Micromanufacturing of Geometrically and Dimensionally Precise Molecular Single-Crystal Photonic Microresonators via Focused Ion Beam Milling

Vuppu Vinay Pradeep and Rajadurai Chandrasekar*

Highly reproducible manufacturing of organic optical crystals with well-defined geometry and dimension is important to realize industrially relevant all-organic microelectronic and nanophotonic components and photonic integrated circuits. Here, programmed shape and size alteration of square-shaped perylene crystal resonators into circular disk and rectangular geometries is demonstrated using the focused-ion-beam milling technique. The fabricated smaller sized circular disk and rectangular crystal resonators display shape- and size-dependent optical modes. Due to generality and high reproducibility, this processing technique can be also extended to other organic crystals to create optical components suitable for commercial nanophotonic device applications.

1. Introduction

Frenkel type molecular optical crystals possess many functional properties such as high exciton binding energy,[1] exciton-polaritons formation,[2] high refractive index, fluorescence (FL),[3,4] phosphorescence,[5] optical non-linearity,[6,7] chirality,[7] hardness/softness,[8,9] bandwidth tunability, surface smoothness,[9] diverse geometries,[9] and lightweight. The past decade has seen tremendous progress in utilizing the naturally grown molecular microcrystals as passive and active optical waveguides,[10,11] resonators,[12] modulators,[13] directional couplers,[14] circuits,[15] polarization rotors,[16] and lasers.[3] However, the main bottleneck that hinders the direct utility of molecular crystals as optical elements to create all-organic PICs is the lack of geometrical and size precisions of crystals compared to inorganic materials, their geometry and dimension cannot be controlled with nanoscale precision during their natural growth. The lack of geometrical and size precisions of crystals severely restricts their entry into the PICs market because the latter demands dimensionally uniform PIC elements with high reproducibility and scalability. As a result, the desire to employ molecular crystals as optical elements to create all-organic PICs with commercially viable precision manufacturing technique grows day by day.

2. Results and Discussion

We developed a mechanophotonics approach[15] to control optical microcrystals’ geometrical shape and dimension down to microscale, and integrate them using atomic force microscopy to fabricate several MCPIC components. Optical microresonators are quintessential components of MCPICs. An optical resonator circumnavigates broad-band light via multiple total internal reflections at the crystal–air interface and subsequently produces optical whispering-gallery-modes (WGMs) via constructive optical interference. The frequency of the modes and their separation (free spectral range, FSR ≈ 1/λ) depends upon the size and shape of the resonator as FSR = −λ_m − λ_m−1) depends upon the size and shape of the resonator as FSR = 1/λ, where λ is wavelength or diameter. Recently, we reported sublimation-mediated...
growth of nearly square-shaped perylene single-crystal optical resonators emitting WGMs (Figure 1a,c,d).[26] Focused ion beam (FIB) milling has been used for etching polymer films[27] and inorganic materials[28] and to convert perylene single crystals into arbitrary shapes.[29] Creating well-defined geometrical shapes such as rings, disks, squares, hexagons, octahedrons, and spheres in crystals is important to produce WGM micro-resonators. Among these geometries, disk-shaped crystal resonators are essential photonic elements to process and route the light into clockwise and counterclockwise directions when coupled with other photonic components. Here, the geometrical precision of the single crystal resonator is crucial to trapping light and observing the optical resonances. For example, the rectangular crystal geometry supports Fabry Pérot (FP) optical resonances by reflecting the light back and forth via their mirror-like opposite facets. To our knowledge, micromachining (by either FIB or electron beam lithography) of a naturally grown crystal into well-defined crystal geometry for direct resonator applications has not been done earlier. Therefore, we envisioned exploiting the FIB milling technique to fabricate two geometrically and dimensionally different perylene micro-resonators. We planned to mill nearly square-shaped perylene single-crystals I and II into disk- and rectangular-shaped crystals, respectively, with size reduction (Figure 1f). Remarkably, single-particle micro-spectroscopy studies revealed that the micromachined disk- and rectangular-shaped crystals act as microresonators by emitting WGM and FP resonance modes, respectively (Figures 2f and 3f).

A nearly square-shaped perylene crystal with \( \approx 5.22 \times 5.28 \, \mu m^2 \) dimensions was identified for micromachining using FIB (Figures 1e,f and 2a). The major crystal facets were found to be (100), (011), and (01-1). First, the single-particle micro-spectroscopy experiments were performed in a transmission mode geometry to determine the resonator characteristics of the selected single crystal. When the crystal was excited with a continuous-wave 405 nm laser on the (100) facet (excitation power: 0.05 mW; objective: 60×), it displayed a bright yellow FL at its four (011), (01-1), (0-1-1), and (0-11) facets. The recorded broad FL (objective: 150×, numerical aperture: 0.95) spectrum covering the bandwidth of \( \approx 525–775 \) nm region exhibited a series of pairs (transverse magnetic, TM and transverse electric, TE) of sharp peaks indicating WGM resonances. The FSR value of the crystal resonator is \( \approx 8.10 \) nm. The resonator characteristics of the square-shaped perylene crystal shown in the FESEM image arise due to multiple circulations of FL by the four-light-reflective facets of the crystal (Figures 2a and 3a). Later, the crystal was gold coated, and milling was
performed orthogonal to the (100) facet using a gallium ion beam (accelerating beam voltage: 30 kV and beam current: 0.4 nA) to fabricate a circular disk-shaped crystal of diameter 4.63 µm (Figure 2a). The gold coating in the sample was removed by repeated washing with KI/Iodine solution (Figure S1, Supporting Information). Photonic experiments on the disk-shaped crystal exhibited an intense FL spectrum supporting relatively broad optical modes with an FSR of 15.39 nm. The number of optical modes depends on the geometry and size of the resonators. From the circular shape of the crystal, it is evident that these optical modes occur due to WGM resonances. The position- and power-dependent FL spectra of fabricated disc-shaped crystals are shown in Figures S4 and S5 (Supporting Information), respectively.

To reduce the size of a large microresonator crystal into a small rectangular microresonator via FIB milling process, a naturally grown perylene crystal of size \( \approx 5 \times 4.7 \) µm\(^2\) was selected. Before milling, during single-particle micro-spectroscopy experiments, the crystal exhibited WGM resonances with an FSR value of 12.16 nm. Milling the crystal into a smaller rectangular crystal of dimensions 1.84 \( \times \) 1.44 µm\(^2\) and subsequent optical experiments displayed relatively broader modes with FSR of 31.29 nm. The increase in the full-width-at-half-maximum of FP modes and FSR values is in line with the inverse relationship of FSR with the resonator dimension. Further, the crystals were stable to up to 20 mW laser pump power.

It is essential to mention that to retain the FL from the milled crystal, the thickness of the crystal chosen for milling and the accelerating beam current need to be optimized. Although the higher ion dose accelerates the milling process, it also causes undesirable amorphization of the crystal surface and deep ion implantation (turning the area black), instigating FL quenching and uneven refractive index of the crystal. The milling resolution depends on the ion beam diameter, and the beam current controls the latter. The smaller the current, the higher the milling resolution that can be attained to mill only targeted areas.

**Figure 2.** a) Schematic of FIB milling of naturally grown square-shaped perylene single crystal into a disk shape. The corresponding FESEM images of crystal before and after milling are shown below the graphics. b,d) Optical microscopy and c,e) FL images of square-shaped perylene single crystal (before milling) and a disk-shaped crystal (after milling). f) The corresponding FL background-subtracted spectra display shape and size-dependent WGMs.
areas. For example, a focused FIB probe of 30 kV at 1 nA current provides a 200 nm beam spot size. To study the effect of beam current on a crystal ($\approx 4.73 \times 5.24 \mu m^2$), FIB milling was performed with a lower (0.1 nA) beam current for the same accelerating voltage (30 kV). These parameters increased the milling time; further, the resultant circular disc-shaped crystal of diameter 3.65 µm showed brighter FL with low laser pump power. This observation is in line with the amorphization reduction as the Ga ion exposure on the unmilled crystal area is minimal (Figures S6 and S7, Supporting Information). As expected, the subsequent optical experiments exhibited broader optical modes (FSR $\approx 18.73$ nm) in the FL spectrum for a smaller resonator.

The mapping of FL and FL-lifetime of perylene crystals before and after gallium ion milling (Figure 4a–c) is shown in Figure 4. The FL images of milled crystals exhibited nearly uniform intensity distribution within the crystal (Figure 4d–f). The disk-shaped resonator showed a well-resolved FL lifetime image with a high FL signal from the rim of the circular cavity due to circumnavigating light at the crystal-air interface. On the other hand, a nearly equal spread of FL was observed for the smaller rectangular cavity. Unlike ordinary crystals, the lifetime values of crystal resonators are different as the resonator’s quality factor ($Q$) determines the photon lifetime, $\tau_P$ (trapped light) of the FL within the crystal by the relation, $Q = $ $\tau_P$. The average lifetime decay values of milled crystals are slightly lowered compared to before milling (Figure 4j–l).

3. Conclusion

In conclusion, FIB milling has been employed to carve perylene single-crystal resonators in different geometries and sizes for the first time. The fabrication of disk- and rectangular-shaped photonic resonators is a proof-of-principle experiment that can also be applied to other molecular crystals. The following points are pertinent for successfully milling FL organic crystals while retaining their optical emission intensities and refractive index homogeneity. Milling parameters and crystal thickness need to
be appropriate to minimize the amorphization of the exposed crystal surface. Thinner crystals take less milling time than thicker ones as the molecular mass to be removed around the crystal is less. This minimizes the amount of Ga ion exposure to the unmilled crystal area. Further, lowering the acceleration current reduces beam spot size, providing higher milling focus and minimizing ion exposure to unmilled crystal area. Thicker gold coating (30–40 nm) not only helps as a conductive layer for SEM imaging but also protects the crystal surface from the Ga ion beam. Milling two different crystals nearby and creating several resonator geometries in a single crystal should be circumvented to reduce the deposition of sputtered ions/molecules/clusters from one crystal to another. Such cases also change the refractive index within the crystal in an inconsistent manner. FIB-based secondary-ion imaging of crystals during milling should be avoided to lessen the ion implantation on the crystal surface.

In general, the presented technique can be used directly to fabricate circular-, ring-, rod-shaped, and any other possible geometries required to create photonic modules such as resonators, waveguides, lasers, interferometers, gratings, couplers, modulators and photonic crystals. As the geometry and dimension of the molecular crystals can be precisely controlled down to microscale, this technique can also be applied to the industrial-scale production of organic crystal photonic modules for PICs.

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

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Authors Contributions
R.C. conceived the research. V.V.P. performed the experiments under the supervision of R.C. Both authors analysed the results. R.C. and V.V.P. wrote the paper and prepared the supporting information.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.
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