

## IRON DOPED CARBON NANODOTS AS EFFICIENT ELECTROCATALYSTS

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**ABSTRACT.** Carbon nanodots (C-dots) doped with iron cations were synthesized as efficient electrocatalysts for oxygen reduction reaction. For that purpose the nanoparticles were immobilized on a graphite rods used as a working electrode. The ultra small iron-doped carbon nanodots produced a substantial reduction peak at  $-0.18$  V in acidic media indicating that the oxygen was reduced at the modified electrode. In conclusion, we consider that iron-doped C-dots are a promising candidate as an alternative to the platinum based catalysts for fuel cells applications.

**Keywords:** carbon nanodots, environmentally friendly electrocatalysts, oxygen reduction reaction

### ВЪГЛЕРОДНИ НАНОТОЧКИ ДОТИРАНИ С ЖЕЛЕЗНИ КАТИОНИ КАТО ЕФИКАСНИ ЕЛЕКТРОКАТАЛИЗАТОРИ

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**РЕЗЮМЕ.** Въглеродните наноточки (C-dots) дотирани с железни катиони бяха синтезирани, като ефикасни електрокатализатори за редукция на кислород. За тази цел наночастиците бяха имобилизирани върху графитни пръчки, използвани, като работен електрод. Ултрамалките въглеродни наноточки, дотирани с железни йони произвеждат значителен редукционен пик при  $-0.18$  V в киселинна среда, което показва, че кислорода се редуцира на модифицирания електрод. В заключение, считаме че тези наночастици са обещаващ кандидат, като алтернатива на катодните катализатори, базирани на платината за приложения в горивни клетки.

**Ключови думи:** въглеродни наноточки, екологосъобразни електрокатализатори, редукция на кислород

## Introduction

The electrochemical oxygen reduction reaction is regarded as a key step for the development of green ecotechnologies, including solar fuel production, fuel cells, rechargeable batteries, etc. (Trotochaud et al., 2012; Suntivich et al., 2011). Nowadays, the fuel cells are in the focus of the research efforts, because they produce water as the main product of the reaction with a few byproducts (Lastovina et al., 2017). Their efficiency is limited by the rate of oxygen reduction reaction (ORR) (Becknell et al., 2015). In the widely used fuel cells the commercially available cathodic catalysts usually contain platinum and its alloys (Pt/C, Pt<sub>3</sub>Co/C). These catalysts are too expensive for common use and they can degrade over time. The high cost of the other noble metal catalysts (as iridium and ruthenium oxides) is a motive to concentrate the efforts on developing high-efficient and cost-effective alternatives, known as efficient platinum-free electrocatalysts. Different compounds have been employed as alternative catalysts for the ORR. Recently, metal-organic frameworks, some nanoparticles and

oxide compounds of cheap and environmental friendly 3d-metals as iron, cobalt, nickel and etc. were investigated as promising electrocatalysts under mild reaction conditions (Liang et al., 2011; Yeo & Bell, 2011; Subbaraman et al., 2012; Gao et al., 2013). Among them, the metal nanocrystals as iron/cobalt nitride, Co<sub>x</sub>O<sub>y</sub>, Fe<sub>x</sub>O<sub>y</sub> and Mn<sub>x</sub>O<sub>y</sub> coordinated to nitrogen-doped carbon materials are of considerable interest. These nano-electrocatalysts produce high oxygen reduction reaction activity due to synergetic chemical coupling effects between the nitrogen-doped carbon and the metal nanocrystals (Liang et al., 2011). The electrocatalytic activity can be increased by change of nanoparticle design as decreasing of its diameter, co-doping with other metals, modification with organic ligands, etc. (Lv et al., 2016). As another kind of electrocatalysts based on metals, the combination of nitrogen doped carbon nanomaterials and nanoparticles synthesized from some transition d-elements is a desired way to promote efficiently ORR catalytic activity (Bo et al., 2015). Previous reports found that the introduction of a trace transition metal as iron effectively increases the activity of nitrogen-doped carbon materials (Liu et al., 2013). Recently it

has been found that catalysts based on iron, nitrogen and carbon can be synthesized by pyrolyzing a wide variety of nitrogen and carbon precursors in the presence of iron sources at high temperature (Byon et al., 2011). Nanocatalysts prepared in such a way exhibited good activity for ORR.

The aim of this report was to develop electrochemically active nitrogen-doped carbon dots with incorporated iron ions as effective ORR catalyst. For that purpose highly-fluorescence nitrogen-doped carbon dots (C-dots) nanoparticles were synthesized by microwave-assisted pyrolysis and iron ion was incorporated into the aromatic core and carboxyl groups by complex-formation chemical reaction. Such prepared nanoparticles were immobilized on the graphite electrode and tested for ORR activity.

## Experimental Procedures

**Materials.** All chemicals were purchased from Wako Company, they are of analytical grade and were used without future purification. The chemicals used in our experiments are as follow, citric acid, 1,2-ethylenediamine, sodium nitrite, sodium bicarbonate, potassium hydroxide, sulfur acid and concentrated hydrochloric acid. The solutions were prepared with ultrapure water (18.0 M 18.2M $\Omega$ -cm, 25°C, Water Purifying System). Commercial graphite rods with 1.2 nm diameter were purchased from Uni 0.5 Mm Hb Nano Dia Blended Hi-quality Mechanical (made in Japan) and used as a working electrode.

### Fabrication of C-dots-Fe<sup>3+</sup> modified graphite electrodes.

The nanoparticles were prepared by the so called microwave assisted pyrolysis, which is a "bottom up" method. For this synthesis 1 g of citric acid was mixed with 10 ml deionized water and 0.2 ml of 1,2- ethylenediamine was subsequently injected into the reaction mixture. Then the precursors were energetically mixed by magnetic stirrer to obtain a final clean and transparent solution. Then the solution was subject to microwave pyrolysis in 150 ml Beher glass for 180 sec in a conventional microwave oven (600 W). After the pyrolytic reaction a yellow-brown pellet was formed at the bottom of the glass vessel. Its aqueous solution was with acidic pH = 3.5. The pellet was dissolved again in 10 ml deionized water and the dispersion was centrifuged at 13500 RPM for 30 min to remove coarse graphite particles and second byproducts. The bare C-dots reacted with solution of FeCl<sub>3</sub> at pH = 4.2 and the reaction solution was neutralized. The reacted nanoparticles were separated from the unreacted iron salt by size-selective desalting column (PD-10 desalting column, GE Healthcare Life Sciences). The supernatant was oven dried at 80°C. The size and morphology of the nanoparticles were characterized by transmission electron microscope. UV-VIS absorption spectra of C-dots were measured using Jasco V-630 UV/VIS spectrophotometer. The commercial graphite electrodes were modified with C-dots-Fe<sup>3+</sup> using simple drop-coating method. Simply, 15  $\mu$ L of C-dots-Fe<sup>3+</sup> dispersion was dropped onto the graphite electrode surface followed by coating with 4  $\mu$ L of Nafion solution (0.5 wt%). Then, the prepared electrode was dried in an oven at 80°C for 60 min.

**Electrochemical characterization.** The modified graphite electrodes were characterized by Cyclic voltammetry (CV) using a Potentiostat (PARSTAT 2263, Princeton Applied Res) in aqueous solution of hydrochloric acid (0.01 M HCl). The applied scan rate was 100mVs<sup>-1</sup> within a potential scan range of - 0.5 to + 0.5 V. The electrochemical measurements were performed at ambient temperature in nitrogen and oxygen-saturated solutions, respectively. A conventional three-electrode electrochemical cell was used, including modified with C-dots-Fe<sup>3+</sup> graphite rod as a working electrode, an Ag/AgCl (saturated KCl) electrode as the reference electrode and polished platinum wire as the counter electrode.

## Result and discussion

### Physicochemical characterization of the nanoparticles.

The preparation of nitrogen-doped carbon nanodots with iron complex is presented on Fig. 1.

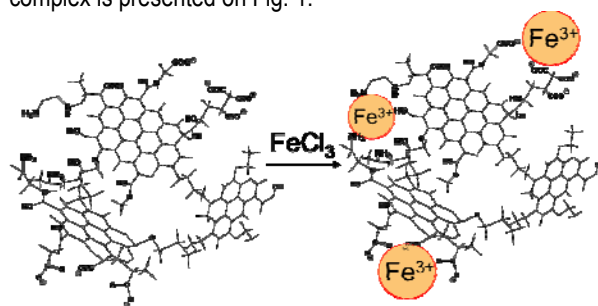


Fig.1. Schematic representation of the formation of chelate complex between iron ions and the surface functional groups of the carbon nanoparticle

It is known that the C-dots contain abundant number of surface functional groups as carboxylates, amines, hydroxyl and etc. The iron ions possess certain affinity to the oxygen atoms from the organic shell and the result is association between the metal ions and the carboxylate groups (Dhenadhayalan & Lin, 2015).

The microscopic data show uniformly dispersed ultra-small nanoparticles with a diameter less than 3 nm ( $d < 3$  nm). Their hydrophilic surface as explained above was abundant with organic groups as carboxyl, amino, hydroxyl and etc., which favors their good solubility in aqueous solutions. The UV-visible spectrum displays the typical for C-dots absorption peaks at 245 nm and 344 nm, which indicate  $\pi$ - $\pi^*$  transition of the aromatic  $sp^2$  domains and  $n$ - $\pi^*$  transition attributed to C=O and C=N groups, respectively (Roy et al., 2015) as shown on Figure 2. The dynamic light scattering analysis confirmed the nanoparticles size distribution in the range 1.0–3.0 nm with 2 nm average diameter. The reaction with iron ions causes quenching of the C-dots emission intensity but does not change the absorption maximum peak. However, the solution color of treated nanoparticles changes to dark, which causes enhancing of the absorbance in the visual wavelength range. This effect remains even after purification of C-dots-Fe<sup>3+</sup> with size-selective desalting column. The darkest color of nanoparticle solution after purification can be seen even with naked eyes. This was an indication that the iron ions are chemically attached to the functional groups of the nanoparticle and they are not in equilibrium with the surrounded aqueous media.

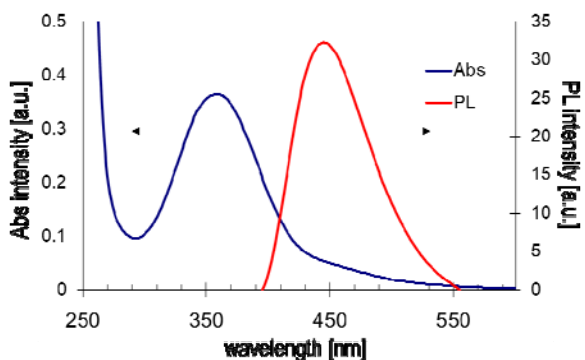


Fig.2. Optical properties of the highly fluorescent C-dots

**Electrochemical oxygen reduction reaction activity of the modified with C-dots-Fe<sup>3+</sup> graphite working electrode.** The electrochemical ORR activity of the unmodified and modified graphite electrode was investigated by cyclic voltammetry. For that purpose the electrode rod was used as a working electrode or cathode in the electrochemical experimental cell. Several parameters were modulated in order to optimize the production of achievable current density of the modified working electrodes. Dilute solution of hydrochloric acid was chosen as it is commonly used as the electrolyte in many electrochemical reactions in fuel cells. Thus, the highest current intensity was achieved by using of 0.01 M HCl as electrolyte. On Fig. 3 are shown the cyclic voltammograms of bare (unmodified) and modified with nanoparticles graphite electrode. The electrode modified with nanoparticles exhibited a remarkably higher anodic peak current intensity as compared with the intensity of the unmodified bare electrode.

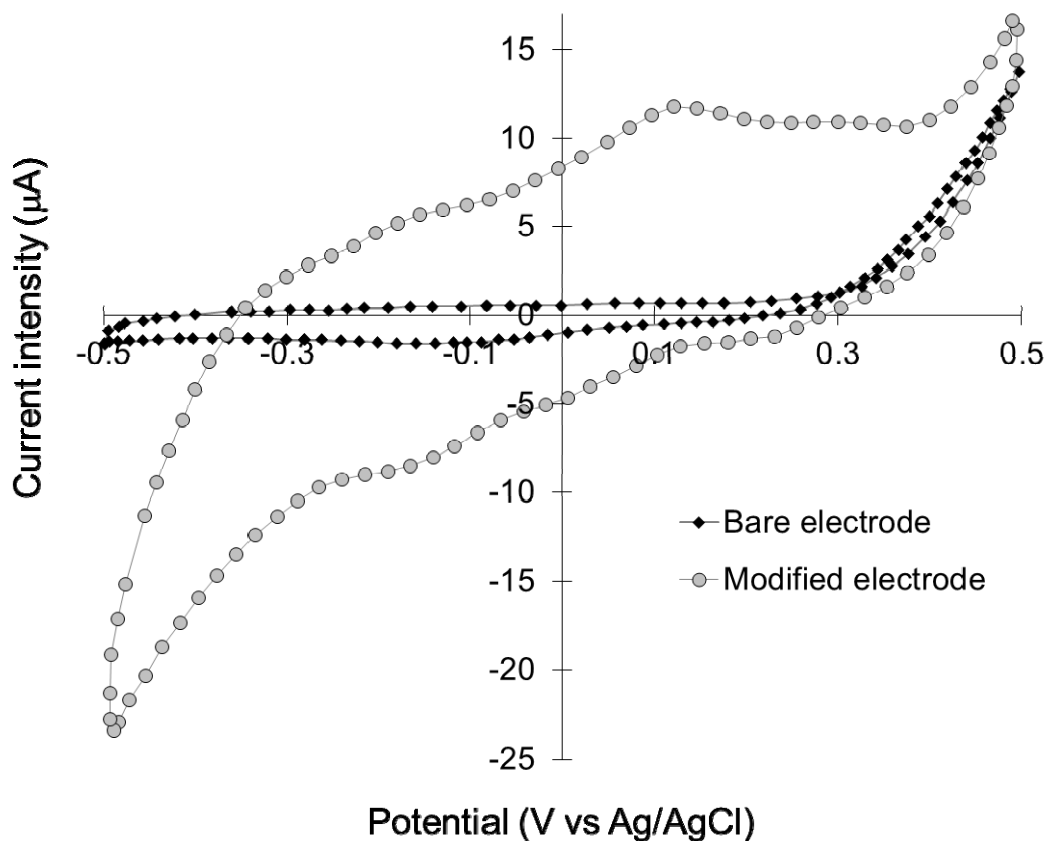


Fig.3. Cyclic voltammogram of bare electrode and modified electrode with C-dots-Fe<sup>3+</sup> nanoparticles in 0.01 M HCl solution, saturated with oxygen at a scan rate of 100 mVs<sup>-1</sup>

This is an indication that the deposition of C-dots-Fe<sup>3+</sup> nanoparticles had substantially enhanced the overall electrical conductivity of the graphite rod. Additional experiments by cyclic voltammetry proved that the current intensity of the modified electrode increased linearly with the increasing of the amount of nanoparticles and iron ions, respectively incorporated in them. This increasing effect could be attributed to the amount of iron ions which are bound to the carboxylate groups on the nanoparticle surface. It is known that -COO- groups have strong coordination affinity towards Fe<sup>3+</sup> ions in

aqueous media as shown on Fig. 1. Thus, they led to higher electrical conductivity of the C-dots-Fe<sup>3+</sup> modified graphite electrode. The cyclic voltammograms of the immobilized nanoparticles show also that in nitrogen-saturated electrolyte C-dots-Fe<sup>3+</sup> produced pseudocapacitive behavior, whereas in oxygen-saturated electrolyte a substantial reduction peak occurred at - 0.18 V as shown on the figure above, indicating that O<sub>2</sub> was reduced on the working electrode. Just for comparison, the commercial Pt/C catalysts exhibit a reduction peak at + 0.53 V for ORR (Bo et al., 2015). If methanol is

introduced into the testing electrochemical cell, then an identical response was observed for C-dots-Fe<sup>3+</sup> modified electrode. This indicates a good selectivity for ORR against methanol. Again, in comparison with the case of commercial Pt/C, the disappearance of oxygen reduction reaction current and methanol oxidation indicated that the ORR process was strongly retarded by the alcohol. These results indicate that the presented graphite electrode with electrocatalytic nano-layer was a potential alternative to platinum as a cathode catalyst.

**C-dots modified electrode as electrochemical sensor for selective detection of metal ions.** The specific electrochemical properties of the carbon nanodots modified electrode can be applied also as a sensor for detection of metal ions in aqueous media. The analytical performance of this electrochemical sensor can be achieved by cyclic voltammetry as well as electrochemical impedance spectroscopy, because of the specific opto-electronic properties as explained above. In our experiment we found that under optimized condition, the electrochemical sensor electrode exhibited a linear detection range of iron ions detection in the interval between 0.5 to 30 ppm with a limit of detection of around 0.4 ppm. The selectivity of the electrode was investigated with a wide range of metal ions (Hg<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, etc.), which are commonly associated with heavy metal pollution in natural water. The solubility of these metal ions is dependent on pH of solution. Due to this reason, in the performed sensor analysis we used HCl and H<sub>2</sub>SO<sub>4</sub> for sample preparation. In our experiment the current intensity of the modified electrode was highest in the case of iron ions among the other evaluated metal ions. The selectivity is attributed to the specific chemical affinity of C-dots to Fe<sup>3+</sup> as we have explained in the text. The investigation of the sensor research project is still under progress.

## Conclusion

An electrode modified with iron-doped carbon nanodots has been fabricated. The electrode has ORR activity in acidic solution and produces higher current density. Therefore, we concluded that C-dots-Fe<sup>3+</sup> nanoparticles are a promising potential candidate as electrocatalytic cathode for oxygen reduction. The obtained data provide also potential alternative approach for preparation of efficient and low-cost metal-doped C-dots electrocatalysts with practical application in fuel cells. In addition, the fabricated graphite electrodes modified with C-dots can be used also as a sensor for electrochemical detection of iron in polluted natural water.

## Competing Interests

The authors declare that there no competing interests regarding the publication of this research article.

## Acknowledgment

Funding from the Bulgarian National Science Fund, Grant № DN07/7, 15.12.2016. This study was accomplished within the bilateral agreement between Saitama University-Japan and the University of Mining and Geology "St. Ivan Rilski"-Bulgaria.

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