

Supporting Information

Two-step adsorption kinetics of malachite green on anionic polystyrene microspheres in aqueous solution probed by second harmonic generation

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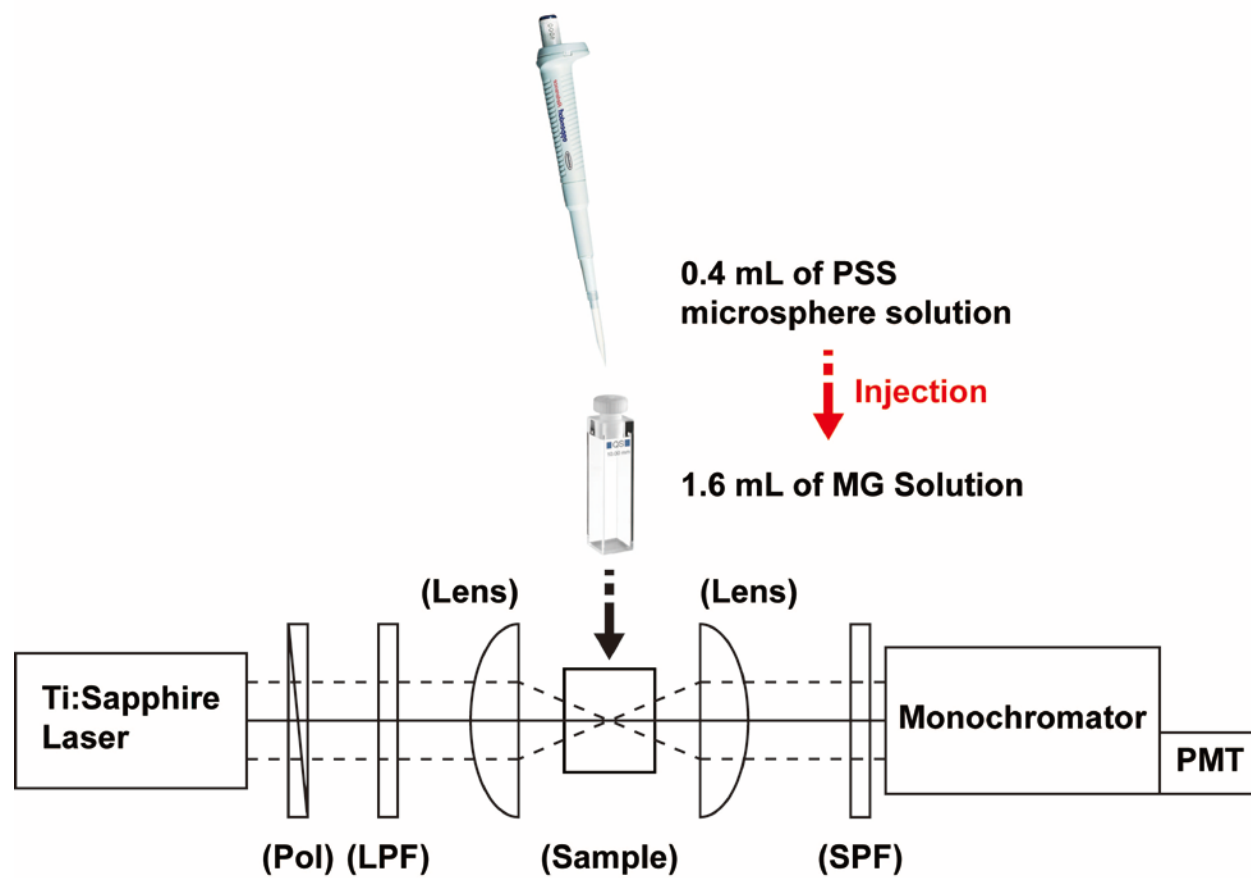
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Fig. S1. Experimental Setup.

Pol: Polarizer, LPF: Long Pass Filter, SPF: Short Pass Filter



< Calculation of the corrected SHG field from the measured SHG intensity >

Absorption of the fundamental light (840nm) by MG was negligible.

Absorption coefficient of the SHG light (420nm) by MG was measured to be 15563 [M⁻¹cm⁻¹].

The measured SHG intensity is

$$\begin{aligned} I_{\text{meas}}(C_D) &= I_{MG}(C_D) + A \times \frac{1}{L} \int_0^L I_{2\omega}(C_D) \times 10^{-\varepsilon_{2\omega} C_D (L-x)} dx \\ &= I_{MG}(C_D) + A \times I_{2\omega}(C_D) \times 10^{-\varepsilon_{2\omega} C_D L} \times \frac{1}{L} \int_0^L 10^{\varepsilon_{2\omega} C_D x} dx \end{aligned}$$

where I_{MG} is the measured intensity at the SH wavelength (420nm) from the bulk MG solution without injection of PSS microspheres. This term includes all the background noise as well as two-photon fluorescence and Hyper-Rayleigh scattering from bulk MG molecules. “A” is a coefficient independent of C_D , which includes a correction factor for the extinction (mostly scattering) of SHG light by polystyrene microspheres.

Because the SHG light can be generated along the optical path in the solution, the locally generated SHG signal with the local attenuation factor is integrated along the optical path. For the experimental range of C_D less than 3 μM , $\varepsilon_{2\omega} C_D L \ll 1$, and

$$\frac{1}{L} \int_0^L 10^{\varepsilon_{2\omega} C_D x} dx = \frac{(10^{\varepsilon_{2\omega} C_D L} - 1)}{\ln 10 \times \varepsilon_{2\omega} C_D L} \approx 1$$

Therefore,

$$I_{\text{meas}}(C_D) = I_{MG}(C_D) + A \times I_{2\omega}(C_D) \times 10^{-\varepsilon_{2\omega} C_D L}$$

Then, the corrected SHG field can be obtained from

$$E_{2\omega}(C_D) = \sqrt{I_{2\omega}(C_D)} = \sqrt{A^{-1} \times 10^{\varepsilon_{2\omega} C_D L} \times (I_{\text{meas}}(C_D) - I_{MG}(C_D))}$$

< Comparison of fittings by a double-exponential and a single-exponential >

As an example, the SHG field data for the MG 0.60 μM solution was fitted by two different, a double-exponential and a single-exponential, functions. The fitting results are as follows.

A single-exponential fitting:

$$y(t) = A_1(1 - e^{-t/t_1})$$

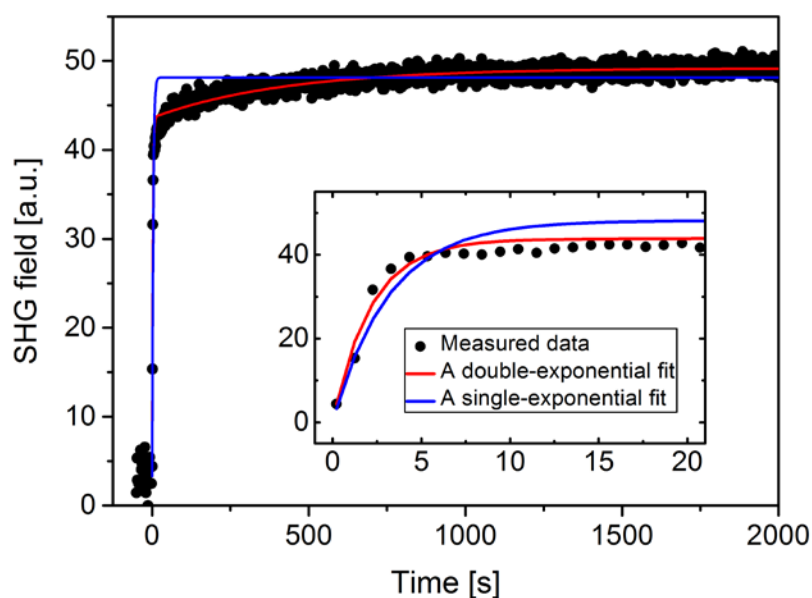
Fitting parameters: $A_1=48.1$, $t_1=3.2$, adjusted $R^2=0.44$.

A double-exponential fitting:

$$y(t) = A_1(1 - e^{-t/t_1}) + A_2(1 - e^{-t/t_2})$$

Fitting parameters: $A_1=43.6$, $t_1=2.1$, $A_2=5.6$, $t_2=423.7$, adjusted $R^2=0.89$.

Fig. S2. Comparison of fittings



< The effect of dilution by total volume change in changing pH or salt concentration of solution in figure 5 >

For the data of figures 5a & 5b, the volume of solution after initial mixing of PS microspheres and MG solution at $t=0$ is 2.0 mL. In order to change pH or NaCl concentration at $t=3200$ s, the 20 μL of concentrated HCl or NaCl solution was rapidly injected to the initial solution of PS microspheres and MG mixtures under magnetic stirring. Thus, the total volume change by additional solution was less than 1 %, which can be confirmed by very small change of the simultaneously measured LS intensity (Fig 5b and Fig S3). Therefore, the observed significant changes of SHG intensity of figures 5a & 5b, which are much larger than 1 %, should not be attributed to the dilution of MG or PS microspheres in the solution.

Fig. S3. Time-dependent change of SHG intensity and LS intensity when changing pH of solution in figure 5a.

