UNIVERSITY "UNION - NIKOLA TESLA"

Nikola Tesla

THE FIRST INTERNATIONAL CONFERENCE ON SUSTAINABLE ENVIRONMENT AND TECHNOLOGIES

PROCEEDINGS

24-25 SEPTEMBER 2021
CARA DUŠANA 62-64, BELGRADE, SERBIA

The First International Conference on Sustainable Environment and Technologies

"Creating sustainable commUNiTy"

Organizer of the Conference: University „Union Nikola Tesla", Belgrad, Serbia

Editors:

Ph.D Ljiljana Nikoluć Bujanović

Ph.D Sanja Mrazovac Kurilić

Publisher: University „Union Nikola Tesla", Belgrad, Serbia

For publisher:

Ph.D Nebojša Zakić

Design:

MSc. Arh. Dunja Bujanović

Mateja Đurić, student

Printed in: Dobrotoljublje, Beograd

ISBN 978-86-89529-33-3

DOMESTIC MATERIAL MADE BY CALCIFICATION OF MODIFIED UF RESINS WITH INCORPORATED Fe-PARTICLES - A SENSITIVE PLATFORM FOR ELECTROANALYTICAL QUANTIFICATION OF GALLIC ACID

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Abstract

In this work, we present domestic high performance electrode material prepared by thermolysis of *in situ* synthesized urea-formaldehyde (UF) resins modified with Fe(III) nitrate. For comparison, material produced by thermolysis of physical mixture of synthesized UF resins and Fe(III) salt was also prepared, and produced materials were electrochemically characterized by cyclic voltammetry. The obtained results have shown that *in situ* synthesized Fe modified UF material (SynFe/UF-TP) prepared by thermolysis, incorporated in carbon paste electrode (CPE), possesses a better electrochemical response and conductivity than the other materials prepared by thermolysis and obtained by physical mixing of UF and Fe salt, and also commercially available classy carbon powder in pure CPE. The morphological and structural characteristics of produced materials were determined by SEM analysis. Then, SynFe/UF-TP incorporated in CPE was applied in sensing of gallic acid (GA), one of the most biologically active phenolic compounds of plant origin. Square wave voltammetry in Britton-Robinson buffer at pH 4 was used to quantify GA in the concentration range of 0.5-100 μM of GA. The limit of detection of developed analytical procedure at proposed electrode was 0.25 μM.

Keywords: Modified urea-formaldehyde resin, thermolysis, voltammetric sensor, gallic acid

INTRODUCTION

Urea-formaldehyde (UF) resin is a kind of amino resin obtained by the polycondensation reactions of formaldehyde with urea. UF resins have various applications and offer unique potential technical advantages, such as low price, non-toxicity, good bonding to wood products etc. Because of that, they are widely used as adhesives in the manufacturing of wood-based composite panels (Conner et al. 1996, p. 8497). Modification of UF resins by metal oxides and other compounds in order to reduce formaldehyde emission as a potential source of indoor air pollution and health problems (Lee et al. 2013, p. 7) is a top priority for this material in an ecological sense (Pizzi et al. 1994, p. 254, Fink 2013, p. 155). In our laboratory, UF resins were improved and modified with different fillers also for the same reasons (Samaržija-Jovanović et al. 2019, p. 161).

Nowadays, scientific interest focuses on materials made from natural or synthetic renewable resources, used for different purposes (Galembeck et al. 2019, e20181160). The goal of our work was to find other possible and effective applications for modified UF resins produced in our laboratory. It is known that UF resin serves for producing glassy carbon, one of the most used "green" electrode materials in electrochemistry. Iron and iron oxide particles also attract much attention due to their specific physical, especially magnetic and chemical properties, and they are, among other applications, used as sensors in electroanalysis (Šljukić et al. 2006, p. 1556). In this work, we present sensitive electrode materials obtained by thermolysis of Fe modified UF composites. The composites were produced by a) physical mixing of synthesized UF resins with an iron salt and b) by *in situ* synthesis of Fe salt and UF. The materials were examined morphologically and electrochemically. The best performance material was used as a voltammetric sensor to determine gallic acid, one of the most important phenols often used as a standard for determining the phenol content of various analytes. The measurement of "total phenols" is a good indication of the level of present antioxidants (Petković et al. 2015, p. 513).

MATERIAL AND METHODS

Materials

The following materials were employed in the study reported here: Urea, $(NH_2)_2CO$, (Alkaloid- Skopje, FYR of Macedonia); 35% Formaldehyde, CH_2O, (Unis-Goražde, Bosnia and Herzegovina); Fe(III) nitrate, $Fe(NO_3)_3 \times 9\ H_2O$;

Gallic acid, $C_6H_2(OH)_3CO_2H$, (Sigma-Aldrich). All the other materials and solvents used for analytical methods were of analytical grade.

Synthesis of modified UF composites

Two samples of iron-modified urea-formaldehyde (UF) composites with formaldehyde to urea (F/U) ratio (0.8) were synthesized. The first sample was a fiscal mixture of pure UF resin with 15% of iron (using Fe(III) nitrate) - hereinafter abbreviated as UF/Fe, and the second sample was prepared by adding the same amount of Fe(III) nitrate *in situ,* during the synthesis (abbreviated as SynUF/Fe). The synthesis of SynUF/Fe was done by the following procedure: 60 cm^3 of distilled water and 0.1 mol of urea are mixed into a reaction vessel with a magnetic stirrer. Then 4.36 g of $Fe(NO_3)_3 \times 9\ H_2O$, 0.12 mol of 35% formaldehyde and 0.6 cm^3 of concentrated sulfuric acid were added into the reaction mixture according to the following order. The reaction mixture is mixed for 3 hours. 0.22 mol of sodium hydroxide dissolved in 6 cm^3 of distilled water and added to the reaction mixture before the stirring was done. The iron-modified UF composite was cured at 110°C for 2 h in a convective drying oven. For the first sample, UF/Fe, the synthesis procedure was the same, except the same amount of $Fe(NO_3)_3 \times 9H_2O$ was mixed and homogenized with pure UF after curing.

SEM measurements

The morphology of UF composites modified with Fe-particles, before and after thermolysis, was observed by TESCAN MIRA 3 XMU field emission scanning electron microscope (FE-SEM), operated at 20 keV. The samples were prepared for analysis by deposition of thin gold layer. The average particle size was determined by the image analysis, using the software ImageJ.

Electrode preparation and electrochemical measurements

Electrode material was prepared by calcination of Fe modified UF composites (UF/Fe and SynUF/Fe) at 950 C for 10 h and then cooled with the muffle furnace. Obtained materials were in 5% added to glassy carbon powder (Sigma-Aldrich) and mixed with paraffin oil to prepare carbon paste electrode. Three electrode systems in the working cell, attached to the PalmSence electrochemical system, consisted of this working electrode, an Ag/AgCl (saturated KCl) reference electrode and a Pt-wire counter electrode. The square wave frequency was varied from 10-100 Hz while pulse amplitude was changed from 10 to 100 mV, and potential step (scan increment) was changed in the range 2-20 mV.

RESULTS AND DISCUSSION

Surface morphology characterization

In order to determine the morphology of the obtained Fe modified composites, as well as the morphology and the particle size of Fe perticles prepared by thermolysis, SEM measurements were performed, and SEM micrographs of all samples are presented in Figure 1.

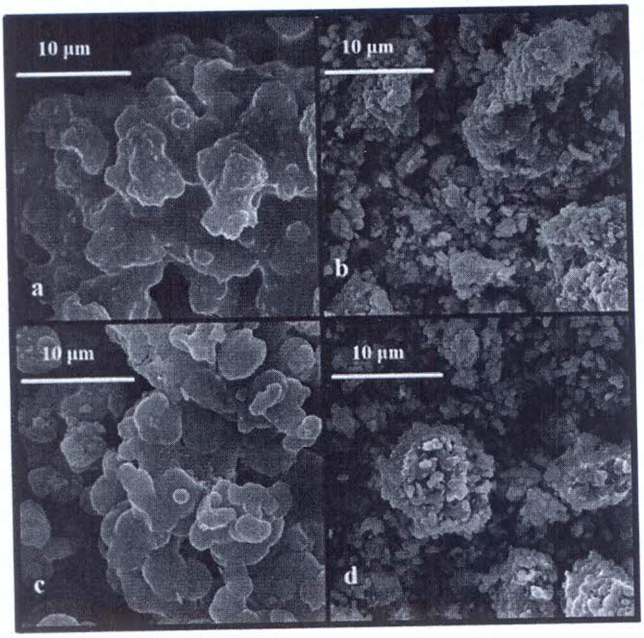

Figure 1. SEM micrograph of a)Physical mixture of UF resin and Fe salt (UF/Fe), b) Physical mixture of UF resin and Fe salt after thermolysis (UF/Fe-TP), c) In situ synthesized UF/Fe composite (SynUF/Fe), and d) In situ synthesized UF/Fe material after thermolysis (SynUF/Fe-TP).

From Fig. 1a, in the physical mixture of UF resin and Fe salt (UF/Fe), one part of the Fe-particles are on the surface of the UF composite covered with resin, and the second is immersed in the UF matrix. After thermolysis of UF/Fe, Fe-particles showed at Fig. 1b have defined shape; they are mostly spherical with the size of 445 ± 168 nm. From SEM micrograph of SynUF/Fe sample obtained by *in situ* synthesis of Fe salt and UF, only UF composite is observed (Fig. 1c). The Fe-particles potentially could be encapsulated with UF composite or incorporated in the structure. However, after thermolysis of SynUF/Fe, Fe-particles are visible. In SynUF/Fe-TP, Fe-particles have a spherical shape, better defined than Fe-particles in UF/Fe-TP, with a smaller average diameter of 357 ± 113 nm.

Electrochemical characterization

In order to electrochemically characterize thermolysis prepared materials obtained from Fe modified UF composites, cyclic voltammetric measurements were performed in test solution of 5 mM $K_3[Fe(CN)]_6/K_4[Fe(CN)]_6$ (1:1) mixture as a redox probe in 0.1 M KCl, and in 100 μM of GA in BR buffer (Figure 2).

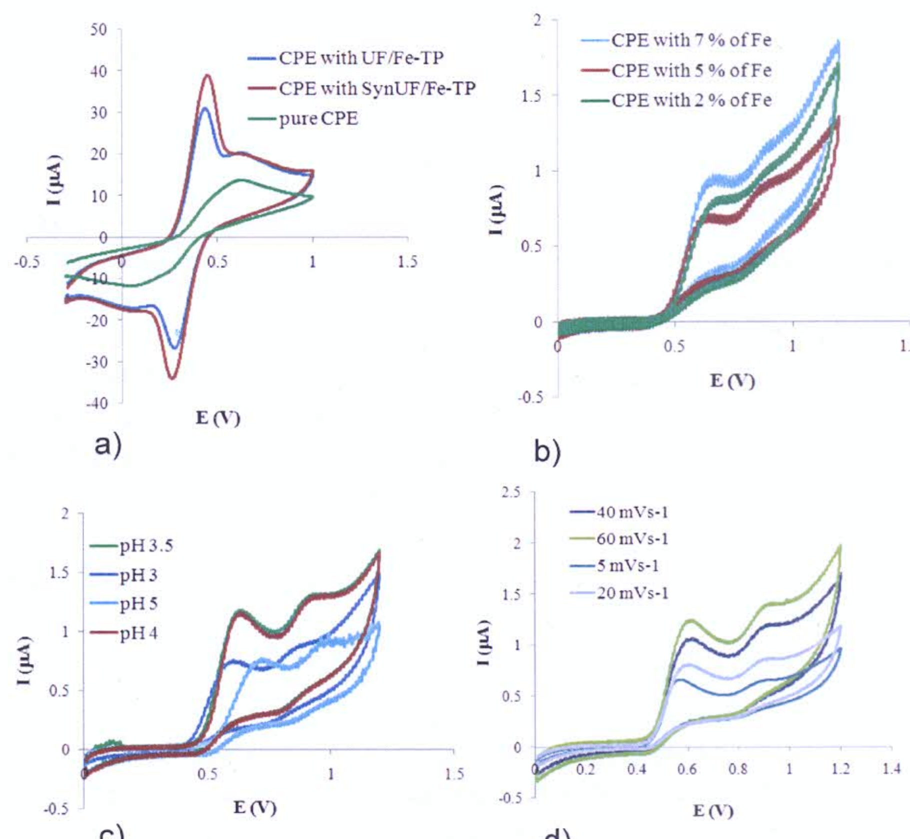

Figure 2. a) CVs of CPE with material doped with 5% of Fe recorded in 0.1M KCl solution containing 5 mM $[Fe(CN)_6]^{3-/4-}$ redox couple (scan rate: 50 mV/s); b) CV profiles of 100 μM of GA in BR buffer pH 3 at SynUF/Fe@CPE with different content (%) of Fe; c)Effect of pH of BR buffer solution and 100 μM of GA, recorded at SynUF/Fe@CPE; d) Effect of scan rate in the same solution and electrode as c).

As the catalytic activity of the material evidently depends mostly on the present iron, From Fig. 2a is evident that peak current in test solution increased in SynUF/Fe@CPE, indicating that *in situ* synthesis of UF and Fe produce material with improved conductivity and electron transfer property. The best voltammetric response to GA was recorded at the electrode with 5% of Fe (Fig. 2b). CV profiles show characteristic peaks for GA recorded in previous works (Petković et al. 2015, p.513). To optimize experimental conditions in terms of pH of supporting electrolyte, cyclic voltammograms of 100 μM of gallic acid in used Britton-Robinsons buffer (pH from 3 to 5) at SynUF/Fe@CPE were recorded (Fig. 2c). The optimal value of pH 4 was chosen for further experiments. From Fig. 2c, which shoves series of CV measurements of 100 μM of GA at different scan rates in BR buffer pH at SynUF/Fe@CPE, it can be seen that the anodic peak currents increased with an increase in scan rate from 5 to 60 mV/s. The relationship between anodic peak current *vs* square root of scan rate showed linear dependence, and it was expressed by regression equation $I\ (\mu A) = 0.11 \times v^{1/2}\ (mV^{1/2}s^{1/2}) + 0.38$; $R = 0.989$. This result suggests that the electrode reaction is controlled by diffusion as a rate-determining step while the adsorption and/or other specific interactions on the SynUF/Fe@CPE surface are negligible.

Development of an analytical procedure

The differential pulse voltammetry (DPV) and square wave voltammetry (SWV) are frequent pulse electroanalytical techniques used in electroanalysis due to good discrimination against background current, which results in lowering of detection limits of voltammetric measurements (Wang 2000, p. 68). SWV technique was chosen for GA determination at SynUF/Fe@CPE due to higher and better-shaped peak current. The optimal working conditions for SWV were found by changing the parameters of the technique (see Materials and Methods), and they were: pulse amplitude of 90 mV, frequency of 70 Hz, and potential step of 18 mV.

The calibration curve (Fig. 3b) was constructed based on values of peak currents from voltammetric SWV profiles and used concentrations of GA (Fig. 3a).

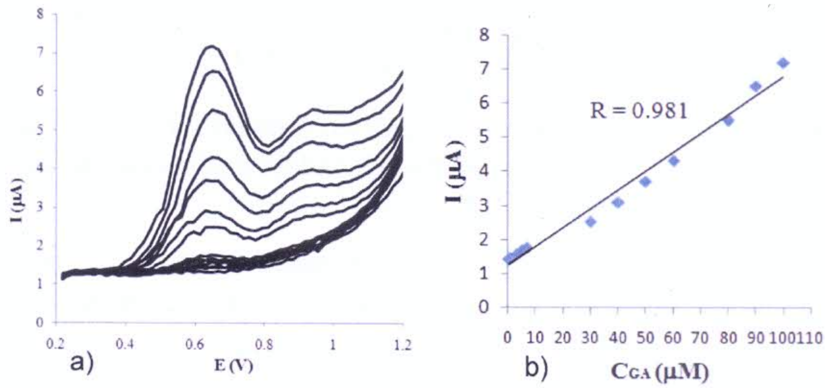

Figure 3. a) SWV profiles of various concentrations (0, 0.5, 1, 3, 5, 7, 10, 30, 40, 50, 60, 80, 90, 100 µM) of GA, in BR buffer at pH 4 at SynUF/Fe@CPE, under optimized experimental conditions;

b) Corresponding calibration curve.

The corresponding regression equation was: I (µA) = 1.243 + 0.055 × C (µM); R = 0.981. The detection limit (calculated as three times the standard deviation for the blank solution divided by the slope of the calibration curve, $LOD = 3s/m$) find to be 0.25 µM. To evaluate the reproducibility of the SynUF/Fe@CPE, 7 successive measurements of 30 µM of GA were determined. The relative standard deviation (*RSD*) of 3.68 % was obtained.

CONCLUSION

This work presents the application of the homely synthesized iron modified UF composite prepared by thermolysis, for the construction of the carbon paste based electrode. This is a new possible application of UF composites primarily used as adhesives in wood panel manufacturing. Electrochemical characteristics of such prepared material in CPE and developed electroanalytical method for determining of gallic acid open novel approaches in the manufacturing electrode materials and their modification.

Acknowledgment

The research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (contract number 451-03-9/2021-14/200123 and 451-03-9/2021-14/200017).

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CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

502/504(082)

INTERNATIONAL Conference on Sustainable Environment and Technologies "Creating sustainable commUNiTy" (1 ; 2021 ; Beograd)
Proceedings / The First International Conference on Sustainable Environment and Technologies [«Creating sustainable commUNiTy»], 24-25 september 2021, Belgrade, Serbia ; [editors Sanja Mrazovac Kurilić, Ljiljana Nikolić Bujanović] ; [organizer University «Union Nikola Tesla», Belgrad, Serbia]. - Beograd : University «Union Nikola Tesla», 2021 (Beograd : Dobrotoljublje). - 378 str. : ilustr. ; 25 cm

Tiraž 50. - Napomene i bibliografske reference uz radove. -

Bibliografija uz svaki rad.

ISBN 978-86-89529-33-3

a) Животна средина -- Зборници

COBISS.SR-ID 46182153