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Light Scattering by Silver Nanoparticles in Colloid Solutions for Improved Photovoltaic Devices

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Incorporation of metal nanoparticles (NPs) into photovoltaic cells attracts much attention last years as a promising way for efficiency improvement by light trapping. Precise characterization of light scattering properties of NPs is essential for their successful application. Scattering diagrams and spectra of absorbed light are studied with custom-assembled automated experimental setups. It was found, that 60-240 nm in diameter Ag NPs demonstrate efficient wide-angle light scattering due to excitation of multipole resonances, which manifest themselves as side lobes in the scattering diagrams. Contributions of the multipole modes were also resolved in the absorption spectra of NPs. Direction of light scattering and a red shift of light scattering efficiency maxima, comparing to absorption maxima, studied aiming its application for efficient trapping of long-wavelength radiation in photovoltaic cells.

Keywords: Localized Surface Plasmon Resonance, Silver Nanoparticles, Extinction Spectra, Scattering diagram.

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1. INTRODUCTION

Increasing the efficiency of solar cells and lowering their costs is the mainstream in modern energy saving technologies. One of the ways to resolve that problem is incorporation of noble metal nanoparticles into photovoltaic cells, which increase the amount of electromagnetic radiation trapped by a solar cell. Noble metal (first of all Au and Ag) nanoparticles feature a number of unique optical properties that result from the excitation of the collective oscillations of electron density termed localized surface plasmon resonances (LSPR). The surface plasmon modes excited in NPs by the incident light result in highly efficient light scattering. At the same time the absorption of light by NPs is low, which leads to light trapping on the surface of the solar cell with low energy losses. In addition, the peak in the light scattering spectrum is red shifted compared to the peak in absorption spectrum. Such red shift is size-dependent and can be tuned by manufacturing NPs of different sizes.

In this work we focus on the size-dependence of the red shift of the maxima of scattering vs absorption and the contribution of different multipoles into this effect. Angular resolved light scattering (ARLS) diagrams of silver NPs in water that strongly depend on the wavelength of the incident light and the size of the particle are presented. Precise characterization of light scattering properties of nanoparticles is essential for their successful application, particularly in photovoltaics.

2. EXPERIMENTAL

2.1 Materials and samples preparation

Silver NPs of arbitrary size between 20 – 250 nm were synthesized by reduction of silver oxide with hydrogen [1]. 0.1% of silver oxide was dispersed in deionized water in a round bottom flask. The flask was heated to 70° C and pressurized to 1atm excess pressure of hydrogen gas. The particle size can be controlled simply by varying the reaction time. The nanoparticle suspension was characterized by UV-vis extinction spectroscopy and scanning electron microscopy (Fig.1). The reaction produces a fairly monodisperse suspension of quasi-spherical nanoparticles with a minor fraction of very small ones and high aspect ratio particles with a short axis of ~30 nm and long axis between 0.1 and 10 μm. To remove those from the suspension, gravity filtration with nylon membranes was used.

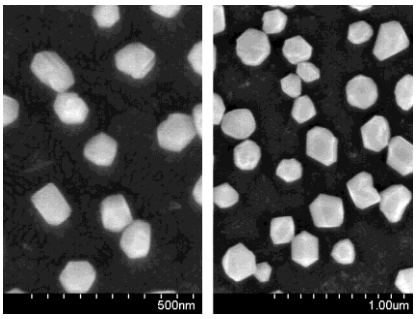

Fig. 1 – SEM image of Ag nanoparticles used in the experiments: sample Ag-1 (left panel), sample Ag-2 (right panel).

Angular resolved light scattering measurements (ARLS) were performed using custom-made automated experimental setup that provides high angular resolution as well as flexibility for the detection of the intensity level of the scattered light. Semiconductor lasers operated at 405 and 532 nm were used as a light source. Scattered light was recorded for 30-150° geometry. To meas-

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ure light absorption by the suspensions of Ag nanoparticles automated experimental based on 1200 mm^{-1} monochromator was assembled. A light incident into the sample was collimated into a parallel beam, while light transmitted through the sample was collected with a set of lenses in such a way that light scattered by the sample within a flat angle of <40° was directed into detector. This allowed elimination of the losses due to forward light scattering. Since forward light scattering for our samples dominating over backscattering, the light extinction measured with our experimental setup is mainly a result of absorption of light.

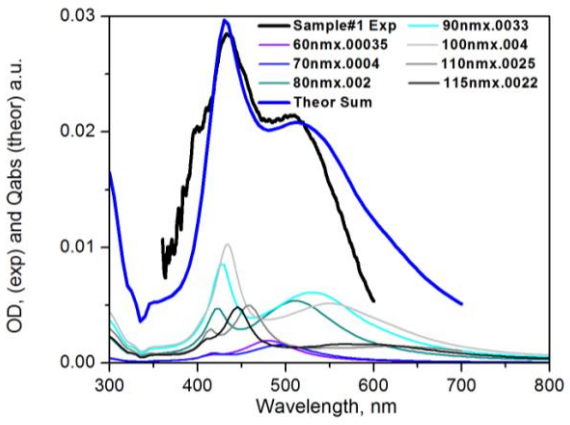
Theoretical modeling of the light absorption by spherical Ag NPs was performed using Mie theory. Dielectric permittivity of silver was taken from [2]. The theoretical scattering diagrams were obtained with freely available Scatlab software (http://www.scattport.org). The Drude model is used in this software for the evaluation of the dielectric function of NPs, which leads to some deviations between theory and experiment. A comparison of the calculated scattering diagrams with experimental ARLS data demonstrate overall good agreement. The contributions of the dipole, quadrupole, and octupole modes into the scattering, absorption and extinction spectra of the silver NPs were evaluated and successfully fitted the experimental data.

3. RESULTS AND DISCUSSION

Two types of suspensions with Ag NPs distributed between 60 – 115 nm (Ag-1) and 130 – 240 nm (Ag-2) were studied, since they exhibit the most interesting effects in absorption spectra and scattering diagrams. It was confirmed experimentally that dipole-related peak in the absorption spectrum shifts towards the "red" side of the electromagnetic spectrum and the quadrupole peak appears at the "blue" side of the spectrum as the size of the NPs increases as it predicted by Mie theory. With further increase of the NPs size, both dipole and quadrupole peaks shift towards the "red" part of the spectrum, and the octupole peak appears at the "blue" side of the spectrum. For the sample Ag-1 the dipole-related peak is positioned at 510 nm while the quadrupole one appears at 430 nm. Corresponding peaks for the sample Ag-2 are centered at 630 nm and 465 nm respectively.). The octupole peak appears at 430 nm.

Analysis of the theoretical fit of the absorption spectrum of the sample Ag-1 reveals that the first peak around 430 nm (Fig.2a) is a result of the quadrupole resonances, and the second peak around 510 nm is a result of the dipole resonances of NPs. Sizes of NPs are shown next to the corresponding lines of different colors in Fig.2a. Coefficients next to the sizes of NPs represent an artificial correction of abundance of NPs in order to construct a Lorentz-like size distribution. As it seen, a sum of absorption efficiency curves for different sizes of NPs (thick blue curve) fits well an experimental optical density spectrum (thick black curve).

Contribution of different plasmon modes into the extinction spectra of 100 nm Ag NPs is presented in Fig.1b. The blue curve represents the octupole-related peak, the green curve represents the quadrupole-related peak, and the red curve represents the dipole-related peak.



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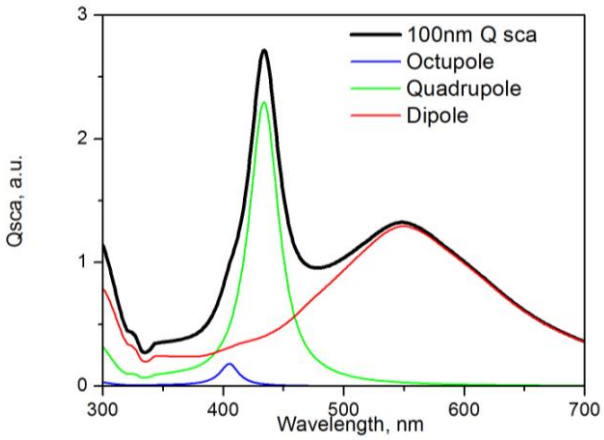
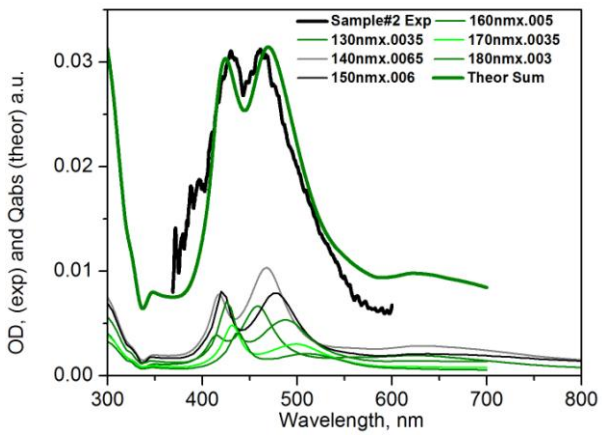


b

Fig. 2 – Experimental (black curve) and calculated (blue curve) extinction spectra of Ag-2 NPs suspension – (a). Thin curves of different colors represent contribution of the absorption efficiencies from NPs of different size. Contribution of the modes of different orders into extinction spectra of 100 nm Ag NPs – (b).

Sample Ag-2 contains NPs of diameters 130-150 nm. The peak centered at 435 nm is associated with octupole resonance, while the second peak at 460 nm is a result of the quadrupole resonances of NPs of different sizes (Fig.3a). Results of theoretical modeling for the dipole, quadrupole and octupole contributions into the absorption efficiency of 140 nm silver NP of are presented in Fig.2b. Both Ag-1 and Ag-2samples exhibit double-peaked absorption spectra, which are the result of a contribution of multipole modes into absorption efficiency of NPs.

Even though positions of the dipole, quadrupole and octupole-related peaks in absorption and scattering spectra of silver NPs are same, the wavelength of light most efficiently absorbed by silver NPs is much different from the wavelength of light most efficiently scattered by NPs. The reason for this is different amplitudes of the multipole modes in absorption and scattering. Most pronounced resonance peaks in scattering are red-shifted in comparison to the strongest resonance peaks in the absorption efficiency. This property of NPs can be used in solar cells to broaden the spectral range of the light converted into the electricity.



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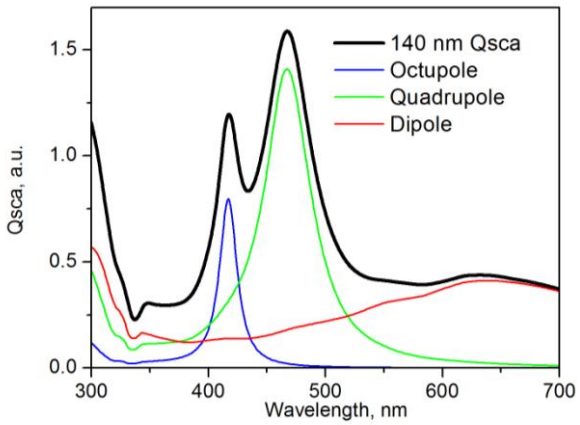
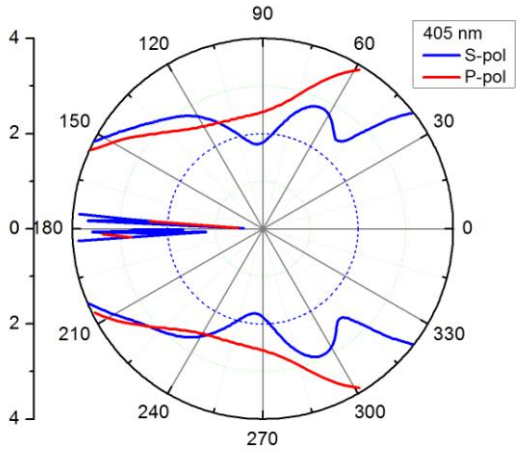


b

Fig. 3 – (a) Experimental (black curve) and calculated (green curve) extinction spectra of Ag-2 NPs suspension. Thin curves of different colors represent contribution of the absorption efficiencies from NPs of different size. (b) Contribution of the modes of different orders into extinction spectra of 140 nm Ag NPs.

Fig. 4 depicts scattering diagrams obtained from angular resolved light scattering (ARLS) measurements for Ag-2 sample at the wavelength of 405 nm which is close to octupole resonance og the NPs (430 nm). The blue curve represents the intensity of scattered light polarized in a plane parallel (p-polarized) to the plane of registration, and red curve represents intensity of scattered light polarized perpendicularly (s-polarized) to the plane of registration.

Side lobes on theoretical and experimental diagrams are the result of the quadrupole mode into scattering. The forward scattering is caused mainly by the dipole mode. Scattering diagram of silver NPs is directed forward, which makes them a good material for light trapping and redirection into the absorbing substrate of a solar cell.



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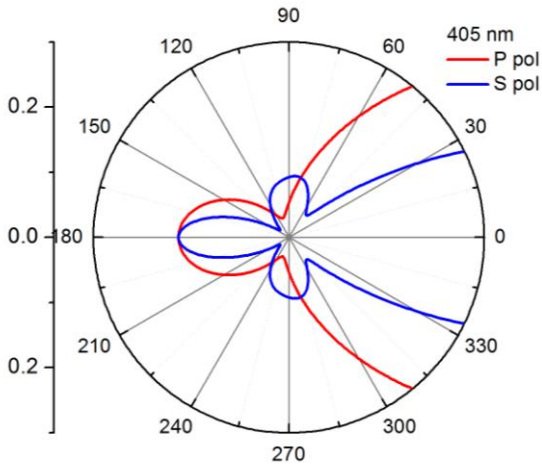

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Fig. 4 – Experimental (a) and calculated (b) scattering diagrams for NPs of sizes 115-240 nm (Ag-1) at the wavelength of 405 nm.

4. CONCLUSIONS

The extinction spectra as well as angular resolved scattering diagrams of silver nanoparticles suspended in water were studied using custom-made experimental setups. The contribution of the octupole and quadrupole modes was separated via fitting the experimental and calculated absorption spectra of silver NPs. Experimental diagrams of angular resolved scattering revealed side lobes, which were identified as a contribution of quadrupole modes. The dipole mode results in the efficient forward scattering. This makes silver NPs a promising material for effective light trapping in solar cells. The fact that forward light scattering is caused by the dipole mode assures efficient light transport from NPs toward the substrate, since dipole field decreases more slowly in comparison with the modes of higher orders.

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