Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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SUBWAVELENGTH MOLECULAR OPTICS: THE WORLD'S SMALLEST LIGHT SOURCE?

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Abstract How does one pass a photon through a tube with a diameter 1/100 or 1/1000 that of its wavelength? This question is relevant to our production of a subwavelength light source. Schematically, it is a concentric, conical, gold-coated, glass tube with an inner diameter tapering down from about 5 to 0.05 microns into which a crystal of anthracene was grown. It is illuminated on the large end by UV light from a CW argon-ion laser. It emits (from the small end) an evanescent beam of blue light (about 10^5 photons/sec). This EXCITOR (exciton transmitted optical radiation) source has been used as a scanning tip for near-field optical microscopy. The theoretical resolution limit is about 100 times below the diffraction limit. the same EXCITOR tip is also a Scanning Forster donor (exciton transfer probe). For instance, it is quenched by a thin (transparent) gold layer at distances below 100 Å.

INTRODUCTION

Recently there has been considerable interest in the development of schemes for subwavelength illumination.[1-4] The aim of most of this research has been to advance near-field light microscopic imaging of surfaces at the resolution of a scanning electron microscope. Indeed, such super-resolution light microscopy has enabled researchers to optically examine a variety of specimens without being limited by the diffraction properties of visible light. The basis of this near-field imaging technique is the following: As an electromagnetic wave emerges from an aperture it is at first highly collimated to the aperture dimension and it is only after the wave has propagated a finite distance from the aperture that the diffraction which limits classical optical imaging takes effect. Thus, in the near field region, a beam

of light exists that is largely independent of the wavelength and determined solely by the size and shape of the aperture.[5] A critical factor in such near-field imaging systems is the nature of the light probe that accomplishes the sub-wavelength illumination. In this paper we present a unique approach for producing sources of light with sub-wavelength confinement and significant amplification. Our method involves aiding the transmission of light through subwavelength dimensions with the introduction of crystals that store light energy as excitons, propagate these excitons in dimensions that are less than 10 nm, and then emit the light in a highly local region of a surface.

The literature contains several approaches for producing sub-wavelength illumination. All of these approaches involve the aperturing of a larger light source with some form of aperture. One of the more successful methods for producing such sub-wavelength apertures has been a metal coated glass micropipette which can be produced readily with inner diameters (at the tip) of less than 50 nm.[6,7] The details of pipette fabrication have been described elsewhere.[6,7] Even though the dimension of these pipettes can be reduced significantly below 50 nm it has been argued that it would be difficult to reduce the spot size of such a light probe below this diameter. The essence of the argument is that the spot size of such an aperture depends ultimately on the finite conductivity of the metallic coating around the pipette. In order to appreciate this point one has to remember that there are no propagating electromagnetic modes in a subwavelength cylindrical metallic waveguide such as a metal coated pipette. The least attenuated mode for a round aperture has been found to be the TE_{11} mode for which the energy decays at a rate of:

$$E = E_0 \exp [-2 \times 1.81 (l/a)]$$

where l is the length of the aperture and a is the radius.[5] With a sufficiently rapid tapering of the pipette, however, this evanescent region can be kept short enough to obtain a fairly large throughput of light. In addition to this effect, consider that the electromagnetic wave penetrates the metallic coating and decays within it at a finite rate given by:

$$E = E_0 \exp (-d/c)$$

where d is the depth of penetration and c is the extinction length of the metal. When the attenuation due to the waveguide effect exceeds the attenuation in the metal, the contrast between the aperture and the surrounding medium becomes insufficient for superresolution applications. The metal with the largest opacity in the visible region is aluminum, for which c = 6.5 nm when the wavelength is 500 nm. This yields a minimum useable aperture of about 50 nm. In practice, multilayered coatings are necessary to obtain good adhesion and a practical aperture is expected to perform with lower efficiency.

The solution presented here is based on the fact that excitons can be confined to molecular and atomic dimensions under appropriate conditions.[8-16] With this approach, energy can be guided directly to the aperture at the pipette tip instead of being allowed to propagate freely in the form of an electromagnetic wave through a region of the pipette whose dimension cannot support a propagating mode. Such energy confining materials can be excited through radiative processes to produce an abundance of excitons that allow light to be effectively transmitted through the "bottleneck" created by the subwavelength dimensions of the tip near the aperture. The excitons can be produced directly at the tip or they can be generated within the bulk of the material and allowed to diffuse to the tip via an energy transfer mechanism.[8-12] In either case, these excitons will then undergo a radiative decay, producing a tiny source of light at the very tip of the pipette.

The proximity of the metal coating along the outer surface of the pipette does not interfere with the exciton transfer. The throughput is basically independent of the wavelength and is a linear function of the aperture size. However, the excitons at the tip can be quenced by a sample brought close to it as shown in preliminary experiments using 200 Å gold films. These experiments are a dynamic version of previous static experiments on excited molecules in front of metallic surfaces.[17-19]

EXPERIMENTAL PROCEDURE

To demonstrate the feasibility and usefulness of the method we chose to work with crystals of molecular anthracene because of its well-characterized electrical and radiative properties. Crystals of anthracene

were grown inside the tip of a pipette from a benzene solution. By varying the concentration of the solution, the size of the deposited crystal could be accurately controlled.

The source of excitation for our experiments was the 363.8 nm line of an argon ion laser. Anthracene exhibits a very strong fluorescence in the blue with a quantum efficiency approaching unity when illuminated in the near U.V. The crystal can be illuminated either by directing the light through the pipette, as in the standard aperturing method, or alternatively, by having an external beam incident on the crystal at the tip of the pipette. Figure 1 is a picture of the pipette with a fairly large crystal of anthracene, shown here magnified about 1000X.

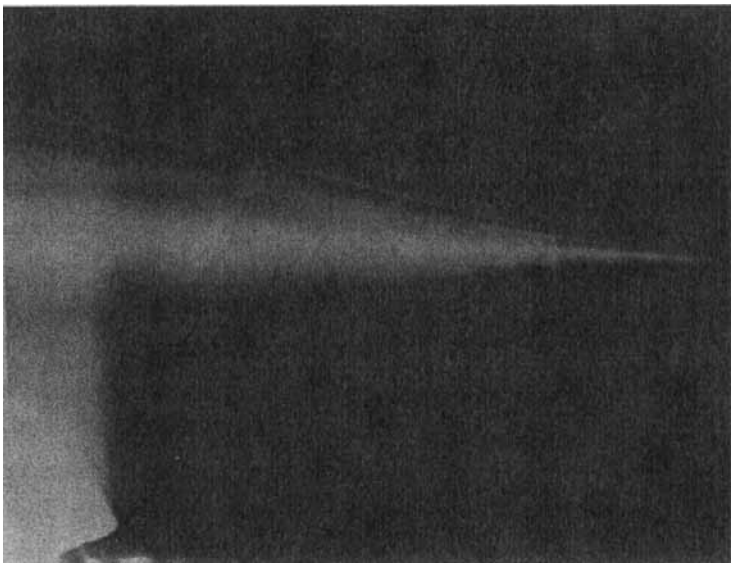

Figure 1. A micro-pipette exciton light source (gold coated) with an anthracene tip.

To show that the anthracene does indeed aid in guiding light through a pipette, the throughput was measured for an empty pipette and compared to the same pipette with a crystal in it. The pipette was illuminated by inserting an 0.21 mm fiber up to the very tip. The

light emerging from the pipette was collected with a photomultiplier using a photon counting system. The pipette was then removed from the system, a small crystal grown inside the tip and replaced in exactly the same position. Both the U.V. and the blue fluorescence was collected, although most of the light was converted to the visible. The experiment was repeated for a large number of pipettes of different dimensions and different illumination intensities. We did not correct for glass (pipette) fluorescence (which was approximately 30% of the signal observed in the empty pipette) and non-linearity in the photomultiplier. The quenching due to a gold film (200 Å) on a glass plate was demonstrated by Z-direction piezoelectric scanning (5-150 Å from the coated plate). We note that the 200 Å gold film is practically transparent to blue light (emitted from the anthracene tip when not quenched). The UV laser light was filtered and did not affect the output of the photomultiplier tube (placed behind the glass plate). This tube measures light *transmitted* through the plate.

RESULTS AND DISCUSSION

Amplification was seen in all the pipettes tested with an inner diameter below several microns. The largest gain observed was a transmission of 2.9 times that of an empty pipette. We note that correcting for fluorescence from the pipette and phototube non-linearity can only increase these values. The actual throughput was dependent chiefly on the dimension of the pipette, but could easily be controlled by adjusting the alignment of the optical delivery system. Counts of several hundred thousand photons per second could be achieved for moderately small (0.25 μ) pipettes, although lower intensities were preferable so as not to saturate the photomultiplier.

The smaller the dimensions of the pipette the greater the gain in transmission should be, although the absolute value of the signal will decrease. This was generally observed to be the case, although quantitative data was difficult to obtain due to the difficulty in characterizing the precise profile of the pipette. In addition, the crystals do not grow uniformly and the size and shape vary from pipette to pipette with a corresponding change in the gain. The crystal also aids in transmitting light through pipettes larger than half a wavelength since

much of the energy exiting the fiber is in higher order modes than TE_{11} and have correspondingly larger cutoff diameters. Geometric factors may also work to increase the throughput in anthracene filled pipettes even when the diameter is larger than the cutoff, since part of the light incident on the inner wall, which otherwise would have been lost, will be re-emitted from the crystal coating the wall along the axis of the pipette and will reach the aperture. It was only when the pipette was broken at the tip to obtain a very large aperture that we saw a decrease in transmission due to the crystal blocking the propagation of the light.

The quenching by the gold film gives an S-shaped curve of light intensity vs. distance from the gold film. The quenching is small at distances above 100 Å and very high at distances below 20 Å. There is good qualitative agreement with previous experiments and theory.[18]

In summary, the observed efficient propagation of excitons in nanometer dimension crystals is in line with previous studies on exciton transport and percolation in mixed crystals,[12] impregnated pores[13] and polymer blends.[16] The metal quenching is closely connected with the problem of an excited molecule in front of a metallic surface.[17-19] The evanescent behavior of our luminescent subwavelength light-source is analogous to light transmitted through nano-apertures.[1-7] Furthermore, we note that the EXCITOR can also be excited via electroluminescence.[11]

APPLICATIONS

The importance and applicability of such light sources for sub-wavelength imaging using the methodologies of near-field microscopy are obvious. However, the availability of such a source of excitons in a confined crystal that can be brought close to a surface, with the micromovement capabilities developed for scanned tip microscopies,[20] could have important implications both for imaging with light and for molecular sensing with light. First, it is interesting to note that if one brought such a crystal within a few nanometers of a surface containing acceptors for its excitons, the excitation of such a surface would be many orders of magnitude more efficient than direct excitation of the same surface with freely propagating light. For example, for a

dye such as rhodamine, the absorption cross-section of a molecule requires 10^9 incident photons for a single photon to be absorbed but the presence of a single exciton of the appropriate characteristics is capable of causing this same effect. Second, given this capability of effective single-molecule excitation with an exciton source, and given the presence of such a source in a pipette that can be scanned with high resolution across a surface, leads to a new way of imaging with light that surpasses any presently available methodologies. Thus, in terms of its use in molecular exciton microscopy, molecular sensing or, for that matter, as a cheap and compact short wavelength light source, the methodologies described in this paper have much potential.

CONCLUSIONS

We have developed a technique for producing a sub-wavelength light source by packing light in the form of excitons within a molecular crystal that is held in the confined space of a pipette tip. We have also demonstrated that such a nanometer exciton light source (EXCITOR) is significantly quenched by closeby exciton acceptors. This opens the way for using the EXCITOR as an energy donor probe in scanning microscopies and as a controlled nanometer photon source. This technique has applicability in a number of areas in both fundamental and applied science.

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