Spatial-Mapping of Photoemission from Plasmonic Nanoparticle Arrays

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The ability of plasmonic nanoparticles to spatially confine light to sub-wavelength volumes and produce strongly enhanced nanoscale optical fields has lent them to a wide-variety of applications. Recently, these capabilities of plasmonic nanostructures have been used to develop ultrafast, surface plasmon-enhanced electron sources.[1,2] Understanding the nanoscale spatial distribution of electrons produced at nanostructured electron sources will be key to their implementation as electron emitters in applications such as ultrafast electron microscopy and spectroscopy, photochemical devices, and lightwave electronics.

Volpe *et al*. recently used poly(methyl methacrylate) (PMMA) as an imaging layer to map hotspots in the optical near-field of plasmonic nanorods.[3] In this work, we have used a similar method to that described by Volpe *et al*. to probe the spatial distribution of electrons emitted from plasmonic Au nanorods.

We fabricated arrays of 20-30 nm wide Au nanorods by electron-beam lithography (EBL) on indium doped tin oxide (ITO) substrates (Figure 1). The nanorod arrays were then coated with a 20-nm-thick layer of PMMA (*Microchem Corp*.) and electron emission was excited by illumination with an Er:fiber seeded supercontinuum (SC) femtosecond laser source producing 9.5 fs pulses, with a central wavelength of 1.2 μm (1.0-1.4 μm), and a repetition rate of 78.4 MHz. The optical excitation was linearly polarized so that the optical field was aligned to the long-axis of the Au nanorods, and the laser was focused to a 5 μm diameter spot on the nanorod array. Typical exposure doses used in this work were estimated to be equivalent to an electron dose of ~ 10^7 electron/nm^2 at the tips of the nanorods for exposure times of 10 s. PMMA was developed in 3:1 IPA:MIBK at 0 °C for 30 s to produce the results shown in Figures 1 and 2. It should be noted that PMMA absorbs light with a wavelength of 200 nm and as such six-photon absorption in the plasmon-enhanced near-field could lead to PMMA decomposition. However, results of bias-dependent measurements shown in figure 2 suggest that electrons are responsible for the formation of the PMMA features observed, and as such, the PMMA features are representative of the spatial distribution of electrons emitted from the Au nanorods.

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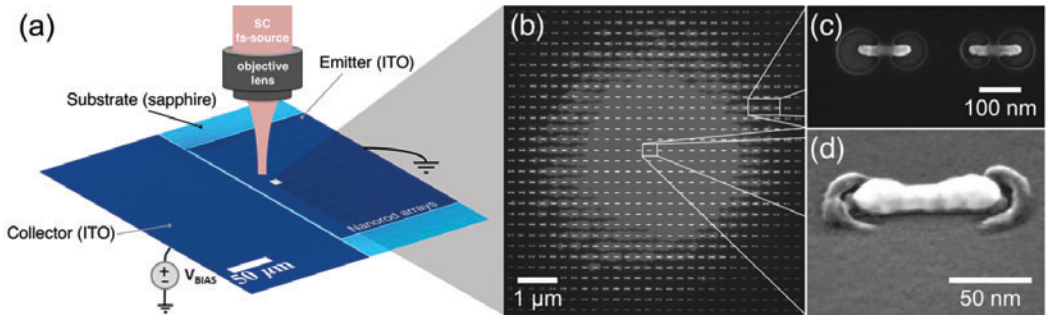

Figure 1: a. *Experimental setup. 9.5 fs laser pulses (central wavelength 1.2 μm) were focused to a 4 μm diameter spot on Au nanorod arrays fabricated on an ITO-coated (dark blue regions) sapphire substrate (light blue regions). A 2 μm gap was etched in the ITO layer to allow a bias to be applied between the nanorod array cathode (dark blue region on right) and the anode or collector (dark blue region on left).* ***b.*** *Top-down SEM micrograph of Au nanorod array coated with 20 nm PMMA following exposure to ~10^9 pulses.* ***c.*** *SEM micrograph of Au nanorods at the periphery of the laser-spot following exposure and development. The regions of developed PMMA at the tips of the Au nanorods define the regions of plasmonic near-field enhancement.* ***d.*** *Tilted-view (45 degree) SEM image of Au nanorod at the center of the laser-spot. The rod displays crescents of cross-linked (negative-tone) PMMA near each pole. The crescents are likely a result of charge recombination at the substrate due to image-charge forces from the substrate acting on emitted electrons.*

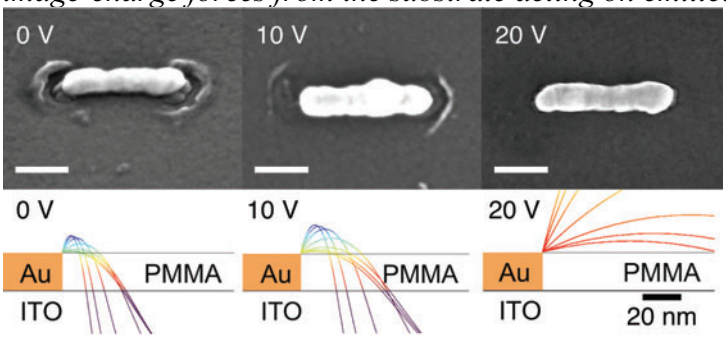

Figure 2*: (top row) SEM micrographs of Au nanorods coated with 20 nm PMMA following 10 s exposures at various anode bias values. The micrographs were acquired following the removal of uncrosslinked PMMA in acetone. At low anode bias values (0 V and 10 V) two regions of crosslinked PMMA are observed, one directly at the nanorod apexes, and a second arc-shaped region 10-20 nm from the nanorod apex. The arc-shaped regions are not observed for higher values of anode bias suggesting that these regions are formed by charged particles and as such depend on the applied anode bias. All scale bars shown represent a length of 50 nm. (bottom row) Simulated electron trajectories for each applied anode bias assuming a constant static field due to image-charge.*

This material is based upon work supported as part of the Center for Excitonics, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001088. The EELS were carried out at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No DE-AC02-98CH10886. We would like to also acknowledge support from the Gordon and Betty Moore Foundation.