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Synthesis of the Nanocomposite SnO_2–Au^0_x–$(H_3PW_{12}O_{40})_y \cdot nH_2O$ Layers on the Silica Surface by the Layer-by-Layer Method

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Abstract—Conditions for the synthesis of the SnO_2–Au^0_x–$(H_3PW_{12}O_{40})_y \cdot nH_2O$ nanocomposite layers by the method of ionic epitaxy were determined for the first time. The layers we investigated by the method of scanning electron microscopy, energy dispersion microanalysis, UV and IR Fourier transmission spectroscopy. On the basis of the experimental data conclusions were drawn on the composition and structure of the synthesized layers.

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The synthesis of nanocomposite layers on the surface of a block or disperse type support is a known promising procedure for the creation of new functional materials like catalysts, sorbents, conductometric gas sensors, and the materials for the nanoionics. Among the methods for the synthesis of the nanocomposite layers those allowing to carry out the synthesis layer-by-layer are especially important because this approach gives rise to precision control over the layer thickness and thus permits to assemble the multilayers consisting of the homolayers differing by the chemical composition.

Earlier the conditions for the synthesis by one of such methods, the method of ionic epitaxy of the SnO_2–$(H_3PW_{12}O_{40})_x \cdot nH_2O$ [1] and SnO_2–$Au^0_x \cdot nH_2O$ [2] nanocomposites nanolayers were found and the properties of the parent and modified SnO_2 layers were tested as the conductometric gas sensors [3].

The aim of this work was the synthesis of the nanocomposite layers of $SnO_2 \cdot nH_2O$ nanoparticles, $H_3PW_{12}O_{40}$ heteropolyacid anions, and Au^0 nanoparticles. It was suggested that by variation of the content of Au^0 nanoparticles in the layer a unique combination of adsorption and catalytic properties could be achieved. As the synthetic method we applied the ionic epitaxy based on the consecutive multiple repeated acts of adsorption of anions and cations on the support surface and their mutual reaction.

Synthesis of SnO_2–Au^0_x–$(H_3PW_{12}O_{40})_y \cdot nH_2O$ nanocomposite by consecutive reactions of ionic epitaxy on the fused quartz surface leads to the appearance of colored layer; its UV transmission spectrum is shown in Fig. 1. The spectrum is characterized by an absorption band in the UV region defined by the presence of tungsten and tin, and by a characteristic absorption band with the maximum at 540 nm related to the gold nanoparticles in the synthesized layer. According to [4, 5] this band can be assigned to the absorption of the plasmons of gold nanoparticles with the size 10–30 nm.

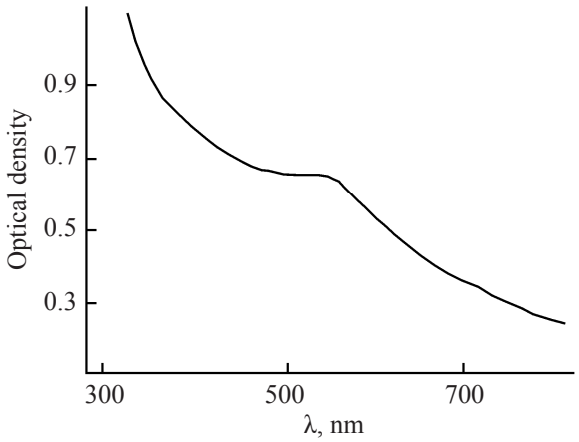

Fig. 1. The transmittion spectrum in UV and visible regions of the layer of $Sn(OH)_x$–Au^0–$H_yPW_{12}O_{40}$ nanocomposite synthesized on the fused quartz surface after 15 cycles of ionic epitaxy.

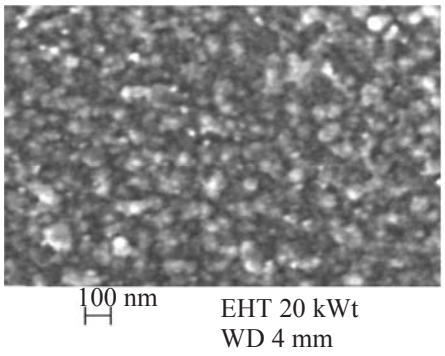

Fig. 2. The view of the surface of $Sn(OH)_x$–Au^0–$H_yPW_{12}O_{40}$ nanocomposite layer synthesized on the surface of silicon single crystal. The image was obtained by the scanning electron micriscopy. The layer was synthesized by 15 cycles of ionic epitaxy.

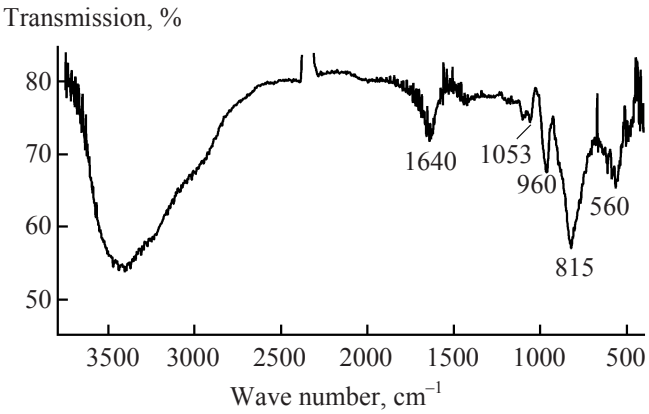

Fig. 3. The IR Fourier transmittion spectum of $Sn(OH)_x$–Au^0–$H_yPW_{12}O_{40}$ nanocomposite layer synthesized on the surface of silicon single crystal by 15 cycles of ionic epitaxy.

Study by the method of scanning electron microscopy showed (Fig. 2) that the layer on the single crystal silocon surface had a globular structure with the globules size 10–50 nm. The composition was characterized by the method of energy dispersive microanalysis, and the presence in the layer of tin, tungsten and gold atoms in the concentration ratio 0.9:0.4:0.5 was established. Unfortunately we failed to detect phosphorus in the layer by this method, due probably to its relatively low concentration.

Indirectly the presence of phosphorus in the composition of the polyoxometallate was confirmed by the IR Fourier transmission spectrum of the nanocomposite layer synthesized on the silicon surface (Fig. 3). In accordance with [6] the absorption bands at 1055, 963 and 820 cm^{-1} might be assigned to the vibrations $\nu(PO_4)$ (800–1100 cm^{-1}), $\nu(W{=}O)$ (900–1000 cm^{-1}) and $\nu(W–O–W)$ (200–900 cm^{-1}). The absorption band at 560 cm^{-1} is caused [7] by $\nu(Sn–O)$ vibrations in the $SnO_2 \cdot nH_2O$ fragment of the synthesized layer. The presence of molecular water in the layer is evidenced by the observed absorption at 3550–3200 cm^{-1} [$\nu(OH)$] and 1640 cm^{-1} [$\delta(OH)$].

On the basis of the experimental data obtained the following scheme of the reactions proceeding at the surface in the course of the synthesis can be suggested. In the first step, when the support is treated with $SnCl_2$ solution it adsorbs tin(II) cations and then, at the treatment with the solution containing $H_3PW_{12}O_{40}$ and $HAuCl_4$ the oxidation Sn(II) → Sn(IV) occurs and the reduction Au(III) → Au^0. Therewith, the gold and $SnO_2 \cdot nH_2O$ nanoparticles are formed, the latter at the given pH of the solution have positive charge of surface and behave as the adsorbents toward the heteropolyacid anions.

Thus, the findings now presented confirm the possibility of the synthesis of SnO_2–Au^0_x–$(H_3PW_{12}O_{40})_y \cdot nH_2O$ nanocomposite on the silica surface by the method of ionic epitaxy. Experimental data allow a conclusion that the layer formed contains heteropolyacid ($H_3PW_{12}O_{40}$), hydrated tin oxide $SnO_2 \cdot nH_2O$, and gold nanoparticles.

EXPERIMENTAL

The transmittion spectra in UV region were registered on a Perkin-Elmer Lambda-9 spectrophotometer at the scanning rate 60 nm min^{-1}, slot program 2 nm. The IR Fourier spectra were registered on a Perkin-Elmer 1760X spectrophotometer. Electron microphotographs were obtained on a Zeiss EVO-40EP scanning electron microscope with LaB_6 cathode, at the accelerating voltage 20 keV. The synthesized layer composition was determined with an Oxford INCA 350 energy dispersion analyzer with a Si(Li) detector 30 mm^2 area.

As the supports for the synthesis of nanolayers were taken fused quartz of KU sort and single crystals of silicon of the <100> orientation, sort KDB-40, the crystals polished to 14th class purity. The quartz supports were washed in acetone and then kept for 10 min at 60ºC in concentrated nitric acid and washed consecutively with distilled water, KOH solution of pH = 9, and again with water. The supports of silicon single crystals were washed with acetone to remove organic impurities, then with duluted (1:10)

hydrofluoric acid, and with water. Then for the formation of oxidized hydrosilylated surface they were kept for 0.5 h in a "pyranha" solution consisting of 30% H_2O_2 and conc. H_2SO_4 (of 3:7 ratio by volume) under the action of the ultrasound (60 W), and then carefully washed with water.

Aqueous solutions of $SnCl_2{\cdot}2H_2O$ (Vecton), $HAuCl_4{\cdot}nH_2O$ (Aurat) with gold content 49.47 wt % and $H_3PW_{12}O_{40}{\cdot}nH_2O$ (Vecton) were used as reagents. The tin salt solution with concentration 0.01 M was prepared along the procedure [8], then a solution of NH_4F in 1:1 proportion and NH_4OH to pH 2.5 were added. The phosphotungstic acid and gold chloride solutions mixture was prepared by dissolving respective weighed samples of $H_3PW_{12}O_{40}{\cdot}nH_2O$ in double distilled water followed by adding a concentrated solution of $HAuCl_4{\cdot}nH_2O$. The $H_3PW_{12}O_{40}$ concentration in the solution for the synthesis was 0.01 M, $HAuCl_4$ 0.001 M, the pH of solution corresponded to the equilibrium one.

Procedure for the synthsis of nanolayers. The supports after an appropriate treatment were fixed in the sample holders of the automatic device for the synthesis controlled with a computer, and were treated consecutively by immersion into solutions according to a predefined scheme comprising an elementary cycle of ionic epitaxy: to solution of tin(II) salt, washing liquid, solution containing phosphotungstic acid and gold chloride, then again to washing liquid. The duration of the sample treatment with a reagent was 0.5 min. At this sequence of treatment on the support surface formed a single nanolayer. Synthesis of next layers was carried our by multiple repeating of the ionic epitaxy cycles.

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