CdSe single-nanoparticle based active tips for near-field optical microscopy

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Abstract

We present a method to realize active optical tips for use in near-field optics that can operate at room temperature. A metal-coated optical tip is covered with a thin polymer layer stained with CdSe nanocrystals or nanorods at low density. The time analysis of the emission rate of the active tips and the analysis of their emission spectra reveal that a very small number of particles—possibly down to only one—can be made active at the tip apex. This opens the way to optics with a single inorganic nanoparticle as a light source.

1. Introduction

Current developments in aperture near-field scanning optical microscopy (NSOM) include the search for improved spatial resolution in the nanometre range where a novel optics is expected to emerge. Active tips made of a fluorescent nano-object attached to a regular tip [4] have much to offer in this context. Apart from challenging the ultimate resolution in optics, there are more fundamental stimuli to this research. For instance, standard electric-dipole selection rules in semiconductor quantum dots are expected to be strongly affected by multipolar contributions at ultra-high spatial resolution [1]. This is especially true when the latter approaches typical length scales of the semiconductor material such as its exciton Bohr radius [2]. In addition, a point-like source of light attached to a NSOM aperture tip has been argued to be the ideal tool for mapping all details of the photonic local density of states (LDOS), which is a fundamental near-field property of a surface [3].

A major breakthrough towards nano-optics with active tips has been realized by Michaelis et al [4] who have performed NSOM imaging with a single molecule serving as a point-like source of light that operates at low temperature. This pioneering work has been extended to other systems like colour centres in a diamond microcrystal [5] and rare-earth doped glass micro-particles [6]. Recently, Shubeita et al [7] have made a further step in the direction of active tips providing high spatial resolution. A thin polymer layer with a large number (of the order of 1000) of CdSe nanocrystals (NCs) has been deposited on coated optical tips. These active tips have been used at 300 K for NSOM fluorescence resonance energy transfer (FRET) imaging of single dye molecules. An optical resolution of 90 nm has been achieved. However, none of the works published so far is free from limitations such as low-temperature operation or/and limited spatial resolution due to the size of the supporting objects or number of active particles involved.

In this paper, we describe the emission properties of active tips made of a few CdSe nanoparticles (NPs), either NCs or nanorods (NRs), deposited at the apex of a tapered and coated tip. Our goal is to make photostable light nanosources working at room temperature and potentially able to offer optical resolution in the sub-10 nm range. Semiconductor NPs have a large potential in this respect because they have natural small dimensions, their optical properties are size-tunable, they possess an absorption threshold—rather than absorption bands as dye molecules, they are optically active at room temperature, and they are more photostable (little bleaching) than single molecules [8].

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2. Materials

ZnSe capped CdSe NCs have been synthesized following the procedure of Reiss et al [9]. The used core NCs have a diameter of 3.8 nm. After growing a ZnSe shell of approximately 1 nm thickness on their surface, the resulting CdSe/ZnSe core/shell NCs exhibit a room-temperature photoluminescence (PL) quantum yield of about 70% in chloroform and a size dispersion < 10%. With the goal to improve their stability against photo-oxidation, the surface of the CdSe/ZnSe NCs has been functionalized with tridecanedithioic acid [10]. Recently, several advances in the synthesis of colloidal semiconductor NCs have been made, allowing for size and shape control [11, 12]. Of particular interest in this context is the possibility to obtain quantum confined CdSe NRs with a narrow distribution of length and diameter. The NRs [12] used in this work have a diameter of 3.9 nm and a length of 13 nm and are coated with a ZnSe/ZnS double shell. The intermediate ZnSe shell provides strain relaxation at the interface between the CdSe core and the outer ZnS shell [13], in a similar manner as in the CdSe/CdS/ZnS system [14]. After shell growth, the NRs have a diameter of 4.4 nm and a length of 21.5 nm (aspect ratio 4.9).

3. Scanning confocal microscopy

Before depositing a small number of CdSe NPs at the optical tip apex, it is necessary to characterize their emission properties in a more conventional environment. This is done at room temperature (all measurements presented in this paper are performed at room temperature) by means of scanning confocal microscopy of a polymer (PMMA) film containing CdSe NPs. Samples are prepared by spin coating the film onto a glass cover slip. CdSe NPs are excited with the 458 nm spectral line of a cw Ar+ laser through a 100× infinity-corrected objective (NA = 1.3). The PL signal, which is selected in the spectral window 540–620 nm with suitable optical filtering, is collected via the same objective.

A series of measurements consists in detecting this PL signal by an avalanche photodiode in photon counting mode. PL images are then acquired by raster scanning the sample through the excitation spot of the microscope. Four fluorescence images of CdSe NP doped PMMA film are shown in figure 1. The typical blinking behaviour [15, 16] of several isolated objects can be clearly observed both for NCs and NRs. The ‘off’ periods of the PL emission can be seen as horizontal dark stripes in some of the PL spots. As a consequence of this blinking, the images are only partly acquired. Nevertheless, up to four individual NCs can be distinguished in figures 1(a) and (b), with possibly a very weak fifth one in the lower left corner, whereas presumably only one NR is seen on each image of figures 1(c) and (d). Although not elucidated so far [17],
the PL intermittency phenomenon is commonly attributed to electron (or hole) ejection via an Auger process [15], which leaves a charged particle switching the nanocrystal in a 'dark' state: other photogenerated electron–hole pairs will recombine non-radiatively until the excess charge leaves the nanocrystal.

In figures 2(a) and (b), the PL intensity is plotted as a function of time for NCs and NRs, respectively. Here, scanning has been stopped, in such a way that the laser spot is focused on a single NP previously isolated in a PL image similar to those of figure 1. It is clearly seen that the single NPs alternate 'on' and 'off' periods with some 'offs' having duration in excess of 100 s. Although this blinking can raise problems in some applications, it turns out to be an advantage here because it helps us to evaluate the number of active NPs at the apex of the optical tip as described later in the paper. Indeed, isolated particles blink in a discrete manner as shown in figure 1 and figures 2(a) and (b) whereas a large ensemble of NCs does not exhibit such a behaviour. This is because individuals of a large ensemble are not synchronized and an average behaviour is revealed.

A second characterization consists in spectrally analysing the filtered PL signal by means of a spectrometer equipped with a cooled charged-coupled device. Figures 2(c) and (d) compare spectra of a single CdSe NC, respectively NR, with spectra of the corresponding ensemble. In both cases, single NPs have Gaussian spectra that are substantially narrower—typically 20 nm in the wavelength domain—than the ensemble. The full width at half maximum (FWHM) of the ensemble is 35 nm for NCs and even 40 nm for NRs, respectively. This reflects the size dispersion of NPs. In principle, the blinking behaviour of single NPs should also manifest itself in the spectra (see below), but the large integration time of 5 min required to have sizable signal strength in our confocal spectrometer hindered such an observation. The behaviour observed here in both the PL time traces (i.e. discrete blinking) and PL spectra (rather narrow spectra) of single NPs serves as a valuable reference for characterizing them when located at the apex of an optical tip as described in the next section.

4. Active optical tips

4.1. Preparation

Since the fluorescence signals emitted by a few NPs attached to an optical tip are expected to have very low intensity, it is most important to start with substrate tips delivering an extremely low parasitic fluorescence signal. Our tips have been prepared by a special chemical-etching process of pure silica optical fibres and they have been subsequently coated with aluminium. They offer a free optical aperture at the apex in the 150 nm range and a large transmission of the order of $10^{-2}$. Details of their fabrication procedure and of their optical properties will be given elsewhere. CdSe single-NP based active optical tips are prepared in the same manner as by
Figure 5. Spectral analysis of CdSe NPs on the active probe. The intensity is normalized and is represented with stretched false colours. Red corresponds to vanishingly small PL intensity, purple to high intensity. (a) A series of 42 successive spectra is shown as a function of time for CdSe/ZnSe NCs. Each spectrum is collected over 30 s. The excitation intensity is 230 W cm⁻². (b) A few experimental spectra selected from the series shown in (a). Also shown is multi-peak fitting of the spectra. (c) A series of 27 successive spectra is shown as a function of time for CdSe/ZnS NRs. Each spectrum is collected over 15 s. The excitation intensity is 170 W cm⁻². (d) A few experimental spectra selected from the series shown in (c).

4.2. Characterization and results

The four successive time traces shown in figure 4(a), respectively figure 4(b), reveal a clear switching between ‘on-like’ and ‘off-like’ intensities for NCs, respectively NRs. This mimics the behaviour of single NPs in a PMMA film described above. This is a strong indication that the number of active NPs involved is certainly of the order of a few units only. This number goes down to zero over some periods of time since the ‘off’ intensity matches the small background fluorescence of the substrate tip. This behaviour is very clear for NCs (figure 4(a)) but is less marked for the optical tip stained with NRs (figure 4(b)) which already showed an unusual strong background fluorescence prior to depositing the thin PMMA layer. This is possibly due to undesired pollution at the tip apex.

The trend, suggested by the time traces of figure 4(a), that only a few NCs contribute to the PL signal is confirmed by the spectral analysis of figure 5(a) which shows in a (time, wavelength) plane 42 successive spectra of the PL emitted by the active probe. A scheme of the experimental set-up is given in figure 3.
PL intensity is represented with a stretched false colour in the (time, wavelength) plane. Clearly, several periods with no PL emission at all (red) can be seen, e.g., at around 200, 400, and 1200 s along the time axis. This corresponds to an ‘off’ state extending at least over 30 s. In addition, it can be seen that the emission wavelength(s) change(s) dramatically with time during the ‘on’ periods. This manifests itself in figure 5(a) as large shifts in peak positions (purple) along the wavelength axis. This is due to a combination of a change in time of the number of NCs being actually active and of possible spectral diffusions of individual NCs [18]. An interesting subsidiary finding in our experiments is that not all of the CdSe nanoemitters are quenched at the tip apex despite the proximity of the aluminium coating; see figure 3.

Figure 5(b) is a selection of a few spectra taken from the above series that confirms that the PL spectra change dramatically with time. The spectrum in the middle (bottom) shows two (one) peak(s) with an FWHM of the order of 15–20 nm similar to that shown in figure 2(c) for a single NC. The upper spectrum does not show any PL at all, which suggests that all of the NCs have turned off during the collection of this spectrum, in agreement with the red lines seen in figure 5(a). Again this is reminiscent of the blinking behaviour observed for single NCs dispersed in a PMMA film. Due to the limited integration time of 30 s, it is indeed possible here to observe the blinking in the spectral domain in contrast with figure 2(c) (integration time ten times longer).

The active tip made of CdSe NRs gives similar results as shown in figure 5(c), which gives 27 successive spectra in a (time, wavelength) plane, and in figure 5(d), which is a selection of a few spectra taken from this series. Here, spectra have been collected over 15 s only. The only noticeable difference is that the active tip has no apparent ‘off’ state over this 15 s time window because of the fastest blinking of NRs, already seen in figure 4(b).

As a complementary test, similar measurements have been made on an active tip stained with a high concentration of CdSe/ZnSe NCs. In figure 6, no blinking is observed either in time traces or in spectra. These observations give a strong indication that only a few NCs contribute to the PL of the active tip in figures 4 and 5.

5. Conclusions

In summary, a method for elaborating CdSe NPs-based active NSOM tips operating at room temperature has been described. Both the spectral and temporal behaviour of the active tips confirm that only a limited number of NPs, either NCs or NRs, are actually active at the tip apex. This opens the way to near-field optics using a single semiconductor NP as light source—a nanosystem potentially much more photostable than a single molecule. An obvious ongoing extension of the present work is to perform NSOM imaging of test surfaces using these active tips.

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