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Experimental identification of unique angular dependent scattering behavior of nanoparticles

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Abstract

Background: Nanoparticles exhibit unique light scattering properties and are applied in many research fields.

Methods: In this work, we perform angular resolved scattering measurements to study the scattering behaviour of random and periodic silver (Ag), and periodic polystyrene (PS) nanoparticles.

Results: The random Ag nanoparticles, with a wide particle size distribution, are able to broadbandly scatter light into large angles. In contrast, both types of periodic nanoparticles are characterized by a strong scattering zone where scattering angles are increasing as the wavelength increases.

Conclusions: Angular resolved scattering measurements enable experimentally revealing the particular scattering properties of different nanostructures.

Keywords: Light scattering, Nanoparticles, Angular resolved measurements, Wide angle scattering, Grating behaviour

Background

Light scattering is a fundamental property of particles and can be adjusted in a great flexibility by finely tuning the particle geometries and surrounding media. This unique feature opens up numerous applications for nanoparticles in spectroscopy, sensors and photovoltaic devices [1–3]. For instance, large-angle scattering of nanoparticles is capable of enhancing the light propagation path beyond the physical thickness of devices for absorption improvement, enabling to reduce material usage and resulting manufacturing cost [3–7]. As the scattering behaviour is highly wavelength-dependent it needs to be identified for specific applications. Mostly the scattering behaviour is either simply predicted by theoretical simulations or characterized experimen-

tally by haze measurements [5–7]. However, the haze only gives the overall scattered fraction for each wavelength, and is not sufficient to resolve angular scattering details. In this contribution, we will apply angular resolved scattering (ARS) measurements [6–8] to characterize the wavelength-dependent scattering behaviour of particles for which only few examples exist so far [9].

Methods

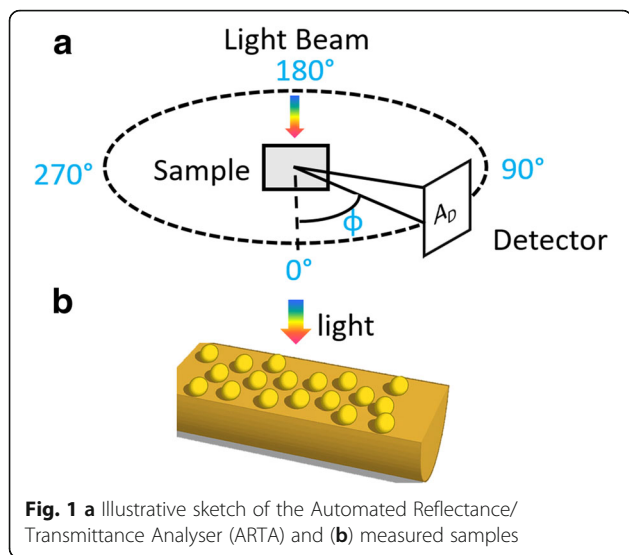
The measurement is done with an UV/VIS setup (PerkinElmer Lambda 950 UV/VIS) and an additional ARS (Automated Reflectance/Transmittance Analyser (ARTA)) extension [10]. The illustrative sketch of ARTA is shown in Fig. 1a. It consists of a fixed sample holder placed in the middle of the moving detector with a detector-sample distance of 92.1 mm (R_{ARS}). Unpolarised light comes from 180° and the scattered light is measured with an angular resolution of 2°. The detection is done by an integration sphere with a slit opening of 6 mm width (w) and 17 mm height (l). Since the detector covers only one plane of the whole scattering space, the measured value at a

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certain angle should be expanded for estimating the volume scattering. The weighting factor F is acquired as [7]:

$$F = 4\pi R_{ARS}^2 / A_D \sin(\phi) \sin(\Delta\theta) \quad (1)$$

where $A_D = w \cdot l$ is the area of the detector slit and ϕ is the measuring angle. $\Delta\theta$ is related to the slit width and is obtained by $\Delta\theta = \arctan\left(\frac{w}{2R_{ARS}}\right)$.

We selected random and periodic Ag nanoparticles as well as closely packed polystyrene (PS) nanospheres, which covers both metallic and dielectric materials. To avoid refraction at the substrate/air interface influencing the scattering angles when light is leaving the substrate, half cylinder glass is applied as substrate and a sketch is shown in Fig. 1b. The investigated wavelength range lies between 400 nm and 800 nm and the range of scanning angle is confined to 30° to 90° (see Fig. 1a), since the transmission is dominant over reflection in intensity for our investigated samples, and direct transmission (scattering angle below 30°) is omitted.

Results and discussion

Figure 2 represents the scanning electron microscopy (SEM) morphologies (left column) and wavelength dependent angular scattering behaviour (right column) of random and periodic Ag nanoparticles and PS spheres. The random Ag nanoparticles in Fig. 2a were fabricated by annealing a 50 nm thick Ag film for 20 min at a temperature of 500 °C in air. The nanoparticle radii range dominantly from 80 nm to 160 nm (see the size distribution in Fig. 3a) with an

averaged spacing of 200 nm. The periodic Ag nanoparticles (Fig. 2b) were prepared using nanosphere lithography [11]: a 30 nm thick Ag film was evaporated onto a hexagonally closely packed monolayer of PS spheres with a radius of 450 nm; subsequently the PS spheres were removed in ultrasonic bath and triangular Ag nanoparticles remained; finally spherical Ag nanoparticles formed after annealing at a temperature of 200 °C for 2 h. Due to the template structure of PS nanospheres, the Ag nanoparticles exhibit a hexagonal order at a uniform radius of 50 nm. Fig. 2c shows the closely packed PS spheres used for the formation of periodic Ag particles in Fig. 2b themselves, which constitute the dielectric nanoparticle sample.

As observed in Fig. 2d, random Ag nanoparticles exhibit a strong scattering ability with a pronounced angular scattering range from 50° to 60°. The scattering is quite broadband and almost covers the whole investigated spectrum, which could be correlated to the broad size and shape distribution of the Ag nanoparticles. Further, as indicated in Fig. 2d, there exists a trend of a moderate increase of scattering angles as the wavelength goes up. To simply explain the scattering behaviour of random Ag nanoparticles, Fig. 3b simulates the angular power distribution of a Ag nanoparticle at air/glass interface using the finite element method as implemented in the software COMSOL [12]. To adapt the simulation geometry to the experimental case, a spherical Ag nanoparticle of $R = 140$ nm radius was cropped off by 20 nm (C) at the substrate interface. Firstly, as shown in Fig. 3b, the large angle scattering ability (a degree beyond 30°) is demonstrated; additionally, the angle corresponding to the large angle scattering peak is increasing as the wavelength increases. This simulation trend is in agreement with the experimental observation of Fig. 2d. In contrast, the periodic Ag nanoparticles (Fig. 2e) exhibit a distinctive scattering feature. It is characterized by a strong scattering zone where scattering angles are increasing from 40° to 70° as the wavelength goes up from 400 nm to 700 nm. We also observe a similar scattering feature in Fig. 2f for the closely packed PS nanospheres. Treating the periodic nanoparticle arrays as line diffraction gratings for PS spheres with the line distance d and considering the refractive index $n = 1.5$ of the glass substrate, the zero-order diffraction angle α can be obtained by the equation [13]

$$d^* \sin\alpha = \lambda/n \quad (2)$$

where λ is the wavelength of incident light. The line distance d according to the shortest spacing is set to $1.15 \cdot R$, with R being the radius of a PS sphere, and taking

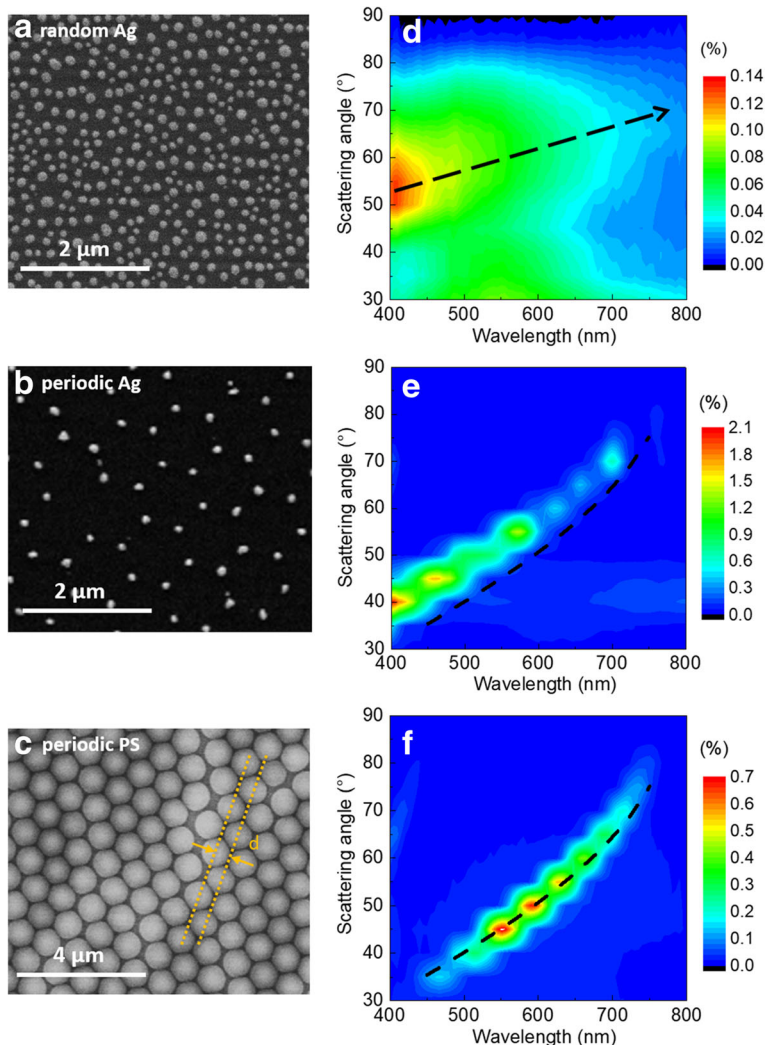


Fig. 2 Scanning electron microscopy (SEM) morphologies (left column) and wavelength dependent angular resolved scattering (ARS) behaviour (right column) of random (a,d) and periodic (b,e) Ag nanostructures and PS spheres (c,f)

into account a finite spacing between the spheres of the order of 15%.

The diffraction angle curve (dashed line) is plotted as a function of wavelength in both Fig. 2e and f. It can be discovered that the zero-order diffraction angle curve fits very well with the scattering feature for the closely packed PS spheres. This suggests that it is the diffraction which determines the strong scattering behaviour for the closely packed PS spheres. Remarkably, the periodic Ag nanoparticles follow the same trend of increasing scattering angles with wavelengths, but shifted to even larger scattering angles. This behaviour can be correlated to the large-angle scattering ability of plasmonic nanoparticles as shown in Fig. 3b, which is well known for

individual metal nanoparticles and less pronounced for dielectric ones [14].

Conclusions

In this work, we prepared random and periodic Ag nanoparticles as well as closely packed PS spheres and studied their scattering behaviour using angular resolved scattering measurements. The different scattering properties of the three nanoparticles are revealed, showing that random Ag nanoparticles have a broadband scattering ability with large scattering angles. In contrast, both periodic nanoparticle types are characterized by a strong scattering zone where scattering angles are increasing as the wavelength goes up. It

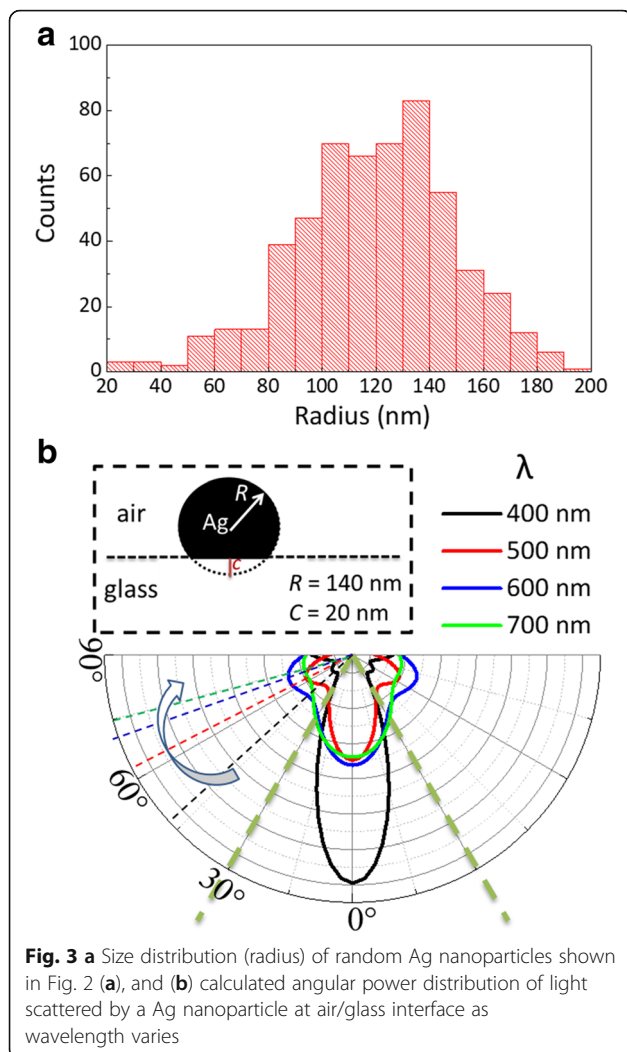


Fig. 3 **a** Size distribution (radius) of random Ag nanoparticles shown in Fig. 2 (a), and **(b)** calculated angular power distribution of light scattered by a Ag nanoparticle at air/glass interface as wavelength varies

can be explained by the zero-order diffraction for closely packed PS spheres. Overall, it is proved that angular resolved scattering measurements are a promising experimental characterization method to identify the scattering properties of nanoparticles and can support their selection for specific applications.

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Availability of data and materials

As given in the paper.

Authors' contributions

M. Schmid proposed the original idea, guided the research and contributed to the manuscript. G. Yin conducted the measurements, evaluated the data and wrote the main manuscript. M. Song prepared the nanostructures, P. Andrae designed and conducted initial measurements and W. Raja provided the simulation templates. All of the authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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