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MODELING OF HYDROGEN ION GENERATION IN THE METALL-GRAPHENE NANOSTRUCTURE CONTAINING ORGANIC COMPLEXES

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Abstract: a computational method is introduced to model the hydrogen ion generation in the metal-graphene nanostructure based on copper (Cu) and reduced graphene oxide (rGO) containing organic complexes (Org) by using COMSOL Multiphysics software tool and calculation of the surface potential and current density distribution in their cross-section. This modeling relies on the water-splitting reactions on the surface of metal-graphene nanostructures, yielding hydrogen ion generation, depending on their average diameter. As a result, the exponential increase of hydrogen ions electrochemically generated in these nanostructures upon enlargement of their average diameter from 1 to 100 nm. The rate of such increase of H^+ generation is the highest in Organic-Cu-rGO and Cu and the lowest in Org-rGO nanostructures, which may be indicative of degradation of such a catalyst caused during the electrochemical redox reactions.

Keywords: copper, graphene oxide, nanostructure, hydrogen, antioxidant.

I. INTRODUCTION

The search for novel functionalities of heterogeneous nanostructures is of increasing research interest in photonics, electronics and nanomedicine. Significant progress has been made in several recent developments of inorganic nanostructures based on graphene oxide (GO) or its reduced form (rGO) with controlled shape, size, crystallinity and functionality. Among such rGO-based nanostructures those modified with Cu and organic substances especially stand out [1, 2]. The big advantage of copper nanoparticles over common ones such as Au, Ag, Co or Ce is their relatively low cost and longer period of chemical stability. It is important to note that the biofunctionality of copper nanoparticles including their antioxidant activity is not limited to their inorganic form but also manifests in various organic complexes. The antioxidant activity, which is least studied, like other important properties of copper nanoparticles depend largely on size, structure, shape and the composition and charge carrier efficiency of the surface layer. Their catalytic activity increases significantly as the nanoparticle size decreases. These properties can be improved and enhanced by conjugation of Cu with rGO due to unique surface area, electronic properties, and biocompatibility of the latter. Overall, the strategy of hybridizing rGO with functional organic substances holds great potential not only for enhancing the existing properties of the resulting nanomaterial's components but also for generating new functionality through such cooperative interaction. We have recently shown that antioxidant efficiency of rGO modified with metal oxide and organic substances, e.g. salicylic acid, can be controlled via hydrogen ion generation in their nanostructure in the electrochemical decomposition of water [3]. However, little is known about the capability of hydrogen ion generation in Cu-modified rGO containing organic complexes so far.

II. EXPERIMENTAL SECTION

Mathematical 3D-modeling of current density distribution on the surface of metal-graphene nanostructures with organic complexes was performed in the use of *Comsol Multiphysics* 4.3 software tool (Equation-Based Models). The modeling is based on the fundamental equation of electrical conduction or the retention of charge on the surface of nanostructures [4]:

$$\Delta(-\sigma \Delta U) = 0, \quad (1)$$

where σ –specific electrical conductivity (S/m); U – electrical potential (V).

$$j = ne\langle v\rangle = \sigma E, \quad (2)$$

where j – current density (A/m^2); n – charge carrier concentration (number/m^3); e = 1,6 × 10^{-19} C; $\langle v\rangle$ − average velocity of charge carriers (m/s); E – electric field strength (V/m).

Equation for current density in the surface layer of nanostructures:

$$j = \partial U/\partial t + \Delta(1-U-\sigma^* d \cdot \Delta U) + (U + \Delta U), \quad (3)$$

where t – time (s); σ* – dynamic specific electrical conductivity (S/m); d – thickness of the surface layer (×10^{-9} m).

In the modeling, the electric potential values U (V) were based on electrochemical cyclic voltammetry measurements, using the peak corresponding to the formation of hydroxyl radicals (•OH). The potential distribution along the surface of the nanostructures was calculated by varying their average diameter under the condition of a current density flow indicated by arrows.

Modeling of the electrochemical decomposition of water, yielding hydrogen ion generation, was carried out by *Comsol Multiphysics* 4.3 software tool (Chemical Reaction Engineering − Electrochemical Engineering module). The model of electrochemical water decomposition is based on the electrochemical reactions of water molecule decomposition and chloride ion oxidation at the anode [5]:

$$2H_2O \rightarrow 4H^+ + O_2 + 4\bar{e}, \quad (4)$$

$$2Cl^- \rightarrow Cl_2 + 2\bar{e}. \quad (5)$$

The Nernst-Planck equations allow determination of hydrogen ion concentration at the interface of two media: of an Ag/AgCl needle electrode with an average diameter of 1 mm and a length of 60 mm and nanostructures [6]:

$$\partial C_i/\partial t = \nabla D_i \nabla C_i - Z/|Z_i| V_i C_i \nabla U + V_i^*, \quad (6)$$

$$V_i = D_i F / RT, \quad (7)$$

where C_i – ion concentration (mol/L); D_i – diffusion coefficient (m^2/s); Z_i – magnitude of the charge (C); V_i – ionic mobility ($m^2/V{\cdot}s$); U – field potential (V); V_i^* – rate of ion formation (mol/(L·s)); R – universal gas constant (8.31 J/(K·mol)); T − temperature (K).

In the computation a saturated aqueous KCl solution (4.76 mol/L) was used as the supporting electrolyte at equilibrium potentials of −0.5 V and 1.2 V, corresponding to hydrogen formation at the cathode and oxygen evolution at the anode. The choice of the potential range is determined by the formation of hydroxyl radicals in the electrochemical Fenton process. The following magnitudes were used in the modeling: diffusion coefficient of K^+ $D_K = 1{,}84 \times 10^{-9}$ m^2/s, concentration of K^+ and Cl^- ions at the electrode inlet $C_{K,0} = C_{Cl,0} = 4{,}76$ mol/L, initial anode voltage $U_0 = -0{,}5$ V, diffusion coefficient of H^+ $D_H = 9{,}31 \times 10^{-9}$ m^2/s, temperature $T = 298$ K, K^+ ion mobility $V_K = 7{,}43 \times 10^{-13}$ s·mol/kg, H^+ ion mobility $V_H = 3{,}76 \times 10^{-12}$ s·mol/kg, Cl^- ion mobility $V_{Cl} = 8{,}19 \times 10^{-13}$ s·mol/kg, initial concentration of H^+ ions $C_{H,0} = 1{,}00 \times 10^{-4}$ mol/m^3 and the potential under equilibrium conditions for the calculation of hydrogen ions $U = 0{,}53$ V. Electrical conductivity value σ of crystalline Cu (at $T = 20$ °C) was 58.0×10^6 S/m. The σ value of rGO 3×10^3 S/m was estimated by using the intensities ratio of D and G bands registered in Raman spectra of these nanostructures as IntD/IntG = 1.08 [7] and of organic ligands as 60×10^{-4} S/m [8]. The model of the effective medium (Bruggeman EMA) of the homogeneous distribution without sharp jump in conductivity was used to calculate the electrical conductivity of Org-rGO (0.75×10^3 S/m) and Org-Cu-rGO (5.43×10^6 S/m) nanostructures considering the volume fraction of Cu as 8.0×10^{-2} vol. % and organic ligands 0.5 vol. %.

III. RESULTS AND DISCUSSION

The results of 3D-modeling of the surface potential and current density distribution j (A/m^2) on the surface of nanostructures with an average diameter 10 nm at the applied potential 0.53 V and the rate of its change 1.0×10^{-2} V/s during 250 s are shown in Figure 1. The analysis of peak j values revealed that its highest magnitudes were observed in Cu (1.67×10^5 A/m^2) and Org-Cu-rGO (1.61×10^5 A/m^2) following Org-rGO (1.53×10^4 A/m^2) and rGO (3.09×10^4 A/m^2) if these nanostructures have an average diameter of 10 nm. The computed concentration of hydrogen ion generation (C H^+, mol/m^3) can reach the highest values in Org-rGO (2.0×10^{-3} mol/m^3) and rGO (1.6×10^{-3} mol/m^3), following Cu and Org-Cu-rGO with their values of 1.0×10^{-3} mol/m^3. It was revealed that the C H^+ values (mol/m^3) exponentially increase in these nanostructures as their average diameter becomes higher starting from 1 nm and ending to 100 nm (see Fig. 1). The rate of such increase of H^+ generation is higher in Org-Cu-rGO ($t_1 = -2.56 \times 10^{-2}$ nm^{-1}) and Cu ($t_1 = -2.59 \times 10^{-2}$ nm^{-1}) than in rGO ($t_1 = -3.02 \times 10^{-2}$ nm^{-1}) or Org-rGO nanostructures ($t_1 = -4.12 \times 10^{-2}$ nm^{-1}). The lowest magnitudes of this rate in Org-rGO nanostructures may indicate the possible enhancement of degradation of such a catalyst caused during the electrochemical redox reactions.

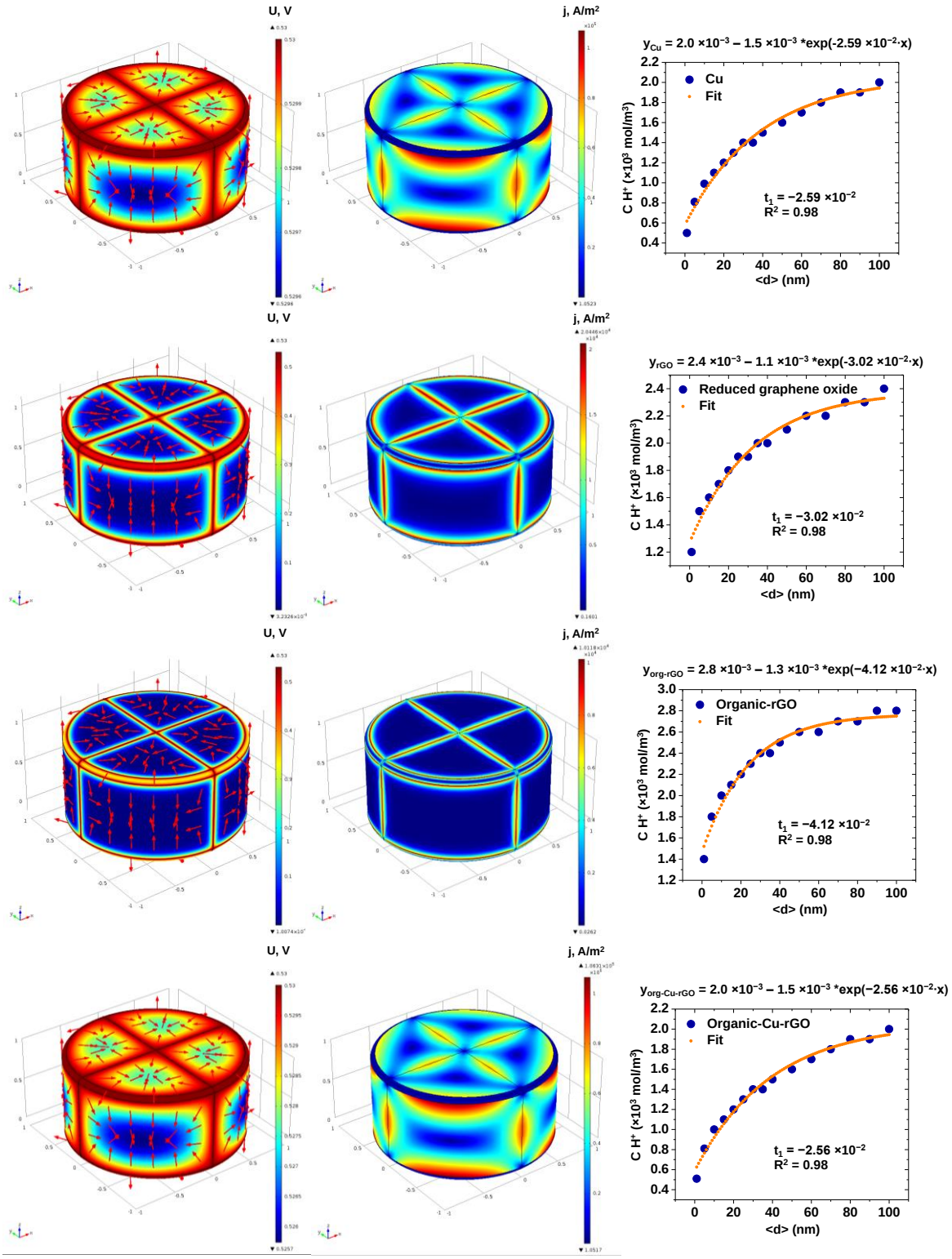


Figure 1. Results of modeling of surface potential distribution (U, V) and current density profile (j, A/m^2) of nanostructures composed of pure Cu and reduced graphene oxide (rGO) before and after complexation with organic substance (Organic-Cu and Organic-Cu-rGO) for calculation of hydrogen ion generation (C H$^+$, mol/m^3) depending on their average diameter (d, nm)

IV. CONCLUSION

A 3D-modeling method is introduced to calculate the hydrogen ion generation in the metal-graphene nanostructure based on copper (Cu) and reduced graphene oxide (rGO) containing organic complexes (Org) using the electrochemical water decomposition. Computation of the surface potential distribution and current density profile of four types of nanostructures (average diameter of 10 nm): Cu, rGO, Org-rGO and Org-Cu-

rGO reveals the highest magnitudes in Cu (1.67×10^5 A/m^2) and Org-Cu-rGO (1.61×10^5 A/m^2) following Org-rGO (1.53×10^4 A/m^2) and rGO (3.09×10^4 A/m^2). However, the amount of hydrogen ions generated in all these nanostructures exponentially increases upon the enlargement of their average diameter from 1 to 100 nm. The rate of such and increase is the highest in Org-Cu-rGO and the lowest in Org-rGO, which may be explained by the possible degradation of the latter due to electrochemical redox reactions.

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Моделирование генерации ионов водорода в металлографеновой наноструктуре, содержащей органические комплексы

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Аннотация: в работе представлен вычислительный метод моделирования генерации H^+ в металлографеновой наноструктуре на основе меди (Cu) и кислородсодержащего графена (КГ) с органическими комплексами (Орг), используя программный инструмент *COMSOL Multiphysics* и расчет поверхностного потенциала и распределения плотности электрического тока в ее поперечном сечении. Это моделирование опирается на реакции расщепления воды, протекающие вблизи поверхности металлографеновой наноструктуры, что приводит к генерации H^+ в зависимости от среднего диаметра. Обнаружено экспоненциальное увеличение H^+, электрохимически образованных в таких наноструктурах, по мере увеличения их среднего диаметра от 1 до 100 нм. Скорость подобной увеличенной генерации H^+ является наибольшей в наноструктурах на основе Орг-Cu-КГ и Cu, а наименьшей в наноструктурах Орг-КГ, что может быть обусловлено деградацией такого катализатора, вызванной протеканием электрохимических окислительно-восстановительных реакций.

Ключевые слова: медь, кислородсодержащий графен, наноструктура, водород, антиоксидант.