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Ultrafast dynamics of near-field enhancements at an off-resonance nano-dimer via femtosecond laser excitations

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Abstract – Giant electric-field enhancements localized on nano-antennas are important for the optical near-field applications in fields such as super-resolution imaging, near-field optical tweezers, and photothermal therapy. Physically, the field enhancement requires plasmon resonance with respect to structure matching. We report a tunable near-field effect, including localized electric-field enhancement and resistive heating at an off-resonance Au nano-sphere dimer via femtosecond laser irradiation. The near field was strongly modified (up to 81 times) with respect to time evolution at a laser fluence of $0.1\,\mathrm{J/cm^2}$. The results are explained as thermal dynamics manipulation of the Au nano-sphere dimer plasmon resonances. This study provides a new alternative route to tailoring the near-field enhancement for wide applications in nano-antennas.

Introduction. – A pair of closely spaced metallic nanoparticles (a nano-dimer), typically used as a nano-antenna supporting "dimer" plasmons, can be considered as bonding and antibonding hybridization of individual nanoparticle plasmons. The enhanced electric field associated with nano-dimer plasmons has been demonstrated to depend, to a large extent, on the nano-dimer shape and structure [1–3]. However, the electric field localized in the gap of a metallic nano-dimer is usually limited by resonance mismatching due to the shape or size deviations from the ideal one, which degrades the performance of a perfect nano-dimer. It becomes potentially important to significantly promote a strong near field in off-resonance nano-dimers to facilitate practical applications, especially those of the near-field imaging, optical tweezers, biosensor and nano-therapy [4–7].

Femtosecond laser excitation of nanostructures has recently found potential applications in photo-excited near-field processes [8–10]. Its prominent advantages can be related to the tiny collateral damage produced in materials [11], which originates from the high non-equilibrium thermal dynamics, in which the electron and phonon are considered as the respective systems. The electron system of a nano-dimer can be excited to high temperature up to 1 eV [12], but the phonon system remains undisturbed during femtosecond laser excitation, leading to the tiny lattice damage. For noble metals, which can exhibit excellent electron excitation for near-field applications, the intraband and interband transitions of the noble-metal electron system can occur under strong femtosecond laser excitation. The dielectric permittivity of a nanoparticle dimer can be substantially modified by ultrashort laser pumping of the nano-dimer's electron system. As a result, femtosecond laser excitation of nano-dimers is suitable for the modification of near-field properties by regulating the non-equilibrium thermal dynamics to generate the desired near-field enhancements on off-resonance nano-dimers. This provides a new opportunity for promoting near-field enhancement in nano-dimers with structural errors. Notwithstanding the underlying interests of femtosecond laser excitation of near-field enhancement, the ultrafast dynamics of near-field effects with off-resonance nanoparticle dimers is still an undeveloped topic.

In this letter, we theoretically investigated the tunable near-field effects, including the field enhancement and resistive heating at an off-resonance Au nano-sphere dimer via femtosecond laser irradiation. The non-equilibrium thermal excitation dynamics is self-consistently coupled into a near-field scattering model to explore the ultrafast dynamics of the near-field enhancement effects for a wide

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range of applications such as super-resolution imaging, femtosecond near-field optical tweezers, and femtosecond near-field nano-surgery.

Modelling and methods. – During femtosecond laser pulse irradiation of an Au nano-sphere dimer, the pulse energy is initially absorbed by the free electrons of the Au nanoparticles in the inverse Bremsstrahlung process. As a result, the electron system can be dramatically excited on femtosecond timescale, producing very high electron temperature. Then the absorbed laser energy in the dimer's electron system is subsequently transferred into the local lattice system by electron-phonon coupling, which occurs on the picosecond timescale. The electron and phonon temperature changes comply with the two-temperature model, which is widely accepted for investigations of ultrashort laser interaction with metal films and metallic nanoparticle [13–15]. In this investigation, the radius of the simulated nano-sphere (6.6 nm) used in the model is set to be quite smaller than the electron ballistic transfer length (100 nm). So the electron thermalization in the nano-sphere dimer can be reasonably considered as a homogeneous process. The two-temperature model describing the homogeneous heating in an Au nano-sphere dimer can be reduced to

$$C_e \frac{\partial T_e}{\partial t} = -\gamma \left(T_e - T_l\right) + Q\left(t\right), \tag{1}$$

$$C_l \frac{\partial T_l}{\partial t} = \gamma \left(T_e - T_l\right), \tag{2}$$

where C_e and C_l are the heat capacities of the electron and lattice subsystems, respectively, and γ is the electron-phonon coupling strength. As the electron temperature of the Au nano-sphere dimer remains smaller than the Fermi energy, the temperature-dependent electron heat capacity can be written as $C_e = C_e' T_e$ [16,17]. $Q(t)$ indicates the laser energy deposition into the target with respect to the nano-sphere scattering section. In fact, the electronic heat capacity is much smaller than the lattice heat capacity. Therefore, the electrons system of the Au nano-sphere dimer can be heated to high temperature ($\sim$1 eV), but the lattice remains undisturbed during laser excitation on the femtosecond timescale. In this case, eqs. (1) and (2) reduce to

$$C_e' \frac{\partial T_e^2}{\partial t} = 2Q(t). \tag{3}$$

$Q(t)$ is calculated in the form of $\sigma A F_a / t_p$. Here, σ denotes the normalized scattering cross-section of the nano-dimer, A is the absorption coefficient treated as constant due to the homogeneous heating process, F_a is the laser pulse fluence and t_p is the pulse duration.

The solution of eq. (3) yields

$$T_e\left(t\right) = \left(T_0^2 + \frac{2\sigma A F_a}{C_e' t_p} t\right)^{1/2}. \tag{4}$$

The dielectric permittivity of Au can be modelled as a set of explicit equations that are functions of wavelength, temperature and time, via the superposition of a Drude-like intraband transition term and interband transition term, in ref. [18,19]:

$$\varepsilon[\omega, T_l(t), T_e(t)] = \varepsilon_{\text{intra}}[\omega, T_l(t), T_e(t)] + \varepsilon_{\text{inter}}[\omega, T_l(t), T_e(t)]. \tag{5}$$

Here, ω is the optical frequency, t is the time, and $T_l(t)$ and $T_e(t)$ are time-dependent lattice and electron temperatures, respectively.

The first term in eq. (5) can be calculated by

$$\varepsilon_{\text{intra}}[\omega, T_e(t), T_l(t)] = 1 + \varepsilon_b - \frac{\omega_p^2}{\omega^2 + \mathrm{i}\gamma\omega}, \tag{6}$$

here

$$\gamma[T_e(t), T_l(t)] = \gamma_0 + \gamma_1 \times T_l(t) + \gamma_2 \times T_e^2(t) + \gamma_3 \times \omega^2, \tag{7}$$

where ε_{b} is the background dielectric constant, γ is the damping constant, ω_p is the bulk plasma frequency, and γ_0, γ_1, γ_2, γ_3 are constant coefficients.

For the second term in eq. (5)

$$\varepsilon_{\text{inter}}[\omega, T_e(t)] = \sum_{j=1}^{M} k_j \int_0^\infty \mathrm{d}\chi \frac{\sqrt{x - E_{g(j)}}}{x^2} [1 - F_{(j)}\left(x, T_e(t)\right)] \frac{\hbar^2\omega^2 - x^2 - \gamma_{ee(j)}^2 - 2\mathrm{i}\hbar\omega\gamma_{ee(j)}}{\left(\hbar^2\omega^2 - x^2 - \gamma_{ee(j)}^2\right)^2 + 4\hbar^2\omega^2\gamma_{ee(j)}^2} \tag{8}$$

with parameter

$$\gamma_{ee(j)}[T_e(t)] = \hbar(\gamma_{a(j)} T_e^2(t) + \gamma_{b(j)}\omega^2), \tag{9}$$

where the summation is composed of M interband terms and each contribution term is denoted by the subscript j, x is the electron energy, κ is a constant related to effective electron mass, E_g is the minimum transition energy from a valence band to an ideal parabolic conduction band, γ_{ee} is the inverse scattering time, $F(x, T_e(t))$ is the electron occupation number, E_f is the electron distribution function, E_{fd} is the transition energy from the band to the Fermi level, k_B is the Boltzmann constant, $\hbar$ is the Planck constant, and γ_a, γ_b are constant coefficients.

Because of the transient changes in the electron and phonon temperatures, the dielectric function can be transiently modified during the two-temperature relaxation process, leading to ultrafast near-field modulations in off-resonance nano-sphere dimers via manipulating femtosecond laser parameters.

Results and discussions. – The electric-field (e-field) enhancement spectra of an Au nano-sphere dimer under the non-equilibrium electron excitation state are shown in fig. 1. We can see that the electric-field enhancement

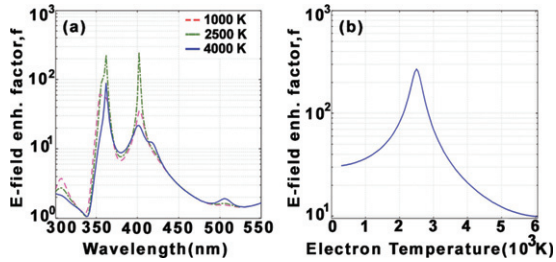

Fig. 1: (Colour on-line) Electric-field amplitude enhancement spectra for the Au nano-sphere dimer at different temperatures of the excited electron system: (a) e-field enhancement factor *vs.* wavelength; (b) e-field factor *vs.* electron temperature at 405 nm wavelength. Radius and distance of nano-sphere dimer are 6.6 nm and 3.5 nm, respectively.

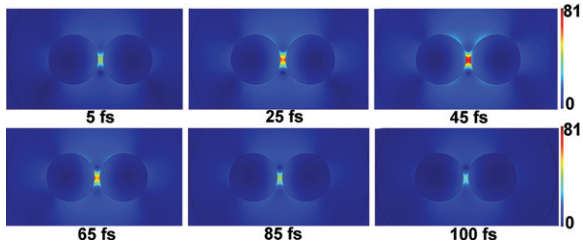

Fig. 2: (Colour on-line) The 2-D evolution of the localized electric-field hotspot in the gap between Au nano-spheres excited by a femtosecond laser pulse, $F = 0.1\,\mathrm{J/cm^2}$, pulse duration 100 fs. The incident laser wavelength is 400 nm. The dimer sphere radius is 26.4 nm.

depends significantly on the electron temperature at the resonant regimes (fig. 1(a)). However, the spectra are not strongly correlated with the temperature as the laser wavelength is detuned from the resonant one. The modified dielectric property of the Au nano-sphere dimer due to thermal dynamics excitation of the intraband and interband electrons of Au significantly enhances the localized electric field at the resonant electron temperature of 2500 K (fig. 1(b)). Our simulations show that the resonance electron temperature can less be affected by changing the dimer size as the sphere radius is less than 30 nm. When the electron temperature departs from the resonant regime, the amplitude of the electric-field enhancement spectrum decreases rapidly. More interestingly, we can observe that the tunable Fano profiles appear during the femtosecond laser excitation of nano-sphere dimers, which was previously observed in a nano-dimer composed of Au and Ag nano-sphere pairs in non-excited state [20]. This is explained by the strong coupling of the Ag nanoparticle to the Au interband transitions. The current investigation indicates a strong interaction of the near-field plasmons between the nano-sphere dimer under moderate external excitation temperature. However, we find that as the electron temperature decreases from the resonance peak, the Fano profile degenerates into single-peak resonant spectra, which is not shown here. This means that the plasmonic coupling between the nano-spheres in the dimer can be impaired at low electron temperature, which is extremely unhelpful for the near-field enhancement in a wide range of applications. It should be emphasised that the observation of the absorption in the ultraviolet region is the important result of the present study, which can be attributed to the absorption due to the interband transition in Au nano-dimer. An interband absorption can be possible at shorter wavelengths due to the transition of an electron from the occupied d-level state to an empty state in the conduction band in noble metal of Au. Theoretical investigations show a considerable interband contribution to the absorption spectra of Au nano-particles at shorter wavelengths [21]. In the current study, we had adopted the Drude-like permittivity model, which considers the mechanism of interband transition term contribution to the absorption spectra. As a result, plasmonics resonances in the UV region are observed with respect to the non-equilibrium electron-phonon state in Au nano-dimer via ultrafast femtosecond laser excitation.

The 2-D evolution of the localized electric field in the gap between off-resonance Au nano-spheres excited by a femtosecond laser pulse is shown in fig. 2. We can see that the electric field localized in the hotspot region increases non-monotonically with increasing delay time. The maximal electric field at the gap of the nano-sphere dimer is increasingly enhanced in the first half of the femtosecond pulse duration with delay time. A large enhancement of the localized electric-field appears at a delay time of 45 fs. As the delay time exceeds 45 fs, the localized electric-field hotspot at the gap in the Au nano-sphere dimer is weakened with delay time. According to the two-temperature model prediction, the electron temperature can normally present monotonous increase during the femtosecond pulse duration. Considering the fact that the nature of the near-field enhancement *vs.* the temperature of the nano-dimer is non-monotonic, as seen in fig. 1(b), the electric-field enhancement consequently presents non-monotonic rise with delay time. The near field was strongly modified (up to 81 times) at 45 fs for the moderate laser fluence of $0.1\,\mathrm{J/cm^2}$. Moreover, it is observed that as the incident laser wavelength significantly differs from the 400 nm resonance wavelength, the electric-field enhancement in the hotspot region can be dramatically reduced, but the basic law of the temporal evolution of the near-field enhancement can be less affected by changing the laser wavelength.

The spatiotemporal distribution of the localized electric-field enhancement and resistive heating in the off-resonance Au nano-sphere dimer via a femtosecond laser pulse excitation is shown in fig. 3. It should be noticed that the resistive heating can be also called as Joule heating. It is defined as the amount of heat dissipated in a resistor (Au nano-dimer herein). We can see from fig. 3(a) and (b) that the temporal evolutions of the localized electric field and heating resistance synchronously exhibit single-peak

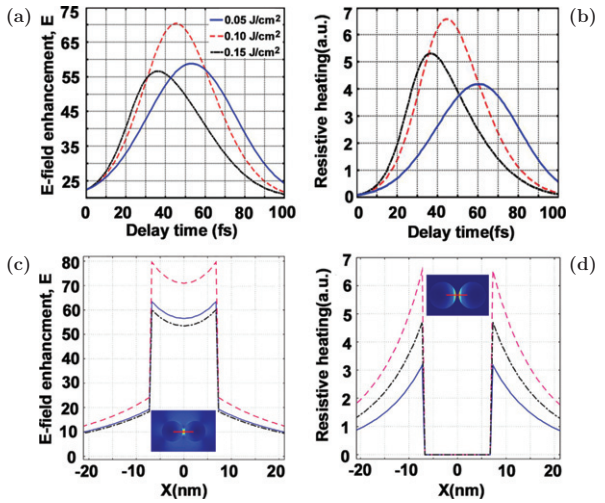

Fig. 3: (Colour on-line) Spatiotemporal distribution of electric-field enhancement and resistive heating of the Au nano-sphere dimer excited by a femtosecond laser pulse, pulse duration 100 fs. The incident laser wavelength is 400 nm. The dimer sphere radius is 26.4 nm.

profiles during the femtosecond pulse. The cross-sectional distributions of the electric field at 45 fs for the nano-sphere dimer (marked by solid line, see the schematic dimer, inset of fig. 3(c)) depends significantly on the laser fluence (fig. 3(c)). It is clearly shown that increasing the femtosecond pulse fluence does not always enhance the localized electric field at the hotspot of the nano-sphere dimer at 45 fs, a time close to the peak of the incident laser pulse. However, the moderate laser fluence of 0.1 J/cm^2 can definitely give rise to the largest transient e-field envelops across most of the pulse duration (fig. 3(a)). It is indicated that the e-field enhancement is predominantly promoted during the whole pulse duration at the moderate fluence of 0.1 J/cm^2 compared to a higher or lower fluence. In addition, we can see from fig. 3(d) that resistive heating of the nano-sphere dimer can be suppressed by excessively increasing the laser fluence. This indicates that the localized electric field and resistive heating of the Au nano-sphere cannot be monotonically tuned by increasing the femtosecond laser fluence at the particular time of 45 fs. The optimal laser fluence for enhancing the localized electric field and resistive heating synchronously appears at the moderate value of 0.1 J/cm^2 during most of the pulse duration in the current simulations. It can be explained as the thermal dynamic manipulation of Au dimer plasmon resonances via tailoring the femtosecond laser fluence. As the laser fluence is 0.05 J/cm^2, the electron system of the off-resonance nano-dimer can be slightly excited, which is still in off-resonance state, leading to a weak near-field enhancement process. Once the laser fluence reaches 0.1 J/cm^2, the electron temperature of the nano-sphere dimer can be pumped to the resonant one of 2500 K according to our calculation using TTM. As a result, the nano-sphere dimer is resonantly excited under the optimal laser fluence of 0.1 J/cm^2, causing strong enhancement of the localized electric field. However, when the laser fluence exceeds 0.1 J/cm^2, the nano-sphere dimer with respect to the electron temperature is again off the resonant state, leading to a weak near-field enhancement. The results are helpful for understanding the ultrafast dynamics of the strong near-field enhancement in off-resonance nano-sphere dimers for a wide range of near-field applications.

Conclusions. – We have theoretically investigated the ultrafast dynamics of near-field effects in an off-resonance Au nano-sphere dimer, including the localized field enhancement and resistive heating via femtosecond laser irradiation. We found that increasing the laser fluence does not always enhance the localized electric field at the hotspot of the nano-sphere dimer. The optimal laser fluence for significantly enhancing the localized electric field of the off-resonance Au nano-sphere dimer is 0.1 J/cm^2 for the current simulation conditions. A strong enhancement of the field, up to a factor of 81 for the off-resonance nano-sphere dimer, was achieved. The phenomena are explained as thermal dynamic manipulation of the Au nano-sphere dimer plasmon using a femtosecond laser. The study provides a strategy for significantly promoting the near-field enhancement at nano-antennas, which are not well fabricated to satisfy the plasmon resonance condition, to advance applications in fields such as femtosecond super-resolution imaging, ultrafast near-field optical tweezers, and femtosecond near-field nano-surgery.

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