Nanoparticles' diffusivity studied by fluorescence recovery and holographic grating relaxation techniques

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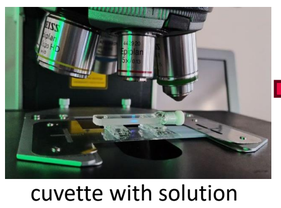
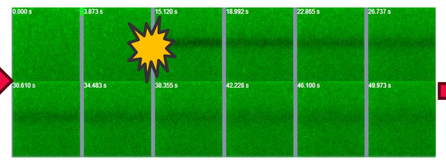
INTERNATIONAL RESEARCH AND EDUCATION CENTRE FOR PHYSICS OF NANOSTRUCTURES

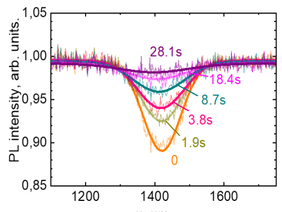
Stripe Fluorescence Recovery After Photobleaching (sFRAP) technique for diffusion studies



cuvette with solution scanned by laser beam

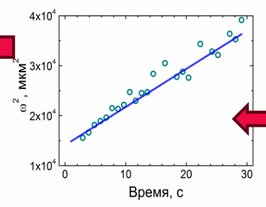


series of luminescent images after laser exposure of a narrow stripe



transversal luminescence intensity profiles

approximation by Gaussian function



dependence of the squared Gaussian width parameter on time

$$y = y_0 + A\frac{\exp\left(-\frac{2(x-x_c)^2}{w^2}\right)}{w\sqrt{\pi/2}}$$

$w^2=8Dt,$

Stokes-Einstein formula

$$D = \frac{k_B T}{6\pi\eta r}$$

D – diffusion coefficient

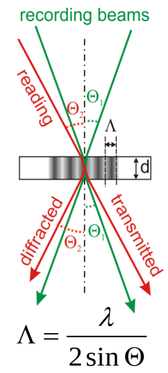
aggregation, gelation, destruction

spatial heterogeneity

r – hydrodynamic radius
h – (micro)viscosity

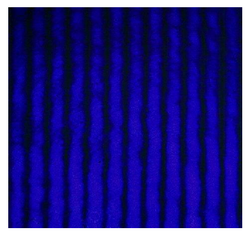
The luminescence recovery approach consists in exposing a narrow stripe of a sample to a focused laser beam, tracking the subsequent change in the spatial distribution of luminescence intensity in its transverse direction, and extracting the diffusion coefficient, then the particle size from the rate of change in its width. The technique was implemented using the Zeiss LSM 710 confocal laser scanning microscope.

Holographic grating relaxation technique (holographic relaxometry)



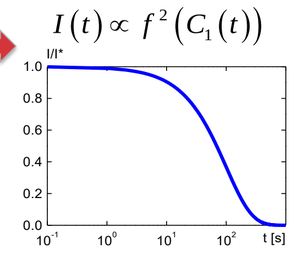
$$\Lambda = \frac{\lambda}{2\sin\Theta}$$

record interference pattern (grating)



monitor diffraction efficiency vs. time

$$I(t) \propto f^2\left(C_1(t)\right)$$



obtain diffusion coefficient, hence particle size

$$D = \frac{\Lambda^2}{4\pi^2\tau}$$

diffusion equation

initial condition (grating)

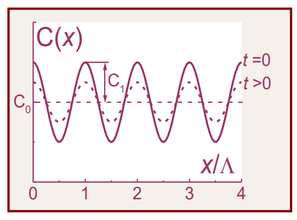
$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$$

$$C(x,0) = C_0 + C_1\cos\left(\frac{2\pi x}{\Lambda}\right)$$

$$C(x,t) = C_0 + C_1(t)\cos\left(\frac{2\pi x}{\Lambda}\right)$$

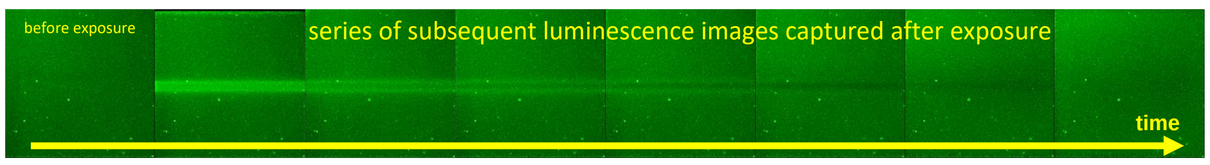
$$C_1(t) = C_1(0)\exp\left(-\frac{4\pi^2 Dt}{\Lambda^2}\right) = C_1(0)\exp\left(-\frac{t}{\tau}\right)$$

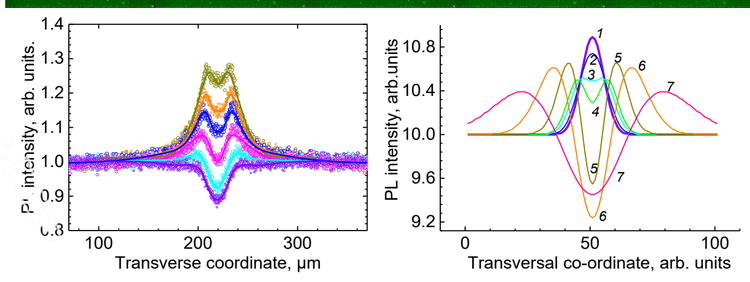
solution



The holographic grating relaxation method involves imprinting a diffraction grating in the sample being studied by exposure to an interference pattern, followed by monitoring its diffraction efficiency, which varies due to a decrease in concentration, hence of the refractive index, modulation, caused mainly by diffusion. The diffusion coefficient can be determined from the dependence of the grating relaxation rate on the spatial period. Both intact and phototransformed species may contribute into diffraction; in such case a biexponential relaxation should be analyzed, and two diffusion coefficients can be extracted.

Laser microscopy of phototransformed diffusivity

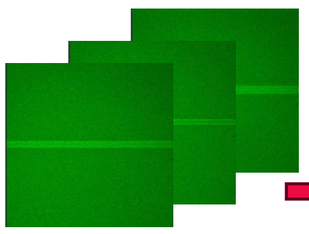




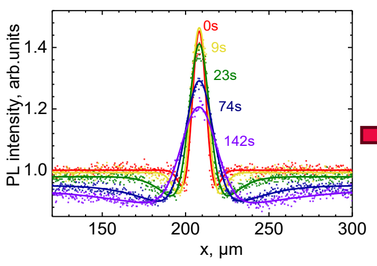
The transverse profiles of the luminescence intensity cannot be described by a Gaussian function, but by the difference of two such functions

$$I(x,t) = A\frac{\exp\left(-\frac{x^2}{4D_A t}\right)}{2\sqrt{\pi D_A t}} - B\frac{\exp\left(-\frac{x^2}{4D_B t}\right)}{2\sqrt{\pi D_B t}}$$

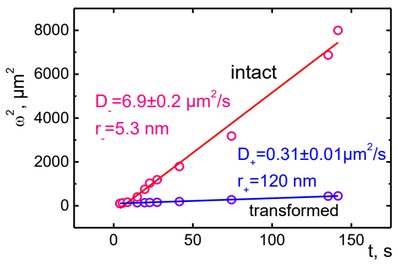
thus obtain information on both intact and phototransformed species



microscopic luminescence images of CD in colloidal solution under 488 nm excitation after exposure to 405 nm laser

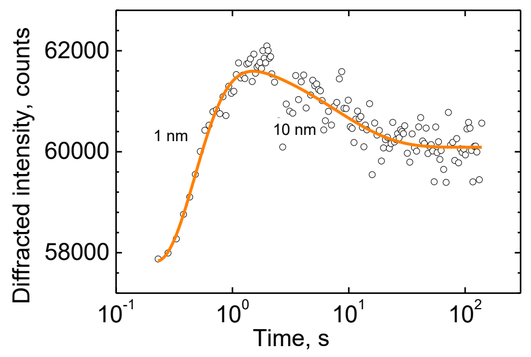


transversal PL profiles



squared Gaussian width vs. time

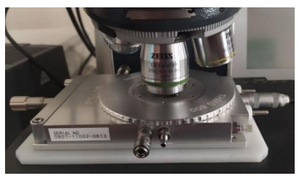
Holographic grating relaxation studies of carbon dots' diffusion

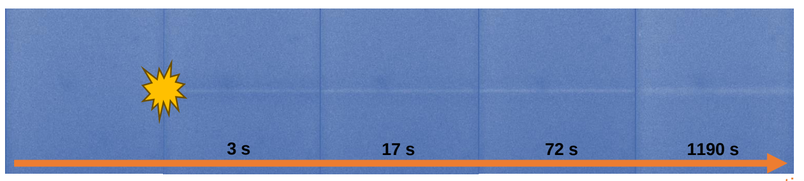


D_1=30 μm²/s, r_1=1nm
D_2=3 μm²/s, r_2=10nm

Study of diffusion in a model system

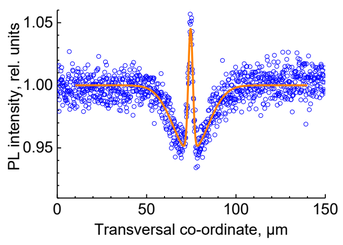
Fluorescence recovery (sFRAP)

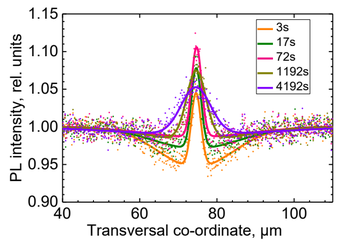


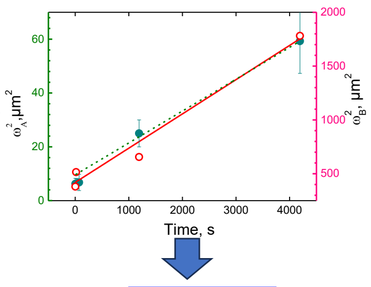


before exposure

luminescence images captured after exposure at 50°C

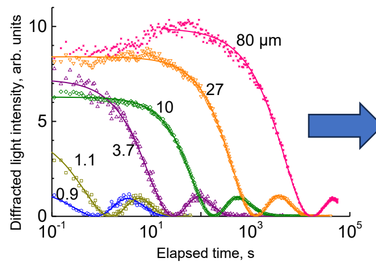


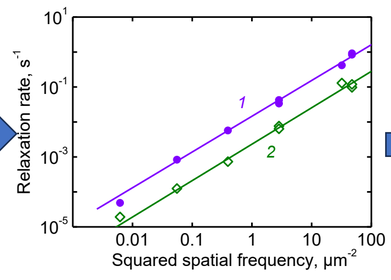




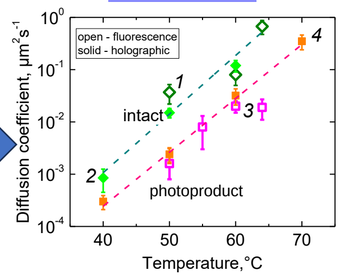
Holographic relaxation

50°C



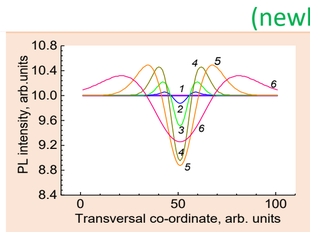
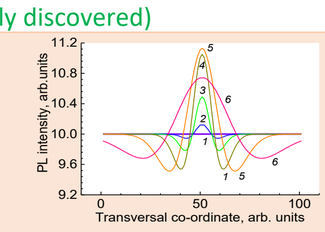
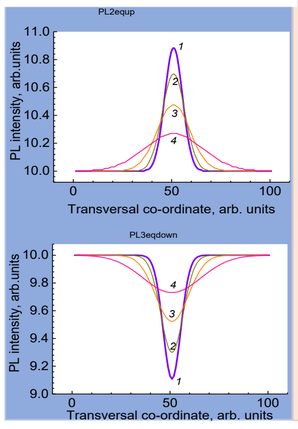
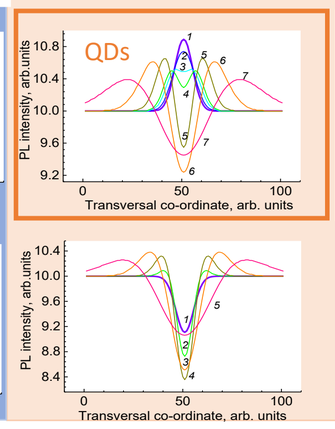
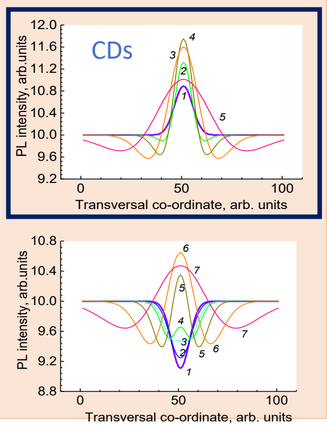
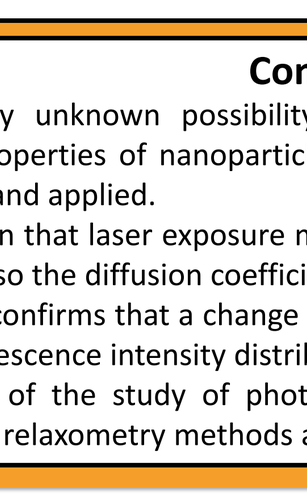
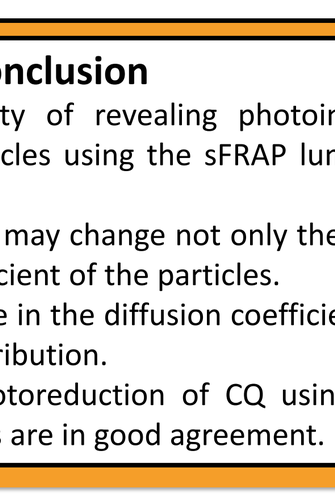
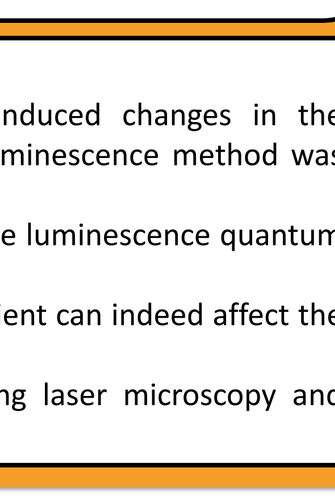


Comparison



The comparative study of camphoroquinone molecular (CQ) diffusion in a viscous melt was fulfilled using the luminescence recovery and the holographic grating relaxation techniques. The nonmonotonic kinetics of grating relaxation with two characteristic times has encouraged us to consider the simultaneous diffusion of two species. The coincidence, within the error bars, of the diffusion data obtained by the two methods confirms the new opportunities of the luminescence method in the study of phototransformations and allows us to interpret the unusual patterns of luminescence as evidencing for the changes in hydrodynamic sizes.

Simulated of luminescence profiles (8 cases)

	D unchanged (ordinary case)	*D increased (newly discovered)*	*D reduced*
PL quantum yield unchanged (yet fluorescence recovery takes place)			
PL quantum yield increased (photoactivation)			
PL quantum yield reduced (photodegradation)			

Conclusion

1. A previously unknown possibility of revealing photoinduced changes in the diffusion properties of nanoparticles using the sFRAP luminescence method was discovered and applied.
2. It was shown that laser exposure may change not only the luminescence quantum yield, but also the diffusion coefficient of the particles.
3. Simulation confirms that a change in the diffusion coefficient can indeed affect the photoluminescence intensity distribution.
4. The results of the study of photoreduction of CQ using laser microscopy and holographic relaxometry methods are in good agreement.

Acknowledgments

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