Enhancement of ultrafast electron photoemission from metallic nanoantennas excited by a femtosecond laser pulse

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Abstract
We have demonstrated for the first time that an array of nanoantennas (central nanotips inside sub-micrometer pits) on an aluminum surface, fabricated using a specific double-pulse femtosecond laser irradiation scheme, results in a 28-fold enhancement of the non-linear (three-photon) electron photoemission yield, driven by a third intense IR femtosecond laser pulse. The supporting numerical electrodynamic modeling indicates that the electron emission is increased not owing to a larger effective aluminum surface, but due to instant local electromagnetic field enhancement near the nanoantenna, contributed by both the tip’s ‘lightning rod’ effect and the focusing effect of the pit as a microreflector and annular edge as a plasmonic lens.

Keywords: nanoantenna, femtosecond laser pulse, ultrafast electron photoemission

(Some figures may appear in colour only in the online journal)

1. Introduction

Strong-field plasmonics, involving excitation of plasmons (collective free-electron oscillations) in different nano-objects by intense femtosecond (fs) laser pulses, is of high interest for basic and applied research. Surface-plasmon-enhanced multiphoton photoelectric emission [1], high-harmonic generation [2], electron acceleration [3, 4] and x-ray enhancement [5] were demonstrated using such nanostructures as diffractive gratings [3], plasmonic bow-tie nanoantennas [2, 4], spherical [6] and non-spherical [4, 5] metallic nanoparticles.

One of the most popular plasmonic elements is a metallic nanotip, providing strong optical field enhancement via the ‘lightning rod’ effect. The nanometer-long decay length of the evanescent field corresponds to its strong gradients, which can be used for nanoscale acceleration of photo-emitted electrons in different regimes (multiphoton [7], above-threshold [8] or optical-field [9] regimes). Interestingly, the strong gradient of localized evanescent field can suppress the quiver motion of the electrons in the oscillating laser electric field [10]. Such a strong-field steering of electrons in the vicinity of nanostructures with large local field enhancement and steep field gradients leads to emission of highly directed, confined coherent electron wavepackets [7, 9–11]. Generally, such a pulsed electron nano-emitter, triggered by femtosecond laser irradiation, could serve as an efficient source for time-resolved nanoscale imaging. For instance, ultrashort electron pulses were employed for time-domain visualization of metal melting [12] and ionization dynamics of H₂ [13].
Fabrication of plasmonic nanotips usually faces problems of long fabrication cycle, chemical treatment and production costs. To provide more efficient fabrication methods, tight focusing of single nanosecond [14] and femtosecond [15] laser pulses into diffraction-limited spots was tested to produce one nanotip per shot. However, femtosecond laser irradiation makes it possible and realistic to easily fabricate huge arrays of nanostructures (down to the sub-100 nm scale) via intense surface plasmon polariton (SPP) excitation, where only weak laser beam focusing on the surface is required [16]. Such a method for surface nanograting formation was successfully used for surface-plasmon-enhanced photoelectron emission [1].

In the same manner, an array of nanotips can also be easily fabricated by means of fs-laser beam weak focusing on a metallic surface [17].

In this letter, we report a simple, double-pulse fs-laser fabrication scheme to produce an array of nanoantennas (nanotips inside sub-micrometer pits) on an aluminum surface and demonstrate their strongly enhanced non-linear electron photoemission, excited by a single fs-laser pulse, in comparison to flat and randomly nanostructured aluminum surfaces. These observations are supported by numerical electromagnetic modeling, indicating high local electromagnetic (EM) field enhancement in the nanoantennas.

2. Experimental details

In our experiments 100 fs, 744 nm linearly polarized Ti:sapphire laser pulses with a maximum pulse energy of 6 mJ in the TEM00-mode were focused by a silica lens (focal distance of 11 cm) onto a 4 mm-thick aluminum sample mounted vertically on an X–Y–Z motorized translation stage. The mechanically polished and ultrasonically cleaned sample was located several mm above the focal plane to obtain a large spot diameter \( D_{1/e} \approx 180 \mu \text{m} \). The nanostructured sample surfaces were characterized using field-emission scanning electron microscopy (FE-SEM).

To measure photoelectron emission, a stationary collecting aluminum electrode (anode) with a 2 mm aperture was mounted at a distance of 1 mm away from the sample surface and a positive voltage of 150 V was applied to extract the emitted electrons (the scheme was described elsewhere [18]). The fs-laser pump pulses were focused on the target surface through the anode aperture. The extracting field (~1 kV cm\(^{-1}\)) in this scheme is two or three orders of magnitude higher than values typical for high-vacuum schemes, where the field values must not exceed \( \sim 1–10 \text{ V cm}^{-1} \) to prevent secondary electron emission, since at atmospheric pressure emitted electrons become attached to oxygen molecules on a nanosecond time scale. Then, the resulting negatively charged ions slowly move in the applied electric field on a sub-millisecond time scale, inducing an image current (potential) in the collector, which was registered using a MΩ-input of a digital oscilloscope. The high extracting electric fields eliminate the space-charge effect even at intense electron emission at fs-laser fluences even as high as several J cm\(^{-2}\) [18].

3. Results

Nanoantenna fabrication on an aluminum surface was performed by two fs-laser pulses at the same peak fluence \( F_0 = 0.85 \text{ J cm}^{-2} \) (slightly below the spallative ablation threshold \( F_{\text{spal}} = 0.73 \text{ J cm}^{-2} \) [19]), following with a delay of a few seconds between them [17]. After the first laser pulse an irregular array of round spallative pits with a surface density \( \sim 10^7 \) cm\(^{-2}\) appeared on the surface (figure 1(a)) at local fluences \( F > F_{\text{spal}} \) along an outer border of a macroscopic spallation crater. Their edges have widths of about \( \Delta \sim 100 \) nm, their bottom is semi-spherical appearing, in average, 100 nm below the initial surface.
Figure 2. (a) Cross-section view of a 3D-model nanotip in a pit on the aluminum surface with the shown notations of their geometrical parameters. (b) Calculated decimal logarithm of squared field enhancement $\lg(|E|^2/E_0^2)$ distribution near the model structure with $H = 550\, \text{nm}$, $h = 100\, \text{nm}$, $R = 100\, \text{nm}$, $R_0 = 650\, \text{nm}$, $r = 20\, \text{nm}$, $\Delta = 100\, \text{nm}$. (c) Image of the nanotip with the decimal logarithm of squared field enhancement and vectors of local electric field (black arrows). The double arrow in picture (b) indicates orientation of the EM wave linear polarization direction.

level (figure 1(b)). The average diameter of the pits depends on local laser fluence, but usually amounts to $1.3\, \mu\text{m}$. They result from intense sub-surface nanovoid generation (homogeneous nucleation) in the melted surface layer [20, 21] at fs-laser fluences slightly lower than the spallation threshold $F_{sp}$.

Such pits with prominent edges respond to EM fields in the optical range as plasmonic nanolenses [22], providing excitation and sub-diffraction focusing of SPPs in their centers. The focusing in plasmonic lenses exposed by fs-laser pulses at $F_0 = 0.85 J \text{cm}^{-2}$ results within each pit in the formation of a single nanojet (figure 1(c)), related to material expulsion and its ultrafast cooling [17] expected for much higher fs-laser fluences, exceeding the threshold $F_{frag} = 1.4 J \text{cm}^{-2}$ for supercritical hydrodynamic (fragmentation) ablation [19].

To evaluate the optical field enhancement in such a nanoantenna (a nanojet in a microscale pit), we performed numerical modeling by solving Maxwell’s equations using the finite-elements method (COMSOL). EM intensity distribution was calculated for a plane EM wave ($\lambda = 744\, \text{nm}$ reaching a nanotip in a pit at normal incidence (figure 2(a)) with the geometrical parameters: $H = 550\, \text{nm}$, $h = 100\, \text{nm}$, $R = 100\, \text{nm}$, $R_0 = 650\, \text{nm}$, $r = 20\, \text{nm}$, $\Delta = 100\, \text{nm}$ (for notations see figure 2(a)), taken from figure 1(c). The dielectric function of unexcited aluminum at the $744\, \text{nm}$ wavelength equals $\varepsilon = -68.9 + 139.9$ [23].

This modeling has revealed an intensity enhancement up to 56 times outside and 5.5 times inside the peak of the nanotip (figures 2(b) and (c)). The enhancement factor inside the nanotip is the ratio between the maximal laser intensity values under the nanotip surface and under the flat metallic surface. The model calculation takes into account all possible interference effects, and, consequently, the enhancement is attributed not only to local phenomena such as the ‘lighting rod’ effect, but also to EM wave reflection from the semi-spherical surface of the pit and SPP excitation from its edges. Calculation of the field for a nanotip on a flat aluminum surface resulted in a corresponding local field enhancement factor 2 times lower (as compared to a nanotip in a pit) outside the nanotip and 1.3 times lower inside. Hence, this proves that the pit works like a reflector in a parabolic antenna, which focuses the incident EM waves onto the nanotip. Additionally, in our case such pits have sharp edges, providing SPP excitation and focusing to the nanotip.

To study the electron emissivity of the fabricated array of the fs-laser-induced nanotips in the micro-craters, we measured the photoemission of electrons from the nanostructured surface in the appropriate intensity regime (~1–10 TW cm$^{-2}$), where the micro-craters and nanotips are typically formed, and compared the yield from a polished surface with the yield from surfaces with laser-induced random nanostructures.

In figure 3 the enhancement of the electron photoemission is shown versus $N$ at two fluences $F_0 = 0.85 J \text{cm}^{-2}$ and $F_0 = 0.5 J \text{cm}^{-2}$. At the highest fluence $F_0 = 0.85 J \text{cm}^{-2}$, the electron yield enhancement is characterized by a maximum of $= 28$ at $N = 3$ and subsequent decrease for increasing laser exposure $N > 3$, since the nanotips are destroyed in the next shot, leaving nanopits underneath them within the sub-micrometer pits (figure 3(d)). The succeeding multi-shot fs-laser exposure results in a random structure of ablative nanoparticles (figure 3(e)), providing the saturated electron yield enhancement is about 20.

Similar multi-shot electron yield enhancement is achieved for smaller fluence $F_0 = 0.5 J \text{cm}^{-2}$, which does not produce high-fluence nanotips, but just lower fluence nanopits (figure 3(g)). Eventually, multi-shot irradiation in this fluence regime leads to similar random nanorelief (figure 3(i)) through cumulative random formation of multiple overlapping surface nanopits via the sub-surface cavitation mechanism [20, 21]. As a result, for large $N$ the surface is again covered by nanoparticles (figure 3(i)) due to enhanced local ablation in the nanopits (figure 3(h)). In this case, the electron yield enhancement factor grows monotonically up to the almost same saturation level of $= 20$.

4. Discussion

The fs-laser induced electron emission enhancement factor of nearly 30 achieved for the nanotipantennas has a straightforward
explanation in terms of the local field enhancement in the nanofeature. For that purpose, we have obtained the experimental dependence of the electron emission yield on fluence for the flat Al surface. The variation of electron emission yield as a function of $F_0$ is represented by the consequent cubic and linear dependences for $F_0 < 1.5 \text{ J cm}^{-2}$ and $F_0 > 1.5 \text{ J cm}^{-2}$, respectively (figure 3(j)). This indicates that, for the incident fs-laser fluence $F_0 \approx 0.85 \text{ J cm}^{-2}$ the electron emission yield from the reference flat surface exhibits in figure 3(j) magnitudes of 0.2–0.4 arbitrary units within the third-power region of its fluence dependence. Following the local intensity enhancement of 5.5 inside the nanotip, the effective fluence becomes equal to 4–5 J cm$^{-2}$, corresponding to the electron emission yield values of 5–8 arbitrary units within the linear region of its fluence dependence (figure 3(j)). As a result, we would expect an enhancement of the photoemission yield due to the nanotips in the range 15–40. However, the surface after the second fs-pulse is covered by nanotips only in part (less than 10% of the irradiated surface). In this case, the total electron photoemission yield has a contribution from the excitation of SPPs outside the pits, where they interfere with the incident laser field and each other on a relatively large area. Such interference SPP–light is the main origin of the yield enhancement in the case of $N = 3$ at $F_0 = 0.5 \text{ J cm}^{-2}$ (figure 3(g)), where the rare subwavelength pits play the role of SPP sources. It should be noted that, in comparison with random nanostructures, a surface with nanotips has evidently a smaller density of nanoelements, but a higher electron emission yield, indicating even stronger local EM field enhancement on individual nanotips.

Moreover, another important characteristic of the nanoantennas is their large (~50) electrodynamical enhancement of optical intensity outside the nanotip, which is significantly higher than the internal enhancement factor of ~5 inside (figure 2). Such discrepancy between both enhancements results from their different electrical field polarizations. Particularly, the internal electric field inside the nanotip appears as a mostly longitudinal one with the predominating $E_z$-component (figure 2(c)), as compared to the external electric field near the nanotip apex with nearly equal $E_x$- and $E_z$-components (figure 2(b)). The EM wave reflected for the pit bottom at the almost normal incidence angle contributes presumably its transversal component ($E_t > E_z$) to the nanotip apex field. Hence, the internal field inside the nanotip apex is contributed by SPP waves with the predominating $E_z$-component, which are rather inefficiently excited at the pit edges.

**Figure 3.** (a) Evolution of the electron yield enhancement with the number of fs-laser shots at $F_0 = 0.5 \text{ J cm}^{-2}$ (blue curve) and 0.85 J cm$^{-2}$ (black curve). The characteristic surface nanofeatures before irradiation by the second (b), (f), third (c), (g), fourth (d), (h) and ninth (e), (i) fs-laser pulse at $F_0 = 0.5 \text{ J cm}^{-2}$ (b)–(e) and 0.85 J cm$^{-2}$ (f)–(i). (j) Single-shot electron emission yield dependence on fluence for the reference flat aluminum surface.
As a result of such a high external EM field enhancement, such a nanoantenna design, accompanied by the related ‘chemical enhancement’ effect of electronic structure of noble metals, can be very promising for diverse nanophotonic applications, such as surface-enhanced absorption [24], Raman scattering [25] and luminescence [26].

In conclusion, we have demonstrated for the first time that an array of laser-induced metallic nanotips within semi-spherical sub-micrometer pits provides 28-fold enhancement of ultrafast electron photoemission. Numerical calculations of the intensity distribution near a nanotip have proven that such an assembly works like nanoantennas with microreflectors, yielding in high EM field concentration near the peak of the nanotip. A comparative study of electron emission from the nanotips versus other types of laser-induced nanotopologies showed that the nanotips provide the highest enhancement, despite relatively low surface density. The experiments were carried out at intensities higher than the damage threshold for the nanotips to show that their simple way of fabrication opens a possibility of their use in a high-fluence (>1 J cm−2) regime.

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