Suopporting Information

Photoisomerization manipulating security covert photonic barcodes

Kun Ge (葛坤)[1,2], Juan Kang (康娟)[1], Yi Li (李裔)[1], Le Wang (王乐)[1*]

[1]College of Optical and Electronic Technology, China Jiliang University, Hangzhou, Zhejiang 310018, China

[2]School of Physics, Peking University, Beijing, 100871, China

*Corresponding author: calla@cjlu.edu.cn

Contents

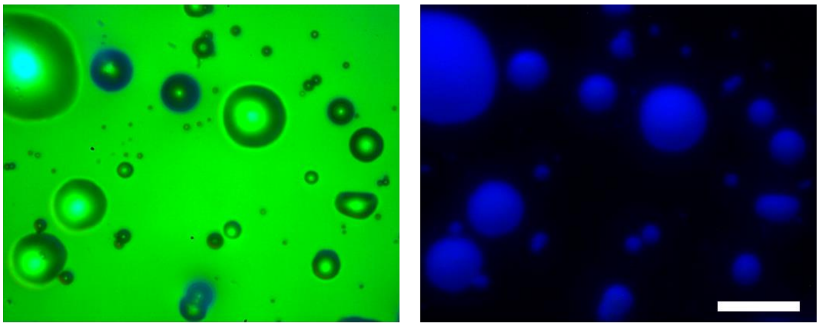

Figure S1 The microscopy images and PL images of microspheres.

A typical highly polarized photo-isomerization light-emitting dye molecule Disodium4,4'-Bis(2-sulfonatostyryl) biphenyl (S420, D-36543, Tianjin Heowns Biochem LLC, Tianjin, China) acts as chemical reagent, and retains two excited gain states such as trans-S420 state and cis-S420 state through optimizing energy levels. Polyvinyl alcohol (PVA) material exhibiting a high compatibility is selected as polymer material along with S420 due to its excellent biocompatibility, non toxicity, and chemical stability. The concentration of gain active (S420) and PVA are 10mg/ml, 16wt% respectively. All these materials (S420, PVA) would be injected into PDMS, slightly stirred to form microspheres, and then heated to solidify. The samples were encapsulated in PDMS solution, which ensure that the size of the microcavity was not changed by stimuli. Moreover, the emission intensity and peak wavelength will be little changed when the microcavity was encapsulated in PDMS solution. It can be ensure the stable output of laser signals.

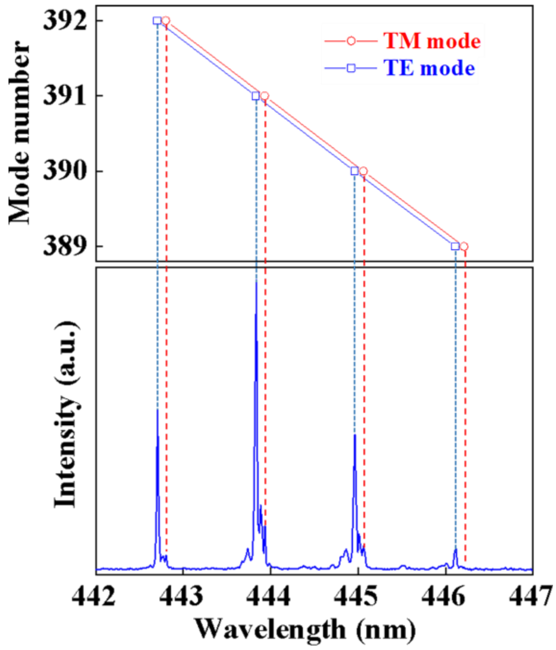

Figure S2 The multimode lasing spectra with TE mode and TM mode.

The theoretical calculation demonstrates the peak wavelength belong to first order transverse magnetic (TM) modes and transverse electric (TE) modes, and the corresponding corresponding mode count is from 389 to 392. The peak wavelength can be well-fitted as shown in Figure S2. According to WGM resonance equation:[1]

$$m\lambda_{\mathrm{m}} = \pi D n_{\mathrm{eff}} \quad (1)$$

where λ_{m} is the peak wavelength, m is the mode number, respectively. The blue squares represent peak wavelength of TE modes and the red circles represent peak wavelength of TM modes.

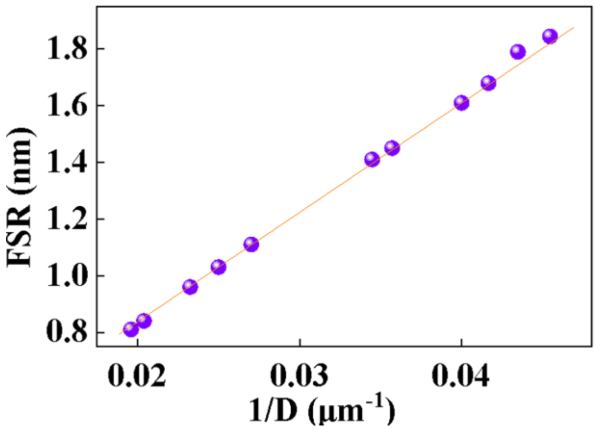

Figure S3 Relationship between FSR and the diameter of microspheres.

To obtain more information about the lasing characteristics, the size related measurements of the isolated micropheres are carried out. Hence, according to the WGM theory:[2-4]

$$\mathrm{FSR} = \frac{\lambda^2}{\pi D n_{\mathrm{eff}}} \qquad (2)$$

Here, λ is the peak wavelength. D represents microfiber diameter and n_{eff} is the effective refractive index, respectively. As shown in Figure S3, the dashed line is fitted with Eq. (1). Further investigation of the FSR shows that an inversely proportional relationship exists between the mode spacing and the diameter. The results demonstrated that the combination of experiment and theory matches very well.

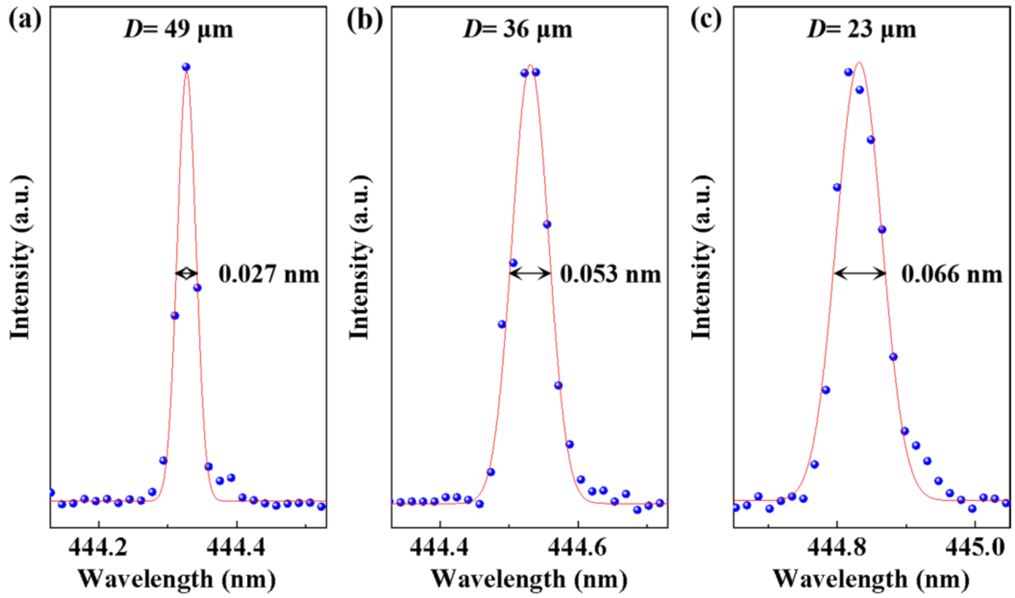

Figure S4 The *Q* factor of microspheres with different diameters. (a) The *Q* factor (~16000) of WGM lasing with diameters (~49 μm). (b) The *Q* factor (~8000) with diameters (~36 μm). (c) The *Q* factor (~6700) with diameters (~23 μm).

The *Q* factor of WGM laser is an important parameter in the optical microcavity and one of the important parameters used to measure the excellent performance of microcavities The *Q* factor can be determined as:

$$Q = \omega \frac{W}{-dW/dt} = \omega\tau = \frac{\lambda}{\lambda_{\mathrm{FWHM}}} \tag{S1}$$

Where ω represents the resonant angular frequency of the resonant mode, W represents the total energy stored in the cavity, $-dW/dt$ indicates the dissipated energy in the cavity per unit time, τ represents the photon lifetime of the microcavity light field, λ and λ_{FWHM} are the peak wavelength and corresponding FWHM, respectively. Figure R1 shows the *Q* factor of WGM laser with different diameters. The calculation of *Q* value is about 16000, 8000, 6700 as displayed Figure S4.

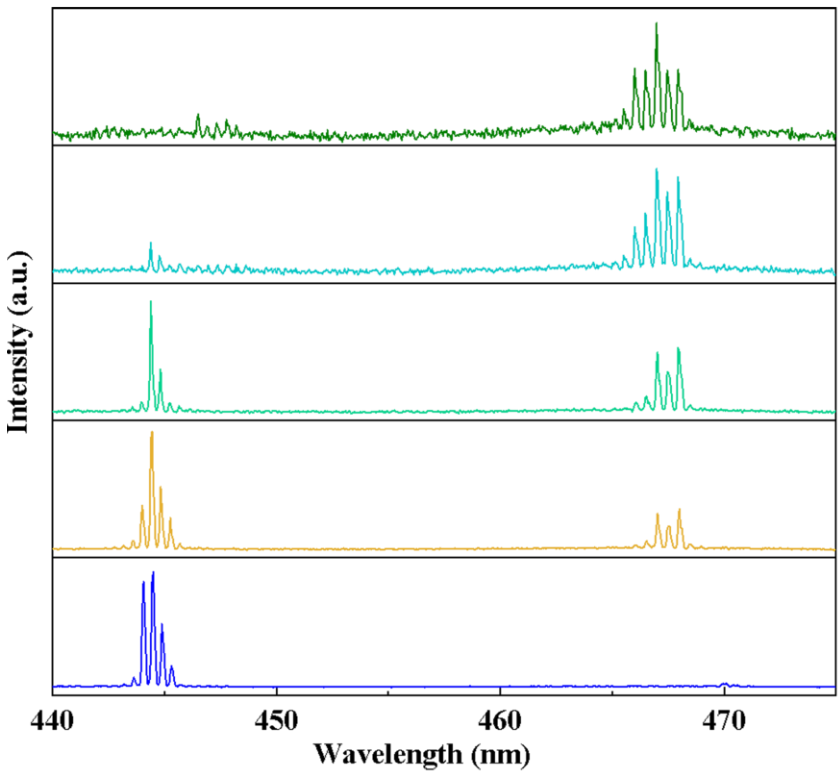

Figure S5 The switchable WGM laser with photo-isomerization activated based on ESIPT process.

The switchable WGM laser with photo-isomerization based on excited-state intramolecular proton transfer (ESIPT) process is achieved when pumped by pulsed laser beam as shown in Figure S5. The microcavity shows two emission regions: one emission band is at about 445 nm and another emission band is at about 468 nm. Lasing emission peak is about 445 nm with trans-form structure. The new lasing peak of 468 nm appears when emission regions excite state is from E structure to cis-form structure.

References

1. J. Zhu, S. K. Ozdemir, Y. Xiao, L. Li, L. He, D. Chen, and L. Yang, "On-chip single nanoparticle detection and sizing by mode splitting in an ultrahigh-Q microresonator", Nat. Photon. **4**, 46-49 (2010).
2. K. Ge, D. Guo, B. Niu, Z. Xu, J. Ruan, and T. Zhai, "Pump-controlled RGB single-mode polymer lasers based on a hybrid 2D-3D μ-cavity for temperature sensing", Nanophotonics **10**, 4591-4599 (2021).
3. X. Jiang, C. Zou, L. Wang, Q. Gong, and Y. Xiao, "Whispering-gallery microcavities with unidirectional laser emission", Laser Photonics Rev. **10**, 40-61 (2016).
4. L. Jin, X. Chen, Y. Wu, X. Ai, X. Yang, S. Xiao, and Q. Song, "Dual-wavelength switchable single-mode lasing from a lanthanide-doped resonator", Nat Commun. **13**, 1727 (2022).