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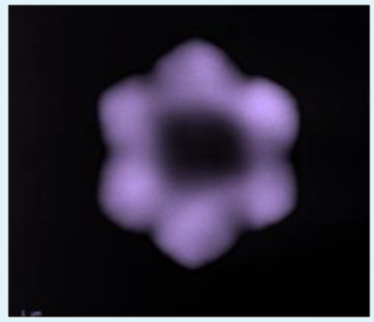
Directional Emission from ZnO Hexagonal Disks

Haimei Dong, Yuhua Yang,* and Guowei Yang*

State Key Laboratory of Optoelectronic Materials and Technologies, Institute of Optoelectronic and Functional Composite Materials, Nanotechnology Research Center, School of Physics & Engineering, Sun Yat-sen University, Guangzhou 510275, Guangdong, P. R. China

ABSTRACT: Lots of theories and experiments have so far tried to acquire the directional emission with whispering-gallery modes (WGMs) from micro- and nanostructures, which will enhance the applications of micro- and nanoscaled whispering-gallery resonators in optoelectronic devices. Here for the first time we report a series of directional emission patterns with WGMs from the single ZnO hexagonal micro- and nanodisk. Based on the cathodeluminescence technique, we observed far-field emissions from ZnO hexagonal micro- and nanodisks in four geometries with different deformations. Mechanisms of directional emissions above were suggested. These investigations facilitated the applications of ZnO hexagonal micro- and nanodisks in photonic devices.



KEYWORDS: *ZnO micro- and nanodisk, whispering-gallery modes, directional emissions, cathodeluminescence, geometry, deformation*

1. INTRODUCTION

Micro- and nanoscaled whispering-gallery resonators with total internal reflection have attracted much interest and have the most potential for the applications of nanolasers and other photonic devices.[1] ZnO hexagonal micro- and nanodisks are regarded as important building blocks for nanoscaled optoelectronic devices, because they provide high Q-factors leading to strong optical feedback within the micro- and nanocavity.[2] But as for the near total internal reflection at the boundary and the perfect symmetry property, the applicability of circular disk lasing cavities is limited by their isotropic light emission.[3] Recently, many attentions have thus been paid to the research of the anisotropic emission, as often desired, directional[4−7] or even unidirectional[8−10] from micro- and nanostructures. Some theoretical works have predicted that the directional emission can be obtained from asymmetric cavities,[11−13] and it is available for triangular,[14] square,[14] and hexagonal cavity.[15] Experimental works have proved that the directional emission can be achieved in the deformed fused-silica microspheres,[16] multisphere photonic molecules,[17] GaN photonic crystals,[3] ZnO twin-spheres,[18] and others.[10,18] All these works above will enhance the applications of micro- and nanoscaled whispering-gallery resonators in fiber-optics communication, medicine, beam splitter, sensor, narrow-linewidth wavelength selective filters and other optoelectronic devices. However, there have not been any reports involved in the directional emission from single ZnO hexagonal micro- and nanodisk.[19,20] In this contribution, we report for the first time the directional emission from ZnO hexagonal micro- and nanodisks. Using the cathodeluminescence (CL) technique attached a scanning electron microscopy (SEM), we directly observe far-field emissions from ZnO hexagonal micro- and nanodisk in four geometries: (i) regular hexagon, (ii) concave-wall hexagon with periodic deformation, (iii) hexagon deformed by bending with all symmetry axes disappeared but the sidewalls smooth, and (iv) hexagon without any symmetry axis and with sidewall curvature. All these geometries can occur in the growth of ZnO hexagonal micro- and nanodisks as their growth conditions are somewhat anisotropic without the carrier gas to balance the atmosphere. And the formation mechanism of ZnO disks is discussed. Furthermore, mechanisms of directional emissions above are discussed.

2. EXPERIMENTAL SECTION

The preparation of ZnO hexagonal micro- and nanodisks is conducted in a horizontal tube furnace by chemical vapor deposition. In short, commercial ZnO and graphite powders with a weight ratio of 1:1 are mixed, ground, and then loaded on a quartz boat and positioned at the higher temperature of the tube. A single-crystal Si wafer, cleaned by a standard procedure without any catalyst, is placed downstream at the lower temperature to act as a deposition substrate. Then, the system is heated to 1050 °C in 50 min and kept at this temperature for 30 min without any carrier gas. Then, it is cooled to room temperature. Gray film is observed on the substrate when it is moved out. Note that we prepare two groups of samples. One is convenient for photoluminescence (PL) observation with larger size and visible luminescence, and the other is good for CL observation. The different growth condition of these two samples is the vacuum. The PL one is synthesized under a pressure of $3x10^4$ Pa, and the CL one is under a pressure of 4×10^4 Pa at the beginning.

The synthesized products are characterized by SEM, X-ray diffraction (XRD) and Micro-Spectrophotometry (MSP). The

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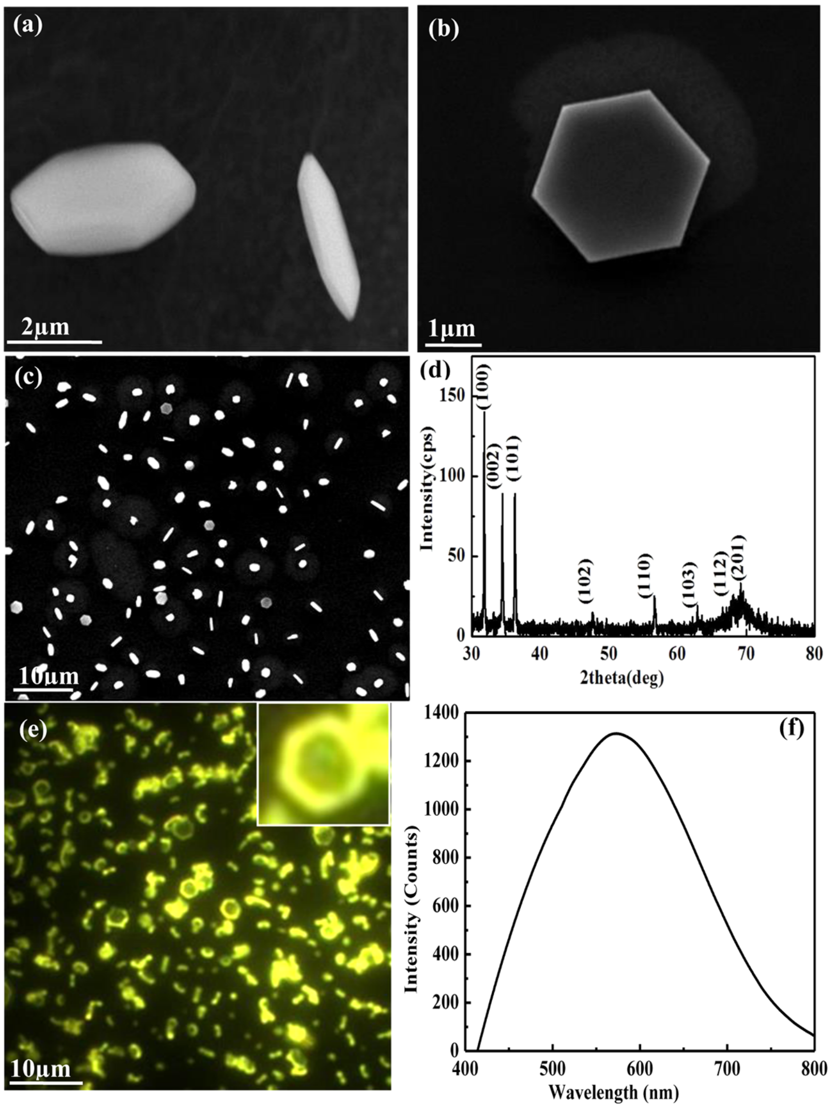

Figure 1. (a−c) Typical SEM images of the prepared ZnO hexagonal disks in different magnification. (d) Corresponding XRD pattern. (e) PL image of ZnO hexagonal disks and the inset shows the enlarged picture of WGM in one ZnO hexagonal disk. (f) Corresponding PL spectrum with 365 nm excitation.

CL measurement is carried out by a Gatan Mono-CL system attached SEM with an accelerating voltage of 10 kV in room temperature.

3. RESULTS AND DISCUSSION

Figure 1a, b shows the typical SEM images of the prepared ZnO hexagonal disks in different magnification. Clearly, the disks have perfect hexagonal shape with the size of about 4−6 μm diagonal and 60−150 nm in thickness. SEM images of lots of ZnO hexagonal micro- and nanodisks are showed in Figure 1c. Every disk is isolated and not all the *c*-axes are perpendicular to the substrate. The XRD pattern is illustrated in Figure 1d. As indexed in the figure, all peaks match with the wurtzite structure ZnO with the lattice constants of a = 3.25 Å and c = 5.207 Å. Figure 1e shows the PL image of the as-prepared ZnO hexagonal disks. We can see the enhanced luminescence from the whispering-gallery modes (WGMs) in every ZnO hexagonal disks clearly. The excitation wavelength is 365 nm in the PL measurements. The spectrum in Figure 1f begins from 400 nm without the intrinsic peak, and there is a broad peak around 580 nm and in the PL image we can just observe the green-yellow light.

In the CL observations, four types of ZnO hexagonal disks with various geometries (Figure 2) are selected to show the different optical patterns inside ZnO hexagonal cavities. All the sizes of four cavities are about 3 μm diagonal. The luminescence patterns of all ZnO hexagonal disks show hexagonal characters. But as their geometries are different, the optical patterns are different. From Figure 2a, we see the normal WGM-like pattern with pseudo-isotropy in a regular ZnO hexagonal disk. A concave-wall hexagonal disk in Figure 2b shows slight directional emission. As its deformation is periodic, the emission pattern is directional that the intensity is brighter in six corners and slight WGM exists. This pattern just meets the prediction from Boriskina.[21] Figure 2c shows a pattern that the center of the bending hexagonal is black with six directions brighter and it still have the WGM profile. We can consider it as the evolution of the normal WGM, but with a clearer hexagonal profile. With a larger deformation, Figure 2d shows that the main intensity of WGM is shifted to the center of the hexagon, and six beams of bright light toward six corners.

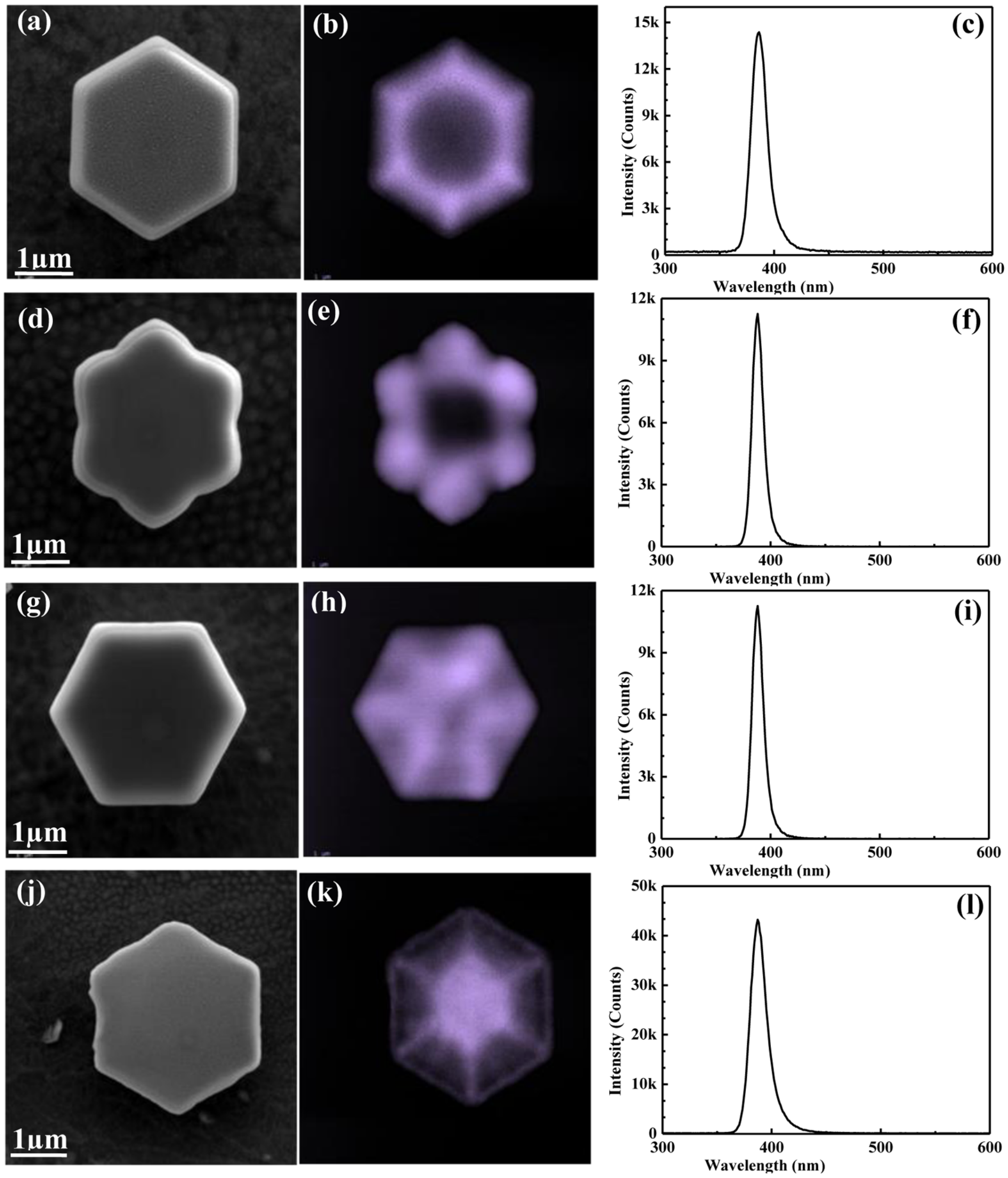

Figure 2. (a, d, g, and j) SEM images of type i, ii, iii, and iv, respectively. (b, e, h, and k) Corresponding panchromatic CL images. (c, f, i, and l) Corresponding CL spectra, respectively.

The radial profile meets the prediction from Grundmann.[22] As we know, a ZnO hexagonal disk without any symmetric axis and with sidewall curvature can distribute a single excitation beam into six well-defined directional beams. Additionally, the four corresponding CL spectra indicate that all the emissions come from 385 nm of ZnO without any defect light. Therefore, the four groups of emission patterns show the evolution of WGM from normal to directional with different deformation degrees.

WGM in a regular hexagonal structure has been studied experimentally in detail in ZnO micro- and nanowires[23] and disks.[24] Light travels around the WGM resonator due to total internal reflection at the resonators boundary. But when its geometry is changed into irregular and asymmetric, six beams of lights emerge. There is a distinct character that the intensity of the six directions is higher. As we know, WGMs are classified as $WG_{m,n}$ modes, m being the azimuthal number, and n being the radial number. In most reports, WGM always displays $WG_{m,1}$ modes and almost all the simulations just calculate $WG_{m,1}$ modes. As the intensity which is angular dependent, hardly changes with increasing n. So it needs much higher energy to excite the mode of $n > 1$ in regular hexagonal disks. But when the geometry of hexagonal disk is broken, the excited energy will decrease. Then we can acquire the mode of $n > 1$. If the resonant wavelength $\lambda = 2\pi/Re(k)$ is comparable with the dimension of hexagonal disks, for small $Re(kR)$[15] and small m and n, the actual shape of resonators can be neglected. $k = w/c$ is the wave number of the resonant and R is the edge length of the disk. The dimensionless quantity kR is considered to describe the resonant modes. In such a case, both the mode patterns as well as the resonant wave numbers do not strongly depend on the respective resonator model chosen and it does not significantly differ from the circular one, although it introduces corners. So within the limit of small $Re(kR)$, hexagon can be understood as a small perturbation of the circular geometry. Hence its WGM performs like the circular one. For larger $Re(kR)$, features of the hexagonal geometry arise, because the resonant waves notice the existence of

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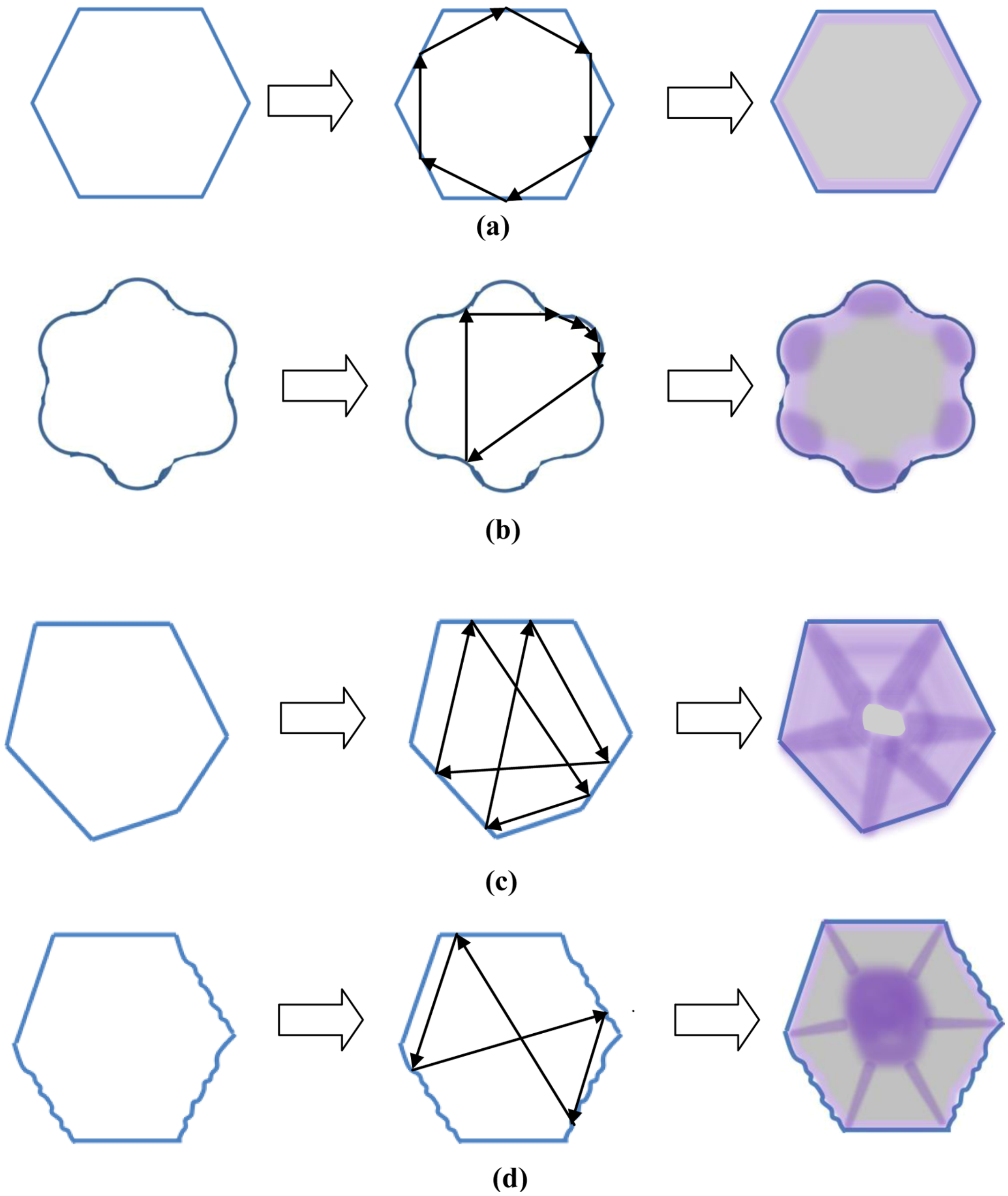

Figure 3. Mechanism patterns of WGM in four types of ZnO hexagonal disks. (a) The normal WGM in a regular ZnO hexagonal disk. (b) Optical pattern in concave-hexagon, (c) transitional profile of WGM in bending hexagon, and (d) directional emission in hexagon with sidewall curvature.

corners as their wavelengths become smaller than the edge length R. Grundmann[22] had concluded that a determination of n cannot be performed clearly if $Re(kR) \gg 1$. Even though we can analyze the particular features of a certain mode pattern. And his calculations have proved that the main intensity of the mode with $n > 1$ is shifted to the center of the hexagon. But to observe this phenomenon with μ-PL and CL measurements in symmetric hexagon is strongly complicated. Recently, many researchers have tried to acquire this pattern in various polygons with different deformations. Interestingly, our investigations above have made it.

Figure 3a shows the normal WGM in a regular hexagonal disk. It performs like the circular disks and the light is pseudo-isotropy. This phenomenon is familiar to us. When the symmetry of the disk is broken, the perturbation of the circular geometry becomes larger. Then, light begins to notice the existence of corners and the pattern with $n > 1$ begins to reveal the hexagonal character. In many practical cases, cavities can be formed with concave-wall and round corners due to the preparation process, as shown in Figure 3b. Boriskina[14] had studied how the change of the resonator sidewall and corner curvature affects its modal characteristics. Its periodic fluctuation at the sidewalls causes different perturbation amplitudes from the mode in Figure 2c, d of which the fluctuation is random. And light can travel around the round corner and obey the triangular mode (3-WGM). Sidewalls in Figure 3(c) are still smooth and $0 < \delta < 0.05$. δ is the degree of the deformation and it contents with $R' = R(1 + \delta)$, where R' is the diameter of the deformed cavity and R is the diameter of the circle circumscribing the cavity. The main intensity just shift near to the center and an embryonic of six beams of light emerges. It begins to be anisotropy. We thus conclude that light in this mode obey the double-triangular mode (3D-WGM).[18] The hexagonal cavity with sidewall curvature which brings larger perturbation with larger deformation totally shows the directional emission pattern in Figure 3d. Also, a slight WGM still exist in these mode because the deformation $0.05 < \delta < 0.2$.[14] Light in this cavity travels around the bow-tie trajectory.[25] Therefore, we can conclude that the pattern in panels b and c in Figure 2 is the transition pattern between panels a and d in Figure 2, and the three kinds of deformations do not break the characteristics of WGM when the random deformation conforms to $0 < \delta < 0.2$ or the periodic deformation satisfies $\delta > 0.2$.

From the CL spectra, we can see that the intensity of the cavity with sidewall curvature is the highest. It is almost 4 times that of the three others including the regular cavity. And all four spectra are measured in the same condition. We use $Q = \nu_0/\Delta\nu_{FWHM} = \lambda/\Delta\lambda_{FWHM}$[26] to estimate the Q factor, in which λ is the wavelength of the resonator and $\Delta\lambda$ is the full width half maximum (FWHM). From the spectra, we can observe the FWHM change with various geometries. The FWHM of the deformed geometrics are narrower than that of the regular one. And as the deformation becomes larger, the FWHM becomes wider but still narrower than that of the regular one. Moreover, according to Wiersig[15] and Wang,[27] diffraction and scattering are expected to influence the direction of emission, but not the escape rate from the resonator. So it does not influence the lifetime of the ray.

4. CONCLUSIONS

In summary, we have performed the PL image of ZnO hexagonal micro- and nanodisks, which clearly exhibited the WGM enhanced emission. On the basis the CL characterizations, we not only showed the regular WGM emission of ZnO hexagonal micro- and nanodisks, but also displayed directional emission patterns and their intermediate state. Meanwhile, we suggested the mechanism of the directional emission form hexagonal disks. Furthermore, we also discussed the Q factor when the geometry of hexagonal disks changes and came to the conclusion that deformations are expected to acquire the directional emission and not influence the lifetime of the ray.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: stsygw@mail.sysu.edu.cn.
*E-mail: yangyuh3@mail.sysu.edu.cn.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Ilchenko, V. S.; Matsko, A. B. Optical Resonators with Whispering-Gallery Modes-Part II: Applications. *Quantum Electron.* **2006**, *12*, 15−32.

(2) Chen, R.; Ling, B.; Sun, X. W.; Sun, H. D. Room Temperature Excitonic Whispering Gallery Mode Lasing from High-Quality Hexagonal ZnO Microdisks. *Adv. Mater.* **2011**, *23*, 2199−2204.

(3) Dettmann, C. P.; Morozov, G. V.; Sieber, M.; Waalkens, H. Directional Emission from An Optical Microdisk Resonator with A Point Scatterer. *EPL* **2008**, *82*, 34002.

(4) K. McGroddy, K.; David, A.; Matioli, E.; Iza, M.; Nakamura, S.; DenBaars, S.; Speck, J. S.; Weisbuch, C.; Hu, E. L. Directional Emission Control and Increased Light Extraction in GaN Photonic Crystal Light Emitting Diodes. *Appl. Phys. Lett.* **2008**, *93*, 103502.

(5) Vukusic, P.; Hooper, I. Directionally Controlled Fluorescence Emission in Butterflies. *Science* **2005**, *310*, 1151.

(6) Coenen, T.; Vesseur, E. J. R.; Polman, A.; Koenderink, A. F. Directional Emission from Plasmonic Yagi−Uda Antennas Probed by Angle-Resolved Cathodoluminescence Spectroscopy. *Nano Lett.* **2011**, *11*, 3779.

(7) Albert, F.; Hopfmann, C.; Eberspacher, A.; Arnold, F.; Emmerling, M.; Schneider, C.; Höfling, S.; Forchel, A.; Kamp, M.; Wiersig, J.; Reitzenstein, S. Directional Whispering Gallery Mode Emission from Limaçon-Shaped Electrically Pumped Quantum Dot Micropillar Lasers. *Appl. Phys. Lett.* **2012**, *101*, 021116.

(8) Huang, Y. Z.; Che, K. J.; Yang, Y. D.; Wang, S. J.; Du, Y.; Fan, Z. C. Directional Emission InP/GaInAsP Square-Resonator Microlasers. *Opt. Lett.* **2008**, *33*, 2170.

(9) Huang, Y. Z.; Lin, J. D.; Yang, Y. D.; Yao, Q. F.; Lv, X. M.; Xial, J. L.; Du, Y. Unidirectional-Emission Single Mode Whispering-Gallery-Mode Microlasers. *Proc. SPIE* **2012**, *8236*, 82360M−1.

(10) Chen, Q.; Hu, Y. H.; Huang, Y. Z.; Du, Y.; Fan, Z. C. Equilateral-Triangle-Resonator Injection Lasers with Directional Emission. *Quantum Electron.* **2007**, *43*, 440−444.

(11) Creagh, S. C. Directional Emission from Weakly Eccentric Resonators. *Phys. Rev. Lett.* **2007**, *98*, 153901.

(12) Nöockel, J. U.; Stone, A. D.; Chen, G.; Grossman, H. L.; Chang, R. K. Directional Emission from Asymmetric Resonant Cavities. *Opt. Lett.* **1996**, *21*, 1609−1611.

(13) Baryshnikov, Y.; Heider, P.; Parz, W.; Zharnitsky, V. Whispering Gallery Modes inside Asymmetric Resonant Cavities. *Phys. Rev. Lett.* **2004**, *93*, 133902.

(14) Boriskina, S. V.; Benson, T. M.; Sewell, P.; Nosich, A. I. Optical Modes in 2-D Imperfect Square and Triangular Microcavities. *Quantum Electron.* **2005**, *41*, 857−862.

(15) Wiersig, J. Hexagonal Dielectric Resonators and Microcrystal Lasers. *Phys. Rev. A* **2003**, *67*, 023807.

(16) Lacey, S.; Wang, H. Directional Emission from Whispering-Gallery Modes in Deformed Fused-Silica Microspheres. *Opt. Lett.* **2001**, *26*, 1943−1945.

(17) Gerlach, M.; Rakovich, Y. P.; Donegan, J. F. Nanojets and Directional Emission in Symmetric Photonic Molecules. *Opt. Express* **2007**, *15*, 17343−17350.

(18) Grundmann, M.; Dietrich, C. P. Whispering Gallery Modes in Deformed Hexagonal Resonators. *Phys. Status Solidi B* **2012**, *249*, 871−879.

(19) Li, F.; Gong, F. L.; Xiao, Y. H.; Zhang, A. Q.; Zhao, J. H.; Fang, S. M.; Jia, D. Z. ZnO Twin-Spheres Exposed in ±(001) Facets: Stepwise Self-Assembly Growth and Anisotropic Blue Emission. *ACS Nano* **2013**, *7*, 10482−10491.

(20) Li, F.; Ding, Y.; Gao, P. X.; Xin, X. Q.; Wang, Z. L. Single-Crystal Hexagonal Disks and Rings of ZnO: Low-Temperature, Large-Scale Synthesis and Growth Mechanism. *Angew. Chem., Int. Ed.* **2004**, *43*, 5238−5241.

(21) Boriskina, S. V.; Benson, T. M.; Sewell, P. D.; Nosich, A. I. Directional Emission, Increased Free Spectral Range, and Mode Q-Factors in 2-D Wavelength-Scale Optical Microcavity Structures. *Quantum Electron.* **2006**, *12*, 1175−1182.

(22) Nobis, T.; Grundmann, M. Low-Order Optical Whispering-Gallery Modes in Hexagonal Nanocavities. *Phys. Rev. A* **2005**, *72*, 063806.

(23) Czekalla, C.; Nobis, T.; Rahm, A.; Cao, B. Q.; Pèrez, J. Z.; STURM, C.; Grund, R. S.; Lorenz, M.; Grundmann, M. Whispering Gallery Modes in Zinc Oxide Micro- and Nanowires. *Phys. Status Solidi B* **2010**, *247*, 1282−1293.

(24) Kim, C.; Kim, Y. J.; Jang, E. S.; Yi, G. C.; Kim, H. H. Whispering-Gallery-Modelike-Enhanced Emission from ZnO Nanodisk. *Appl. Phys. Lett.* **2006**, *88*, 093104.
(25) Stone, D. Classical and Wave Chaos in Asymmetric Resonant Cavities. *Phys. A* **2000**, *288*, 130−151.
(26) Bhowmik, K. Polygonal Optical Cavities. *Appl. Opt.* **2000**, *39*, 3071−3075.
(27) Wang, N. W.; Chen, X. D.; Yang, Y. H.; Dong, J. W.; Wang, C. X.; Yang, G. W. Diffuse Reflection inside A Hexagonal Nanocavity. *Sci. Rep.* **2013**, *3*, 1298.