Supporting Information

**Plasmon Enhanced Photoacoustic Generation from Volumetric Electromagnetic Hotspots**

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**Relation between the photoacoustic generation and electric field intensity**

The photoacoustic waves are generated by the consecutive transformation of optical energy into heat energy and then to mechanical energy. Subsequently, nanosecond laser radiation causes a pressure rise, ΔP, in the irradiated volume:

\[ \Delta P = \frac{1}{\gamma} \beta \Delta P = \frac{1}{\gamma} \beta E_a \]

where \( \gamma \) is thermodynamic coefficient of isothermal compressibility, \( \beta \) is thermal coefficient of volume expansion, \( \Delta T \) is a local temperature modulation, \( C_v \) is the heat capacity at constant volume, \( \rho \) is the density of a medium, \( c_0 \) is the sound velocity in medium. Simply, the pressure rise \( \Delta P \) is proportional to the thermal coefficient of volume expansion \( \beta \) of a given medium and the absorbed energy \( E_a \). Then the absorbed energy in non-magnetic medium is obtained from absorption distribution defined by

\[ E_a = \int -\frac{1}{2} \nabla \cdot S dV = \int \frac{\omega_0}{2} |\varepsilon''| |E|^2 dV \]

where \( S \) is Poynting vector, \( \omega_0 \) is angular frequency, \( \varepsilon'' \) is imaginary permittivity, and \( E \) is electric field. While imaginary permittivity of metal is larger than that of absorbing polymer (\( \varepsilon''_{\text{metal}} = 0.2 \sim 0.4 \), \( \varepsilon''_{\text{polymer}} = 0.04 \sim 0.08 \) at visible), total products of material constants are comparable in photoacoustic generation due to higher thermal expansion coefficient of absorbing polymer than that of metal. Thus, with assumption of comparable material constants of metal and absorbing layer, we employed sum of \( |E|^2 \)
under each medium to compare photoacoustic generation between the plasmonic structure and the absorbing layer.

**Electric field distribution in the 2D and 3D plasmonic absorbers**

Figure S1 shows the electric field distribution in the 2D and 3D nanostructure calculated by using a FDTD method and the total electric field intensity, sum of $|E|^2$, on the absorbing medium (area from $y=0$ nm to $y=200$ nm). The 3D nanostructure shows the strongly localized electric field within the interstitial gap spacing between Ag nanoislands in larger volume than that of the 2D nanostructure. Thus, the 3D structures clearly show much higher total electric field intensity than that of 2D over the whole visible range. In addition, both the 2D and 3D structures show the enhanced electric intensity at excitation wavelengths of 600–700 nm, which shows a good agreement with the experimental results in Fig 3(c).

![Electric field distribution of the 2D and 3D plasmonic nanostructures](image)

**Figure S1. Electric field distribution of the 2D and 3D plasmonic nanostructures.** Electric field distribution of (a) 2D plasmonic absorber and (b) 3D plasmonic absorber with highly localized electric field. (c) The total electric field intensity over the absorbing medium of 2D and 3D plasmonic absorber depending on excitation wavelengths.
Dominant contribution of EM hotspot to photothermal effect

Figure S2 (a-b) shows the electric field distribution in the absorbing polymer or in the Ag nanoislands calculated by a FDTD method. E-field distribution in the absorbing polymer shows that the electric field of an excitation laser beam is strongly localized within the interstitial gap spacing between Ag nanoislands, i.e., within the volumetric EM hotspots, whereas E-field distribution in the Ag nanoislands shows relatively weak electric field intensity. Figure S2c clearly exhibits that total electric field intensity, sum of $|E|^2$, in the absorbing polymer is much higher than that in the Ag nanoislands over the whole visible range. Moreover, the total intensity drastically increase at plasmonic resonance wavelength (600–650 nm) due to volumetric hotspot generation. At an excitation wavelength of 650 nm, the total electric field intensity in the absorbing polymer takes 86% of electric field intensity in the whole area. The calculated total electric field intensity also shows an excellent agreement with the experimental results of both the optical enhancement factor and the photoacoustic enhancement factor (Fig. 3 in the original manuscript). Figure S3d also shows the calculated total power absorption, sum of $\epsilon^*|E|^2$, in absorbing polymer and Ag nanoislands. Even though the imaginary permittivity of metal is much higher than that of absorbing polymer, the total absorption at each region is comparable in the plasmonic resonance wavelength due to volumetric hotspot generation on the absorbing polymer.

Figure S2. Comparison of electric field and intensity between the absorbing polymer and Ag nanoislands. (a, b) Electric field distribution in the absorbing polymer, (a), and the silver nanoislands, (b). (c) The total electric field intensity on each area of Ag nanoislands (red solid), absorbing polymer (blue solid), and contribution of Ag nanoisland in total absorption (black dash). (d) The total power absorption on each area of Ag nanoislands (red solid), absorbing polymer (blue solid), and contribution of absorbing polymer in total absorption (black dash).