MEMORY IN BLINKING DYNAMICS OF SILVER NANOPARTICLES

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We present experimental results on emission dynamics of silver nanoparticles (NPs) deposited on a glass substrate. Upon continuous-wave excitation at 488 nm, Ag NPs emit light in the yellow, orange, and red spectral ranges. This emission is intermittent, consisting of distinct on- and off-periods (blinking) with on- and off-times showing power-law distributions. We find that subsequent on- and off-times of Ag NP emission are not independent, exhibiting correlation that extends for a few tens of blinking events, thus indicating the presence of memory in the process governing the NP blinking dynamics. To the best of our knowledge, this is the first observation of the presence of memory in blinking dynamics of metal nanoparticles.

1. Introduction

Single nanoemitters (semiconductor nanocrystals, organic molecules, and metal nanoparticles) under continuous optical excitation usually exhibit intermittent emission, switching between the bright (on) and dark (off) states, the phenomenon known as blinking [1]. The on- and off-times typically obey the power-law statistic, and this is one of the reasons why this phenomenon attracted so much attention during the last decades. Previously, it has been found [2] that on- and off-times of semiconductor nanoparticles, when considered as a function of the on-off switching event number, demonstrate the presence of memory in the system which persists for several tens of switching events. Very recently, the similar effect was observed for single molecules [3], albeit the correlation was found only for adjacent switching events. This puzzling phenomenon reflects the presence of memory in the process governing the emission blinking.

Here we present results of video-microscopy observations of emission from silver nanoparticles (NP) adsorbed on a glass substrate upon continuous-wave laser excitation and report what we believe to be the first experimental observation of memory in blinking dynamics of metal nanoparticles.

2. Experimental

Silver nanoparticles were produced using the method of Lee and Meisel [4] and characterized by scanning electron microscopy (SEM) and optical absorption

measurements. Samples for video-microscopy experiments were prepared by drying a droplet of Ag NP sol on a glass cover slide (Mentzel, Germany). Video-microscopy experiments were carried out on a setup built around an Axiovert 200 microscope (Zeiss, Germany). Continuous-wave optical excitation was provided using the 488 nm line of an Innova70C-Spectrum Ar/Kr ion mixed gas laser (Coherent, UK) focused at the back aperture of an α Plan-FLUAR 1.45 NA 100x oil-immersion objective (Zeiss, Germany). The excitation power density at the sample did not exceed 8 W/cm^2. Emission from nanoparticles was detected via the same objective using the Andor iXon3 EMCCD camera (Andor Technologies, UK) with the spatial resolution of 0.156 μm per pixel. The detection range (> 495 nm) was selected using a 495 DCXRV dichroic mirror, and the residual scattered excitation light was removed using a Raman RazorEdge 488 filter (both AHF-Analysetechnik, Germany). To study the emission dynamics, movies with the total duration of 1190 s were recorded with the frame rate of 72.5 frames/s. The movies were stored and processed off-line using a dedicated software written in Matlab (The MathWorks, USA).

3. Results and discussion

3.1. *Sample characterization*

Analysis of SEM images of Ag NPs deposited on a surface (data not shown) yielded the estimate of the Ag NP diameter of $d_{\mathrm{SEM}} = 73 \pm 15$ nm. Measurements of optical extinction spectra of Ag nanoparticle solution and their comparison with the predictions of the optical scattering theory [5] produced a value of $d_{\mathrm{abs}} \approx 55$ nm. These data are consistent with the ones previously reported [6] for Ag NPs produced by the same method.

3.2. *Emission dynamics of Ag nanoparticles*

Upon CW optical excitation at 488 nm of Ag NPs adsorbed on a glass substrate, bright spots of sizes below optical resolution are observed (Figure 1a) with distinct colors in the yellow, orange, and red regions. These single emitters[a] show characteristic on/off switching (blinking) with on- and off-periods having durations up to a few tens of seconds (Figure 1b). Our Ag NP samples do not show any signs of bleaching or other photodegradation, and the emission can be observed without changes in the mean intensity for hours. This allowed us to obtain reliable data on the distribution of on- and off-times t_{on} and t_{off} (Figure

[a] At the moment, it is unclear whether the emitting center involves just one or more Ag NPs.

1c,d). The distributions of t_{on} and t_{off} follow the power law $P(t_x) \propto t_x^{-m_x}$ with exponents $m_{on} \approx 1.94$ and $m_{off} \approx 1.70$, which agrees well with the recent data on Ag nanoparticle blinking [7].

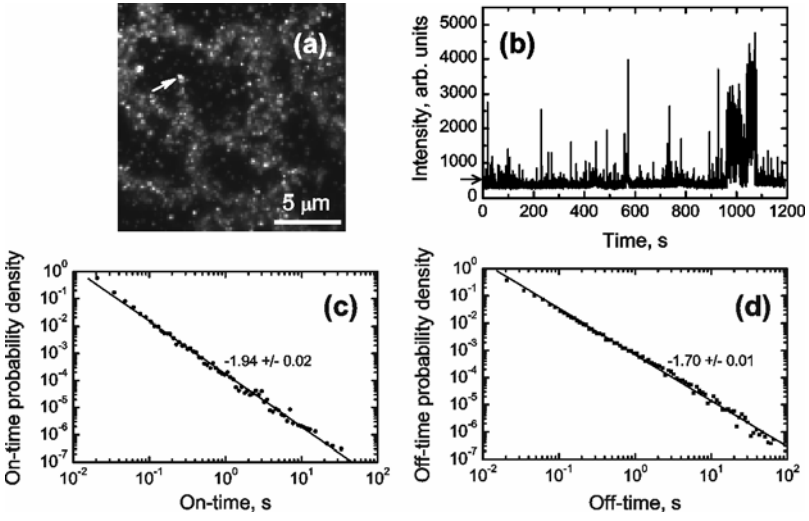

Figure 1. (a) Emission micrograph of an Ag NP sample; (b) Time dependence of the emission intensity of the single emitting center marked by the arrow in panel (a), the arrow at the Y-axis marks the on/off threshold; (c, d) on- and off-time distributions averaged over 11 distinct single emitting centers along with their power-law fits.

3.3. *Non-random patterns in Ag nanoparticle blinking*

A further insight into the mechanisms governing the blinking dynamics can be gained by studying the on- and off-times as a function of the on–off (off–on) switching event number *n*. Interestingly, both $t_{on}(n)$ and $t_{off}(n)$ do not behave completely randomly, but rather show correlated patterns (Figure 2a,b). Additionally, anticorrelation between $t_{on}(n)$ and $t_{off}(n)$ can be observed.

This behavior can be characterized in more detail by calculating the auto- and cross-correlation functions of on- and off-times or their logarithms $g_{xy}(\Delta n) = \left\langle \left(x(n) - \langle x \rangle\right)\left(y(n+\Delta n) - \langle y \rangle\right)\right\rangle \Big/ \left(\mathrm{var}\{x\}\,\mathrm{var}\{y\}\right)^{1/2}$; ($x, y = t_{on}, t_{off}$ or $x, y = \log t_{on}, \log t_{off}$). Notice that the correlation functions $g_{xy}(\Delta n)$ and $g_{xy}^{\log}(\Delta n)$ are mostly sensitive to the (cross-) correlation between large and short on- and off-times, respectively. Both correlation functions (Figure 2c,d) clearly indicate that the durations of the on- and off-states of single emitters in the Ag nanoparticle sample are correlated on the scale of a few tens of on-off (off-on) switching events. Taking into account that the mean on- and off-times

in our experiments were $\langle t_{on} \rangle = 0.08$ s and $\langle t_{off} \rangle = 0.7$ s, the memory in the system persists on the time scale of seconds.

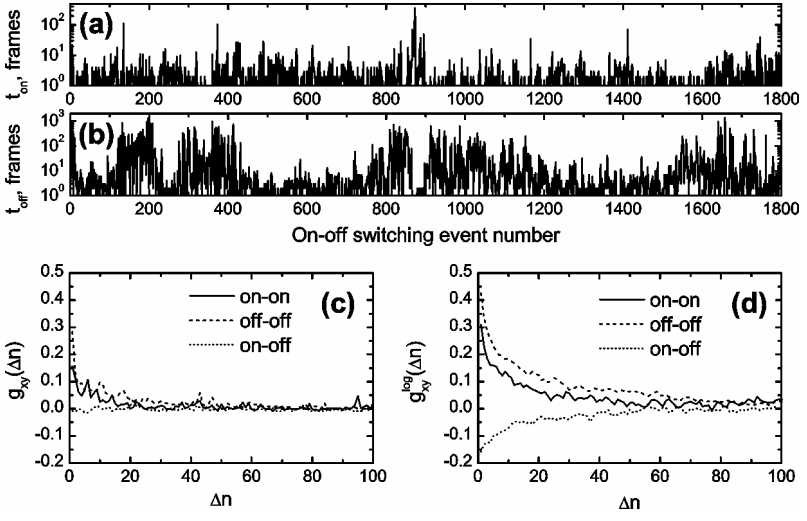

Figure 2. (a, b) Durations of the on- and off-times (1 frame = 13.8 ms) for the single emitting center of the Ag NP sample marked in Fig. 1a; (c, d) auto- and cross-correlation functions of on- and off-times and their logarithms averaged over the data for 11 distinct emitting centers.

Our observations of the presence of memory in emission blinking for metal NPs, put together with similar findings for semiconductor nanocrystals [2] and molecules [3], suggest the universal character of this phenomenon.

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