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Self-Assembling Ensembles of Silicomolybdic Acid–Diamines

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Abstract—Modification of the surface of the conductive glass [conductive layer is indium–tin oxide (ITO)] by diamines (1,8-diaminooctane and piperazine) and organic polycations [poly(diallyldimethylammonium chloride) and poly(allylamine) hydrochloride] followed by the formation of electroactive composites with silicomolybdic acid $H_4SiMo_{12}O_{40}$ was carried out. The two-layer ITO/cationic/anionic coatings were shown to differ by the shape of cyclic voltammograms depending on the cationic component.

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An effective way of the surface modifying in order to obtain electroactive and photochromic coating is electrostatic layer-by-layer deposition (LbL) [1, 2]. A brief overview of some composites using electrostatic heteropolymolybdates $PMo_{12}O_{40}^{3-}$ (PMo_{12}) and $SiMo_{12}O_{40}^{4-}$ ($SiMo_{12}$) as anionic layers was given in [3]. The acids corresponding to these molybdates are available, stable, and well-studied compounds. [3, 4]. In an acidic aqueous medium both compounds undergo several stages of reduction, of which the first three redox transition are highly electrochemically reversible [3, 4]. Anions of the heteropolymolybdates can be readily chemisorbed irreversibly from acidic aqueous solutions on carbon materials (glassy carbon or carbon nanotubes) with retention of ability to subsequent interaction with organic polycations. However, in the case of the conductive glass there is a problem of forming the first layer, because the indium-tin oxides (ITO) used for making the conductive layers are incapable of chemisorption of heteropolyacids anions.

In this paper, the problem of forming coatings with $SiMo_{12}$ on the surface of ITO is solved by functionalizing the surface with diamines. Besides, to simulate the coating formed on the ITO surface we studied interaction between the diamine (or its protonated form) and $SiMo_{12}$ in solution.

The heteropolymolybdate $SiMo_{12}O_{40}^{4-}$ like the phosphomolybdic acid anion $PMo_{12}O_{40}^{4-}$ [5, 6]) practically is not fixed on the conducting glass (Fig. 1b). Poly(diallyldimethyl)ammonium chloride, poly(allyammonium chloride), 1,8-diaminooctane, and piperazine required for forming the first layer are well adsorbed on the ITO, as follows from the subsequent formation of a bilayer with $SiMo_{12}$. Due to the surface activity of poly(allyammonium chloride) and poly(diallyldimethyl)ammonium chloride, they can be deposited on the conducting glasses simply by immersing the latter into the aqueous solution of the polycation. To modify the ITO surface with diamines it is necessary to keep the electrode in the diamine alcoholic solution for a rather long time, in dark, isolated from air.

The active sites on the ITO are either negatively charged surface oxygen, O^-, or the positively charged metal centers M^+ [7]. Modifying the ITO electrode with diamine occurs as a result of adsorption of the amino group on the surface of conductive glass and the subsequent restructuring due to van der Waals and hydrogen bonding interactions. The diamine concentration in the alcoholic solution used for the application of 1,8-diaminooctane on the conducting glass is high enough (5×10^{-3} M), and the formation of

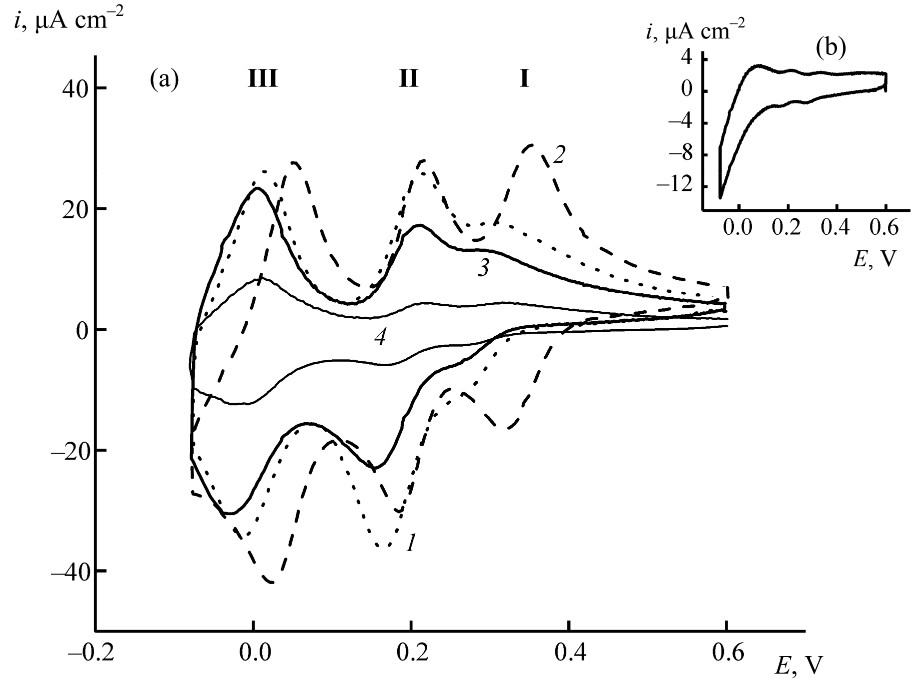


Fig. 1. Voltammograms of the initial anionic $SiMo_{12}$ layers assembled by LbL method through assembled cationic layers: (*1*) poly(diallyldimethylammonium chloride), (*2*) poly(allylamino)hydrochloride, (*3*) 1,8-diaminooctane, and (*4*) piperazine, adsorbed preliminary on (a) an ITO electrode and (b) $SiMo_{12}$/ITO electrode.

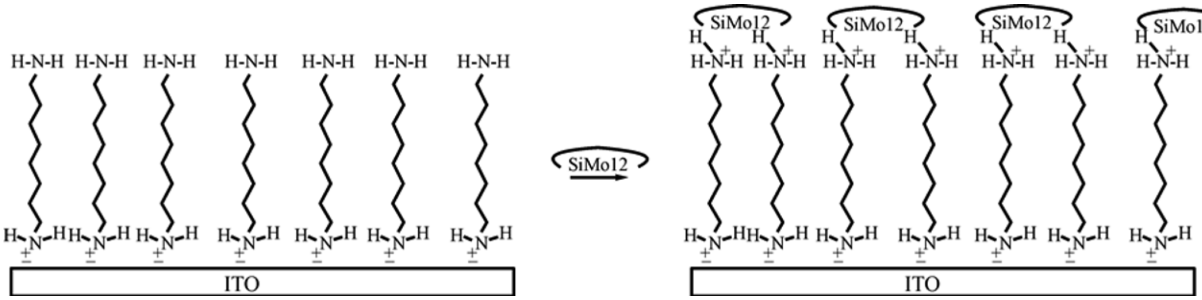
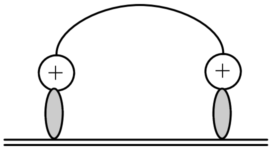


Fig. 2. The scheme of formation of double-layer coating ITO/1,8-diaminooctane/$SiMo_{12}$.

Ω-structures [8] based on it would lead to a strain in the molecule. Therefore the probability of adsorption of 1,8-diaminooctane on ITO to form structures like those shown in Scheme 1 at these concentrations of diamine is rather low.

Scheme 1.



As a result, free amino groups that conserve the nucleophilic properties are capable of forming the second (anionic) layer through the formation of acid–base complex with a strong Brønsted acid, $H_4SiMo_{12}O_{40}$. Figure 2 shows the formation of the ITO/1,8-diaminooctane/$SiMo_{12}$ coating.

Figure 1a shows cyclic voltammograms of initial anionic $SiMo_{12}$ layers assembled by the LbL method on the cationic layers that were preliminary adsorbed on the ITO electrode. The nature of the cationic sublayer defines the shape of the voltammograms of the anionic layers of $SiMo_{12}$.The CVA in Fig. 1a differ also from those obtained for the $SiMo_{12}$ dissolved in or adsorbed on the glassy carbon substrates of silicododecamolybdate anions. For the latter the three redox processes are characterized by close values of the currents [3, 9]. In contrast, in the case of bilayers a relative increase in the current is observed in going from the first to the second, and especially to the third

IR spectral parameters of the compounds based on $SiMo_{12}O_{40}^{4-}$ [a]

Compound	ν_{as}(Mo–O$_d$)	ν_{as}(Mo–O$_b$–Mo)	ν_{as}(Si–O$_a$)	ν_{as}(Mo–O$_c$–Mo)	δ_{N-H}
$H_4SiMo_{12}O_{40}$ [11]	957 (967)	855 (858)	904 901	770 765	
I	948 (947)	862 (863)	896 (895)	773 (773)	1594
II	943	866	898	794	
$(Bu_4N)_4SiMo_{12}O_{40}$ [11]	945 пл, 940	868	899	795	

[a] In parentheses are the data for the $H_4SiMo_{12}O_{40}$ used in the work and for the system of $SiMo_{12}$–$[H_3N^+(CH_2)_8NH_3^+]2Cl^-$ Designations: Mo–O$_d$ denotes Mo=O$_{end}$ which has a double bond character, Mo–O$_b$–Mo and Mo–O$_c$–Mo are bridge bonds in the $SiMo_{12}$ anion (betweeen the Mo_3O_{13} groups and between the octahedrons inside the Mo_3O_{13} groups, respectively).

stage of reduction. Apparently, a common cause of the transformation of CVA obtained on the electroactive bilayers is the presence on the electrode surface of an electrochemically inert barrier (cation layer), causing the necessity of electron tunneling, and moreover, leading to a change in the degree of protonation of the anion. The electrochemical responses are the least distorted in the case of poly(allyammonium chloride), and the degree of transformation of CVA increases in going from poly(allyammonium chloride) to piperazine (Fig. 1).

It is assumed that with 1,8-diaminooctane the ITO surface is covered by $SiMo_{12}$ anions close to the formation of a monolayer, like in the case of PMo_{12}. For the perfectly smooth surface of ITO the calculated surface concentration of the PMo_{12} monolayer is 1.7×10^{-10} mol cm^{-2} [5, 6]. According to the atomic force microscopy data, the roughness factor for the used ITO glasses is 1.2. As a result, the number of $SiMo_{12}$ units on the ITO/1,8-diaminooctane surface should be about 2.04×10^{-10} mol cm^{-2}. The integration of the anodic part of curve *3* (Fig. 1a) made it possible to calculate the concentration of $SiMo_{12}$: it equaled ~2.34×10^{-10} mol cm^{-2}. This means that the surface concentration of 1,8-diaminooctane for the ratio diamine:$SiMo_{12}$ = 4:1 is ~9.4×10^{-10} mol cm^{-2}. Note that this is the first layer. During the assembly of the next layers the cation/anion ratio may vary. For piperazine, the surface concentration of the diamine calculated in a similar way is much lower. Apparently, the use of a cyclic diamine instead of the linear one decreases the cationic species concentration in the layer due to steric reasons: piperazine in crystal is known to have the ideal chair conformation with equatorial NH bonds [10]. This leads to a corresponding decrease in the surface concentration of $SiMo_{12}$. The formation of a self-assembled organic monolayer on the ITO surface in the case of phosphomolybdic acid did not occur at all when the number of carbon atoms in the alkyl chain of linear diamine was less than 8 (1,8-diaminooctane) [6].

The interaction of $H_4SiMo_{12}O_{40}$ with 1,8-diaminooctane ($SiMo_{12}$:1,8-diaminooctane = 1:4) or 1,8-diammoniooctane dichloride ($SiMo_{12}$:1,8-diammonio-octane dichloride = 1:4) in 0.5 M H_2SO_4 leads to the formation of compounds $[NH_3^+(CH_2)_8NH_3^+]_6(SiMo_{12}O_{40}^{4-})_2(SO_4^{2-})_2$ (**I**), which can be regarded as a model of the coating formed on the ITO at the modification with 1,8-diaminooctane followed by the formation of the anion layer at the contact with a solution of heteropolymolybdate. Salt **II** with the composition $[(C_8H_{17})_4N]_4SiMo_{12}O_{40}$ was separated at the treatment of a solution of $(C_8H_{17})_4NBr$ in chloroform with aqueous silicomolybdic acid. Like tetraoctylammonium bromide, this salt was used as the salt matrix in the study of electrochemical behavior of C_{60} in aqueous solution. The compounds were characterized using the methods of elemental analysis and IR spectroscopy. The absorption bands of silicomolybdic acids and the compounds based on it are shown in the table.

The IR spectrum of pure $H_4SiMo_{12}O_{40}$ contains the bands (957, 904, 855, and 770 cm^{-1}) typical of the heteropolyanion of the Keggin geometry (Fig. 3). The spectra of compounds **I** and **II** include the bands of both inorganic (heteropolymolybdate) and organic fragments of the molecules. The bands of heteropolyanion in **I** and **II** compounds are shifted relative to the bands of parent $SiMo_{12}$, which may indicate some distortion of its structure. The presence of the band at 1594 cm^{-1} (NH_3^+ group) in the IR spectrum of compound **I** confirms the protonation of 1,8-

diaminooctane at the interaction of the latter with $H_4SiMo_{12}O_{40}$, and the bands at 1080–1150 cm^{-1} are characteristic of the anions SO_4^{2-}. A shift of the band of Mo–O$_d$ (948 cm^{-1}) relative to its position in the free acid (957 cm^{-1}) indicates the interaction of the dication $NH_3^+(CH_2)_8NH_3^+$ with the multiply charged heteropolymolybdate anion. Note also that in the spectrum of compound **I** the bands of C–H bending vibrations of CH_2 group and N–H in the NH_3^+ group compared with the 1,8-diaminooctane·2HCl are broadened. This may indicate a change in packing of the cations $H_3N^+(CH_2)_8NH_3^+$ and ordering of its alkyl fragment (or the existence of different structures) in compound **I** compared with $[H_3N^+(CH_2)_8NH_3^+]$·2HCl. In addition, the stretching C–H vibrations in CH_2 groups of compound **I** appear at 2861 and 2939 cm$^{-1,}$ whereas in the spectrum of $[H_3N^+(CH_2)_8NH_3^+]$·2HCl they are at 2849 and 2928 cm^{-1}. The structure of 1,8-diammoniooctane dichloride obtained by heating 1,8-diaminooctane in hydrochloric acid is characterized by layered packing in which the organic cations $H_3N^+(CH_2)_8NH_3^+$ are separated by inorganic layer consisting of chloride ions and water molecules [12].

Stretching vibration frequencies of C–H in CH_2 and CH_3 groups of octyl radical of the tetraoctylammonium cation in compound **II** remain almost unchanged compared with tetraoctylammonium bromide. When comparing compounds **II** and $(Bu_4N)SiMo_{12}O_{40}$, it is obvious (see the table) that the size of the cation $(C_nH_{2n+1})_4N^+$ (butyl and octyl in our case) at $n > 4$ does not affect the Mo–O$_d$ vibration frequency, which agrees with the conclusions of [11].

Similarly to the self-assembled ensembles (see Fig. 1), the cyclic voltammograms of compound **II** deposited on ITO, in an aqueous KCl[1] solution show redox activity of $SiMo_{12}$, and the potentials of the two revealed redox transitions correspond to the potentials of the first and the third processes in bilayers. At adding fullerene C_{60} to the $(Oct_4N)_4SiMo_{12}$ salt matrix we succeeded to detect also the process of C_{60} reduction. However, the reversibility of the electrochemical response for C_{60} in the $(Oct_4N)_4SiMo_{12}$ matrix is impaired significantly compared with its redox transformations in the Oct_4NBr matrix [13]. Note that in the case of electrode with the fullerene embedded in a cationic lipid matrix the process of the fullerene C_{60} reduction is controlled by the electrolyte anion. To preserve the electroneutrality of the covering, the Br$^-$ anion comes from the lipid matrix bulk into the solution, and for the reduced form of C_{60} the Oct_4N^+ acts as the cation [13]. Apparently, the $SiMo_{12}O_{40}^{4-}$ heteropolyanion as the leaving particle contributes to the coating destruction. In addition, the composition of the matrix that differs from Oct_4NBr will determine also its structure and, consequently, environment for the C_{60}. The replacement of Oct_4NBr by $(Oct_4N)_4SiMo_{12}$ reduces dramatically the adhesion of the coating to the surface of the ITO electrode, which can lead to difficulties in the formation of the bilayer structures. However, just the ability of Oct_4NBr to form the layered structure and create suitable hydrophobic microenvironment around the fullerene molecules through non-covalent CH–π interactions allows the fullerene to form extended ordered nanostructures, and the interaction of C_{60} with hydrophobic parts of the matrix provides a microenvironment of the fullerene necessary for the occurrence of the reversible electrochemical processes in aqueous medium [13]. It was noted earlier that the films obtained from tetralkylammonium, in particular, didodecyldimethylammonium, salt of copper tetrasulfophthalocyanine or by the introduction of the latter in the prepared film of artificial lipid showed different electrocatalytic properties [14]. These data may serve as confirming indirectly our assumptions on different structure of the films in the case of Oct_4NBr and $(Oct_4N)_4SiMo_{12}$ and its role in redox trans-formations of C_{60}.

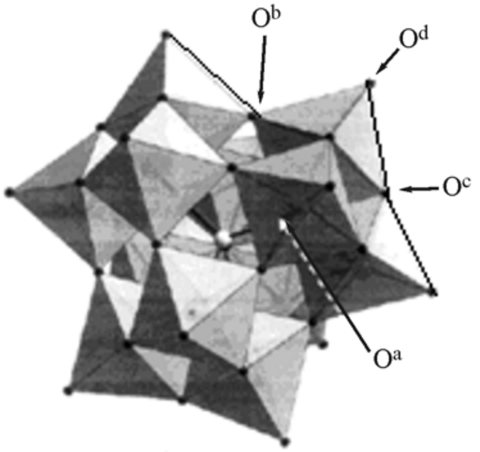


Fig. 3. The geometry of the heteropolyanion $SiMo_{12}O_{40}^{4-}$.

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[1] Inasmuch as the redox processes of C_{60} embedded into the matrix of tetraoctylammonium bromide were studied in water solutions in the presence of KCl as electrolyte we used the same solution in the study both of compound **II** and the composition **II**–C_{60}.

Thus, we have demonstrated the formation of bilayered electroactive diamine coating on the ITO glass involving silicomolybdic acid on the basis of stable self-assembling monolayers. The combination of amine adsorption by active centers of the ITO surface, the van der Waals interactions of alkyl chains and the interaction between the terminal amine groups ensure its high stability. Use of $(Oct_4N)_4SiMo_{12}O_{40}$ instead of Oct_4NBr as a cationic matrix impairs the reversibility of electrochemical response of C_{60} in aqueous solution.

EXPERIMENTAL

We used hydrated silicomolybdic acid, $H_4SiMo_{12}O_{40}\cdot xH_2O$ (Aldrich) (M = 1860, x = 2) and tetraoctylammonium bromide (Lancaster). The cationic layers were poly(diallyldimethyl)ammonium chloride (M 200,000–350,000, 20% aqueous solution, Aldrich, M_{eq} 126), poly(allyammonium chloride) (M 15 000, Aldrich; M_{eq} 58), 1,8-diaminooctane (Aldrich), piperazine (Aldrich), methylene chloride for spectrophotometry (Aldrich). For preparing the reaction, background, and washing solutions we used sulfuric acid of extra pure grade (Russia). These reagents were not purified. Aqueous solutions were prepared with bidistilled water.

To prepare coatings, the conductive glass ITO (In_2O_3–SnO_2 oxides on the glass substrate) with an area of 1.0 cm^2 (0.5×2 cm) was washed in an ultrasonic bath with anhydrous ethyl alcohol, acetone (extra pure, Russia), and dried in argon.

Electrochemical measurements were carried out in a standard three-electrode cell on an IPC-4M (Russia) potentiostat-galvanostat. Auxiliary electrode was platinum wire, the potentials were measured relative to saturated aqueous calomel electrode. Working solutions were purged with argon.

The IR spectra in the range 4000–670 cm^{-1} were recorded on a Spectrum 100 infrared spectrometer.

Formation of coatings. Prepared electrodes were immersed in a solution of polycation [poly(diallyldimethyl)ammonium chloride 0.2 mg or poly(allyammonium chloride 0.3 mg)/1 ml of 1 M H_2SO_4] for 30 min, washed with a solution of 1 M H_2SO_4 and then placed for 30 min in 1M solution of H_2SO_4 containing 5×10^{-3} M $H_4SiMo_{12}O_{40}$.

The surface modification of the conductive glass with 1,8-diaminooctane (or piperazine) was carried out by keeping the ITO electrode in a solution of diamine (5×10^{-3} M) in anhydrous ethanol for three days in an inert atmosphere at room temperature in the dark. After repeated washing with alcohol, the electrode was dried. For the application of the anion layer the glass was kept in a 0.5 M solution of H_2SO_4 containing 5×10^{-3} M of $H_4SiMo_{12}O_{40}$.

Synthesis of $[H_3N^+(CH_2)_8NH_3{}^+]_6(SiMo_{12}O_{40}^{4-})_2\cdot(SO_4)_2^{2-}$ (I). *a.* To a solution of 0.036 g (2.47×10^{-4} mol) of 1,8-diaminooctane in 1 ml of 0.5 M aqueous H_2SO_4 was added slowly 5.25 ml of $H_4SiMo_{12}O_{40}$ ($[H_4SiMo_{12}O_{40}] = 0.24\times10^{-3}$ M) in 0.5 M aqueous H_2SO_4. A weak turbidity was observed, accompanied by the formation of yellow crystals (0.08×0.15 mm) in the form of transparent layered plates. The precipitate was filtered off, washed with 0.5 M solution of H_2SO_4 (2 ml), then with water to neutral reaction and dried at room temperature in a vacuum. After drying, some of crystals were turbid. Found, %: N 3.7, S 1.33. $C_{48}H_{132}\cdot N_{12}O_{88}S_2Mo_{24}Si_2$. Calculated, %: N 3.56, S 1.36.

b. To a solution of 0.021 g of $[H_3N^+(CH_2)_8NH_3^+]\cdot 2Cl^-$ in 1 ml of H_2O was slowly added 10 ml of aqueous solution of $H_4SiMo_{12}O_{40}$ ($[H_4SiMo_{12}O_{40}] = 0.24\times10^{-3}$ M) in 0.5 M H_2SO_4. The reaction product was isolated as above. The reaction on the presence of the Cl anion was negative. Found, %: N 3.75, S 1.5. $C_{48}H_{132}N_{12}O_{88}S_2Mo_{24}Si_2$. Calculated, %: N 3.56, S 1.36.

Synthesis of $[(C_8H_{17})_4N]_4SiMo_{12}O_{40}$ (II). 0.062 g (1.13×10^{-4} mol) of Oct_4NBr in 5 ml of CH_2Cl_2 was added at vigorous stirring to a solution of 0.056 g (0.028×10^{-4} mol) of $H_4SiMo_{12}O_{40}$ in 2.5 ml of 0.5 M aqueous H_2SO_4. When the aqueous solution became colorless, the organic layer was separated and washed with dilute H_2SO_4 and water. After drying over calcined molecular sieves (4 Å), the organic solvent was removed almost to dryness and then were added in succession 1.5 ml of alcohol, 1.5 ml of ether, and 5 ml of hexane. The precipitate formed was filtered off and dried in a vacuum. Found, %: N 1.7. $C_{128}H_{272}N_4O_{40}Mo_{12}Si$. Calculated, %: N 1.52.

Preparation of coatings based on compound II and C_{60}. *a.* A sample of compound **II** (0.0052 g, 1.4×10^{-6} mol) was dissolved in CH_2Cl_2 (1 ml), filtered, and then the solution was applied in 0.1 ml portions to the ITO electrode. After each application the glass was dried in a glass chamber. On the whole ~1.15×10^{-7} mol cm^{-2}, of compound **II** was deposited.

b. To 0.9 ml of a solution of compound **II** in CH_2Cl_2 was added 0.1 ml of C_{60} in toluene ($[C_{60}] = 1.3\times10^{-3}$ M) and then 0.05 ml of this mixture was applied to the ITO electrode. The substrate contained on the whole 1.15×10^{-8} mol cm^{-2} of C_{60} (**II**/C_{60} ~ 10).

The obtained electrodes were evacuated, purged with argon, and kept in the dark. The method of application used does not provide complete uniformity of film thickness, however, it was possible to obtain reproducible electrochemical characteristics.

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