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Successive ionic layer deposition of Fe_3O_4@$H_xMoO_4 \cdot nH_2O$ composite nanolayers and their superparamagnetic properties

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The Fe_3O_4@$H_xMoO_4 \cdot nH_2O$ nanolayers were synthesized on the solid surface for the first time by Successive Ionic Layer Deposition (SILD) method with using an aqueous Fe_3O_4 suspensions and $(NH_4)_2MoO_4$ solutions. The obtained nanolayers were investigated by XRD, SEM, EDX, FTIR spectroscopy and magnetization measurement techniques. SEM images showed that the nanolayers formed by nanoparticles of size approximately 15–20 nm. The synthesized nanolayers exhibited superparamagnetic properties with the saturation magnetization value of 55 emu/g.

Keywords: magnetite, SILD, nanolayers, core-shell nanoparticles, superparamagnetism.

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1. Introduction

It is known that iron oxide nanomaterials are very important in a big number applications because of their magnetic properties. Iron oxides particles are prepared with solid-state reactions [1], coprecipitation from solutions [2], hydrothermal treatment [3–5], oxidation of solutions of iron (II) salt [6], combustion method [7] and etc. Iron oxides in nano-scale have a great potential for their applications as ion exchangers, adsorbents, catalytic materials, magnetic data storage devices, superparamagnetic materials and etc. The nanoparticles and nanolayers with superparamagnetic properties are very important for fabrication of new advanced materials in MRI diagnostics [8], drug delivery [9], mixture separation [10], hyperthermia [11], as well as new multi-functional materials, in particular luminescent and magnetic materials [12] and etc.

The Layer-by-Layer (LbL) method is used for such nanolayers obtaining as one of the best methods among other [13].This method of synthesis based on a successive and multiple treatments of substrate in salt solutions and polyelectrolytes, forming an insoluble layer of new compound at interaction on the surface. The SILD method is one of LbL synthesis methods without the using of polyelectrolite solutions. It has been used previously to synthesize nanolayers of metal oxides [14], noble metal nanoparticles [15], hydroxides [16] and etc. The SILD method is based on a sequential adsorption of anions and cations or colloid particles on the substrate surface with formation of nanolayer of insoluble compounds [17].

The major advantages of this method is a simplicity of the process and equipment, the application of substrates with irregular shapes and sizes and precision control of the thickness of the multilayer. These special features of the SILD method give a possibility to obtain nanolayers of wide number of substances, which can be applied in optics, microelectronics, energy storage devices.

In this paper, we describe a novel simple route for SILD synthesis of the Fe_3O_4@$H_xMoO_4 \cdot nH_2O$ composite nanolayers with using a Fe_3O_4 suspensions and $(NH_4)_2MoO_4$ solutions, as well as their magnetic properties study.

2. Experimental methods

The single crystalline silicon plates of size $10 \times 25 \times 0,3$ mm with $< 100 >$ orientation were used as substrates for synthesis of nanolayer. All substrates were cleaned in an ultrasonic acetone bath for 10 minutes before synthesis. Then plates were sequentially treated for 10 minutes in 40 % HF, distilled water, 70 % HNO_3, distilled water, 0.1 M KOH solution and flushed out by deionized water.

For SILD synthesis we used an aqueous Fe_3O_4 suspensions ($C_{Fe_3O_4} = 0,01$ M, pH 4,0) and $(NH_4)_2MoO_4$ solutions (C = 0.01 M, equilibrium pH). The Fe_3O_4 suspension was prepared by the method [18] from 0.01 M $FeCl_2$ and 0.0202 M $FeCl_3$ mixed solution. The $HClO_4$ was added in mixed solution to pH = 4.0 to enhance the suspension stability. All reagents used were of analytical grade. Deionized water with resistively 18.2 MΩ cm (Mili-Q) was used for preparation of reagent suspensions and solutions.

$Fe_3O_4@H_xMoO_4{\cdot}nH_2O$ nanolayers were synthesized by SILD. First, plates were sequential immersed for 60 second into Fe_3O_4 suspension, then washed in distilled water. Then plates were dipping for 30 second in solution of $(NH_4)_2MoO_4$ and again washed in water. The sequence corresponds to one SILD cycle, which is repeated 30 times to obtain desired nanolayer thickness.

The composition and morphology of $Fe_3O_4@H_xMoO_4{\cdot}nH_2O$ layers were investigated by energy-dispersive X-ray spectroscopy (EDX) using Oxford INCA350 detector and scanning electron microscopy (SEM) using Zeiss EVO-40EP microscope. X-ray diffraction (XRD) was carried out on Rigaku Miniflex II diffractometer with CoK_α radiation, 30 kV voltage, and 10 mA current. FT-IR transmission spectra of synthesized nanolayers on silicon surface were registered by FSM-2201 spectrophotometer using differential scheme related to spectra of bare silicon.

Magnetization measurement of the Fe_3O_4/molybdate nanocomposite nanolayers was performed with a vibrating sample magnetometer VSM Lake Shore-741 in the ± 17.8 kOe window at room temperature.

The sizes of Fe_3O_4 particles in aqueous suspensions were determined with the help of Dynamic Light Scattering (DLS) method. The measurements were carried out with a Zetasizer Nano ZS analyzer in a DTS 1060 universal capillary U-shaped cell at 20°C. The electrokinetic potential was calculated by the Smoluchowski equation. The values of the ζ potential were corrected within the approximation of the Overbeek-Booth-Wiersema model [19].

3. Result and discussion

DLS experiments demonstrated that average particle size of Fe_3O_4 suspension is 16 nm. Their ζ potential equals +47,1 m.

SEM investigation of synthesized layers showed that they formed by nanoparticles with sizes about 15–20 nm (Fig. 1). The dispersive X-ray spectroscopy research has determined the significant energy signal intensity of Fe, Mo, and O elements in the sample (Fig. 2). The concentration ratio of Fe : Mo corresponds $13,5 : 1,0$.

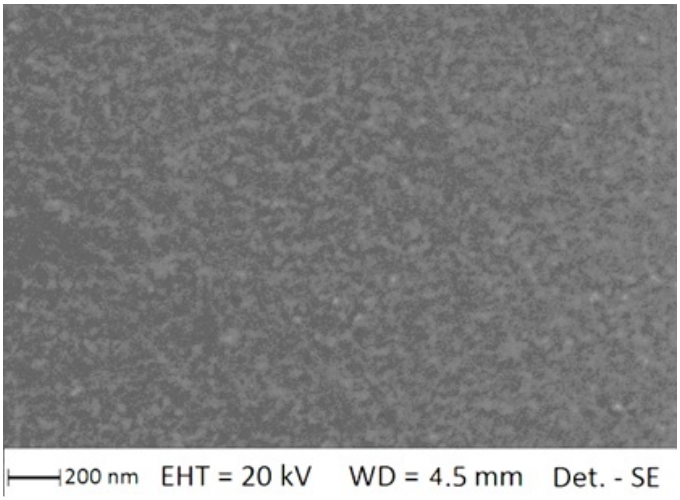

FIG. 1. SEM image of $Fe_3O_4@H_xMoO_4{\cdot}nH_2O$ nanolayer on silicon

The XRD pattern of synthesized sample is presented in Fig. 3. Five diffraction peaks at 35.2, 41.5, 50.6, 67.4, and 74.3° can be indexed as the diffractions of magnetite Fe_3O_4 (ICDD PDF # 01-071-6336).

As can be seen from the experimental FT-IR spectra (Fig. 4) a water molecules are included in composition of nanolayer, which can be identified by the valence band (3400 cm^{-1}) and the deformation band (1640 cm^{-1}). The band at 594 cm^{-1} may be assigned to valence vibrations of Fe-O bonds in magnetite Fe_3O_4 [20], and bands at 950–750 cm^{-1} region connected with valence vibrations of Mo-O bonds in molybdate-anions [21].

For the explanation the obtained results it can be suggested the following schemes of chemical reactions on the surface of silicon. At the first SILD cycle after dipping in the Fe_3O_4 suspension and wash in distilled water on the surface silicon the layer of Fe_3O_4 nanoparticles (NP) is formed:

$$\equiv \mathrm{Si} - \mathrm{OH} + (\mathrm{Fe_3O_4})_{\mathrm{NP}} \rightarrow \equiv \mathrm{Si} - \mathrm{OH} \cdot (\mathrm{Fe_3O_4})_{\mathrm{NP}}, \quad (1)$$

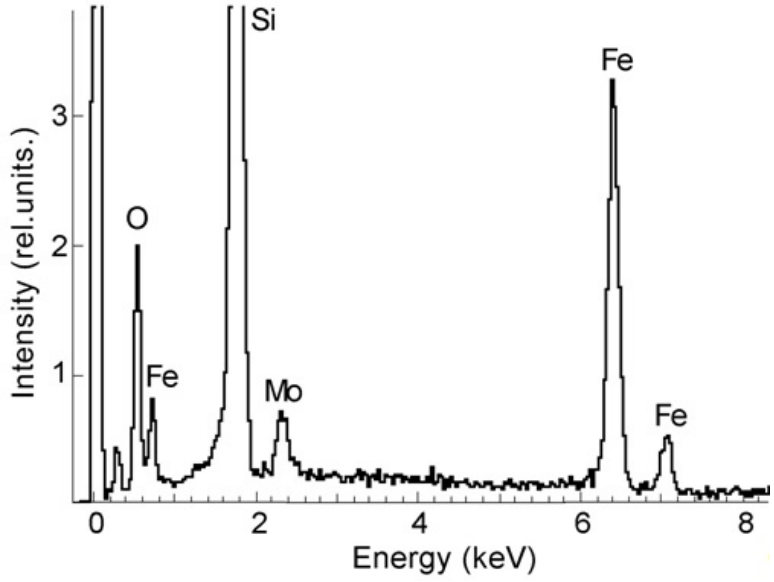

FIG. 2. EDX spectrum of $Fe_3O_4@H_xMoO_4{\cdot}nH_2O$ nanolayer on silicon

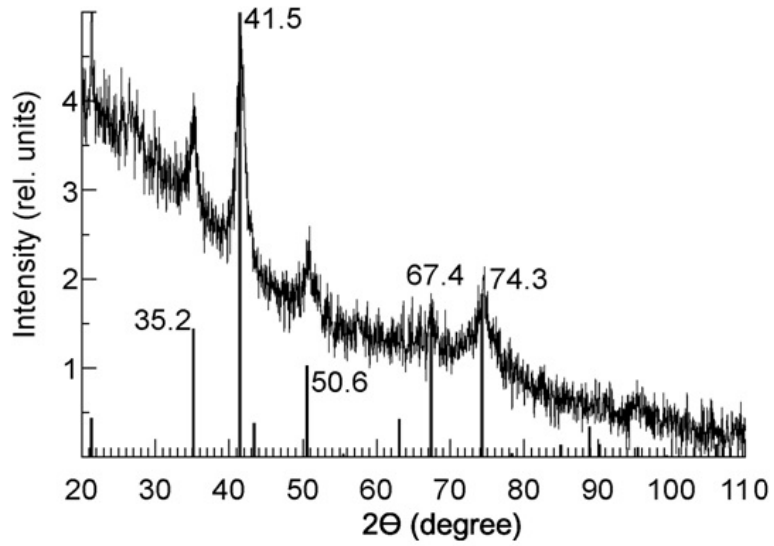

FIG. 3. XRD pattern of synthesized sample

Then after treatment in the excess of $(NH_4)_2MoO_4$ solution and washing the MoO_4^{2-}-anions adsorbed on Fe_3O_4 surface and core-shell nanoparticles layer is formed:

$$\equiv Si - OH \cdot (Fe_3O_4)_{NP} + MoO_4^{2-} + H_2O \rightarrow \equiv Si - OH \cdot (Fe_3O_4@H_xMoO_4)_{CS}. \quad (2)$$

On the second SILD cycle during the treatment in the Fe_3O_4 suspension, the nanoparticles of Fe_3O_4 are adsorbed on the substrate surface again:

$$\equiv Si - OH \cdot (Fe_3O_4@H_xMoO_4)_{CS} + (Fe_3O_4)_{NP} \rightarrow \equiv Si - OH \cdot (Fe_3O_4@H_xMoO_4)_{CS} \cdot (Fe_3O_4)_{NP} \quad (3)$$

Thus, as a result of multiple repetitions of SILD cycles the $Fe_3O_4@H_xMoO_4{\cdot}nH_2O$ omposite nanolayer is created on the surface. It is evident that thickness of this layer can be control by number of SILD cycles.

Magnetic characterization of the $Fe_3O_4@H_xMoO_4{\cdot}nH_2O$ nanolayer is shown in Fig. 5. The analyzed sample demonstrated superparamagnetic properties with the saturation of magnetization value of 55 emu/g and very low remanence magnetization (Mr$\sim$4 emu/g) and coercivity (Hc$\sim$30 Oe).

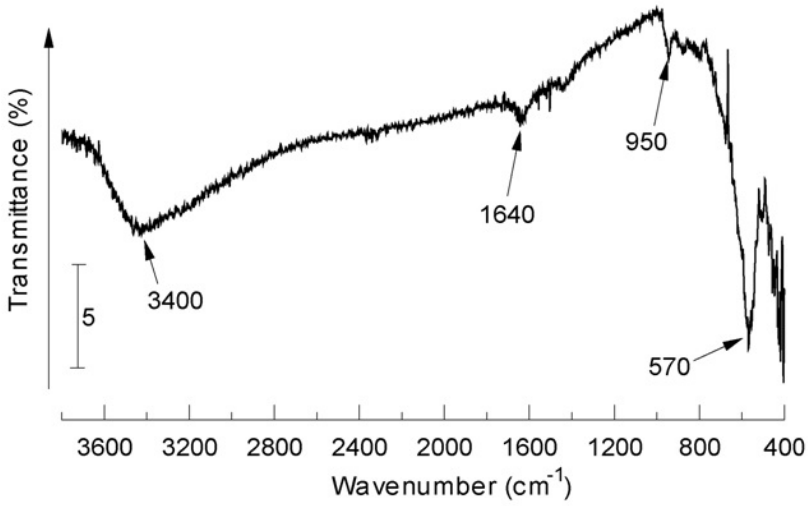

FIG. 4. FT-IR transmission spectrum of $Fe_3O_4@H_xMoO_4{\cdot}nH_2O$ layer on silicon surface

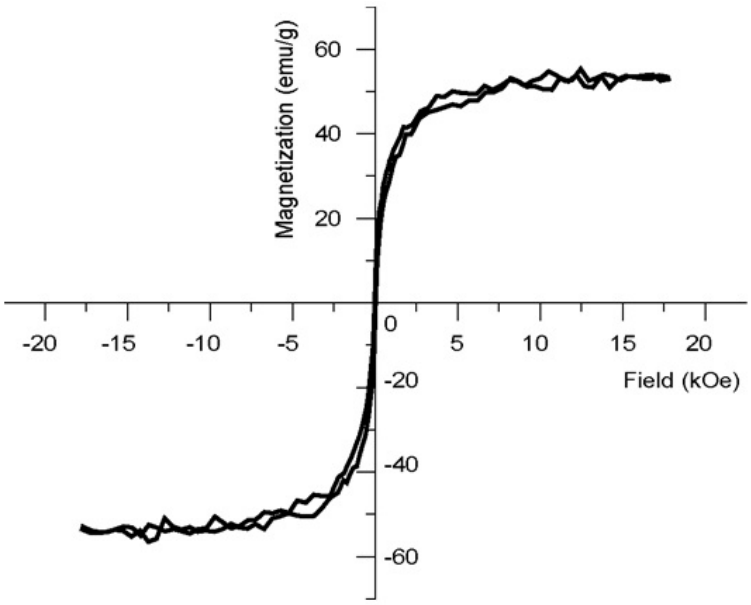

FIG. 5. Magnetization curves of $Fe_3O_4@H_xMoO_4{\cdot}nH_2O$ nanolayer synthesized on silicon surface in result 30 SILD cycles

We believe that nanolayers with such composition and morphology can be apply as superparamagnetic materials for separation of mixtures. The promoted approach to the synthesis provides a good opportunity to adjust the properties of the new multilayered materials in the synthesis process by changing the number of SILD cycles.

4. Conclusion

In this work, we obtained the $Fe_3O_4@H_xMoO_4{\cdot}nH_2O$ nanolayers by SILD method using a Fe_3O_4 suspension and $(NH_4)_2MoO_4$ solution as reagents. These nanolayers exhibit superparamagnetic behavior with saturation magnetization value of 55 emu/g.

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