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Chemical deposition of silver shells on the surface of hollow glass microspheres

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Abstract This article reports the chemical deposition of silver shells on the surface of hollow glass microspheres. This was accomplished by using titanium dioxide, derived from titanium (IV) tetra-*n*-butoxide, as the surface modifier. Two routes of formation of thin titanium dioxide layers on the substrate were compared in terms of composition and properties: photochemical approach and atmospheric hydrolysis. The structure and composition of the samples were characterized by atomic force microscopy, scanning electron microscopy, IR spectroscopy, electron paramagnetic resonance spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. The resulting thickness of uniform silver shells on the surface of microspheres averaged out at 1.0–1.25 μm.

Introduction

Composite particles with the core–shell structure consist of microspheric cores covered with nano- or micro-sized shells. Novel materials based on such composite core–shell structures have attracted extensive attention lately due to their unique properties that could be tailored by varying the diameter of cores or the thickness of shells. Recently a great number of composites with dielectric core–metallic shell structures have been synthesized. Such particles could be used in catalysis [1], sensory and optical devices [2, 3], and for surface enhanced Raman spectroscopy (SERS) [4]. Silver-contained composite materials are especially promising for medical application. For example, silver-coated glass microspheres have been used for the development of a new diagnostic technique for cancer treatment [5].

There are several methods to generate composite nanoparticles with metallic shells, such as chemical reduction [6], sonochemical approach [7], synthesis in reversed micelles [8], and sol–gel technique [9]. However, sodium tetrahydroborate, glucose, and potassium sodium tartrate used in many of these methods lead to non-autocatalytic metal plating in the bulk solution and result in coarse suspensions that cause major metal precursor consumption and necessity of their regeneration. Due to the fact that metal reduction takes place in solution the final thickness of shells is insufficient.

Peeling of metallic shells from ceramic or glass dielectric substrates remains the problem of common use of the composite nanomaterials. To achieve durable metallic shells with high adhesion characteristics some preparatory modifications of dielectric surface should be done. There are two main routes for such modification: (a) mordanting of the surface with fluorine containing compounds (hydrofluoric acid or sodium tetrafluoroborate) so the surface of glass or ceramics becomes uneven, (b) attaching of bifunctional organic agents with an affinity to both a dielectric core and a metal of use (for example, treatment with 3-aminopropylnrimetoxosilane [10]), or (c) application of promoting tin- [6] or palladium-containing [11] agents that enhance metallic shell deposition by vigorous redox reactions between Sn^{2+} or Pd^{2+} and metal ions in the near-surface region of substrate.

Dielectric microspheres doped with metals have been obtained using a sol–gel [12] and an electroless wet-plating methods [13, 14]. Novel reliable techniques for producing

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composite particles with dielectric core–metallic shells, however, still need to be developed.

We propose an alternative method for the preparation of composite nanoparticles: photochemical approach. It is relatively simple, neat, environmental friendly and can be applied at ambient temperature. This method for producing nanoparticles allows to study the reaction mechanism (unlike most other abovementioned methods).

Previously [15], we have shown that photochemically induced excitation of transition metal complexes at the ligand-to-metal charge regions results in a one-electron reduction of the central metal ions. These low-valence metal forms are unstable and display strong reductive properties which could be used for initiation of metal ion autocatalytic plating [16].

Therefore, searching for the new photoactive precursors with high adhesive characteristics is of great interest for researchers whose work focused on surface chemistry. Acting as substrate modifiers and seed-mediators, these compounds would make synthesis of composite nanoparticles with core–shell structure easier and more effective.

Our preliminary experiments indicated that certain titanium containing compounds (e.g., titanium (IV) alkoxides) exhibit desirable properties. Besides, these alkoxides have the ligand-to-metal charge transfer band at 260 nm and that enables the use of commercially available low-pressure mercury-vapor lamps with the wavelength of 254 nm.

Considering the abovementioned, modification of the surface of dielectric substrates with titanium (IV) alkoxides for further metal deposition are of utmost interest.

Herein, we report a simple photochemical synthesis route for deposition of silver uniform shells on the titanium (IV) tetra-*n*-butoxide modified surface of sodium borosilicate hollow glass microspheres, thus producing highly reflective materials with the conductivity of the precious metal but without the high cost or weight.

Experimental section

Chemicals and materials

Hollow sodium borosilicate glass spheres with the size range 46–100 μm were used as substrates for silver shells deposition ("MicroComposite," Russia). Prior to use, all the substrates were cleaned by boiling in 30% hydrogen peroxide for 10 min, then rinsed in bidistilled water and air-dried. For modification of microspheres titanium (IV) tetra-*n*-butoxide, $Ti(OC_4H_9)_4$ (TTB), (Aldrich, 97%) and 2-propanol (Aldrich, HPLC) were used. Silver nitrate (Aldrich, 99.9%) and glucose (Aldrich, 97%) were used for silver shells producing via simple chemical reduction. All the chemicals were used as received without further purification.

Substrate modification

2% solution of TTB in 2-propanol prepared by dissolution of 1 mL of titanium (IV) tetra-*n*-butoxide ($\rho = 1$ g/mL) in 62.4 mL of 2-propanol ($\rho = 0.785$ g/mL) was used for production of TTB layers. This solution was applied to the portion of microspheres on a funnel, air-dried, and stored in a vacuum desiccator.

Formation of thin titanium dioxide layers on the substrate was achieved by two routes. The first route implied watering of $Ti(OC_4H_9)_4$ on the surface of glass microspheres for 5 min. The second route—atmospheric hydrolysis of $Ti(OC_4H_9)_4$ on the surface of glass microspheres in the open air for 15 h and then its photolysis with the monochromatic UV light. All the experiments were conducted at constant air humidity (55%).

We used glucose as a reducing agent for silver deposition on the surface of glass substrate. For metallization of 1 g of microspheres 20 mL of 10% silver nitrate water solution was added to 20 mL of 0.5% solution of glucose under constant stirring.

UV irradiation was carried out using a TUV 4W/G4 05 Philips lamp, which produces a monochromatic 254 nm radiation at 4 W of power. The intensity of light was 4.0×10^{16} quant/cm^2 s.

IR spectra were recorded between 3500 and 500 cm^{-1} on a Schimadzu IR-21 Prestige Fourier Transform Infrared Spectrophotometer, using the KBr pellet technique [17].

Thermogravimetric analysis (TGA) of microspheres with titanium containing layers was conducted using a Mettler Toledo TGA/SDTA 851. The temperature range was 50–800 °C and the heating rate was 10 °C/min. A sample of titanium dioxide powder, Degussa P-25 was analyzed as a reference. All the measurements were performed in the atmosphere of argon.

Characterization of the shells

The atomic force microscopy (AFM) topography images were acquired in the semi-contact mode with Smena-A NT-MDT scanning microscope at room temperature. AFM imaging was performed at a scanning speed of 1 Hz using high frequency 239 kHz silicon cantilevers (NSG10S) with a tip radius of 10 nm and a force constant of 11.5 N/m. Profiles of the substrates and dimensions of the produced particles were treated using the Nova 1.0.26.1324 software. Infrared (IR) analysis of titanium (IV) butoxide films was performed with a MIDAC M 2200 IR spectrometer. Polytetrafluoroethylene disposable IR cards (Performance Systematix Inc) were used as a substrate in IR analysis of titanium (IV) butoxide films.

Electron paramagnetic resonance (EPR) measurements were performed using a Bruker ER200D instrument operating in the X-band using a double T-type cavity. Irradiation treatments were carried out for 15 min at 77 K by placing a quartz cell with the samples in an Dewar flask filled with liquid N_2. This low operation temperature is crucial for increasing the sensitivity and stabilizing labile species.

The scanning electron spectroscopy (SEM) was conducted on a Carl Zeis EVO-40 microscope.

Reflection of the silver-coated glass microspheres were measured using Shimadzu spectrometer UV-2550 PC.

For chemical analysis of synthesized shells X-ray photoelectron spectroscopy (XPS) was conducted on a Perkin-Elmer PHI 5400. The Mg K_α line ($h\nu = 1253.6$ eV) was used as an excitation source.

To reveal detailed information about the chemical composition and crystallographic structure of titanium containing layers X-ray diffraction (XRD) layers was performed using the Rigaku MiniFlex benchtop system.

Results and discussion

Formation of modifying titanium containing layers

AFM images of modified glass microspheres (Fig. 1) show that the structure of the titanium containing layer produced by hydrolysis was non-uniform and loose. The roughness of the sample profile varied up to 100 nm. The layer had low adhesion characteristics and peeled from the glass surface as a result of attrition between microspheres during storage and maintenance. The titanium containing layer obtained via long-term atmospheric hydrolysis (15 h) of titanium alkoxide was smooth and the level difference was 5–30 nm. This coating is nonuniform, tended to rift during drying, and peeled from the glass surface in the course of maintenance of the samples. To eliminate these surface defects photochemical approach was applied. Corresponding AFM images shows that selected route led to the formation of a smooth uniform coating with level difference not more than 2–20 nm (Fig. 1).

IR spectroscopy results (Fig. 2) show that after UV irradiation of the samples with TTB layers for 30 min, the intensity of the band at 1005–1205 cm^{-1} attributed to valent vibrations of the C–O bond (NIST Chemistry WebBook. http://webbook.nist.gov/chemistry) decreased, as well as the intensity of the bands at 951, 1463 cm^{-1} and at 2863, 2933, and 2968 cm^{-1} associated with valent and deformation vibrations of C–H bonds, respectively. The intensity of the valent vibrations of C–C bonds in C_4H_9O groups of TTB with the band at 819 cm^{-1} also decreased. Several bands associated with deformation vibrations of Ti–O bonds were detected at 500–670 cm^{-1}. These changes in the spectra indicate that UV irradiation of the samples resulted in elimination of C_4H_9O and/or C_4H_9 groups.

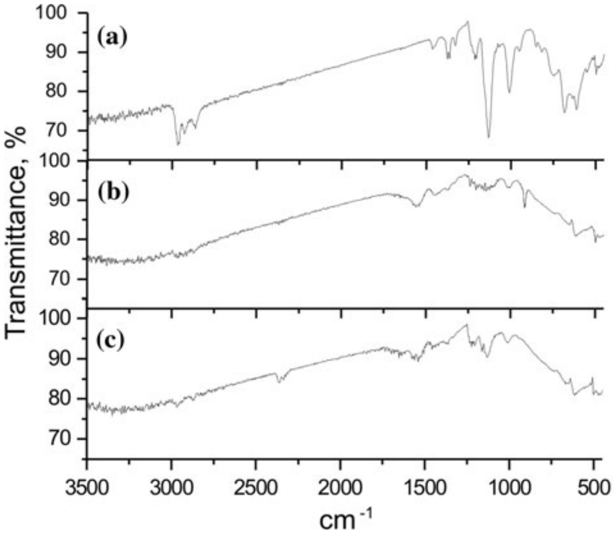

Fig. 2 IR spectra of a single-layer coating of TTB on the glass microspheres (*a*) initial, (*b*) irradiated by UV light for 30 min, and (*c*) after 15 h of atmospheric hydrolysis

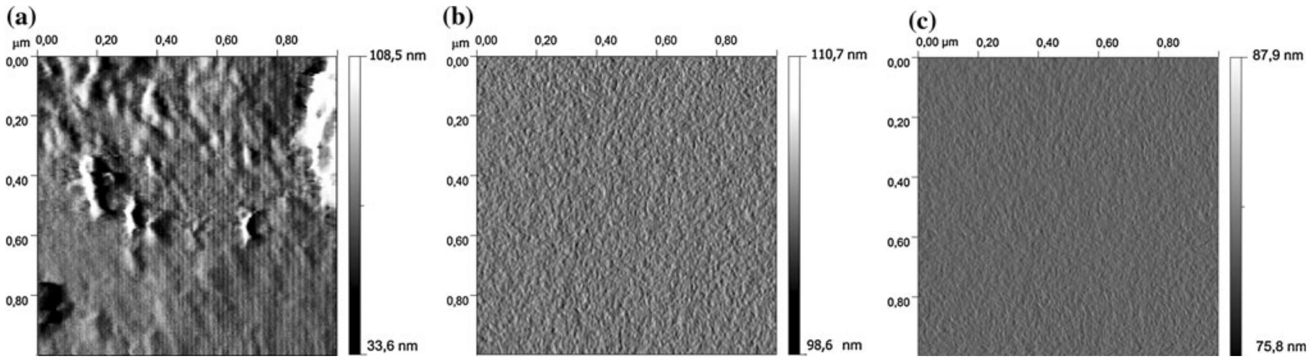

Fig. 1 AFM images of the surface morphology of the titaniferous layers obtained by **a** hydrolysis of TTB, **b** long-term atmospheric hydrolysis of TTB, and **c** photolysis

Simultaneously with the changes in chemical composition of the titanium containing layers improved hydrophilic characteristics of the surface, and the intensity of the band at 3100–3500 cm^{-1} attributed to O–H vibrations increased. This effect based on elimination of non-polar organic groups from TTB molecules with eventual formation of OH groups on the layer's surface. $TiO_2 \cdot nH_2O$ structures are formed as a result of hydrolysis. In IR spectra of TTB modified microspheres irradiated for 30 min we detected a band at 930 cm^{-1} associated with valent vibrations of $\equiv$Si–O–Ti$\equiv$ bonds [18]. This fact proves that UV irradiation of the samples induces formation of bridged complexes, which are the products of photolytic reaction between TTB and silica constituent of glass. Thus, high adhesion characteristic of the final titanium containing layers is due to their chemical photo-induced linking with the glass surface.

During storage in air, TTB layers on the microspheres underwent similar changes confirmed by IR spectra (Fig. 2, after 15 h). The intensity of IR bands at 1005 and 1133 cm^{-1} for C–O valence vibrations, at 951 and 1463 cm^{-1} for valence vibrations and at 2863, 2933, and 2968 cm^{-1} for deformation vibrations of C–H bonds of C_4H_9O groups in TTB decreased; absorption bands at 500 and 1560 cm^{-1} for Ti–O bonds appeared. Obviously, the process of hydrolysis occurred due to the presence of water molecules in the surrounding air. In contrast to the dark hydrolysis of TTB, which occurs without any changes of an oxidation state of the central ion, photo-induced hydrolysis is of reductive-oxidative pathway. At room temperature the rate of photo-induced hydrolysis of TTB layers is two orders of magnitude faster than in case of their dark hydrolysis, even using low intensity light (10^{15} quanta/cm^2 s). This fact is important for the practical use.

IR spectra of hydrolyzed TTB layers show only bands at 760 and 736 cm^{-1} attributed to the deformation vibrations of $\equiv$Si–O–Si$\equiv$ bonds in SiO_2 and $\equiv$Ti–O–Ti$\equiv$ in TiO_2, respectively, as well as growth of band intensity of O–H bond vibrations at 3100–3500 cm^{-1}. No bands for $\equiv$Si–O–Ti$\equiv$ bonds for unirradiated samples were detected.

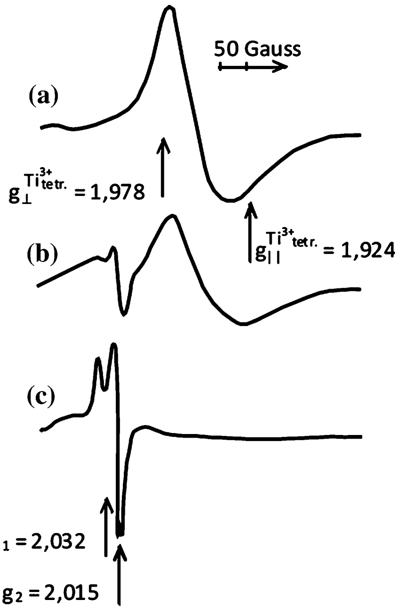

Fig. 3 EPR spectra of the TTB layers irradiated in aerobic conditions (*a*) at 77 K, (*b*) melted to 170 K, and (*c*) 298 K, respectively

EPR is a sensitive, specific method for studying both radicals formed in chemical reactions and the reactions themselves. Organic and inorganic radicals can be detected in the materials exposed to UV light. EPR spectra of the irradiated at 77 K TTB layers show an anisotropic signal at $g_{\perp} = 1{,}978$ and $g_{||} = 1{,}924$ (Fig. 3), attributed by [19–21] to alkoxy-titanium complexes with a distorted tetrahedral geometry. Air melting of the samples resulted in rapid oxidation of tetrahedral Ti(III) into Ti(IV) forms, with hydroperoxide $Ti^{IV}\text{–}{}^{\bullet}O_2H$ radical as an intermediate (c $g_1 = 2{,}032$ and $g_2 = 2{,}015$), derived from superoxide radical $O_2^{\bullet-}$ [22, 23]. No EPR signals from free radicals were detected in the irradiated TTB layer, which indicated that oxobutyl radicals ($^{\bullet}$OBu) had reduced titanium (IV) ions from the photodecomposed complex:

$$\begin{aligned}&\left[Ti^{IV}-(OBu)_4\right]\cdots\left[Ti^{IV}-(OBu)_4\right]\overset{hv}{\leftrightarrows}\\&\left\{Ti^{III}(OBu)_3,{}^{\bullet}OBu\right\}\cdots\left[Ti^{IV}(OBu)_4\right]\rightarrow\\&\left[Ti^{III}(OBu)_3\right]\cdots\left[Ti^{III}-(OBu)_4\right]+C_4H_8O+H^+\end{aligned}$$

New experimental data suggested the following mechanism for photo-enhanced and dark hydrolyses of TTB layers in aerobic conditions:

$$\begin{tikzcd}
{[Ti^{IV}(OBu)_4]\cdots[Ti^{IV}(OBu)_4]} \arrow[rr, "hv"] \arrow[drr, "H_2O"'] & & {[Ti^{III}(OBu)_3]\cdots[Ti^{IV}(OBu)_4]} \arrow[rr, "O_2"] & & {[Ti^{IV}\text{-}O_2^{-}]} \arrow[dll, "H_2O"] \\
& & {[(H_2O)_x(OH)_{5-x}Ti^{IV}\text{-}O\text{-}Ti^{IV}(H_2O)_x(OH)_{5-x}]} & &
\end{tikzcd}$$

TGA shows that there was substantial mass loss in the titanium containing layers, obtained either by hydrolysis or by photochemical approach (Fig. 4). Concurrently, TiO_2 content of the samples, calculated by taking the difference between masses before and after heating, was strongly

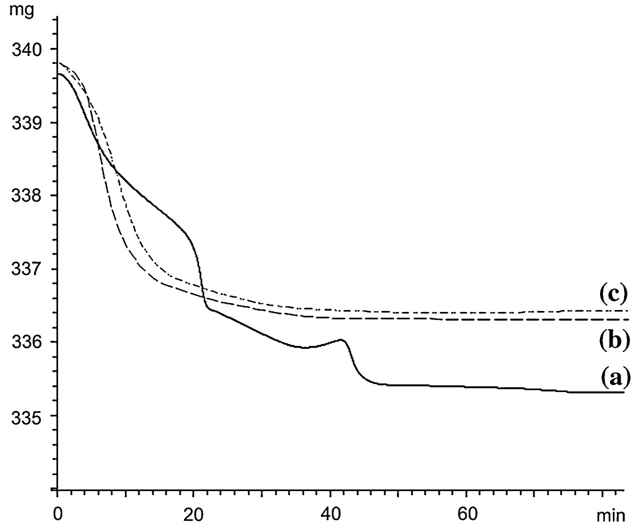

Fig. 4 Thermogravimetric curves of the titaniferous layers on the glass microspheres: (*a*) fresh-prepared layer, (*b*) air-dried for 15 h layer, and (*c*) 30 min UV irradiated layer

Table 1 Thermogravimetric analysis results for the glass microspheres with titanium containing layers

Sample	Mass loss (%)	TiO_2 content (%)
a	42.00	58.00
b	30.08	69.91
c	27.17	72.83
d	11.7	97.83

(a) Fresh-prepared layer, (b) air-dried for 15 h layer, (c) 30 min UV irradiated layer, and (d) standard Degussa P-25

dependent on its synthetic route. Table 1 shows that heating of the samples with hydrolytic titanium containing layers resulted in low TiO_2 content (58.0 wt%). UV irradiation of TTB layers for 30 min provided 72.8 wt% TiO_2 in the samples. Heating of the samples with air-dried hydrolytic titanium containing layers showed a similar result—69.91 wt% of TiO_2.

TGA shows that the main mass loss of the samples during heating occurred at 220 °C, which can be attributed to the elimination of water molecules adsorbed on the titanium containing coating and OH groups produced by photo-enhanced and dark hydrolyses. Further heating up to 700 °C led only to insignificant changes in the thermograms.

Thus, modifying films in question proved to be oxo- and hydroxoforms of titanium.

Metal shell formation

For silver deposition on the glass microspheres both chemical and photochemical approaches were tested using several identical sets of substrate samples.

Photocatalytic activity of titanium dioxide enabled the use of photochemical route for metal coating formation. Small amount of glass microspheres samples were placed in water solutions of silver nitrate, forming monolayers, and then irradiated with monochromatic UV light. Photochemical cells were placed in the shaker for uniform irradiation of the samples and hence uniform metal coating of the glass substrate. The images of these samples after irradiation show that by that route continuous silver layers on the surface of glass microspheres could not be obtained. AFM image analysis indicated that the surface coverage of silver on a single microsphere was not more than 5% regardless of the modification method applied. Formation of scattered metallic patches on the glass microspheres surface was caused by two main reasons: first, the titanium containing coating we obtained was not the pure titanium dioxide modification but contained different byproducts of TTB hydrolysis, which considerably depressed catalytic properties of TiO_2. Second, microspheres tended to disperse light substantially.

Application of standard method of ammoniacal silver nitrate solution reduction by glucose on the glass microspheres led to uncontrolled metal reduction in the bulk solution which resulted in black precipitate at the bottom of the cells.

To avoid abovementioned problems and obtain uniform metal deposition on the substrate, the next set of microspheres underwent preheating with glucose at 60–70 °C, then water washing to remove an excess of the reductant following an injection of ammoniacal silver nitrate solution. Removed excess of silver compound could be reused.

Glucose as a reducing agent furnished uniform shells with metallic luster only on the surface of glass microspheres modified with titanium containing coatings obtained by photo-induced hydrolysis of TTB, resulting in chemical linking between the modifier and the glass surface (Fig. 5). Metal shells on all the other samples (obtained by hydrolysis and atmospheric hydrolysis) flaked away during heating process of ammoniacal silver nitrate solutions with microspheres, forming black bulky agglomerates on the bottom of reaction vessels. The surface coverage of silver the microspheres with a hydrolytically induced layer of TiO_2 was 30–40%, for the microspheres with a titanium containing layer produced by atmospheric hydrolysis of TTB—50–60%.

There was a dramatic difference between the silver-coated microspheres with hydrolyzed and photolytic titanium containing layers. The images show that after hydrolysis of TTB most of the samples contained conglomerates made of 3–5 microspheres. By contrast, the samples of microspheres obtained from photolysis, did not agglomerate (Fig. 6). Thus, the further characterization of

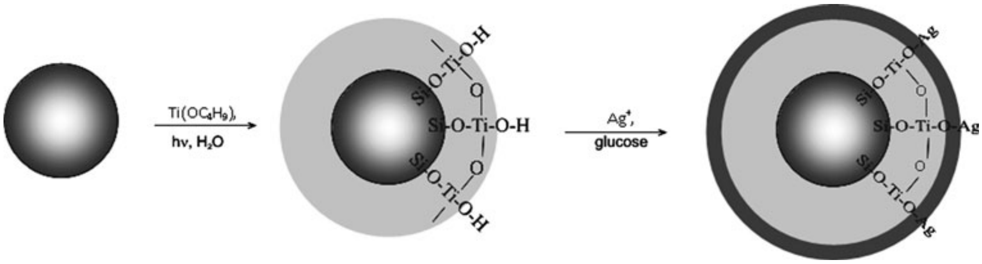

Fig. 5 Schematic sketch of the metallization process of the hollow glass microspheres

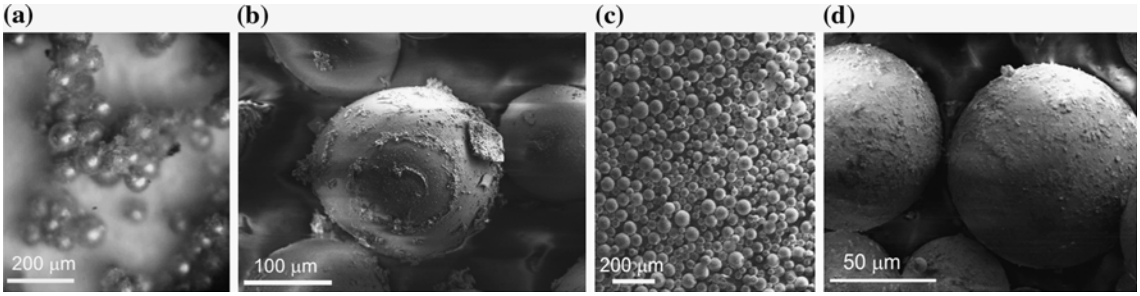

Fig. 6 The microphotographs of the silver-coated glass microspheres modified with (**a**, **b**) hydrolytically induced titaniferous layers and (**c**, **d**) those obtained upon the photolytic route

metallic coatings was performed for the glass microspheres modified by UV irradiation.

The average thickness of synthesized metallic shells estimated by SEM analysis of chips was 1.0–1.25 μm that corresponded to the previous data for silver coatings on flat surfaces originated from ammoniacal silver nitrate solutions (2 μm according [24]). Obtained metal shells had good glass adherence and were tenacious as opposed to the coatings deposited on unmodified glass microspheres.

According to XPS analysis, the magnitude of 3d electron-binding energy for Ag in electronic shell Ag $3d_{5/2}$ 367.2 eV corresponded to those of the bulk metal. XPS spectra also show signal for O 1s at 530.9 eV corresponded to the Ag–O chemical bond in silver oxide (NIST X-ray Photoelectron Spectroscopy Database. NIST Standard Reference Database 20, Version 3.5. http://srdata.nist.gov/xps/Default.aspx). The oxide content was 7–10%.

XRD spectra of metal-coated samples of glass microspheres contained two intense peaks at $2\theta = 38.44°$ which attributed to silver cubical lettuce (111) and (200). Calculated lattice constant was 4.0862 Å in agreement with literature (X-ray Powder Diffraction File JCPDS-ICDD (Joint Committee on Powder Diffraction Standard-International Centre for Diffraction Data, Swarthmore, PA) 04-0783, fcc-Ag). TiO_2 peaks were not present in these XRD spectra.

Reflectance of as-plated silver coatings was 50–60%, after air storage for the first 24 h reflectance receded for 5–10% due to oxidation.

Conclusions

Effectiveness of the silver coating process on microspherical glass substrate depends on the following characteristics of a modifying agent: adhesion capacity to the substrate and the degree of adsorption of a metal precursor's ions on its surface.

UV irradiation of modified microspheres resulted in intermolecular cross-linking between the modifying agent and glass surface that yielded in high adhesion characteristics of titanium containing layers. Unirradiated samples exhibited low adhesion with the glass substrate and peeled off during metal deposition procedure.

Although a requirement of high adsorption degree of a metal precursor's ions on the surface of modifying agent for successful metal deposition considerably limits the range of suitable reductants, similar results were achieved using dextrose for the reduction of $AgNO_3$ in ammonia solutions as well as D-fructose and D-maltose. Furthermore, our technique offered the possibility to avoid the usage of expensive palladic activation dopants.

Suggested route for metal deposition on glass microspheres modified with titanium containing layers resulted in production of uniform and bright silver coatings. Synthesized composite material shows high stability and granularity, which facilitated its further utilization. The main physical characteristics of the final product corresponded with all-metallic silver microspheres.

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