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# Seven-Photon-Excited Upconversion Lasing at Room Temperature

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**In contrast to conventional harmonic generation, realized using nonlinear crystal, the multiphoton-excited (MPE) laser has critical applications in fluorescence imaging probe and biological photonics. Here, lasing emission from a crystal plate under 7-photon excitation at room temperature is reported for the first time, which is the highest order MPE lasing reported up to date. Moreover, MPE lasing spikes and high-order harmonic peaks are observed simultaneously. The saturation behavior of harmonic generation and abnormal fluorescence enhancement identify that the interaction of photon–electron in 7-photon-excited lasing transits from photon-excited to a more field-driven regime. The results may pave the way for short wavelength laser by taking advantage of the processability and larger scale of solid crystals.**

With development of strong short-duration laser pulse, nonlinear interaction of photon and material has got remarkable progress, such as double frequency,[1] four-wave mixing,[2] multiphoton flourescence,[3,4] and recent attosecond ultrashort pulse.[5,6] The exploration of high-order interaction between photon and atom has been a furious and innovational topic. Especially, multiphoton-excited/absorption upconversion laser has versatile applications, such as optical storage memory and laser spectroscopy.[7–9] In contrast to 2nd or 3rd harmonic generation, strict phase matching and polarization orientation are not necessary in multiphoton-excited (MPE) laser.[10,11] Therefore the tuning region of pumping light for MPE laser can be significantly extended. Since 3-photon-excited amplified spontaneous emission in organic materials was observed,[12] several interesting phenomena of 3-photon-excited stimulated emission have been reported.[13–15] Especially, the 5-photon-excited stimulated emission was successfully realized through organic materials solution.[16] Nevertheless, low damage threshold of organic materials would be a bottleneck for its practical application. Therefore, special attention had been paid to semiconductor materials.[17–19] However, no report is on MPE lasing above 4-photon until now. In traditional theory about MPE lasing, the light field–induced electron dynamic effect was ignored.[10] Indeed, the exploration of light field–driven electron in crystal indicates that intense infrared (IR) laser field will induce ultrafast interband transport.[20,21] This may open the possibilities of studying high-order MPE upconversion lasing through light field-assisted tunneling.

In this letter, we used the femtosecond IR pulse to explore 7-photon-excited lasing in crystal plate. Under strong optical field, the interaction of photon–electron transits from photon-excited to a more field-driven regime.[22] In this case, electron transient absorption exhibits sub-femtosecond dynamics in the oscillating electrical field.[23] Therefore, the electron transition by light field–induced tunneling can happen for the photons with energy below bandgap. Moreover, the saturation behavior of high harmonic generation (HHG) and abnormal fluorescence enhancement can be illustrated by light field-assisted tunneling mechanism. The light field–driven tunneling transition for MPE lasing may be an effective solution for frequency conversion laser device.

**Figure 1**a illustrates the experiment setup for MPE fluorescence and lasing measurements. High quality as-grown ZnO crystal was used as the active media, and its crystalline and optical qualities were given (Figure S1, Supporting Information). Typical near bandedge emission (NBE) of sample was realized through tunable MPE scheme (Figure 1b). Remarkably, 3rd and 5th harmonic (3rd/5th-h) peaks of pumping light were also clearly seen in spectra. This phenomenon indicates that NBE peak resulted from intrinsic band to band transition

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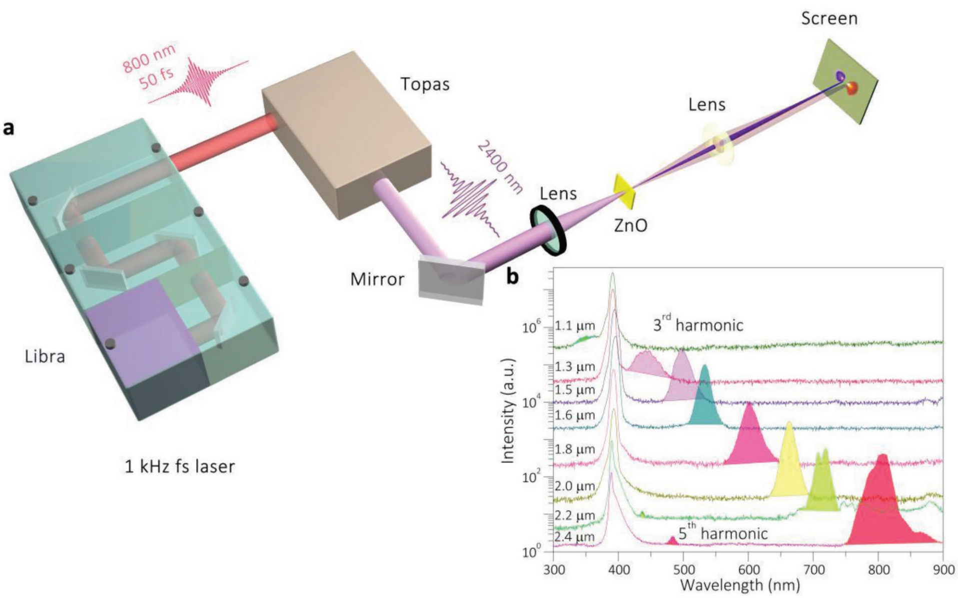


**Figure 1.** Experimental setup and MPE optical characteristic analysis. a) Experimental setup of femtosecond laser pumping system for MPE lasing. The wavelength can be varied from 800 nm to 2.5 µm with the temporal width (repetition rate) of 50 fs (1 kHz). b) The upconversion NBE located at 390 nm was realized through MPE in tremendous tunable region (1.1–2.4 µm). Moreover, the 3rd- and 5th-h peaks of tunable pumping light were also indicated obviously in spectra.

in media, while harmonic peak is associated with incident light. Recently, the HHG has been attributed to electron dynamic nonlinear response in energy band.[24]

Benefiting from high optical gain and antiradiation, ZnO is a promising candidate for MPE laser.[25,26] The MPE nonlinear optical gain characteristics of samples were investigated by variable stripe length method (Figures S2 and S3, Supporting Information).[27] 7-photon (2418 nm)-excited stimulated emission in m-face crystal plate was measured at room temperature (**Figure 2**a). A broad spontaneous NBE with a linewidth of 15 nm emerges at low excitation intensity (<250 GW cm$^{-2}$). Furthermore, NBE collapses into a multimode lasing peak at

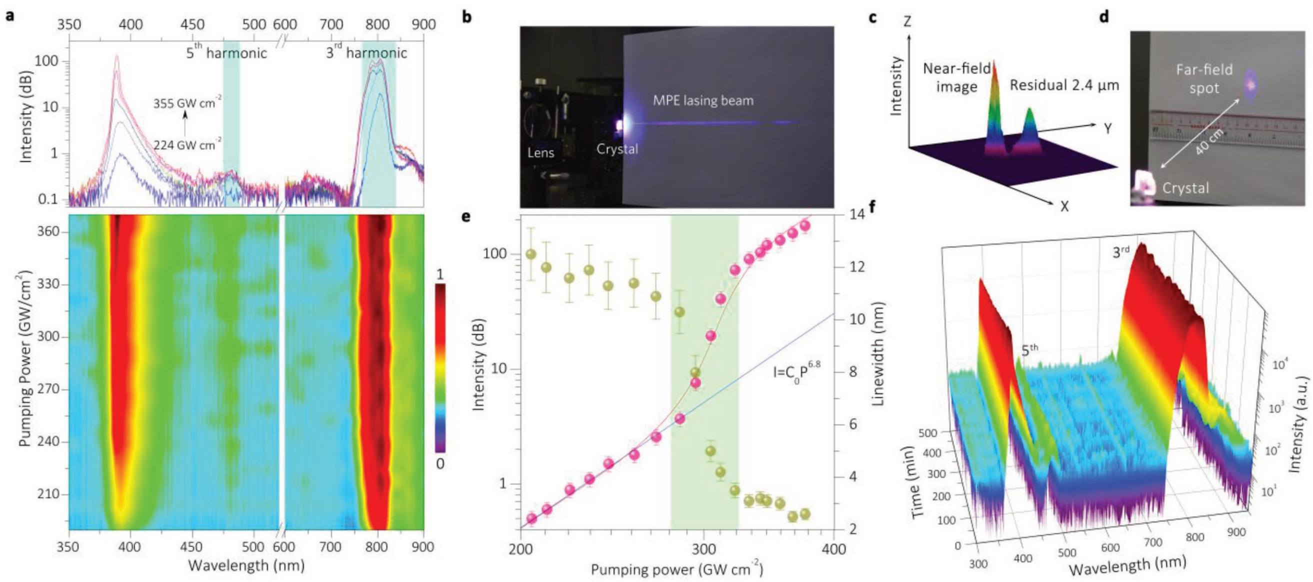


**Figure 2.** Seven-photon excited lasing and lifetime stability. a) Plot of emission spectra under various powers with 2418 nm laser excitation. Detailed evolution of NBE versus pumping intensity (bottom). b) Lasing emission beam of the sample through MPE. c) Charge-coupled device (CCD) image of lasing beam, which shows a Gauss-type intensity distribution. Meanwhile, the residual pumping light was also shown obviously. d) Far-field pattern of lasing beam. Divergence angle of lasing beam was extracted to be about 0.08 rad (≈5.0°). e) The intensity and width of peak versus excitation intensity. In shaded region, the light was transiting from spontaneous emission to lasing. f) Lifetime stability of 7-photon-excited lasing, in which the spectra were recorded with 2 min interval.

higher power. It is noted that 3rd- and 5th-h peaks of pumping light were displayed clearly in the spectra, which unambiguously confirmed that the lasing was resulted from 7-photon-excited upconversion. Detailed evolution of NBE and HHG as a function of pumping intensity was presented in bottom part of Figure 2a. Here, it should be noted that fine structure of lasing from crystal Fabry–Pérot (F–P) cavity was not detected due to the relatively large cavity length (300 µm). It is worthy to point out that this is the first observation of coexisted MPE lasing and HHG signal up to date, which indicates that MPE lasing and HHG were generated synchronously.

The intensely coherent and highly directional lasing with blue-violet beam can be observed on screen above excitation threshold (Figure 2b). Near-field spatial intensity distribution of lasing was a typical Gauss-type, and nearby peak indicates the residual pumping light (Figure 2c). In addition, the divergence angle was extracted to be about 5.0° according to far-field pattern (Figure 2d). To obtain pumping threshold, the peak intensity and width versus excitation power were studied (Figure 2e). The NBE intensity increases superlinearly, meanwhile the width decreases to 4.1 nm when excitation intensity raises to threshold ($P_{th}$) of about 295 GW cm$^{-2}$. The output exhibits a well-known kink behavior, which represents the transition from spontaneous emission to typical lasing oscillation, and the fitting of curve using equation $I \propto P^n$ gives the value of $n$-factor to be about 6.8. In addition, lasing characteristics of sample through 4-, 5-, and 6-photon excitation were also investigated (Figures S4–S6, Supporting Information). Remarkably, the decay lifetime of upconversion lasing (6.5 ps) is much longer than HHG (1.0 ps), as shown in transient-absorption spectra (Figure S5c, Supporting Information).

7-photon-excited lasing emission from sample shows no signs of optical damage, even after operating for 6–10 h every day over a few weeks, which can also be revealed by the evolution of 3rd- and 5th-h peak intensity (Figure 2f). The slight variation can be attributed to thermal fluctuation originating from environment. In order to investigate the fine structures of lasing spike, upconversion lasing in thinner F–P cavity was realized (**Figure 3**). The spectra show spontaneous emission at low excited power ($0.3P_{th}$), while the well-defined lasing modes (linewidth $\delta\lambda$ = 0.8 nm) were emerged at high power ($1.5P_{th}$). Schematic diagram of lasing oscillation was given (inset of Figure 3), which indicates the coherence optical feedback was supplied by F–P cavity.

Another feature of 3rd-h and 5th-h peak originated from pumping light (2418 nm) is that their intensity exhibits a saturation behavior obviously at high excited power (**Figure 4**a). This saturation trend of HHG was observed in series of experiment, for example, 4th-h of 1800 nm (Figure S7d, Supporting Information), which was distinguished from thermal effect because HHG was slightly influenced by temperature. In contrast to HHG, the intensity of upconversion lasing was enhanced strongly at high pumping power. Therefore, the deep insight into high-order MPE lasing is crucial for this extreme nonlinear optics, however, there is no detailed report about MPE lasing under strong laser field. For exploring the MPE lasing mechanism, temperature-dependent 4-photon (1.3 µm)-excited fluorescence measurements were performed (Figure 4b). In contrast to 3rd-h peak, the NBE shows an obvious redshift

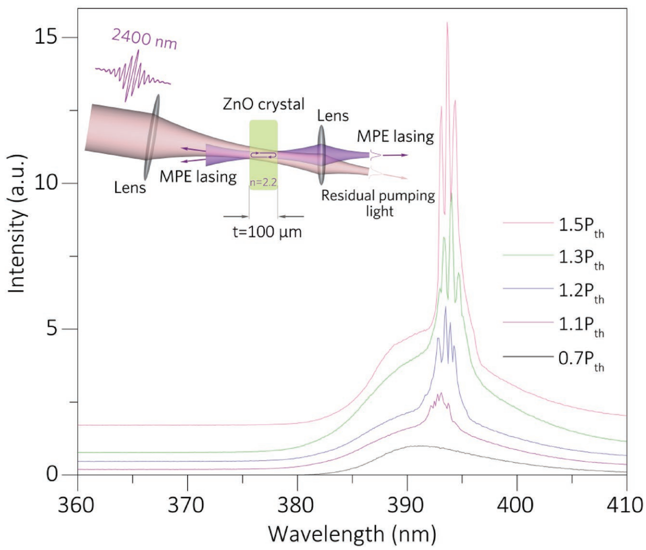


**Figure 3.** Lasing spectra in F–P resonator via 7-photon excitation. Fine structure of lasing spectra from crystal plate with increasing of excitation power, which illustrates the evolution from spontaneous emission to well-defined lasing modes. Inset, schematic of light feedback that supplied by F–P resonator.

with increasing of temperature. Meanwhile, NBE intensity was affected significantly by measuring temperature. The analogous evolution of NBE and 7th-h peak under 7-photon (2.5 µm) excitation can also be observed clearly (Figure 4c,d). Although NBE intensity decreases monotonously in region of 77–150 K, it was enhanced anomalously from 150 to 220 K. Upon 220 K, NBE intensity decreases gradually as normal case. Above anomalous behavior exhibits more obviously under higher power conditions (240 and 280 GW cm$^{-2}$). It is emphasized that the anomalous evolution is not occasional because it appears in a series of measurements. In addition, 5-photon-excited temperature-dependent upconversion fluorescence also shows the similar behavior (Figure S7, Supporting Information).

Here, we present a light field-assisted tunneling mechanism to illustrate the above anomalous upconversion photoluminescence (PL) evolution. Actually, the oscillating electric field of femtosecond pulse is about $10^8$ V cm$^{-1}$ ($10^{11}$ W cm$^{-2}$) or more.[28] In such large electric field regime, the band dressing,[29] dynamic Franz–Keldysh effect will occur.[30] Electrons will be driven in sub-femtosecond timescale, and tunnel from top of valence band (VB) into bottom of conduction band (CB). In schematic of MPE electron transition (Figure 4e), $E_i$ is virtual energy state in bandgap, $E_C$ and $E_V$ are CB and VB, respectively. First, electrons can be excited into a serial of virtual states. Meanwhile, the electrons in virtual state $E_i$ can tunnel into nearby point CB through triangular potential barrier under light-field driven. As a result, a large number of electron–hole pairs will be generated in CB and VB, respectively. In our experiments ($3 \times 10^{11}$ W cm$^{-2}$), photon-excited and field-driven coexist in the excitation process. Therefore total transition probability of electron can be calculated using a phenomenological expression including above two effects. The tunneling probability $T_i$ of $i$th path in bandgap can be described by Wentzel–Kramers–Brillouin approximation.[31,32]

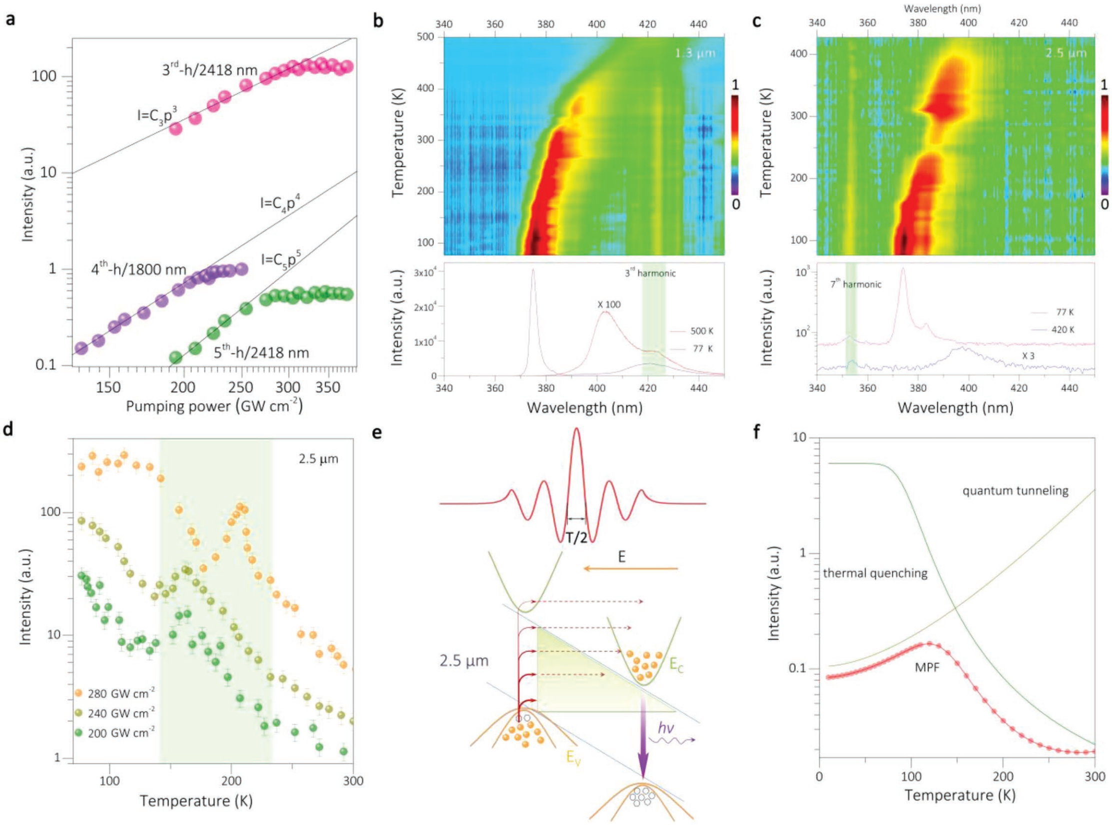


**Figure 4.** Light field-assisted tunneling for MPE lasing. a) Output intensity of 3rd-h/5th-h of 2418 nm and 4th-h of 1800 nm versus pumping power. Under strong excitation power, the HHG exhibits a saturation behavior obviously. Solid lines are fitting according to $I_{\text{harmonic}} = C_n p^n$. b) Detailed temperature-dependent MPE PL in the range of 77–500 K with 1.3 µm excitation (100 GW cm$^{-2}$). c) Evolution of MPE PL versus temperature with 2.5 µm excitation (280 GW cm$^{-2}$). d) NBE intensity as a function of temperature under various powers. An abnormal enhancement behavior of PL intensity exhibits more obviously under high power condition. e) Schematic view of the light field-assisted electron tunneling transition. The energy bands were pulled under intense laser field during the half period, which enables electrons tunnel from $E_i$ state into CB. f) Calculated result about light field-assisted MPE fluorescence intensity versus temperature according to Equation (2).

$$T_i = \exp\left[-\frac{4\sqrt{2m^*}\left(E_g - i\hbar\omega_0\right)^{\frac{3}{2}}}{3e\hbar E}\right] \tag{1}$$

where $E_g$ is bandgap energy, $m^*$ is effective mass of electron, $\hbar\omega_0$ is excited photon energy, and $E$ is light-field intensity. Combining the effect of photon-excited and field-driven, MPE electron density in CB is given by

$$\Delta N_C = \sum_{i=0}^{n} N_V B_i \int_0^{\tau} E(t)^{2i} \exp\left[-\frac{4\sqrt{2m^*}\left(E_g - i\hbar\omega_0\right)^{\frac{3}{2}}}{3e\hbar E(t)}\right] dt \tag{2}$$

where $N_V$ is electron density in VB, $B_i$ is $i$th order transit coefficiency, and $\tau$ is pulse duration. The transition probabilities of paths under 7-photon excitation with different field intensities were calculated (Figure S7d, Supporting Information). As light field ($E$) increases two times, the density of excited electrons will be enhanced ten orders. According to Equation (2), simulated result (dotted line) about MPE NBE intensity versus temperature displays an enhancement behavior in the region of 90–180 K (Figure 4f). Thus, anomalous enhanced PL phenomenon can be well explained by light field-assisted tunneling upconversion transition. With increasing of temperature, tunneling probability $T_i$ of electrons on virtual state will be promoted due to the shrink of bandgap. As a result, NBE intensity was enhanced significantly. Nevertheless, thermal effect will dominate in the CB to VB recombination process as temperature increases further. Consequently, NBE intensity will decrease in higher temperature region. In addition, the saturation behavior of 3rd-h and 5th-h peak can also be interpreted using electron tunneling mechanism. Under high light-field driven, tunneling probability of electrons on 3rd-h (5th-h) related energy state will be enhanced dramatically. Therefore, the electron density on virtual states was restricted, which induces the saturation evolution about the output intensity of 3rd-h (5th-h) peak versus pumping power.

We first demonstrated 7-photon-excited upconversion lasing from crystal plate. The coexistence of MPE lasing and HHG was observed under femtosecond pulse excitation. Furthermore, saturation behavior of 3rd-h (5th-h) peak and anomalous enhanced fluorescence phenomenon were studied comprehensively. These typical evolutions identified that the interaction of photon–electron in 7-photon-excited lasing transits from photon-excited to a more field-driven regime. Our results prove that it is feasible to realize higher order MPE upconversion lasing as a substantial number of electrons were injected into CB by means of light field-assisted tunneling. The light field–driven tunneling mechanism moves a step toward a full understanding of MPE lasing, and it is anticipated that this study will motivate numerous experimental efforts and theoretical passion to further investigate the high-order MPE lasing.

## Experimental Section

*Crystalline quality of sample*: The ZnO crystal was grown by hydrothermal method, meanwhile the double faces of sample were polished carefully. The crystalline quality of sample was studied using a JEM-2010 X-ray diffraction (XRD).

*Multiphoton excited lasing measurements*: The MPE lasing measurement was carried out at room temperature. The femtosecond pulses with 50 fs duration (700-2600 nm) were generated from optical parametric amplifier (OPA) system. The OPA system was pumped by a regenerative amplified mode-locked *T*i:Sapphire oscillator at a center wavelength of 800 nm with power of 5 W operation at 1 kHz repetition rate. The emission light was collected from the forward direction through a focus lens and an optical fiber. An Aceton monochromator (SP2500) attached with a thermoelectric cooling silicon CCD was used to analyze the emission spectra. To eliminate the fundamental frequency light from OPA, filters were used to remove the residual signals.

*Theoretical modelling*: As described in the paper, ZnO was illustrated by a two-band model and the bandgap was acted as the energy barrier for electron tunneling under the intense light-field driving. The quantum-tunneling probability $T_i$ through the triangular energy barrier was calculated by the WKB approximation. In the calculation of electron transition, nonradiation recombination was neglected.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

lasing mode, multiphoton excitation, quantum tunneling, solid crystals, upconversion lasing

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