Real space and real time observation of plasmon wavepacket dynamics in single gold nanorod

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Abstract: We applied ultrafast time-resolved near-field optical microscopy to spatio-temporal observation of plasmon dynamics in a gold nanorod. We found prominent changes of transient near-field images as time evolves, indicating coherent excitation of multiple plasmon modes.
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1. Introduction

Noble metal nanostructures attract much attention in various research fields because of their unique optical properties arising plasmon such as confinement of optical fields into nano space. Full understanding of plasmonic properties of metal nanostructures is of fundamental importance to achieve nanoscale control of optical fields. Direct observation of the dynamic behavior of the spatial feature of plasmons is essential for that purpose, but is quite challenging because we need nanometer spatial resolution and sub-20-fs time resolution, considering the spatial scale and the dephasing time scale of plasmons [1].

Combination of scanning near-field optical microscopy (SNOM) with ultrafast spectroscopy achieves nanometric spatial resolution and sub-20-fs time resolution simultaneously [2], and we applied the ultrafast SNOM to spatio-temporal observation of plasmon wavepacket dynamics in a gold nanorod. Broadband ultrashort pulse can coherently excite two or more plasmon modes with different resonance frequencies and spatial structures. In the present study, two longitudinal plasmon modes of a gold nanorod were excited with femtosecond pulses. We found in the transient near-field images two plasmon-mode features appear alternately with time at the delay region around ~20 fs. This is a characteristic behavior for coherent superposition of more than two states.

2. Experimental section

The experimental setup for ultrafast SNOM system is similar to that reported previously [2]. The system consists of an interferometer, dispersion compensation devices and SNOM system. The output pulse of Ti:sapphire laser (~800 nm, 12 fs) was delivered to a Michelson interferometer for time-resolved measurement. Then, the sequence of pump and probe pulses passed through a grating pair and chirped mirrors so that a large amount of material dispersion arising from the optical components in the SNOM system (optical fiber of the aperture probe, in particular) was compensated up to the 3rd order. A 4-f-sytem based pulse shaper equipped with a deformable mirror was also used to compensate the higher order dispersion adaptively. The SNOM system consists of a commercial aperture near-field probe (aperture diameter of ~100 nm), an XYZ piezo-driven stage and a detection system. The pulse was introduced into the optical fiber of the near-field probe and near-field radiation at the probe tip illuminated the sample. The distance between the sample surface and the probe tip was regulated at ~10 nm by shear-force feedback method. To obtain shortest pulse after probe tip, we adaptively controlled the pulse shape adaptively to maximize the second harmonic (SH) generated at the near-field probe tip. We placed a BBO crystal at the sample stage to generate the SH signal. The pulse duration was evaluated by SH autocorrelation. The full width at half maximum of the autocorrelation trance was 23 fs, corresponding to ~15fs pulse duration. To get transient near-field images of the sample, we detected two-photon-induced photoluminescence (TPI-PL) from gold in the wavelength region of 500–675 nm as the signal, at every point in the scanning area of the sample. Because of the two-photon induced nature of the luminescence, we can obtain time-correlated signal by detecting the luminescence while scanning the delay time between the pump and probe pulses, which reflects the dynamics occurred in the intermediate state (plasmon resonance in the present case) of the two-photon excitation. We constructed a transient near-field image by collecting TPI-PL signals at a fixed time delay. We also obtained static near-field transmission and two-photon excitation images. For the static transmission measurement, we used a Xe discharge lamp as a light source and detected the transmitted light by a spectrometer. Static two-photon excitation images were obtained by detecting TPI-PL under irradiation of narrow spectral-band pulses from wavelength-tunable Ti:sapphire laser (λ = 680–1600 nm, >140 fs). The sample gold nanorod was fabricated by electron-beam lithography lift-off technique. The designed size of the rod was 1000 nm in length, 40 nm in width, and 20 nm in height.

3. Result and Discussion

Near-field absorption spectrum of the nanorod is shown in Fig. 1(a). Two broad absorption bands, whose peaks are at 805 nm and 870 nm, respectively, are found in the spectral region of irradiated pulses. The transmission image observed at 865 nm (shown in Fig 1(b)) shows a spatially oscillation pattern along the long axis of the nanorod. This feature reflects the standing wave function of higher-order plasmon mode (*m*=6) of the nanorod [3]; at the antinodes of the wave function, strong extinction is observed due to high transition probability of the plasmon resonance. Since the plasmon excitation enhances the local optical field, two-photon excitation image at the excitation wavelength of 870 nm (Fig. 1(c)) also provides similar spatial pattern with higher contrast. The wave function of another resonant plasmon mode (*m*=7) can also be visualized by changing excitation wavelength (800 nm, Fig. 1(d)).

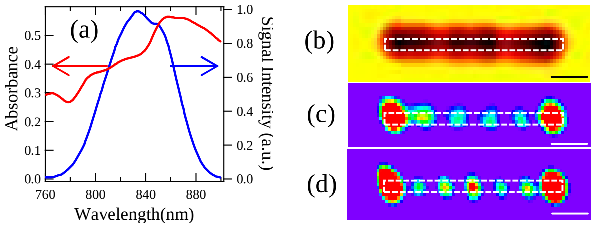

Fig. 1 (a) Near-field absorption spectrum and spectral profile of the irradiated pulses. (b) Near-field transmission image of the gold nanorod probed at 865 nm. (c, d) Near-field two-photon excitation images of the same nanorod excited at (c) 870 nm and (d) 800 nm. Dashed lines represent the outlines of the rod. Scale bar: 200nm.

Typical time-resolved TPI-PL signal is shown in Fig. 2(a). The time-resolved signal becomes broader than SH autocorrelation from BBO crystal. This broadening involves effects of lifetime of the intermediate state of two-photon excitation, most representatively plasmon dephasing. The temporally oscillating signal remains even after the correlation between the pump and the probe pulses disappeared, because the plasmon retains the coherence. The time-resolved signal involves even much longer (>50 fs) decay component than the plasmon lifetime (<20 fs), which indicates the existence of long-lived species. This species is attributed to hot electrons after plasmon dephasing [4].

Here, we focus on transient images at shorter timescale. At zero time delay (Fig. 2(b)), spatial oscillation is obscured in the image due to simultaneous excitation of two plamon modes with different spatial features. As time delay increases, transient images changes gradually. Especially, at the time delay of about 20 fs, transient image alternates with time between two patterns: one is similar to the image in Fig. 1(c) observed upon excitation of the *m*=6 mode as shown in Fig. 2(c), and the other is similar to that in Fig. 1(d) of the *m*=7 mode as shown in Fig. 2(d). This observation can be explained by the difference of oscillation period between the two modes. After excitation, each plasmon mode oscillates at its characteristic resonant frequency (oscillation period of 2.68 fs for *m*=7 and 2.88 fs for *m*=6). The intensity of the time-resolved TPI-PL signal is related with not only the population of the plasmons but also the relative phases. Since the phase difference between the two modes is 0.16 rad per fs, the two modes are expected to be out of phase at the time delay of ~20 fs. This is consistent with our present experimental findings.

From these results, we are sure that wavepacket dynamics of the plasmons can be visualized as the dynamic near-field images. We believe that this experiment can be extended to coherent control of plasmon wavepackets.

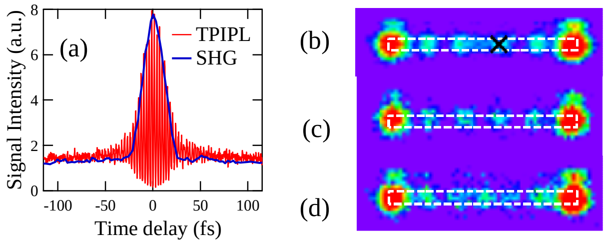

Fig. 2 (a) Time-resolved TPI-PL signal measured at the position × in (b) and envelope of SH autocorrelation from BBO crystal. (b,c,d) Transient TPI-PL image of a gold nanorod at the time delay of (b) 0 fs, (c) 19.8 fs and (d) 21.2 fs. Dashed lines represent the outlines of the rod.

4. References

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