Optical Materials 58 (2016) 439–444

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Absorption and scattering cross-section extinction values of silver nanoparticles

May Hlaing [a], Bellsabel Gebear-Eigzabher [b], Azael Roa [a], Aristides Marcano [b, *], Daniela Radu [b, c], Cheng-Yu Lai [b]

[a] Department of Physics and Engineering, Delaware State University, 1200 North DuPont Highway, Dover, DE 19901, USA
[b] Department of Chemistry, Delaware State University, 1200 North DuPont Highway, Dover, DE 19901, USA
[c] Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA

ARTICLE INFO

Article history:
Received 25 April 2016
Received in revised form
7 June 2016
Accepted 9 June 2016

Keywords:
Silver nanoparticles
Extinction cross-section
Photothermal methods

ABSTRACT

We determine the extinction values of silver nanoparticles as a function of their diameter for three different wavelengths (*405* nm, *532* nm, and *671* nm) from the values of absorbance and their photothermal lens response. We show that for particles of small diameters (*<50* nm) the extinction grows as the cube of the diameter for all three wavelengths. For larger particles the extinction determined from absorbance exhibits a sixth order dependence on the diameters for *532* nm and *671* nm. This kind of behavior is typical of scattering processes that should dominate for large particles. For *405* nm the plasmonic resonant absorption dominates over scattering making difficult the observation of the sixth order dependence even for particles larger than *50* nm. The absorption cross-section measured by the photothermal method does not show the sixth order dependence. It depends on the cube of the particle's diameter for all nanoparticles confirming the scattering free character of this absorption technique and validating the results of the absorbance experiment.

1. Introduction

Silver nanoparticles (Ag NPs) have been the subject of numerous studies for many years because of their potential uses as bactericides and fungicides [1–4], as biological and chemical sensors [5–8], as conductive inks, as pastes and fillers, among other uses in molecular diagnostics, electronics, and photonics devices [7–10]. Despite the evident advances, determination of optical, electrical, and thermal properties of silver nanoparticles is still an open area of research. In this work we propose the combined use of regular absorption spectroscopy and photothermal lens (PTL) spectrometry for the determination of the extinction cross-section and the contribution of the absorption and scattering cross-sections values of Ag NPs of different dimensions. We show that absorption and scattering components of the extinction cross-section can be distinguished in a regular absorption experiment by their different dependence on the particle dimensions. According to the Rayleigh model, the absorption of one individual nanoparticle grows proportional to the third order of the particle's diameter while its scattering cross-section is proportional to the sixth order of the same magnitude [11–14]. We provide experimental evidence that such substantially different behaviors can be actually observed from the data obtained using regular absorbance spectroscopy. We show that these differences are remarkable for light wavelengths shifted toward the red, far from the region of plasmonic resonances, for which absorption dominates over the scattering effects. By fitting the experimental results based on this model we determine the contribution of the absorption and scattering effects to the total extinction cross-section values of an individual Ag NP.

We validate the results of the absorbance experiments using a PTL method which basically provides only the absorption contribution to the NPs extinction cross-section values [15–18]. Indeed, the PTL method measures the amount of heat released by the nanoparticles, following the absorption of light photons. In this regards, scattering effects cannot contribute. This particular property of the PTL methods has been demonstrated by different authors [19–23]. Furthermore, the combined use of absorbance and PTL method allows the determination of scattering and fluorescence quantum yields of the sample [24–26]. In this work, we use a pump-probe PTL approach to determine the corresponding

* Corresponding author.
E-mail address: amarcano@desu.edu (A. Marcano).

http://dx.doi.org/10.1016/j.optmat.2016.06.013
0925-3467/

absorption cross-section of Ag NPs of different dimensions. As expected, we show that this contribution is proportional to the cube of the nanoparticle diameter. The sixth order dependence on the particle's dimensions was not observed in the PTL experiment. Comparison of the PTL and absorbance results allows validation and identification of absorption and scattering contribution to the total extinction value of the nanoparticle. Although this study is limited to Ag NPs, the method bears general character and can be applied for other nanoparticles.

2. Theoretical considerations

2.1. Determining absorption and scattering cross-sections based on absorbance spectroscopy

We consider that the loss of light energy upon propagation through the solution of nanoparticles results only in the generation of heat and scattering. In this situation, the extinction cross-section of the nanoparticle can be written as:

$$\sigma(\lambda) = \sigma_{abs}(\lambda) + \sigma_{sca}(\lambda), \tag{1}$$

where λ is the light wavelength, and σ_{abs} and σ_{sca} are the absorption and scattering cross-sections, respectively. For a nanoparticle with dimensions much smaller than the wavelength of the propagating light, we have [27]:

$$\sigma_{abs}(\lambda) = 8\pi^2 \mathrm{Re}(i\alpha(\lambda))\Big/\lambda, \tag{2}$$

$$\sigma_{sca}(\lambda) = 128\pi^5 |\alpha(\lambda)|^2 \Big/ \left(3\lambda^4\right), \tag{3}$$

where α is the polarizability of the nanoparticle, and $i = \sqrt{-1}$. Lorentz formula provides the value of the polarizability $\alpha(\lambda)$ for a spherical particle of diameter d as:

$$\alpha(\lambda) = [(\varepsilon(\lambda) - 1)/(\varepsilon(\lambda) + 2)]d^3\Big/8, \tag{4}$$

where $\varepsilon = \varepsilon' - i\varepsilon''$ is the complex permittivity of the nanoparticle, and ε' and ε'' are its real and the imaginary part, respectively. Taking into account Eqs. (2) Through (4) the extinction cross-section can be written as:

$$\sigma(\lambda) = B(\lambda)d^3 + D(\lambda)d^6, \tag{5}$$

where:

$$B(\lambda) = \pi^2 \mathrm{Re}[i(\varepsilon(\lambda) - 1)/(\varepsilon(\lambda) + 2)]\Big/\lambda, \tag{6}$$

$$D(\lambda) = 2\pi^5 |(\varepsilon(\lambda) - 1)/(\varepsilon(\lambda) + 2)|^2 \Big/ \left(3\lambda^4\right). \tag{7}$$

Eq. (5) shows that the extinction cross-section is basically due to absorption for small nanoparticles. For large nanoparticles the scattering contribution becomes dominant. Experimental values of the extinction cross-section of the nanoparticles can be determined according to the Beer-Lambert law as

$$\sigma(\lambda) = A(\lambda)\ln 10/NL, \tag{8}$$

where $A(\lambda)$ is the absorbance expressed as a function of the light wavelength, L is the pathlength of the sample, and N is the concentration of nanoparticles. For a sample of spherical nanoparticles of diameter d (m) and sample's concentration C (kg/m^3), N (m^{-3}) can be calculated from the formula:

$$N = 6C\Big/\left(\pi d^3 \rho\right), \tag{9}$$

where $\rho = 10.5 \cdot 10^3$ kg/m^3 is the density of silver. Based on the dependence of the extinction cross-section on the dimensions of the nanoparticles we estimate the values of the absorption and scattering extinction cross-sections using Eqs. (1) and (5).

Determination of scattering cross-section using this method is limited when absorption dominates the interaction between the nanoparticle and the light. In this case, sixth order dependence on the particle diameter might not be observed. Another limitation is related to the dimensions of the particle. If the particle has a diameter of the order of the wavelength ($d \geq 200$ nm) the penetration of light into the particle is not complete. In this case, we expect a reduction of the extinction cross-section because of the limited coupling between the light and the particle.

2.2. Determining absorption cross-section using the PTL method

PTL experiment is an alternative way to study absorption. The method is based on the detection of the amount of heat released in the sample following the absorption of light photons. In a pump-probe PTL experiment, the light from a pump laser is focused onto the sample generating a local field of the refraction index of thermal origin or thermal lens (TL). The TL is then tested by a collimated probe beam of light which propagates collinearly to the pump beam. The presence of the TL distorts the wavefront of the probe beam inducing changes in its diffraction pattern at the far field. We measure the relative transmission of the probe light through a small aperture located at the far field. Thus, the PTL signal can be defined as:

$$S(z,t) = (T(z,t) - T_o)/T_o, \tag{10}$$

where T_o is the probe light transmission through the aperture in the absence of the pump field and $T(z,t)$ is the probe light transmission in the presence of the pump field. The signal has been written as a function of time t and sample position z. We consider that the pump and the probe beam are Gaussians with Rayleigh ranges z_e and z_p, and wavelengths λ_e and λ_p, respectively. We also consider that the pump beam waist is at position $z = 0$ and the probe beam waist is at position $z = a_p$. A Fresnel diffraction model shows that for small changes in probe light transmission ($|T(z,t) - T_o| << T_o$) the PTL signal is given by Ref. [18]:

$$S(z,t) = S_o \tan^{-1}\Big(4m(z)V(z)[t/t_c(z)]\Big\{\Big[1 + 2m(z) + V^2(z)\Big]2t/t_c(z) + [1 + m(z)]^2 + V^2(z)\Big\}^{-1}\Big), \tag{11}$$

$$S_o = P_e \psi A L_{ef}(\mathrm{d}n/\mathrm{d}t)/(\kappa\lambda_p), \tag{12}$$

$$V(z) = (z - a_p)/z_p + \left[(z - a_p)^2 + z_p^2\right][z_p(d_e - z)]^{-1}, \tag{13}$$

$$m(z) = \lambda_p z_p \left[1 + (z - a_p)^2 \Big/ z_p^2\right]\left[\lambda_e z_e \left(1 + z^2 \Big/ z_e^2\right)\right]^{-1} \tag{14}$$

$$t_c(z) = \lambda_e z_e \left(1 + z^2 \Big/ z_e^2\right)\Big/(4\pi D), \tag{15}$$

P_e is the total power of the pump beam, ψ is the fractional thermal load, A is the sample's absorbance, $L_{ef} = [1 - exp(-AL)]/A$, L is the sample's pathlength, $\mathrm{d}n/\mathrm{d}t$ is the thermal gradient of the