Optical extinction spectra of the aqueous suspensions of Ag nanoparticles

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Abstract

The experimental results on the extinction spectra of aqueous suspensions of silver nanoparticles are presented. It is shown that optical properties of suspensions are strongly affected by the size and shape of the particles. Extinction spectra of monodisperse Ag colloid consist of two characteristic bands centered at about 430 and 540 nm, which can be explained in terms of Mie theory. These bands arise from the excitation of dipole and quadrupole components of surface plasmon resonance respectively. Presence of rod-like particles in colloid leads to broadening and tailing of the dipole component of the extinction spectra.

Keywords: silver nanoparticles, extinction, surface plasmon resonance

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Introduction

Michael Faraday was the first who has systematically studied optical properties of finely dispersed noble-metal particle suspensions as early as in 1850's. He has synthesized characteristic ruby-red Au particle suspensions and demonstrated that the color of Au colloids changes while varying the size and aggregation state of the particles. In 1908, Mie has presented his phenomenological theory based on the Maxwell's equations and calculated for the first time the extinction, scattering and absorption cross-sections of spherical Au particles of arbitrary sizes. Now it is well known that small metal particles strongly scatter light, due to resonant plasma oscillation of conducting electrons, termed surface plasmon polaritons or surface plasmons. When confined to sub-wavelength dimensions, plasmons can be excited by a visible light and their frequency tuned efficiently with varying the size and dielectric environment of the particles [1]. Remarkably, silver is the only metal whose plasmon resonance might be tuned to any wavelength within the visible spectral range.

Silver nanoparticles are known as strongly interacting with the incident electromagnetic radiation. The overall cross-section of the light interaction for Ag

nanoparticles is almost ten times larger than the geometric cross-section, which indicates that the nanoparticles capture more light than is physically incident upon them [2]. High efficiency for the interaction with light, tunability of optical properties, chemical robustness and the ability to withstand high-intensity radiation without photobleaching make silver particles a very appealing system for various optical and photonic applications [3]. Those include guided-wave propagation [4], nonlinear spectroscopy [5], surface-enhanced techniques [6], infrared absorption [7] and sensors [8].

Despite a great deal of theoretical and experimental works devoted to metal nanoparticles, studies of spectral properties of interacting and non-interacting Ag nanoparticles are still desired. The aim of the present work is to examine optical extinction spectra for the aqueous suspensions of silver nanoparticles, prepared using the method of chemical reduction.

Experimental

Silver nanoparticles of arbitrary sizes in the limits from 10 and 100 nm were synthesized by involving a chemical reduction of supersaturated Ag_2O solution by pressurized hydrogen gas. One can control the particle size when simply varying the reaction time. The detailed procedure of the nanoparticle synthesis can be found elsewhere [2]. Particle stability is achieved through electrostatic repulsion between thick double electrical layers resulting from a limited dissociation of silver oxide. Typical concentrations of the Ag particle suspension synthesized by this method are around 10^{10} cm^{-3}. The reaction produces a fairly monodispersed suspension, with a minor fraction of particles much smaller than those of the average size for the given suspension and high aspect ratio particles (‘rods’ or ‘whiskers’). High aspect ratio particles may be easily removed from the suspension using a gravity filtration with nylon membranes. However, we concentrate in our work on the studies of spectral properties of the as-prepared silver colloids.

Because hydrogen, water and silver oxide are the only components used in the reaction, no other chemicals are present in the final colloidal suspension. The synthetic method used in this work has many advantages over the other methods, since it provides homogeneous size distribution of the particles, their crystallinity and is highly productive.

The extinction spectra of the samples were measured using a LOMO (St. Petersburg, Russia) SF-46 spectrophotometer. Both scanning electron microscopy (SEM) and atomic-force microscopy (AFM) techniques were used to determine the size and shape of the particles.

Results and Discussion

The SEM and AFM studies have revealed that the Ag colloids are mainly composed of polyhedral shaped nanoparticles, each of which having the same dimensions along the coordinate axes and so a spherical symmetry. The total number of nanoparticles of the same size and shape in the suspensions exceeds 80%. The rest of the particles are ‘whiskers’, with the short axes of about 30 nm and the long axes between 0.1 and 10 μm.

Notice that, for the reason of conciseness, the corresponding SEM and AFM images of the nanoparticles are not presented in this paper.

As mentioned above, the particle size may be controlled with varying the reaction time. The aliquots were taken in the 0.5–120-min interval, so that the total reaction time is approximately 8 h, thus representing 25 different particle sizes (see Fig. 1). The initial suspensions (the reaction times 30–150 s) appear as lemon-yellow and totally transparent. The mean size of the particles in these suspensions ranges approximately from 10 to 20 nm. The particles are small enough and the absorption contribution dominates in the extinction spectrum.

Fig. 1. Aliquots of silver nanoparticle suspension taken during a single chemical reaction. Labels on the vials indicate the reaction times (in seconds and minutes).

The colour of the suspension changes continuously to fulvous, sorrel and then foxy with increasing size of the particles. The contribution of resonant scattering becomes noticeable for the particles larger than 50 nm in size. The scattering component appears as

a weak opalescence. Then, when it prevails over the absorption, the suspension becomes opaque. The aqueous suspension of Ag nanoparticles about 100 nm in size appears turbid greenish, due to a strong resonance scattering of light in this spectral region. Hence, the colour of the aqueous silver suspension can be used as a qualitative indicator of the mean particle size. Notice that the problems of determination of the colour for finely dispersed metal particles have also been discussed in the work [9].

The extinction spectra of the aliquots collected in the course of single reaction are shown in Fig. 2. The evolution of the maximum in the extinction spectra starts from the initial peak position around 410 nm, which represents the dipole component of the plasmon resonance of silver particles smaller than 30 nm (see seven lower curves in Fig. 2).

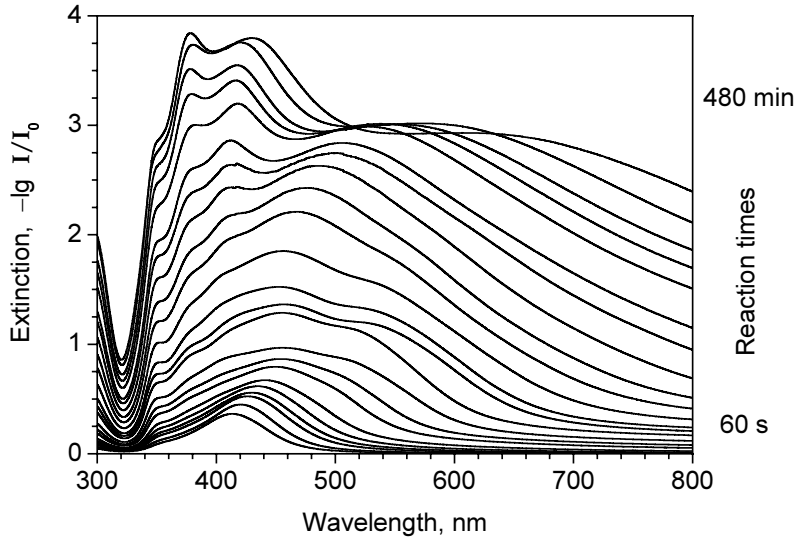

Fig. 2. UV/Vis extinction spectra of the as-prepared aqueous suspensions of silver nanoparticles. The aliquots are collected in the time intervals indicated on the vials (see Fig. 1). The mean diameter of the particles represented by the corresponding extinction curves ranges from 10 to 100 nm.

The two main features may be observed in the extinction spectra of non-interacting Ag nanoparticles of the size about 80–100 nm (see the middle and upper curves). The first one is centred in the spectral range of 450–550 nm for different aliquots, while the second is located at 430 nm. In their theoretical work, *Schatz* and the co-authors [1] have shown that the spectral position of these spectral bands is a function of particle size, shape and the dielectric function of external medium.

Usually the optical response of small individual spherical metal particle or the suspension of those particles could be successfully described in terms of the Mie's theory [10]. For the metal particles much smaller than the wavelength of incident light, the electromagnetic field is uniform across a particle, so that the conduction electrons move in-phase producing only dipole-type oscillations. These oscillations appear in the absorption spectrum as a single narrow peak. As the particle size increases, the field across it becomes non-uniform and the phase retardation broadens the dipole resonance

and excites higher multipole resonances, such as quadrupole, octupole, etc., thus leading to several peaks in the spectra. As the size increases, the dipole maximum shifts to longer wavelengths and the quadrupole peak at about 430 nm is also revealed. This shift results from the influence of surrounding medium, which slows the electron oscillations down more efficiently, due to a larger surface area of the particles [10].

Silver nanoparticles less than 30 nm in size do not interact with light as efficiently as the particles lying in the 50–100 nm range and this interaction is owing to the energy absorption. Plasmon resonances, which can be excited for the larger Ag particles, have a significant light scattering component. Hence, for the particles larger than 50 nm in size it is more correct to consider total energy losses for the beam passed through the sample and detected in the far field, i.e. the extinction of light.

As it might be expected, the spectra of suspensions comprised by ensembles of nanoparticles of different sizes and shapes are more complex, when compare to those for the suspensions of spherical particles. A presence of particles with different aspect ratios in the suspension leads to broadening and tailing effects in the extinction spectra (see Fig. 2). Besides, a new spectral band appears at 370 nm, which may be assigned to the excitation of multipole component of the surface plasmon resonance. This agrees qualitatively with the numerical calculations that utilize discrete dipole approximation performed for the nanoparticles of silver with the spherical, ellipsoidal, cubic, tetrahedral, cylindrical and pyramidal shapes [11]. The excitation of multipolar plasmon resonances in the silver 'whiskers' may be described in terms of standing plasmon waves [12]. The plasmon emission near the plasmon resonance frequencies may also complicate a scattering pattern by the rod-like nanoparticles or 'whiskers' [13].

Conclusions

We have observed experimentally the size and shape effects in the extinction spectra of aqueous suspensions of Ag nanoparticles, prepared with the chemical reduction of silver oxide. The measured spectra are quite different from those derived on the basis of the Mie theory. A presence of particles with high aspect ratios in the suspensions leads to broadening and tailing in the extinction spectra. We have also shown that the colour of aqueous silver suspensions could be used as a qualitative indicator of the mean particle size.

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