Optical properties of silver and silver-cluster-decorated dielectric core nanoparticles

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Application Note

Introduction

In the last decades, engineering of light-matter interactions at nanoscale level has become one of primary interests of science. The ability to manipulate light localization and propagation as well as its use to probe or induce local change is expected to revolutionize many fields such as optics, computing, imaging, telecommunication, health, and many others. The basic requirement for light manipulation at this scale is the confinement of light down to a sub-wavelength size. Unfortunately, this is known to be intrinsically unfavorable. Dielectric materials usually used in conventional photonics suffer from diffraction. The diffraction limits the lowest achievable light confinement to half of the wavelength of light.

Metallic nanostructures, despite significant losses at optical frequencies, were found to be able to overcome the diffraction limit due to the excitation of Surface Plasmon Polaritons (SPPs). SPPs are collective oscillations of the conduction band electrons of metals at a metal-dielectric interface. Meanwhile SPP-induced optical properties of metallic nanostructures led to a broad range of applications, like waveguiding[1], enhancing absorption in a solar cell [2], lasing [3], sensing [4], cancer imaging and treatment [5], and nonlinear optics [6]. Moreover, collective SPP excitation of a cluster of metallic nanoparticles may induce artificial magnetism. Magnetic permeability can be designed even to have a negative value. Realization of nanostructures having simultaneously negative permittivity and permeability would lead to fascinating phenomena like a negative refractive index, electromagnetic cloaking, the reversed Doppler shift and Cerenkov radiation [7].

The negative effective permittivity and permeability at optical frequencies are, however, difficult to realize. The original design8 working at microwave frequencies is difficult to shrink even with advanced nanofabrication methods. Therefore, recent attempts are focused on employing Mie resonances of metal particle clusters.[9,10,11] Metal-cluster-decorated dielectric core particles can be considered as a more promising approach.[12] They are easy to synthesize and exhibit isotropic magnetic response.

In this work, the optical properties of chemically grown silver particles and silver-cluster-decorated dielectric core nanoparticles are investigated by linear transmission spectroscopy. The results provide information about the growth process and the quality of the silver particles.

Experimental Methods

Silver ions were added to a solution of sodium polyacrylate (NaPA) in bi-distilled water. After mixing, the solution was illuminated under UV light for 7 minutes. The size of synthesized silver nanoparticles was tuned by varying the ratio (r) of silver ions to NaPA. The UV illumination initiates reduction of silver ions and leads to formation of silver nanoparticles. Details on the synthesis can be found in literature.[13,14] Similar procedure was employed to synthesize silver-cluster-decorated dielectric core particles. In this case poly-acrylate chains, instead of simply dissolved in water, were grafted on the surface of polystyrene particles covered by a thin layer of photoinitiator. Polystyrene particles were synthesized using conventional emulsion polymerization method. Each single silver-cluster-decorated particle consists of big (D = 120 nm) polystyrene core covered by evenly-distributed small (D = 20 nm) spherical silver nanoparticles.

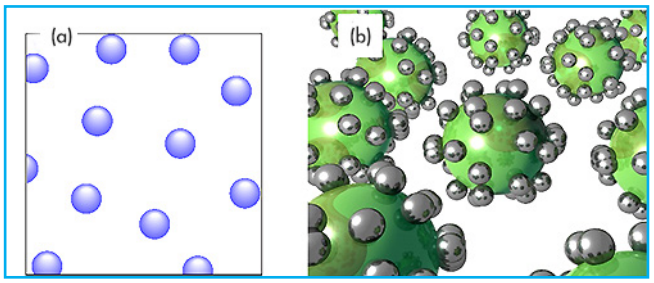

Figure 1 (a) Silver, and (b) silver-cluster-decorated dielectric core nanoparticles.

A home built transmission set-up was used for optical characterization (see Figure 2). Light from a Tungsten halogen lamp (Ocean Optics) was guided to optical set-up by using optical fiber. The diverging beam of the fiber was re-focused into a cuvette filled with the suspension of nanoparticles. The transmitted light from the sample was filtered and measured using a Shamrock spectrograph SR-303i-B combined with an Andor CCD-detector iDus DU420A-BR-DD. A cuvette filled with bi-distilled water was used as a reference sample. All measurements were carried out using non-polarized light.

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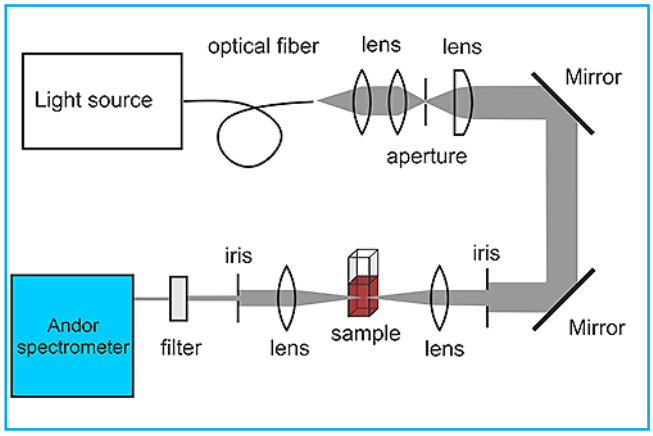

Figure 2 Measurement set-up. Suspension of silver particles was inserted into a cuvette. Transmission measurement was carried out using non-polarized light and spectrometer.

Experimental Results

Extinction (-log T) spectra of silver nanoparticles synthesized with different concentration of silver ions are shown in Figure 3(a). From this figure, it is obvious that there is a minimum content of silver ions to form silver nanoparticles. The extinction peak, indicating formation of silver nanoparticles, is hardly visible for ratio of silver ions below 5%. Furthermore, the extinction peak grows, red-shifts, and broadens with the increase of the ratio of silver ions. Further increase of the ratio leads to a monotonous increase of the intensity and resonance wavelength. The intensity and resonance wavelength reach their saturation values when the ratio of silver ions reach 80% (data are not shown).

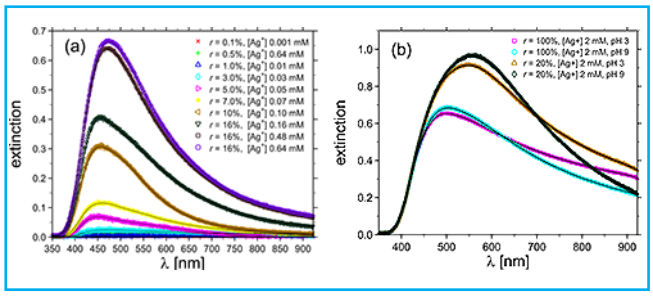

Figure 3 Extinction spectra of (a) silver nanoparticles, and (b) silver-cluster-decorated dielectric core particles.

The existence of minimum content of silver ions can be explained as follows. For low content of silver ions, the ions sitting on NaPA matrix are separated apart to each other. Large separation avoids formation of silver nanoparticles under UV illumination. At high content, silver ions influence the coiling of NaPA matrix. Closely-separated silver ions and dense NaPA matrix result in the formation of big particles. A TEM investigation reveals that at high content of silver ions, the resulting particles deviates from spherical shape.

For real application, silver particles with a high quality factor is necessary. The quality factor can be determined from the resonance frequency and the linewidth of the resonance peak. Mathematically, it can be calculated by $Q = \omega_r / \Delta\omega$. For the synthesized particles, it was found that a high quality factor is obtained for ratio of silver ions 5–10%. This range of silver ion content leads to formation of nearly monodisperse particles. Moreover, the resonance wavelength of silver nanoparticles for a silver ion ratio of 5–10% is around 450 nm.

Figure 3(b) shows extinction spectra of silver-cluster-decorated dielectric core nanoparticles. The nanoparticles synthesized with low ratio of silver ions have surprisingly a higher extinction intensity. From this figure it is visible that pH value of the solution seems to have noticeable but non-significant influence on the optical properties. The linewidth of the extinction spectra seems to be more dependent on pH. A higher pH results in narrower peak indicating better monodispersity of the particles. The resonance wavelength is less affected by pH. During synthesis, the pH is expected to influence the morphology and density of the grafted NaPA. Hence, it influences the size of nanoparticles.

Conclusion and outlook

We reported an investigation of optical properties of silver nanoparticles. We observed an intense and narrow extinction peak for a large range of synthesis parameters. Furthermore, we show that we can tune the size and monodispersity of the resulting particles. The silver ion content was found to have a major influence on the size and monodispersity of the synthesized particles. We were able to determine the range of silver ion content resulting monodisperse particle with resonance at intended wavelength.

Further work will be to investigate the magnetic properties of disordered and ordered silver-cluster-decorated dielectric core particles. Particle ordering is expected to influence the directionality of the magnetic response.

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