Original article

One-step synthesis of organic microwire-disk interconnected structure for miniaturized channel filters

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ABSTRACT

Miniaturized channel filters are in high demand for many applications such as photonic integrated circuits, information-based technology, and platforms for investigation of light-matter interactions. Recently, several photonic schemes have been proposed to achieve nanofilters, which require sophisticated growth techniques. Here, we have fabricated microdisk whispering-gallery-mode (WGM) resonators through controlled assembly of organic materials with an emulsion-solvent-evaporation method. Based on this emulsion assembly method, the diameters of microdisks can be easily controlled, and more importantly, a microwire-disk interconnected structure is able to be constructed via one-step assembly. This microwire-waveguide-connected microdisk heterostructure can be utilized as a channel drop filter. Our results have demonstrated a facile way to achieve flexible WGM-based photonic components which can be integrated with other functional devices.

1. Introduction

Achieving filters in micro/nanoscale cavities is crucial to realize promising applications in on-chip optical communication [1-3]. With the development of fabrication techniques, a series of photonic materials with various structures such as nanofibers [4], nanorings [5] and nanotubes [6], have been readily synthesized to realize filtering. In optical resonators, whispering gallery mode (WGM) cavities with tight confinement of photons [7-11] allow profound engineering of light emission to achieve specific functionalities [12-20]. Practical applications of these artificial optical geometries are still hindered for their inconvenient fabrication, which requires sophisticated planar epitaxial technology to incorporate with optical gain medium.

With advantages in chemical versatility, good processability and flexible nature, organic materials have been utilized to fabricate many kinds of micro/nano-assemblies [21,22] including highly bent waveguides [23], platelets [24], hemispheres [25] and also rings [26], which have already served as WGM resonators. Moreover, the ease of molecular design [27] and chemical compositing [28] enables organic matrixes to incorporate with various optical dyes to display tunable and diverse photonic properties [29]. Therefore, organic materials are ideal candidates for the fabrication of flexible WGM microresonators. To integrate with other functional components, the resonating light in WGM resonators should be efficiently exported [30]. It is known that wire-disk connected structure provides a promising approach to break the rotational symmetry and efficiently collect the WGM signals. Up to now, several wire waveguide-coupled WGM resonators have been constructed using sophisticated multistep procedures. The ever-increasing demand in high-speed photonic processing chips requires more facile and controlled ways for waveguide-coupled microdisks.

In this work, we have proposed a controlled emulsion assembly strategy to fabricate flexible organic microdisk WGM resonators. The diameters of the microdisks can be finely tuned by altering the micelle size of the emulsion during the assembly process. The phosphorescent dye fac-tris(2-phenylpyridine) iridium ($\text{Ir}(\text{ppy})_3$) has been doped in the microdisks in order to realize WGM spectral modulation of the outcoupled light signals. More importantly, waveguide-coupled WGM resonators comprising microdisks and microwires have been obtained by one-step assembly via a controllable phase separation between the doped dye and the matrix material, which acted as a channel drop filter. The results offer a facial way to construct flexible microwire-disk interconnected structures and enlightenment for their potential applications in high-speed and high-density photonic processing chips.

2. Results and discussion

2.1. Microdisk resonators

The flexible composite microdisks are obtained by an emulsion-solvent-evaporation method, as shown in Fig. 1. In the process, polystyrene (PS) was chosen as a host material for the microdisk due to its high transparency, thermal stability against oxidization, and outstanding flexibility, which is suitable to form a high-quality and stable microresonator. Fac-tris(2-phenylpyridine) iridium ($\text{Ir}(\text{ppy})_3$) (Fig. S1 in Supporting information) was selected as a dopant because of its high luminescence efficiency and broad spectral range of

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photoluminescence (PL). First, PS and Ir(ppy)₃ molecules were dissolved in *N,N*-dimethylformamide (DMF), and then slow precipitation of PS was induced by adding a small amount of water [31]. After the sonication, the polymer molecules with low crystallinity prefer to aggregate into spherical micelles [32], because of the interfacial tension. At the same time, the Ir(ppy)₃ were doped in the PS matrix through molecule interactions. Finally, the composite microdisks were obtained on the substrate after the evaporation of solvents.

Fig. 1. Schematic diagram of the composite microdisks fabrication process.

The top- and side-view SEM images in Fig. 2 verify the disk-shape structure with a perfect circular boundary and ultra smooth surface. The thickness of the microdisk is about 2 μm , which is suitable to confine the light in the PS matrix with negligible leakage to the substrate. According to the assembly process, the diameter of the microdisk is in direct proportion to the size of the micelles in the emulsion solution that strongly relies on the interfacial tension between PS and the solvent. When more water is added, the size of the polymer micelles tends to increase, because large micelles have small specific surface areas and enable to reduce the interfacial energy of the system. Hence, as illustrated in Fig. 3a-c, the microdisk diameter ranging from 3 μm to 15 μm can be easily controlled by changing the amount of water (from 10 $\mu\text{L}/\text{mL}$ to 30 $\mu\text{L}/\text{mL}$). The corresponding PL microscopy images in Fig. 3d-f demonstrate green fluorescence emission under UV excitation, confirming uniform doping of the Ir(ppy)₃ dye in the PS matrix.

Fig. 2. Top (a) and side view (b) SEM images of the Ir(ppy)₃/PS microdisks.

Fig. 3. (a-c) SEM images of the Ir(ppy)₃/PS microdisks prepared by adding water (10, 20, and 30 μL , respectively) to the PS solution (1 mL). (d-f) PL images of the microdisks excited with the UV band (330-380 nm) light source. All scale bars are 10 μm .

When microdisks were excited locally by a focused UV laser beam (351 nm), a brighter ring shape pattern located at the outer boundary of the microdisk was observed (Fig. 4a-c insets). It indicates that the fluorescence emission is efficiently guided along the edge of the microdisk. A series of sharp peaks from the WGM modulation were found over the emission band in the outcoupled spectra, as shown in Fig. 4a-c. The mode spacing between the peaks decreases rapidly with an increase in disk diameter from 3.4 μm to 5.3 μm , and to 9.5 μm . This optical modulation is based on the confinement of photons within the rings. In other words, the disks function as optical WGM resonators of fluorescence.

Fig. 4. (a-c) PL spectra of the microdisks with different diameters recorded at the microdisk edge. Insets: corresponding PL images. All scale bars are 5 μm .

The fluorescent backgrounds were removed in order to fully understand the optical modulations of WGM resonance, as shown in Fig. 5a. The spacings between the peaks at 515 nm for disk 1, 2 and 3 are about 16 nm, 10 nm and 6 nm, respectively. The spacing between the spectral peaks $\Delta\lambda$ is given by $\Delta\lambda = \lambda^2/n\pi D$, where λ is the wavelength of guided light, n is the group refractive index, and D is the diameter of a disk. The value of $\Delta\lambda$ exhibits a quadratic growth with emission wavelength λ , and is in inverse proportion to the optical path length $n\pi D$. More disks have been measured and the relationship between $\lambda^2/\Delta\lambda$ and D was plotted in Fig. 5b. The value of n is estimated to be 1.57, according to fitting the function $\Delta\lambda = \lambda^2/n\pi D$. This calculated n is consistent with the intrinsic refractive index of the PS polymer (1.59), indicating that the optical WGM modes are tightly confined in the polymer matrix with negligible optical leakage to the substrate.

Fig. 5. (a) WGM modulation within the range of 480-600 nm in disks 1-3 by removing the fluorescence backgrounds. (b) Relationship between $\lambda^2/\Delta\lambda$ and the diameter of the microdisk (D). The red line is a fit to a function $\lambda^2/\Delta\lambda = n\pi D$.

2.2. Wire waveguide-coupled microdisks for filters

With tight optical confinement, these doped flexible microdisks can serve as ideal active photonic components for integrated photonics. To demonstrate the applicability of the microring resonators to photonic devices, we used one-step strategy to fabricate the wire waveguide-coupled microdisks by easily changing the concentration of the $\text{Ir}(\text{ppy})_3$ molecules in solution (see the experimental section and Fig. S2 in Supporting information for details). Because $\text{Ir}(\text{ppy})_3$ has a twisted molecular structure (Fig. S1) and a resulting weak interaction with PS molecule, it leads to separating out of the PS matrix during the self-assembly. In this case, it facilitates the one-step fabrication of phase separated heterostructures. It has been reported that $\text{Ir}(\text{ppy})_3$ molecules preferentially self-assemble to form one-dimensional structures [33, 34]. Hence, the phase separation between $\text{Ir}(\text{ppy})_3$ dopant and PS matrix will result in a wire-disk hybrid structure.

When increasing the amount of $\text{Ir}(\text{ppy})_3$, some of $\text{Ir}(\text{ppy})_3$ molecules diffused into the polymer matrix during the nucleation of PS, while more $\text{Ir}(\text{ppy})_3$ molecules preferred to stay in the solvent. Upon the evaporation of the solvent, the $\text{Ir}(\text{ppy})_3$ -doped PS microdisks formed as mentioned above, and the remained $\text{Ir}(\text{ppy})_3$ in the solvent turned to nucleate at the edge of the squashed PS microdisks because the small radius of curvature and high surface energy of the disks allow them to serve as preferential condensation nuclei [35, 36]. Then the $\text{Ir}(\text{ppy})_3$ molecules aggregated to form 1D nanostructures via epitaxial growth driven by its own intermolecular interactions. These wire-disk interconnected structures enable to collect the WGM signals output coupling efficiently. Fig. 6a shows the SEM images of some typical assembled hybrid structures. It can be seen that most of the doped microdisks are tangentially connected with $\text{Ir}(\text{ppy})_3$ wires. In the PL microscopy images taken under UV excitation (Fig. 6b), the $\text{Ir}(\text{ppy})_3$ wire emit green with very bright luminescence spots at both tips and relatively weaker emission from the bodies of the wires, which is a typical characteristic of an optical waveguide. In a typical hybrid structure, the disk and microwire show the same emission colors, due to the same optical gain media ($\text{Ir}(\text{ppy})_3$ dye).

Fig. 6. SEM image (a) and PL image (b) of the microwire-connected microdisks, showing the junctions between the disk and the wires. Scale bars are 10 μm .

The tangentially connected heterostructure facilitates light coupling from the waveguide to the WGM resonator. When the microwire is excited locally at one end with a focused UV laser at 351 nm, the excited PL signals are steered from the excitation spot toward the other tip (Fig. 7a, inset). Moreover, the whole edge of the microdisk illuminated and emitted the same color of light, indicating the fluorescence emission of the wire has transmitted into the microdisk resonator. As illustrated in Fig. 7a, a series of sharp dips and peaks from the WGM modulations of the microdisk are found in the spectra outcoupled (O1 and O2) from the end of the microwire waveguide and the edge of microdisk. Interestingly, the dip positions are consistent with those of the peaks, revealing that the device functions as a channel drop filter.

The corresponding spectra were analyzed by removing the fluorescent background in Fig. 7b. The observed spacing of a 5 μm microdisk is about ~ 12 nm, which is in fine accordance with the evaluated mode spacing $\Delta\lambda$ from the above mentioned equation $\Delta\lambda = \lambda^2 / n\pi D$. And the spacing between two adjacent dips in wire spectra (~ 12 nm) is almost the same with that in disk spectra, indicating that these dips were originated from the WGM modulation of the disk, and there is a strong optical coupling between the microwire and the microdisk. The refractive index n is nearly constant around 1.6 over the entire emission regime (Fig. 7c), which is consistent with the intrinsic refractive index of the PS polymer, further indicating the dips in the spectrum outcoupled from the end of the microwire waveguide comes from the WGM modulation of the disk.

Fig. 7. (a) Spatially resolved PL spectra collected from the O1 and O2, respectively. Inset: PL image of a wire connected microdisk locally excited at one end of the microwire. (b) The corresponding WGM modulations of the spectra collected from the O1 and O2 by removing the fluorescence backgrounds. (c) Plots of n evaluated from the PL spectra of O1 and O2.

3. Conclusion

The flexible organic microdisk WGM resonators have been fabricated via a emulsion-solvent evaporation method. The assembled microdisks can well confine their fluorescence as active WGM resonances. Tuning the micelle size of the emulsion enables facile control on the diameters of the disks. Furthermore, based on our proposed assembly strategy, Ir(ppy)₃ wire waveguide-coupled microdisks have been prepared by one-step self-assembly to explore the applicability of the microring resonators to photonic devices. The tangentially connected heterostructures lead to the strong optical coupling between the microwires and the microdisks, which can function as a channel drop filter. We believe our demonstration of self-assembled WGM microdisk resonators would pave a new way to the extensive exploration of organic active components for integrated photonics.

4. Experimental

Polystyrene (PS, M.W. 250,000) was purchased from Acros Organics; Fac-tris(2-phenylpyridine) iridium (Ir(ppy)₃) was purchased from Sigma-Aldrich.

4.1 Organic composite microdisks preparation

Firstly, 10 mg PS and 0.1 mg Ir(ppy)₃ molecules were dissolved in 1 mL *N,N*-dimethylformamide (DMF). Then, a small amount of ultrapure water (10-50 μL) was added into 1 mL mixed solution in order to induce slow precipitation of PS. The mixed solution was subsequently treated with sonication for 30 s. Driven by the interfacial tension, the polymer molecules with low crystallinity prefer to aggregate into spherical micelles. At the same time, the Ir(ppy)₃ were doped in the PS matrix through molecule interactions. After that, a drop of the as-prepared mixed solution (15 μL) was drop-cast onto a glass slide, and then another glass substrate was covered. In this

case, a tiny gap was formed between the two glasses, which could act as a template for the self-assembly. Finally, the composite microdisks were obtained on the substrate after the evaporation of solvents.

4.2 Microwire-disk interconnected structure preparation

As shown in Fig. S2 in Supporting information, 10 mg PS and ~3 mg Ir(ppy)₃ molecules were dissolved in 1 mL DMF. Then, a small amount of ultrapure water (10-50 μ L) was added into 1 mL mixed solution. The mixed solution was subsequently treated with sonication for 30 s. Some of Ir(ppy)₃ molecules diffused into the polymer matrix during the nucleation of PS, while more Ir(ppy)₃ molecules preferred to stay in the solvent. After that, a drop of the as-prepared mixed solution (15 μ L) was drop-cast onto a glass slide, and then another glass substrate was covered. Then the Ir(ppy)₃ molecules aggregated to form 1D nanostructures via epitaxial growth driven by its own intermolecular interactions. After aging of the assembly system for 10 hours, the wire waveguide-coupled microdisks were obtained.

4.3 Characterization

The morphologies of the composite microdisks were examined by scanning electron microscopy (SEM, Hitachi S-4800). The absorption and fluorescence spectra were measured on a UV-visible spectrometer (Perkin-Elmer Lambda 35) and a fluorescent spectrometer (Hitachi F-7000), respectively. Bright-field optical images and fluorescence microscopy images were taken from an inverted fluorescence microscope (Nikon Ti-U), by exciting the samples with a mercury lamp.

The optical measurements were performed on a home-built confocal microphotoluminescence system (Fig. S3 in Supporting information). The single composite microdisk was locally excited with a 351 nm laser beam (Spectra-Physics, Beamlok2065) focused by an objective lens (Nikon CFLU Plan, 50 $\times$, N.A.=0.8). The spatially resolved spectra were measured with a monochromator (Princeton Instrument Acton SP 2300i) connected with an EMCCD (Princeton Instrument ProEM 1600B).

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References

- [1] P.P. Absil, J.V. Hryniewicz, B.E. Little, et al., Compact microring notch filters, *IEEE Photon. Technol. Lett.* 12 (2000) 389-400.
- [2] B.E. Little, S.T. Chu, H.A. Haus, J. Foresi, J.P. Laine, Microring resonator channel dropping filters, *J. Lightw. Technol.* 15 (1997) 998-1005.
- [3] F. Xia, M. Rooks, L. Sekaric, Y. Vlasov, Ultra-compact high order ring resonator filters using submicron silicon photonic wires for on-chip optical interconnects, *Opt. Express* 15 (2007) 11934-11941.
- [4] K. Takazawa, J.I. Inoue, K. Mitsuishi, Optical microring resonators constructed from organic dye nanofibers and their application to miniaturized channel drop/add filters, *ACS Appl. Mater. & Inter.* 5 (2013) 6182-6188.
- [5] B.E. Little, S.T. Chu, P.P. Absil, et al., Very high-order microring resonator filters for WDM applications, *IEEE Photon. Technol. Lett.* 16 (2004) 2263-2265.
- [6] A. Srivastava, O.N. Srivastava, S. Talapatra, R. Vajtai, P. M. Ajayan, Carbon nanotube filters, *Nature Mater.* 3 (2004) 610-614.
- [7] M. Humar, M. Ravnik, S. Pajk, I. Musevic, Electrically tunable liquid crystal optical microresonators, *Nature Photon.* 3 (2009) 595-600.
- [8] S.K.Y. Tang, R. Derda, Q. Quan, M. Loncar, G. M. Whitesides, Continuously tunable microdroplet-laser in a microfluidic channel, *Opt. Express* 19 (2011) 2204-2215.
- [9] H.B. Lin, A.L. Huston, B.L. Justus, A.J. Campillo, Some characteristics of a droplet whispering-gallery-mode laser, *Opt. Express* 11 (1986) 614-616.
- [10] S.X. Qian, J.B. Snow, H.M. Tzeng, R.K. Chang, Lasing droplets: highlighting the liquid-air interface by laser emission, *Science* 231 (1986) 486-488.
- [11] J. Schäfer, J.P. Mondia, R. Sharma, et al., Quantum dot microdrop laser, *Nano Lett.* 8 (1709) 1709-1712.
- [12] C. Zhang, C.L. Zou, Y. Yan, et al., Self-assembled organic crystalline microrings as active whispering-gallery-mode optical resonators, *Adv. Opt. Mater.* 1 (2013) 357-361.
- [13] P.J. Pauzauskie, D.J. Sirbully, P. Yang, Semiconductor nanowire ring resonator laser, *Phys. Rev. Lett.* 96 (2006) 143903.
- [14] R.M. Ma, X.L. Wei, L. Dai, et al., Light coupling and modulation in coupled nanowire ring-fabry-pérot cavity, *Nano Lett.* 9 (2009) 2697-2703.
- [15] K. Takazawa, J.I. Inoue, K. Mitsuishi, T. Takamasu, Micrometer-scale photonic circuit components based on propagation of exciton polaritons in organic dye nanofibers, *Adv. Mater.* 23 (2011) 3659-3663.
- [16] H. Baek, C.H. Lee, K. Chung, G.C. Yi, Epitaxial GaN microdisk lasers grown on graphene microdots, *Nano Lett.* 13 (2013) 2782-2785.
- [17] R. Chen, S. Gupta, Y.C. Huang, et al., Demonstration of a Ge/GeSn/Ge quantum-well microdisk resonator on silicon: enabling high-quality Ge(Sn) materials for micro- and nanophotonics, *Nano Lett.* 14 (2014) 37-43.
- [18] A.W. Clark, A. Glidle, D.R.S. Cumming, J.M. Cooper, Plasmonic split-ring resonators as dichroic nanophotonic DNA biosensors, *J. Am. Chem. Soc.* 131 (2009) 17615-17619.
- [19] D.K. Armani, T.J. Kippenberg, S.M. Spillane, K.J. Vahala, Ultra-high-Q toroid microcavity on a chip, *Nature* 421 (2003) 925-928.
- [20] L. Mahler, A. Tredicucci, F. Beltram, et al., Vertically emitting microdisk lasers, *Nature Photon.* 3 (2009) 46-49.
- [21] R. Chandrasekar, Organic photonics: prospective nano/micro scale passive organic optical waveguides obtained from π -conjugated ligand molecules, *Phys. Chem. Chem. Phys.* 16 (2014) 7173-7183.
- [22] Y. Yan, Y.S. Zhao, Organic nanophotonics: from controllable assembly of functional molecules to low-dimensional materials with desired photonic properties, *Chem. Soc. Rev.* 43 (2014) 4325-4340.
- [23] S. Basak, R. Chandrasekar, Passive optical waveguiding organic rectangular tubes: tube cutting, controlling light propagation distance and multiple optical out-puts, *J. Mater. Chem. C* 2 (2014) 1404-1408.
- [24] Q. Zhang, S.T. Ha, X. Liu, T.C. Sum, Q. Xiong, Room-temperature near-infrared high-Q perovskite whispering-gallery planar nanolasers, *Nano Lett.* 14 (2014) 5995-6001.
- [25] V. D. Ta, R. Chen, H.D. Sun, Self-assembled flexible microlasers, *Adv. Mater.* 24 (2012) OP60-OP64.

- [26] N. Chandrasekhar, R. Chandrasekar, Reversibly shape-shifting organic optical waveguides: formation of organic nanorings, nanotubes, and nanosheets, *Angew. Chem. Int. Ed.* 51 (2012) 3556-3561.
- [27] Q. H. Cui, Y. S. Zhao, J. Yao, Photonic applications of one-dimensional organic single-crystalline nanostructures: optical waveguides and optically pumped lasers, *J. Mater. Chem.* 22 (2012) 4136-4140.
- [28] Q.H. Cui, Y.S. Zhao, J. Yao, Controlled Synthesis of Organic Nanophotonic Materials with Specific Structures and Compositions, *Adv. Mater.* 26 (2014) 6852-6870.
- [29] L. Cerdan, E. Enciso, V. Martin, et al., FRET-assisted laser emission in colloidal suspensions of dye-doped latex nanoparticles, *Nature Photon.* 6 (2012) 621-626.
- [30] C. Wei, S.Y. Liu, C.L. Zou, et al., Controlled self-assembly of organic composite microdisks for efficient output coupling of whispering-gallery-mode lasers, *J. Am. Chem. Soc.* 137 (2014) 62-65.
- [31] R. Deng, S. Liu, J. Li, et al., Mesoporous block copolymer nanoparticles with tailored structures by hydrogen-bonding-assisted self-assembly, *Adv. Mater.* 24 (2012) 1889-1893.
- [32] T. Adachi, L. Tong, J. Kuwabara, et al., Spherical assemblies from π -conjugated alternating copolymers: toward optoelectronic colloidal crystals, *J. Am. Chem. Soc.* 135 (2013) 870-876.
- [33] H. Wang, Q. Liao, H. Fu, et al., Ir(ppy)₃ phosphorescent microrods and nanowires: promising micro-phosphors, *J. Mater. Chem.* 19 (2009) 89-96.
- [34] Y.J. Li, Y. Yan, C. Zhang, Y.S. Zhao, J. Yao, Embedded branch-like organic/metal nanowire heterostructures: liquid-phase synthesis, efficient photon-plasmon coupling, and optical signal manipulation, *Adv. Mater.* 25 (2013) 2784-2788.
- [35] J. Y. Zheng, Y. Yan, X. Wang, et al., Wire-on-wire growth of fluorescent organic heterojunctions, *J. Am. Chem. Soc.* 134 (2012) 2880-2883.
- [36] R. Chikkaraddy, A. Dasgupta, S. Dutta Gupta, G. V. Pavan Kumar, Microsphere-coupled organic waveguides: preparation, remote excitation of whispering gallery modes and waveguiding property, *Appl. Phys. Lett.* 103 (2013) 031112.

Graphical Abstract

One-step synthesis of organic microwire-disk interconnected structure for miniaturized channel filters

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The microwire-disk interconnected structure have been fabricated *via* one-step assembly, which can be utilized as a channel drop filter.