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Reduction of colloidal Ag_2S to binary $Ag_{2-x}S/Ag$ nanoparticles under UV and visible irradiation

Svetlana V. Rempel,*[a,b] Yulia V. Kuznetsova[a] and Andrey A. Rempel[a]

[a] *Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620990 Ekaterinburg, Russian Federation. Fax: +7 343 374 4495; e-mail: svetlana_rempel@ihim.uran.ru*
[b] *Ural Federal University, 620002 Ekaterinburg, Russian Federation*

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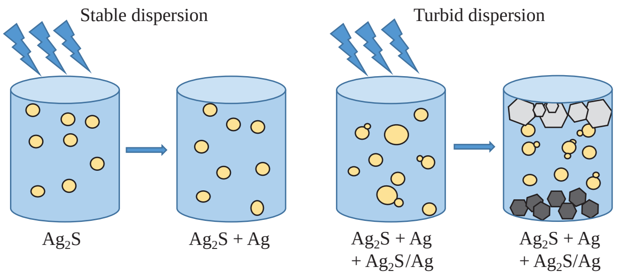
The formation of $Ag_{2-x}S/Ag$ binary nanoparticles in an aqueous colloid dispersion of Ag_2S under irradiation leads to an asymmetry in the optical absorption spectrum as a consequence of the Fano resonance due to the interaction between the excitons of semiconductor nanoparticles and the plasmons of metallic nanoparticles. Aqueous dispersions from different stability regions containing Ag_2S nanoparticles have been studied. Sunlight, UV and laser irradiation leads to the partial reduction of silver in the dispersion and the formation of the $Ag_{2-x}S/Ag$ particles depending on the initial state of the dispersion and the conditions of irradiation.



The organic[1] and inorganic hybrid systems[2,3] of semiconductor and metallic nanoparticles are of interest because of their unique properties.[4–9] The generation and transport of hot carriers, energy transfer and related optical, magnetic, photoconducting and catalytic properties of metal/semiconductor heterostructures have been studied.[10–15] The mobility of Ag^+ ions in Ag_2S promotes the formation of heterostructures depending on ambient conditions and concomitant components.[16] Irradiation and applied voltage may change the stoichiometry of Ag_2S up to complete reduction of silver.[17] The x/y ratio in $(Ag_2S)_xAg_y$ was varied by applying an electron beam.[18] The stability of colloidal gold and silver dispersions was changed under exposure to visible and UV light.[19,20]

The aim of this work was to study the processes occurring within a colloidal dispersion containing Ag_2S nanoparticles with time and under irradiation. The dispersion of Ag_2S nanoparticles was synthesized in accordance with a published procedure[21] using aqueous solutions of silver nitrate and sodium sulfide. In order to achieve long-term aggregative stability, sodium citrate $Na_3C_6H_5O_7$ ($CitNa_3$) was used as a complexing and stabilizing agent. In preliminary experiments, we determined the stability region of Ag_2S colloidal dispersion depending on a ratio between initial components. To examine the aging of dispersion containing Ag_2S nanoparticles, we used two samples from the stability region (dispersion I) of 0.3125 mM and turbidity region (dispersion II) of 2.5 mM (Table 1).[†]

Table 1 Conditions for the synthesis of dispersions I and II.

Dispersion	Initial dispersion concentrations/mM			After synthesis		In a month	
	$AgNO_3$	Na_2S	$CitNa_3$	Turbidity	Average D_h/nm	Turbidity	Average D_h/nm
I	0.625	0.3125	1.25	0	8	0	3
II	5	2.5	2.5	14.34	17	34.38	12

The results of DLS showed that the aqueous dispersion of nanoparticles is a dynamic system, and its equilibration time is about a day. Thus, the average values of D_h in dispersions I and II after synthesis were 8 and 17 nm, respectively. Within a month, the turbidity of dispersion II increased in contrast to that of dispersion I, which remained stable. In a month, the average values of D_h reached minima at 3 and 12 nm in dispersions I and II, respectively, and remained unchanged for more than half a year (see Table 1). As a result of UV irradiation, the average values of D_h nanoparticles in the dispersions increased to 5 and 19 nm, respectively. However, the zeta potential of nanoparticles in dispersion I increased in modulus, which is indicative of a rise in the stability of the system. At the same time, the zeta potential of nanoparticles in dispersion II decreased in modulus, and the instability of the system was confirmed by the formation of a precipitate.

The DLS measurements during 3 h exposure to the helium-neon laser light revealed the formation of a spot with metallic luster on the cell wall, which had a diameter corresponding to that of the laser beam. This can be due to the reduction of silver

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[†] The hydrodynamic diameter D_h of Ag_2S nanoparticles in the dispersion was determined by dynamic light scattering (DLS) on a Zetasizer Nano ZS device (Malvern Instruments). The measurements were performed by a backscattering method at an angle of 173° with the use of a helium-neon laser (633 nm) at 25 °C. The turbidity was controlled by an HI 93703 Microprocessor Turbidity Meter. The samples were analyzed by optical spectroscopy in the UV, visible and near-IR regions from 190 to 2300 nm at room temperature by means of an FS5 spectrofluorometer (Edinburgh Instruments) and a UV-3600 two-beam spectrophotometer (Shimadzu). The UV radiation source was a HB0 103/W2 mercury lamp with a 325–420 nm filter. The exposure times were 15 and 30 min. The energy dispersive X-ray (EDX) analysis and the examination of the morphology of dried dispersion samples were carried out on a JSM JEOL 6390LA scanning electron microscope.

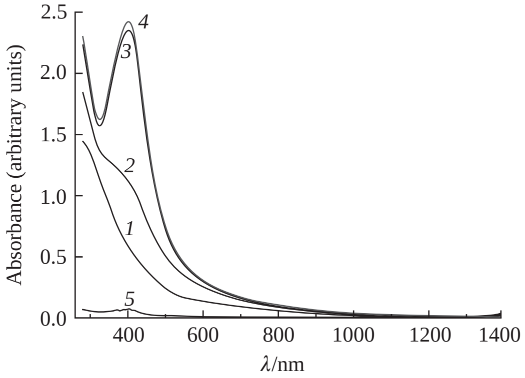

Figure 1 Optical absorption spectra of dispersion I containing Ag_2S nanoparticles (*1*) after the synthesis, (*2*) after six-month storage, (*3*) before irradiation, (*4*) after UV irradiation for 15 min, and (*5*) the difference spectrum before and after irradiation.

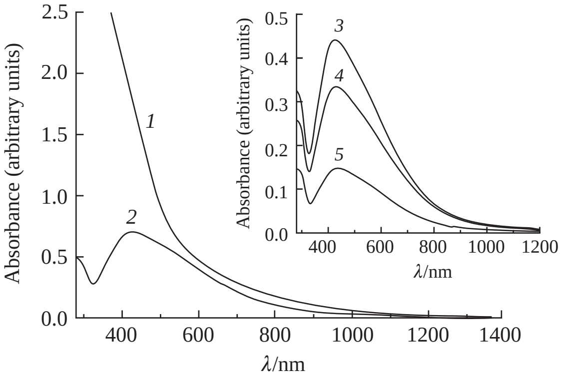

Figure 2 Optical absorption spectra of dispersion II containing Ag_2S nanoparticles (*1*) after synthesis, (*2*) after six-month storage, (*3*) after seven-month storage and before irradiation, after (*4*) 15 min and (*5*) 30 min UV irradiation.

on the wall under laser irradiation. The optical absorption spectra of dispersion I before and after UV irradiation are shown in Figure 1. After daylight six-month storage of dispersion I, a step appeared in the spectrum (see Figure 1, curve *2*), whose position coincides with the position of the plasmon peak of Ag nanoparticles.[6,10] Consequently, the step is due to the appearance of Ag nanoparticles in the dispersion. During the next month, the amount of reduced silver increased, and the main contribution to the spectrum was made by silver nanoparticles. The absorption maximum at 402 nm is determined by the environment and adsorbed ions.[10]

The mechanism of Ag nanoparticle growth in the presence of citrate during irradiation was described.[22,23] The reduction of Ag^+ by citrate ions in a dispersion occurs on the surface of nanoparticles under exposure to light. The plasmon-induced growth is directly proportional to the energy of incident light. The particles may grow to a so-called light-controlled size depending on the wavelength of incident light.[22] The formation of binary nanoparticles on the surface of Ag_2S proceeds during the migration of Ag^+ ions to the surface of nanoparticles, as described previously.[17,18]

On the other hand, an increase in light absorption in the presence of metal nanoparticles is due to plasmon resonance. When light is scattered by the surface plasmons of metallic nanoparticle into a distant region, light absorption by other particles at a distance of hundreds of nanometers is possible, *i.e.* the fraction of light absorbed by the system increases. Thus, reduction with the formation of metal nanoparticles leads to an increase in optical absorption.[9] Therefore, a considerable part of Ag_2S in dispersion I transformed with time into Ag on exposure to daylight in the presence of citrate.

Figure 2 shows the optical absorption spectra of turbid dispersion II. After the synthesis, the spectrum was typical of a dispersion containing silver sulfide nanoparticles. According to the DLS data, particle aggregation and the subsequent deposition occurred in the dispersion with time and under UV irradiation; this can be due to dipole interaction intensified by light absorbed in the plasmon resonance band. Medium-sized particles of ~20 nm remained in the dispersion, and the particle size distribution after irradiation became monodisperse. After 30 min UV irradiation, a very thin pink film appeared at the cell bottom. According to earlier TEM data, this film colour corresponds to Ag particles with a diameter of 10–20 nm. A similar effect of Ag nanoparticle aggregation on the optical spectra was described previously.[15] The absorption maximum of the turbid dispersion was displaced by 24 nm to the red region, as compared with that of stable dispersion I.

The peak asymmetry in the plasmon resonance region of silver nanoparticles in the spectra of dispersion II is of interest. This asymmetry is due to the Fano resonance owing to exciton–plasmon interaction in a metal and semiconductor,[9,24] and this effect depends on the size and mutual arrangement of the semiconductor and metal nanoparticles. The theoretical and practical investigations[9,25] revealed that the optical absorption spectra become asymmetric and strongly antiresonance because of interactions between the dipoles of semiconducting and metallic nanoparticles. On the other hand, resulting from strong adhesion, the electronic states of the semiconductor and metal can be mixed in the interface, which leads to a considerable suppression of the plasmon wave and excitonic excitation.[8,26]

The absorption peak asymmetry in dispersion II is indicative of the existence of $Ag_{2-x}S/Ag$ binary particles. A thin smooth film of a silver colour was formed on the dispersion surface with time, and a black precipitate was deposited at the bottom. As found by HRTEM,[27] binary particles with a common interface were present in the dispersions.

The initial turbidity of the dispersion may also be caused by $Ag_{2-x}S/Ag$ binary particles. Random distribution of a local resonance addition to the absorption coefficient (because of exciton–plasmon interaction), additions in amplitude and the dispersion volume may result in an optical opalescence effect.

The dispersion surface films and bottom deposits were analyzed by SEM. Aggregated particles 100 to 200 nm in diameter from the surface of dispersion II in the form of regular polyhedra were found. The EDX results indicate that the film consisted mainly of Ag, and S occurred in a small amount. The bottom deposit particles were smaller; they formed a network structure and had a shape similar to that of the dispersion surface particles with a size of about 100 nm. The deposit contained Ag_2S.

Thus, Ag_2S nanoparticles were formed in stable dispersion I, and Ag nanoparticles were generated during storage under the daylight. The irradiation increased the amount of Ag nanoparticles and, partially, led to their agglomeration (Figure 3).

In turbid dispersion II, the Ag_2S, Ag and $Ag_{2-x}S/Ag$ particles were formed during the synthesis. The Ag_2S particles were deposited, the Ag particles formed a smooth film on the dispersion surface, and the non-agglomerated particles $Ag_{2-x}S/Ag$ remained in the colloidal dispersion. The negative surface charge induced the migration of silver ions from either the dispersion or silver sulfide. The absorption of Ag^+ ions from the dispersion caused the enlargement of particles. When the size of the particles reached 100–200 nm, they formed a film on the dispersion surface or a deposit at the bottom (see Figure 3).

Under irradiation at the absorption band of both Ag_2S and Ag, a photon can be absorbed on the excitation of the $Ag_{2-x}S/Ag$ binary structure by both metallic and semiconducting nanoparticles. If the photon is absorbed by metallic nanoparticle, the plasmon–

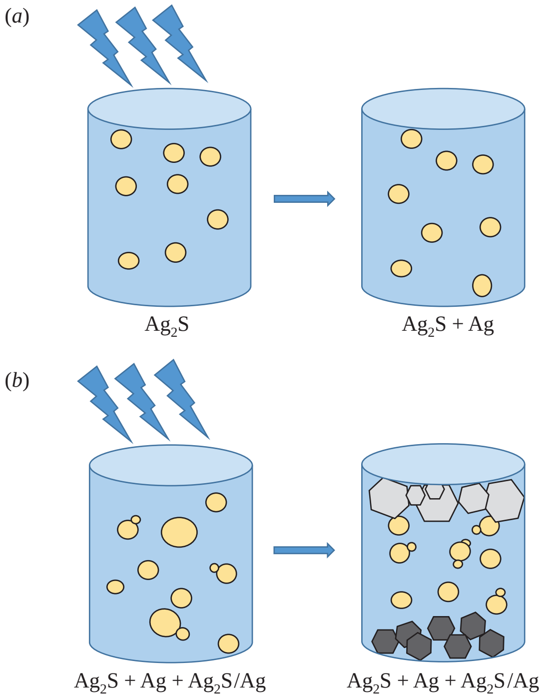

Figure 3 Formation of nanoparticles under irradiation in (*a*) stable and (*b*) turbid dispersions.

resonance energy transfer (PRET) is probable. Since the photon energy is greater than the forbidden bandwidth of Ag_2S, the semiconducting nanoparticle can also be excited. Thus, during the excitation of Ag_2S nanoparticle, the dipole in the semiconductor excites surface plasmons; *i.e.*, energy is transferred owing to the Forster resonance energy transfer (FRET). Hence, in the Ag–Ag_2S system of nanoparticles, the FRET and PRET effects are possible. These effects compete with each other, but they exhibit an inverse dependence on the distance between semiconductor and metal.

In transparent stable colloidal dispersion I (after storage for seven months and after irradiation), if the Ag content is large, the Ag_2S content is small and the arrangement of nanoparticles is random, no conditions are created for exciton–plasmon interaction between semiconducting Ag_2S and metallic Ag nanoparticles. The enlargement of nanoparticles under exposure to light can be due to electron transfer from citrate ions to Ag nanoparticles. In turbid dispersion II, the presence of Ag_2S and Ag promotes the formation of $Ag_{2-x}S$/Ag particles where FRET from Ag_2S to Ag takes place, and the exciton–plasmon interaction appears as the absorption peak asymmetry.

Thus, in citrate-stabilized colloidal dispersions of Ag_2S, silver is reduced under irradiation. The deposition of nanoparticles on the walls and precipitation are observed depending on exposure time, radiation intensity and the initial state of dispersion.

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