General Method for Determining Light Scattering and Absorption of Nanoparticle Composites

1. Introduction

Nanoparticles have unique optical properties, that can be exploited in a multitude of applications. Noble metal nanoparticles exhibit localized plasmon resonances, forming the basis for the rapidly expanding field of plasmonics. Plasmonic materials exhibit enhanced light absorption and scattering and large electric field enhancement at the resonances. They have attracted extensive attention for solar energy harvesting,[1] color displays,[2] optical antennas,[3] and biosensing.[4] Recently, dielectric nanostructures have also attracted considerable interest,[5] due to their strong electric and magnetic Mie resonances[6] and low absorption at optical frequencies.[7] Metal oxide nanoparticles show interesting optical as well as magnetic properties. Iron oxide can be used in diagnostic applications[8] and titanium oxide is a well-known white pigment with applications in photocatalysis[9] and dye-sensitized solar cells.[10]

Nanocomposites consisting of functional nanoparticles embedded into polymers are used in many applications, for example pigmented paints,[11] translucent sheets,[12] UV-absorbing films,[13] radiative cooling layers,[14] and dichroic materials.[15] In these cases, nanoparticles are stabilized by inclusion in a surrounding matrix material, forming a composite layer. When the nanoparticles are much smaller than the wavelength of incident light, the optical properties of such composites can be described by effective medium theory[16] and the effective optical constants of the composite layer can be obtained by inversion of experimental transmittance (T) and reflectance (R) measurements by the well-known methods of thin film optics.[17] However, when the particles are of the order of or larger than the wavelength of incident light, light scattering becomes significant. In this case, the description of the optical properties becomes complicated and the definition of the effective optical parameters of a composite layer is not straightforward. The simplest theoretical description of the optical properties of a plane-parallel layer of an absorbing and scattering medium is the two-flux theory.[18] The theory is formulated in terms of effective backscattering (S) and absorption (K) coefficients of the light-scattering material. However, the calculation of these parameters from optical measurements is problematic, because the angular dependence of the radiation...
field in the material as well as the surface reflection coefficients are often not well characterized.

Previous methods for obtaining scattering and absorption coefficients from \( R \) and \( T \) measurements have disadvantages. The two-background method\(^{[19]} \) depends on the accurate characterization of a white and a black reference material. Other approaches to the inverse problem are computationally complex and involve Monte-Carlo simulations\(^{[20]} \) and numerical solutions of the general radiative transfer equation.\(^{[21]} \) A simpler alternative is offered by inversion schemes using the two-flux theory\(^{[22]} \) but it has been found that the \( T \) and \( R \) values obtained from the solutions for \( S \) and \( K \) sometimes do not converge to the experimental data.\(^{[22a]} \) We have identified this deficiency as being due to an assumption of isotropic diffuse scattering in the composite layer, as shown below. An advantage of the Kubelka–Munk theory is that it can be formulated in matrix form\(^{[23]} \) and hence can be extended to multilayers in a straightforward way. This provides a possible route to determine the optical parameters of an unknown layer in an otherwise known multilayer stack.

In this article, we put forward a methodology for the determination of the Kubelka–Munk coefficients from experimental data, thereby correcting deficiencies in previous approaches. In addition to ordinary \( T \) and \( R \) measurements, we make use of angle-resolved scattering (ARS) measurements from the composite layer. Our method was validated by experiments on plasmonic Au, ferromagnetic Fe\(_3\)O\(_4\), and dielectric TiO\(_2\) nanospheres (NSs) with diameter around 200 nm and embedded in a polymer matrix. We also propose a simplified approach for determining \( S \) and \( K \) that can be used when angle-dependent information is not available.

### 2. Structural Characterization

The optical parameters of three types of light-scattering NSs with diameters of the order of visible wavelengths were investigated in this work. NSs of Au, Fe\(_3\)O\(_4\), and TiO\(_2\) with diameters of \( \approx 200 \) nm were prepared by a wet-chemistry bottom-up approach (see Experimental Section). The X-ray diffraction (XRD) patterns of the nanoparticle powders and the corresponding Joint Committee on Powder Diffraction Standards (JCPDS) cards show good agreement (Figure S1, Supporting Information) with data for cubic Au, orthorhombic Fe\(_3\)O\(_4\), and tetragonal anatase TiO\(_2\).

The particles were hosted in a weakly absorbing polymer matrix (Figure 1a), thus forming a nanocomposite layer. The size distributions of the three types of NSs, dispersed in water at a volume fraction of 0.1%, were obtained from scanning electron microscopy (SEM) images and show similar diameters around 200 nm (Figure 1b–g). The Au NSs have a smoother surface and a narrower size distribution as compared to the Fe\(_3\)O\(_4\) and TiO\(_2\) spheres. Dynamic light scattering revealed the hydrodynamic diameters of the three types of NSs in water (Figure S2, Supporting Information). Au and Fe\(_3\)O\(_4\) NSs were well dispersed; however, a lower degree of dispersion was obtained for the TiO\(_2\) NSs due to their high surface energy.\(^{[24]} \) Polyvinylpyrrolidone (PVP) was further added to the NS/water solution, and the volume fraction in the resultant water+PVP mixture was 0.066%. The scattering layer consisting of the NS–water+PVP mixture was placed between two glass slides separated by an \( \approx 80 \) \( \mu \)m.
thick epoxy spacer (Experimental Section). The transmittance and reflectance of a glass/(water+PVP)/glass sample without adding the nanoparticles is close to that of a single glass slide (Figure S3a–c, Supporting Information), as measured in an integrating sphere (Figure S3d, Supporting Information). Due to the similarity between the refractive index of the glass and the PVP, the reflection from the glass/(water+PVP) interface is negligible, and we can treat our sample as a slab where the nanoparticles are dispersed homogeneously. The absorption coefficient of the glass/(water+PVP)/glass sample (Figure S3e, Supporting Information and Experimental Section) shows that the matrix is optically transparent at wavelengths above 350 nm.

3. Results and Discussions

3.1. Spectrophotometric Transmittance and Reflectance Spectra

Total, regular/specular and diffuse transmittance and reflectance of the nanocomposite samples were measured in the wavelength range 300–1300 nm by a spectrophotometer equipped with an integrating sphere (Experimental Section). The regions of regular ($T_{\text{reg}}$) and diffuse ($T_{\text{diff}}$) transmittance and the specular ($R_{\text{spe}}$) and diffuse ($R_{\text{dif}}$) reflectance are set by the geometry of the integrating sphere (Figure S3d, Supporting Information and Experimental Section). Total transmittance ($T_{\text{tot}}$) is the sum of $T_{\text{reg}}$ and $T_{\text{diff}}$, while total reflectance ($R_{\text{tot}}$) is the sum of $R_{\text{spe}}$ and $R_{\text{dif}}$.

Transmittance and reflectance components were obtained after standard corrections for the sphere geometry and reflectance standard (Experimental Section), and the results are depicted in Figure 2. The specular reflectance is slightly above 4% for all samples and primarily originates from the reflectance of the front side of the glass. The minimum in the total and regular transmittance at a wavelength of 580 nm of the Au sample (Figure 2a) originates from the localized surface plasmon resonance, which is the collective oscillation of free electrons in metallic particles.[25] Magnetite, $\text{Fe}_3\text{O}_4$, is a conducting oxide with optical intraband absorption extending down to zero energy and no well-defined bandgap.[26] The absorption coefficient increases steeply above $\approx 1.5$ eV due to interband transitions,[26] which is in qualitative agreement with the drop in transmittance below a wavelength of 800 nm in Figure 2b. Anatase $\text{TiO}_2$ is an indirect semiconductor[9] with a bandgap of 3.39 eV for anatase films and 3.20 eV for bulk anatase.[27] In Figure 2c, a sharp drop of transmittance below 400 nm signifies the absorption onset.

3.2. Angle- and Wavelength-Resolved Light Scattering

To characterize the radiation field inside the sample, the angular distribution of scattered light from the sample must be investigated. Measurements by a 3D goniometer at a wavelength of 633 nm showed that (Figures S4 and S5, Supporting Information) light scattering depends only on polar/scattering angle and not on azimuthal angle. Hence, the intensity distribution outside the sample can be obtained from measurements by an in-plane angular and spectrally resolved spectrometer (Figure S6a, Supporting Information). Figure 3 shows the ARS intensity for wavelengths from 350 to 1000 nm as a function of the scattering angle $\beta_o$ in the forward and backward directions from 0° to 2° (Figure 3a–c), 2° to 90° in forward (Figure 3d–f) and backward (Figure 3g–i) directions for the three nanoparticle samples. The high reproducibility of the instrument is shown in Figure S6b in the Supporting Information. By integration of the intensity from the angle-resolved spectrometer
over the proper range of angles, we obtain the regular and diffuse transmittance as well as the specular and diffuse reflectance as a function of wavelength (Experimental Section). The results agree well with the direct measurement of these quantities from the Lambda 900 spectrophotometer (Figure S6c–e, Supporting Information).

In the small-angle region depicted in Figure 3a–c, the scattering intensity is mainly given by collimated incident light not absorbed or scattered by the nanoparticles. The minor portion of the scattered light at small angles can be estimated by extrapolation from scattering profiles at angles larger than 2°. In the large-angle region, Figure 3d–i, the scattered intensity in the transmittance and reflectance regions drops rapidly for angles up to 15°, and is an order of magnitude higher in the transmittance region than the reflectance region. The scattering behavior is angle- and wavelength-dependent in a complex and sample-dependent manner. The plots in Figure 3 can be converted to the scattering intensity as a function of wavelength at different angles, as well as forward-to-backward ratios (Figure S7, Supporting Information).

3.3. Phase Functions within the Scattering Layer

The scattering phase function is the angular distribution of light intensity scattered by the particles at a given wavelength. To obtain an effective phase function for the scattering layer, we use the inner intensity distribution close to the front and back surfaces. This is achieved by first converting the outside scattering angle $\beta_o$ into the angle $\beta_i$ of light incident on the interface from inside the layer, by Snell’s law (Experimental Section, inset in Figure 4a). We then relate the measured ARS$_o(\beta_o)$ (Figure 3) to the inner scattering distribution ARS$_i(\beta_i)$ by considering the interface reflection. The interface reflection coefficient, $r_i(\beta_i)$, for light coming from the inside of the film is obtained from the Fresnel relations (Experimental Section). Subsequently, we transform the ARS$_i(\beta_i)$ in forward and backward directions into the bidirectional scattering distribution function (BSDF)$^{[28]} f(\theta)$, where $\theta$ is the polar angle.

Figure 4a shows a typical example of converting the observed outer forward ARS$_o(\beta_o)$ and backward ARS$_o(\beta_o)$
intensities into $\text{ARS}_{\text{f,b}}(\beta)$ for the Au sample at a wavelength of 600 nm. The conversion was carried out for angles $>1.3^\circ$ inside the film, equivalent to the diffuse region at $>2^\circ$ outside the film, up to the critical angle of total internal reflection (Experimental Section). Evidently, the values derived from the ARS measurement are only a part of the phase function and an empirical fit is needed to fill the gap at intermediate polar angles. We use a revised Reynolds–McCormick\cite{29} phase function (denoted rRM, Experimental Section), which can simultaneously fit peaked scattering intensities in forward and backward directions. The critical angle varies with wavelength (Figure S8a,b, Supporting Information), but we restrict the fit to be from $1.3^\circ$ to $39^\circ$ because of lower measurement accuracy at outer angles close to $90^\circ$, together with errors due to scattered light from the sample edge. A good agreement between the experimental forward and backward branches of $f_{\text{f,b}}(\theta)$ (orange and cyan lines) to the fitted rRM (dashed green curve) can be seen in Figure 4b–d at 600 nm. The final phase function inside the scattering layer was obtained by combining the experimental forward and backward portions (orange and cyan) with the rRM fitting curve (solid green).

### 3.4. Determination of Backscattering and Absorption Coefficients

The Kubelka–Munk model\cite{18} is formulated in terms of two differential equations for radiation fluxes moving in the forward and backward directions in a material (Experimental Section). It was originally derived for the case of completely diffuse radiation fluxes, but can be reformulated in terms of total fluxes in order to be applied to situations where the sample exhibits partly diffuse transmittance and reflectance.\cite{22b} The solutions of the coupled differential equations together with the boundary conditions at the interfaces of the material, give analytic expressions for the total transmittance and reflectance.\cite{22b} The Kubelka–Munk model is used to determine the backscattering and absorption coefficients $S$ and $K$ of the light scattering material as well as the interface reflectances $R_c$ (the collimated reflectance of the incident light at the front interface of the slab), $R_i$ (the internal reflectance at the front interface), and $R_g$ (the internal reflectance at the back interface). In order to invert the equations for $R$ and $T$ to determine $S$ and $K$, knowledge of the interface reflectance parameters is necessary. It is straightforward to obtain $R_c$ from measurements of regular
transmittance and specular reflectance (Figure S8c, Supporting Information and Experimental Section) and here we use data for the glass/(water+PVP)/glass sample. However, the internal reflectances $R_g$ and $R_j$ of the nanocomposite layer present greater challenges, and methods to estimate them are essential to obtain $S$ and $K$. The reflectances can be computed from the angular distribution of light scattering at the interfaces. First, the internal diffuse reflectances at the back and front interface $R_{df,db}$ are calculated by averaging the effective phase function $f_{t,r}(\beta_i)$, multiplied with the interface reflection coefficient $r(\beta_i)$, over the angles $(0^\circ, 90^\circ)$ (Experimental Section). However, the total interface reflectances $R_{g,j}$ also involve contributions from collimated light; the respective collimated and diffuse fractions can be calculated from experimental reflectance and transmittance measurements (Experimental Section).

Previous methods$^{[22a,b]}$ assumed isotropic diffuse fluxes propagating in both directions in order to derive $R_g$ and $R_j$, and thereafter obtaining $S$ and $K$. However, in certain cases, the inversion procedure failed to converge, i.e., the computed $T$ and $R$ could not reproduce the experimental values.$^{[22a]}$ This discrepancy was most serious in wavelength ranges where the computed backscattering coefficient $S$ reached values close to zero. We tested this method on the three nanoparticle composites (the method is denoted $\text{dif}$; Experimental Section). Residual spectra verify that $R$ and $T$ calculated from $S$ and $K$ did not converge to the experimental total transmittance and reflectance (Figure S9a–f, Supporting Information). Another possibility would be to calculate the phase function from Mie theory for spherical particles with the measured size distribution and use it to derive $R_g$ and $R_j$ (Mie method; Experimental Section). However, discrepancies between the calculated and experimental $R$ and $T$ were also observed (Figure S9a–f, Supporting Information). This shows that an inversion routine based on the Mie phase function does not work well in many cases.

In our work, we calculated the scattering phase function from ARS, as described above. From these measurements and the fit to the rRM phase function, we first computed $R_{df,db}$ and the diffuse light fractions (Figure S10, Supporting Information and Experimental Section). Wavelength-dependent $R_g$ and $R_j$ derived from this ARS method are shown in Figure 5a–c for

![Figure 5](https://www.advancedsciencenews.com/...)

Figure 5. Backscattering and absorption coefficients derived from back and front interface reflectances. a–c) Back interface reflectance $R_g$ and front interface reflectance $R_j$ (inset) calculated by the ARS, cri, and cri/dif methods for Au, Fe$_3$O$_4$, and TiO$_2$ samples. d–f) Backscattering coefficient $S$ derived from $R_g$, $R_j$ by ARS, cri, and cri/dif methods. g–i) Absorption coefficient $K$ derived from $R_g$, $R_j$ by ARS, cri, and cri/dif methods.
our samples. A higher $R_\text{f}$ than $R_\text{g}$ shows that the backscattering fluxes are more isotropic than the forward ones. Now $S$ and $K$ can be obtained numerically and the results are given in Figure 5d–f ($S$) and Figure 5g–i ($K$) (Experimental Section). A very good convergence has been achieved (Figure S9g–i, Supporting Information) for the ARS method. By comparing with the phase function patterns used in the ARS method, we can readily understand the failure of the dif method. It assumes isotropic diffuse scattering in forward and backward directions. However, in our cases the scattering patterns are anisotropic, exhibiting strong increases toward small forward and backward angles.

We have also used the ARS method as a benchmark to devise approximations for cases when experimental ARS data are not available. In the cri method, we assume that the forward/backward scattering angles are restricted to those below the critical angle $\theta_c$. This approximation should be valid for forward/backward peaked scattering patterns, like the ones in Figure 4. In the cri/dif method, we define the forward scattering to be confined to angles below $\theta_c$, while the backward scattering is assumed to be isotropic (Experimental Section). Both the cri and cri/dif methods show good convergence for our samples (Figure S9g–i, Supporting Information). A comparison of $S$ and $K$ calculated by the cri, cri/dif, and ARS methods (Figure 5d–i) shows that $K$ is quite insensitive to the details of the model used to derive it. However, $S$ derived by the cri method is much closer to the exact value from the ARS method, than the cri/dif result. It is seen that $R_\text{f}$ derived from the ARS method is between 0.05 and 0.25, indicating a weaker forward peaked scattering pattern than assumed in the cri and cri/dif methods. On the other hand, $R_\text{g}$ from the ARS method is always between the values obtained from the cri and cri/dif methods, which indicates that the real backscattering pattern is somewhere between these assumptions.

4. Conclusion

In this work, we have combined spectrophotometry and ARS measurements in order to establish a method to thoroughly characterize the optical parameters of light-scattering materials, in particular nanoparticle composites. We study the integrated reflectance and transmittance as well as the angular and spectral light scattering for Au, Fe$_3$O$_4$, and TiO$_2$ nanoparticles dispersed in a polymer matrix. The light-scattering pattern was represented by an effective phase function as a function of wavelength, and it was accurately fitted with the rRM expression. By using a generalized Kubelka–Munk two-flux model, backscattering and absorption coefficients ($S$, $K$) were determined from reflectance, $R$, transmittance, $T$, and angle resolved scattering measurements. The inversion procedure from experimental $R$ and $T$ to the material parameters $S$ and $K$ is far from trivial, and earlier approaches did often not converge in part of the wavelength range. These problems are solved when we employ resolved scattering measurements in addition to the experimentally determined $R$ and $T$ to obtain the light scattering parameters. However, in many practical cases, data from ARS measurements may not be available. We found that results from the approximate cri method were very close to those of the ARS method. In this method, it is assumed that the light-scattering pattern is uniform for angles up to the critical angle of total internal reflection, and that no light scattering takes place at larger angles. This approximation should be useful at least for samples containing particles of the order of or larger than the wavelength of light, where strongly forward peaked scattering patterns would be expected. Our approach establishes a scheme for the optical characterization of coatings containing light-scattering particles, which is not restricted by particle size, shape, or state of aggregation. We expect that our method will be highly useful in the fields of optical coatings, displays, solar cells, metamaterials, biological materials, and tissues as well as others.

5. Experimental Section

Material Synthesis and Characterization: All chemicals were purchased from Sigma-Aldrich, Merck, or VWR, and used as received. The three NS samples were prepared using a bottom-up wet chemistry method, which allowed for good control of the shapes and sizes of nanostructures. Au NSs were obtained by a seed-mediated growth together with mild oxidation, starting from small Au NSs, growing to nanopolyhedra, and reshaping to $\approx$200 nm diameter Au NSs by etching the edges.[20] In a typical synthesis of Fe$_3$O$_4$ NSs, FeCl$_3$·6H$_2$O (0.1 g), PVP (MW: 40,000, 4 g), sodium acetate trihydrate (NaAc·3H$_2$O, 0.3 g), and 1 mL of polyethylene glycol (PEG, MW: 300) were dissolved in ethylene glycol (20 mL) under stirring and ultrasonic treatment. The homogeneous yellow mixture was then transferred to a Teflon-lined stainless steel autoclave which was sealed and heated to 200 °C for 4 h. The Fe$_3$O$_4$ NSs were formed and collected by a magnet, washed with distilled water (50 mL), and collected by centrifugation at 1700 rpm for 20 min. The washing and centrifugation processes were repeated 5 times. The Fe$_3$O$_4$ NSs were eventually collected by drying overnight at 80 °C. The TiO$_2$ NSs were synthesized using a similar procedure previously described by Han et al.[21] with minor modifications. Briefly, CaCl$_2$ solution (0.05 M, 200 mL) was added to methanol (50 mL) into an one-necked flask and stirred for 10 min. Then of titanium (IV) isopropoxide (850 μL) was added dropwise. The resulting solution was magnetically stirred for 24 h at room temperature. The synthesized TiO$_2$ NSs were subsequently washed with distilled water (50 mL) and collected by centrifugation at 1700 rpm for 20 min. The washing and centrifugation processes were repeated 5 times. The TiO$_2$ NSs were obtained by calcination at 450 °C for 2 h with a ramp rate of 5 °C min$^{-1}$.

The Au, Fe$_3$O$_4$, and TiO$_2$ NSs were added to water at a concentration of 19.3, 5, and 4 mg mL$^{-1}$, corresponding to 0.1% in volume fraction, equivalent to a particle concentration of 2.39 × 10$^{11}$ mL$^{-1}$. Then PVP solution was added into the NS/water solution at a mass ratio of 0.8 (PVP/water). PVP has high viscosity and good binding capability with water. It dissolves at room temperature and is highly stable and nontoxic. The NS/water/PVP solution was vigorously shaken in a vortex mixer until the PVP powders dissolved completely. The viscous solution was deposited on a glass slide, and then another glass side with a spacer $\approx$80 μm in thickness was added on top. The as-made particle-incorporated sample was sealed with glue and measurements took place when the sample was stable.

SEM imaging was performed on a Zeiss (LEO) 1530 FEG microscope at an acceleration voltage of 5 keV. The XRD patterns were measured by a SIEMENS D5000 diffractometer with Cu K$\alpha$ ($\lambda = 1.54 \AA$) radiation at a scanning speed of 0.1° s$^{-1}$. The hydrodynamic size of the NSs at a concentration of 20 μg mL$^{-1}$ in water was determined by a Zetasizer Nano ZSP.

Optical Characterization: The total and diffuse transmittance and reflectance spectra were measured in the wavelength range 300–1300 nm using a commercial Perkin-Elmer Lambda 900 UV–vis–NIR spectrophotometer equipped with a 150 mm Spectralon-coated integrating sphere. Total transmittance ($T_{\text{tot}}$) is the sum of
regular transmittance \((T_{\text{reg}})\) and diffuse transmittance \((T_{\text{dif}})\), while total reflectance \((R_{\text{tot}})\) is the sum of specular reflectance \((R_{\text{spec}})\) and diffuse reflectance \((R_{\text{dif}})\). Hence, the regular transmittance and specular reflectance were derived by subtracting the diffuse component from the total transmittance or reflectance. The regular transmittance was defined as the directly transmitted light within an angle of \(+/- 4.6^\circ\) from the normal and the specular reflectance is the directly reflected light within \(+/- 7.4^\circ\), owing to the geometry of the integrating sphere. Scattered light at angles larger than \(4.6^\circ\) in transmittance and \(7.4^\circ\) in reflectance is denoted diffuse transmittance \((T_{\text{dif}})\) and diffuse reflectance \((R_{\text{dif}})\). The reflectance and transmittance were measured relative to a Spectralon \((R_{\text{spec}}})\). To obtain the total, regular, specular and diffuse transmittance \((T_{\text{reg}}, T_{\text{tot}}, R_{\text{spec}}, R_{\text{dif}})\), the measured total, regular, and diffuse transmittance signals \((S_{\text{tot}}, S_{\text{reg}}; S_{\text{dif}})\) and reflectance signals \((U_{\text{tot}}, U_{\text{spec}}, U_{\text{dif}})\) were corrected according to the relations below.

\[
T_{\text{reg}} = S_{\text{tot}} - S_{\text{dif}}
\]

\[
T_{\text{dif}} = S_{\text{dif}} \times R_{\text{spec}}
\]

\[
T_{\text{tot}} = T_{\text{reg}} + T_{\text{dif}}
\]

\[
R_{\text{spec}} = (U_{\text{tot}} - U_{\text{dif}}) \times 0.96
\]

\[
R_{\text{dif}} = U_{\text{tot}} \times R_{\text{spec}}
\]

\[
R_{\text{tot}} = R_{\text{spec}} + R_{\text{dif}}
\]

The factor 0.96 is a correction for the difference between the reflectance of the reference plate and the coating on the integrating sphere, as well as for geometrical factors. The port angle for the regular transmittance was \(+/- 4.6^\circ\) and it was \(+/- 7.4^\circ\) for specular reflectance; light scattered at angles larger than these contributed to the diffuse transmittance and reflectance. In the reflectance mode, the measurements were performed at an incident angle of \(8^\circ\). A photomultiplier was used in the UV–vis range and a lead sulfide (PbS) detector was used in the near infrared (NIR) range. The detector change occurred at 900 nm. The scan speed was 250 nm min\(^{-1}\), using a slit width of 3 nm in VIS and 2 nm in NIR region.

The “in-plane” angular and spectrally resolved spectrometer \((1,2)\) consisted of a tungsten–halogen lamp, a monochromator, two gratings, a parabolic aluminum mirror, and a silicon diode detector with a port dimension of 6.4 \(\times\) 6.4 mm\(^2\). The lock-in technique was used to record the signal from the detector. The sample was centrally mounted and illuminated, and the silicon detector could be positioned at various angles from \(0^\circ\) to \(180^\circ\). To increase the dynamic range of the measurement, different neutral density filters \((\text{Thorlabs})\) were applied for measurements at different wavelengths. A 50% filter was used for 350 nm, a 1% filter was used for 400 nm, a 0.01% filter used for 600 nm, and a 0.007% filter was used for 800 nm. The incident light spot was much smaller than the port of the Si detector. The incident light intensity \(P_{\text{i}}\) was calculated using the measured intensity with the filter \(f_{\text{filter}}\) divided by the filter transmittance at the specific wavelength. The light spot spanned an angle within \(+/- 1^\circ\). The transmittance and reflectance were measured as a function of angle with fixed wavelength. An angle of \(10^\circ\) of the sample normal to the incident light was used for reflectance measurements, to be able to measure the specular and near-specular reflected intensity; subsequently, the data were shifted by Harvey’s method.\(^{(3,4)}\) The measured radiant intensity was represented in the form of ARS, by normalizing with the incident light intensity \(P_{\text{i}}\) and the solid angle \(\Omega\) of the detector\(^{(5,6)}\).

\[
\text{ARS}(\beta) = \frac{S(\beta)}{R \times \Omega} = \frac{S(\beta)}{S(0) \times \frac{A}{R^2}}
\]

where \(S(\beta)\) is the measured radiant intensity of the sample. In the small-angle region, i.e., smaller than \(2^\circ\), the measurements were conducted together with a filter and thereby the intensity was divided by the filter transmittance. \(S(0^\circ)\) is the measured intensity of the incident light with filter and without sample. \(T_{\text{filter}}\) is the transmittance of the filter at the desired wavelength, \(A\) is the surface area of the detector port, \(R\) is the distance from the sample to the detector, i.e., 20 cm. The solid angle \(\Omega\) was equal to \(6.4^2/200^2 = 0.001024\) sr\(^{-1}\).

The ARS \((\beta)\) can be integrated over angle to obtain \(T_{\text{reg}}, T_{\text{spec}}, R_{\text{spec}}, R_{\text{dif}}\) in order to compare those with measurements from the Lambda 900 spectrophotometer\(^{(2,6)}\).

\[
T_{\text{dif}} = \int_{0}^{\beta} 2\pi\text{ARS}(\beta)\sin(\beta)d\beta
\]

\[
R_{\text{spec}} = R(0^\circ) + \frac{1}{2} \pi\text{ARS}(\beta)\sin(\beta)d\beta + \int_{0}^{\beta} 2\pi\text{ARS}(\beta)\sin(\beta)d\beta
\]

\[
R_{\text{tot}} = R(0^\circ) + \frac{1}{2} \pi\text{ARS}(\beta)\sin(\beta)d\beta + \int_{0}^{\beta} 2\pi\text{ARS}(\beta)\sin(\beta)d\beta
\]

where \(\beta\) was \(4.6^\circ\) for transmittance and \(7.4^\circ\) for reflectance. \(T(0^\circ)\) and \(R(0^\circ)\) were the measured transmittance and reflectance at \(0^\circ\), that was the ratio of intensity with the sample and without sample at \(0^\circ\).

In order to obtain an estimate of small-angle diffuse scattering between \(0^\circ\) and \(2^\circ\), ARS \((\beta)\) was extrapolated from the measured data at angles larger than \(2^\circ\). The main contributions to \(T_{\text{reg}}\) and \(R_{\text{spec}}\) came from \(T(0^\circ)\) and \(R(0^\circ)\).

The “out-of-plane” spatial scattering intensity distribution was measured using a home-built goniometer\(^{(1,2)}\). The light source was a red HeNe laser (wavelength \(\lambda = 633\) nm). The position-controlled detector was mounted on a movable arm, thereby allowing the detector to move in a hemisphere. The radius of the semicircular arc was 45 cm. The sample was fixed at the center of the arc, and was free to rotate around a horizontal axis, to vary the angle of incidence. The sample holder, the detector, and the arc were controlled by stepping motors. The lock-in technique was used to monitor the signal from the detector. A relatively small spot was illuminated on the sample and the amount of light scattered into a known solid angle (under-illumination method) was measured\(^{(3,4)}\). The detector was a silicon diode with a spectral response region from \(300\) to \(1100\) nm with port dimension \(2.5 \times 2.4\) mm\(^2\). The incident light intensity was measured using a neutral density filter with a transmittance of \(0.000482\) at 633 nm. The shortest steps corresponded to an angle shift of \(0.0015^\circ\). In the transmittance mode, the incident light was parallel to the normal of the sample surface. In the reflectance mode, the incident light was incident at \(10^\circ\) to the sample normal, the same as in the in-plane scattering measurement. The position of the sample to the incident light was fixed, a half hemisphere was measured both in transmittance and reflectance regions and then we mirrored the intensity distributions to the other half hemisphere. The data analysis was similar to the in-plane spectrometer; the intensity was divided by the incident light intensity \(P_{\text{i}}\) and the solid angle \(\Omega\) of the detector port. The arm moved from \(-90^\circ\) to \(90^\circ\) while the detector moved in the range from \(-68^\circ\) to \(68^\circ\) on the arm due to the geometry of the instrument.

Phase Function within the Scattering Layer: The inner intensity distribution within the slab was derived by converting the measured outside scattering angle \(\beta_i\) into the angle \(\beta_o\) of light incident on the interface from the inside, by Snell’s law,

\[
\beta = \arcsin \left( \frac{\sin(\beta_i)}{n_i} \right)
\]

Here, \(n_i\) is the refractive index of the outer medium, in this case air, and \(n_o\) is the refractive index of the polymer matrix inside the scattering layer. We use the refractive index \(n_i\) from glass/(water+/PVP)/glass.
determined from the obtained front surface reflectance, $R_f$, (Figure S8c,d, Supporting Information). The measured ARS($\beta$) (Figure 4) was then related to the inner scattering distribution ARS$^\alpha$($\beta$), using the reflection coefficient, $r(\beta)$, at the interface, for light coming from the inside of the film:

$$ARS(\beta) = \frac{ARS^\alpha(\beta)}{1 - r(\beta)}$$

(13)

The surface reflection coefficient of light coming from inside the film $r(\beta)$ was obtained from the Fresnel equations for unpolarized light incident from an angle $\beta$ = $\beta_0$ on the interface from the light scattering layer to air:[30]

$$r(\beta) = \frac{2}{n_{air}} \left[ \frac{\cos(\beta) - n_{air}}{\cos(\beta) + n_{air}} \right]$$

(14)

Here $r_0(\beta)$ and $r_p(\beta)$ represent reflectance for s-polarized and p-polarized light, $n$ is the refractive index of the sample and $n_{air}$ is the refractive index of air, equal to unity. The diffuse reflectance $R_{df,db}$ reached 0.6 when scattering was Lambertian.

Subsequently, the ARS was transformed into the BSDF, denoted $f_{\alpha}$, where the subscripts $t$, $r$ represent the transmittance (forward) and reflectance (backward) regions of the scattering fluxes:

$$f_{\alpha}(\beta) = \frac{ARS^\alpha(\beta)}{cos(\beta)}$$

(15)

**Determination of Optical Constants:** The reflectance at the air/glass interface $R_c$, the imaginary part of extinction coefficient $k$, and refractive index $n$ can be determined as follows:[30]

$$R_c = \frac{(T_{out}^2) - (R_{spe} - 1)^2}{2(R_{spe} - 1)} - \frac{(T_{out}^2) - (R_{spe} - 1)^2}{2(R_{spe} - 1)}$$

(16)

$$k = -\frac{\lambda}{4n} \ln \left( \frac{R_{spe} - R_c}{R_{spe} R_c} \right)$$

(17)

$$n = \frac{1 + R_c}{1 - R_c} \left[ 1 + \sqrt{1 - R_c^2 \left( 1 + k^2 \right)} \right]$$

(18)

The absorption coefficient of the matrix was assumed to be equal to the extinction coefficient $k$ of the glass/(water+PVP)/glass sample as no scattering occurred. The critical angle $\theta_c$ was determined from the refractive index $n$ of a single glass slide:

$$\theta_c = \arcsin \left( \frac{n_{air}}{n} \right) = \arcsin \left( \frac{1}{n} \right)$$

(19)

The same equations are applicable to the collimated components of light in scattering samples, although the extinction coefficient in this case is equal to the sum of absorption and scattering coefficients.

**Fitting Forward and Backward Scattering Spectra with the rRM Approach:** The inner forward and backward scattering intensities as functions of the scattering angle $f_{\alpha}(\beta)$ were fitted to an empirical phase function. An expression was developed starting from the Reymonds–McCormick (RM) approximation:[30]

$$\rho_{F\alpha RM}(\theta, \alpha, g) = \frac{a g (1 - g^2) \alpha}{\alpha [1 + g^2 - 2g \cos(\theta)]^{\alpha/2} \left[ (1 + g) \alpha^2 - (1 - g) \alpha^2 \right]}$$

(20)

where the polar angle $\theta$ ranged from $0^\circ$ to $180^\circ$, $g$ is the asymmetry factor which ranged from 0 to ±1 and $\alpha$ is a fitting parameter.

The experimental forward and backward branches were fitted to a rRM approximation, which was analogous to the previously used two-term Heney–Greenstein approximation:

$$\rho_{F\alpha RM}(\theta, \alpha, g) = f \rho_{E\alpha RM}(\theta, g) + (1 - f) \rho_{F\alpha RM}(\theta, g)$$

(21)

where $f$ and $g$ are new fitting parameters introduced to describe the amplitude of the two terms.

**Kubelka–Munk Theory for the Reflectance and Transmittance of a Slab of Material:** The Kubelka–Munk model was formulated in terms of two differential equations for radiation fluxes moving in the forward and backward direction in a slab of material. The total intensity in the forward $I$ and backward $J$ directions were coupled according to the differential equations:

$$\frac{dI}{dz} = -(S + K)I + S\alpha$$

(22)

$$\frac{dJ}{dz} = (S + K)J - SJ$$

(23)

The solutions for the transmittance and reflectance for a case of a slab with backside internal reflectance $R_d$ were given by:

$$R_{KM} = \frac{1 - R_d}{a - R_d + b \cosh(bSd)}$$

(24)

and

$$T_{KM} = \frac{b(1 - R_d)}{a - R_d + b \cosh(bSd)}$$

(25)

where $a$ is equal to $(1 + K/S)$ and $b$ is equal to $(a^2 - 1)^{0.5}$. Taking into account multiple reflections in the slab and reflections at the front interface, one finally obtains:

$$R = R_c + \frac{(1 - R_c)(1 - R_{KM})}{1 - R_{KM} R_d}$$

(26)

and

$$T = \frac{(1 - R_c)T_{KM}}{1 - R_{KM} R_d}$$

(27)

where $R_c$ is the reflectance of the incident light on the front interface of the slab while $R_d$ is the frontside internal reflectance of the slab. It was seen that in order to invert the equations for $R$ and $T$ to determine $S$ and $K$, knowledge of the interface reflectance parameters was necessary.

**Determination of $R$ parameters:** In this work, the scattering phase function was measured by the angle-resolved spectrometer, as described above. From these measurements and the fit to the empirical rRM phase function, the forward and backward internal diffuse reflectance at the back and front interface $R_{df,db}$ was first derived:

$$R_{df,db} = \frac{\int_{0}^{\theta_c} f_{\alpha}(\theta) R(\theta) \sin(2\theta) d\theta}{\int_{0}^{\theta_c} f_{\alpha}(\theta) R(\theta) \sin(2\theta) d\theta}$$

(28)

$R_{df,db}$ was derived by averaging the inner angular scattering pattern $f_{\alpha}(\theta)$ at the front and back interfaces, multiplied with the interface reflectance coefficient $\rho(\theta)$, Equation (14), over the angles $(0^\circ, 90^\circ)$ from the forward and backward directions. $R_{df,db}$ considered the diffuse light component of the reflectance, but the total interface reflectances $R_{df}$ also involved a collimated light contribution.

$$R_{df} = (1 - q_d)R_c + q_d R_{df,db}$$

(29)

where $q_d$ and $q_{db}$ are defined as the diffuse light fractions in the film close to the back interface and front interface, according to

$$q_d = \frac{I_d(\theta) - I_s(\theta)}{I_d(\theta)}$$

(30)

and

$$q_{db} = \frac{J_d(\theta) - J_s(\theta)}{J_d(\theta)}$$

(31)
The intensity passing toward the back interface is denoted \( I \) and the intensity toward the front interface is denoted \( J \). In addition, the coordinates \( 0 \) and \( d \) represents the back and front interfaces, respectively, and the subscript \( c \) signifies the collimated light. \( q_{df,c} \) was calculated from transmittance and reflectance spectra according to Barrios et al.\(^{[22a]}\)

\[
q_{df,c} = \frac{T_{df}(1-R_c)}{T_{df}(1-R_{d})} - T_{df}(R_{df} - R_{c})
\]

\[
q_{df,b} = \frac{T_{df}(1-R_b)}{T_{df}(1-R_{d})} - T_{df}(R_{df} - R_{b})
\]

From the knowledge of diffuse interface reflectance \( R_{df,b,d} \) and the diffuse light fractions \( q_{df,c} \), the total interface reflectances \( R_0 \) were determined by Equation (29).

If forward and backward diffuse interface reflectances \( R_{df,b} \) and \( R_{df,d} \) could not be determined directly from ARS measurements, one had to assume a scattering profile, i.e., a phase function of the nanoparticle coating, so that the front/back interface scattering distributions could be approximated.

In the \( d \)-approximation, an isotropic scattering profile of diffuse light was assumed for both forward and backward directions for the nanoparticle samples. \( R_0 \) was defined as the total diffuse interface reflectance when light was incident from the sample to air; \(^{[35]} \) therefore, \( R_{df} = R_{df} = R_{df} \) was computed in analogy to the \( R_{df,c} \) method, but the scattered light was restricted in the forward and backward directions to angles less than the critical angle; hence, \( \theta_c \) is the angle above which total internal reflection occurs so that \( r_c = r_0 = 1 \), and it is wavelength dependent. In this case, it was determined for the glass/air interface.

In the \( d \)-approximation, the scattering angle was restricted by the critical angle in the forward direction and went to the full \( 90^\circ \) in the backward direction.

\[
R_{df} = R_{df} = R_{df} = \int_{0}^{\theta_c} \frac{P_{f} (\beta) (\sin(2\beta)) d\beta}{\int_{0}^{\theta_c} \sin(2\beta) d\beta}
\]

Mie Theory Modeling: The electrodynamic response of particles of spherical shape was analytically and effectively solved with Mie theory. The scattering phase function for the three types of NSs was computed using the program MiePlot version 4.6.\(^{[38]} \) The calculations by the Mie theory took into consideration the particle size distributions measured from SEM images. The refractive index database of \( \text{Au}^{[39]} \), \( \text{Fe}_2\text{O}_3^{[40]} \) and \( \text{TiO}_2^{[27]} \) were used as input for the optical properties of the NSs while the optical constants of the surrounding medium were taken from the calculated \( n, k \) obtained from \( T_{df,b} \) and \( R_{df,b} \) of the glass/(water+PVP)/glass sample.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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angle-resolved scattering, nanoparticle composites, radiative transfer, scattering coefficient, absorption coefficient


