Electrochemical Behavior of Novel Composite Based on Reduced Graphene Oxide, Poly-*o*-Phenylenediamine, and Silicotungstic Acid¹

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Abstract—The behavior of novel electroactive material based on reduced graphene oxide (RGO), polyphenylenediamine (PPD), and silicotungstic acid (SiW) is studied using the methods of cyclic voltammetry (CVA) and electrochemical impedance. It is found that graphene oxide (GO) has a catalytic effect on the electrochemical codeposition of PPD and SiW onto the GO film during fabricating the RGO–PPD–SiW composite. It is shown that the composite has at least six redox transitions depending on the chosen range of cycling potentials. It is found that, at the potentials of 200 and 500 mV (Ag/AgCl), the conductivity of the composite is by 4 orders of magnitude higher than that of PPD. By the example of quinone-hydroquinone and ferro-ferricyanide redox reactions, it is shown that, in this potential range, the composite exhibits electrocatalytic properties, though neither PPD nor SiW individually exhibit pronounced redox transitions in this potential range.

Keywords: graphene oxide (GO), reduced graphene oxide (RGO), poly-*o*-phenylenediamine (PPD), electrocatalysis, silicotungstic acid

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INTRODUCTION

Electroactive polymers (EP) [1], graphene oxide (GO) [2] and polyoxometallates (POM) [3] separately form three large fields of scientific and technical research. In each of them, one can find major achievements that largely determined the development of material science for many decades. Although the above fields of science began to develop at different times, a large number of works have already appeared at their intersection. It should be noted that the development and study of composites of EP and GO or its reduced form (RGO) became the point of growth. The composites of EP with GO (or RGO) are already successfully used in the anticorrosion coatings, supercapacitors, sensors, and other devices [4]. POM are also widely used in various fields of science and engineering. The examples of their main areas of application are highly diverse: in the anticorrosion coatings, analytical chemistry, catalysis, membranes, sensors, etc. [5]. It is also worth noting the application of POM in

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the proton-exchange devices [6, 7]. For electrochemistry. POM are of interest due to their numerous redox transitions. However, in contrast to EP, which can be easily applied onto the electrodes in the course of electrochemical polymerization, it is important for POM to find appropriate methods for their immobilization [5]. A number of POM can be strongly adsorbed on the surfaces of carbon-containing materials. These are, for example, some heteropolyacids (HPA): phosphomolybdic (PMo), phosphotungstic (PW), and silicomolybdic (SiMo) acids [5]. For other HPA, various methods of immobilization are used. Their codeposition with EP is one of the methods. Earlier [8, 9], we began to study the codeposition of silicotungstic acid (SiW) and poly-o-phenylenediamine (PPD). It should be noted that SiW is a promising POM, which is used, for example, in the electrocatalysis [10] and for the anticorrosion coatings [11]. The ladder-type redox PPD polymer is also widely used for various scientific and practical purposes [12–14].

We fabricated the RGO–PPD–SiW composite, which also exhibits the properties of a mediator catalyst. In this work, we continue to study the novel electroactive material.



Fig. 1. Planar screen-printed carbon electrode, SPCE.

EXPERIMENTAL PROCEDURE

Devices and Materials

All electrochemical measurements were performed on the planar screen-printed carbon electrodes (SPCE), Fig. 1. The measurements were carried out in a drop of solution (approximately $30-50 \mu$ L) placed on the surface of SPCE.

To obtain the GO coating on the electrode, the GO aqueous dispersion (5 g/L) (www.graphenox-ru.com) was diluted in the 1 : 3 ratio, applied onto the substrate with a micropipette, and then dried in air.

Monomer *o*-phenylenediamine (OPD), as well as SiW (Aldrich), were used as delivered.

To fabricate the RGO–PPD–SiW composite, first, a drop of the GO suspension was applied to the center of SPCE, where the working electrode is located (Fig. 1), and then dried. After that, $50 \,\mu L \, 10^{-2} \,M \,OPD + 10^{-3} \,M$ SiW in 1 M H₂SO₄ solution was applied with a micropipette. Then, the PPD–SiW codeposition was performed in the CVA mode.

The electrochemical studies were performed with an IPC-compact potentiostat–galvanostat (Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Russia).

The impedance spectra were measured using a P-45X potentiostat-galvanostat equipped with an FRA-24 M frequency response analyzer unit (Electrochemical Instruments, Chernogolovka, Moscow oblast, http://potentiostat.ru). The impedance measurements were carried out under the potentiostatic conditions at the potentials of 0.2 and 0.5 V, in the range of 1 MHz-0.1 Hz, with 10 mV ac perturbation.



Fig. 2. (1) CVA of synthesis of PPD–SiWon SPCE in 10^{-2} M OPD + 10^{-3} M SiW solution in 1 M H₂SO₄ and (2) CVA of SPCE + PPD–SiW in 1 M H₂SO₄. Potential scan rate is 50 mV/s.

RESULTS AND DISCUSSION

Synthesis of RGO-PPD-SiW Composite

Figure 2 gives (curve 1) the cyclic voltammograms (CVA) of PPD and SiW codeposition on SPCE without GO and (curve 2) CVA of produced PPD–SiW composite in 1 M H₂SO₄ solution. Comparing curves 1 and 2, we can see that a small amount of redox-active composite is attached to the electrode (curve 2) as compared with the species involved in the electrochemical reactions from the bulk solution (curve 1).

Figure 3 (curve 1) gives the CVA of the synthesis of RGO–PPD–SiW composite. As it was shown earlier [8, 9], the electrochemical codeposition of OPD and SiW on GO proceeds at 500 mV, which is significantly lower than the potential of synthesis of pure PPD (1200 mV). This is due to the oxidative properties of GO, which acts as the mediator catalyst and, thereby, itself is reduced, which was earlier supported by the data of the IR and Raman spectra [8, 9].

Electrochemical Behavior of RGO-PPD-SiW Composite

After the synthesis, the electrode was repeatedly washed with deionized water and 50 μ L of 1 M H₂SO₄ was applied. Figure 3 (curve 2) shows the CVA of the composite. It is seen that it possesses a large number of redox transitions. Some peaks can be clearly referred to the redox transitions of SiW or PPD. However, a couple of reversible peaks at approximately 500 mV do not correspond to the CVA of PPD [15] or CVA of SiW [16, 17].

Comparing the currents on Figs. 2 and 3, one can see that the rate of the composite synthesis is higher in

the presence of GO. In addition, it is firmly attached to the GO-coated electrode, whereas a very small amount of PPD–SiW composite remains on the pure SPCE when the electrode is washed after the synthesis (Fig. 2).

In addition, when the composite is synthesized in the absence of GO, no peak is observed in the vicinity of 500 mV (Fig. 2). Probably, one more redox center forms in the presence of GO.

Let us consider the electrochemical behavior of RGO-PPD-SiW by the example of two pronounced pairs of peaks: at the lowest (A) and highest (B) potentials in the range of cycling potentials used. Figure 4a shows the CVA measured at various potential scan rates. Figures 4a and 4c show the dependences of peak current on the potential scan rate for the anodic peaks A and B. Figures 4d and 4e show the dependences of $\ln (I_{max})$ on $\ln (V)$ for peaks A and B. It can be seen that, in the case of peak A, the dependence is almost linear, and for peak B, the deviation from linearity is small. Peak A is clearly caused by the presence of SiW [16, 17]. The silicon tungstate anion can be considered as a counterion to the oxidized cation-radical form of the polymer. However, it differs from the anions of the supporting electrolyte in that it is fixed in the matrix and, as a result, it is not deintercalated in the reduction cycle (i.e., the conversion of the cation-radical form of the polymer to the neutral one). In this case, according to the concepts accepted in the literature, protons act as the counterions during doping/dedoping (oxidation/reduction). This is very important, because, in this case, there are no diffusion limitations (Grotthuss mechanism). Correspondingly, the rate of the redox reaction will increase. Sulfuric acid molecules in the electrolyte fill the pores of the composite; therefore, protons can freely move within the matrix and cannot limit the rate of doping-dedoping. The linear dependence indicates that the charge transfer is not considerably retarded in the bulk composite coating. In accordance with the Randles-Ševčik equation for reversible electron transfer involving freely diffusing species, the dependence of the peak current on the square root of potential scan rate should be linear [18]. In our case, no root dependence is observed. In the presence of electrochemically active species adsorbed on the electrode surface, the dependence should be linear [18]. In the novel composite, all redox species are firmly attached to the electrode surface. From the bilogarithmic curves (Figs. 4d and 4e), the exponents for $I_{\text{max}} \sim V^x$ of 1.21 (peak A) and 0.89 (peak B) are determined; this also brings the dependence closer to linear one. For quasi-reversible processes ($\Delta E >$ 120 mV), the potential difference between the anodic and cathodic peaks will increase. If the redox-active species are adsorbed, this will not take place. In the case of the RGO-PPD-SiW composite (Fig. 4a), the potential difference between the anodic and cathodic peaks is 15.5 mV (peak A) and 52 mV (peak B).



Fig. 3. (1) CVA of synthesis of RGO–PPD–SiW on the SPCE + GO electrode in 10^{-2} M OPD + 10^{-3} M SiW solution in 1 M H₂SO₄ and (2) CVA of SPCE + RGO–PPD–SiW in 1 M H₂SO₄. Potential scan rate is 50 mV/s.

Earlier [19], the formation of RGO–PPD composite was studied. It was found that when the GO film, which was applied onto the electrode, was impregnated with the OPD solution, OPD was firmly attached to the GO nanosheets; GO started to oxidize the monomer and was reduced. The oxidation of the monomer initiated the polymerization and the formation of the RGO-PPD composite. After the impregnation, GO was washed, placed into 1 M H₂SO₄ solution, and potential was cycled in the range from -250to +450 mV. The observed increase in the current was the evidence for further synthesis of the composite, which was conventionally named (RGO-PPD)1. Then, the potential was cycled in the range corresponding to the synthesis of the PPD polymer with no additives, i.e., up to 1.2 V, and the current increased from cycle to cycle. This phase of the composite was designated (RGO-PPD)2. The main methods of fixing OPD on GO are the formation of hydrogen bonds between various oxygen-containing groups of GO and protons at nitrogen atoms in OPD (because everything occurs in the acidic medium, 1 M H₂SO₄) and the interaction of aromatic rings of OPD with double bonds in GO, which lie in the parallel planes $(\pi - \pi$ stacking). When SiW, which has several redox transitions, is added to such a system, the variety of bonds between GO and OPD and the binding of OPD to SiW can lead to the additional redox peaks, for example, peak B.

In [9], we studied the impedance spectra for PPD, GO and RGO–PPD, PPD–SiW, and RGO–PPD–SiW composites at –200 mV, because at approximately this potential, the redox peaks of pure PPD and RGO–PPD composite are observed in the CVA, and



Fig. 4. (a) CVA of SPCE + RGO–PPD–SiW in 1 M H₂SO₄, potential scan rates: 20, 40, 50, 100 mV/s; (b) and (c) dependences of current in peaks A and B on the potential scan rate; (d) and (e) dependences of $\ln(I_{max})$ on $\ln(V)$ for peaks A and B.

for the RGO–PPD–SiW composite, a wide peak is also observed at approximately this potential. It was shown that at -200 mV, the conductivity of RGO–PPD–SiW is higher than that of PPD and RGO–PPD.

It was of interest to study the electrochemical properties of RGO–PPD–SiW in the range of anodic peak at 500 mV and compare them with the previous potential region, where almost a plateau is observed in the CVA (at approximately 200 mV).

Impedance Spectra of RGO-PPD-SiW Composite

Figures 5 and 6 show the impedance spectra for PPD and RGO–PPD–SiW at the potentials of -200, +200, and +500 mV. Figure 5 also shows the equivalent circuit that adequately describes the behavior of both pure polymer and the composite. The equivalent circuit is widely used to describe the electroactive polymers, composite materials, and supercapacitors based on them [20–22]. It consists of the electrolyte



Fig. 5. The Nyquist diagrams. On the left: a general view, on the right: the same curves on a larger scale. The spectra are obtained at the potentials of -0.2 V (triangles), 0.2 V (squares), and 0.5 V (circles) for PPD (open symbols) and RGO–PPD–SiW composite (solid symbols). The results of fitting are shown with lines.

resistance R_s , the Faradaic film resistance R_f , which is inversely proportional to the electric current associated with the electron hopping mechanism in the bulk redox polymer or composite containing redox-active centers. The electron hopping is accompanied by the diffusion of protons in the film, which is associated with the proton-exchange properties of heteropolyacids incorporated into the composite [6, 7]. The Faradaic pseudocapacitance in the form of constant-phase element CPE_n simulates the accumulation of charge in the film [23]. In contrast to the pure polymer, in the composite, this mechanism is more pronounced due to an addition of redox centers from POM. Therefore, for the polymer, the proton-exchange properties are much weaker, and CPE_p is not used. As indicated in [24], the ideal impedance spectrum is rarely observed for real redox polymers. For real systems, the low-frequency limit is commonly a straight line at an angle less than 90° to the X axis; therefore, a capacitancetype constant-phase element was chosen [25]. The double-layer capacity is also simulated by the constant-phase element CPE_{dl} that takes into account the energetic and morphological inhomogeneity of film surface.

Table 1 lists the parameters of equivalent circuit for spectra presented in Figs. 5 and 6. It should be noted that, as well as in our previous work [9], in order to compare various films, the resistance R_f and the Faradaic pseudocapacitance CPE_p -T were normalized to the anodic peak currents as a measure (to the first approximation) of the amount of redox-active polymer in the studied systems. In Table 1, this is indicated by subscript "norm."

	Normaliza- tion factor <i>I</i> _{max} , A	$E_{\mathrm{appl}},$ V	$R_{\rm f}, \Omega$	$R_{\rm fnorm}, \Omega {\rm A}$	CPE _p -T, F	CPE _p -T _{norm} , F/A	CPE _p -P	CPE _{dl} -T, F	CPE _{dl} -P	$R_{\rm s},$ Ω
RGO– PPD– SiW	1.1×10^{-5}	-0.2	465	2.1×10^{-3}	9.4×10^{-5}	21.2	0.95	1.0×10^{-5}	0.68	10.7
		0.2	404	1.8×10^{-3}	4.5×10^{-5}	10.1	0.91	5.2×10^{-6}	0.71	10.5
		0.5	345	1.5×10^{-3}	2.0×10^{-5}	4.5	0.92	2.7×10^{-6}	0.76	10.6
PPD	4.4×10^{-6}	-0.2	2715	3.0×10^{-2}	4.6×10^{-5}	4.1	0.94	5.8×10^{-6}	0.72	15.7
		0.2	9.39×10^{6}	104	_	—	_	4.2×10^{-7}	0.87	16.2
		0.5	1.77×10^{7}	197	_	_	_	1.3×10^{-7}	0.93	16.1

 Table 1. Parameters of equivalent circuit for spectra presented in Figs. 5 and 6



Fig. 6. The Bode diagrams. The spectra are obtained at the potentials of -0.2 V (triangles), 0.2 V (squares), and 0.5 V (circles) for PPD (open symbols) and RGO–PPD–SiW composite (solid symbols). The results of fitting are shown with lines.

From the data of electrochemical impedance spectra, the following conclusions were drawn:

(1) At the potential of inherent polymer redox activity of -0.2 V, the impedance spectra of both pure polymer and composite are close; they can be described by a common equivalent electrical circuit.

(2) In the case of pure polymer, with an increase in the potential (0.2 and 0.5 V), the CPE_p element is excluded from the equivalent circuit due to the apparent absence of electrochemical reaction. This can be seen both from an abrupt increase in the resistance R_f and from the absence of peaks at the aforementioned potentials in the CVA.

(3) For the composite, the film resistance $R_{\rm f}$ decreases monotonically with increasing potential. This can be associated with the redox activity of other composite components (see Fig. 4a).

(4) For the composite, the Faradaic capacitance CPE_p -T decreases with increasing potential, probably, because the polymer ceases to participate in the redox reaction.

Electrocatalytic Properties of RGO–PPD–SiW Composite

The mediator-assisted electrocatalysis requires a high rate of the catalyst redox reaction, which depends

on the number of electrons and protons in the nearsurface reaction layer. The number of electrons in the reaction layer depends on the conductivity of the electrode, in our case, composite coating. According to the impedance data, the conductivity of RGO–PPD– SiW is by several orders of magnitude higher than that of the redox polymer (PPD); therefore, it should be expected that the novel composite will exhibit the properties of mediator catalyst.

Figure 7a shows the CVA for SPCE + RGO-PPD-SiW in (1) 1 M H_2SO_4 and (2) 10^{-3} M solution of hydroquinone (HQ) in 1 M H₂SO₄. For comparison, Fig. 7b shows the CVA for pure SPCE. It is seen that the reversibility of reaction is significantly lower on the unmodified electrode. The dependence of the HQ oxidation current in the anodic peak (B') on the potential scan rate (Fig. 7c) is nearly linear (dashed line). Figure 7d shows the same dependence on the bilogarithmic coordinates. From this plot, it was determined that $I_{\text{max}} \sim V^{0.72}$. The relationship is neither root nor strictly linear. In addition, the difference between the anodic and cathodic peaks is only 30 mV, which indicates the reversibility of the reaction. We can suppose that the adsorption of hydroquinone on the composite surface makes a contribution by affecting the exponent at V. Then, the Q/HQ redox transition on the modified electrode is a reversible and surface-controlled electrochemical process [26].



Fig. 7. (a) CVA of SPCE + RGO–PPD–SiW in (curve *I*) 1 M H₂SO₄ and (curve *2*) 10^{-3} M hydroquinone solution in 1 M H₂SO₄; (b) CVA of SPCE in 10^{-3} M hydroquinone solution; (c) dependence of current in peak B' on the potential scan rate; (d) dependence of ln(I_{max}) on ln(V).

The RGO-PPD-SiW mediator catalyst has a similar effect also on the $K_3[Fe(CN)_6] \leftrightarrow K_4[Fe(CN)_6]$ redox reaction (Fig. 8).

Comparing CVAs for (b) the pure electrode and (a) the electrode modified with RGO-PPD-SiW, we can see the application of the composite onto the electrode surface raises he reversibility of reaction. It should be noted that the distances between the anodic and the corresponding cathodic peaks varies only from 30 to 80 mV with increasing potential scan rate. The reversibility of the redox peaks B', as well as the nearly linear dependence of $I_{\rm max}$ on the potential scan rate (Fig. 8c), also correspond to the surface-controlled electrochemical process involving a mediator catalyst. From the bilogarithmic dependence (Fig. 8d), an exponent of 0.75 is obtained, i.e. $I \sim V^{0.75}$. This result is similar to the result obtained for hydroguinone. In the case of the diffusion control, the peak currents in the CVA are directly proportional to the square root of the potential scan rate. In a surface-controlled process (also known as the process controlled by adsorption), the peak currents are linearly proportional to the potential scan rate [26]. For the

 $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ and Q/HQ redox reactions, which proceed on the surfaces modified with the novel composite, PPD and POM, which are fixed in the porous matrix, serve as the mediators. Hydroquinone or ferrocyanide is present in the electrolyte that impregnates the matrix. Therefore, there can be no diffusion limitations for such processes. In addition, the adsorption of dissolved species on the modified electrode is not excluded. If the exponent at the potential scan rate on the bilogarithmic coordinates is 0.5, we can speak of the diffusion control in accordance with the Randles-Ševčik equation. When the exponent at V is higher than 0.5, we are talking about adsorption [27], which itself plays an important role for the electrocatalysis, including the mediatorassisted electrocatalysis. If the exponent at V were equal to one, we could suppose that both redox couples $(K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ and Q/HQ) are firmly attached to the electrode and behave similarly to the redox-active composite (Fig. 4). The exponents of 0.72 (for the quinone/hydroquinone couple) and 0.75 (for the ferro/ferricyanide couple) are most likely due to a combination of two factors: the adsorption of



Fig. 8. (a) CVA of SPCE and (b) CVA of SPCE + RGO–PPD–SiW in 10^{-2} M K₃[Fe(CN)₆] + 10^{-2} M K₄[Fe(CN)₆] solution in 1 M H₂SO₄; (c) dependence of current in peak B' on the potential scan rate; (d) dependence of ln(I_{max}) on ln(V).

reacting species and the effect of mediator-assisted catalysis.

CONCLUSIONS

A novel composite material based on reduced graphene oxide, poly-o-phenylenediamine, and silicotungstic acid is fabricated. The composite exhibits redox activity in a wide range of potentials. Using the method of electrochemical impedance, it is shown that the resistance of the polymer film is by 4-5 orders of magnitude higher than that of the composite. Due to the fact that the composite retains the faradaic pseudocapacitance in the studied potential range $(\sim 0.9 \text{ V})$, it becomes possible to use it as the material for supercapacitors. In addition, the composite has pronounced properties of mediator catalyst. The model electrochemical redox reactions for guinonehydroquinone and ferro-ferricyanide couples on the planar electrode coated with the novel composite proceed with a high reversibility under the surface control of the mediator-assisted reaction. The novel material has proven itself well when operating with a planar electrode. This can be used to develop the catalysts and sensors based on RGO-PPD-SiW.

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CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interests.

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