Polyurethane foam modified with borohydride: preparation and possibilities of using for synthesis of gold nanoparticles and their nanocomposites

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Polyurethane foam modified with borohydride: preparation and possibilities of using for synthesis of gold nanoparticles and their nanocomposites

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Abstract. The present work describes preparation of polyurethane foam modified with borohydride. Adsorption of borohydride from alkaline solutions in presence of a cationic surfactant is discussed. The polyurethane foam modified with borohydride possesses reductive ability with respect to Au(III). Possibilities of the new material for synthesis of gold nanoparticles are described. This solid reducting agent is convenient for use in the synthesis of nanoparticles, since it ensures precise dosing of a reductant while desorbed from polymer. Gold nanoparticles can be synthesized both in solution and on the polymer surface by varying reagents concentrations during the preparation of modified polyurethane foam.

1. Introduction

Gold nanoparticles possess a number of valuable qualities: unique optical properties due to surface plasmon resonance (SPR), highly developed surface, low toxicity, chemical inertness, catalytic activity, etc [1-6].

The method and conditions of gold nanoparticles preparation in many cases determines their properties: morphological, optical, and other features [1-5, 7]. Often, nanoparticles functionalization occurs during their preparation, which determines selectivity and sensitivity of the synthesized reagent. Modern research is aimed at obtaining gold nanoparticles with various sizes and a narrow size distribution.

Spherical gold nanoparticles are most often obtained by chemical reduction of hydrochloric acid with sodium borohydride. The main feature of sodium borohydride is its great reducing ability. Sodium borohydride is quite stable in solid form and convenient for use in the synthesis of nanoparticles in both aqueous and organic media.

The size and dispersion of the resulting nanoparticles, as well as their stability over time, are controlled by varying the nature of a stabilizer and its amount. As stabilizers, an excess of a reducing agent is used, as well as specially introduced substances. Often for the synthesis of monodispersed gold nanoparticles, ionic surfactants are used, for example sodium dodecyl sulfate [8] or

cetyltrimethylammonium bromide [9], as well as synthetic and natural polymers — polyvinylpyrrolidone [10], polyethylene glycol [11], cyclodextrins [12], polyamidoamine [13] and etc.

To stabilize and improve the operational performance of gold nanoparticles, they can be immobilized on various solid matrices. The nanocomposites obtained in this way can advantageously differ in their optical and analytical characteristics. A large number of different matrices used to obtain nanocomposite materials is described. Among the variety of matrices, polyurethane foams (PUFs) should be considered specifically as having a number of quite important advantages: good sorption ability, low density (0.015 ─ 0.045 g cm^{-3}), monolithicity, resistance to thermo-oxidative degradation, chemical inertness to many compounds, low cost and the availability of these materials [14-15].

In this work the features of polyurethane foam modification with borohydride for subsequent use as a reducing agent in the preparation of gold nanoparticles and their nanocomposites is studied and discussed.

2. Experimental

2.1. Materials

The following reagents at least of analytical grade were used: sodium borohydride, cetyltrimethilammonium bromide (CTAB), sodium hydroxide, hydrogen tetrachloroaurate, hydrochloric acid. Stock solutions of these reagents were prepared by dissolving their weighed portions or aliquots in deionized water.

Polyether-based polyurethane foam (PUF) was used. The polymer was cut into cylindrical tablets of 16 mm in diameter. The weight of each tablet was (20 ± 2) mg. To clean samples, the PUF tablets were placed in acetone and shaken for 10 minutes. The procedure was repeated twice, and then the tablets were dried under stream of air. The tablets were stored in a light-protected place.

2.2. Instruments

Absorption spectra of solutions were recorded using SF-103 spectrophotometer (Akvilon, Russia), diffuse reflectance measurements were carried out using an Eye-One Pro mini-spectrophotometer (X-Rite) [16, 17] on a white base. The diffuse reflectance coefficients (R) were recalculated into the Kubelka-Munk function (F) values to get absorption spectra in a solid phase according to the formula: $F = \frac{(1-R)^2}{2R}$. pH was measured using Ekspert 001 pH-meter (Ekoniks Ekspert). TEM-images were recorded using transmission electron microscope Libra 200 (Zeiss, Germany) at the accelerating voltage of 200 kV. Aqueous dispersions of the samples were deposited onto copper grid support with a formvar film covered by amorphous carbon Formvar®/Carbon Reinforced Copper Grids 3440C-MB (SPI, USA). Scanning electron microscopic studies of PUF samples microstructure was carried out using scanning electron microscope JSM 7100 F (Jeol, Japan) at the accelerating voltage of 2–5 kV. Deionized water was obtained using the Millipore Simplicity purification system (Millipore).

2.3. Adsorption of borohydride onto polyurethane foam

Adsorption of borohydride onto PUF was carried out in a static mode. The PUF tablet was placed into a test-tube containing 5 mL of an following mixture: 0.01 mol L^{-1} sodium hydroxide, 0.01 mol L^{-1} sodium borohydride and 0.0001 mol L^{-1} CTAB for further application of the modified polymer in the synthesis of nanocomposites or 0.1 mol L^{-1} sodium borohydride and CTAB for further application of the modified polymer in the synthesis of gold nanoparticles colloids. The tablets were thoroughly pressed with a glass rod to remove air bubbles from pores and shaken on an electromechanical shaker for some time. After that, the tablets were removed and dried between sheets of filter paper.

To control adsorption of borohydride, freshly prepared modified tablets were placed in 5 mL of hydrogen tetrachloroaurate containing 20 μg mL^{-1} of gold. The tablets were thoroughly pressed with a glass rod and stirred by shaking on an electromechanical shaker for 30 minutes. Then, the tablets were removed and dried between sheets of filter paper

3. Results and discussion

In this work, PUF has been first modified with borohydride aiming for its following use as a new reductant for synthesis of gold nanoparticles colloids and nanocomposites.

Sorption of sodium borohydride onto PUF was carried out from a solution containing sodium hydroxide and CTAB. Sodium borohydride is a polar compound that dissociates well into ions in aqueous solutions. In order to overcome the interfacial boundary and ensure transition of borohydride anions to the PUF phase, CTMA was added to the solution as a hydrophobic counterion. Since in aqueous solutions, especially in an acidic environment, borohydride is unstable, NaOH was added to the system as a stabilizer.

Adsorption of borohydride onto PUF in the mentioned conditions was studied in detail. Sorption of sodium borohydride onto PUF was carried out from a solution containing sodium hydroxide and CTAB. Sodium borohydride is a polar compound that dissociates well into ions in aqueous solutions. In order to overcome the interfacial boundary and ensure transition of borohydride anions to the PUF phase, CTMA was added to the solution as a hydrophobic counterion. Since in aqueous solutions, especially in an acidic environment, borohydride is unstable, NaOH was added to the system as a stabilizer.

Adsorption of borohydride onto PUF in the mentioned conditions was studied in detail.

3.1. Adsorption kinetics of borohydride on polyurethane foam

For kinetics study of borohydride adsorption by polyurethane foam, a number of experiments were carried out according to the scheme described above with different mixing times at the first stage at $NaBH_4$ concentration of 0.01 M. Diffuse reflectance spectra for borohydride-modified tablets treated with a solution of hydrogen tetrachloroaurate were recorded (figure 1a). The dependence of the Kubelka-Munk function obtained at the absorption maximum at 540 nm on the time of adsorption of borohydride is shown in figure 1b.

According to the graphics, 15 minutes is enough to achieve a maximum of the function. This time was used in further experiments. A slight decrease at times greater than 20 min can be explained by the gradual decomposition of sodium borohydride with subsequent stirring.

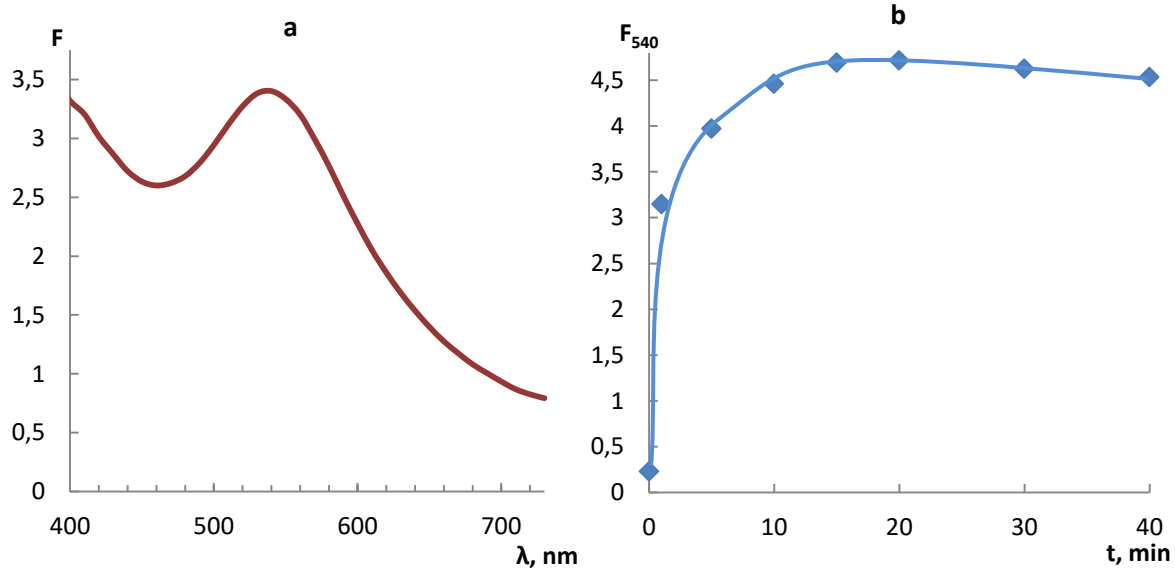

Figure 1. a) Diffuse reflectance spectrum of PUF modified with gold nanoparticles; b) dependence of the Kubelka-Munk function at 540 nm on the phases contact time of the PUF with a borohydride solution.

For numerical evaluation of adsorption kinetics of sodium borohydride on polyurethane foam several classical kinetic models of adsorption were used: the Lagergren pseudo first order model

($\ln(1 - a/a_{eq}) = -k_1 t$) and the pseudo second order model ($t/a = t/a_{eq} + 1/k_2 \cdot a^2_{eq}$), where k_1 is the pseudo first order reaction rate constant, min^{-1}; k_2 is the pseudo-second order reaction rate constant, $g \cdot \mu mol^{-1} \cdot min^{-1}$); a_{eq} — adsorption value upon reaching the sorption equilibrium between the sorbent and sorbate, $\mu mol \cdot g^{-1}$; t is the adsorption time, min.

In order to ascertain the sorption mechanism and select the kinetic model that most adequately describes the sorption of borohydride on polyurethane foam, the integral kinetic curve was processed and linearized taking into account the fact that the Kubelka-Munk function is directly proportional to the specific adsorption. The obtained dependences are presented in figure 2.

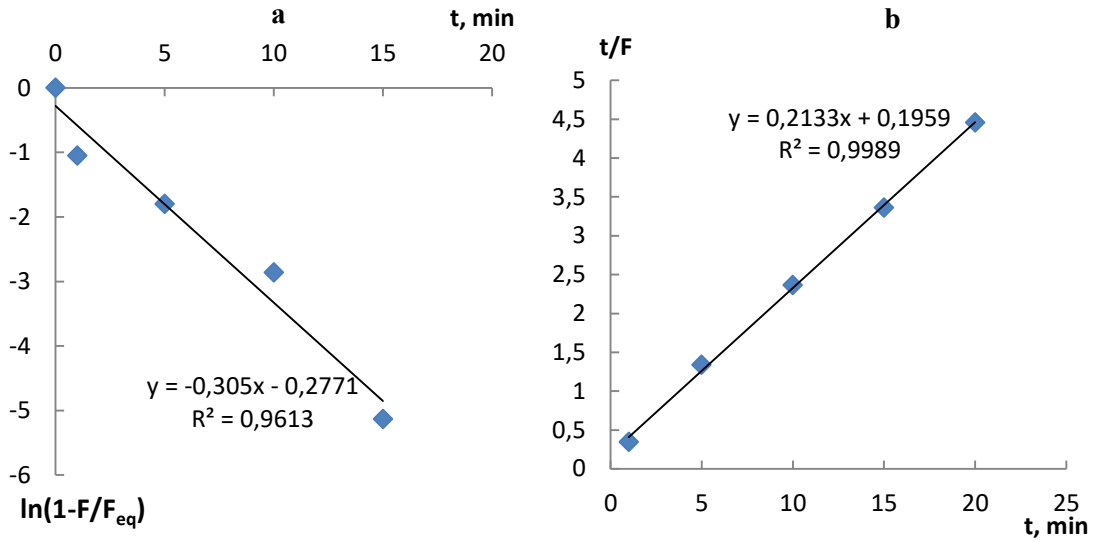

Figure 2. Kinetic dependences of the adsorption of sodium borohydride on polyurethane foam linearized using the pseudo-first (a) and pseudo-second (b) order models.

According to the obtained graphics, the adsorption kinetics is best described by the pseudo-second order model ($R^2 = 0.999$), $F_{eq} = 4.69$. The calculated value of the pseudo-second order adsorption rate constant was 0.232 min^{-1}. The proportionality coefficient between the Kubelka-Munk function and the specific adsorption of borohydride is 18385 $g \cdot mol^{-1}$, therefore the pseudo-second order adsorption rate constant can be calculated as $4.3 \cdot 10^{-3}$ $g \cdot \mu mol^{-1} \cdot min^{-1}$.

3.2. Adsorption isotherm.

In order to construct the adsorption isotherm of borohydride on polyurethane foam, a number of experiments were carried out according to the scheme described above, varying the concentration of sodium borohydride in the range of 0.001 ─ 0.02 M.

After removing PUF tablet, the solution was neutralized with an excess of hydrochloric acid of known concentration. Hydrochloric and boric acids in the joint presence were determined using potentiometric titration with alkali with a glass pH-selective electrode. First, hydrochloric acid was titrated until a sharp change in pH. Since boric acid cannot be titrated directly by acid-base titration due to the low acidity constant ($pK_a = 9.24$), glycerol was added to the system during its determination. After this, titration was continued until a second pH increase, which corresponded to boric acid. From the obtained data, equilibrium concentration of borohydride in the aqueous solution was calculated. The specific adsorption of the reducing agent was found by the difference between the initial and equilibrium concentrations divided by the mass of polyurethane foam. The obtained adsorption isotherm of borohydride is shown in figure 3.

It has two stages. It was determined that the first step can be described by the Langmuir adsorption isotherm with parameters K = 724 L mol^{-1}, $a_{max} = 3.1 \cdot 10^{-4}$ mol g^{-1}. Presumably, it is related to the adsorption of borohydride on the surface of polyurethane foam and its absorption near the surface of polymer membranes. The second stage — more pronounced — can be caused by the absorption of

borohydride in the polymer volume, which is often observed when studying the sorption of various organic substances on polyurethane foam [14]. This is also confirmed by the significant difference between the experimental and theoretically calculated values for the maximum adsorption of borohydride, which amounted to $8.0 \cdot 10^{-6}$ mol g^{-1} ($a_m = s_{sp} / (s_{mol}N_A)$), the specific surface of the polyurethane foam is 0.3 m^2 g^{-1} [14], and the size of the BH_4^- ion is 2.5 Å).

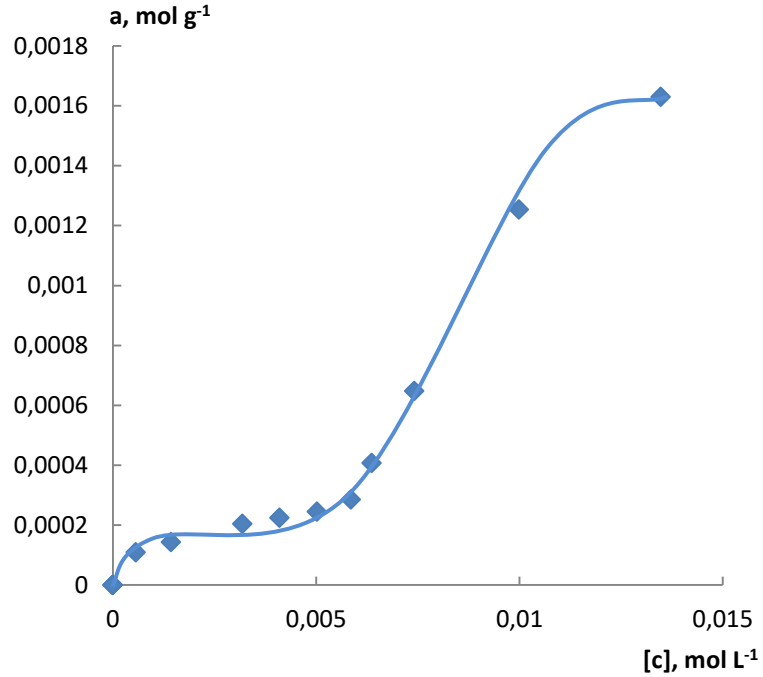

Fig. 3. Adsorption isotherm of borohydride on polyurethane foam.

3.3. Synthesis of gold nanoparticles and their nanocomposites

We found that polyurethane foam modified with borohydride reduces Au(III) from a solution to form gold nanoparticles on PUF surface. The resulting material is a polymer-based nanocomposite with a characteristic SPR band in the spectrum located at 540 nm.

The supposed mechanism of the nanocomposite formation includes slow diffusion-controlled desorption of borohydride anions from polyurethane foam and their interaction in the surface layer with Au(III) to form gold nanoparticles. In absence of a stabilizer that facilitates gold nanoparticles transition to a colloidal solution, they attach onto the surface. In this case, PUF plays a role of a solid-phase stabilizer, forming the nanocomposite.

In this view, it is important to discuss the role of CTAB. On the one hand, this substance promotes sorption of borohydride anions onto PUF, forming a hydrophobic ionic associate. On the other hand, CTAB is a stabilizer of nanoparticles [18] that promote formation of a colloidal system in a solution at high concentration. Depending on the concentration of CTAB, the higher amount of gold nanoparticles on PUF, the lower their amount in the solution can be obtained, and vice versa. At CTAB concentration of 0 and 0.1 M, gold nanoparticles preferably exist in the aqueous solution, at 0.0001 ─ 0.001 M CTAB they form the nanocomposite. It shows the possibility of controlling distribution of nanoparticles between phases. Increasing $NaBH_4$ concentration up to 0.1 M leads to a sharper dependence of the nanocomposite absorbance on concentration of CTAB.

Nanocomposites of gold were studied using scanning electron microdcopy. Formed nanoparticles are attached on a polymer network. A SEM image (Fig. 4a) shows that they are evenly distributed over the surface of the polymer. Nanoparticles on PUF surface have mainly spherical shape. Their average diameter is 12 ± 5.

Colloids of gold nanopaticles by increasing the concentration of CTAB and $NaBH_4$ during preparation of borohydride-modified PUF were obtained. Fig. 4b shows a TEM image of gold nanopaticles synthesized. Their average diameter is (4 ± 1) nm. They have narrow size distribution, which can be ascribed to the slow release of borohydride during desorption from PUF avoiding high local supersaturation and formation of many small particles. On the other hand, this can be ascribed to the stabilizing action of the polymer matrix with respect to nanoparticles forming near its surface.

a b

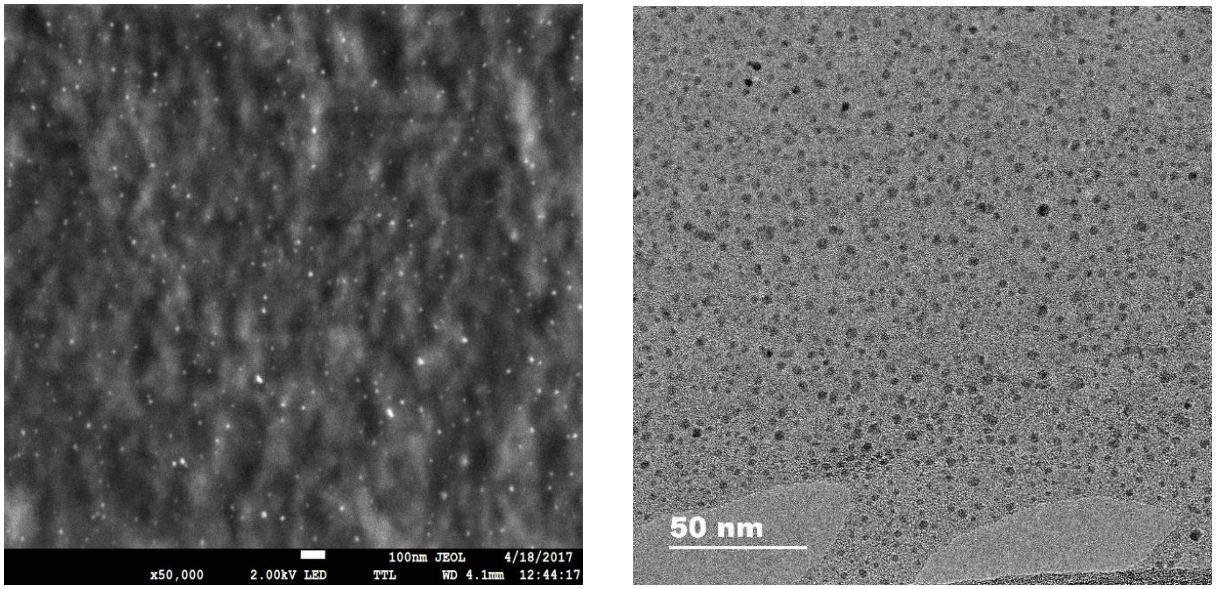

Figure 4. *A SEM image of gold nanocomposites with PUF (a) and TEM image of gold nanoparticles in solution (b).*

4. Conclusions

The features of borohydride-modified polyurethane foam synthesis were studied. This solid-phase reagent can be obtained by a simple adsorption technique. The kinetics of adsorption of sodium borohydride on polyurethane foam was studied. The kinetic sorption curve is well described by a pseudo-second order model. The adsorption isotherm of sodium borohydride on polyurethane foam consists of two stages indicating complex mechanism of adsorption. First stage can be described by the Langmuir equation.

Polyurethane foam modified with borohydride was found to reduce Au(III) from solution to form nanocomposites or colloidal solutions of gold nanoparticles. Due to the controlled desorption of borohydride from polyurethane foam, the synthesized nanoparticles has a narrow size distribution. Control of nanoparticles distribution between polymer and solution can be easily performed by varying CTAB and $NaBH_4$ concentration during the adsorption. The presence of optical properties in the nanocomposites allows their possible use as sensitive materials for optical sensors.

Acknowledgments

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