

Heteronanoparticles of silicon dioxide with shell of Pt nanocrystals

*N.A.Matveevskaya, M.V.Dobrotvorskaya,
S.V.Dukarov, Z.I.Kolupaeva*

Institute for Single Crystals, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

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The results of preparation and study of core-shell heteronanoparticles are represented based on monodisperse spherical SiO₂ colloidal particles of 40, 120, 250, and 350 nm diameter and shell consisting of Pt nanocrystals. The heteronanoparticles surface structure and composition have been studied by transmission electron microscopy, photoelectron spectroscopy and X-ray diffraction.

Приведены результаты по получению и изучению свойств гетеронаночастиц типа "ядро-оболочка" на основе монодисперсных сферической формы коллоидных частиц SiO₂ диаметром 40, 120, 250 и 350 нм и оболочкой из нанокристаллов Pt. Методами просвечивающей электронной микроскопии, фотоэлектронной спектроскопии и рентгеновской дифракции исследованы состав и структура поверхности гетеронаночастиц.

The latest decades are characterized by a great interest in the preparation and research of metal nanoparticles as promising materials for development of biological and chemical highly selective sensors, new catalysts, and magnetic markers. Numerous works are aimed at researching properties of noble metal nanoparticles, their use as catalysts in various organic reactions, for purification of gaseous industrial wastes and engine exhaust gases from toxic agents [1]. Lately, there are two trends in the ways to nanostructural catalysts: volumetric structurization of nanoparticles in porous matrices (SiO₂, Al₂O₃, zeolites, carbon materials) and formation of nanoparticles on surface of nanograins. Nanomaterials of the surface type are more chemically active than those with nanoiclusions in volume and thus more promising for development of new efficient catalysts.

To structurize and concentrate the metal nanocrystals, most convenient are colloidal silicon dioxide nanospheres obtainable with

narrow size distribution in a wide size range from dozens of nanometers to one micrometer [2]. The nanoparticles structurized on SiO₂ nanospheres (nanotemplates) are suggested to present certain advantages as compared to the ordinary supporting materials, since the nanoparticle absorption must to occur much easier due to their high surface energy. When concentrating nanoparticles on SiO₂ nanospheres surface, it is necessary to provide a reproducible process of metallic shell formation from isolated nanocrystals of certain size, to control the SiO₂ surface covering degree with them till the whole shell of pre-specified thickness, and to prevent the agglomeration of metal nanoparticles in the solution and on SiO₂ sphere surface [3–6]. Before, the core-shell heteronanoparticles with dielectric silicon dioxide core and conducting shell consisting of metal particles (Au, Ag) were obtained, and their structure and optical characteristics defined [3–10]. The preparation of heteronanoparticles with Pt

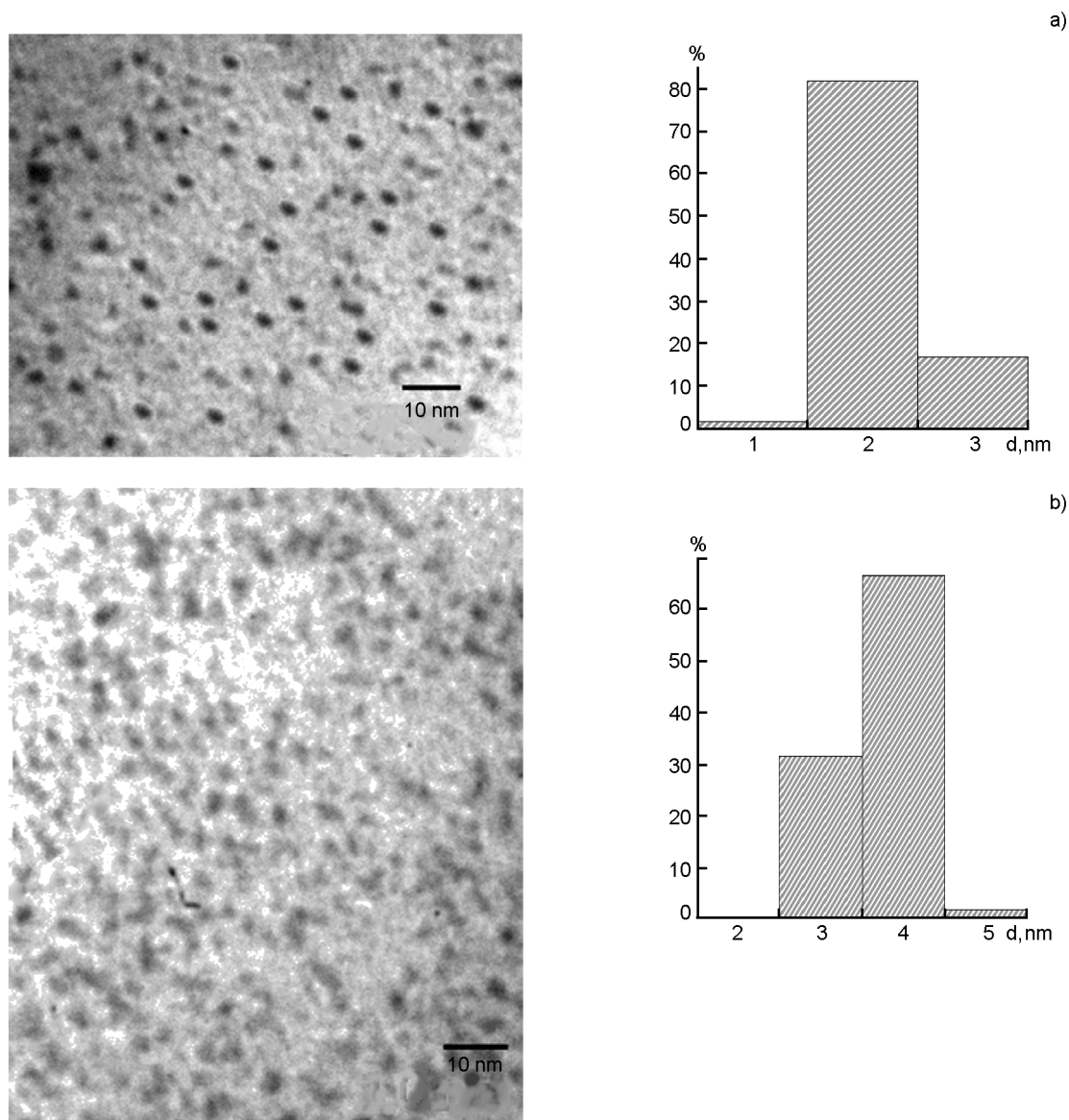


Fig. 1. Transmission electron microscopy images and size distribution histograms of Pt nanocrystals of the mean diameter (nm): 2.4 (a); 3.6 (b).

nanocrystal shell on SiO_2 core surface is not described in literature. The aim of our research was to obtain heteronanoparticles with monodisperse SiO_2 spherical cores and outer surface consisting of Pt nanocrystals, to study the conditions of metallic shell formation from Pt nanocrystals on the core surface at different diameters, and to identify the heteronanostructures obtained.

SiO_2 monodisperse spherical nanoparticles (with the size dispersion not exceeding 10 %) were obtained by hydrolyzing tetraethyl orthosilicate according to Stober [2–6]. The nanoparticle size was controlled by the ratio of reagents, temperature and the process rate. The SiO_2 colloidal solutions (sols) are transparent and stable for a long time

(2–3 months). The nanotemplate surface was modified using bifunctional organic compound, 3-aminopropyl triethoxysilane (APTES) (99.8 %, Aldrich), that was covalently bound to silicon dioxide and provide the metal shell connection to the core. To obtain isolated Pt nanocrystals, the reduction of H_2PtCl_6 (99.9 %, Aldrich) in aqueous solution was used [11]. The synthesis was conducted under N_2 atmosphere to prevent platinum oxidation. As the reducing agent, sodium borohydride NaBH_4 (special purity grade, Sinbias) was used. The Pt nanocrystals obtained were stabilized by polyvinyl pyrrolidone (PVP) ($M_w = 360000$, Merck) at the concentrations varying from 0.01 % to 0.07 %. By varying precursors

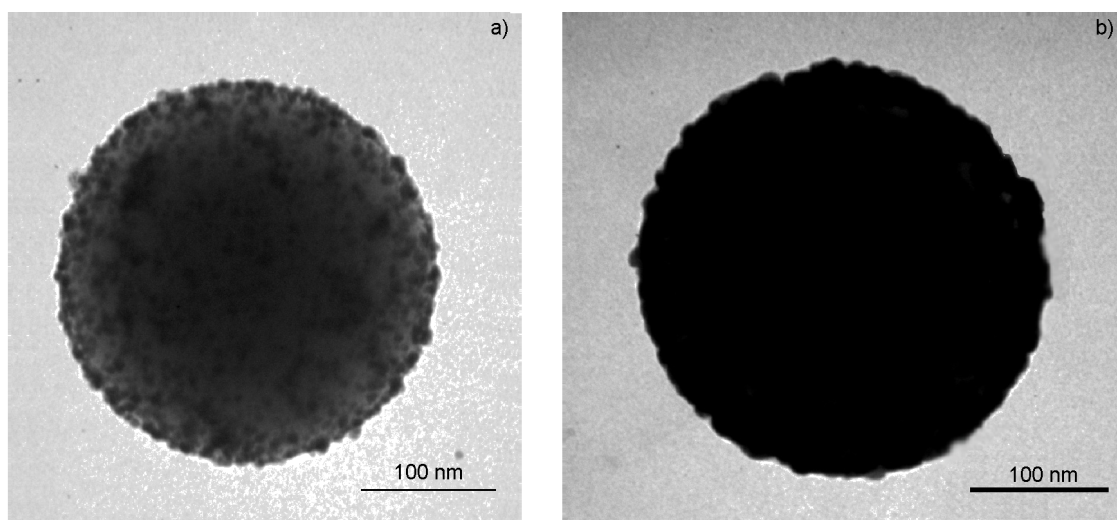


Fig. 2. Transmission electron microscopy images of SiO_2/Pt heteronanoparticles, SiO_2 diameter 250 nm; Pt shell: (a) isolated nanocrystals, diameter 6 nm, covering degree about 60 %; (b) 6 nm thick continuous shell.

and stabilizer concentrations, Pt nanocrystals of the diameter ranging from 1 to 7 nm were obtained. To obtain SiO_2/Pt nanoparticles, the suspension of organosilane modified SiO_2 nanoparticles was mixed with aqueous solution of stabilized Pt nanocrystals. The mixture was centrifuged using an OPN-3 centrifuge, the heteronanoparticulate precipitate was separated and dispersed in a small amount of water using an ultrasonic disperser UZDN-A. The procedure was repeated to increase Pt nanocrystals coverage of the core surface. To prevent the spontaneous agglomeration of nanocrystals both in the solution and on SiO_2 surface, and to provide the even covering of the nanotemplate surface, the absorption was conducted at low concentrations of Pt nanocrystals (10^{-4} – 10^{-5} mole/L). Under such conditions, the core outer shell formation is controllable and reproducible up to formation of a continuous shell.

Transmission electron microscopy of synthesized nanostructures was performed using a PEM-125 instrument at 100 kV accelerating voltage. The samples were prepared according to standard procedure by depositing colloidal solutions on copper grids covered with carbon film. Atomic concentration of elements in SiO_2/Pt heteronanoparticles surface layer and the ratio of Pt/ SiO_2 concentrations, characterizing nanotemplates surface covering with Pt nanocrystals, were determined by X-ray photoelectron spectroscopy (XPS-800 Kratos) using areas under C1s, O1s, Na2s, Pt4f, B1s, Cl2p, Si2p lines. The coating

phase structure was studied by X-ray diffraction using DRON-4, (Fe K_α radiation, $\lambda = 1.93728 \text{ \AA}$, the 2θ scanning range 10° to 70°). The samples were prepared by depositing heteronanoparticles from suspensions on titanium substrates (VT1-0) and drying the precipitate obtained.

Fig. 1 presents electron microscopic images and histograms of Pt nanocrystals size distribution. The obtained Pt crystals are monodisperse, with average particle diameter 2.4 nm (Fig. 1a) and 3.6 nm (Fig. 1b) with the size dispersion 11 % and 13 %, respectively.

Varying size of Pt nanocrystals and the SiO_2 core surface covering degree, SiO_2/Pt heteronanoparticles were obtained with various structure of outer shell (from the ensemble of isolated nanocrystals of 2–7 nm size with the covering degree 30–70 % up to the continuous surface up to 7 nm thickness), Fig. 2. As the covering degree of the core surface exceeds 70 %, a shell is formed on SiO_2 surface, consisting of Pt nanocrystals monolayer. The shell thickness is determined by the nanocrystal size.

SiO_2/Pt heteronanoparticles specific reflections in X-ray diffraction pattern corresponding to the planes (111), (200), (220) suggests that the Pt nanocrystals have face-centered cubic lattice, which corresponds to the bulk phase with the space of 3.92 \AA (Fig. 3). The peak broadening specific for nanocrystals as compared to bulk crystals evidences a small size of Pt crystals being researched. Estimations based on the reflections width in diffraction patterns have

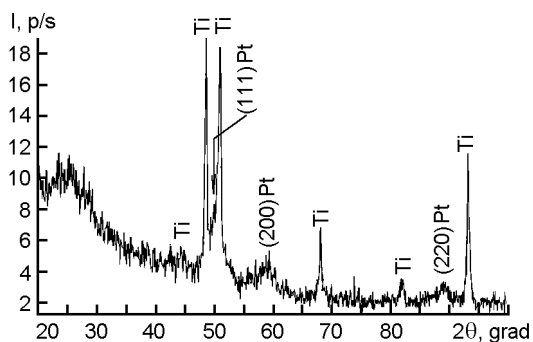


Fig. 3. X-ray diffraction of SiO₂/Pt heteronanoparticles.

shown that the coherent scattering area (Pt nanocrystal size) is of 6 nm, which agrees with Pt nanocrystal size in the sol deposited on core surface when SiO₂/Pt heteronanoparticles are being obtained.

SiO₂/Pt heteronanoparticles with core diameter of 250 nm, Pt nanocrystals diameter of 6 nm and covering degree of 40 %, 60 % and 6 nm thick continuous coating were examined by photoelectron spectroscopy to study the outer conducting shell surface state. Fig. 4 shows X-ray photoelectron spectrum of Pt4f_{7/2,5/2} — level for the samples of bulk standard platinum specimen (a) and platinum nanoparticles on SiO₂ (b). Pt4f binding energy (E_b Pt4f_{7/2} = 70.5±0.1 eV) in nanoparticles corresponds to platinum in metal state Pt⁰ (E_b Pt4f_{7/2} = 70.9±0.1 eV). Moreover, a small (about 0.4 eV) line shift towards lower binding energy is observed in Pt nanoparticles spectrum. Such low-energy shift was observed earlier for aurum and platinum nanoparticles with size smaller than 5–7 nm on various support [12, 13] and might be connected to electron density change on metal atom in nanoparticles under the decreasing of their sizes. The shift towards lower binding energies was observed for Pt in all samples of SiO₂/Pt heteronanoparticles with them covering core surface in different degrees. This confirms the absence of Pt nanoparticles agglomeration on template surface and the formation

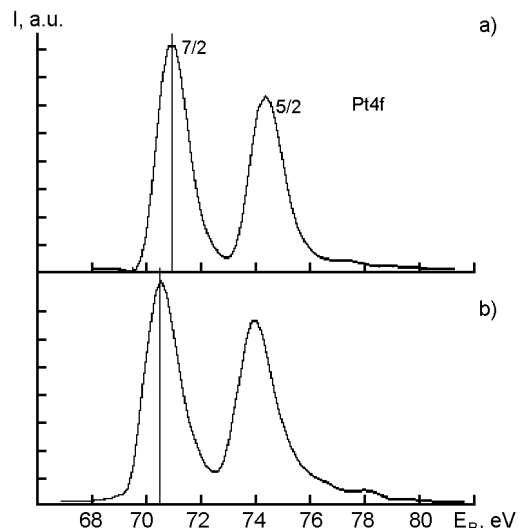


Fig. 4. Pt4f-XPS spectra for bulk standard platinum sample (a) and Pt nanoparticles on SiO₂ (b).

of the external shell out of isolated Pt nanocrystals, whose thickness is determined by nanocrystals size.

To determine SiO₂ size impact on forming SiO₂/Pt heteronanoparticles external shell for the samples with core diameter of 40, 120 and 350 nm and Pt nanocrystalline shell with the diameter of 4 nm obtained under the equal process conditions, the degree of nucleus surface core with Pt nanocrystals was estimated. In accordance to the transmission electron microscopy data, covering degree was calculated as the ratio of total Pt nanocrystals surface to SiO₂ core hemisphere surface.

Atomic concentration C_{Pt} and C_{Si} of SiO₂/Pt heteronanoparticles in samples surface layer and their ratio n was determined by means of XPS. Assuming that only the SiO₂ surface part not covered with Pt nanocrystals contributes to silicon signal (the photoelectrons escape depth for the lines used for the study is about 2 nm) and, not taking into consideration particles sphericity, the Pt nanoparticles covering degree

Table. Heteronanoparticles SiO₂/Pt characteristics

SiO ₂ diameter, nm	Pt diameter, nm	Covering degree (according to EM data), %	Atomic concentration ratio $n = c_{Pt}/c_{Si}$	Covering degree (according to XPS data), %
40	4	80	6.1	71
120	4	70	5.6	69
350	4	25	0.3	15

p on SiO_2 surface can be estimated by the following formula:

$$p = \frac{n}{n + \frac{\rho_{\text{Pt}}}{\rho_{\text{SiO}_2}} \cdot \frac{M_{\text{SiO}_2}}{M_{\text{Pt}}}} \cdot 100\%,$$

where n — atomic concentration ratio between Pt and Si;

ρ_{Pt} , ρ_{SiO_2} — Pt and SiO_2 density, g/cm^3 ;
 M_{Pt} , M_{SiO_2} — Pt and SiO_2 molecular weight, g/mol .

The results are represented in the following table. The data concerning SiO_2 surface covering degree with Pt nanocrystals estimated with the help of transmission electron microscopy data and photoelectron spectroscopy correlate.

Method of analysis using XPS gives a more accurate value of covering degree due to elements atomic concentrations in the surface layer being integrated quantities. The probability of inaccurate covering degree estimation increases with SiO_2 core diameter growing and its covering degree in connection with difficulties during defining the area of Pt nanocrystals on SiO_2 with the diameter greater than 120 nm.

The greatest SiO_2 surface covering with Pt nanocrystals is observed for heteronanoparticles with SiO_2 diameter of 40 nm. With SiO_2 surface spheres curvature growing, the number of active silanol groups on SiO_2 surface is known to increase [14]. A greater number of active centers where Pt nanocrystals are absorbed are formed on SiO_2 nanoparticles, 40 nm in diameter, having the biggest surface curvature among nanotemplates samples researched, under the fictionalization of their surface. Low covering degree of SiO_2 spheres surface with the diameter of 350 nm is connected to decreasing the number of active silanol groups on the surface because of their partial binding through hydrogen combining. The same dependence of covering degree from SiO_2 core diameter was earlier discovered for nanoparticles with external shell consisting of Au nanocrystals [15].

Thus, by means of template synthesis in colloidal solution core — shell SiO_2/Pt isolated heteronanoparticles with the dielectri-

cally core diameter varying from 40 to 350 nm and various external shell structure were obtained (from isolated nanocrystals ensembles 2–7 nm in size with SiO_2 surface covering degree of 30 % to even shells 7 nm thickness). It has been found experimentally that under such conditions the shell out of Pt isolated nanocrystals monolayer is formed, with its thickness being determined by nanocrystals diameter. It has been shown that in the external heteroparticles shell Pt is in metallic state. Great specific surface and mobility of such nanostructures offer the challenge of using them as new efficient catalysts in oxidation-reduction reactions.

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Гетеронаночастинки на основі діоксиду кремнію з оболонкою з нанокристалів Pt

***Н.А.Матвеевська, М.В.Добротворська,
С.В.Дукаров, З.І.Колупаєва***

Подано результати з одержання та вивчення властивостей гетеронаночастинок типу "ядро-оболонка" на основі монодисперсних сферичної форми колоїдних наночастинок SiO₂ діаметром 40, 120, 250 та 350 нм та оболонкою з нанокристалів Pt. Методами просвічуваної електронної мікроскопії, фотоелектронної спектроскопії та рентгенівської дифракції досліджено склад та структуру поверхні гетеронаночастинок.