydrogen production.

The aim of this study was to develop methods for loading silica coated iron oxide nanoparicles on carbon felt and examine the electrochemical performance of the prepared nanomodified materials in neutral electrolyte in respect to their potential applications as electrodes in MFCs and/or MECs.

MATERIALS AND METHODS

Materials

Chemicals used in experiments were of analytical grade and used without any further purification. Ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous

chloride ($FeCl_2·4H_2O$), sodium hydroxide (NaOH), ammonia (NH_4OH), tetraethylorthosilicate (TEOS) and ethanol were purchased from Merck. Aminosilane coupling agent 3-aminopropyl-triethoxysilane (APTES) was obtained from Sigma Aldrich. In this study, only deionized water (18 MΩ) was used. Carbon felt (SPC-7011, 30 g/m^2) was purchased from Weißgerber GmbH & Co. KG.

Preparation and silica coating of the magnetic nanoparticles

Magnetic nanoparticles (NP's) of Fe_3O_4 were synthesized by a conventional chemical co-precipitation method [13-14]. Aqueous solutions of Fe^{2+} and Fe^{3+} chlorides in a molar ratio of Fe^{2+}/Fe^{3+} = 0.5 were precipitated by NaOH, under N_2 flow in order to prevent oxidation. The precipitate was aged for 10min and ultrasonicated for another 10min. The resulting magnetic nanoparticles underwent washing with water.

In order to coat the surface of the nanoparticles with thin silica (SiO_2) layer, 40mg of the synthesized Fe_3O_4 nanoparticles were dispersed in a solution of ethanol/water (4:1) and the pH of the solution was adjusted to 9 by addition of NH_4OH. Finally the Si-source, TetraEthylOrthoSilicate (TEOS) was added dropwise and the solution was stirred mechanically for 10 hrs [15-16]. The precipitate was washed several times with water. Subsequently, water was added to redisperse ultrafine magnetic particles. The obtained magnetite dispersion will be called in the next paragraphs magnetic fluid (MF).

Two types of NP's were prepared, with different TEOS concentration, which resulted in different silica layer thickness (S0.008 has thinner silica layer than S0.016).

Loading of silica coated Fe₃O₄ nanoparticles to carbon felt samples

Circular pieces of carbon felt with diameter 1cm are used. Prior to the deposition of the nanoparticles the carbon felt samples are rinsed with ethanol, unless otherwise mentioned. Two different methods were used for attaching the magnetic nanoparticles, either by simple physical adherence or through the formation of covalent bonds.

Impregnation of carbon felt samples in suspension of silica coated Fe_3O_4 nanoparticles (Method No1): The magnetic fluid is ultrasonicated for 15 minutes in order to achieve the best dispersion of the NP's and to become homogeneous. Then a piece of carbon felt is added in the dispersion and stirred at room temperature for 2 hrs. The carbon felt is removed, washed with water and dried at room temperature.

Attachment of silica coated Fe_3O_4 nanoparticles to carbon felts samples with covalent bonding through amine functional groups (Method No2): 3-aminopropyl triethoxysilane (APTES), as a source of amine groups, is added to the suspension of silica coated iron oxide nanoparticles. After stirring for 2 min, a circular piece of carbon felt with diameter 1cm, previously washed with ethanol (unless mentioned otherwise), is inserted in the solution and stirred for 5 hrs. In the end the carbon felt specimen is removed, washed with water, ultrasonicated in water for 30 min and dried at room temperature.

Physicochemical Characterization

The crystalline phases present in the prepared nanoparticles are identified by X-ray diffraction (XRD). Powder XRD patterns are recorded with a Siemens D 500 X-ray diffractometer, with an autodivergent slit and graphite monochromator using CuKa radiation, with a scanning speed of 2°min^{-1}. The characteristic reflection peaks (d-values) are matched with JCPDS data files and the crystalline phases are identified.

Scanning electron microscopy (SEM) is used for inspecting the morphology of the prepared samples. The instrument used is a JEOL JSM 6300 scanning electron microscope equipped with an Oxford ISIS 2000 energy dispersive analysis system (EDS).

High-resolution transmission electron microscopy (HRTEM) images are obtained in a JEOL JEM 2010 microscope operating at 200 kV and equipped with an Oxford Instruments INCA EDS detector. In order to prevent eventual agglomeration, the sample was mixed with pure ethanol in an ultrasonic apparatus and superimposed on a lacey carbon film supported on a 3 mm Cu grid.

Electrochemical characterization

The electrochemical performance of the newly produced nanomodified carbon felt materials in phosphate buffer (PBS, pH 7.0) solutions was investigated by means of Linear Sweep Voltammetry (LSV). The studied samples with a geometric area 1 cm^2 were connected as a working electrode in a three electrode arrangement. A platinum-titanium mesh (10 cm^2) was used as a counter electrode. All potentials were measured against Ag/AgCl reference electrode.

To examine the corrosion behaviour of the materials, the potential was swept with a scan rate 2

mV/s in a positive direction in the range from -400 mV to 600 mV (vs. Ag/AgCl). To evaluate the electrocatalytic activity of the studied materials towards hydrogen evolution reaction (HER), LSV measurements with the same scan rate were performed in a negative direction from 0 to -1200 mV (vs. Ag/AgCl).

The electrochemical studies were performed by using potentiostat - galvanostat PJT 35-2 (Radiometer-Tacussel) with IMT 101 interface and VoltaMaster 2 data acquisition system. LSV tests were carried out in triplicate and the third scan was used for analysis of the performance.

RESULTS AND DISCUSSION

Two types of nanoparticles were used in these experiments, nanoparticles with thin silica layer (samples 1,5) and nanoparticles with a relatively thick silica layer (samples 2,3).

Physicochemical properties of the Si-coated magnetic nanoparticles

Only stable magnetic fluids were used in the further steps of the study. Optical inspection gave a first indication whether the prepared samples had properly dispersed nanoparticles. The prepared nanoparticles were examined by X-ray diffraction in order to identify the crystalline phases formed. The experimental peaks were perfectly matched with the theoretical data of the JCPDS card No 19-629, thus indicating the presence of pure magnetite. The crystallite size, determined from the line broadening by the Scherrer formula, was in the range 9-12 nm.

The Si-coating efficiency was monitored by HR-TEM, in combination with X-ray EDS Microanalysis. Figure 1 presents a characteristic image of crystalline magnetite nanoparticles, coated with a surface silica layer. The nanoparticles are visible as agglomerates of small nanoparticles of 10-20nm, coated with a thin layer of silica.
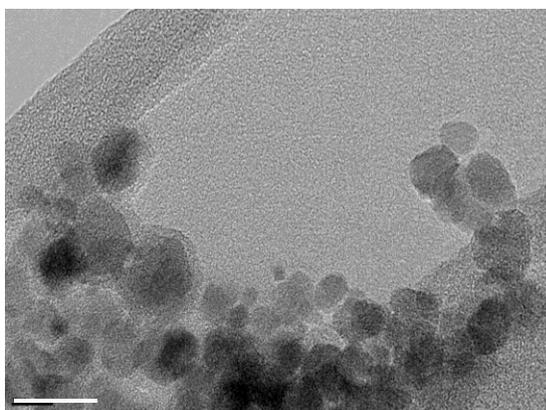

Fig. 1. TEM image of silica coated Fe_3O_4 nanoparticles

Physicochemical Characterization of NP-loaded Carbon Felt Samples

Samples prepared by Method No1: Magnetite nanoparticles after different treatment were used for the preparation of each of the following samples:

Sample P0: Pure Fe_3O_4 nanoparticles, without further modification were loaded on the carbon felt sample. In Figure 2, SEM images of the prepared sample show that only few big aggregates have been attached to the carbon felt fibers.
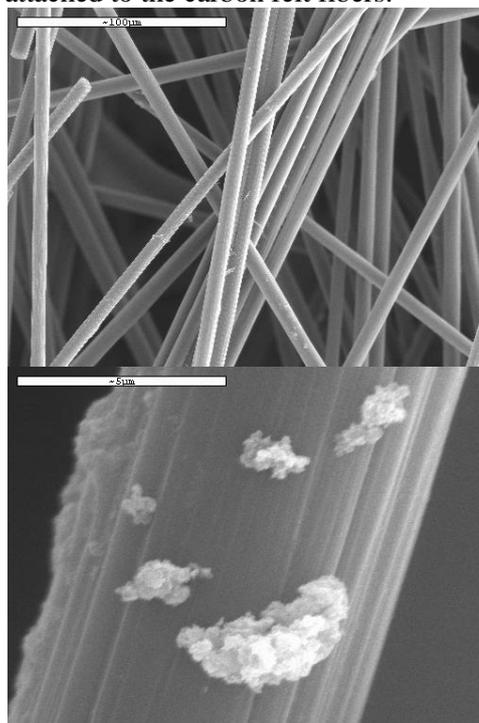

Fig. 2. SEM images of sample P0

Sample P1: Magnetite (Fe_3O_4) nanoparticles, treated with TEOS in order to obtain a silica layer (S0.016) were loaded on this sample. SEM images reveal that the silica coating increases the number of attached NP's and also reduces the size of the aggregates, however the results are still not acceptable.

Sample P2: The carbon felt sample was immersed in an aqueous suspension of silica coated (S0.016) magnetite (Fe_3O_4) nanoparticles, functionalized with surface amine groups, after treatment with 3-AminoPropyl-ThriEthoxySilane (APTES). As shown in Figure 3, the presence of amine groups of the surface of the nanoparticles has greatly enhanced their affinity to the carbon felt fibers. However, the NP's are still loosely attached as aggregates, not forming a homogeneous layer of the surface of the fibers.
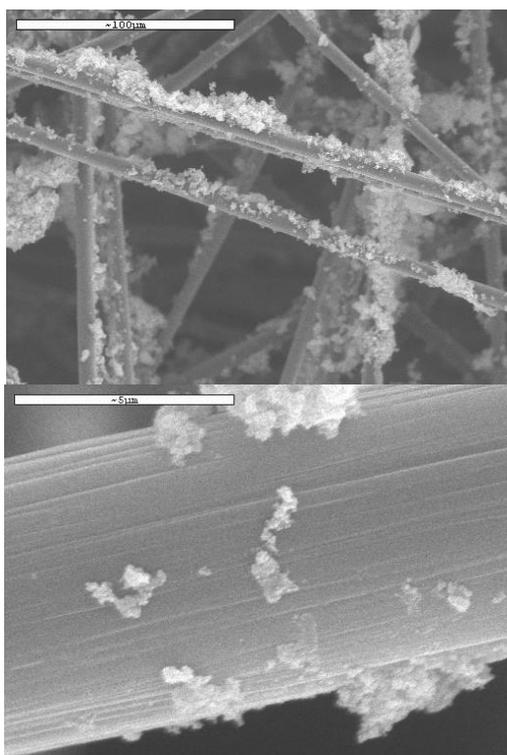
Fig. 3. SEM morphology of sample P2

Sample P3: Finally the effect of reducing the thickness of the silica layer has been examined. Sample P3 was prepared by using an aqueous suspension of amine functionalized magnetite (Fe_3O_4) nanoparticles coated with a thinner silica layer (S0.008). By observing the morphology of the prepared carbon felt sample, no major difference from sample P2 can be seen, thus it is concluded that the thickness of the silica layer does not have a significant effect on the adhesion behavior of the NP's on the carbon felt fibers.

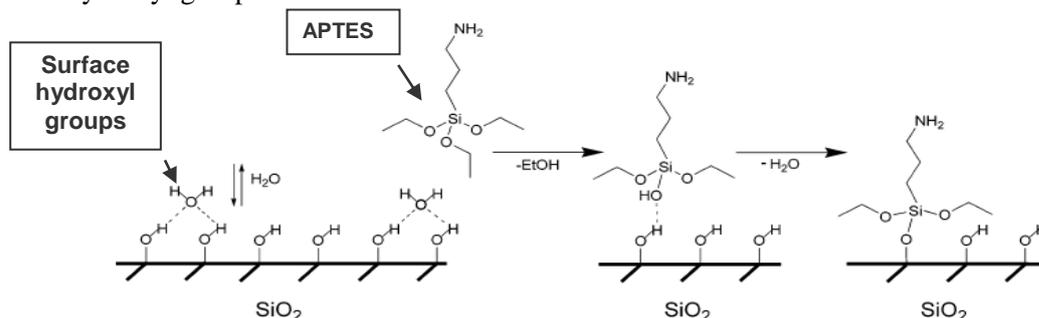Samples prepared by Method No2: The reaction of the surface hydroxyl groups of silica with the amine source, which leads to the formation of functional surface amine groups, is shown schematically in Figure 4.

The parameters studied for the samples loaded through the formation of covalent bonding between the nanoparticles and the carbon felt fibers were:

- the pretreatment of the carbon felt samples with ethanol
- the thickness of the surface silica layer of the nanoparticles
- the quantity of nanoparticles available to be attached to a carbon felt specimen

Sample C1: The carbon felt sample used for preparing sample C1 was pretreated with ethanol for 120 minutes before the nanoparticles loading procedure. Magnetite (Fe_3O_4) nanoparticles, treated with TEOS in order to obtain a silica layer (S0.016) were loaded on the sample, the same NP's as those used in Sample P1. In Figure 5 the SEM images obtained from sample C1 are shown. It is clear that the affinity of the nanoparticles to the carbon felt fibers has been greatly enhanced. The NP's have been attached almost uniformly around the fibers, forming a continuous magnetite layer. Local elemental analysis with X-ray EDS (Figure 6) clearly reveals the presence of iron and silica, thus confirming that the deposited layer is composed from the magnetic NP's.

At this point it should be emphasized that prior to the SEM morphology observation, the samples have been placed in the ultrasonic bath for 30 minutes, nevertheless the adherence of the nanoparticles remained strong, showing that Method 2 for the deposition of the NP's is superior than Method 1.
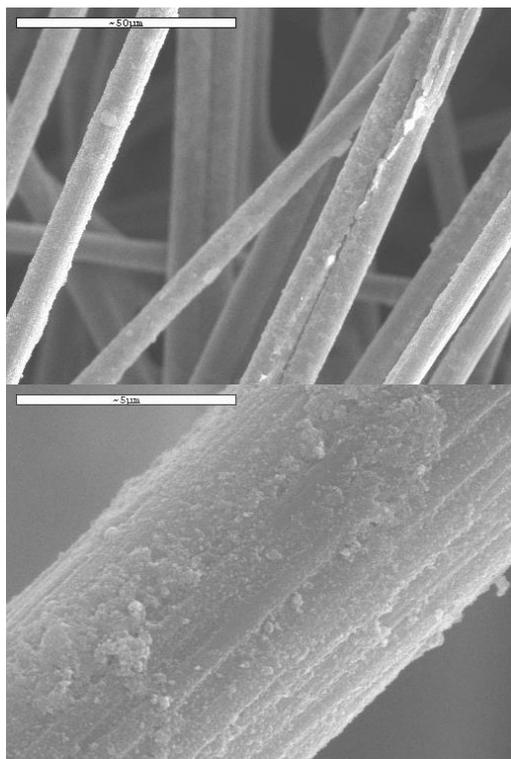

Fig. 4. Reaction scheme for the formation of surface amine groups.

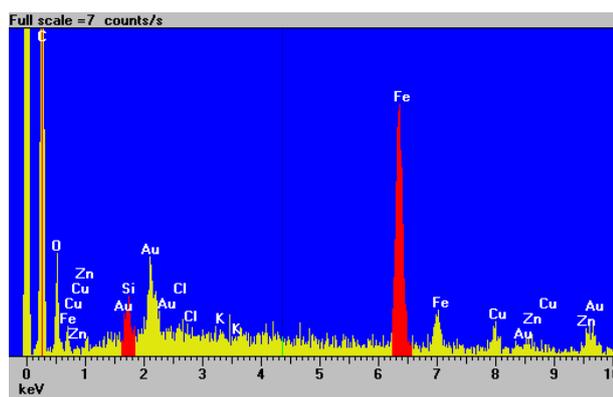**Fig. 5**. SEM morphology of sample C1

Fig. 6. Elemental analysis (X-ray EDS) of sample C1.

Sample C2: Sample C2 was prepared to investigate the effect of the pretreatment of the carbon felt with ethanol. Thus the preparation of sample C2 was exactly the same as sample C1, but without pretreatment with ethanol. The results, presented in Figure 7a, indicate that there is not a significant difference in the morphology of the fibers, from sample C1.
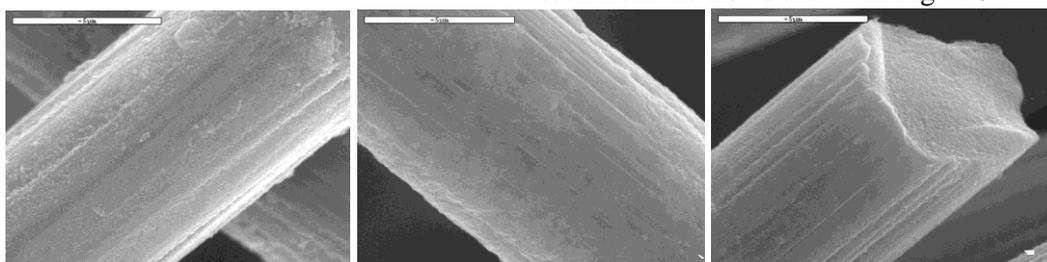
Sample C3   Sample C3 was prepared in order to study the effect of reducing the thickness of the silica layer. Magnetite (Fe_3O_4) nanoparticles, treated with TEOS in order to obtain a thinner silica layer (S0.008) were used, the same NP's as in sample P3. By comparing the SEM images of the prepared carbon felt specimens, shown in Figure 7b, to the images of samples C1 and C2, it is concluded that the effect of the silica layer thickness on the fibers morphology is not significant.

Sample C4   Finally, the quantity of nanoparticles available to be attached to the carbon felt specimen was investigated by preparing sample C4. Magnetite (Fe_3O_4) nanoparticles, treated with TEOS in order to obtain a thinner silica layer (S0.008) were used, the same NP's as in sample C3. However, 30% less nanoparticles were used for the deposition. The morphology of the obtained sample C4 is shown in Figure 7c. The number of attached nanoparticles on the fiber surface is significantly smaller than in the previous samples, eventually there were not enough NP's to form a continuous layer as in the previous samples C1-C3. However, the NP's are still not aggregated and very firmly attached to the fibers.

Electrochemical performance

The LSV studies performed in a positive (anodic) direction indicate a good corrosion stability of all studied materials in neutral PBS solution. As a measure of the corrosion rate, the exchange current density values estimated from the Tafel plots, presented in Figure 8, varies in the range $10^{-8} \div 10^{-7}$ mA/cm^2. These low corrosion rates reveal the potential possibility to use the modified materials, produced by covalent bonding of Fe_3O_4 nanoparticles to carbon felt, as electrodes in MFCs or MECs, in which neutral PBS solution is commonly used as an electrolyte. The performed potentiodynamic measurements with modified materials at negative potentials from 0 to -1200 mV (vs.Ag/AgCl), however, show an absence of reduction process in a broad range of potentials, as seen from the LSVs shown in Figure 9.
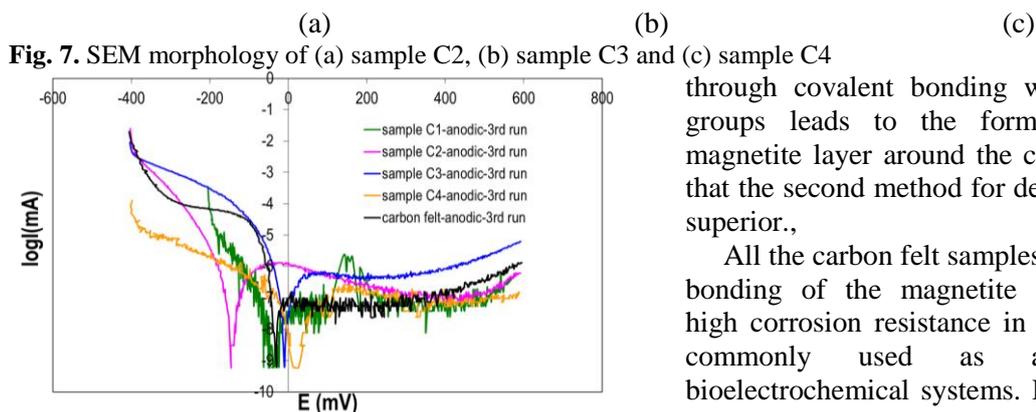

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(a)　　　　　　　　　　(b)　　　　　　　　　(c)

Fig. 7. SEM morphology of (a) sample C2, (b) sample C3 and (c) sample C4

Fig. 8. Tafel plots of modified and non-modified carbon felt samples obtained by LSV with a scan rate 2 mV/s in PBS (pH 7)
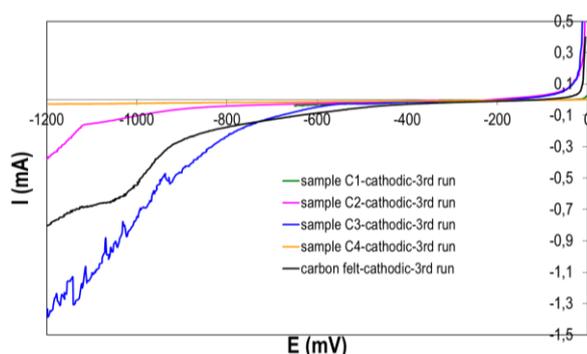

Fig. 9. Linear voltammograms of modified and non-modified carbon felt samples obtained with a scan rate 2 mV/s in PBS (pH 7)

The highest electrochemical activity at potentials more negative than -700 mV (vs.Ag/AgCl), corresponding to a noticeable hydrogen evolution, is observed with sample C3. Although the rate of HER, estimated from the slope of the linear region in voltammogram is twice higher for sample C3 than that for the non-modified carbon felt, it is rather small in comparison with the hydrogen production rates of electrode materials with a practical impact [10-12]. The rest of the studied modified materials exhibit even less than the carbon felt or negligible electrocatalytic activity towards HER. This exludes these materails as potential cathodes for bio-hydrogen production in MECs.

CONCLUSION

Two different methods were used for attaching magnetic Fe_3O_4 nanoparticles on carbon felt in order to obtain modified electrode materials for BESs application. The direct immersion of carbon felt samples in an aqueous suspension of silica coated magnetite nanoparticles results in loose attachment of NPs aggregates. In the contrary, the attachment of silica coated Fe_3O_4 nanoparticles

through covalent bonding with amine functional groups leads to the formation of a uniform magnetite layer around the carbon fibers, showing that the second method for deposition of the NPs is superior.,

All the carbon felt samples modified by covalent bonding of the magnetite nanoparticles possess high corrosion resistance in neutral PBS solution, commonly used as an electrolyte in bioelectrochemical systems. However the prepared samples are not suitable for use as cathodes for bio-hydrogen production in MECs.

The newly synthesized Fe_3O_4/carbon felt materials need to be further examined as anodes in MFCs using metal respiring bacteria (e.g. *G.metalloredusence*, *S.oneidensis*) as biocatalysts, since they combine high corrosion stability in neutral medium and specific properties due to the attached NPs.

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СИНТЕЗ И ОХАРАКТЕРИЗИРАНЕ НА ПОКРИТИ СЪС СИЛИКАГЕЛ СУПЕРПАРАМАГНИТНИ НАНОЧАСТИЦИ ЗА БИОЕЛЕКТРОХИМИЧНИ ПРИЛОЖЕНИЯ

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(Резюме)

В настоящата разработка, наночастици от магнетит, покрити със силикагел, бяха нанесени върху въглеродно кече чрез две различни техники – импрегниране на образци от въглеродно кече в суспензия от Fe_3O_4 наночастици, покрити със силикагел (Метод 1) и ковалентно свързване на покритите със силикагел Fe_3O_4 наночастици с въглеродното кече чрез функционални амино-групи (Метод 2). Повърхностната морфология на новосъздадените наномодифицирани въглеродни материали бе охарактеризирана чрез сканираща електронна микроскопия (СЕМ). Ефективността на Si-покритие бе оценена чрез високо-разделителна трансмисионна електронна микроскопия (ВР-ТЕМ) в комбинация с енерго-дисперсионна рентгенова спектроскопия. Проведените физикохимични анализи показаха, че Метод 2 е по-добър за отлагане на наночастиците от магнетит. Въз основа на това, бе изследвано електрохимичното поведение на образци, изготвени по Метод 2, в неутрален фосфатен буфер с оглед на потенциалното им използване като електроди в микробиални горивни елементи (МГЕ) и/или микробиални електролизни клетки (МЕК).