June 4, 2012

(Channels of Entangled Nanoparticles Discovered by Visualization in Space and Time)

Supporting Online Material

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EXPERIMENTAL METHODS

Experiments were carried out in Caltech's second-generation ultrafast electron microscope (UEM-2). A high power femtosecond laser system is integrated with a modified transmission electron microscope (TEM) which operates at 200 kV and is equipped with a post-column spectrometer. In a UEM, photo-electron packets are used for imaging, in contrast to a continuous beam of electrons produced either thermally or by field-emission in a conventional TEM. A femtosecond optical pulse (250 fs), with an average photon energy of 4.8 eV (wavelength of 260 nm), extracts electrons from the cathode via the photoelectric effect. This ultrashort electron pulse is then accelerated to 200 keV. For optimal temporal and energy resolution, experiments were carried out near the single electron limit of UEM operation [1, 2]. Another optical pulse, at 519 nm wavelength (2.4 eV), excites the nanoparticles and induces the near-fields. These fields follow the Gaussian temporal shape of the inducing pulse; *i.e.* they rise and decay within the ultrashort pulse duration.

The PINEM imaging is accomplished by controlling the pulse arrival times using an optical delay line, thereby achieving synchronous temporal overlap of these fields with the probing electrons. Since both pulses have similar durations, a scan of time delay yields a cross-correlation-type PINEM intensity profile. All the reported data in the main text is acquired with the delay set for maximum PINEM intensity, defined as time-zero, *i.e.* when fields are arrested at the peak incident fluence.

The laser system, which has variable repetition rates, operated at 400 KHz, and the green beam was focused to a spot size on the specimen measured accurately, by a newly designed apparatus to be described elsewhere (J.S. Baskin & A.H. Zewail), to be 35 μm in diameter, resulting in a peak pulse fluence ranging from 2.1 to 3.9 mJ/cm^2. These values correspond to peak electric fields of $2.3 \cdot 10^6$ V/cm and $3.2 \cdot 10^6$ V/cm, respectively (using the above-mentioned pulse duration). The linear polarization of the green laser was controlled with a half-wave plate outside the microscope.

The PINEM images were obtained by analyzing the scattered electrons with the GIF spectrometer. An energy selecting slit, 10 eV wide, was placed at the energy gain side of the zero-loss-peak in order to filter only those electrons that have gained energy. The slit was centered at +6 eV, selecting electrons with energies between +1 eV and +11 eV. This window corresponds to ~ 4 peak orders (10/2.4 = 4.1) which is sufficient to capture essentially all of the inelastically scattered electrons at the peak electric fields employed. To minimize the effects of sample drift and to increase signal-to-noise ratio, the measurement protocol consisted of acquiring between 12 and 20 images with 20 seconds acquisition time for each image. These data were then digitally averaged after correcting for the sample drift. No further image processing was applied and the results are displayed in the paper. For both PINEM and UEM images, an objective aperture was used in order to minimize the spurious effects that may have resulted from the diffracted beams.

The silver nanoparticle sample was prepared by pipetting a commercially available 100 nm particle solution from *nanoComposix* onto a graphene/graphite sample purchased from

Graphene Supermarket. After letting the sample dry in open air, it was directly transferred to the electron microscope. Before the measurements, the sample was treated with the green laser at high powers (10 mJ/cm^2 pulse fluence) for one minute. This process heated up the particles and caused them to acquire more spherical shapes, where facets were generally not observed.

DIFFRACTION CONTRAST OF THE PARTICLES

Besides the inelastic scattering of ultrafast electrons with the near-fields, the diffraction of electrons by crystalline nanoparticles could contribute to the contrast of the particles themselves. Although this contrast is irrelevant for the void-channel region, it is the primary reason for the relatively lower intensities seen on the particles. As the ultrafast electrons interact with the lattice of a crystalline material, they undergo elastic Bragg scattering that deflects the electrons out of the range of the objective aperture. This process decreases the number of electrons in the primary beam and, therefore, nanoparticles appear darker in the bright field UEM images. The same process is operative in PINEM images, but scattering from the dipolar fields at the top and bottom half-planes of the particle also occurs, causing in Figure 1A,B, for example the straight low intensity feature that crosses the particle from the joining point (zero-charge point) of the void-channel to the opposite edge (mapped with light blue color in PINEM images shown). This indicates that the image intensities inside the particles' boundaries are composed of diffraction and PINEM contrast.

The fraction of the incident electrons undergoing diffraction will generally depend on the particle orientation and thickness, on the extinction coefficient of the diffracting crystalline planes, and on the size of the objective aperture. Nevertheless, this fraction can be experimentally measured using bright field images, such as those shown in Figure 1. For instance, the particle pair in the inset of Figure 1A transmits 20% (left particle) and 6% (right particle) of the incoming electrons. As a result, it is expected that the left particle will show more field contrast in the PINEM image than the right particle. Indeed, this is what is experimentally observed in Figure 1A where the straight feature in the inside of the left particle is more visible than the one in right. The particles in Figure 1B transmit 15% of the incoming electrons and, hence, their contrast is similar to that of the left particle in Figure 1A.

REFERENCES

[1] A.H. Zewail & J.M. Thomas, "4D Electron Microscopy", Imperial College Press, London, 2009.

[2] A.H. Zewail, "Four-Dimensional Electron Microscopy", *Science*, **328**, 187-193 (2010).