Composite nanoparticles: applications, creation mechanism, properties

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Annotation This article presents data on the use of Janus-like and core-shell composite nanoparticles consisting of two substances—metal and semiconductor—in nanophotonics and spectroscopy. Investigations were carried out of the mechanism of formation of composite nanoparticles, based on the principle of minimum surface energy of the system and the results of molecular dynamics modelling. Integral representation was employed to analyse size distribution function of nanoparticles, and it was concluded that coagulation predominates during particle formation.

Keywords: composite nanoparticle, surface energy, core-shell particle, Janus nanoparticle, size distribution function of nanoparticles, nanophotonics, high-index dielectric nanoparticles

Introduction

Composite metal and dielectric/semiconductor nanoparticles are promising as the elemental base of nanophotonics, due to the combination of unique properties of both plasmon resonance metal particles and polariton resonant dielectric/semiconductor particles with a high refractive index (high index). In dielectric nanophotonics, the property of high-index dielectric/semiconductor nanoparticles is used to interact intensively with the magnetic component of an electromagnetic wave in the visible spectral region. The spectral position of the corresponding magnetic Mi-resonance can be varied by changing the radius of the spherical nanoparticle, which allows the position to be changed in a wide spectral range, in contrast to plasmon nanoparticles, in which the magnetic response can be obtained only in complex nanostructures and is limited by the IR region for high Joule losses in the optical range. Composite nanoantennas, which combine high-index nanoparticles with plasmon elements, exhibit both electrical and magnetic resonance, suitable for various advanced applications as basic elements for ultrafast optical switching and nonlinear optics [1].

Silicon is used in dielectric nanophotonics due to its high refractive index, about 3 in the visible spectral region, as well as its biocompatibility and biodegradability. A high refractive index leads to local amplification of the electric field near the nanoparticles on nanoantennas created from silicon. Photochemical synthesis of Si nanoparticles coated with Au and Ag along with pure Au and Ag nanoparticles was carried out recently, using IR nanosecond laser treatment of a bulk silicon wafer in aqueous solutions of hydrochloric acid (HAuCl4) and silver nitrate (AgNO3) [2]. Silver is used because
of their outstanding plasmonic properties, and, in combination with high-index dielectric nanoparticles of Si, is important as potential building blocks for nonlinear nanophotonics and spectroscopy.

The resonance properties of nanoparticles depend on their shape and structure. The magnitude of the Schottky electric potential at the interface between particles is also determined by the metal / semiconductor interface. Therefore, the synthesis of composite nanoparticles and the mechanisms of their formation are especially relevant at the present time. Composite nanoparticles are used in catalysis to protect particles from oxidation, and in biomedical applications. For example, the antimicrobial effect of Cu/Zn bimetallic nanoparticles is a combination of factors such as a change in the permeability of the bacterial membrane due to zinc ions and the oxidation process caused by copper ions; Fe-Ag particles form a galvanic pair which contribute to the dissolution of nanoparticles, the formation of ions, and enhanced antitumor properties [3]. Under the action of a relativistic electron beam, we obtained the following metal/semiconductor composite nanoparticles with a dielectric silicon part: core shell Cu@SiO₂, Ag@Si, Janus-like TaSi₂/Si [4-6]. The authors have presented some electrophysical properties and applications of these composite nanoparticles in the following articles [7-9]. We propose, below, some mechanisms for the formation of composite nanoparticles created by a one-stage gas-phase synthesis method based on two approaches: energy, and molecular dynamics.

Results and discussion

The mechanism for creating composite core/ shell nanoparticles based on the principle of minimum surface energy.

It is known that redistribution occurs at the interface between two liquid media—particles with a lower surface energy diffuse to the interface. In other words, the addition of a small amount of a substance with low surface energy leads to a significant decrease in the surface energy of a two-component liquid, in contrast to the small change in its surface energy following the addition of a small amount of liquid with a large value of surface energy. This is due to the fact that a substance with a small value of surface energy reduces the surface energy of a two-component liquid as a result of segregation to its surface.

![Fig. 1. a - Dependence of the surface energy of a two-component substance on the content of its components; b - surface energy of the core-shell particle.](image)

These substances tend to concentrate in the surface layer, reducing the surface tension of the bicomponent substance. The qualitative behaviour of changes in surface tension depending on the relative content for two-component liquids is shown in Fig. 1a. The surface energy W₁ of the composite core-shell particle composed of the sphere with surface area S₁ and surface energy G₁ and the sphere with the surface area S₂ and the surface energy G₂ is W₁ = G₁S₁ + G₂S₂. In the case when G₁ > G₂ and S₁ > S₂, the surface energy W₁ is less than W₂ (Fig. 1b). Figure 2 shows a Cu@Si nanoparticle and calculation of the surface energies of the particle. The condition W₁ < W₂ creates conditions for the segregation of silicon to the surface of the particle, with the formation of a copper core.

Molecular dynamics simulation
Modelling of the process of formation of composite nanoclusters [8] is consistent with experiments on the production of core-shell nanoparticles. The estimated time, based on the results of molecular dynamics modelling, for phase separation does not exceed 1 μs, and the diffusion rate increases significantly with increasing temperature. In the electron beam method used in this work, wherein evaporation by a relativistic electron beam is followed by condensation of vapours in an inert gas stream, high temperatures are reached; therefore, the diffusion rate is high enough for phase separation and there will be enough time for the process of separation and formation of a core-shell particle. The creation of a Cu@Si core-shell nanoparticle from a liquid fcc phase of randomly distributed silicon and copper atoms in a lattice with a 10% silicon content occurs at a cooling rate of 1 K / ps. The formation of Janus-like nanoparticles in the initial configuration in the form of two liquid contacting nanoclusters with a high silicon content of 50% occurs at high cooling rates compared to core-shell nanoparticles. Cu@Si forms a Janus-like nanocluster with a decrease in the cooling rate. The structure and internal structure of the Cu@Si composite cluster depend on the type of initial objects, the concentration of silicon in the alloy, and the crystallisation rate.

**Analysis of the size distribution function of composite nanoparticles**

Information on the particle formation mechanism is provided by the particles’ size distribution. The particle size distribution function was determined from their images obtained using a transmission electron microscope. The number of particles in the statistical sample ranged from 300 to 500. The data obtained for the core-shell particles Cu@SiO₂ are well described by the lognormal distribution (Fig.2), which is observed when the coagulation process prevails at all stages of particle growth at their condensation in the gas phase [1]. It is known that the coagulation process of particle growth is well described by the Smoluchowski kinetic equation [10].

![Cu@SiO₂ size distribution](image1)

![Cu size distribution](image2)
Fig. 2. Histogram of particle size distribution: a - Cu @ SiO₂, b – Cu

The size distribution function of copper particles is visually close to the lognormal distribution (Fig. 2a), although its deviation from the lognormal will be shown below. As a rule, to estimate the propinquity of the distribution to the lognormal one, the integral probability distribution function on the particle diameter in semilogarithmic coordinates is used. The dependence obtained should be linear. More informative is a comparison of the experimentally obtained distribution with a true lognormal distribution. In this case, the integral probability distribution function in semilogarithmic coordinates is also constructed, and we determine the smallest and largest probabilities where the dependence is linear. The histogram of the experimental values is approximated by the lognormal distribution, and the mean value and the logarithm of the standard deviation are determined. Further, this distribution is constructed in semi-logarithmic coordinates, the probability interval where this dependence is linear is determined, and the obtained interval is compared with the experimental one.

Thus, a large fraction of large sized particles are present in Cu nanopowder as compared to Cu@SiO₂ nanopowder. From these data it follows that the same formation mechanisms are characteristic of the first stages of the formation of Cu@SiO₂ and Cu nanoparticles, whereas a difference is observed at the final stages. The first stage, by the coagulation mechanism, obviously occurs before the formation of the SiO₂ shell and its hardening.

Fig. 3. a - integral probability distribution function depending on the particle size Cu in semilogarithmic coordinates, b - true integral probability distribution function depending on the particle size in semilogarithmic coordinates for an average particle size of 147 nm.

Fig. 4. a - integral probability distribution function depending on the particle size Cu@SiO₂ in semilogarithmic coordinates, b - true integral probability distribution function depending on the particle size in semilogarithmic coordinates for an average particle size of 90.5 nm.
At the second stage, the coagulation of copper nanoparticles under the shell does not occur due to hardening of the silica shell. This leads to a deviation from the lognormal law when large particles are “not enough” in the distribution, starting with $\ln(d) = 4.6$ (Fig. 4a). This process most probably occurs at temperatures close to the crystallisation temperature of silicon dioxide, 1400°C. In the case of copper nanoparticles, the situation is the opposite—in the distribution, there is an “excess” of large particles, starting with $\ln(d) = 5$, which is most likely due to the manifestation of the liquid-drop mechanism of their formation.

Obviously, one can influence the final particle sizes by choosing a shell material with different condensation temperatures. The arithmetic average size of copper nanoparticles in the shell (90.5 nm) is significantly smaller than the size of pure copper nanoparticles without a shell (190 nm).

For example, if we take a substance for a shell with a high condensation temperature (titanium, tungsten, etc.), the coagulation process will be limited at high temperatures, which will lead to a small particle size. It should be added that the substance of the nucleus should be selected taking into account its surface tension, intermolecular interaction, and the formation energies of chemical reactions with the shell material.

Conclusions

As follows from a review of the published data, Janus-like and the core-shell composite nanoparticles, consisting of a metal and a semiconductor with the dielectric constant of more than 3, are promising for nanophotonics, because of the effects in the particles: plasmon and polariton.

It is shown that the main driving force for the formation of core-shell nanoparticles is the difference in the surface energies of the substances that make up this particle. Addition of a small amount of a substance with a small value of surface energy into a substance with a large value of surface energy leads to a sharp decrease in the total surface energy of the system. Moreover, for nanoscale, due to the high Laplace pressure, and consequently large values of surface energy, this mechanism is predominant.

Based on the experimental data of the authors, on obtaining particles under the action of a relativistic electron beam using the integral size distribution function, it was found that for large particle sizes deviations from the lognormal law, described by the Smoluchowski equation, are observed. The reason for this is the formation of a shell of silicon oxide, as well as the manifestation of a liquid-droplet mechanism.

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