# Integrating Sphere Microscopy for Direct Absorption Measurements of Single Nanostructures

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# I. INTEGRATING SPHERE DETAILS

An integrating sphere (or Ulbricht sphere) is a tool frequently used to determine the absorptance of scattering macroscopic samples or suspensions. In brief, it comprises an extremely reflective surface, which reflects light diffusely (lambertian, equally in all directions). As a result, light inside the integrating sphere is quickly randomized, and ultimately covers the inner surface with equal intensity, independent of the distribution of the initial excitation and scattering pattern of the sample. The surface of a photodetector attached to the integrating sphere will therefore also be illuminated with the same intensity, and as a result the photodetector signal is proportional to the total power inside the integrating sphere. If the integrating sphere is designed properly, this proportionality factor also does not depend on the exact angular distribution of the initial excitation. Hence, even if a sample is strongly scattering into a certain direction, the photodetector signal is still proportional to the total intensity of light inside the integrating sphere with the same proportionality factor. By comparing the measurement on the sample to a reference measurement (where there was no absorption), we can use the fact that this collection efficiency of the integrating sphere remains the same to determine the fraction of absorbed power.

#### A. Technical details of our integrating sphere

The integrating sphere that we used in this experiment is a customized integrating sphere ordered from Labsphere, which has a 50.8 mm internal diameter and three ports (of which two can be closed). Fig. 1a shows a schematic of the integrating sphere from the side, which shows two ports: one 1" port for the sample to enter the integrating sphere, and one 1" port for access to the photodetector, which is filled with a baffle. On the front of the sphere the custom indentation on the front for the microscope objective is clearly visible, as shown in Fig. 1b. This indentation is required due to the focal length of the objective, which in our case is 17mm (Mitutoyo M Plan APO NIR  $50 \times$ ). The indentation runs all the way to the bottom of the integrating sphere, allowing for the integrating sphere to be lowered over the sample and objective. Under normal operating conditions the bottom

port is also has a plug, which reduces the port size. In this plug, the sample enters through a  $5 \times 15 \text{ mm}^2$  slit in spectralon. The photodetector sits behind a plug with a baffle (not shown) in front of a 1/2" diameter port.

Under the conditions used in this article, the integrat-



FIG. 1. Technical drawings for integrating sphere and sample holder. a. Side view of the integrating sphere, showing the 1" port for sample entrance (plug not shown) and the baffle for the photodetector. On the front the indentation facilitating objective placement is shown. b. Front view of the integrating sphere, with sizes shown in mm. The indentation for microscope objective is now clearly visible, together with a 17 mm port through which the objective focuses light. c. Top perspective showing width and depth of the indentation as well as the attaching mechanism. d. Schematic drawings of the baffle, a crucial part of the system that prevents direct illumination of the photodetector. e. Sizes of our glass sample holder, with two holes: one to fix the sample to the piezoelectric stage, and one for reference measurements. The sample holder is cut from regular microscope slides, and is therefore  $\sim 1.5$ mm thick.

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FIG. 2. Detection efficiency of the integrating sphere system. The photodetector attached to the integrating sphere detects just below 2% of all incident light. This detection efficiency is determined by the surface reflectivity, the multiplier, the photodetector size relative to other ports, and the detector's field of view. This collection efficiency is without sample holder in the integrating sphere.

ing sphere port fraction (the fraction of the sphere area that is open) is  $f \approx 0.05$ . Since spectralon, the material that the integrating sphere is made of, has a diffuse reflectivity of > 99%, the so-called multiplication factor is in excess of 16. This multiplier describes the average number of times a photon is expected to reflect within the sphere before it escapes through a port or is absorbed in the coating. The probability that a photon is detected is just below 2%, as shown in Fig. 2. This probability naturally depends on the multiplier and size of the photodetector relative to the other ports, but also on the detector field of view and the solid angle of integrating sphere that it is exposed to. Due to the extremely small size of the nanoscale sample, the probability that light is absorbed in the sample on second pass is negligible. For macroscopic samples, on the other hand, second pass absorption is frequently considerable and must be taken into account.

The width of the indentation in the front is 34 mm (Fig. 1c), while the illumination port has a diameter of 17 mm. This is about the size of the microscope objective front lens, and can therefore be changed if a different microscopy objective is used. In any case, the port needs to be just large enough to not block parts of the focused beam emanating from the objective. On the top of Fig. 1c, a construction can be seen to attach the integrating sphere to a lift, which enables loading and removing of the sample.

The baffle blocking direct illumination of the photodetector is a crucial part of the integrating sphere system, as it must be ensured that light homogenizes before it reaches the photodetector. In our case the baffle is 11 mm wide (1d) in front of a 1/2" inch port, and enters the integrating sphere (see Fig. 1a). The distance from the front of the baffle to the back of the integrating sphere ensures that the (at this point) diverging excitation beam cannot reach the photodetector directly.

# B. Sample holder

The sample holder is another crucial part of the experimental setup. A good sample holder for integrating sphere microscopy measurements satisfies at least these requirements:

- it facilitates a reference measurement;
- it is made from a nonabsorbing material;
- it does not provide other escape paths.

In our case the sample holder is shown schematically in Fig. 1e, and is made from regular glass microscopy slides. We use fiducial markers to locate the nanoscale specimen, and take reference measurements through the hole close to the fiducial markers. This ensures that the sample does not need to be significantly displaced between the measurement and reference measurement, which could alter the collection efficiency of the integrating sphere significantly (since the multiplication factor can be high).

If the sample holder is absorbing, it will not be possible to distinguish between absorption in the sample itself and absorption in the sample holder. Likewise, if the sample provides another escape path from the integrating sphere that is not probed in the reference measurement, it is also not possible to distinguish between absorbed power in the specimen, or power that was not absorbed but escaped from the integrating sphere *via* the sample holder. The latter may contribute to collection losses in our experiment, and can in the future be prevented by using an improved sample holder design.

# **II. DATA ANALYSIS**

In this section we will discuss details on data analysis in integrating sphere microscopy. In brief, we combine two signals to determine the absorption. These two signals constitute the total reflected light (specular reflection from the substrate and backscattered light from the sample) on the one hand, and the sum of transmitted and other scattered light on the other hand. Specifically, we have for the absorptance A:

$$A = 1 - \frac{R}{R_{ref}} - \frac{IS}{IS_{ref}} - C, \qquad (1)$$

where R and IS are the reflection and integrating sphere photodetector signals at the position where we want to measure the absorptance (*e.g.* with a gold nanoparticle in the center of the focus).  $R_{ref}$  and  $IS_{ref}$  are reference signals with known reflection and transmission, such as a mirror (for reflection) or a hole in the sample (for transmission). These fractions are shown in Fig. 1a (for the integrating sphere) and Fig. 1b (for reflection and the offset C) for a clean sample holder. The fraction IS/IS<sub>ref</sub> in this case is determined by focusing the light on a clean glass



FIG. 3. Clean sample reflection and transmission. a. The transmission of the glass sample holder over a range of wavelengths, showing that the total transmission is approximately 93%. b. The reflection of the sample holder, which is lower than the expected 7%, because the reflection from the second interface is not efficiently collected. This results in a correction factor of  $\sim 3\%$ .

sample holder and as a reference the beam is sent through a hole in the sample. The detection efficiency of the integrating sphere is sensitive to sample placement, and it is therefore important to minimize moving the sample between the measurement and reference measurements. We obtain a transmissivity of the glass slide of almost 93%, which is in good agreement with a refractive index of ~1.45.

While the glass sample holder should reflect  $\sim 1 -$ 0.93 = 0.07%, the reflected signal is only ~4-4.5%. This is largely because the reflection is recorded through a microscope objective, which only efficiently images light on the photodetector if that light originates from the focal plane of the microscope objective. The second interface of the glass sample holder, which is responsible for approximately half of the reflected power, is too far away for the objective to image, and hence the recorded reflection signal is lower than 7%. As a result, a small offset  $C \approx 0.03$  is required to satisfy the power balance (since the sample holder itself does not absorb). This constant is thus determined by requiring that the absorption from Eq. 1 is zero in absence of an absorbing sample. As mentioned in the main text, some small systematic errors are introduced due to the presence of this constant: if a nanoparticle scatters strongly and significantly alters the amount of power reflected from the second interface, the constant C no longer represents the amount of power that is not collected by either photodetector, but also is

not absorbed. While this systematic error is likely to be small, efforts may be taken to reduce it further. This can for example be achieved by using a sample holder with an antireflection coating on the back side of the glass sample holder.

In practice, it is sufficiently accurate to assume a constant reflectivity and transmission of the substrate. This simplifies data analysis, because signals on and off the nanostructure can now be directly compared:

$$A = 1 - 0.04 \times \frac{R_{hit}}{R_{miss}} - 0.93 \times \frac{IS_{hit}}{IS_{miss}} - 0.03.$$
(2)

Here the subscripts hit and miss refer to measurements on and next to the nanostructure. While very small fluctuations occur with wavelength as shown in Fig. 3, these do not strongly affect the results. For example, assuming that the transmission of the glass is in fact 92% and not 93% will usually result in an error in the absorptance of less than 1% relative. However, it is crucial that the offset does indeed compensate the power that is not covered by the reflection or integrating sphere signal: if we set C to 2% instead of 3%, that will directly lead to an *absolute* error in absorptance of 1%.

It is important to emphasize that these constants (0.04, 0.93, 0.03) are specific to each experimental setup and depend on *e.g.* microscope objective, sample holder, and reflection photodetector placement. These constants therefore have to be determined *everytime* even small changes are made to the setup, let alone when making large changes or starting to use a completely new setup.

#### A. Conversion to cross section

In the main text we show all spectra in terms of the absorption cross section  $\sigma_{abs}$ , a quantity that describes the interaction of the structure with an incident plane wave and enables comparison to theory or simulations. To convert between absorptance and cross section we use a formula also given in the main text:

$$\sigma_{\rm abs} = A \sqrt{\pi w_0^2 / 2} \tag{3}$$

for an extended structure such as a nanowire, and

$$\sigma_{\rm abs} = A\pi w_0^2 / 2 \tag{4}$$

for point-like structures such as the gold nanoparticles. In these formulas A is the absorptance as measured with integrating sphere microscopy and  $w_0$  is the beam radius. The derivation of these formulas is briefly discussed in the main text, and more information on the derivation and also on the procedure to find  $w_0$  can be found in [1]. The beam width is determined based on a "knife-edge" measurement, which is done by scanning the focused spot

over a sharp edge between glass and a thin gold film. Such a measurement, as shown in Fig. 4, results in a monotonically increasing signal as more and more of the focused beam is reflected by the gold film. The functional shape of this increasing signal is given by an error function, and the derivative is a gaussian with width equal to the width of the focused beam. In this case, the scan is performed at  $\lambda = 550$  nm and the beam width is determined at  $w_0 = 660$  nm. Note that for tightly focused beams more care needs to be taken [2].

# III. REFLECTION AND INTEGRATING SPHERE SIGNALS

In the following we will show all signals from the reflection and integrating sphere photodetectors before they are combined to generate the spectra as shown in the main text. To facilitate figure placement, we discuss the data in a different order than in the main text. We begin with the gold nanoparticles, than move on to the GaAs nanowire, and finally the silicon nanowire. In any of the figures the reflection and integrating sphere signals are already shown normalized to the total incident power, such that they give the absorptance spectrum according to Eq. 1.

### A. Figure 5: Gold sphere spectra

The reflection and integrating sphere intensities for the 60 nm gold sphere are shown in Fig. 5a. Due to the small absorption cross section of this sphere, only very small modulations of the reflection and integrating sphere signals occur relative to the baseline reflectance and trans-



FIG. 4. Knife edge measurement. The reflection signal at  $\lambda = 550$  nm is recorded over a sharp gold edge, resulting in a typical error function reflectance curve. The derivative is a gaussian, which here is shown in blue cross, together with a fit (red curve). From the fit the spot size is determined to be 660 nm.



FIG. 5. Au nanoparticles in Fig. 5. Reflection (top) and integrating sphere (middle) signals combined to give the absorptance (bottom) for **a**. a 60 nm diameter gold nanoparticle and **b**. a 200 nm diameter gold nanoparticle.

missivity of the glass sample holder. Due to the larger size, these variations are stronger in the case of the 200 nm gold particle. Both signals contain features corresponding to the resonance feature shown in the absorption spectrum, but in particular the reflection signal may have a more complicated shape.

# B. Figure 4: GaAs nanowire

The reflection and integrating sphere signal maps of the GaAs nanowire are shown in Fig. 6a, together with the absorption maps as in Fig. 4 in the main text. Interestingly, it is immediately apparent that in this polarization (electric field along the nanowire axis) the nanowire is strongly backscattering, such that the signal on the reflection photodetector is increased by almost a factor of 3. This is therefore also accompanied by a big drop in the integrating sphere signal, which is bigger than what would be expected just from the absorption. For example, for 540 nm the absorptance is  $\sim 6\%$ , while the integrating sphere signal is  $\sim 13\%$  below the background signal. This difference is thus compensated for by the increase in reflected power. Interestingly, for the reflection map at 460 nm, the nanowire locally appears invisible, which is solely because it backscatters just the right amount to compensate for the extinction. On the other hand, in the integrating sphere signal the nanowire does not disappear at all.



FIG. 6. GaAs nanowire data for Fig. 4 in the main text. a. Spatial maps for different wavelengths as shown in the main text in Fig. 4, decomposed in the (normalized) reflection and integrating sphere signals. The scale bar is 2  $\mu$ m. b-c. Reflection (top) and integrating sphere (middle) spectra, combined into absorptance spectra (bottom) for the two polarizations as shown in the main text, Fig. 4g and h. From the maps (and the reflection spectrum in b) it is clear that the nanowire backscatters strongly.

The variation in signals with wavelength is more clearly visible in Fig. 6b. On resonance (at  $\sim 475$  nm) the nanowire does not scatter back as strongly and indeed reaches 4%, but as the wavelength increases, the backscattered power increases as well. On the other hand, the integrating sphere signal displays the largest drop right at the resonance, and then increases with wavelength. The net absorptance is shown in the bottom curve. In the other polarization, shown in Fig. 6c, the nanowire does not scatter back significantly, and the reflection signal is lower than background over the whole frequency range.

#### C. Figures 2 and 3: Silicon nanowire

The reflection and integrating sphere signal maps of the Si nanowire are shown in Fig. 7a, together with the absorption maps as in Fig. 2 in the main text. Contrary to the GaAs case, the reflection signal is now lower than the glass background signal over the whole length of the nanowire, and all wavelengths. There are small variations within the reflection signal as a function of wavelength, but they are hard to observe accurately. One can just notice a localized increase in backscattering, which occurs spatially just below the peak of the resonance (as determined from the absorption image). Variations are more clearly visible in the integrating sphere signal: there is a large dip in the signal where the nanowire is resonant, corresponding to strong absorption, as shown in the bottom row. Fig. 7b-e show the reflection and integrating sphere spectra taken at two different positions and two different locations, resulting in the absorptance spectra shown in the main text in Fig. 3. Interestingly, we can now see that at the bottom of the wire, in the TM polarization, the nanowire starts to backscatter strongly at longer wavelengths. This behavior is similar to that of the GaAs nanowire, as observed in Fig. 6. We can also observe that the nanowire backscatters strongly at resonance in the TE polarization at larger diameters (position 1, Fig. 6c). Strong forward scattering is not directly visible, as this would require a large dip in the reflected signal, but only a very small decrease, or even an increase, in the integrating sphere signal.

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FIG. 7. Silicon nanowire data for Fig. 2 and Fig. 3. in the main text. a. Spatial maps for different wavelengths as shown in the main text in Fig. 2, decomposed in the (normalized) reflection (top) and integrating sphere (bottom) signals. The scale bar is 2  $\mu$ m. b-e. Reflection (top) and integrating sphere (middle) spectra, combined into absorptance spectra (bottom) for the two polarizations and two positions on the silicon nanowire as shown in the main text, Fig. 3.