

SiO₂/Au core-shell nanoparticles: synthesis and characterization

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Preparation of heteronanoparticles of the core-shell type has been described based on single-dispersed spherical nanoparticles of silicon dioxide and gold. Using the colloid chemistry techniques, nanoparticles having different dielectric core diameters and different metal shell thickness have been obtained. The effect of the nanoparticle structure on the absorption spectra thereof has been investigated. The maximum position in the absorption spectra has been shown to be defined by dielectric core diameter ratio to the gold shell thickness in the SiO₂/Au nanoparticles.

Приведены результаты по получению гетеронаночастиц типа "ядро-оболочка" на основе монодисперсных сферической формы наночастиц диоксида кремния и металлического золота. Методами коллоидной химии получены наночастицы с различным диаметром диэлектрического ядра и толщиной металлической оболочки. Изучено влияние структуры наночастиц на спектры поглощения. Показано, что отношение диаметра диэлектрического ядра к толщине золотой оболочки определяет положение максимума в спектрах поглощения гетеронаночастиц SiO₂/Au.

Unusual optical properties of small particles are known for a long time [1]. For example, colloidal solutions of metal particles exhibit the highest known 3rd order susceptibility, absorption coefficient, and ultrafast nonlinear optical response. These properties are interpreted usually in the frame of concept of surface mode excitation in the small particles, in particular, for metal particles, within the concept of the surface plasmon excitation.

The optical absorption by homogeneous spherical gold particles of a 2.6 to 10 nm radius is known to exhibit a spectral maximum near to the Froehlich frequency ($\omega_t = 520$ nm). As the radius increases from 10 nm up, the absorption spectral curve is broadened significantly while its maximum shows a shift as small as about 50 nm towards longer

wavelengths. As to particles of a radius smaller than 2.6 nm, the absorption maximum position is independent of the particle size but the spectral line shape changes significantly. In this size range, the metal nanoparticles exhibit the dimensional quantum effects of the charge carrier motion caused by the spatially restricted path length of free electrons. The slight dependence of the plasmon resonance frequency on the size of small homogeneous metal spheres, and thus lack of possibility to control the plasmon resonance frequency therein, restricts the practical use fields of materials based on such structures.

Now, synthetic methods have been developed providing the complex nanoparticles consisting of a thin metal shell (gold or silver as a rule) and a dielectric core [2–7].

The optical properties of those particles have been shown to depend on the particle size and shape, the number of coating layers and sequence thereof, as well as on dielectric constants of the core and shell materials and environment.

In [4], the formation growth and conditions of gold clusters at the surface of large nanoparticles of silicon dioxide have been studied. The effects of solvent and the nature of the ligand functional groups on the cluster formation at the surface of functionalized silica has been studied. A general approach to metal nanoshells based on the molecular self-assembly using the colloid chemistry methods is described in [5]. The optical spectra calculated in the frame of the classical Mie theory of electromagnetic scattering have been shown to agree well with the absorption spectra of the obtained core-shell type complex nanoparticles consisting of a dielectric silica core (of 120 and 340 nm diameter) and a gold metal shell.

In spite of the available publications, the methods and conditions for the dielectric core/metal shell complex nanoparticles and the properties thereof (in particular, at the dielectric core diameter smaller than 50 nm) are still insufficiently studied in experiment. The aim of this work is to obtain the heterogeneous nanoparticles containing a silica core in a gold shell with different core diameters (including those of < 50 nm) and to study the manifestations of dimensional effects in the absorption spectra.

The monodispersed spherical silica particles were prepared using a technique similar to that described in [8]. To synthesize SiO₂, 50 mL of absolute ethanol were mixed in a 100 mL conical flask with 4 mL of 25 % ammonia solution (Makrokhim, Kyiv) under continuous stirring at 22°C and 2 mL tetraethyl orthosilicate (TEOS) (special purity grade, SUREL, St. Petersburg). Assuming that the whole TEOS is reacted and knowing the SiO₂ nanoparticle density to be of 2.2 g/cm³ [9], the number of nanoparticles in the solution can be determined to be $7 \cdot 10^{15} \text{ L}^{-1}$.

To provide the heterogeneous nanoparticles, the dielectric core (SiO₂ nanoparticle) surface was modified using bifunctional organic molecules, namely, 3-aminopropyltriethoxysilane (APTES) (99.8 %, Aldrich) that provides the adhesion of the metal shell to the core. To 10 mL of SiO₂ suspension in alcohol, 0.04 mL of APTES was added, the solution was stirred and refluxed under periodic addition of ethanol to pro-

vide the constant mixture volume. Then the suspension was centrifuged using an OPN-3 centrifuge (3000 rpm) for 20 min, the residue was re-suspended in ethanol using ultrasound (UZDN-1 device) to remove the organic impurities.

The gold reduction method in solution [10] was used to prepare the SiO₂/Au heteronanoparticles. Tetrakis(hydroxymethylphosphonium)chloride (THMP) (80 % aqueous solution, Aldrich) was used as the reducing agent to provide colloidal gold. The mixture containing water (45 mL), 1 M NaOH (0.3 mL), and freshly prepared 1 % aqueous THMP solution (1 mL) was stirred for 10 min and then 2 mL of $25 \cdot 10^{-3} \text{ M}$ HAuCl₄·3H₂O (99.99 %, Aldrich) were added. The synthesis process resulted in formation of a stable gold sol with 1 to 3 nm particle size. The colloidal gold solution was stored in a refrigerator and used within 7 days after preparation. To obtain the SiO₂/Au nanoparticles, the suspension of SiO₂ nanoparticles modified with organosilane was mixed with the colloidal gold solution. The mixture was stirred for 3 h, then the unreacted gold colloid was separated from the SiO₂/Au nanoparticles by centrifugation at 1000 rpm for 5 min. The heteronanoparticles were purified by twice-repeated centrifugation and dispersion in ethanol using ultrasound. To obtain the SiO₂/Au core-shell nanoparticles, the alcoholic solution of SiO₂ nanoparticles modified with organosilane was mixed with the aqueous solution of colloidal gold with 1 to 3 nm particle size. The gold nanoparticles are bound at the silica particle surface due to electrostatic interaction with the positively charged amino group at the modified silica surface. The concentration and size of the metal clusters on the SiO₂ core can be varied by changing the HAuCl₄·3H₂O concentration.

The electron microscopy was carried out using an EM-125 transmission electron microscope (100 kV accelerating voltage) and a JEOL-820 scanning electron microscope. The samples were prepared according to the standard procedure by application of the nanoparticle solutions onto copper films coated with a carbon film, the excess solution was removed using filter paper. The absorption spectra of the obtained colloidal nanoparticle solutions were taken using a Specord M-40 spectrophotometer in the wavelength range 200 to 900 nm using a 1 cm long quartz cell, an ethanol/water mixture was used as the reference solution.

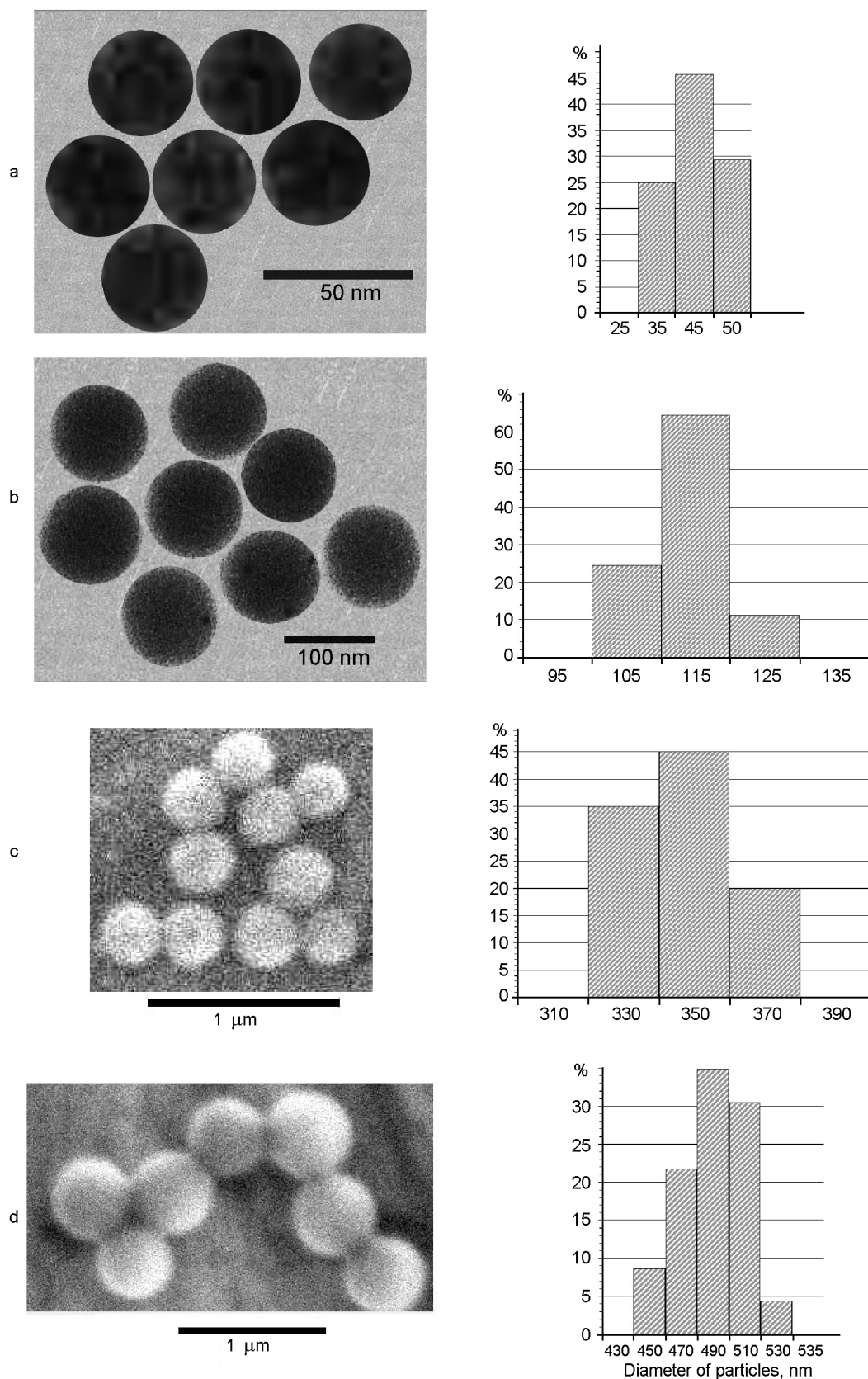


Fig. 1. Electron-microscopic images and size distribution histograms of SiO₂ nanoparticles of the mean diameter (nm): 40 (a), 115 (b), 350 (c), 500 (d).

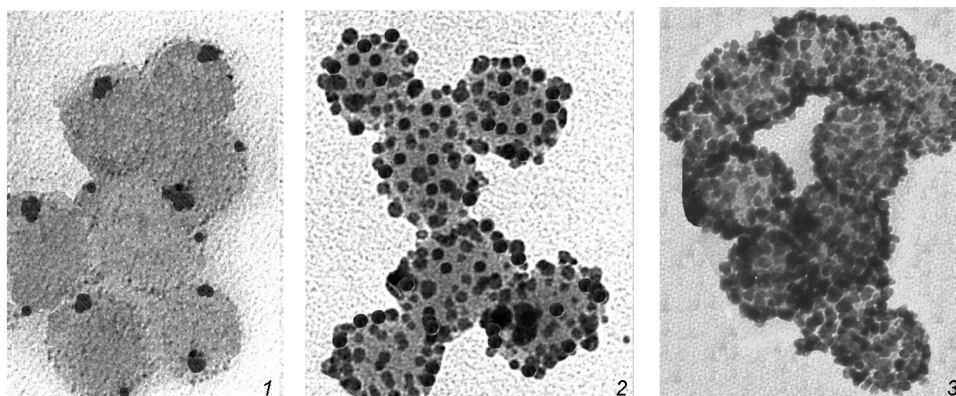


Fig. 2. Electron-microscopic images of SiO₂/Au heteronanoparticles, SiO₂ diameter 40 nm, Au shell thickness (nm): individual clusters (1), 5 (2), 7 (3).

The monodisperse spherical SiO₂ nanoparticles exhibit a complex fractal structure. The particle size and polydispersity depend on the synthesis conditions, namely, the concentrations of reagents (TEOS, ethanol, water, ammonia hydrate) and the mixing sequence thereof, the solution pH value, the reaction temperature, etc. The synthesis of SiO₂ nanoparticles consists of the following stages: TEOS hydrolysis, polymerization of the molecular SiO₂, condensation of polymer clusters, and aggregation of the primary SiO₂ nanoparticles into monodisperse colloidal particles of amorphous SiO₂ [9].

We have selected the TEOS hydrolysis conditions providing the spherical silica nanoparticles of 30 to 500 nm in diameter at a good reproducibility and low dispersity. The colloidal solutions of SiO₂ nanoparticles are transparent and stable for prolonged time periods (2 to 3 months).

Fig. 1 presents the electron-microscopic images of SiO₂ nanoparticles. The nanoparticles are almost ideal spheres and a high size uniformity. The histogram of the particle size distribution shows the r.m.s. deviation does not exceed 10 % for each particle size value obtained in this work.

The SiO₂/Au heteronanoparticles were obtained at different filling density of the dielectric core surface with metal particles. To increase the metal shell thickness at the SiO₂ nanoparticle surface, the chemical reduction of gold hydrogen chloride in solution with hydroxylamine hydrochloride. Fig. 2 presents the electron images of 40 nm diameter SiO₂ nanoparticles with gold particles fixed at the surface. It is seen that the metal shell is not continuous.

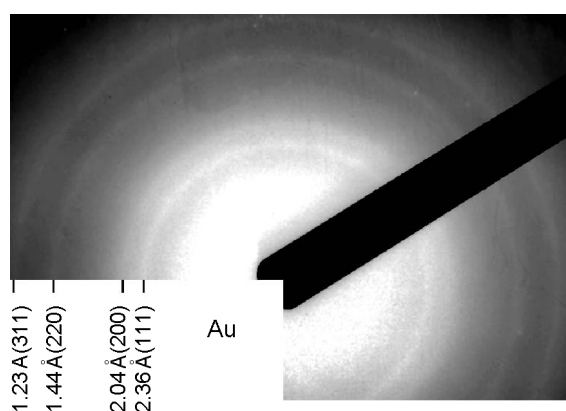


Fig. 3. Electron diffraction pattern of a SiO₂/Au heteronanoparticle.

Therefore, the shell thickness has been defined as the "effective thickness" determined as the ratio of the total volume of gold nanoparticles to the core surface area.

The electron diffraction pattern of SiO₂/Au heteronanoparticles shown in Fig. 3 allows us to conclude that there is a polycrystalline gold coating with fcc lattice at the amorphous SiO₂ surface.

The absorption spectra of the core-shell nanoparticles have been interpreted using the theory of light absorption and scattering by small particles [11]. The excitation condition of surface plasmons in a thin metal shell of a thickness d and dielectric constant ϵ_2 formed at the surface of a small spherical particle having dielectric constant ϵ_1 (r is the core radius, λ , the exciting wavelength, $r \ll \lambda$) is

$$K_{eff} + 2\left(x + \frac{12}{5}x^5\right) = 0, \quad (1)$$

where

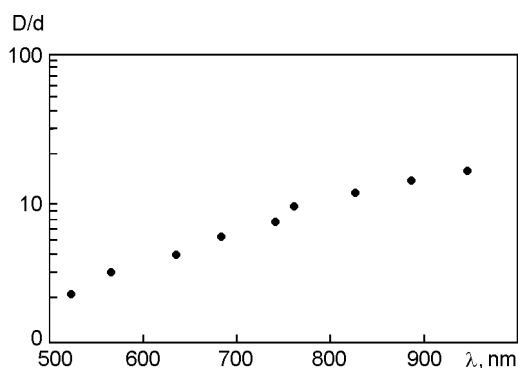


Fig. 4. Dependence of the optical absorption maximum position for a heteronanoparticle on the core diameter (D) ratio to the metal shell thickness (d).

$$K_{eff} = \frac{\varepsilon_2(\omega)}{\varepsilon_3} \frac{(\varepsilon_1 - 2\varepsilon_2(\omega)) + 2(\varepsilon_1 - \varepsilon_2(\omega))(L/D)^3}{(\varepsilon_1 + 2\varepsilon_2(\omega)) - (\varepsilon_1 - \varepsilon_2(\omega))(L/D)^3}, \quad (2)$$

$$x = \frac{D}{\lambda}, \quad L = D + d.$$

According to the Drude-Lorentz model, the dielectric function for a metal shell can be presented as

$$\varepsilon_2(\omega) = \varepsilon_0 \left\{ 1 - \frac{\omega_{pf}^2}{\omega^2 + i\omega\gamma_f + \frac{\omega_{pb}^2}{\omega_0^2 - \omega^2 - i\omega\gamma_b}} \right\}, \quad (3)$$

where ω_{pf} is the contribution to the plasmon frequency due to free electrons; ω_{pb} , that from the bound electrons of the metal; ω_0 , the resonance frequency of the bound electrons; γ_f , γ_b , the damping constants of the free and bound electrons, respectively. The solution of Eq.(1) taking into account (2) is the frequency $\omega = \omega_F$ (Froehlich frequency) that depends both on the volume ratio of the whole spherical nanoparticle to the core and on dielectric constants of the core and shell materials and the surrounding medium.

Assuming the contribution from bound electrons to the metal dielectric constant to be small as compared to that from free electrons, the real and imaginary parts of the metal shell, $\varepsilon'_2(\omega_F)$ $\varepsilon''_2(\omega_F)$, respectively, can be presented as $\varepsilon'_2(\omega_F) = 1 - \omega_{pf}^2/\omega_F^2 + \gamma_f^2$, $\varepsilon''_2(\omega_F) = \omega_{pf}^2\gamma_f/\omega_F(\omega_F^2 + \gamma_f^2)$, where for gold, $\omega_{pf} = 1.3 \cdot 10^{16}$ Hz, $\gamma = 1.12 \cdot 10^{15}$ Hz [12].

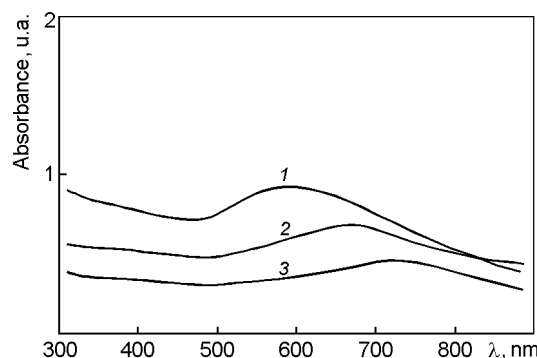


Fig. 5. Absorption spectra (plasmon resonance) for SiO₂/Au heteronanoparticles with the core diameter (nm): 40 (1), 115 (2), 350 (3). Shell thickness 5 nm.

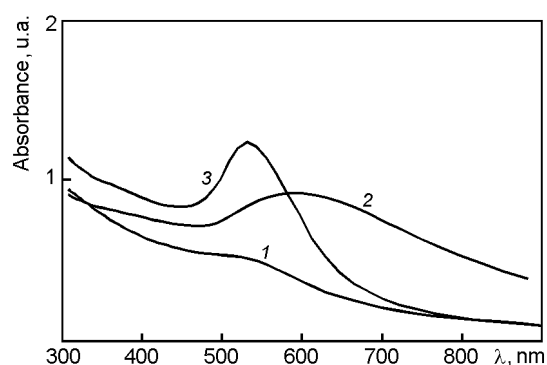


Fig. 6. Absorption spectra of SiO₂/Au heteronanoparticles, SiO₂ diameter 40 nm, Au shell thickness (nm): individual clusters (1), 5 (2), 7 (3).

Substituting the expressions for ε_2' and ε_2'' into (2) and solving the Eq.(1) with respect to ω_F , we obtain an analytical expression for as a function of the core and shell sizes.

Fig. 4 presents the calculated dependence of the absorption maximum position on the dielectric core diameter ration to the metal shell thickness.

The optical absorption spectra of colloid solutions containing the obtained heteronanoparticles having various dielectric core diameters and the metal shell thickness were studied. Fig. 5 shows the absorption spectra of such solutions containing the SiO₂/Au nanoparticles of 40, 115, and 350 nm in diameter at the effective shell thickness of 5 nm. It is seen from the Figure, as the dielectric core diameter increases, the metal shell thickness being the same, the absorption maximum becomes shifted towards longer wavelengths at a si-

multaneous considerable broadening of the absorption band.

Fig. 6 presents similar absorption spectra for a constant dielectric core diameter of 40 nm and various thickness of the Au shell. As follows from the Figure, the absorption maximum position is defined by the surface density of the gold metal clusters on the core. The core size being the same, the higher the surface density of metal clusters is, the larger is the absorption maximum shift towards shorter wavelengths. As the effective thickness of the gold shell increases up to 8 or 10 nm at the small dielectric core diameter, the absorption maximum position becomes shifted into the absorption region of colloidal gold particles. It is obvious that at a relatively thick metal shell, the surface plasmons will be excited at the metal/solution interface and the effect of the small dielectric core on the position of the plasmon resonance maximum for the heteronanoparticle will be insignificant.

In Fig. 7, presented are the obtained experimental dependences of the plasmon resonance maximum position on the SiO₂ core diameter ratio to the shell thickness for various core diameters at a constant metal shell thickness (curve 1) and for various shell thickness at a constant small (40 nm) core diameter (curve 2). The plasmon resonance maximum position dependence on the core diameter/shell thickness in the first case is seen to be linear within the studied wavelength range, thus agreeing well with the theoretically calculated dependence. In the second case (the same small core size and varying shell thickness), the above-mentioned dependence is linear, too. The small dielectric core diameter provides the plasmon resonance maximum shift even if the metal shell thickness is changed insignificantly. The maximum position is defined by the gold shell thickness.

Thus, the monodisperse spherical nanoparticles of silica have been obtained within a wide diameter range (40 to 500 nm) and an insignificant (<10 %) size dispersion as well as SiO₂/Au heteronanoparticles of core-shell type with various outer-to-inner diameter ratio. The dimensional effects have been revealed in the absorption spectra of the heteronanoparticles. The absorption maximum position (plasmon resonance) is defined by the dielectric core diameter/metal shell thickness ratio. As the dielectric core diameter increases at a con-

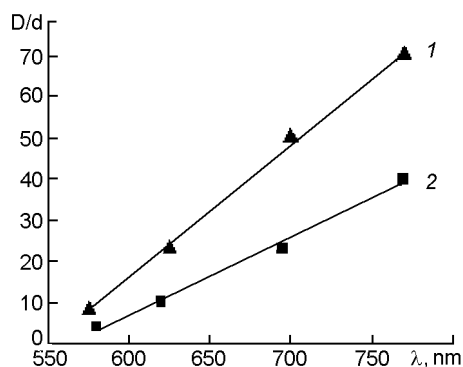


Fig. 7. Dependences of the plasmon resonance maximum position on the core diameter (D) ratio to the metal shell thickness (d): constant $d = 5$ nm, $D = 40$ to 350 nm (1); constant $D = 40$ nm, $d = 1$ to 10 nm (2).

stant metal shell thickness, the spectral maximum position becomes shifted towards longer wavelengths at a simultaneous considerable broadening of the absorption band. When the core size is small (<50 nm), the plasmon resonance maximum position is defined by the gold shell thickness. As the effective thickness of the metal shell is increased up to 7–10 nm, the absorption maximum position is shifted into the absorption region of colloidal gold particles.

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Наночастинки ядро-оболонка SiO₂/Au: синтез та характеристики

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Наведено результати з одержання гетеронаночастинок типу "ядро-оболонка" на основі монодисперсних сферичної форми наночастинок діоксиду кремнію та металевого золота. Методами колоїдної хімії одержано наночастинки з різним діаметром діелектричного ядра і товщиною металевої оболонки. Вивчено вплив структури наночастинок на спектри поглинання. Показано, що відношення діаметра діелектричного ядра до товщини золотої оболонки визначає положення максимуму в спектрах поглинання гетеронаночастинок SiO₂/Au.