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One-pot electrosynthesis and physicochemical properties of multifunctional material based on graphene oxide, poly-o-phenylenediamine, and silicotungstic acid

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Abstract

The methods of silicotungstic acid (SiW) immobilization on conducting substrates were studied. For SiW immobilization by codeposition, poly-o-phenylenediamine (PPD) redox polymer was used. The most effective codeposition of SiW and PPD was demonstrated on a graphene oxide (GO) film. Meanwhile, GO is reduced to form RGO-PPD-SiW electroactive composite. The structure of the novel material was evidenced by cyclic voltammetry and IR and Raman spectra. PPD-SiW and RGO-PPD-SiW composites were studied by impedance spectroscopy, where an equivalent circuit was proposed. Film resistance $R_{\rm f}$ was shown to decrease in the series of PPD \rightarrow RGO-PPD \rightarrow RGO-PPD-SiW. Further, RGO-PPD-SiW has better transfer properties (bulk film diffusion rate). This enabled suggesting that the composite has better electrocatalytic properties than PPD and RGO-PPD as was evidenced for example of $[\text{Fe}(\text{CN})_6]^{4-/3-}$ redox transfer on the electrode coated with the novel material.

Keywords Silicotungstic acid · Graphene oxide · Poly-o-phenylenediamine · Modification

Introduction

Due to their various properties, polynuclear metal oxide complexes (polyoxometalates or POMs) draw attention of experts in a wide range of sciences and applications. POMs are used in catalysts, photochemistry, material science, and medicine [1–3]. Heteropolyacids (HPAs) can be considered a POM subclass. For example, a silicotungstic acid (SiW)-based composite takes part in photocatalytic decomposition of methyl orange [4] and can be used for decomposition of some organic impurities to purify water. A range of POMs in nanomolar quantities can inhibit CK2 specific kinase protein, which enzyme is highly active in some cancer diseases [3]. The unique behavior of POM is its capacity of accepting up to 24 electrons

E. Yu. Pisarevskaya elena_pisarevska@bk.ru per one cluster [5]. Along with other properties, this determined numerous POM applications.

It was especially interesting to use POMs as redox mediators (RM), which take a key part in acceleration of electrochemical reactions [6], for example, in electrocatalysis, energy accumulation, and conversion systems (rechargeable batteries and supercapacitors), and in the sensors detecting biologically active substances. So a great attention is paid to both experimental and theoretical studies of RM influence to the electrochemical systems making the basis of redox mechanisms and reaction kinetics. With respect to the reaction media, where RMs are used, they are classified as bulk and solid state interface. If introduced to an electrochemical system, RM can radically alter the chemistry, in particular, significantly decrease polarization of the electrode reaction.

The catalytic properties of heteropolyoxometalates have been sufficiently studied and are interesting for their use as mediators in catalysis of some electrochemical processes. Mediators enable accelerating the heterogeneous process of electron transfer between the substrate and the electrode if complicated for some reasons. Furthermore, a redox active catalyst can be used in selective sensors [7, 8].

To achieve these purposes, heteropolyanions should be immobilized on a substrate. The substrate to be selected for immobilizing an active catalyst or sensor material will depend

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upon the type of catalytic reaction. For example, to catalyze glycerol oxidation to acrolein, Al_2O_3 is impregnated with silicotungstic acid solution and further calcined [9]. In the case of electrochemical catalysts, a conducting electrode material serves as the catalyst substrate. The general POM immobilization methods are specified in [7]. These methods rely on the basic POM properties: adsorption of some POMs on the electrode surface, POM inclusion in the polymer coating in the course of synthesis, and POM electrodeposition on electrode from solution in potentiostatic mode (E = -1.2 V, SCE).

According to [7], POMs can be reliably integrated in the polymer matrix by two methods. First, POMs can be electrostatically drawn into the polymer preformed on the electrode surface (two-step method), wherein polymer-coated electrodes are impregnated with POM-containing solutions. Second, POMs can be immobilized along with oxidative electropolymerization in the POM presence (single-step method). The same study states that the interaction between polymers and POMs is stronger than the interaction between polymers and smaller counter ions such as, for example, sulfate, chloride, and perchlorate in the electrolyte solution. Therefore, POMs can be effectively immobilized in a polymer matrix to prevent their exchange with anions from the bulk electrolyte solution that is accounted for by spatial hindrance due to bulky POMs. In most cases, electrochemical polymer-integrated POMs behave virtually like in a solution. In some cases, the polymeric medium affects the behavior of immobilized heteropolyanion [7].

Regarding the electrode material as the POM substrate, Pt or Au metals are less suitable for these purposes due to release of hydrogen at cathodic potentials and oxygen at anodic potentials. Therefore, in this case, we consider more suitable, for example, ITO or SnO_2 sprayed glasses or carbon materials.

Unlike GO + SiMo composite formation, which we studied earlier [10], SiW is not adsorbed on carbonaceous substrates. Given that SiW is a rather promising material from existing HPAs, and continuing our studies of GO used as the basis for molecular design, it was interesting to study GO-SiW or RGO-SiW composite. As compared to SiMo, CVA of SiW shows redox peaks at further cathodic potentials. In an acid aqueous solution, SiW demonstrates five redox transitions, wherein three further cathodic peaks are reversible (with respect to pH, about - 0.22, - 0.42, and - 0.58 V vs. SCE). Two more anodic peaks are accompanied with HPA irreversible decomposition [7]. SiMo also demonstrates five transitions, wherein three reversible ones are between 0 and 0.4 V [10, 11] falling beyond the range of irreversible redox potentials for SiW. Therefore, it seems interesting to prepare the materials that could have a different application field, for example, in sensors being active in the ranges of potentials, where SiMo demonstrates no electroactivity.

We have earlier discussed [10, 12, 13] introduction of redox particles in graphene oxide (GO)-based materials. As we have already shown, GO and RGO-PPD composite thereof are good

bases for introduction of various particles. We proposed a simple method of preparing an RGO-PPD composite [13]. We showed that the contact of GO film applied on an electrode with OPD monomer initiates the redox reaction, wherein OPD is oxidized and partially polymerizes, and GO is reduced to RGO. This composite was arbitrarily referred to as RGO-PPD. If GO is exposed in an OPD solution for some time and then rinsed with twice-distilled water and potential is cycled in a narrow range between - 400 and 450 mV in 1 M H₂SO₄ without monomer in the bulk solution, the composite is further synthesized with participation of OPD adsorbed by GO nanosheets. This composite was referred to as (RGO-PPD)1. Finally, upon shifting to potential of PPD synthesis (1.2 V), also without monomer in the solution, we prepared (RGO-PPD)2 composite. This classification was somewhat arbitrary but the composites differed in CVA with respect to the aforesaid conditions; therefore, the prepared composite types should be differently referred to. Unlike the synthesis of (RGO-PPD), (RGO-PPD)1, and (RGO-PPD)2 composites, which is initiated by impregnating GO films with an OPD monomer solution, we obtained no clear experimental evidences that the synthesis of PPD-SiW, GO-SiW, and GO (or RGO)-PPD-SiW can be initiated similarly. Therefore, we attempted codeposition of SiW together with PPD polymer when synthesized on GO film based on our assumptions that due to various surface bonds GO is a good basis for molecular design [10]. To this end, we first prepared a GO film (by pouring GO slurry on SnO₂ glass). Further, we attempted a precaution: to prepare RGO-PPD-SiW composite without uncontrolled growth of PPD polymer, which could suppress other possible processes, we selected the "short synthesis" like that for the synthesis of (RGO-PPD)1 composite, which approach was to prevent achievement of the PPD polymerization potential [13]. Meanwhile, due to mediator catalysis with the interaction of GO and OPD, PPD synthesis takes place at smaller anodic potentials with simultaneous GO reduction to RGO [10, 12, 13].

POM composites with nanotubes or reduced graphene oxide (RGO) can be further used as electrode materials to save power in electrochemical pseudocapacitors [5]. As we know, pseudocapacitors achieve their high capacity due to addition of the electrochemical double layer capacity to pseudocapacity (Faradaic pseudocapacity) arising from reversible redox reaction. Due to their high proton mobility and high redox activity, the protonated POM (heteropolyacid or HPA) based materials can become perfect components for supercapacitors. The same study described use of POM composites with polymers in preparation of proton-exchange membranes for fuel cells [5].

Earlier, we have already attempted immobilizing SiW by codeposition with OPD on a GO-coated substrate [14]. Now, we are going to compare different methods of SiW immobilization.

The goal of this work was a comparative study of the methods for synthesis of an electroactive composite coating containing immobilized silicotungstate as a mediator of electrode redox reactions on different conducting substrates as well as a study of its electrochemical behavior.

Instruments and materials

We used two types of electrodes: glass spray-coated with SnO_2 conducting layer and planar screen printed carbon electrode $SPCE^1$, Fig. 1. The operation with SnO_2 electrode used a three-electrode electrochemical cell with an Ag/AgCl reference electrode. The measurements with SPCE were carried out in a solution droplet (about 30 μ L) placed on the electrode surface.

To apply GO films on the substrate, we used a 1:3 diluted aqueous GO (5 g/l) produced GRAPHENOX Ltd^2 , which was micropipetted and spread over the electrode surface.

In RGO-PPD synthesis on SPCE a droplet of aqueous GO dispersion was applied and dried on the electrode. A droplet of OPD solution in 1 M H_2SO_4 was applied on the SPCE with GO film and exposed for 2.5 h. Then, CVA was recorded in the same droplet.

SiW and o-phenylenediamine (OPD) monomer (Aldrich) were used as received.

(RGO-PPD)1 composite was synthesized according to the method described in [13]. Upon micropipetting GO dispersion on the electrode and drying, the system was exposed in 0.05 M OPD + 1 M H₂SO₄ solution. Then the electrode was rinsed, dried, placed in 1 M H₂SO₄ and polarized under cyclic potential scanning between 450 and – 400 mV. With a higher upper polarization limit, for example, up to 1200 mV, CVA takes a different form, and the prepared composite was referred to as (RGO-PPD)2.

SiW and PPD codeposition was carried out from 10^{-2} M OPD + 10^{-3} M SiW solution in 1 M H₂SO₄.

The electrochemical studies were carried out with an IPCcompact³ potentiostat-galvanostat.

The impedance spectra were recorded with a P-45X potentiostat-galvanostat equipped with an FRA-24 M^4 frequency response analyzer unit. EIS measurements were performed in 10^6-10^{-1} Hz with 10 mV ac perturbation in potentiostatic mode.

In three-electrode cells, potential was measured against saturated Ag/AgCl electrode. A platinum gauze was used as the counter electrode.



Fig. 1 SPCE. (1) Working electrode (graphite paste), (2) Counter electrode, (3) Reference electrode (Ag/AgCl), (4) Insulator, (5) Terminals. Electrode dimensions, 8×28 mm

IR spectra were recorded with a Perkin Elmer System 2000 FT-IR spectrometer equipped with a diffuse reflection unit.

Raman spectra were recorded with a Renishaw inVia Reflex spectrometer with the following experimental parameters: laser source wavelength 633 nm, used lens \times 20, and radiation power under 0.5 mW.

Results and discussion

SiW + PPD on SnO₂

Our aim was to provide optimum SiW immobilization on a conducting substrate. As aforementioned, unlike SiMo, this HPA forms no strong bonds with carbon materials. Since one of POM immobilization options is introduction in a polymer, we attempted PPD synthesis in the presence of SiW.

Figure 2a shows CVA of codeposition in 10^{-2} M OPD + 10^{-3} M SiW solution in 1 M H₂SO₄. Then, the electrode together with the film were rinsed and placed in 1 M H₂SO₄, Fig. 2b.

We see that currents gradually decrease; therefore, the prepared PPD + SiW film is unstable and this method of SiW immobilization fails to provide a reliable result.

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⁴ Produced by Electrochemical Instruments (Chernogolovka, Moscow Region). http://potentiostat.ru



Fig. 2 SiW and PPD codeposition on SnO_2 in 10^{-2} M OPD + 10^{-3} M SiW solution in 1 M H₂SO₄ (**a**). CVA of PPD-SiW on SnO₂ in 1 M H₂SO₄ (**b**)

RGO-PPD-SiW on SnO₂

Figure 3 shows CVA recorded on the SnO₂ sprayed glass with GO film applied in 10^{-2} M OPD + 10^{-3} M SiW solution in 1 M H₂SO₄. The gradually increasing current from cycle to cycle evidences the growth of some electroactive coating. However, this figure does not enable concluding whether only (RGO-PPD)1 composite [13] is synthesized or SiW is also deposited. When the current growth ceased, the electrode was rinsed and placed in 1 M H₂SO₄, and CVA was recorded at various cathodic limits of potential cycling. Figure S1 (1–4) shows CVA recorded under these conditions.

We see that the more potential shifts to the cathodic region, the more expressed is SiW contribution. Remind that there are no redox active particles in the solution.

SPCE

Along with SnO₂ sprayed glasses, we also used SPCE. These electrodes allow carrying out studies in a small volume of



Fig. 3 SiW and PPD codeposition on SnO₂-supported GO film in 10^{-2} M OPD + 10^{-3} M SiW solution in 1 M H₂SO₄

solution as well as they can be used in sensors, especially upon modifying their surface with other materials.

Figure 4 shows final CVA for the synthesis of (RGO-PPD)1 composite on SPCE in a droplet of 1 M H_2SO_4 . We see that the form of these curves is approximately the same as in our earlier studies with other electrode materials (glassy carbon, SnO₂) [10, 13]. Therefore, SPCE is also suitable for the synthesis of composite.

PPD-SiW on SPCE

Figure 5a shows CVA for the synthesis of PPD-SiW composite in 10^{-2} M OPD + 10^{-3} M SiW solution in 1 M H₂SO₄. We can see the growing current in the course of synthesis, whereas the shape of curves differs from those characterizing the synthesis of unmodified PPD in the absence of SiW. Figure 5b shows CVA recorded in a droplet of 1 M H₂SO₄ after the synthesis of PPD-SiW composite. A comparison of Fig. 5a



Fig. 4 CVA in 1 M $\rm H_2SO_4$ for SPCE-GO after OPD solution exposure for 1.5 h



Fig. 5 Synthesis of PPD-SiW composite on SPCE (CVA in 10^{-2} M OPD + 10^{-3} M SiW solution in 1 M H₂SO₄) (**a**). CVA after synthesis of PPD + SiW composite (**b**)

and **b** demonstrates the currents strongly decreasing upon rinsing the electrode coated with the composite. In other words, under the given conditions of synthesis, like in the case of SnO_2 , a portion of PPD-SiW composite is weakly attached to the substrate or SiW anions are poorly captured in the course of polymer synthesis.

To strengthen SiW capture by the polymer, we slightly altered the method of synthesis, namely, shifted the upper limit of potential scan to the anodic region by 50 mV (Fig. S2a). We see that this shift of the anodic limit of synthesis to 1.25 V yielded a more stable SiW composite (Fig. S2b).

RGO-PPD-SiW on SPCE

Further, we carried out the synthesis of RGO-PPD-SiW composite on SPCE. To this end, SPCE was preliminarily coated with GO film. Figure S3 shows continuous CVA of synthesis and its gradual changes Fig. 6a–e. Unlike the aforementioned synthesis on SnO₂ electrode, here, we used a somewhat different cathodic potential limit, where the contribution of SiW is clearly seen.

Figures 6e and 7a show that the synthesis of composite yields a redox active material having several redox transitions.

Figure 7b shows current vs. potential scan rate for the anodic peak at -0.55 V. The linear dependence evidences no significant deceleration of charge carriers in the bulk electrode, therefore their transfer speed is sufficiently high and controlled only by proton diffusion from the solution to the electrode surface.

IR spectra

Figure 8 shows IR spectra of silicotungstic acid powder and PPD, PPD-SiW, and RGO-PPD-SiW films applied on SnO₂ sprayed glasses. The authors of [15] carried out the theoretical simulation for IR spectrum of $[SiW_{12}O_{40}]^{4-}$ and distinguished the major vibration frequencies for W=O, W-O, Si-O, and W–O–W bonds between 378 and 1011 cm⁻¹. The strongest bands are observed at 785 and 920 cm⁻¹. A comparison of spectra of unmodified SiW and its composites with PPD and GO-PPD clearly demonstrates the presence of heteropolyanion within the said wavelength range. In the case of RGO-PPD-SiW, we see some changes caused by the interaction of HPA and PPD. For example, the band at 874 cm^{-1} (Si–O, W–O–W) splits into two bands at 882 and 833 cm⁻¹ due to the interaction of SiW with the polymer as well as with RGO. The interaction of SiW with the polymer is also evidenced by Raman spectra (spectrum of the composite shows a split band of the polymer at 600 cm^{-1} , Fig. 9).

As to attribution of other bands, GO appears at 1746 cm⁻¹, in which the wavelength corresponds to C=O (carbonyl/ carboxy) stretching vibrations, 1654 cm⁻¹ C=C (aromatics), but this band may be also attributed to the aromatic structures in PPD, 1232 cm⁻¹ C–O (alkoxy) [13]. The fact of low intensity of the peaks corresponding to oxygen-containing groups evidences a significant reduction of GO to RGO in the composite formation.

PPD contributes to the bands of C=C (benzenoid) at 1512 cm^{-1} for PPD-SiW and 1507 for RGO-PPD-SiW; 1654 cm^{-1} C=N (quinoid) for RGO-PPD-SiW composite and close values for PPD-SiW [13].

Raman spectra

The structural properties of PPD-SiW and RGO-PPD-SiW nanocomposites were characterized by Raman spectroscopy. Figure 9 shows the spectra of GO-based composite comprising two well-expressed characteristic peaks at 1331 cm⁻¹ (D band) and 1603 cm⁻¹ (G band), respectively, due to the that structural defects and planar vibrations of sp² carbons [16]. Given a high intensity ratio ID/IG = 1.66 of D and G bands, we can surely assume that in the course of electrochemical composite synthesis, GO is reduced to RGO that is further evidenced by [16] and our earlier studies [13, 17].

PPD spectrum (Fig. 9) shows characteristic bands at 606 cm^{-1} for Def (ring), 1160 cm^{-1} (C–H), 1368 cm^{-1} (C–N⁺), and 1478 cm^{-1} (C–N) [18–20]. Our records further show a band at 750 cm^{-1} . Most probably, it can be also attributed to



Fig. 6 Consequent CVA changes in the course of RGO-PPD-SiW composite synthesis



Fig. 7 CVA of RGO-PPD-SiW composite synthesized on SPCE in 1 M H_2SO_4 at various scan rates, mV/s (a). First anodic peak (peak I) current vs. scan rate (b)

Def (ring). Several spectral bands at $\lambda > 600 \text{ cm}^{-1}$ were recorded but not discussed in details [20].

Thus, the spectra of both PPD-SiW and RGO-PPD-SiW composites show the characteristic peaks of SiW and PPD in the low wavelength region.

Impedance studies

All measurements were carried out on SPCE. We studied the following systems: GO, RGO-PPD, PPD, PPD-SiW, and RGO-PPD-SiW. Figure 10 shows pre-impedance CVA for these samples.

Pre-impedance CVA

To compare the shape of CVA for the studied samples, the curves were normalized by the anodic peak current (at $E \approx -220 \text{ mV}$) since it is proportional to the weight of polymer. All four CVA curves except GO (Fig. 10) show an anodic peak at $E \approx -220 \text{ mV}$ attributed to the redox reaction of PPD dopingundoping. The corresponding cathodic peak is shifted to the cathodic region more strongly in the series of PPD (-237 mV) < PPD-SiW (-270 mV) < RGO-PPD -SiW (-320 mV) < RGO-PPD (-410 mV). Formally, this fact evidences lower



Fig. 8 IR spectra of SiW powder and PPD, PPD-SiW, and RGO-PPD-SiW films applied on SnO_2 sprayed glasses

process reversibility upon the polymer modification but it may also be due to the contribution of SiW own redox activity.

The presence of strongly expressed process for RGO-PPD-SiW (anodic peak at + 450 mV and corresponding cathodic peak at + 340 mV) and its absence for PPD-SiW allows attributing to the properties of heteropolyacid bound with graphene oxide. Similarly, there are weakly expressed processes at + 200/+ 100 and - 50/- 100 mV that also correspond to the redox behavior of SiW.

Post-Impedance CVA changes

Figure S4 shows the pre- and post-impedance CVA of the polymer-containing samples (PPD, PPD-SiW, RGO-PPD-SiW). We see reversible CVA evidencing no degradation of the polymer in the course of impedance measurements. The polymer-graphene oxide composite (RGO-PPD) changed insignificantly: pair of redox peaks shifted to the cathodic region



Fig. 9 Raman spectra of PPD, PPD-SiW, and RGO-PPD-SiW films applied on SnO₂-sprayed glasses



Fig. 10 Sample CVA normalized on anodic peak current at $E \approx -220$ mV. Scan rate 50 mV/s, cycle 5. (1) PPD, (2) RGO-PPD, (3) PPD-SiW, and (4) RGO-PPD-SiW

by 100 mV (probably, the composite partially degraded despite of no essential change in the total charge).

Impedance at E = -200 mV peak of polymer own redox activity

The electrochemical properties of the prepared composites were compared at the anodic peak potential in the CVA of initial polymer. According to the spectra (Figs. 11 and 12), within the studied frequency range at E = -200 mV, all samples can be formally described by the same equivalent electric circuit (Fig. 11a) [21, 22]. R_s is the high-frequency limit of the impedance-frequency dependence (|Z| vs. f), which simulates the resistance of bulk electrolyte in the cell. $R_{\rm f}$ is the film resistance that is inversely proportional to the polymer oxidation/reduction rate in the bulk film. CPE_f is the constant phase element simulating the double layer capacity at the film/ solution interface, $Z_{\text{CPE}} = T^{-1} \times (j\omega)^{-P}$, where T is a factor similar to capacity and *P* is the exponent. If $1 \ge P \ge 0.7$, then, CPE simulates the capacity behavior (distributed capacity arising due to irregular energy or geometry as well as coarse surface or electrode porosity, unlike the "perfect capacity", where P = 1 [23].

The diffusion of ions (protons) in the bulk polymer film is simulated by the Warburg open circuit terminus of finite length W_0 . It comprises three parameters: *W-R*, diffusion resistance; $W-T = \frac{L^2}{D}$, characteristic diffusion time being the ratio of effective film thickness square to effective diffusion coefficient (the lower is W-T, the faster is diffusion of protons); and $W-P \approx 0.5$, exponent.

Analysis of equivalent circuit parameters

A criterion of good redox polymer-mediated electrocatalysis is a high polymer redox reaction rate, which depends upon the



Fig. 11 Nyquist plots of samples exposed for 10 min at E = -200 mV: a general view + equivalent electric circuit and b enlarged view

amount of electrons and protons in the subsurface reaction layer. The amount of electrons in the reaction layer depends upon the electron conductivity; in our case this is the conducting polymer film. The amounts of protons in the reaction layer depend upon their diffusion rates from the solution through the conducting polymer film. The same can be attributed to active composites.

Upon normalizing the film resistance R_f by the anodic peak current at E = -200 mV, we see that unmodified PPD has the highest normalized resistance R_f norm (Table S1) and PPD-

SiW composite has the lowest resistance (lower by two orders of magnitude than unmodified PPD). The film resistance $R_{\rm f norm}$ decreases in the series PPD > PPD-GO > RGO-PPD-SiW > PPD-SiW that may be accounted for by higher electron conductivity of the composite film due to both GO introduction and PPD electroactivity.

The transfer properties (proton diffusion rate in bulk film) improve in the series of RGO-PPD \rightarrow PPD-SiW \rightarrow PPD \approx RGO-PPD-SiW. The higher is the proton diffusion rate (the lower are *W*-*R* norm and *W* – *T* parameters) and the higher is

Fig. 12 Bode plots. Impedance spectra recorded for samples exposed for 10 min at E = -200 mV



the polymer redox reaction rate, the better are electrocatalytic properties of the polymer. The lowest diffusion resistance and proton diffusion rate characterize unmodified PPD and RGO-PPD-SiW composite (by an order of magnitude lower as compared to RGO-PPD and PPD-SiW). This allows assuming that unmodified PPD and RGO-PPD-SiW composite have the best catalytic properties. However, RGO-PPD-SiW composite has a higher conductivity than unmodified PPD. The given fact distinguishes RGO-PPD-SiW composite as the best electrocatalyst as compared to other electrodes.

The film capacity $CPE_f - T$ does not depend upon the polymer weight, and all composite samples have close values. Further, $CPE_f - P$ shows similar values close to 0.75 ± 0.05 evidencing strongly irregular surface of the composite film.

A special consideration should be provided for GO. Formally, GO spectrum is described by the same equivalent circuit as the PPD containing electrodes. However, in the case of GO, R_f and W-R are not normalized since GO is not electroactive in this range of potentials. The values of W-Tand GO film capacity CPE_f -T are lower by two orders of magnitude as compared to the PPD containing electrodes. The value of CPE_f -P = 0.98 is very close to the "perfect" capacity that evidences smoother and more regular surface of GO film as compared to PPD composites.

Thus, the growth of polymer globules between GO nanosheets with simultaneous capture of silocotungstate counter ions allows improving both transfer and electroactive features of the polymer. This enables assuming that RGO-PPD-SiW composite has better electrocatalytic properties than PPD and RGO-PPD.

Catalytic behavior of composite electrode

As was predicted on the basis of the impedance spectra, RGO-PPD-SiW composite film has electrocatalytic properties; Fig. 13 shows CVA for $K_3[Fe(CN)_6] + e^- \neq K_4[Fe(CN)_6]$ redox transition in acid medium on unmodified planar electrode and on SPCE coated with PPD and RGO-PPD-SiW. We see that in the curve peak bifurcates in the cathodic course for PPD: first peak appears about 130 mV and second peak appears at -237 mV. Already in [24], we showed by means of PPD-coated rotating disk electrode that the reduction halfwave potential for some substances, in particular, $K_3[Fe(CN)_6]$ on the modified electrode is near to the PPD standard (formal) potential. In this case, reactions take place at the polymer/solution interface. A further wave (in Fig. 13 at 130 mV) is observed for negatively charged redox particles, for example, $K_3Fe(CN)_6$, due to the reaction arising at the metal/polymer interface under the semi-infinite diffusion conditions. Meanwhile, in the case of RGO-PPD-SiW composite, the reaction reversibility is higher as compared to other electrodes and there is no PPD characteristic bifurcation. This evidences a mediated catalysis type reaction taking place on the polymer/solution interface on RGO-PPD-SiW composite.



Fig. 13 CVA for 10^{-2} M K₃[Fe(CN)₆] + 10^{-2} M K₄[Fe(CN)₆] solution in 1 M H₂SO₄ on SPCE, SPCE + PPD, and SPCE + RGO-PPD-SiW

Conclusions

This study of SiW heteropolyanion immobilization on various conducting substrates showed that SiW codeposition in the course of PPD synthesis provides better results in the presence of graphene oxide, which affects catalytically the process of synthesis being reduced to RGO. Thus, prepared film demonstrates redox activity at the potentials close to those of PPD and SiW own redox activity. Since the composite ingredients exhibit their own mediator properties in some reactions, it would be reasonable to assume retention of these properties in the composite structure. This may be promoted by better transfer properties of the composite as was demonstrated by means of impedance spectroscopy for example of redox-species $[Fe(CN)_6]^{4-/3-}$ reaction. Further, based on the studied electrochemical properties, this composite may be considered a promising material for use in the field of electrochemical power engineering (supercapacitors with Faradaic pseudocapacity and proton-exchange materials), in electrocatalysis and sensors.

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