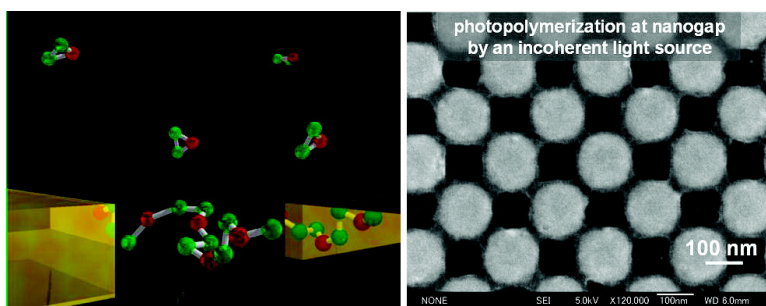


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Nanoparticle Plasmon-Assisted Two-Photon Polymerization Induced by Incoherent Excitation Source

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The second law of photochemistry states that each absorbed photon activates one molecule for a photochemical reaction. An exception to this rule is nonlinear absorption, in which more than one photon is consumed. The lowest-order nonlinear two-photon absorption (TPA) was predicted in 1931,¹ but it took three decades to obtain its first experimental evidence, when coherent laser excitation sources with sufficiently high irradiance levels, on the order of 10^6 – 10^9 W·cm⁻², became available.² Since then, TPA and higher-order nonlinearities became quintessential for triggering of photochemical reactions, in three-dimensional (3D) optical memories,³ scanning microscopy,⁴ and laser lithography.⁵ These and other applications rely on the excitation by tightly focused beams of powerful lasers in order to achieve locally enhanced irradiance levels needed to reach substantial TPA rates. Even tighter, diffraction-free nanoscale “super-focusing” is possible using the localization of plasmonic near-field modes at the surfaces of metallic nanoparticles.^{6,7} Despite the potentially high field intensity enhancement achievable in the latter case, it is commonly accepted that excitation of substantial nonlinear absorption requires a coherent laser source. Here we demonstrate for the first time that nanoparticle plasmons can induce a detectable TPA even under irradiation by incoherent continuous-wave (cw) sources. For this purpose, arrays of gold nanoblocks were specially tailored for maximum near-field localization and intensity enhancement. Two-photon polymerization (TPP) of the photoresist surrounding the nanoparticles was found in the high-plasmonic field regions after irradiation by an incoherent light source, demonstrating that TPA triggered a photochemical reaction without a laser source.

For plasmonic field enhancement, gold nanoblocks measuring $120 \times 120 \times 40$ nm³, arranged into a checkerboard pattern with 6 nm wide nanogaps at their nearest corners, were fabricated on glass substrates by electron-beam lithography and lift-off techniques^{8–11} as shown schematically in Figure 1a. Such structures possess localized surface plasmon (LSP) modes whose near field is predominantly localized in the nanogaps with enhanced intensity.⁸ Therefore, even a weak photoexcitation by laser at 800 nm wavelength excites TPA-mediated photoluminescence from the regions of gold adjacent to the nanogaps.⁸ Here, we concentrate on TPA in the photosensitive material in which nanoblocks are embedded. The structures were spin-coated by a 1 μm thick film of epoxy-based negative photoresist SU-8 (formulation 2002 from Microchem Co.). SU-8 molecules have 16 epoxy functional side groups providing a dense 3D network of cross-links. SU-8 is doped by triarylium–sulfonium salt-based photoinitiator, which is converted into acid upon optical exposure at ultraviolet wavelengths shorter than 360–400 nm. The acid molecules react with the epoxy

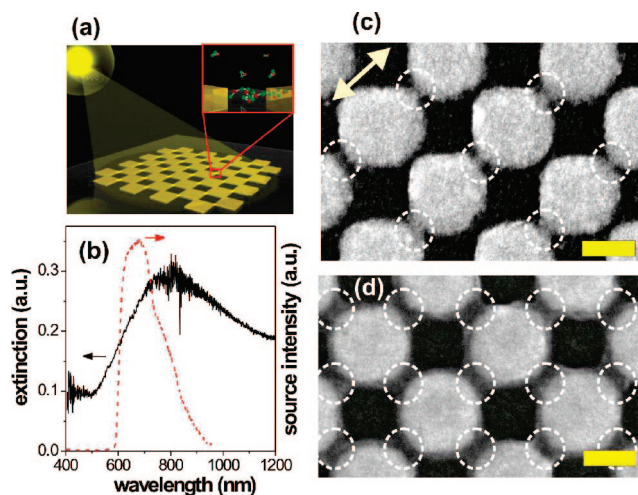


Figure 1. (a) Schematic of the checkerboard pattern of nanoblocks separated by nanogaps; the nanoblocks are coated by a thin film of photoresist SU-8 and exposed to radiation from an incoherent source; the inset illustrates polymerization of SU-8 in the intense near-field existing in the nanogap. (b) Optical extinction spectrum of the checkerboard pattern and the spectrum of the incoherent source. (c) SEM image of the structure after 3 h exposure to the incoherent source polarized linearly along the direction indicated by the arrow. Panel (d) is the same as (c), after exposure by unpolarized source. The polymerized regions are emphasized by dashed circles. The scale bar length is 100 nm.

side groups, producing radicals attached to the backbone of SU-8 molecule and cross-linking SU-8 via cationic photopolymerization.¹² At visible and near-infrared wavelengths, SU-8 is optically insensitive, and photopolymerization resulting from exposure in this spectral region is commonly ascribed to two-photon polymerization.¹³

The plasmonic extinction spectrum of the gold nanoblock structure is given in Figure 1b. The incoherent excitation source was a halogen lamp, spectrally filtered to the wavelength range of 600–1000 nm, as illustrated in Figure 1b. Linear absorption of SU-8 is negligible in this range.¹⁴ The source was polarized linearly and provided an average irradiance of 0.2 W·cm⁻². Figure 1c shows a scanning electron microscopy (SEM) image of the structure after 3 h exposure to the source polarized linearly along the arrow, and postprocessing of SU-8. It can be seen that lines of nanogaps parallel to this direction are filled by polymerized SU-8, whereas along the perpendicular direction the nanogaps are empty. This arrangement indicates the dominant collective longitudinal plasmon (LP) mode excited *only* in the chains of nanoblocks oriented along the polarization direction (the chains oriented along the perpendicular direction remain inactive). Theoretical analysis of these modes indicates that, at the central wavelength of the cw source (800 nm), LP modes are strongly localized in the nanogaps with

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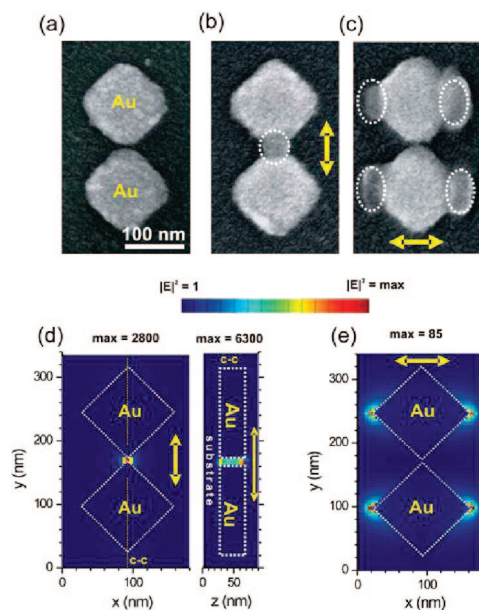


Figure 2. (a) SEM image of a pair of gold nanoblocks measuring $100 \times 100 \times 40 \text{ nm}^3$ and separated by a 5.6 nm wide nanogap before irradiation by an attenuated femtosecond laser beam. (b) SEM image of other nanoblock pairs after 0.01 s exposure to the laser beam polarized linearly along the long axis of the pair. (c) SEM image of another pair after 100 s exposure to the laser beam polarized in the perpendicular direction. (d and e) Theoretically calculated near-field patterns at selected planes for the excitation conditions of the samples shown in (b) and (c), respectively. In (d), the field pattern is shown on the x - y plane bisecting the nanoblocks at half of their height (i.e., 20 nm above the substrate), and in (e), the field is calculated on the plane coincident with the line c - c shown in (d). The field intensity is normalized to that of the incident wave and therefore represents the intensity enhancement factor.

high local intensity. Thus, nonlinear absorption and photopolymerization of SU-8 in the nanogaps is the most likely reason behind our observations. In contrast, exposure by unpolarized source, which excites LP modes along both chain directions, leads to polymerization in *all* nanogaps as shown in Figure 1d.

These results were duplicated under conditions that are easier to control experimentally and to describe theoretically. For field enhancement, pairs of closely spaced nanoblocks (Figure 2a), separated by hundreds of nanometers and hence essentially isolated from each other electro-dynamically, were used. Collective LP modes within the pairs have frequencies and field localization very similar to those in checkerboard patterns. For irradiation, a femtosecond Ti:sapphire laser having a pulse length of 150 fs , a central wavelength of 800 nm , and a repetition rate of 80 MHz was used.

SEM images in Figure 2b,c show pairs of gold nanoblocks with regions of photopolymerized SU-8 resulting after the exposure at an average fluence of $2.0 \times 10^3 \text{ W} \cdot \text{cm}^{-2}$. Energy-dispersing spectrometry conducted in the SEM apparatus confirmed the presence of carbon in the exposed structures, whereas unexposed reference structures exhibited only the signatures of gold. When the laser beam was polarized linearly along the axis of the pairs (Figure 2b), LP modes localized in the nanogaps induced significant local photopolymerization after a short exposure of 0.01 s (8×10^5 pulses). When the laser beam was polarized perpendicular to the axis of the pair, transverse plasmon (TP) modes whose field is concentrated on the left and right tips of the nanoblocks were excited and induced photopolymerization in the corresponding regions

(Figure 2c).¹⁵ Photopolymerization in the nanogap remains negligible even after much longer exposure of 10 s (8×10^8 pulses).

The near-field intensity patterns of plasmonic modes responsible for photopolymerization were obtained from finite-difference time-domain (FDTD) calculations. The field intensity patterns shown in Figure 2d,e correspond closely to the experimental photopolymerization patterns. For the LP mode, the field is localized predominantly in the nanogap where it has a local enhancement factor of up to 6.3×10^3 . For the TP mode, the maximum enhancement of up to 85 is reached at the left and right corners of the nanoblocks. The lower field enhancement factor for TP modes explains why longer exposure was needed during the experiments.

These results suggest that the same absorption process is responsible for SU-8 photopolymerization under excitation by the incoherent source and the laser. SU-8 photopolymerization by laser near 800 nm wavelength has been well studied and is commonly assigned to TPA.^{12,16} However, neither intensity nor wavelength-dependent photopolymerization yields can help validate the TPA nature of SU-8 photopolymerization observed in this study. Intensity thresholds for photopolymerization and optical damage in SU-8 differ by the factor of only 2.5,¹³ which severely limits the available range of incident intensities, while spectrally nonlinear photoexcitation depends not only on SU-8 but also on the resonant plasmonic field enhancement (Figure 1b).

Although two-photon sensitivity of photopolymers has already been exploited for the near-field imaging of nanoparticle plasmon modes under laser excitation,^{12,16} our work is crucially different from the previous studies because it demonstrates that TPA can be induced under exposure to a continuous-wave, incoherent radiation source. This result can be considered an illustration that the TPA theory proposed in 1931 can be verified experimentally without a coherent light source. From a practical viewpoint, nonlinear photoexcitation by low-intensity sources may enable cost- and energy-efficient nanofabrication, microscopy, and exploitation of nonlinear absorption in the solar energy conversion.

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References

- (1) Göppert-Mayer, M. *Ann. Phys.* **1931**, *401*, 273.
- (2) Kaiser, W.; Garrett, C. G. B. *Phys. Rev. Lett.* **1961**, *7*, 229.
- (3) Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843.
- (4) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73.
- (5) Sun, H.-B.; Matsuo, S.; Misawa, H. *Appl. Phys. Lett.* **1999**, *74*, 786.
- (6) Xu, H.; Aizpurua, J.; Käll, M.; Apell, P. *Phys. Rev. E* **2000**, *62*, 4318.
- (7) Hao, E.; Schatz, G. C. *J. Chem. Phys.* **2004**, *120*, 357.
- (8) Ueno, K.; Juodkazis, S.; Mizeikis, V.; Sasaki, K.; Misawa, H. *Adv. Mater.* **2008**, *20*, 26.
- (9) Ueno, K.; Juodkazis, S.; Mizeikis, V.; Sasaki, K.; Misawa, H. *J. Am. Chem. Soc.* **2006**, *128*, 14226.
- (10) Ueno, K.; Mizeikis, V.; Juodkazis, S.; Sasaki, K.; Misawa, H. *Opt. Lett.* **2005**, *30*, 2158.
- (11) Ueno, K.; Juodkazis, S.; Mino, M.; Mizeikis, V.; Misawa, H. *J. Phys. Chem. C* **2007**, *111*, 4180.
- (12) Sundaramurthy, A.; Schuck, P. J.; Conley, N. R.; Fromm, D. P.; Kino, G. S.; Moerner, W. E. *Nano Lett.* **2006**, *6*, 355.
- (13) Witzgall, G.; Vrijen, R.; Yablonovitch, E.; Doan, V.; Schwartz, B. *J. Opt. Lett.* **1998**, *23*, 1745.
- (14) See http://www.microchem.com/products/pdf/SU8_2-25.pdf.
- (15) El Ahrach, H.; Bachelot, R.; Vial, A.; Lerondel, G.; Plain, J.; Royer, P.; Soppera, O. *Phys. Rev. Lett.* **2007**, *98*, 107402.
- (16) Hubert, C.; Romyantseva, A.; Lerondel, G.; Grand, J.; Kostcheev, S.; Billot, L.; Vial, A.; Bachelot, R.; Royer, P.; Chang, S. H.; Gray, S. K.; Wiederrecht, G. P.; Schatz, G. C. *Nano Lett.* **2005**, *5*, 615.

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