Accessory publication

Aggregation of titanium dioxide nanoparticles: role of calcium and phosphate

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FCS Technique

A laser light is focussed into a sample of interest using confocal optics. In this manner, an open, illuminated volume element with dimensions of ~0.5–1.0 μm^3 (confocal volume) is created. At any point in time, the confocal volume is occupied by one or only a few fluorescent molecules. In the absence of chemical reactions or other dynamic processes, temporal fluctuations in the measured fluorescence intensity in the confocal volume can be attributed solely to the translational diffusion of the fluorescent particle. Variations in the fluorescence intensity are analysed using an autocorrelation function that assumes a three-dimensional Gaussian distribution, $G(t)$. For example, for a one-component system in the absence of phosphorescence[1]:

$$G(t) = a + \frac{1}{N}\left(1+\frac{t}{\tau_D}\right)^{-1}\left(1+\frac{t}{\left(\frac{\omega_0}{z_0}\right)^2 \tau_D}\right)^{-1/2} \quad \text{(A1)}$$

where a is the limiting value of $G(t)$ for $t \to \infty$ (usually $a = 1$), N is the average number of fluorescent particles diffusing in the confocal volume, τ_D is the characteristic diffusion time of the fluorescent species through the sample volume, t is the delay time, and ω_0 and z_0 are the transversal and longitudinal radius of the sample volume respectively. The values of ω_0 and z_0 can be determined by calibration of the system with Rhodamine 110 (R110, Fluka), which has a known diffusion coefficient of 4.4×10^{-10} m^2 s^{-1}. [2]

The values of diffusion times for the bare TiO_2 nanoparticles (labelled with R6G), and for the TiO_2 nanoparticles complexed with SRFA were determined from a best fit of the autocorrelation function that assumed a three-dimensional Gaussian distribution, and which was given as a weighted sum of a number *i* of individual G_i in the presence of phosphorescence[3]:

$$G(t) = \frac{1}{\langle N \rangle} \prod_{i=1}^{n} \left(1 + A_i \exp\left(-\frac{t}{\tau_i} \right) \right) \frac{1}{\left(1 + \frac{t}{\tau_D} \right) \left(1 + \frac{t}{\left(z_0 / \omega_0 \right)^2 \tau_D} \right)^{1/2}} \quad \text{(A2)}$$

where $A_i = F_i / (1 - F_i)$. *F* corresponds to the fraction of molecules that resided in the dark state at any time. Diffusion coefficients (*D*) were subsequently calculated from measured diffusion times using the following relationship:

$$D = \omega_0^2 / 4\tau_D \quad \text{(A3)}$$

References

[1] S. R. Aragón, R. Pecora, Fluorescence correlation spectroscopy as a probe of molecular dynamics. *J. Chem. Phys*. **1976**, *64*, 1791. doi:10.1063/1.432357

[2] P.-O. Gendron, F. Avaltroni, K. J. Wilkinson, Diffusion coefficients of several rhodamine derivatives as determined by pulsed field gradient-nuclear magnetic resonance and fluorescence correlation spectroscopy. *J. Fluoresc*. **2008**, *18*, 1093. doi:10.1007/s10895-008-0357-7

[3] J. Widengren, U. Mets, R. Rigler, Fluorescence correlation spectroscopy of triplet states in solution: a theoretical and experimental study. *J. Phys. Chem*. **1995**, *99*, 13368. doi:10.1021/j100036a009