Future Opportunities in Nanophotonics

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ABSTRACT

Nanophotonics, dealing with optical science and technology at nanoscale, is an exciting new frontier, which provides numerous opportunities both for fundamental research and new applications of photonics. The Institute for Lasers, Photonics and Biophotonics at Buffalo has a comprehensive multidisciplinary program in Nanophotonics funded by the United States Department of Defense. This program focuses on three major areas of Nanophotonics: (i) interactions involving nanoscale confined radiation, (ii) use of nanoscale photoexcitation for nanofabrication and (iii) design and control of excitation dynamics in nanostructured optical materials.
Selected examples of our accomplishments in nanophotonics are presented here which illustrate some of the opportunities.

1. INTRODUCTION

Nanophotonics involves a fusion of Photonics with NanoScience and Technology.[1] It offers challenging opportunities for studying fundamental processes of interaction between the light and matter on a nanoscale, much smaller than the wavelength of radiation, as well as for development of nanostructured optical materials suitable for novel applications. Furthermore, the use of such confined interactions to spatially localize photochemical processes also offers exciting technological opportunities for nanofabrication. These potentials for Nanophotonics are being recognized worldwide as is evident by a considerable growth of new programs both at academia and industries.

Our Institute for Lasers, Photonics and Biophotonics leads a multiinstitutional, multidisciplinary program in organic and polymeric Nanophotonics, funded by the Chemistry and Life Sciences Directorate of the Air Force Office of Scientific Research under the Defense University Research Institute on Nanotechnology Program. The focus is on information technology covering communication, signal processing, storage and display, where nanotechlogogy is used to provide significant gain at each stage.

The work on nanoscale confinement of matter has focused on near field studies of nonlinear optical interactions. The research on the nanoscale confinement of matter for photonics has focused on nanoparticles, nanocomposites, dendrimers and self-assemblying or externally directed ordering of nanostructures. Nanoscale photofabrication has been used for optical memory applications.

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2. NANOSCALE-CONFINEMENT OF NONLINEAR OPTICAL INTERACTIONS

Experimental studies of nanoscale nonlinear optical interactions have utilized the arrangement shown in Figure 1 which consists of a combination of near-field scanning optical microscopy (NSOM) and photon scanning tunneling microscopy (PSTM).[1]

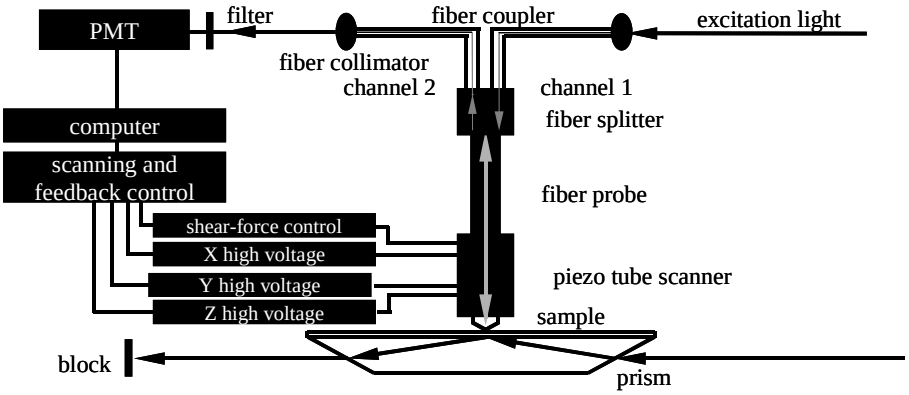

Figure 1. Schematics of experimental arrangement used for combined NSOM and PSTM.

In NSOM, either the sample is excited in the near field by the light emanating from the fiber tip (near field excitation), or the emitted light from the sample, now excited in the far-field, is collected by the fiber tip (near field collection). In the PSTM geometry, the sample is excited by an evanescent wave (tunneling photon) emanating from a prism surface at which light is incident at a total internal reflection angle. A combination of NSOM and PSTM has been utilized in our laboratory in which a sample interacts with the incident light in the PSTM geometry, and the nonlinear optical response (e.g., second harmonic generation or third harmonic generation) is collected in the near field by the fiber tip (near field collection). The spatial resolution is determined by the fiber tip size. This method provides the advantage that high intensity pulses can be conveniently used for nonlinear optical interaction studies. We have studied both second-order and third-order nonlinear optical processes.

An example is provided by the study of third order nonlinear optical interactions in organic nanocrystals of DEANST having dimensions ~100 nm. Excitation in this case was provided at 1064 nm, from a nanosecond Nd:Yag laser.[2] Figure 2 shows the spectra of the nonlinear optical response from a single nanocrystal. It generates two types of nonlinear optical response: (i) third-harmonic generation, seen as a sharp peak at precisely $\lambda/3$ = 355 nm, derived from the absolute value of $\chi^{(3)}$ of the sample and (ii) two-photon emission, seen as a broad peak at ~585 nm, derived from the imaginary part of $\chi^{(3)}$.

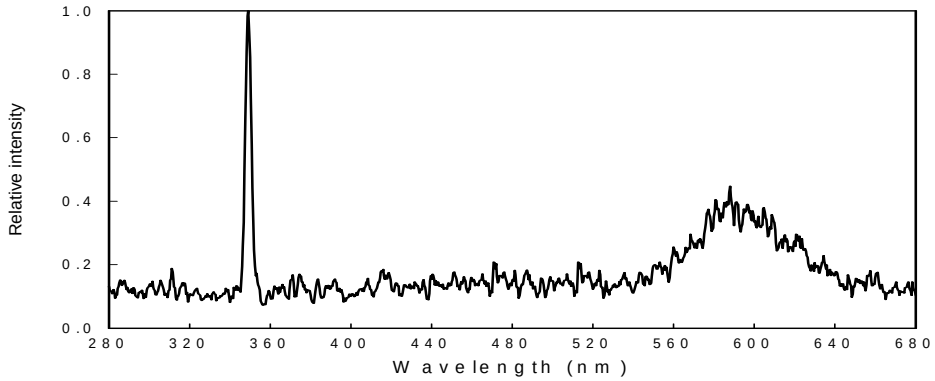

Figure 2. Near field third harmonic generation and two-photon emission from a ~100 nm size nanocrystal of the organic molecule, DEANST.

The angular distribution of both the third-harmonic generation and the two-photon emissions obtained by rotation of the polarization of the linearly polarized incident beam were the same. They fitted well with the anisotropy of the $\chi^{(3)}$ tensor, showing nanoscale ordering in the nanocrystal with the same $\chi^{(3)}$ tensor property as in the bulk sample.

More recently, our study has focused on the study of dynamical processes in nanodomains using time-resolved pump-probe experiments. In a recent study, we used femtosecond pulses at 800 nm to saturate, by two-photon excitation, a transition in a highly efficient two-photon absorbing material.[3] The recovering of saturation was monitored by using linear absorption of a 400 nm probe pulse, time-delayed with respect to the pump pulse. The transmitted probe was collected by the fiber tip (near field collection). The advantage of this approach is that the pump and the probe, derived from the same laser source (~400 nm is obtained by frequency doubling of 800 nm), are widely separated in frequency to be easily discriminated. The recovery time of the saturation provides information on the excited state lifetime. It was found that the excited state lifetime is strongly dependent on the distance between the fiber tip and the sample, the shorter the distance the faster the observed decay. The result was quantitatively fitted into a non-radiative decay model involving interaction between the sample dipole and the metal coating of the outer surface of the fiber tip.

3. NANOSCALE-CONFINEMENT OF OPTICAL MATERIALS

Nanoscale confinement of optical materials can be utilized to produce novel classes of nanomaterials with control of their optical interactions and dynamics. Nanostructure control also provides integration of inorganic and organic nanodomains to produce hybrid materials with unique optically multifunctional properties.

Nanomaterial technology allows one to achieve the followings: (i) produce quantum confined structures with the prospect to judiciously control the electronic bandgap, (ii) control the excitation dynamics and photo-induced carrier dynamics, (iii) disperse in a polymer matrix or a sol-gel glass to form nanocomposites and (iv) control the dynamics at the hybrid interface between an inorganic and an organic component.

An example of nanostructure control of excited state dynamics in a nanoparticle to enhance a particular optical manifestation is provided by the rare earth doped nanoparticles. In the rare-earth ion containing nanostructures, phonon interactions with the surrounding lattice and subsequently the excited state relaxation are controlled to produce enhancement of a particular emission. An important type of emission is that of the Er^{3+} ions at 1,550 nm which forms the basis for optical amplification. We have shown that the nanostructure control produces significant increase of the emission lifetime, from 8 m sec to 17 m sec to provide improved optical amplification ability.[4] Another important type of emission is up-conversion, where excitation by a CW-IR laser beam at 974 nm produces up-converted emission in the red, green or blue regions, depending on the nanostructure composition and interactions of the rare-earth ion containing nanoparticles.[5] This up-conversion process finds important applications for bioimaging and light-activated therapy.

Another major thrust of our program in development of nanomaterials is on producing inorganic:organic nanocomposites. We are focusing on nanocomposites containing inorganic quantum dots dispersed in a polymer matrix. These are novel systems providing opportunities for fundamental studies of photogeneration of charge-carriers, charge-transfer across the inorganic:organic interface and the carrier mobilities.[6, 7] We are also exploring the applications of these hybrid nanocomposites for photorefractivity and for electroluminescence. From the point view of charge carrier mobility, a quantum dot:polymer nanocomposite is a novel system with the inorganic nanoparticles providing photosensitization. In these systems, we are investigating if the nanoparticles enhance charge carrier transport or they contribute to trapping. Another aspect being investigated is if one can improve the speed of response of a hybrid nanocomposite photorefractive material by enhancing the mobility of the polymer host in the presence of the quantum dots.

The carrier mobility was measured in a CdS quantum dot:polymer nanocomposite using a time-of-flight measurement.[7] Figure 3 shows the mobility of the nanocomposite as a function of field. Our results of charge-carrier mobility provides the following information:

- A dispersive transport is observed for holes.
- The mobility data, activation energies, field dependences are similar to those of PVK.
- There is a discernible enhancement of carrier mobility (a factor of less than an order of magnitude at the best) due to the presence of nanoparticles.
- The concentration of nanoparticles is too low for percolation. The enhancement more likely arises from local field effects.

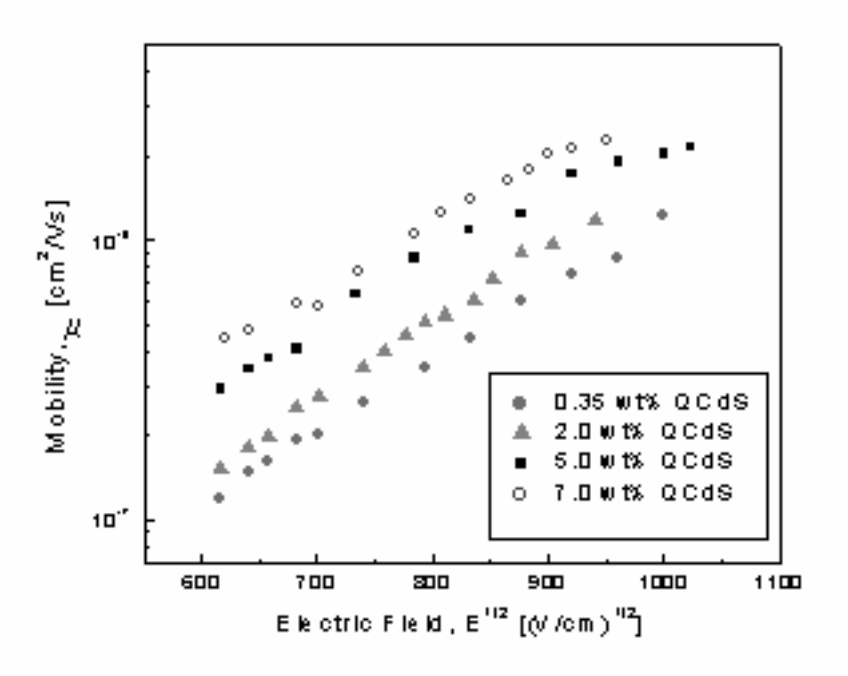

Figure 3. Comparison of field dependencies of hole mobilities in samples having varying concentrations of CdS nanoparticles at 297K.

We have used a photorefractive nanocomposite containing HgS or PbS nanocrystals dispersed in the PVK matrix containing electro-optic chromophore NPP and the TCP platicizer to obtain photorefractivity at the communication wavelength of 1.3 μm.[8] A net two-beam coupling gain was observed.

More recently, we have used a polymer dispersed liquid crystal nanocomposite for photorefractivity, which consists of the following components: (i) a quantum dot such as CdS for photosensitization, (ii) liquid crystal nanodroplets for electro-optic effect and (iii) a hole transporting matrix consisting of hole transporting molecules, ethyl carbazole (ECZ) dispersed in the PMMA polymer.[9] This nanocomposite exhibited a very photorefractive figure of merit with a net diffraction efficiency reaching a very high value of over 70% as the applied bias field was increased. This result is shown in Figure 4.

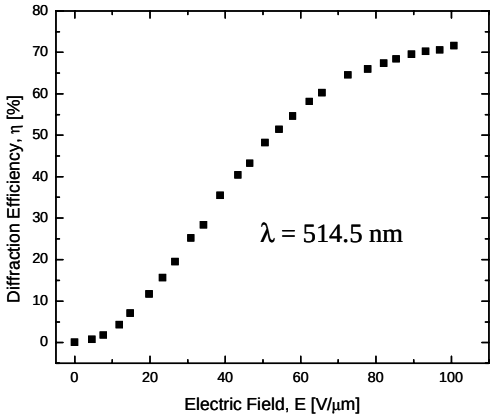

Figure 4. Net diffraction efficiency of the polymer dispersed liquid crystal nanocomposite containing CdS quantum dots for photosensitizations. The wavelength used is 514.5 nm from an argon-ion laser.

Another area of nanoscale material development is ordering of nanoparticles to produce amplification or co-operative interactions leading to new manifestations. An example is provided by our work on investigating nonlinear optical effects in photonic crystals. Photonic crystals are periodic dielectric structures of domains of two different refractive indices.[10] The periodicity is of the order of a specific wavelength of light, at which a band gap (or a pseudo gap) opens up. At this gap wavelength, light transmission through the photonic crystal medium is significantly altered. We have observed a dramatic enhancement of third harmonic generation in 3-D polystyrene photonic crystals pumped by a near infrared laser beam.[11] As the pump wavelength is tuned, the peak of the enhancement occurs when the third harmonic wavelength approaches the short-wavelength edge of the band gap. We show that the origin of the enhancement is phase matching provided by the periodic structure of the photonic crystals. We have observed enhancement of two-photon emission at the edge of the pseudogap in a photonic crystal.[12] This effect is derived from local field enhancement near the edge.

4. NANOSCALE PHOTOFABRICATION

Near field excitation can be used for photofabrication and nanolithography. Two-photon excitation which, because of quadratic dependence on excitation intensity, shows enhanced spatial localization compared to one-photon excitation, provides better spatial resolution. We have utilized photobleaching of dyes to achieve pixels of ~70 nm dimensions which can be read by fluorescence method for optical data storage .[13]

5. NANOMATERIALS FOR BIOPHOTONICS

A major application of nanoparticles being investigated at our Institute is in the area of biophotonics. Biophotonics is an emerging hot field dealing with interaction of light with biological matters.[14] The applications range from optical bioimaging to light activation of drugs using a nanoparticle platform.

A major development at our Institute is the use of nanochemistry to form Nanoclinics.[15] Nanoclinics are nanoscale silica bubbles containing optical probes, magnetic probes and drug delivery systems. The surface of these nanoparticles are functionalized with appropriate carrier groups to carry them to cancer (or diseased) cells. Another development targeting application to biophotonics is that of up-converting Y_2O_3 nanoparticles containing Er^{3+}. Er^{3+}

ions in these nanoparticles can be excited at 975 nm in the IR to generate efficient emission in the visible (green and red).[16] We are using these nanoparticles for bioimaging and for photodynamic therapy.

6. FUTURE OPPORTUNITIES

The opportunities are multidisciplinary, ranging from understanding of physics of optical processes and their dynamics on nanoscopic scale, to development of novel optical materials, to their applications in information technology and biotechnology. Some of these opportunities are listed in Table 1.

Table 1: Future Directions

- Ordered and Self-Assembled Nanocomposites and Superlattices
- Novel Photonic Crystal Media
- Nanoscale Nonlinear Processes
- Dynamics of Excitation on Nanoscale
- Nanomedicine
- Nanotechnology for Photodynamic Therapy
- Nano-Biophotonic Probes (Nanofluorophores)

7. ACKNOWLEDGEMENTS

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