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Review

Near-field microscopy with a scanning nitrogen-vacancy color center in a diamond nanocrystal: A brief review

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AD, AC, OM, MB and SH wish to dedicate this review article to their co-author and colleague Yannick Sonnefraud who passed away in September 2014. Yannick initiated this research in 2008 (Sonnefraud et al., 2008)

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ABSTRACT

We review our recent developments of near-field scanning optical microscopy (NSOM) that uses an active tip made of a single fluorescent nanodiamond (ND) grafted onto the apex of a substrate fiber tip. The ND hosting a limited number of nitrogen-vacancy (NV) color centers, such a tip is a scanning quantum source of light. The method for preparing the ND-based tips and their basic properties are summarized. Then we discuss theoretically the concept of spatial resolution that is achievable in this special NSOM configuration and find it to be only limited by the scan height over the imaged system, in contrast with the standard aperture-tip NSOM whose resolution depends critically on both the scan height and aperture diameter. Finally, we describe a scheme we have introduced recently for high-resolution imaging of nanoplasmonic structures with ND-based tips that is capable of approaching the ultimate resolution anticipated by theory.

Contents

1. Motivation: beyond classical near-field microscopy

Since its birth in the early 80s (Pohl et al., 1984), NSOM (Courjon, 2003) became a versatile tool for optical imaging at very high spatial resolution in the nanometer range (Novotny and Hecht, 2006). Yet one fundamental issue with NSOM is the optical resolution offered by a given system. Standard systems based on aperture-NSOM (Pohl et al., 1984) with a hole at the apex of a metal-coated conical tip are fundamentally limited by the size of the optical aperture (Betzig and Chichester, 1993; Gersen et al., 2001; Obermüller et al., 1995a; Obermüller and Karrai, 1995b; Drezet et al., 2002, 2004a). In order to improve the optical resolution one could ideally use a point-like emitting source.

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Recently, inspired by the pioneer work by (Michaelis et al., 2000) who used a fluorescent single molecule at low temperature as basis for a NSOM, we developed a high-resolution NSOM tip that makes use of an NV center in a diamond nanocrystal as a scanning point-like light source (Cuche et al., 2009a) (see also Schröder et al., 2011). In this active tip the 20 nm nanocrystal is glued in situ to the apex of an etched optical fiber probe. The NV center acts as a photostable (non blinking, non bleaching) single-photon source working at room temperature (RT) (Beveratos et al., 2002; Sonnefraud et al., 2008). As such, the NV-center based tip proves to be superior to quantum-dot based tips (Chevalier et al., 2005), which suffer from insufficient photostability (Sonnefraud et al., 2006), to insulating-nanoparticle based tips, which, despite remarkable photostability, cannot reach the single-photon emission rate (Cuche et al., 2009b), and to tip-embedded light-emitting-diodes (Hoshino et al., 2012), which are quite involved to fabricate. Therefore, the ND-based NSOM probe opens new avenues for microscopy and quantum optics in the near-field regime.

In this paper we review our contribution to this field and discuss the potentiality of such active-tip based NSOM in terms of spatial resolution. Note that high-resolution apertureless NSOM (Zenhausern et al., 1994; Bachelot et al., 1995) or NSOM based on specially nanostructured passive tips (Mivelle et al., 2014; Eter et al., 2014; Singh et al., 2014) are not covered by the present brief review. In Section 2 we describe in detail the fabrication process of such tips and show how to characterize them. We emphasize in particular the quantum properties of the NV emitters and show how to characterize the photon emission statistics of the NV emitters at the NSOM tip apex. In Section 3 we show how to use such an active tip for imaging and analyze its optical resolution. The theoretical limit of the optical resolving power is discussed in Section 4 and the potentiality of the NV-based NSOM tip in the emerging field of quantum plasmonics is shortly reviewed in Section 5. Finally, we present in Section 6 some recent results concerning nano-manipulation and displacement of NVs using a NSOM tip.

2. NV center-based active tip

Color centers in diamond (Gruber et al., 1997), in particular NV centers, are very promising for the purpose of developing active NSOM. They are room-temperature single-photon emitters (Beveratos et al., 2001, 2002), their photostability is well established (Beveratos et al., 2001) and they are hosted by nanocrystals with steadily decreasing sizes thanks to progress in material processing (Chang et al., 2008; Sonnefraud et al., 2008; Boudou et al., 2009; Smith et al., 2009). Early use of NV-center doped diamond nanocrystals in NSOM active tips (Kühn et al., 2001) was, however, limited by the size of the hosting crystal, which was beyond the 50 nm range, so that the promise of single NV-occupancy, i.e. single-photon emission, was counterbalanced by size excess that prevents positioning with nanometer accuracy. The recent spectacular reduction in size (Chang et al., 2008; Sonnefraud et al., 2008; Boudou et al., 2009; Smith et al., 2009) of fluorescent nanodiamonds (NDs), down to approximately 5 nm (Smith et al., 2009), suggests that such limitation no longer exists and that active optical tips made of an ultra-small (well below 50 nm in size) ND with single NV-occupancy should be possible to achieve.

Our scanning single-photon sources are produced in a single transmission NSOM (Sonnefraud et al., 2006, 2008) environment. We successively use the optical tip for the imaging and selection of the very ND to be grafted at the tip apex, for controlled attachment of the latter, and subsequent NSOM imaging of test surfaces. A sketch of the optical setup is shown in Fig. 1. After pre-selection of the NDs in the confocal geometry, the NV-center emission is excited with the 488 or 515 nm line of an Ar^+-Kr^+ CW laser that is injected by an uncoated optical tip and is collected into a multimode optical fiber through a microscope objective. The remaining excitation light is removed by means of a dichroic mirror complemented either by a band-pass filter centered at 607±35 nm for photon counting and imaging or a long-pass filter (> 532 nm) for spectra acquisition of the neutral and negatively-charged NV centers (Dumeige et al., 2004). The collection fiber can be connected either to an avalanche photodiode (APD) for imaging and optical control of the ND manipulation, to a charge-coupled device attached to a spectrometer, or to a Hanbury-Brown and Twiss (HBT) correlator for photon correlation measurements. In the HBT module, a long-pass filter (750 nm) and a diaphragm placed in front of each detector eliminate most of the detrimental optical cross-talk.

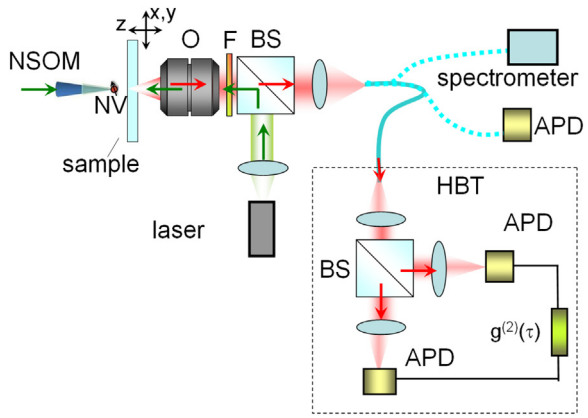

Fig. 1. Scheme of the optical setup used for tip functionalization with a single fluorescent ND; (O = microscope objective, F = optical filters and dichroic mirror, BS = beamsplitter, APD = avalanche photodiode in the single-photon counting mode). The optical excitation from an Ar^+-Kr^+ CW laser is launched from the polymer-coated optical tip and the NV-center fluorescence is collected by a high NA objective, filtered, and injected into a multimode optical fiber. The latter can be connected either to an APD, a spectrometer, or a HBT correlator, which involves a 50/50 BS, two APDs and a time-correlated single-photon counting module (for details see Cuche et al., 2009a). The latter delivers the second-order time-intensity correlation function $g^{(2)}(\tau)$: see text. Note that a rapid pre-selection of the NDs is usually made prior to the ND grafting: this is achieved by using the setup first in the confocal mode with the excitation being launched to the sample through the microscope objective O directly (green beam on the figure). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The method that we have designed (Cuche et al., 2009a) to trap in a controlled way a well-selected single ND at the optical tip apex is as follows (see Fig. 2). The uncoated optical tip is covered with a thin layer of poly-l-lysine, a polymer able to cover homogenously the tip, including the apex (radius of curvature below 30 nm). In addition, poly-l-lysine is positively charged. This facilitates electrostatic attraction of the NDs, which bear negatively charged carboxylic groups on their surface. This polymer-covered tip is glued on one prong of a tuning-fork (Karrai and Grober, 1995) for shear-force feedback and mounted in the NSOM microscope.

The first step is to image the sample fluorescence to the far-field by scanning the surface under the optical tip with a very large tip-sample distance of 3 μm. This allows for selecting an interesting area with isolated NDs. In a second step, the tip is brought into the surface near-field by using shear-force regulation. A near-field fluorescence image together with a shear-force topography image are simultaneously recorded at a rather large tip-sample distance of about 50 nm (usual cruise altitudes for NSOM imaging are between 20 nm and 30 nm) in order to identify an isolated small sized ND with a fluorescence level among the lowest-intensity spots detected in the entire scanned area. This last point is taken as a hint that this very ND presumably hosts a single color center. This essential point can be checked in situ by photon-correlation

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