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ORIGINAL ARTICLE

Borohydride-modified polyurethane foam: a new form of a widely known reducing agent in synthesis of metal nanoparticles for sensing applications

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Abstract
Currently a lot of synthetic routs have been proposed for preparation of various metal nanoparticles for sensing applications. A majority of them are based on the borohydride approach. We have found that some polymers (e.g. polyurethane) can be a promising support for immobilization of borohydride. The present work describes a method for preparation of polyurethane foam modified with borohydride as a new form of the widely known reducing agent and its possibilities for synthesis of metal nanoparticles. This new reagent is quite stable when stored at low temperature and is convenient for use in the synthesis of nanoparticles since it ensures precise dosing of a reductant. Metal nanoparticles could be synthesized both in solution and on polymer surface by varying reagents concentrations during the modified polyurethane foam preparation. It was illustrated that nanoparticles prepared using the borohydride-modified polymer have a narrower size distribution that probably should be ascribed to the stabilizing effect of the polymeric matrix. Optical properties of polyurethane foam-based nanocomposites with metal nanoparticles open a possibility of their using for sensing substances that affect formation of nanoparticles or their distribution between the polymer and the solution.

Keywords Metal nanoparticles · Nanocomposite · Polyurethane foam · Sorption · Analytical application

Introduction

The first article devoted to methods of synthesis and properties of colloidal gold was published by Michael Faraday as early as 1857. Since then, researches on metal nanoparticles (NPs) and their various applications are of increasing interest, as evidenced by the significant growth of scientific publications in this field (Zhang et al. 2016; Gawande et al. 2016; Amendola et al. 2017; Lim et al. 2015; Sirelkhatim et al. 2015; Kuznetsov et al. 2016).

The main efforts of modern researchers are aimed to synthesis of NPs with various sizes, shapes, and narrow size distributions, to search for new substances that stabilize them, to reveal the relationship between the size, shape, and properties of NPs and used reducing agents, stabilizers, and formation conditions, as well as further expansion of the NPs application (Apyari et al. 2014; Terenteva et al. 2017; Das et al. 2018; Goud et al. 2018; Malik and Mukherjee 2018; Xiao et al. 2018; Georgakilas et al. 2016; Zhu et al. 2015; Huang et al. 2017; Kaushik and Moores 2016).

Special attention is paid to the creation of new nanocomposite and hybrid materials. Inclusion of NPs into various solid matrices makes it possible to create new nanocomposite materials, often favorably distinguished by their performance, optical, chemical, mechanical, catalytic, electrical, and other characteristics. Therefore, detailed studies on synthesis and applications of NP-based materials is of great interest (Liu et al. 2017; Ahmad et al. 2015; Merino et al. 2015; Khalil et al. 2016; Rie and Thielemans 2017; Ferhan and Kim 2016).

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Among NPs, gold (AuNPs) and silver nanoparticles (AgNPs) are quite interested and widely studied. First of all, this is due to their unique optical properties. They are based on the surface plasmon resonance phenomenon (SPR) (Amendola et al. 2017; Dykman et al. 2008; Dykman and Bogatyrev 2007; Wang and Ma, 2009; Ghosh and Pal 2007; Saarinen et al. 2009). It leads to appearance of the SPR bands in their absorption spectra. The optical properties of AuNPs and AgNPs are widely used in various fields of science and technology. In particular, these NPs are used to develop the spectrophotometric and colorimetric methods of analytical chemistry for the determination of various substances (Apyari et al. 2014; Terenteva et al. 2017; Priyadarshini and Pradhan 2017; Majdalawieh et al. 2014; Howes et al. 2014; Zhou et al. 2015). Size, shape and chemical surrounding of the NPs play a crucial role for their analytical properties and range of possible use. Therefore, a special attention should be paid to the method of synthesis and processes during NP formation.

Formation of nanoparticles proceeds through a series of successive stages: the emergence of individual atoms; nucleation and formation of an initial atomic cluster; growth of the cluster to a certain size; stabilization of NPs. Dimensions and dispersity of the NPs formed, as well as their stability over time, are regulated by varying the nature of the stabilizer and the synthetic process conditions. As stabilizers in the synthesis of monodisperse NPs, one can use excess of a reducing agent as well as specially introduced substances: ionic surfactants, e.g. sodium dodecyl sulfate or lauryltrimethylammonium chloride, ionic liquids, synthetic and natural polymers—polyvinylpyrrolidone, polyethylene glycol, cyclodextrins, chitosan and others (Dykman and Bogatyrev 2007).

As the reducing agent, sodium borohydride is used most often (Tan and Cheong 2013). Main feature of this widely used reductant is its high reduction ability, which makes it possible to obtain NPs of various metals differing greatly in their redox potentials. Sodium borohydride is quite stable in solid form and is convenient for use in the synthesis of nanoparticles in both aqueous and organic media.

The present work describes a method for preparation of polyurethane foam modified with borohydride as a new form of the widely known reducing agent and its possibilities for synthesis of metal nanoparticles.

Experimental

Reagents and instruments

The following reagents were used in the study: sodium borohydride, sodium hydroxide, cetyltrimethylammonium bromide (CTAB), hydrogen tetrachloroaurate, silver nitrate, hydrochloric acid, cysteamine hydrochloride. All they were at least of analytical grade. Stock solutions of these reagents were prepared using deionized water.

Polyether-based polyurethane foam (PUF) was cut into cylindrical tablets of 16 mm in diameter of (20 ± 2) mg each from an industrial sheet of the polymer. PUF tablets were cleaned in acetone by shaking for 10 min. The cleaning was repeated twice. After that the tablets were dried under stream of air. They were stored in a place protected from light.

Absorbances were recorded by SF-103 spectrophotometer (Akvilon, Russia), diffuse reflectance measurements were carried out using Eye-One Pro mini-spectrophotometer (X-Rite) (Apyari et al. 2011, 2013) on a white base.

The content of NPs in phase of polyurethane foam was estimated using values of the Kubelka–Munk function (F) at a wavelength of an absorption maximum (λ_{max}): $F = \frac{(1-R^2)}{2R}$, here R is the diffuse reflection. pH was measured using Ekspert 001 pH-meter (Ekoniks Ekspert). TEM-images were recorded using a transmission electron microscope Libra 200 (Zeiss, Germany). The accelerating voltage was 200 kV. 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 a 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). A mechanical shaker was also used.

Preparation of borohydride-modified polyurethane foam (PUF/BH_4)

The polyurethane foam modified with borohydride was prepared by a sorption method. Sorption was carried out in a static mode. The PUF tablets were placed in a test-tube containing 5 mL of an aqueous solution of the following composition: 0.01 mol L^{-1} sodium borohydride, 0.01 mol L^{-1} sodium hydroxide and CTAB (0.0001 mol L^{-1} for the synthesis of nanocomposites or 0.01 mol L^{-1} for the synthesis of NPs colloids). The tablets were thoroughly pressed with a glass rod to remove air bubbles from pores and shaken on an electromechanical shaker for 15 min. After that, the tablets of PUF/BH_4 were removed and dried between sheets of filter paper.

Synthesis of metal nanoparticles and nanocomposites with PUF/BH_4 as a reducing agent

For the synthesis of metal NPs (gold and silver), freshly prepared PUF/BH_4 tablets were placed in 5 mL of a suitable precursor solution (hydrogen tetrachloroaurate or silver

nitrate respectively) of the concentration of 20 μg mL^{-1} in terms of atomic metal. The tablets were thoroughly pressed with a glass rod and stirred by shaking on an electromechanical shaker for 30 min. Then, the tablets were removed and dried between sheets of filter paper. Depending on the concentration of CTAB used during preparation of PUF/BH_4, either NPs colloids or PUF/NPs nanocomposites can be prepared.

Analytical application of the PUF/AuNPs nanocomposites for the determination of cysteamine

To build the calibration curve, different amounts of cysteamine (0–26 μ mol L^{-1}) were added during the synthesis of nanocomposites. After preparation of PUF/AuNPs, the diffuse reflectance of the resulting tablets was measured. The calibration curve was plotted as the decrease of the Kubelka–Munk function compared to the blank without cysteamine (ΔF) versus the concentration of cysteamine.

Results and discussion

General approach and scheme of the experiments

In this study, polyurethane foam was proposed as a solid matrix for preparation of a new form of a reducing agent for the synthesis of NPs. This choice was primarily justified by the unique sorption properties of this material, caused by the presence in its structure groups of different nature—urethane, ether, carbonyl, amino, phenylene, and alkyl. Owing to them, PUF effectively absorbs substances of different polarity, dissolving them in its polymeric membranes (Dmitrienko and Apyari 2010; Dmitrienko et al. 2012; Ramazanova et al. 2013). Additional advantages of this sorbent are the continuity and softness of the structure. These properties make it easy to separate the polymer from solution and remove residual liquid from pores by compressing between the sheets of filter paper. High efficiency of PUF sorption centers allows anchoring its network to not only chemical compounds, but also nanoparticles (Jain and Pradeep 2005; Jeon et al. 2008; Chou et al. 2006; Apyari et al. 2012; Gorbunova et al. 2017; Furletov et al. 2018; Arkhipova et al. 2015). This reveals possibility of creating nanocomposites based on this sorbent, which are promising for use in chemical analysis, medicine, healthcare, and other spheres. Moreover, polyurethane foam can be industrially produced as large soft and flexible pieces of various forms and reversibly compressed mechanically for many times. This opens prospects for application of the proposed approach for bulk preparation of the nanocomposites at an industrial scale.

In this work, PUF has been first modified with borohydride and studied as a new form of this widely known reductant for the synthesis of nanoparticles. The general scheme of the experiment is illustrated in Fig. 1a. It included two stages. In the first stage, sorption of sodium borohydride on PUF was carried out from a solution containing sodium hydroxide and CTAB. Sodium hydroxide is necessary as a stabilizer which reduces the concentration of hydrogen ions and, accordingly, the rate of borohydride decomposition. CTAB was added as an ion-pair reagent to form a hydrophobic ionic associate with borohydride anion to facilitate its transition to the polyurethane phase. The second step involved interaction of PUF/BH_4 with hydrogen tetrachloroaurate (or other precursor), resulting in the formation of PUF nanocomposite with AuNPs (or AuNPs colloids depending on the conditions, as discussed below). In Fig. 1b the spectrum of the resulting nanocomposite of PUF with AuNPs (PUF/AuNPs) is shown. One can see a characteristic SPR band with a maximum at 540 nm in the spectrum of the nanocomposite. The shift of this band of about 20 nm in comparison with the characteristic SPR band of AuNPs in solution located at 520 nm is probably due to the influence of the polymer matrix on the plasmon oscillation frequency, as well as the more compact arrangement of AuNPs on the polymer surface compared to the aqueous solution.

The supposed mechanism includes slow diffusion-controlled desorption of borohydride anions from polyurethane foam and their interaction in the surface layer with a precursor to form NPs. In absence of a stabilizer that facilitates NPs transition to a colloidal solution, they attach onto the surface of the polymer, which in this case, in fact, plays a role of a solid-phase stabilizer, forming the nanocomposite.

PUF/BH_4 synthesis optimization

The synthesis conditions have a significant effect on characteristics of the borohydride-modified polyurethane foam and its possibilities for the synthesis of nanoparticles.

First of all, modifying of PUF with borohydride can be accompanied with trapping of the solution drops containing redundant amounts of this reagent. This excess will affect reproducibility of PUF/BH_4 properties. To choose appropriate initial conditions for preparation of PUF/BH_4, a reproducibility study was done. Optical properties of the nanoparticles formed in the PUF phase were used to control their state. The data derived are represented in Table 1. One can see that high concentrations of the reagents (first three data rows) result in low reproducibility (the relative standard deviation, RSD of about 8–19%). This is assumed due to the redundant amounts of the reagents remaining on PUF that can be hardly eliminated by pressing of PUF samples with filter paper. Decreased concentrations of $NaBH_4$ and CTAB (data rows 4–5) lead to improved reproducibility, however

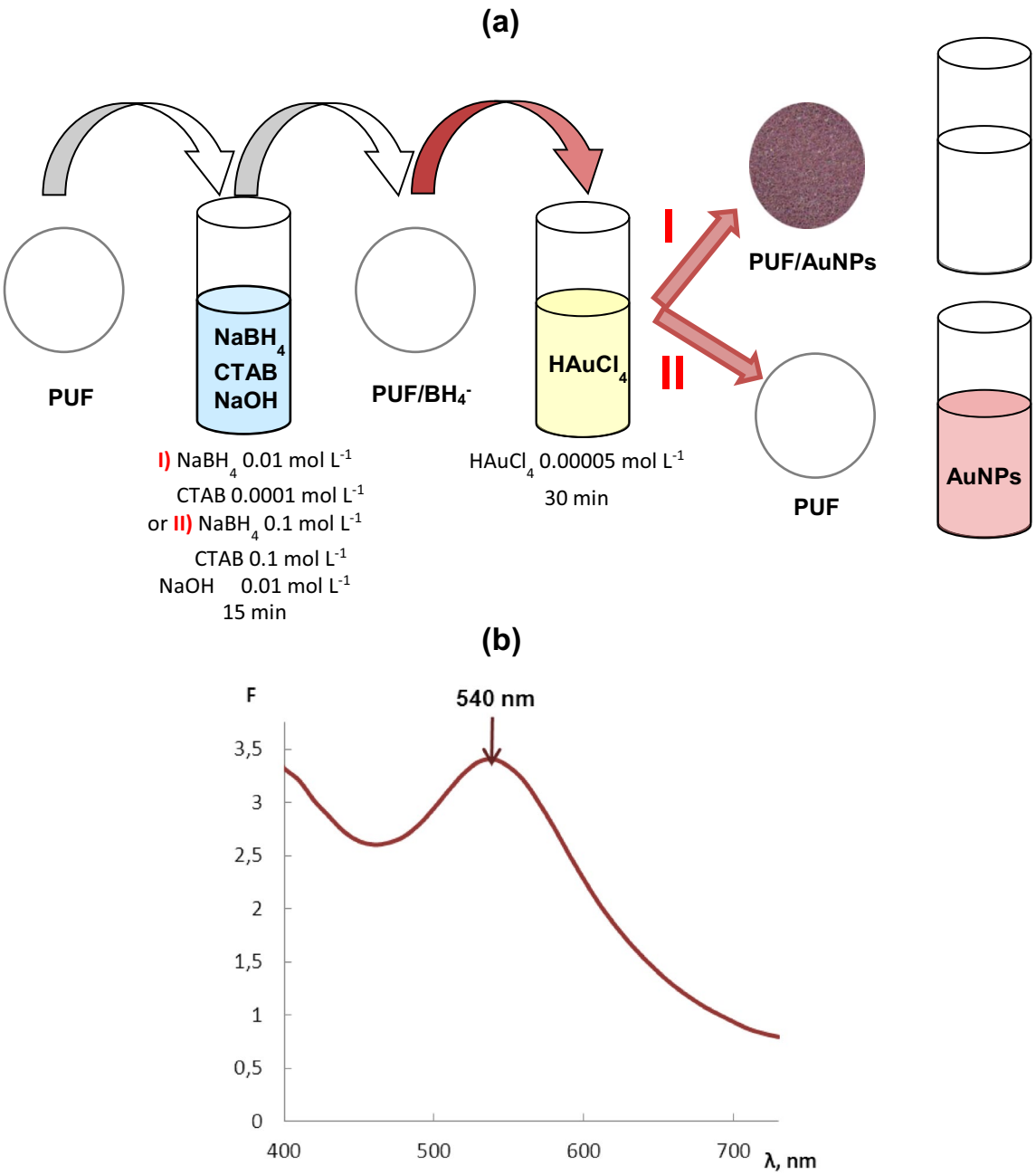

Fig. 1 **a** General scheme of the experiments; **b** diffuse reflectance spectrum of PUF/AuNPs nanocomposite

Table 1 Reproducibility of PUF/AuNPs preparation at different concentrations of the reagents

Concentration of a reagent (mol L^{-1})			Relative standard deviation (%)
$NaBH_4$	NaOH	CTAB	
0.1	0	0	8.4
0.1	0.01	0	18.8
0.1	0	0.001	15.8
0.0001	0	0.0001	–
0.0001	0.01	0.0001	6.3
0.01	0.01	0.0001	6.6

intensity of the spectrum becomes insufficiently low. Finally, a solution containing 0.01 mol L^{-1} $NaBH_4$ and NaOH, and 0.0001 mol L^{-1} CTAB (data row 6) was considered as appropriate for preparation of PUF/BH_4 with RSD of 6.6%.

Effect of the phases contact time and the concentration of reagents on sorption of borohydride onto PUF was studied. Effect of these factors on the intensity of an SPR band of the resulting nanocomposite is illustrated in Fig. 2.

From the data represented, it is evident that about 2/3 of the maximum possibly amount of sorbed borohydride is extracted within 1 min (Fig. 2a). This indicates a high

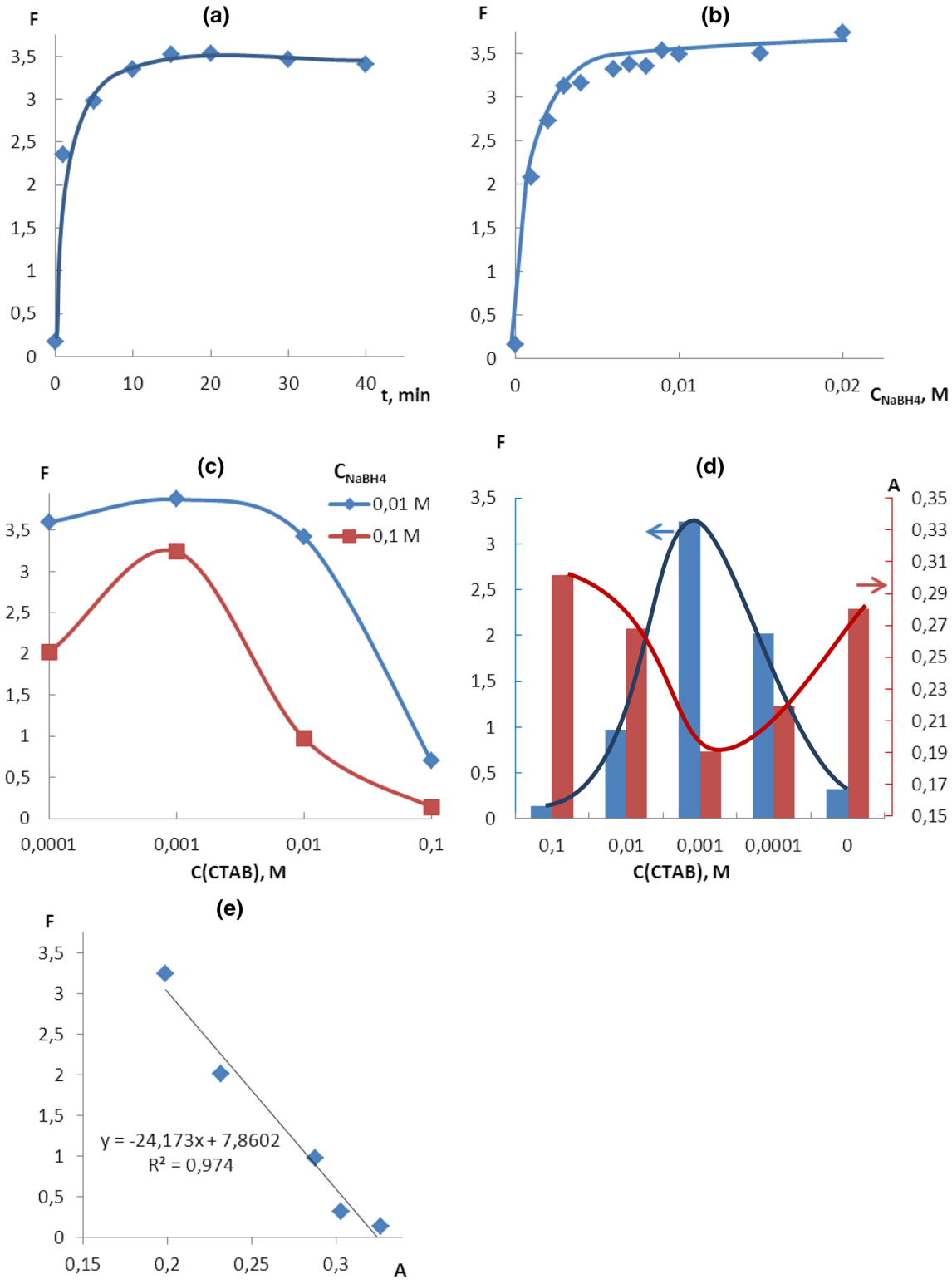

Fig. 2 Dependence of F on phases contact time (**a**), concentration of $NaBH_4$ (**b**), and CTAB (**c**). Meanings of F of the nanocomposite and absorbance of the solution at various concentrations of CTAB (**d**). Dependence of *F* of the nanocomposite on absorbance of the solution (**e**)

rate of sorption, which is valuable from a practical point of view. To achieve the maximum signal, 10–15 min of the phase contact is required. In all subsequent experiments, sorption was carried out for 15 min.

An important factor affecting the characteristics of PUF/BH_4 is the concentration of sodium borohydride in the solution for modification (Fig. 2b). With increasing concentration of $NaBH_4$ up to 0.003 M, the number of NPs produced increases, which can be used to regulate optical and other properties of the resulting material. At high concentrations of $NaBH_4$, the signal growth stops because of the full consumption of the precursor. Introducing large amounts of $NaBH_4$ (> 0.01 M) is impractical because of both consumption of the reagent and the greater contribution of the surface-deposited reductant, amount of which is difficult to control, impairing reproducibility of the final material. To achieve the best reproducibility, $NaBH_4$ concentration was chosen as 0.01 mol L^{-1} in subsequent experiments.

Unlike other factors, the concentration of alkali does not significantly affect the amount of gold nanoparticles formed. However, this reagent is necessary for stabilization of borohydride, which has a positive effect on reproducibility of the results. Therefore, in further experiments, its concentration was set to 0.01 mol L^{-1}.

The role of CTAB is quite interesting. On the one hand, this substance promotes sorption of borohydride anions on the polyurethane foam, forming a hydrophobic ionic associate. On the other hand, it is known that CTAB is a stabilizer of nanoparticles (Tan and Cheong 2013) that promote formation of a colloidal system in solution at high concentration. It was shown (Fig. 2c) that increasing its concentration up to 0.001 M leads to an increase in the optical signal of the nanocomposite. At the same time, one can observe increasing formation of gold nanoparticles in the solution (Fig. 2d). At concentrations > 0.001 M, a decrease in the nanoparticles signal in both nanocomposite and solution is observed. However, a band of Au(III) complexes at 400–430 nm grows in the solution, i.e. formation of nanoparticles is suppressed under these conditions.

Increasing $NaBH_4$ concentration up to 0.1 M leads to a sharper dependence of the nanocomposite absorbance on concentration of CTAB. Figure 2e illustrates that, depending on the concentration of CTAB, the higher amount of gold nanoparticles on PUF, the lower their amount in the solution is, 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. In fact, one can assume that there is a competition between two stabilizers—a solid phase one (PUF) and a dissolved one (CTAB). This can be proved by an antibate linear relation between Kubelka–Munk function of the nanocomposite and absorbance of the solution (Fig. 2f). It shows the possibility of controlling distribution of NPs between phases.

On the basis of experimental data, the following conditions were chosen for the preparation of PUF/BH_4 as a new form of a reducing agent for synthesis of nanocomposites: $NaBH_4$ sorption time—15 min, $NaBH_4$ concentration—0.01 M, sodium hydroxide and CTAB concentrations—0.01 and 0.0001 M, respectively. For synthesis of NPs colloids, the concentrations of $NaBH_4$ and CTAB should be increased up to 0.1 M.

Stability of PUF/BH_4

From a practical point of view, it is important to know stability of a reagent during storage. It is well known that aqueous solutions of $NaBH_4$ are unstable and should be used immediately after preparation. It was of interest to study stability of PUF/BH_4 in time (Fig. 3). It was shown that PUF modified

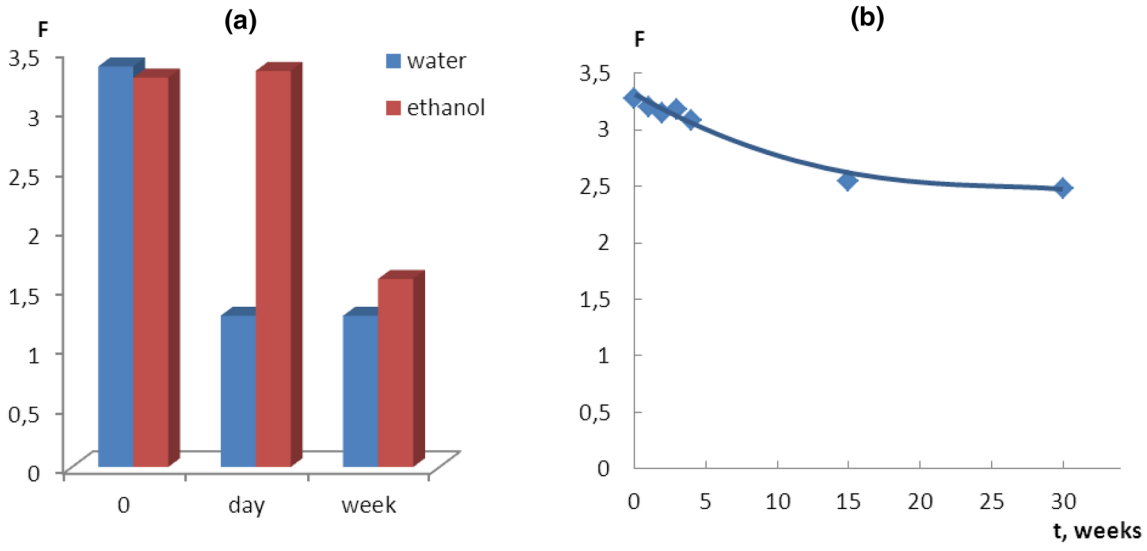

Fig. 3 The time stability of PUF/BH_4 obtained in aqueous and ethanol solution when stored at room temperature (**a**); and PUF/BH_4 obtained from an aqueous solution when stored in a freezer (**b**)

in aqueous solution is stable only for several hours and loses its activity in a day (Fig. 3a). By analogy with the aqueous solution, it can be assumed that this is because of hydrolysis of borohydride by residual water in PUF structure. It was found that the modification from alcohol allows achieving increase in stability of the reagent. In this case, its activity remains at the same level even after 1 day (Fig. 3a).

The decomposition rate of borohydride can be reduced by cooling. From Fig. 3b it is clear that storage at low temperature (− 20 °C) in a freezer allows this reagent to be used for at least 1 month without any loss of activity (Fig. 3b), and even after half a year, the loss is not significant.

Thus, PUF/BH_4 obtained even from aqueous solution is stable at low temperature and can be used for a long time. Preparation from aqueous solution is economically more justified, so synthesis PUF/BH_4 from alcohol is unnecessary except for some special cases.

Application of PUF/BH_4 for synthesis of metal nanocomposites

The new solid-phase reagent can be used to synthesize nanocomposites of metals. We have studied preparation of nanocomposites of gold and silver. Formed nanoparticles are attached on a polymer network. From a magnified image, by the example of a PUF/AuNPs cutoff shown in Fig. 4, it can be seen that the most intense coloration of polymeric membranes occurs at the edges. Within individual nodes, being cut perpendicularly to the direction of vision, the color is much weaker than around. This suggests that NPs are located on the surface of the polymer membranes and are practically absent inside. A SEM image represented in Fig. 4 shows that they are evenly distributed over the surface of the polymer. In our opinion, such a monolithic honeycomb structure of PUF/NPs is very interesting for practice.

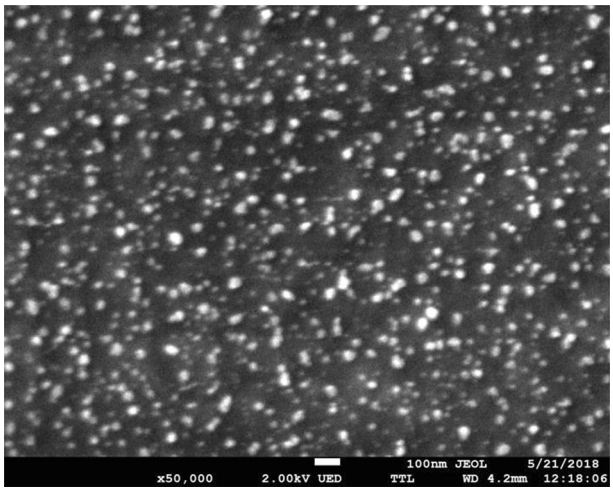

Fig. 5 A SEM image of silver nanocomposite with PUF

In particular, it may prove promising for the development of catalysts, sorbents, sensors, etc.

Similarly, using an $AgNO_3$ precursor, nanocomposites of PUF and silver NPs can be obtained. Electron microscopy showed that NPs on PUF surface are basically spherical in shape (Fig. 5). Their average diameters were 12 ± 5 and 34 ± 14 nm for gold and silver, respectively.

Figure 6 shows histograms of size distribution of NPs on PUF surface. Histograms can be characterized by a distribution close to normal. Polydispersity indices of these NPs calculated as $PDI = s^2/\langle d \rangle^2$ (here s is the standard deviation of the diameter, $\langle d \rangle$ is the average diameter) are 0.0364 and 0.0413 for gold and silver, respectively.

All obtained nanocomposites possess characteristic resonance optical properties inherent in the corresponding nanoparticles. Diffuse reflectance spectra of the nanocomposites obtained are given in Fig. 7. The maxima of the SPR bands

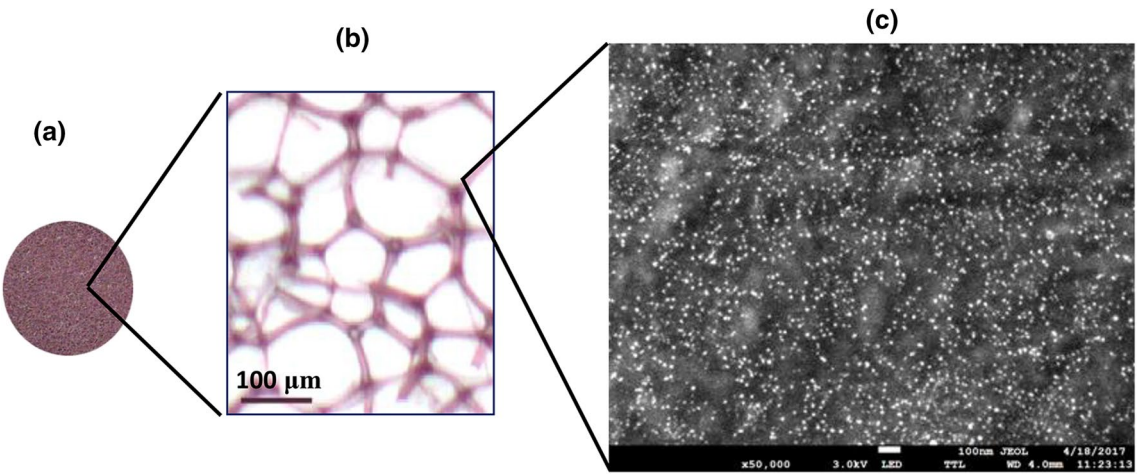

Fig. 4 A sample of PUF/AuNPs nanocomposite (**a**), a magnified visible image of its structure (**b**) and its SEM image (**c**)

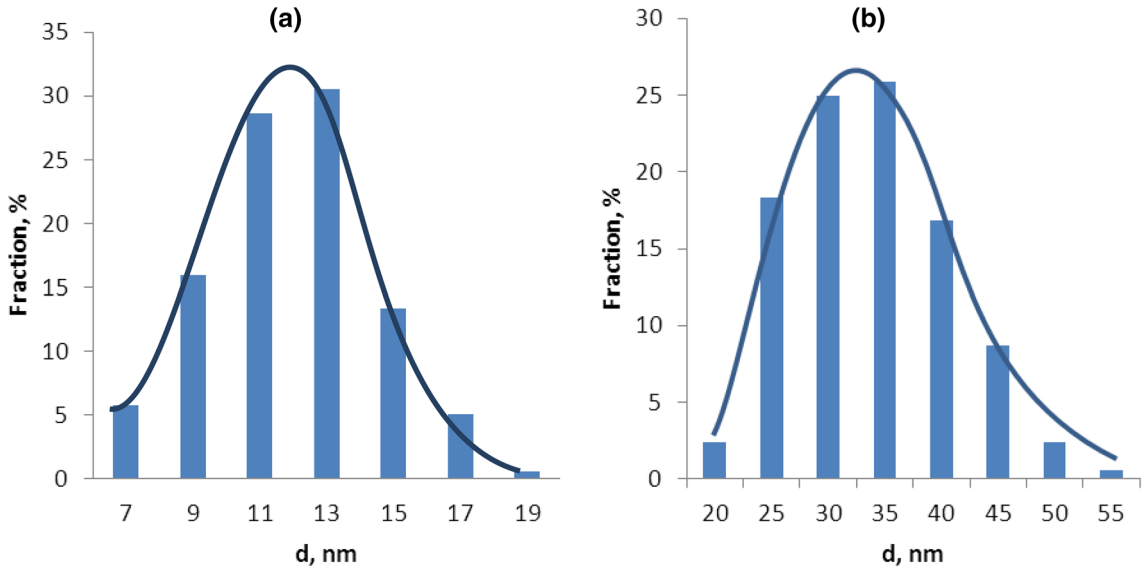

Fig. 6 Size distribution histograms of the gold (**a**) and silver (**b**) nanoparticles on PUF surface

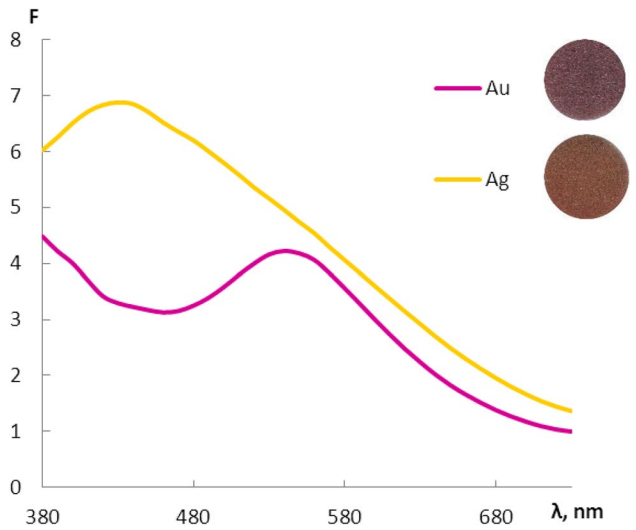

Fig. 7 Diffuse reflectance spectra of gold and silver nanocomposites with PUF

of gold and silver are at 540 and 430 nm, respectively. The presence of optical properties in nanocomposites allows their possible use as sensitive materials of optical sensors.

Application of PUF/BH_4 for synthesis of metal nanoparticles colloids

As was said above, control of distribution of the formed NPs between PUF and solution can be carried out by varying the concentration of CTAB and $NaBH_4$ during preparation of PUF/BH_4. Addition of excess CTAB and 0.1 M sodium borohydride leads to a colloid of nanoparticles (Fig. 1). No nanocomposite formation can be observed in this case. By the example of gold, characteristics of the NPs formed in solution were studied. Figure 8a shows a TEM image of AuNPs synthesized using PUF/BH_4. In Fig. 8b, c TEM images of AuNPs obtained under the similar conditions but in the absence of PUF are given. In these cases, $NaBH_4$ was added as an aqueous solution directly into the reaction mixture. It can be seen that the NPs obtained with the use of PUF/BH_4 have a shape close to spherical and approximately equal size. Their average diameter is (4 ± 1) nm. The size distribution of these NPs is much narrower than when solutions of the corresponding reagents are mixed in the absence of PUF (Fig. 8d). The calculated polydispersity index (PDI) for AuNPs obtained using PUF/BH_4 was 0.0264. This value is 5–10 times smaller than for the cases shown in Fig. 8b,c (PDI = 0.1069 and 0.2176, respectively). This value is also 10 times less than for AuNPs obtained by the classical Turkevich method (PDI = 0.282) (Manson et al. 2011; Kimling et al. 2006). Apparently, this is due to the slow release of borohydride during desorption from PUF, which avoids 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. Thus, PUF/BH_4 is promising for obtaining not only nanocomposites based on PUF, but also colloid solutions of NPs, which significantly expands its practical applications.

Practical application in analytical chemistry

Optical properties of PUF nanocomposites with metal NPs open a possibility of using PUF/BH_4 as an analytical reagent.

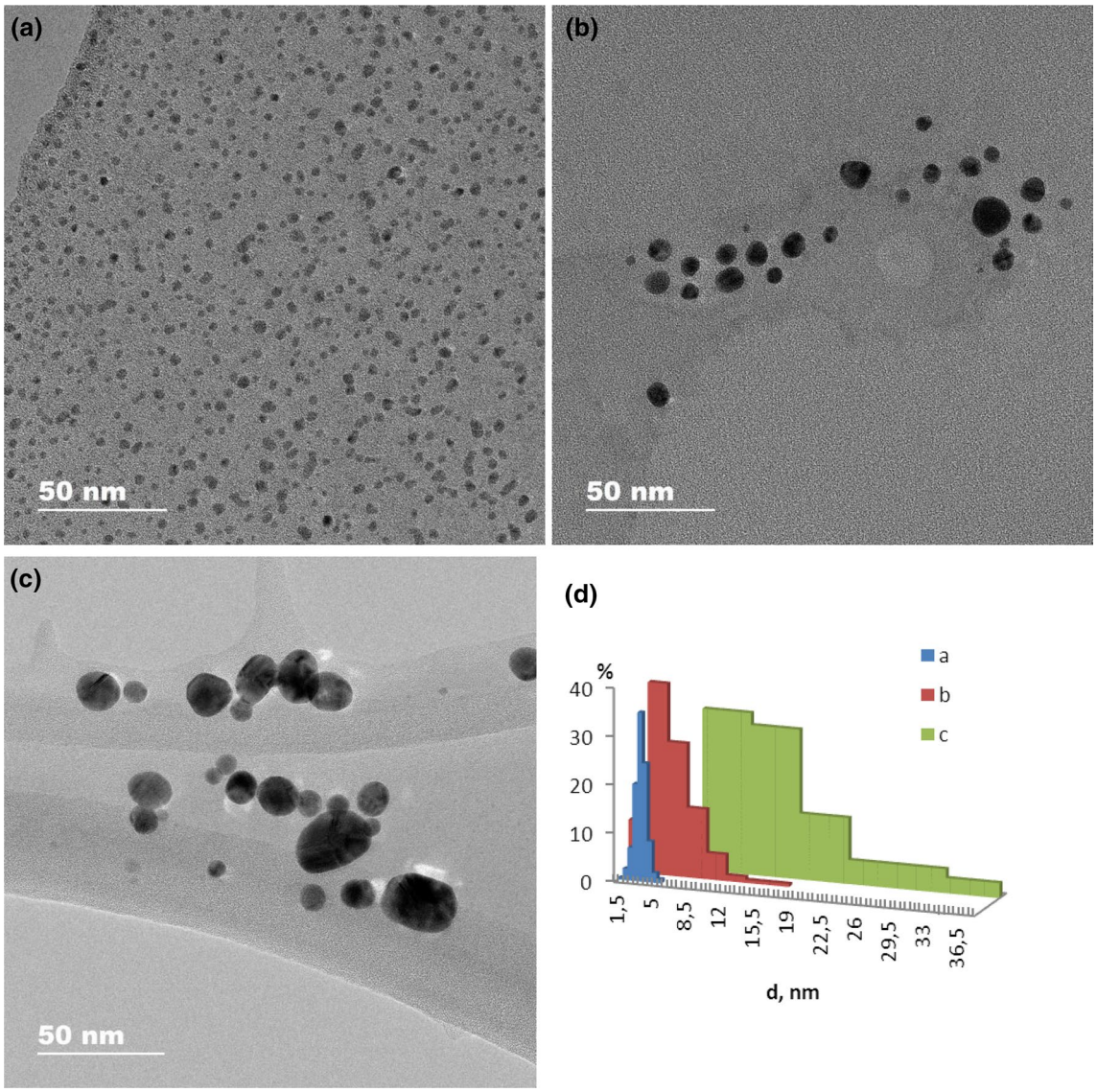

Fig. 8 TEM images (**a**–**c**) and histograms of size distribution (**d**) of AuNPs in solution prepared using **a** PUF/BH_4; **b** by adding solution of $NaBH_4$ to solution of $HAuCl_4$; **c** by adding solution of $HAuCl_4$ to solution of $NaBH_4$

On the one hand, it can be used to determine gold and silver, on the other hand—substances that affect formation of NPs or their distribution between the polymer and the solution. An important advantage of this reagent is an ability to detect an analytical response using simple equipment or visually. At the same time, the stabilizing effect of PUF in relation to the formed NPs should provide good analytical performance and, accordingly, the ability to determine small contents of an analyte.

Within the second option, a possibility of determining cysteamine using PUF/BH_4 has been demonstrated. Cysteamine is able to form a strong bond with gold due to the presence of the mercapto and the amino group. Addition of this compound at the stage of interaction between PUF/BH_4 and $HAuCl_4$ influences formation of the nanocomposite, which is manifested by a decrease in the SPR band and color of the sample (Fig. 9a). This effect can be used for cysteamine determination. Decrease of the Kubelka–Munk function at 540 nm was used as an analytical signal. I was shown that it depends linearly on the concentration of cysteamine in solution, which was used to construct a calibration curve (Fig. 9b). The method allows to determine the content of cysteamine in the range of 1.8–18 μmol L^{-1}, the detection limit is 0.6 μmol L^{-1}, which indicates good sensitivity of the determination.

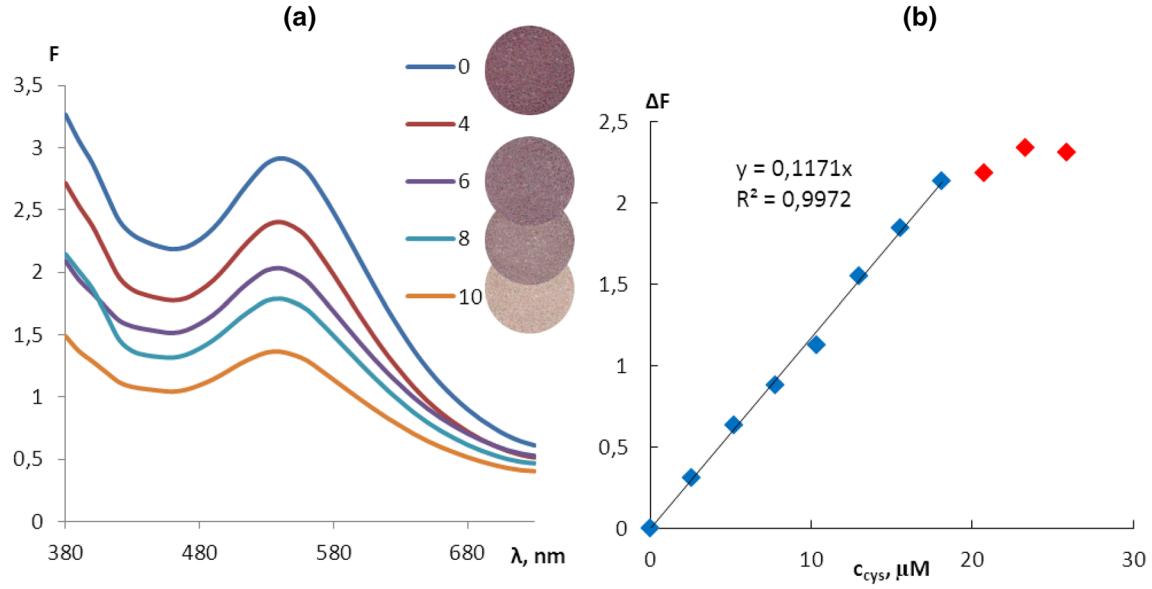

Fig. 9 Diffuse reflectance spectra and images of the nanocomposite samples obtained in the presence of different concentrations (μmol L^{-1}) of cysteamine (**a**) and the calibration curve for the determination of cysteamine (**b**). C_{HAuCl_4} = 0.05 mM, t = 30 min, pH 3.7, **b** λ = 540 nm

Conclusions

Borohydride-modified polyurethane foam has been proposed as a new form of the well-known reducing agent to obtain nanocomposites and colloidal solutions of nanoparticles of various metals. This solid-phase reagent can be obtained by a simple sorption technique. 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 preparation of the borohydride-modified polyurethane foam. The change in distribution of nanoparticles between the phases in the presence of cysteamine makes it possible to propose an approach to its determination using diffuse reflectance spectroscopy. The advantages of the proposed scheme include simplicity, high throughput, availability of the equipment used, and facility of a semi-quantitative test-version implementation. Synthesized nanocomposites have a potential to be used in medicine, catalysis, analytical chemistry.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, Vladimir V. Apyari states that there is no conflict of interest.

References

Ahmad R, Griffete N, Lamouri A, Felidj N, Chehimi MM, Mangeney C (2015) Nanocomposites of gold nanoparticles@molecularly imprinted polymers: chemistry processing and applications in sensors. Chem Mater 27:5464–5478

Amendola V, Pilot R, Frasconi M, Maragò OM, Iatì MA (2017) Surface plasmon resonance in gold nanoparticles: a review. J Phys Condens Matter. https://doi.org/10.1088/1361-648X/aa60f3

Apyari VV, Dmitrienko SG, Batov IV, Zolotov YuA (2011) An Eye-One Pro mini-spectrophotometer as an alternative to diffuse reflectance spectrometer. J Anal Chem 66:144–150

Apyari VV, Volkov PA, Dmitrienko SG (2012) Synthesis and optical properties of polyurethane foam modified with silver nanoparticles. Adv Nat Sci Nanosci Nanotechnol. https://doi.org/10.1088/2043-6262/3/1/015001

Apyari VV, Dmitrienko SG, Zolotov YuA (2013) Unusual application of common digital devices: potentialities of Eye-One Pro mini-spectrophotometer—a monitor calibrator for registration of surface plasmon resonance bands of silver and gold nanoparticles in solid matrices. Sens Actuators B 188:1109–1115

Apyari VV, Arkhipova VV, Dmitrienko SG, Zolotov YuA (2014) Using gold nanoparticles in spectrophotometry. J Anal Chem 69:1–11

Arkhipova VV, Apyari VV, Dmitrienko SG (2015) Determination of polyhexamethylene guanidine hydrochloride using gold nanoparticles and polyurethane foam. Moscow Univ Chem Bull 70:28–33

Chou C-W, Hsu S-H, Chang H, Tseng S-M, Lin H-R (2006) Enhanced thermal and mechanical properties and biostability of polyurethane containing silver nanoparticles. Polym Degrad Stabil 91:1017–1024

Das P, Sedighi A, Krull UJ (2018) Cancer biomarker determination by resonance energy transfer using functional fluorescent nanoprobes. Anal Chim Acta 1041:1–24

Dmitrienko SG, Apyari VV (2010) Penopolyurethany: sorbtsionnye svoistva i primenenie v khimicheskom analize (Polyurethane

foams: sorption properties and application in chemical analysis). Krasand, Moscow
Dmitrienko SG, Apyari VV, Kudrinskaya VA, Stepanova AV (2012) Preconcentration of flavonoids on polyurethane foam and their direct determination by diffuse reflectance spectroscopy. Talanta 102:132–136
Dykman LA, Bogatyrev VA (2007) Gold nanoparticles: preparation functionalization and applications in biochemistry and immunochemistry. Usp Khim 76:199–213
Dykman LA, Bogatyrev VA, Shchegolev SYu, Khlebtsov NG (2008) Gold nanoparticles: synthesis properties and biomedical use. Nauka, Moscow
Ferhan AR, Kim D-H (2016) Nanoparticle polymer composites on solid substrates for plasmonic sensing applications. Nanotoday 11:415–434
Furletov AA, Apyari VV, Garshev AV, Volkov PA, Tolmacheva VV, Dmitrienko SG (2018) Sorption of triangular silver nanoplates on polyurethane foam. Rus J Phys Chem A 92:357–360
Gawande MB, Goswami A, Felpin F-X, Asefa T, Huang X, Silva R, Zou X, Zboril R, Varma RS (2016) Cu and Cu-based nanoparticles: synthesis and applications in catalysis. Chem Rev 116:3722–3811
Georgakilas V, Tiwari JN, Kemp KC, Perman JA, Bourlinos AB, Kim KS, Zboril R (2016) Noncovalent functionalization of graphene and graphene oxide for energy materials biosensing catalytic and biomedical applications. Chem Rev 116:5464–5519
Ghosh SK, Pal T (2007) Interparticle coupling effect on the surface plasmon resonance of gold nanoparticles: from theory to applications. Chem Rev 107:4797–4862
Gorbunova MV, Matveeva MA, Apyari VV, Garshev AV, Volkov PA, Dmitrienko SG, Zolotov YuA (2017) Sorption of gold nanorods on polyurethane foam as a way to obtain a nanocomposite material with a surface plasmon resonance for chemical analysis purposes. Nanotechnol Russ 12:185–192
Goud KY, Kalisa SK, Kumar V, Tsang YF, Lee SE, Gobi KV, Kim K-H (2018) Progress on nanostructured electrochemical sensors and their recognition elements for detection of mycotoxins: a review. Biosens Bioelectron 121:205–222
Howes PD, Rana S, Stevens MM (2014) Plasmonic nanomaterials for biodiagnostics. Chem Soc Rev 43:3835–3853
Huang Y-B, Liang J, Wang X-S, Cao R (2017) Multifunctional metal-organic framework catalysts: synergistic catalysis and tandem reactions. Chem Soc Rev 46:126–157
Jain P, Pradeep T (2005) Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter. Biotechnol Bioeng 90:59–63
Jeon HJ, Kim JS, Kim TS, Kim JH, Yu W-R, Youk JH (2008) Preparation of poly(e-caprolactone)-based polyurethane nanofibers containing silver nanoparticles. Appl Surf Sci 254:5886–5890
Kaushik M, Moores A (2016) Review: nanocelluloses as versatile supports for metal nanoparticles and their applications in catalysis. Green Chem 18:622–637
Khalil I, Julkapli NM, Yehye WA, Basirun WJ, Bhargava SK (2016) Graphene–gold nanoparticles hybrid—synthesis functionalization and application in a electrochemical and surface-enhanced Raman scattering biosensor. Materials. https://doi.org/10.3390/ma9060406
Kimling J, Maier M, Okenve B, Kotaidis V, Ballot H, Plech A (2006) Turkevich method for gold nanoparticle synthesis revisited. J Phys Chem B 110:15700–15707
Kuznetsov AI, Miroshnichenko AE, Brongersma ML, Kivshar YS, Luk'yanchuk B (2016) Optically resonant dielectric nanostructures. Science. https://doi.org/10.1126/science.aag2472
Lim SY, Shen W, Gao Z (2015) Carbon quantum dots and their applications. Chem Soc Rev 44:362–381
Liu X, Iocozzia J, Wang Y, Cui X, Chen Y, Zhao S, Li Z, Lin Z (2017) Noble metal-metal oxide nanohybrids with tailored nanostructures for efficient solar energy conversion photocatalysis and environmental remediation. Energy Environ Sci 10:402–434
Majdalawieh A, Kanan MC, El-Kadri O, Kanan SM (2014) Recent advances in gold and silver nanoparticles: synthesis and applications. J Nanosci Nanotechol 17:4757–4780
Malik P, Mukherjee TK (2018) Recent advances in gold and silver nanoparticle based therapies for lung and breast cancers. Int J Pharm 553:483–509
Manson J, Kumar D, Meenan JB, Dixon D (2011) Polyethylene glycol functionalized gold nanoparticles: the influence of capping density on stability in various media. Gold Bull 44:99–105
Merino S, Martín C, Kostarelos K, Prato M, Vázquez E (2015) Nanocomposite hydrogels: 3D polymer-nanoparticle synergies for on-demand drug delivery. ACS Nano 9:4686–4697
Priyadarshini E, Pradhan N (2017) Gold nanoparticles as efficient sensors in colorimetric detection of toxic metal ions: a review. Sens Actuators B 238:888–902
Ramazanova GR, Tikhomirova TI, Apyari VV (2013) Sorption of food dyes on polyurethane foam and aluminum oxide. Moscow Univ Chem Bull 68:175–180
Saarinen JJ, Vartiainen EM, Peiponen KE (2009) Surface plasmon resonance reflectance from nanoparticles in a liquid matrix: retrieval of the optical properties using the maximum entropy model. Sens Actuators B 138:383–395
Sirelkhatim A, Mahmud S, Seeni A, Kaus NHM, Ann LC, Siti SKM, Hasan H, Mohamad D (2015) Review on zinc oxide nanoparticles: antibacterial activity and toxicity mechanism. Nano Micro Lett 7:219–242
Tan KS, Cheong KY (2013) Advances of Ag Cu and Ag–Cu alloy nanoparticles synthesized via chemical reduction route. J Nanopart Res. https://doi.org/10.1007/s11051-013-1537-1
Terenteva EA, Apyari VV, Kochuk EV, Dmitrienko SG, Zolotov YuA (2017) Use of silver nanoparticles in spectrophotometry. J Anal Chem 72:1138–1154
Van Rie J, Thielemans W (2017) Cellulose–gold nanoparticle hybrid materials. Nanoscale 9:8525–8554
Wang Z, Ma L (2009) Gold nanoparticle probes. Coord Chem Rev 253:1607–1618
Xiao H, Yan L, Dempsey EM, Song W, Qi R, Li W, Huang Y, Jing X, Zhou D, Ding J, Chen X (2018) Recent progress in polymer-based platinum drug delivery systems. Prog Polym Sci 87:70–106
Zhang X-F, Liu Z-G, Shen W, Gurunathan S (2016) Silver nanoparticles: synthesis characterization properties applications and therapeutic approaches. Int J Mol Sci. https://doi.org/10.3390/ijms17091534
Zhou W, Gao X, Liu D, Chen X (2015) Gold nanoparticles for in vitro diagnostics. Chem Rev 115:10575–10639
Zhu C, Yang G, Li H, Du D, Lin Y (2015) Electrochemical sensors and biosensors based on nanomaterials and nanostructures. Anal Chem 87:230–249