Close-to-Atom Scale Laser Manufacturing for 30-Color Turn-key Single-Photon Emitters

Hong-Bo Sun (✉ hbsun@tsinghua.edu.cn)  
Tsinghua University  https://orcid.org/0000-0003-2127-8610

Xiao-Jie Wang  
Tsinghua University

Hong-Hua Fang  
https://orcid.org/0000-0003-3636-1011

Zhen-Ze Li  
State Key Laboratory of Integrated Optoeletronics, College of Electronic Science and Engineering, Jilin University

Dan Wang  
Jilin University

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Abstract

Atomic and close-to-atom scale manufacturing is now considered an avenue toward single-photon emitters, single-electron transistors, single-atom memory, and quantum-bit devices for future communication, computation, and sensing applications. Laser manufacturing is outstanding to this end for ease of beam manipulation and batch production, and no requirement for photomasks. It is, however, suffering from optical diffraction limit and lacks atomic and close-to-atom scale precision. Herein, we circumvent this limitation by exploiting a threshold tracing-and-lock-in method, whereby the 2-order gap between atomic point defect complexes and optical diffraction limit is surpassed. As a result, bright (up to 10 Mcounts s$^{-1}$) single-photon color centers are deterministically created from few-layer hBN with feature size of less than 5 nm and a near-unity yield. Around 94% of them emit monochromatically at around 30 individual wavelengths from 500 nm to 800 nm. A turn-key monochromic single-photon emitter of demanded color is attained by integrating it with 5-V blue laser diodes.

Introduction

Since early demonstrations of femtosecond laser as a three-dimensional (3D) processing tool,$^{1-4}$ microdevices with exciting optical, electronic, mechanical, and magnetic functions have been manufactured,$^{5-9}$ by which novel concepts from 3D quantum photonic integrated circuits to intelligent micro-robots are enabled.$^{10-12}$ Much effort in the past decade in this field has been devoted to improving manufacture resolution, and several tens of nanometer feature sizes, far beyond the optical diffraction limit, have been reported based on multiphoton absorption,$^1$ stimulation emission depletion,$^{13,14}$ far-field-induced near-field enhancement,$^{15}$ and photoexcitation-induced chemical bonding effects.$^{16}$ Nevertheless, single-electron transistors, single-photon emitters, single-atom memory, and quantum-bit devices require higher manufacturing accuracy, i.e., the ability to address single-atom defects complex (SADC) for initiating functions such as single-photon emission, as is still missing. Along this line, a recent progress is direct laser writing in wide-bandgap semiconducting materials, such as diamond, silicon carbon, and hexagonal boron nitride (hBN),$^{17-22}$ in which color centers that emit single photons are readily created and randomly distributed at edges of the several hundred-nanometer damaging areas. The relatively low positioning accuracy and low yield of color centers are challenging its usage on nano-integrated photonic quantum devices.

In this work, we propose and experimentally demonstrate close-atomic-scale manufacturing using a threshold tracking and lock-in (TTL) method, by which feature sizes are as small as a few nanometers, e.g., $< 5$ nm, $\sim \lambda/100$, approaching statistic uncertainty limit, are realized. It enables the deterministic fabrication of single-photon color centers with a yield of 99.9% from few-layer hexagonal boron nitrides (hBN). Different from electron-beam or focus-ion-beam generated color centers,$^{23-26}$ here they show high purity, high stability (no spectral diffusion and blinking), and so far, the highest brightness with single-photon count rates of more than 10 Mcounts s$^{-1}$.

Threshold Tracking And Lock-in (TTL) Technology For Close-to-atom Scale Precision

Material damages occur only if an irradiation laser is sufficiently strong, while the damaging area becomes invisible under optical imaging and not spectroscopically detectable due to the signal weakness when its size is reduced to atomic or close-to-atom scale. A primitive unit that is geometrically small but optically large enough to initiate unique absorption, emission, and scattering functions different from the background materials, for example, single-photon emission at a certain wavelength, is here defined as single-atom defect complex (SADC). Under the extreme case, a SADC consists solely of a single-atom defect like a vacancy, an interstitial atom, or a broken bond. Its size, therefore, ranges from an atom
diameter to several nanometers, defined by the maximum local electron or energy transfer distance. Now a question arises, is it possible to deterministically produce such a small size SADC by optical fabrication?

A threshold tracking and lock-in (TTL) technology is proposed to solve this problem (Fig. 1). It is known that a femtosecond laser damaging threshold ($E_{\text{thr}}$ reported values) of most solids, particularly crystalline matter, is considered an unambiguous numerical value, a reflection of chemical bond strength of the material. It seems that this damage can be characterized by a sudden appearance of some sort of irreversible modification. However, observations are strongly dependent on the characterization method and its sensitivity. Furthermore, the experimentally defined threshold $E_{\text{thr}}$ differs strongly for different experimental standards set. Figure 1b shows the damaging area reduces from $\Phi \sim 200$ nm to $\sim 6$ nm by keeping the pulse energy at $E_p = 4.66$ nJ, while changing the shot number $N$ from 3 to 1 (see more detailed data in Supplementary Fig. 4). This fact enlightens us the experimentally defined $E_{\text{thr}}$ is dependent on the experimental criteria, and the visibility of damaged area doesn't reflect the real “threshold” for bond cleavage. Figure 1c shows the dependence of shot number on pulse energy for the visibility of laser processed area under an optical microscope. 4.83 nJ is required for single-shot irradiation, while 2–5 pulses are needed for $E_p = 4.70$ to 4.66 nJ. A critical value, $E_{\text{th0}} = 4.65 \pm 0.01$ nJ, which is close to the lowest energy to produce a visible defect, is therefore deduced by the curve extrapolation when the material is processed with infinite laser shots.

The new parameter, $E_{\text{th0}}$ is significantly smaller than $E_{\text{thr}}$. In comparison, the physics of $E_{\text{th0}}$ is clearer: single-shot pulse creates, by mechanisms like multi-(n)-photon absorption, the smallest possible material damage, i.e., a SADC as a seed, and then it is easily magnified by ensuing pulses via multiphoton absorption of smaller $n$ or even by linear absorption, due to appearance of defect energy levels contained in SADC (Fig. 1a). Lower energy irradiation leads to reversible photoexcitation and no permanent defects occur. With multiple shots amplification, the experimental determination of $E_{\text{th0}}$ become independent either on observation methods (by imaging or by spectroscopy, optically or electronically) or on their sensitivity. It is, therefore, a factor more accurate than $E_{\text{thr}}$ and intrinsic to a solid. Figure 1d exhibits the high-resolution transmission electronic (TEM) image of a SADC created by femtosecond laser. Although the morphology varies from spot to spot, the appearance of sub-5 nm feature sizes is highly reproducible (Supplementary Fig. 5). The advent of sub-5 nm SADC immediately evokes a question, what is the ultimate limit in femtosecond laser fabrication? Conventional laser damage threshold refers to a specific optical energy flux density, the critical energy absorbed per unit area that leads to excitation and collapse of lattice-electron subsystems. In the view of statistical thermodynamics, the threshold is associated with a critical temperature of the subsystem that is scalable to a radius of a Gaussian beam, regardless of damaging mechanisms. In this regard, the laser damaging area could be arbitrarily small until the single atom level if we lower the laser pulse energy sufficiently near the threshold. However, the model, based on the continuous medium hypothesis, fails due to the statistic uncertainty limit. The energy of particles in a solid distributes following probabilistic law. Single-atom ablation means that an atom gains sufficient kinetic energy to overcome binding energy $\varepsilon_b$ and escapes from the system. The probability of the event occurrence, according to the Maxwell-Boltzmann distribution, is:

$$P(E \geq \varepsilon_b) = 1 - \text{erf}(r) + \frac{2r}{\sqrt{\pi}} e^{-r^2}$$

1

where $r = \sqrt{\varepsilon_b/k_BT}$ with $\text{erf}(x)$ being the error function. When the $E_p$ decreases towards the threshold, the light intensity gradient at the Gaussian beam center becomes less steep and ineffective in defining local atom kinetic energy, in another world, the probability isn't geometrically truncated by statistic $k_BT$, that is, when $r \ll 1$, we have:

$$P(E \geq \varepsilon_b) = \frac{2}{\sqrt{\pi}} \sqrt{\varepsilon_b/k_BT} e^{-\frac{\varepsilon_b}{k_BT}}$$

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Following the analysis, laser ablation of a single atom doesn’t necessarily occur at the geometric center of a laser focus when the laser pulse energy is reduced towards the SADC threshold, but appears randomly in the small range. The uncertainly limit $r_m$, is estimated using $\gamma = \Delta E_{kin}/U_p$<sub>1</sub>, where $\Delta E_{kin}$ is the statistical fluctuation of the electron kinetic energy, $\Delta E_{kin}E_{kin}/\sqrt{N}$, ($N$ is the total number of excited electrons) and $U_p$ is the pondermotive energy.<sup>30,31</sup> For hBN, we have $r_m \sim 3$ nm (Supplementary Note 1), in accordance with the experimental observation of less than 5 nm. It means that the size of SADC may be further reduced till the single-atom level, but its positioning uncertainty limit of 3 nm, the precision limit, has almost been reached.

**Deterministic Manufacturing Of High Purity Color Centers**

SADC requires not only a geometrically small size, but also possesses a completely novel optical or electronic function. To reach this end, the laser-written hBN samples are annealed at 1000 °C in a vacuum for activating defects, and 2-µm spaced written sites exhibit stable emission under 405-nm photoexcitation (Fig. 2a). More than 10 peaks are discernible in photoluminescent (PL) spectra collected from the site 1 (4.86 nJ, Fig. 2b), and the peak number drops to 4 (site 2, Fig. 2c) and 1 (site 3, Fig. 2d) for $E_p = 4.78$ nJ and 4.68 nJ, respectively. The latter has approached the SADC creation threshold, exhibiting a single-color emission peak with full width at half maximum of 3 nm.

For deep insight into SADC physics from the sharp peak emission, we perform photon autocorrelation measurement with Hanbury Brown-Twiss (HBT) method. The antibunching curve at the isolated spectral window gives $g^2(0)$ value, an indicator of single-photon purity, as it is lowered from 0.48 (right, Fig. 2b) to 0.09 (right, Fig. 2d). Thus, it is reasonable to conclude that the multiple peaks in Fig. 2b and Fig. 2c come from a large population of color centers, emitting varied wavelengths. When the dot size shrinks to a certain value, here < 5 nm for hBN, short-range inter-defect energy, or electron transfer functions. It allows electronic excitation moves from a donor emitter to an acceptor, jointly enhancing single radiative recombination with a sharp peak (Fig. 2d). Similar energy or electron transfer mechanism has been the basis of and clearly described by Förster and Dexter transfer effects.<sup>32–34</sup>

The physical connotation of SADC in laser-written hBN is thus manifest. Optically it emits single photon at a single wavelength. The upper limit of its size is prescribed by the donor-acceptor energy transfer range, to several nanometers, a combination of single atomic defects. In the lower limit, it may be a real single atom defect but situated with a positioning uncertainty of several nanometers. Experimentally, by tuning writing laser pulse energy from $\sim 0.5–5\%$ over $E_{th0}$, the yield of bright color centers that emit single photons at not less than one wavelength is 99.9% (see large-scale patterns of single-photon emitters in Supplementary Fig. 10). Narrowing the laser writing pulse energy window to $0.5\%$ ~ $0.8\%$ above $E_{th0}$ brings about a 94% yield of single-color single photon emission (Fig. 3a), on which no similar reports have been found. The high yields (from the function point of view) and the high precision of SADC positioning with an uncertainty of several nanometers (from the geometry point of view), set a new milestone in deterministic laser manufacturing of single-photon color centers.

**High Reproducibility, High Brightness, And High Durability**

The single-color single-photon emission feature preserves if the size of SADC in hBN remains less than a critical value, here 5 nm. Fixing $E_p = (1 + 0.5\%) E_{th0}$ (with fluctuation of 0.3% from pulse to pulse, see Supplementary Fig. 6) produces high purity single-photon emitters of high homogeneity, as shown by the confocal PL image of a dot array (Fig. 3a). All the written sites are identified with single sharp emission peaks (Supplementary Fig. 13) and low photon correlations $g^2(0)$ (Supplementary Fig. 14). Statistic data shows the yield of single-color single-photon emitter reaches 94%, guaranteeing high manufacturing reproducibility.
The single emitters retain high brightness, as shown by the room-temperature PL intensity as a function of excitation laser power (Fig. 3b). The fitting yields $I_{\text{sat}} = 9.0 \text{ Mcounts s}^{-1}$ with the saturation power $P_{\text{sat}} = 764 \mu\text{W}$. Approximately 91% of emitters exhibit single-photon count rates more than 5 Mcounts s$^{-1}$, and 20% of them exceed 10 Mcounts s$^{-1}$ (More information see Supplementary Note 3). The high brightness is attributed to minimized nonradiative channels and reduced energy loss in a SADC, as is further proved by the high polarization visibility of 77% (Fig. 3c), indicating that the emission center consists of a single dipole.

Another unique feature of the SADC single-photon emitters is their high durability. 94% of them exhibit high spectral and intensity stability with negligible spectral diffusion or intensity fluctuations under one milliwatt continuous-wave laser excitation (Figs. 3d,e). From the time-series spectra of a single-photon emitter over a period of 5 minutes and time trajectory with a binning time of 50 ms, no blinking or bleaching was observed (Supplementary Fig. 20, Supplementary Fig. 21). The color centers also exhibit a long shelf lifetime since no emission intensity degradation has been found after 6-month storage in atmospheric environment (Supplementary Fig. 23).

**Compactly Integrated Turn-key Monochromatic Single-photon Emitters**

Given a pulse repetition rate of 1MHz, single-pulse writing makes it theoretically possible to produce $10^6$ single-photon color centers in a second. Although the wavelength of individual centers among them is unlikely to be precisely tailored by tuning laser pulse energy, each emits a definite color (Fig. 4a). The initial atomic structure of a tiny, damaged area immediately after laser irradiation may possess higher diversity; the 1000°C annealing reforms them, which are finally stabilized to limited SADC configurations. A histogram of the spectral distribution of zero-phonon-line for approximately ten thousand centers indicates that a maximum of 30 colors are present, each from a specific SADC, and they emerge under the current experimental condition with definite probabilities (Fig. 4b), for example, 6.7% at 565 nm, the highest probability. Single-photon emitters of different colors, from green, 500 nm, to red, 800 nm, are sorted from batch-produced samples, and thus those with demanded colors are readily available.

Single photon emission at such a broad spectral range is accomplishable by a blue laser diode pumping. A turn-key single photon emitter is thus enabled by packaging a particular color SADC-contained hBN patch with an 0.6-mm focal length mini-lens and a commercially available 450-nm laser diode. Experimentally, the laser diode, powered by a 5-V coin cell battery, provides power up to 1 mW, and the light is focused by the mini-lens onto a pre-selected single photon color center. The optical performance of emitters, including high purity, high reproducibility, high brightness, high durability, and multiple colors, are well retained after the package (Fig. 4d). Furthermore, the emitters, consisting of limited devices with no movable parts, exhibit high robustness, small size (1.9-cm in length including 1-cm pin), lightweight (20 gram), and allow for turn-key usage (right, Fig. 4c). It may find immediate use in quantum physics and device applications.

**Summary And Outlook**

In summary, we report sub-5-nm close-to-atom-scale precision femtosecond laser fabrication by threshold-tracking and lock-in technology, which is approaching the statistic uncertainty limit, a new milestone after the optical diffraction limit. The technology is employed for deterministically producing SADC in a few-layer hBN, an atomic configuration that is geometrically small but optical large enough to initiate a novel function. The SADC, recognized, in nature, as a single-photon-emission single-color center, exhibits excellent performance such as high purity, reproducibility, high brightness, and high durability. It emits a definite single color among 30 options from green, 500 nm, to red, 800 nm, under a simple blue laser diode pumping. This allows for a turnkey package of single-photon emitters with demand colors. The compactly integrated 30-color turnkey monochromatic single-photon emitters are prospective in quantum physics and device applications.
Methods

hBN Sample preparation

We used hBN crystals obtained from 2D Semiconductors Inc. to generate flakes using a Scotch-tape mechanical exfoliation method. The desired hBN flake was transferred onto a flat quartz substrate via a “dry transfer” technique based on a polydimethylsiloxane (PDMS) framework. The sample was then mounted on the three-dimensional stage for laser position and pattern.

Laser Writing Setup

The setup for laser writing is illustrated in Supplementary Fig. 1. A commercial femtosecond laser (Pharos, light conversion) was used as a light source, which delivered a laser pulse with a duration of around 230 fs, and a wavelength of 1030 nm. For the writing, the second harmonic generation was produced by using a BBO crystal. A high numerical aperture objective lens (NA = 0.95, 50× Olympus) was used to tightly focus the laser pulse for fabricating color centers. The measured full width at half maximum (FWHM) of the focal spot is ~ 357 nm. A precision translation stage is used for the three-dimensional scanning. The pulse energy was controlled using a combination of a half-wave plate and a polarizer and monitored by a photodetector before the objective lens.

High-temperature Annealing

High-temperature annealing was performed in a tube furnace following the laser-writing process. The samples were annealed at 1000 °C for 2 hours at a 10⁻⁴ Pa vacuum. Then, the samples were cooled down to room temperature for 4 hours.

Room-temperature Optical Characterization

Optical measurement, including the confocal imaging, the fluorescence spectrum, and antibunching experiments, was based on our home-built confocal microscope, as shown in Supplementary Fig. 8. A continuous-wave 488 nm laser was used for excitation. The laser was focused onto the sample using a high-numerical-aperture (NA = 0.95, Olympus) objective lens. The FWHM of the focal spot is 339 nm. A polarizer combined with a half-wave plate was used to control excitation power. For PL mapping and position, an X-Y-Z piezoelectric stage (PI instruments) was used. The collected fluorescence was filtered using a 500nm dichroic mirror and an additional long-pass filter (Thorlabs FELH0500 or FELH0550). The signal was split by a beam splitter (30:70) and coupled into a grade-index fiber, one into the spectrometer (Princeton instruments) for collecting PL spectra, and the other into the two avalanche photodiodes (Excelitas) for autocorrelation measurements. The fiber aperture serves as a confocal pinhole. Antibunching measurements were done using a time-correlated single-photon counting module (PicoHarp 300, PicoQuantum). The $g^2(t)$ data were not corrected for background luminescence.

Cryogenic PL Spectra Characterization

Cryogenic PL measurement in Supplementary Fig. 19 was performed using a Montana S50 (Montana Instruments, s-series). The sample of hBN on a quartz substrate was anchored onto a cold finger using silver paste. The cryostat is cooled down to 10 K at a high vacuum (< 1 · 10⁻⁵ mbar). The 515 nm excitation from a continuous wave diode laser was focused by a long-distance infinity-corrected objective with a numerical aperture of 0.6 (40× Nikons). Emission was collected by the same objective in confocal geometry.
High-resolution TEM Characterization

High-resolution transmission electron microscopy (TEM) was conducted on JEOL (JEM-2100F) operating at 200 kV accelerating voltage.

Declarations

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Author contributions

X.-J.W., H.-H.F. and H.-B.S. conceived the idea. H.-H.F., H.-B.S. supervised the work. X.-J.W. designed, and conducted the fabrication and characterization experiments. Z.-Z.L. provides analysis and calculation of ultrafast laser fabrication. D.W. provided a theoretical analysis of defect types. All authors participated in the discussion of the results and wrote the manuscript.

Additional Information

Supplementary Information is available for this paper

Correspondence and requests for materials should be addressed to Hong-Hua Fang, or Hong-Bo Sun.

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References


27. **Note:** The damaging threshold is accurately described by power density (W/cm$^2$), here we use the energy unit (Joule) without inducing confusion since the objective lens numerical aperture, wavelength, and pulse width are identical for all experiments.


**Figures**

**Figure 1**

**Creation of SADCs at the uncertainty limit.** a, Schematic of the threshold tracking and lock-in technology. b, Relationship between the damaging size on hBN versus pulse numbers. c, Dependence of pulse number for producing optically visible defects on laser pulse energy, $E_p$. d, TEM image of the laser-induced damaged region.
Deterministic creation of single-photon color centers. a, PL image after laser writing. The laser pulse energy decreases from the top to the bottom (from b, 4.86 nJ to d, 4.68 nJ). Typical spectra of laser-written multiple single photon emitters and corresponding second-order autocorrelation measurement $g^2(t)$. The $g^2(0)$ value is marked for each curve. d, Typical spectra of laser-written single-photon single-color centers with low fluorescence background and its second-order autocorrelation measurement $g^2(t)$. 

Figure 2
Figure 3

High reproducibility, high brightness, and high durability of single-photon single color centers. a, Fluorescence image of a 4 × 4 array of single-photon single color centers induced by the same pulse energy. b, Fluorescence saturation curve with a saturation count of 9 Mcounts s⁻¹ with a saturation power of 764 mW. c, Emission polarization curves from the emitter. d, The time series of PL spectra from the emitter. e, Intensity time trace with a binning time of 50 ms acquired by APDs through the time-gated time-resolved method. The intensity histogram is plotted on the right.
**Figure 4**

**Compactly integrated turn-key monochromatic single-photon emitters.**

- **a,** PL Spectra of laser written single-photon single color centers with emission ranging from 500 nm to 800 nm.
- **b,** Histogram of ZPL wavelength distribution taken from more than ten thousand quantum emitters.
- **c,** Schematic configuration (left) and a photograph (right) of a packaged emitter.
- **d,** Excellent optical performance preserves after package, for example, the PL spectra, and the inset is its antibunching curve.

**Supplementary Files**

This is a list of supplementary files associated with this preprint. Click to download.

- SupplementaryInformationNatureClosetoAtomScaleLaserManufacturingfor30ColorTurnkeySinglePhotonEmitters.docx