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Spectroscopic ellipsometry study of silver nanospheres and nanocubes in thin film layers

(Optical properties of heterogeneous thin films: silver nanoparticles in PVP
Optical study of silver nanocubes and nanospheres in a PVP thin film layers
Optical behavior of heterogeneous thin film layers including silver nanoparticle)

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Abstract:

Selective control of the optical properties of thin film layers is necessary in various domains such as photovoltaics and optoelectronics. Through localized surface plasmon resonance, silver nanoparticles exhibit selective optical properties in the visible wavelength range depending on their size and shape. The tremendous progress in nanoparticle synthesis methods, leads to easy fabrication of nanoparticles of various sizes and shapes. By embedding various nanoparticles in a thin film layer, the optical properties are engineered. Silver nanospheres and nanocubes are synthesized by a modified polyol process and randomly deposited in a non-absorbing polymer host matrix. Spectroscopic ellipsometry characterizations determine the complex optical indices of single shape nanoparticles, two shaped nanoparticles and multilayer configuration thin film layers. The spectroscopic ellipsometry data are fitted by a Cauchy law, accounting for the optical properties of the polymer host matrix, and one or several Gauss laws, accounting for the optical properties of the nanoparticles. The extinction coefficient of the blend and multilayer layers show a simple superposition of the extinction coefficients. Therefore, the nanoparticles do not interact in the thin film layers.

Recent progress in nanoparticle synthesis methods have lead to the ability of nanoparticle production of various sizes, shapes and materials.¹⁻⁴ Among them, noble metals are especially interesting for various applications in the field of optoelectronics, photovoltaics, thermal solar cells, color filters and color materials.⁵⁻⁷ This non-exhaustive list of applications results from noble metal nanoparticle size and shape dependent optical properties over the visible wavelength range, driven by localized surface plasmon resonances (LSPR).⁸

We propose randomly distributed silver nanospheres and nanocubes in a non-absorbing polymer thin film layer to control the light absorption in the visible spectrum. The polymer host matrix is chosen according to its chemical and physical properties: poly vinyl pyrrolidone (PVP) is a transparent and non-absorbing polymer.⁹ PVP is also used as a surfactant specially for silver nanocubes.^{10,11} A PVP host matrix is therefore a mild environment for silver nanoparticles. Silver nanocubes are obtained by polyol process through slight modifications from the synthesis published by Zhang et al.¹² Silver nanospheres are obtained by the same procedure by decreasing reaction time to 7 min, thus avoiding the nanocubes formation. Successive centrifugation steps remove the excess reactants and increase the nanoparticle density in the colloidal solution. Thin film layers are deposited by spin coating on glass and Si substrates. The nanospheres in PVP samples have a density of about 20 nanoparticles. μm^{-2} and the nanocubes in PVP have a density of about 375 nanoparticles. μm^{-2} .

The optical characterizations of the thin films include spectrophotometer measurements, performed by a UV-Vis-NIR Perkin Elmer lambda 950, and spectroscopic ellipsometry (SE) measurement. Spectroscopic ellipsometry is an indirect technique to determine the complex optical index.^{13,14} To fit the SE data, an optical dispersion model needs to be derived. This model contains several mathematical laws accounting for the optical properties of the probed thin film layer. The nanoparticles in polymer thin film layers are considered as a homogeneous material containing the properties of silver and the polymer, according to the Maxwell-Garnett effective medium approach. The fit is validated by checking the fit quality and its root mean square error (RMSE). The determined indices are then injected into a transfer matrix method (TMM) to calculate the reflectance and compare it with the reflectance measured by the spectrophotometer.¹⁵ A good overlap of the calculated reflectance and measured reflectance validates the physical meaning of the dispersion model and by extend the complex refractive indices.

In order to verify the hypothesis of addition of the optical properties of the various types of nanoparticles embedded in a thin film layer, the complex refractive index of nanospheres in PVP and nanocubes in PVP are compared to the complex refractive index of nanospheres and nanocubes mixed together in a thin film layer. The SE data are fitted in the Maxwell-Garnett effective medium approach considering a model consisting of silver and PVP.¹⁶⁻¹⁸ In other words, the obtained indices correspond to an effective medium having the optical properties of the nanoparticles and the polymer host matrix.

Silver nanospheres in PVP display a unique dipolar absorption peak at 420 nm. The dispersion model used to analyze for the nanospheres in PVP samples is a mathematical addition of a Cauchy law accounting for the non-absorbing polymer and a Lorentz or Gauss law, accounting for the absorbing property of the nanospheres. Several publications discuss spectroscopic ellipsometry measurements on noble metal nanoparticles on substrates and embedded various dielectric matrices.¹⁹⁻²⁵ The use of a Cauchy law for an inert host matrix is well accepted by the community, but there is an open discussion on the laws to be used to account for the optical properties of the nanoparticles. **Table 1** briefly list the laws used in these publications and their physical origin.

Sample	Laws	Meaning	Ref
Ag in PVA	1 Lorentz	1 Lorentz oscillator for main LSPR	¹⁹
35 nm Ag nanocubes	2 Lorentz	2 Lorentz oscillators for main LSPR	²⁰
Au nanospheres on gold substrate	2 Lorentz	1 Lorentz oscillator for main LSPR 1 Lorentz oscillator for background absorption	²²
Ag nanospheres in Al ₂ O ₃	2 Lorentz + 1 Drude		²¹
Ag nanospheres and nanorods on Si substrates	1 Lorentz + 1 Tauc Lorentz	1 Lorentz oscillator for main LSPR 1 Tauc-Lorentz for bulk silver	²³
Au islands on glass substrate	4 Gauss	1 Gauss oscillator for main LSPR 2 Gauss oscillators for interband transitions of gold 1 Gauss oscillator for inhomogeneous broadening of LSPR	²⁴
Ag islands on glass substrate	3 Gauss + 1 Tanguy	2 Gauss oscillators for main LSPR 1 Gauss oscillator for bulk plasmon resonance 1 Tanguy oscillator for interband transitions	²⁵

Table 1. Review of the laws accounting for the optical properties of noble metal nanoparticles.

The main trend is to model the LSPR absorption by a Lorentz law and add another law for the interband transitions. According to band structure calculations, the interband transition of silver occurs at 312 nm.²⁶ In order to determine which laws are suited for our samples, we compare the parameters and the results for the use of a Lorentz law and for the use of a Gauss law on the nanospheres in PVP sample. The thickness of the sample is measured to be 270 ± 5 nm. Both models are fitted for the measurement angles 72° , 73° , 74° and 75° to increase precision.¹³ The optical indices fitted by a Lorentz law and a Gauss law are shown on **Figure 1** (a) and (b) respectively. The Cauchy parameters are equal for both fits, only the parameters accounting for the optical properties of the nanoparticles change. As the nanospheres only display one dipolar absorbance peak, a unique law centered at the plasmonic resonance energy 2.91 eV is used. The fit quality of the Lorentz based model is 94.3% accuracy and a RMSE of 7.4 for the four angles. For the Gauss law the accuracy is 94.7% and the RMSE is equal to 6.7. Based on these fit results, the Gauss law should be used.

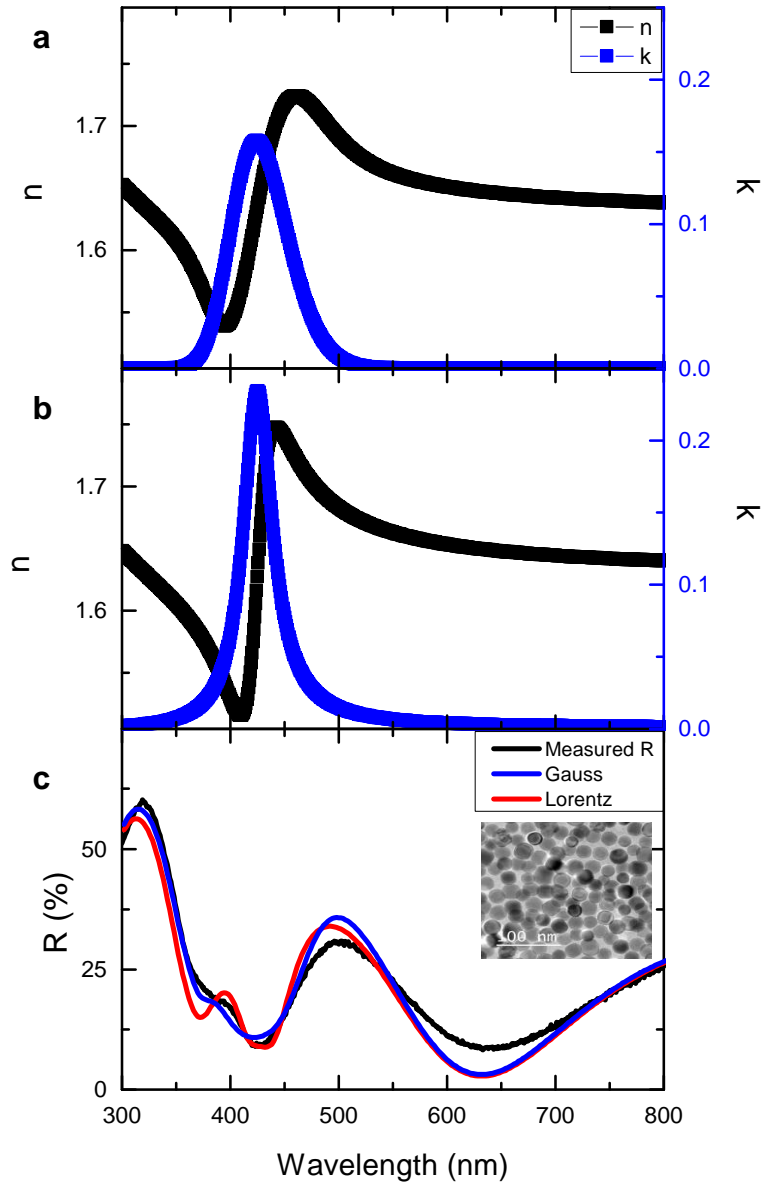


Figure 1: Complex optical indices for SE data fitted with (a) a Cauchy and a Gauss law and (b) a Cauchy and a Lorentz law. (c) Measured reflectance compared to calculated reflectance from (a) and (b) of silver nanospheres in PVP as depicted in insert.

A second validation of this result is obtained by comparing the reflectance calculated by TMM using both laws and the measured reflectance, **Figure 1** (c). The overlap is higher for the model using the Gauss law.

Therefore, the Gauss law is chosen to account best for the absorption properties of the embedded nanoparticles. The complex refractive indices n and k in **Figure 1** (b) are used in the following.

Arising from their more complex geometry, nanocubes present more than one plasmonic absorption peak. Complex geometries imply different charge distribution on the nanoparticle surface and sharp corners induce larger localized electric field enhancements.²⁷ Several Gauss laws will account for the different peaks. Let us note that SE only measures the specular reflected light. The determined indices are used to calculate the reflectance. This reflectance will be compared to the measured specular reflectance, i.e. the diffuse reflectance is subtracted from the total reflectance. It has to be kept in mind, that the different scattering peaks of the nanocubes are not included into the optical model.

The Gaussian oscillator centered at 2.67 eV (464 nm) corresponds to the main dipolar LSPR absorption peak. The origin of the oscillator centered at 3.54 eV (350 nm) is associated to the bulk plasmon resonance of silver.²³ This peak was not necessary for the nanospheres. As the nanocubes are present in a higher density, i.e. the extinction coefficient is higher for the nanocubes than for the nanospheres, this peak might have reached a non-negligible intensity. The oscillator centered at 3.2 eV is associated with the cubic shape of the nanoparticles.¹¹ **Figure 2** (a) displays the optical indices of the nanocubes in PVP. The quality of this optical model is optimized to 97.1 % and a RMSE of 4.8. The overlap of the calculated and measured R is good, **Figure 2** (b), but it has to be kept in mind, that the scattering is not taken into account.

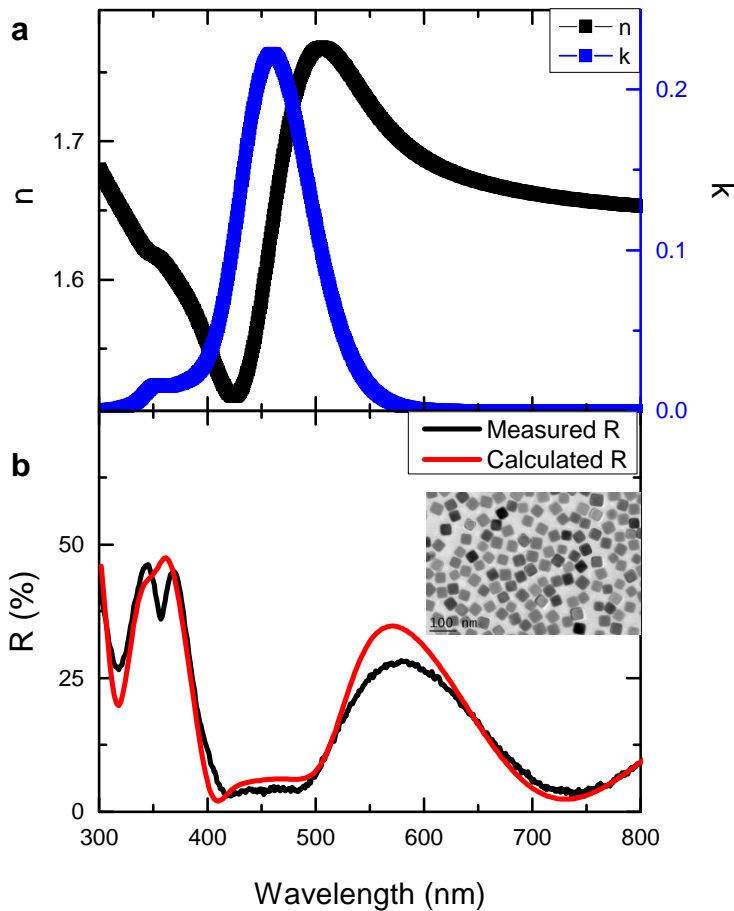


Figure 2: (a) Complex refractive index of nanocubes in PVP and (b) calculated and measured reflectance of the nanocubes shown in the insert in PVP on Si substrate.

Having characterized the silver nanospheres and silver nanocubes in PVP, both nanoparticles solutions are blended and embedded into a single layer of 284 ± 5 nm.

The fit quality using these laws equals 96.9 % and the RMSE equals 4.6 for four angles from 72° to 75° . **Figure 3** (a) displays the optical indices of the nanospheres and nanocubes in PVP. As the density of the nanoparticles in the layer changes the intensity of absorption, the determined extinction coefficients are normalized to 1 in order to be comparable. It is then obvious, that the extinction coefficient of the mixed nanospheres and nanocubes sample is a simple superposition of the extinction coefficient of the spheres and the cubes in PVP, **Figure 3** (b). It seems that there are no further absorption peaks arising from interparticle coupling or array effects are measured.

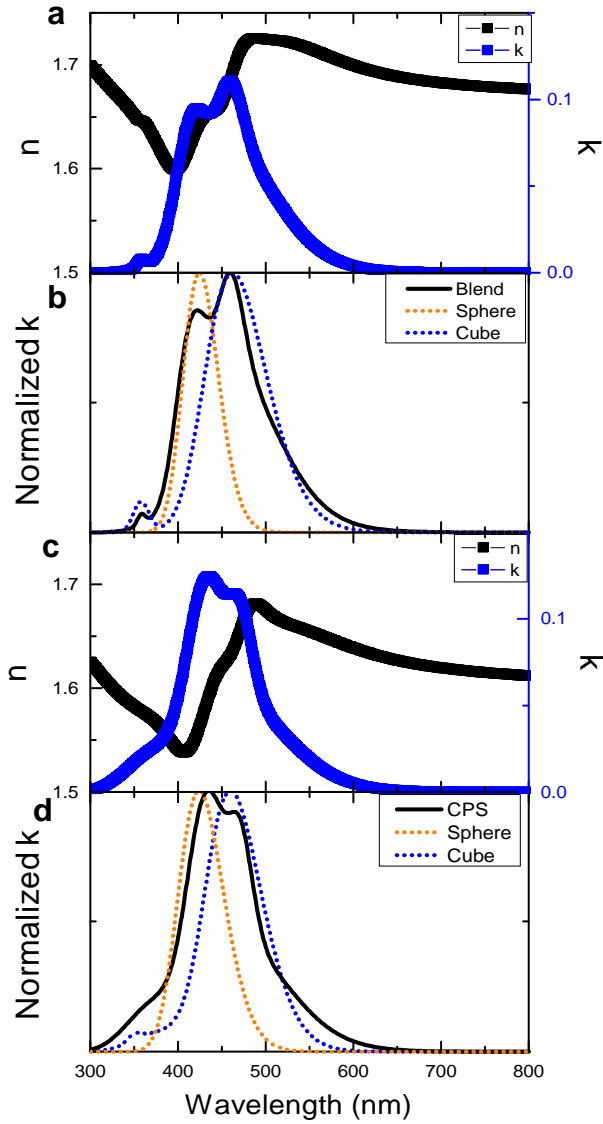


Figure 3: (a) Complex refractive index of nanospheres and nanocubes blend in PVP and (b) the normalized extinction coefficient compared to the one of nanospheres in PVP and nanocubes in PVP, (c) complex refractive index of of the nanocubes shown in the insert in PVP on Si substrate.

The nanoparticles are then deposited in a multilayer configuration. Nanocubes in PVP are deposited on the substrate in a first step, followed by the deposition of about 70 nm PMMA layer to protect the first layer from the nanospheres in PVP deposited in a third step. The optical analyses of the nanocube/PMMA/nanosphere (CPS) and nanosphere/PMMA/nanocube

stacks yield the same conclusion, therefore only the analysis of the CPS sample is reported here.

The SE measurement is performed on the complete stack, i.e. a single layer is sensed. The difference of indices in the different layers is not high enough to treat them separately and the thicknesses of each layer are rather difficult to measure as every deposition may dissolve and therefore decrease the thickness the underlying layer.

The complete layer has a thickness of 620 ± 5 nm and is fitted by one Cauchy law accounting for the PVP and PMMA layers and several Gauss laws accounting for the optical behavior of the nanospheres and the nanocubes. The optical indices are displayed on **Figure 3** (c). The fit quality is 92.7% and the RMSE is 7.21 for four angles from 72° to 75° .

For clarity, the normalized extinction coefficient is compared to the normalized extinction coefficients of nanospheres and nanocubes, **Figure 3** (d). The multilayer sample seems to result from a simple superposition of the extinction coefficients of both the nanospheres and nanocubes. As for the blend sample, the multilayer does not exhibit any coupling between the particles in the two layers.

In summary, the optical indices n and k of the PVP layer can be varied at wish by introducing differently shaped nanoparticles. The optical properties of the nanoparticles are simply added to the properties of the polymer layer and their deposition configuration does not induce any coupling phenomena.

In conclusion, SE measurements on silver nanospheres in PVP, silver nanocubes in PVP, silver nanospheres and nanocubes in PVP and a stack configuration of silver nanocubes, PMMA and silver nanospheres are performed. The dispersion model used to fit the data is composed of a Cauchy law and several Gauss oscillators. Gauss oscillators are found to fit the data better than Lorentz oscillators, as demonstrated on the nanospheres in PVP sample. Introducing the nanoparticles into the PVP layer, modifies the optical indices in a nanoparticle shape dependent way. When mixing nanospheres and nanocubes together into one layer, the comparison of the normalized extinction coefficients shows that there is a simple addition of each particle's optical contribution. Nevertheless, the SE does not evaluate the diffuse reflectance originating from the scattering of the nanocubes. Furthermore, the results are valid only for well dispersed nanoparticles in the thin film layer, as aggregates modify the optical properties of the thin film layers.

Further optical studies will be performed on nanoparticle aggregates.

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(a)

(b)

Figure 1. (a) TEM image of nanospheres and (b) TEM image of nanocubes.

Figure 2. Optical indices n and k by fitting with a Cauchy law and a (a) Lorentz law or a (c) Gauss law accounting for the absorption of the nanospheres, (c) comparison between calculated and measured specular reflectance.

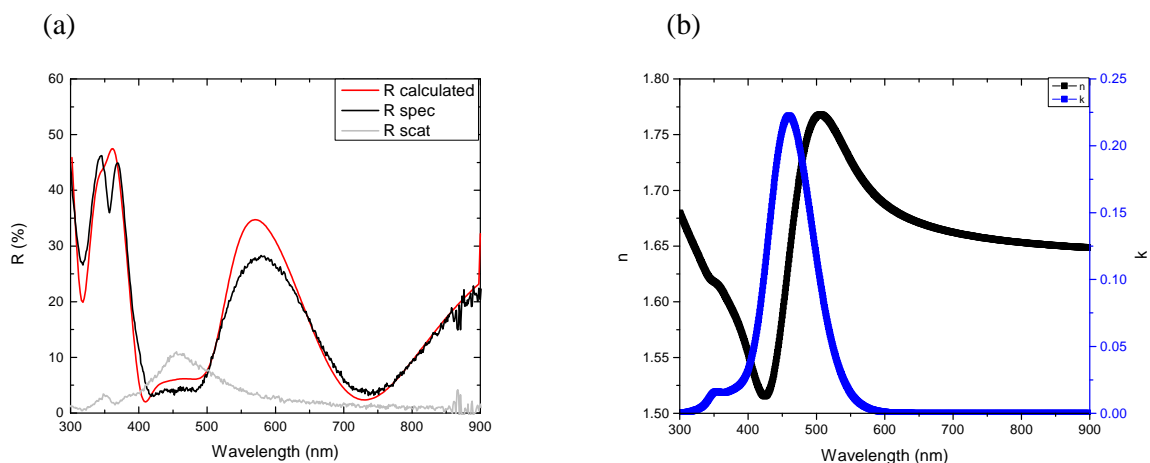


Figure 3. (a) Calculated and measured specular reflectance and the measured diffuse reflectance not taken into account into the spectroscopic ellipsometry data, (b) n and k indices of nanocubes in PVP.

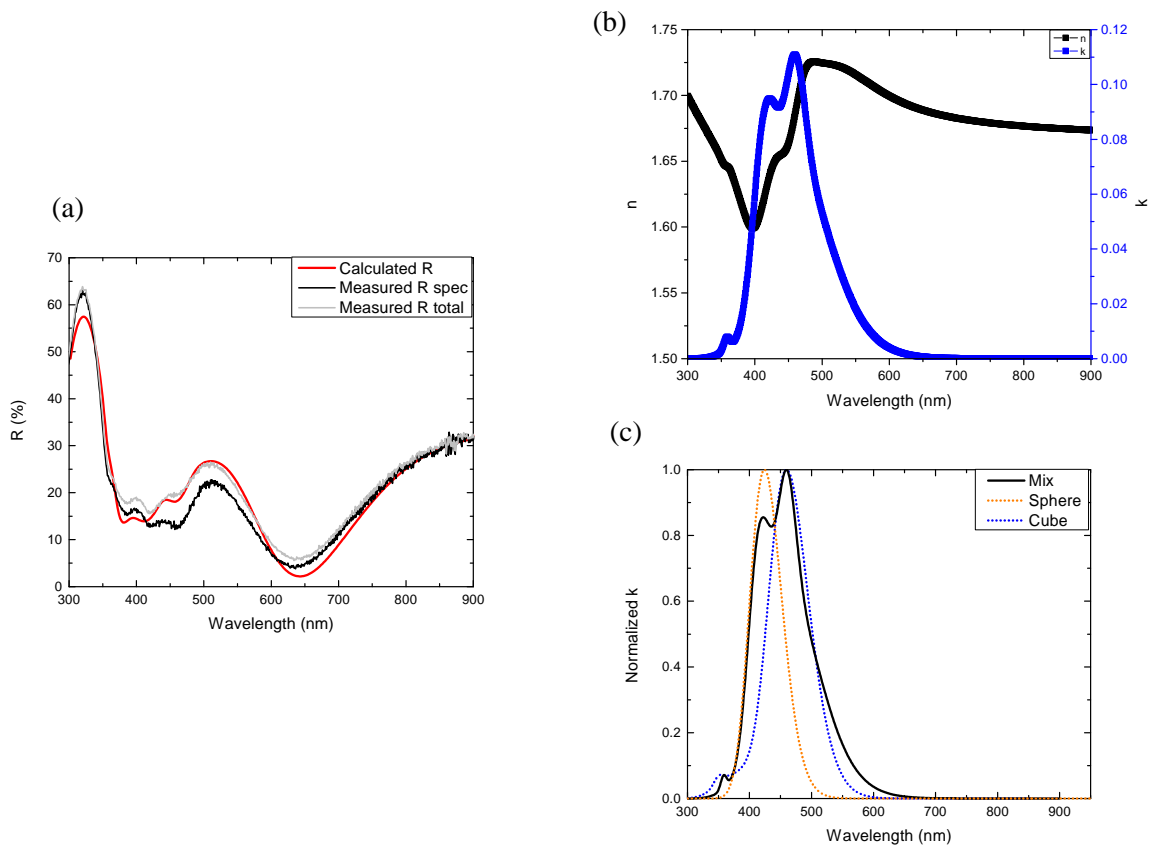


Figure 4. (a) Calculated and measured total and specular reflectance, (b) n and k indices of nanospheres and nanocubes in PVP and (c) normalized k of nanospheres, nanocubes and nanospheres and nanocubes in PVP.

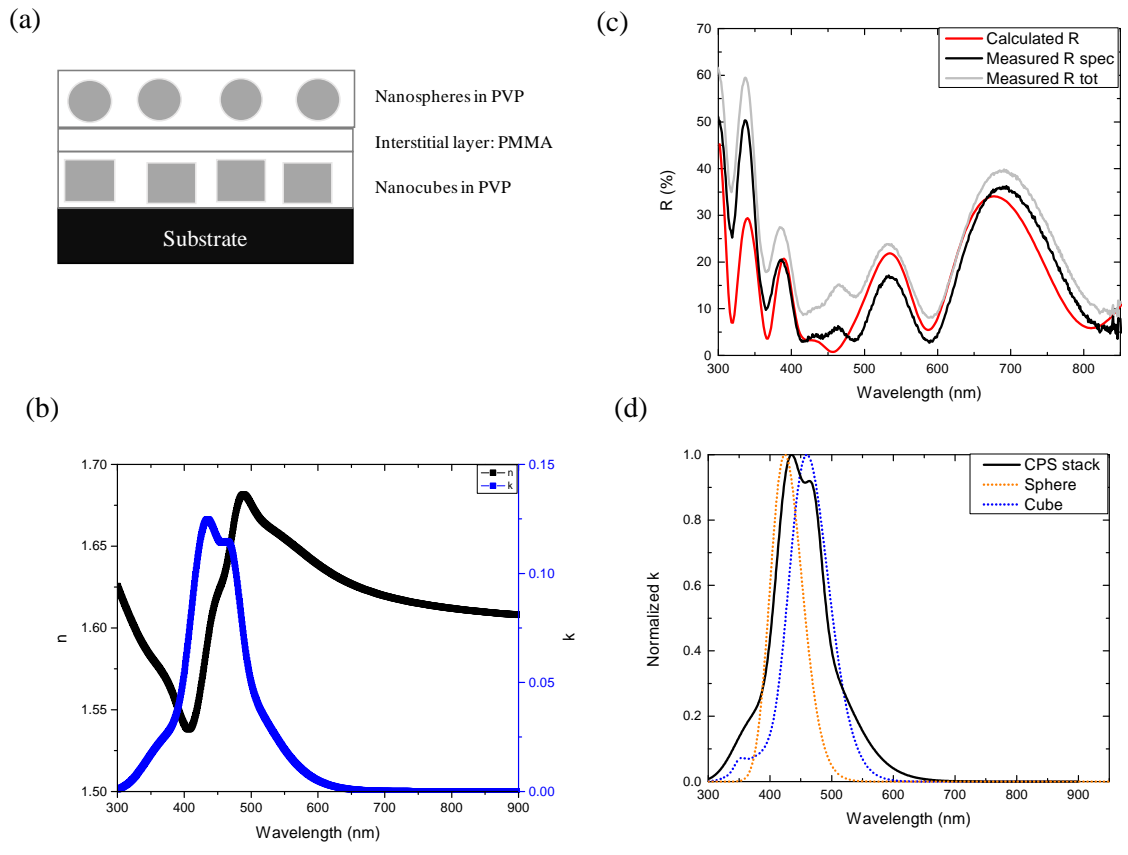


Figure 5. (a) Scheme of the multilayer sample, (b) measured refractive index and extinction coefficient, (c) measured and calculated reflectance, and (d) normalized extinction coefficients for comparison.

Table 2. Fit parameters for nanospheres in PVP by a model using Cauchy and Lorentz laws and a model using Cauchy and Gauss laws. The Lorentz law is centered at the resonance energy E_0 , has a broadening Γ and a force f . The Gauss law is centered at the resonance energy E_0 , has a broadening Br and an amplitude A .

Cauchy		Lorentz			
$n_\infty = 0$	$A = 0.037$	$f = 0.065$	$E_0 = 2.91 \text{ eV}$	$\Gamma = 0.32 \text{ eV}$	$\varepsilon_\infty = 2.60$
Cauchy		Gauss			
$n_\infty = 0$	$A = 0.037$	$A = 0.52$	$E_0 = 2.91 \text{ eV}$	$Br = 0.42 \text{ eV}$	$\varepsilon_\infty = 2.61$

Table 3. Fit parameters for nanocubes in PVP. Several Gauss laws account optical properties arising from the complex geometry.

Cauchy		Gauss			
$n_\infty = 0$	$A = 0.045$	$A = 0.072$	$E_0 = 2.67 \text{ eV}$	$Br = 0.43 \text{ eV}$	$\varepsilon_\infty = 2.64$
		$A = 0.025$	$E_0 = 3.54 \text{ eV}$	$Br = 0.19 \text{ eV}$	
		$A = 0.091$	$E_0 = 3.2 \text{ eV}$	$Br = 0.59 \text{ eV}$	

Table 4. Fit parameters for nanospheres and nanocubes in PVP.

Cauchy		Gauss			
$n_\infty = 0$	$A = 0.042$	$A = 0.22$	$E_0 = 2.64 \text{ eV}$	$Br = 0.57 \text{ eV}$	$\varepsilon_\infty = 2.72$
		$A = 0.13$	$E_0 = 2.69 \text{ eV}$	$Br = 0.19 \text{ eV}$	
		$A = 0.21$	$E_0 = 2.98 \text{ eV}$	$Br = 0.32 \text{ eV}$	
		$A = 0.016$	$E_0 = 3.2 \text{ eV}$	$Br = 0.59 \text{ eV}$	
		$A = 0.015$	$E_0 = 3.46 \text{ eV}$	$Br = 0.11 \text{ eV}$	

Table 5. Fit parameters for a nanocube in PVP/PMMA/nanosphere in PVP stack layer.

Cauchy		Gauss			
$n_\infty = 0.11$	$A = 0.033$	$A = 0.13$	$E_0 = 2.53 \text{ eV}$	$Br = 0.54 \text{ eV}$	$\varepsilon_\infty = 2.27$
		$A = 0.13$	$E_0 = 2.62 \text{ eV}$	$Br = 0.17 \text{ eV}$	
		$A = 0.29$	$E_0 = 2.86 \text{ eV}$	$Br = 0.36 \text{ eV}$	
		$A = 0.084$	$E_0 = 3.2 \text{ eV}$	$Br = 0.86 \text{ eV}$	