

White Light Photothermal Lens Spectrophotometer for the Determination of Absorption in Scattering Samples

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We developed a pump-probe photothermal lens spectrophotometer that uses a broadband arc-lamp and a set of interference filters to provide tunable, nearly monochromatic radiation between 370 and 730 nm as the pump light source. This light is focused onto an absorbing sample, generating a photothermal lens of millimeter dimensions. A highly collimated monochromatic probe light from a low-power He-Ne laser interrogates the generated lens, yielding a photothermal signal proportional to the absorption of light. We measure the absorption spectra of scattering dye solutions using the device. We show that the spectra are not affected by the presence of scattering, confirming that the method only measures the absorption of light that results in generation of heat. By comparing the photothermal spectra with the usual absorption spectra determined using commercial transmission spectrophotometers, we estimate the quantum yield of scattering of the sample. We discuss applications of the device for spectroscopic characterization of samples such as blood and gold nanoparticles that exhibit a complex behavior upon interaction with light.

Index Headings: **Photothermal spectroscopy; Photothermal effects; Absorption spectroscopy; Spectrophotometers.**

INTRODUCTION

The photothermal lens (PTL) method measures the amount of heat generated by the absorption of light photons. Photon absorption generates a spatial gradient of the refraction index of thermal origin or thermal lens. The thermal lens affects propagation of the light beam, yielding distortions of its wave-front. By measuring the transmission of light through a small aperture located at some distance from the absorbing medium, a signal proportional to the amount of absorbed heat can be obtained. The method exhibits sensitivities well above the sensitivity of the transmission method commonly used for determination of absorption.^{1–4} Different studies have pointed out the intrinsic scattering-free character of the photothermal lens method.^{5–7} Other studies have shown the usefulness of the technique for determination of absorption in highly scattering samples.^{8–13} However, the majority of these studies were conducted at fixed wavelength values. Tuning the excitation wavelength yields a PTL spectrum. PTL spectroscopy is in principle different from the usual absorbance spectroscopy.

Traditional transmission-based spectroscopy measures the total loss of electromagnetic energy upon propagation through the sample. The differences become evident when other processes such as fluorescence; Raman, Brillouin, or Rayleigh scattering; or photoacoustic, photochemical, or other effects take place. Hung et al. have shown the differences between transmission and PTL spectroscopy of fluorescent dye solutions.¹⁴ In this regard, PTL spectroscopy is a fundamentally new way to characterize the optical response of samples that exhibit a complex behavior upon interaction with light. Despite this evident application and the universal character of photothermal effects, no commercial PTL spectrophotometers have been developed to date. The main limiting reason is that PTL spectroscopy generally requires tunable laser technology such as dye lasers, optical parametric oscillators, or tunable solid state or diode lasers, among other costly and complex technology. However, PTL spectrophotometers can be developed using white light and other technologies generally used in commercial transmission-based spectrophotometers.^{15,16} Chartier and Bialkowski demonstrated the production of the PTL signal using a wide spectral band width incoherent excitation source.¹⁵ The signal was analyzed as the integrated absorbance of the sample with no intentions to detect the PTL spectra. Kitamori et al. have developed a tunable thermal lens spectrophotometer using a Xe lamp for microchip analysis using microchannel-assisted thermal lens spectrometry (MATLS), demonstrating the ability of the method to detect absorption in the presence of turbidity.¹⁶ The MATLS method is based on the creation of a high-temperature gradient through heat generation in a microchannel and rapid thermal conduction between the channel glass wall and solution.¹⁷ Marcano et al. have demonstrated that a broadband incoherent white source can be used to generate PTL spectra of fluorescent and nonfluorescent dyes in bulk samples without the use of microchannel technology.¹⁸ In this work, we develop further the idea of a white light PTL spectrophotometer to demonstrate the importance of PTL spectroscopy for characterization of bulk scattering samples with relatively high levels of scattering. By using interference filters, we filter the spectrally broadband light to generate quasi-monochromatic radiation with 10 nm spectral width in the spectral region 370–730 nm. This light is focused onto the sample by using a conventional converging lens generating a thermal lens

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of millimeter dimensions. A low-power He–Ne (632 nm) laser probes the thermal lens. We collimated the probe beam of light by using a telescope to a beam spot several times larger than the spot of the excitation light at the sample position. This configuration has been reported as optimal for a PTL experiment¹⁹ and provides low chromatic aberrations.²⁰ The configuration is also fundamentally different from the configuration used in previous work where the probe and excitation beam are focused by the same lens.^{15,16} To test the proposed PTL spectrophotometer, we measured the PTL spectra of nonfluorescent dyes: water solution of malachite green oxalate and Nile blue. As expected, the PTL spectra reproduced the obtained absorbance spectra well using a commercial transmission-based spectrophotometer. The similarity breaks down when scattering effects are present. We added polystyrene microspheres to the dye solution to increase the levels of scattering. The absorption spectra were substantially affected because of the presence of scattering losses. However, the PTL spectra remained unaltered due to the scattering-free character of the method. By comparing the absorption and PTL spectra of the samples, we estimated the scattering quantum yield of the sample as a function of the excitation wavelength. We further used the PTL spectrophotometer to study the spectra in gold nanoparticles and blood samples. The results show similarities and differences when compared with the transmission method, demonstrating the importance of the PTL approach as a new kind of spectroscopy. Depending on the type of sample, the device can also be used for determination of quantum yields of fluorescence, Raman, photoacoustic, photochemical, or other properties of a given optical sample.

BACKGROUND

We consider a sample that exhibits only absorption and elastic scattering upon interaction with light. We also consider that the not scattered, absorbed electromagnetic energy is totally converted into heat and that reflection, fluorescence, Raman, photochemical, or other effects are negligible. If $P_i(\lambda)$ is the power of the propagating light wave, we can write the following equation based on energy conservation principles

$$P_i(\lambda) = P_T(\lambda) + P_H(\lambda) + P_S(\lambda) \quad (1)$$

where λ is the wavelength of the light and $P_T(\lambda)$, $P_H(\lambda)$, and $P_S(\lambda)$ represent the transmitted power, the amount of power used for heating, and the amount of scattered power, respectively. Transmission based spectrophotometers yield the absorption spectrum as

$$\alpha(\lambda) = -\frac{1}{L} \ln(T(\lambda)) \quad (2)$$

where $T(\lambda) = P_T(\lambda)/P_i(\lambda)$ is the sample's transmission and L is the length of the sample. The absorption coefficient $\alpha(\lambda)$ includes contributions of both heating and scattering losses. In a first approximation, we consider that these contributions are independent one from another. Consequently, we write

$$\alpha(\lambda) = \alpha_H(\lambda) + \alpha_S(\lambda) \quad (3)$$

where $\alpha_H(\lambda)$ accounts for losses due to heating of the sample and $\alpha_S(\lambda)$ accounts for scattering losses. According to Beer's law, $\alpha(\lambda) = 2.303 N \varepsilon(\lambda)$, where N is the molar concentration and $\varepsilon(\lambda)$ is the molar extinction coefficient that is generally used to characterize absorption. We denote $\alpha_H(\lambda)$ as thermal absorption coefficient. In the presence of low losses we obtained from Eqs. 1–3

$$\alpha_H(\lambda) = (1/L)P_H(\lambda)/P_i(\lambda) \quad (4)$$

and

$$\alpha_S(\lambda) = (1/L)P_S(\lambda)/P_i(\lambda) \quad (5)$$

The scattering coefficient $\alpha_S(\lambda)$ is an integration factor that accounts for scattering losses in all directions and for all states of polarizations. Its direct experimental determination is generally difficult. However, this factor can be determined by a simple comparison of absorption and thermal absorption losses. The thermal absorption coefficient $\alpha_H(\lambda)$ can be determined by measuring the PTL signal generated by the distortions of the probe beam. The PTL signal is defined as the relative change in the transmission of probe power through a small aperture located at some distance from the sample. Therefore, we can write

$$S_H(\lambda) = W_P(\lambda)/W_{po}(\lambda) - 1 \quad (6)$$

where $W_P(\lambda)$ is the probe light power transmitted through the aperture in the presence of the excitation beam, and $W_{po}(\lambda)$ is the probe light power transmitted through the aperture in the absence of the excitation beam. A Fresnel diffraction approximation provides a practical model to describe the PTL signal as a function of coefficient $\alpha_H(\lambda)$.^{20,21} For small PTL signal values, we have the relation^{4,19}

$$\alpha_H(\lambda) = S_H(\lambda)\alpha(\lambda)\lambda_p\kappa \times \left[KP_i(\lambda)(dn/dT)\left(1 - \exp(-\alpha(\lambda)L)\right) \right]^{-1} \quad (7)$$

where λ_p is the probe light wavelength; κ is the sample's thermal conductivity; dn/dT is the sample's thermal refraction coefficient; and K is a unitless coefficient that depends only on Rayleigh ranges, sample position, and waist positions of the excitation and probe beams. For the situation when the pump beam is focused and the probe beam is highly collimated, the value of this coefficient is close to $\pi/2$.¹⁹

To characterize the scattering properties of the sample $\alpha_S(\lambda)$, instead we define the quantum yield of elastic scattering, Ω_S , as the number of scattered photons divided over the number of photons lost during propagation of the excitation light. Using Eqs. 1–5, we estimate

$$\Omega_S(\lambda) = 1 - \alpha_H(\lambda)/\alpha(\lambda) \quad (8)$$

EXPERIMENTAL

In Fig. 1, we show the scheme of the white light PTL spectrophotometer. An ozone-free Xe 150 W arc-lamp

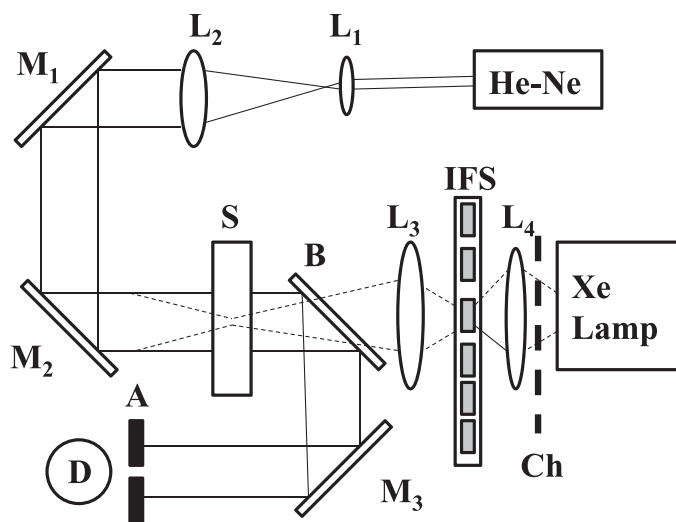


FIG. 1. Simplified scheme of the experimental setup that consists of Xe arc-lamp; a He-Ne laser; an optical chopper (Ch); a set of interference filters (IFS); lenses L_1 , L_2 , L_3 , and L_4 ; a beamsplitter (B); mirrors (M_1 , M_2 , and M_3); an aperture (A); and a semiconductor detector (D).

provides a broadband excitation light. An optical chopper modulates the pump excitation at low frequency (2 Hz). This low frequency provides the conditions for the PTL signal to achieve maximal stationary values. The excitation light is collimated by a telescope in which we place 2.54 cm (1 in) diameter interference filters. By using a total of 36 interference filters (ultraviolet [UV]-Vis bandpass filters, Thorlabs, Inc.) of different wavelengths, we obtain tunable partial monochromatic light within the spectra range 370–730 nm with a spectral resolution of ± 10 nm. The filtered light is then focused onto the sample up to a beam with a rectangular spot of 2×4 mm. A 4 mW He-Ne probe laser (632 nm) tests the thermal lens. The probe beam is collimated using a telescope up to a diameter of 1 cm and directed collinearly by mirrors M_1 and M_2 in a counterpropagating direction to the excitation beam. Both beams are centered, illuminating the same area of the sample. Behind the sample, a glass wedge and a mirror redirect the probe beam toward a small aperture located in front of a semiconductor detector. At this detector, we use interference laser line

filters to deplete any remaining excitation light. The signal is then amplified and averaged using a digital oscilloscope. We record the power $P_i(\lambda)$ available for each particular wavelength using a calibrated detector. The system provides a nearly flat response in the region 400–700 nm, with a power spectral density of about 0.2 mW/nm. Absorption of the samples $\alpha(\lambda)$ is determined using a Cary 100 UV-Vis-near-infrared (UV-Vis-NIR) commercial spectrophotometer (Agilent). Using the values of the PTL signal, $P_i(\lambda)$ and $\alpha(\lambda)$ and Eq. 5, we estimate thermal absorption coefficient $\alpha_H(\lambda)$ apart from a constant calibration factor. This calibration factor can be determined from the fact that in the absence of scattering thermal absorption coefficient and absorption values are the same.

The samples are water solutions of commercial nonfluorescent dyes malachite green oxalate (ACROS) and Nile blue (ACROS). The samples are used without further purification. The samples are contained in 1 mm-thick glass cells. To increase scattering we add 0.5 μL drops of 1% water solution of 200 nm diameter polystyrene microbeads (Polysciences, Inc.) to 0.3 mL of each dye solution. As an example of the uses of PTL spectroscopy, we also measure and compare PTL and absorption spectra of water colloid of 50 nm diameter gold nanoparticles and blood taken from a meat sample.

We should note that the probe light is also absorbed and scattered. However, these losses do not affect the final spectra apart of a constant factor because the amount of the probe field losses are the same for the different wavelengths of the excitation light.

RESULTS AND DISCUSSION

In Fig. 2a, we show the absorption and the PTL spectrum of malachite green oxalate at the concentration of 1.06×10^{-4} mol/L with no polystyrene microbeads added in terms of molar extinction coefficients. We obtain good agreement of the two spectra signaling on the heating character of the absorption in the dye solution. Figure 2b shows the same spectra when 1.5 μL of 1% polystyrene microbeads solution is added to 300 μL of the solution. The resulting concentration is 0.005% by weight. The extinction spectrum measured using the transmission

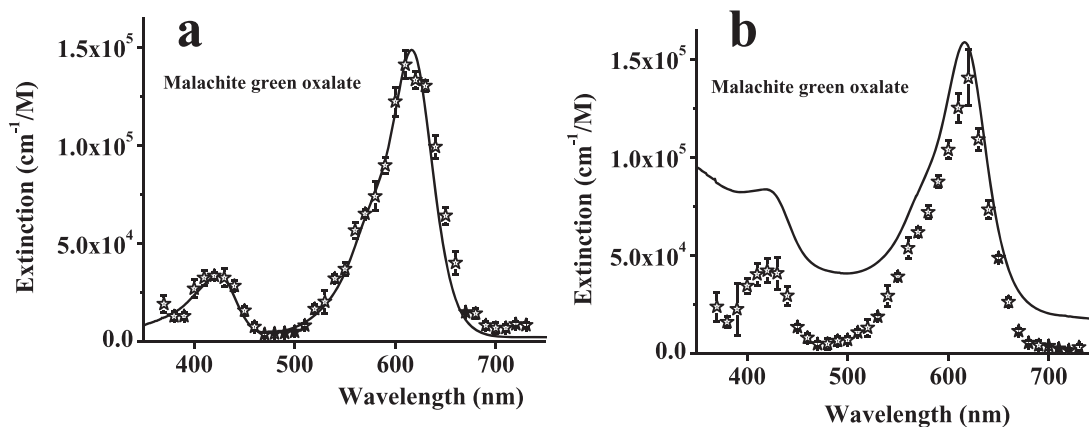


FIG. 2. (a) PTL and extinction spectra of malachite green oxalate with no polystyrene microbeads added. (b) PTL and extinction spectra of malachite green oxalate containing polystyrene microbeads at concentration of 0.005% by weight. The SD is estimated averaging over five different experiments.

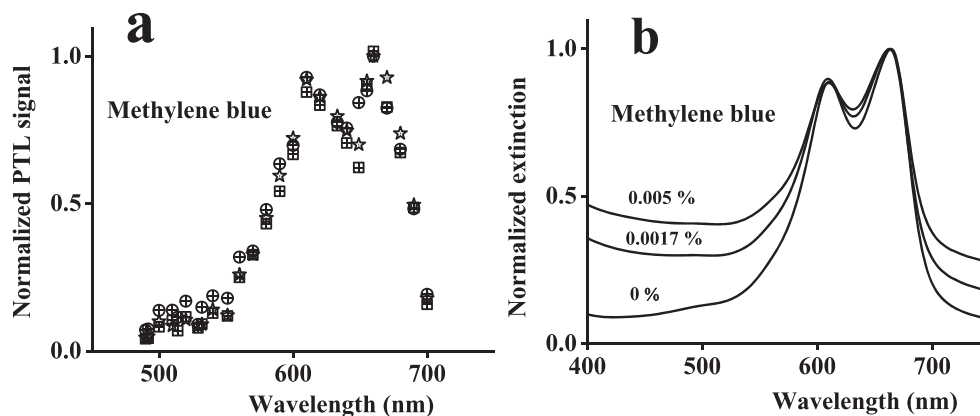


FIG. 3. (a) Normalized PTL spectra of Nile blue with polystyrene microbeads added at a concentration of 0 (crossed circles), 0.0017% (stars), and 0.005% (crossed squares) by weight. (b) Normalized extinction spectra of Nile blue containing polystyrene microbeads at a concentration of 0, 0.0017, and 0.005% by weight. The SD is estimated averaging over five different experiments.

method shows a substantial change. The PTL spectrum shows no measurable change. The comparison between both results demonstrates that PTL, as expected, does not include the scattering contribution. In Fig. 3a, we show the normalized PTL spectra of a 1.79×10^{-4} mol/L water solution of methylene blue with 0, 0.5, and 1.5 μL of polystyrene microspheres solution. The resulting concentrations of polystyrene microspheres are 0, 0.0017, and 0.005% by weight, respectively. Despite the presence of substantial losses due to scattering, the shape of the PTL spectra show no effect. Meanwhile, the absorption spectra measured using the transmission methods exhibit dramatic changes. In Fig. 3b, we show the normalized extinction spectra of the methylene blue solution when adding 0, 0.5, and 1.5 μL of 1% polystyrene microspheres solution. For wavelengths around 480 nm, the extinction increases about 8 times from their values when no microspheres are present.

We use Eq. 7 to estimate the quantum yield of scattering $\Omega_S(\lambda)$ of the solutions for malachite green oxalate (Fig. 4a) and methylene blue (Fig. 4b) when 1.5 μL of polystyrene spheres is added. The increase of signal-to-noise ratio for high $\Omega_S(\lambda)$ values observed in Fig. 4 is

due to the reduced value of the effective experimental signal obtained when thermal absorption is small. We observe small $\Omega_S(\lambda)$ values when thermal absorption is present.

We have also compared the PTL and extinction spectra of a solution of 50 nm diameter gold particles in a water solution at a concentration of 1 mg/mL. For this sample, we have estimated a molar concentration of nanoparticles of 2.6×10^{-6} M/L using the method reported by Liu et al.²¹ In Fig. 5, we show the extinction of this sample and the PTL spectrum. We observe a good fit between both spectra. We conclude that the main component of the absorption for this gold nanoparticle sample has thermal origin. Scattering and other effects are negligible, at least for the spectral region 370–730 nm. The lack of scattering and the high values of extinction confirm the character of this gold nanoparticle sample as an excellent thermal absorber.

In Fig. 6a, we show the PTL and extinction spectra of a blood sample taken from a piece of meat. The effect of scattering is evident because of the differences observed in both spectra, in particular in the spectral regions 420–500 and 600–730 nm. In Fig. 6b, we show the quantum

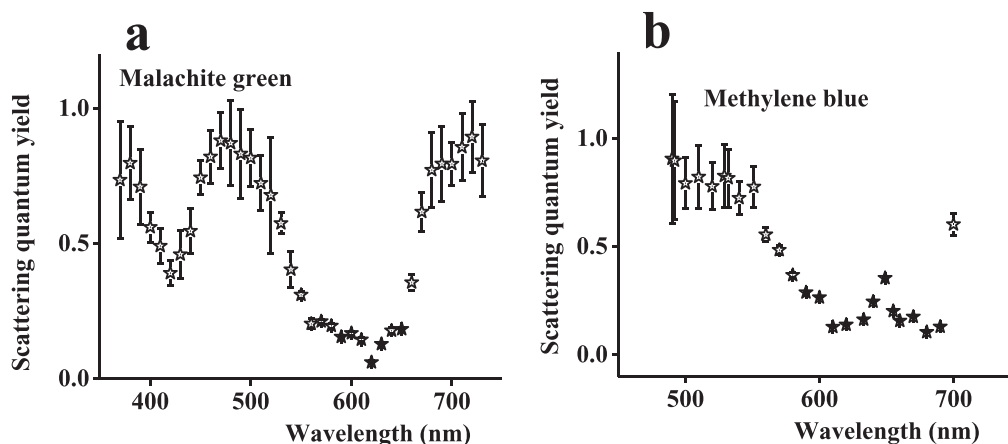


FIG. 4. (a) Scattering quantum yield of the malachite green oxalate sample with added polystyrene microparticles at a 0.005% concentration by weight. (b) Scattering quantum yield of the Nile blue sample with added polystyrene microparticles at 0.005% by weight. The SD is estimated averaging over five different experiments.

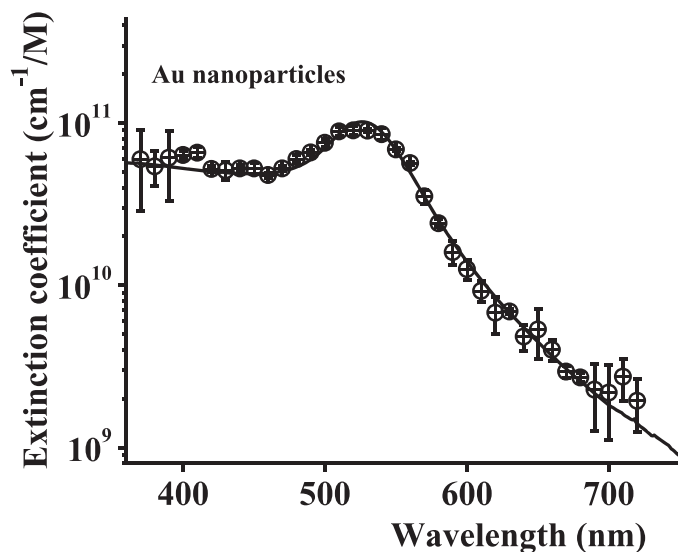
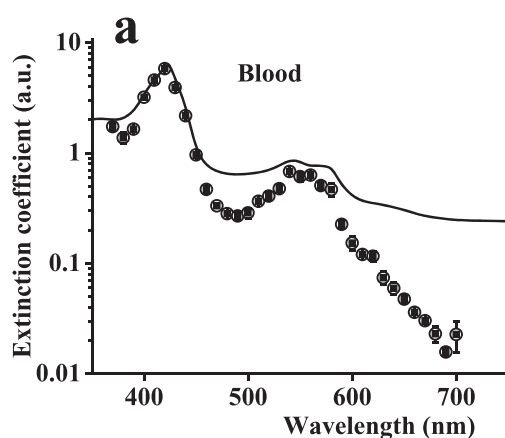


FIG. 5. Extinction (solid line) and PTL (crossed circles) spectra of a solution of 50 nm diameter gold nanoparticles at concentration of 1 mg/mL. The SD is estimated averaging over five different experiments.

yield of scattering that clearly shows the spectral regions where scattering becomes dominant.

CONCLUSIONS

We demonstrated the use of PTL spectroscopy to characterize the scattering and absorption of an optical sample using a broadband incoherent light source. The original design is based on a mode-mismatched scheme where the excitation beam is focused and the probe beam is collimated, yielding optimal conditions for the PTL experiment. We confirm that PTL and commonly used transmission spectroscopic methods provide different spectra if the sample exhibits scattering losses. The comparison of both spectra yields the sample's scattering quantum yield. In this regard, the combination of traditional and PTL spectroscopy provides a new tool for characterization of materials that exhibit a complex behavior upon interaction with light.



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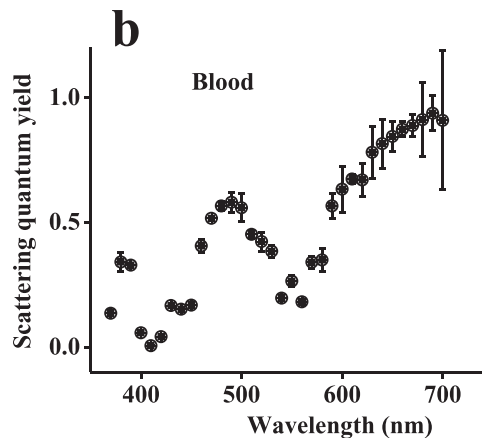


FIG. 6. (a) Extinction (solid line) and PTL (crossed circles) spectra of a blood sample. (b) Scattering quantum yield of the same blood sample. The SD is estimated averaging over five different experiments.

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