Switchable Multimode Microlaser based on AIE Microsphere

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ABSTRACT: Switchable multimode microlasers are of great significance to the development of photonic devices with high integration levels. Herein, we demonstrate an acid/alkaline gas responsive multimode AIEgen@starch microsphere-based microlaser. The aggregation-induced emission (AIE) active fluorescent dye ASCPI is used as the gain medium in this study. ASCPI was weakly emissive in water but became highly emissive when introduced to the starch microsphere as a guest molecule. The resultant ASCPI@starch microsphere worked well as a typical whispering-gallery-mode microlaser. The laser mode wavelengths were size dependent. Due to the sensitivity of ASCPI to pH, the output wavelength of the microlaser could be switched to shorter wavelength by acetic acid vapor treatment or longer wavelength by NH₃ vapor treatment. This work will provide a useful enlightenment for the rational design of effective switchable lasers using AIE materials with a simple preparation procedure.

1. INTRODUCTION

Miniaturized lasers have gained an increasing interest owing to their applications in chemical and biological sensing,¹⁻³ laser display,⁴⁻⁶ imaging⁷, and on-chip optical interconnects⁸⁻¹¹. Wavelength-tunable lasers with capability of delivering intense coherent light signals across broad spectral range represent particularly interesting opportunities for highly integrated photonic devices. Compared to inorganic material based lasers, organic materials with tailorable excited-state processes and facile fabrication offer an alternative to realize wavelength-switchable

microlasers.¹²⁻¹⁵ To date, wavelength tunable lasers based on organic materials can be realized by modulating the energy level of excited state¹⁶⁻²⁰ or mode variation of the optical resonator^{13, 21-23}. The excited-state energy level of gain materials can be tuned by external stimuli including humidity²⁴, temperature^{19, 25}, light²⁶, vapor¹⁶⁻¹⁷, solvent²⁷, *etc.*. However, reports on gas responsive micro-/nanolasers are limited.^{16-17, 27}

Aggregation-induced emission luminogens (AIEgens) are new type of luminescent materials which are non-emissive when molecularly dissolved, but induced to luminesce by aggregate formation.²⁸⁻³² AIEgens used as optical gain materials of microlasers can take advantages of the inherent AIE characteristics to improve lasing performance including dramatic threshold reduction and favorable lasing stability.³³ In addition, these AIEgen-based miniaturized lasers can improve their laser performance with much higher doping concentration.³³ However, there are only few reports of AIEgen-based miniaturized lasers.³³⁻³⁴ The environmental-responsive emission behavior of AIEgen-based miniaturized lasers was more elusive in the literature. Excited-state intramolecular charge transfer (ICT)³⁵⁻³⁸ effect endows the AIEgens with high sensitivity to the microenvironment. Therefore, AIEgens with ICT effect might be ideal candidates to fabricate robust wavelength-switchable microlasers.

Herein, we report a switchable multimode microlaser based on the ASCPI@starch microsphere. The cationic AIEgen, ASCPI, was originally weakly emissive in water solution due to its AIE and ICT properties. When mixed with starch granules, ASCPI could readily bind to the starch. The host-guest interaction restricted the intramolecular motion of the AIE molecules and strong fluorescence was triggered with blue-shifted emission color. The acid gas could protonate ASCPI, which would consequently weaken the electron density of the donor system and therefore led to blue shift of gain region. In contrast, alkaline gas (NH₃) provided a more polar environment for these ICT chromophores and thus led to a red-shifted gain behavior. As a result, we discover a method of tuning lasing wavelength in the starch microparticles based on the acid/base-responsive AIEgen. These results offer a novel understanding on the stimulated emission of AIEgens and provide a useful enlightenment for the rational design of miniaturized lasers with desired performance.

2. EXPERIMENTAL SECTION

2.1. AIEgen preparation. AIEgen (ASCPI) was synthesized according to the previous literature.³⁹ **2.2. Extraction Process of Potato Starch Granules.** Potato starch granules were extracted from a fresh potato purchased at a local market. The potato was sliced into flakes, soaked in pure water, and vigorously shaken for 30-60 mins. Potato starch granules were collected by centrifuging the solution (4000 rpm for 5 min), followed by further washing and purification through three times centrifugation with pure water. Finally, the as-prepared fresh potato starch granules were collected and dried in oven at 40 °C.

2.3. Preparation of ASCPI@starch. 0.4 mg starch granules were immersed in 1 mL of pure water and sonicated for 5 s. Then 10 μ L of ASCPI (10⁻³ M in DMSO) was dropped into the starch/H₂O solution, shaken by hand and left at ambient temperature for 24 h. The the mixture was centrifagued and washed with pure water for several times until no characteristic emission was observed in the supernatant upon excitation, and then dried in oven at 40 °C.

2.4. Measurements. The absorption and fluorescence spectra were measured with PerkinElmer Lambda-950 spectrophotometer and Edinburgh FLS-1000 instruments, respectively. The time-resolved photoluminescence (TRPL) was measured with Edinburgh FLS-1000 spectrofluorometer system equipped with EPLED-360. The absolute luminescence quantum yield were measured on

a Edinburgh FLS 980 fluorescence spectrophotometer equipped with an integrating sphere (0.1 nm step size, 0.3 second integration time, 5 repeats). The morphology of the microsphere was examined with scanning electron microscopy (SEM, FEI Nova NanoSEM450). X-ray diffraction measurements were conducted on a D/max-2550 PC X-ray diffractometer with Cu K α radiation. 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. Lasing measurements were performed on a home-built far-field microphotoluminescence system. The microsphere was locally excited with a focused 400 nm femtosecond laser (fs-laser), which was generated from the second harmonic of the fundamental output of a regenerative amplifier (Solstice, Spectra-Physics, 800 nm, 100 fs, 1 kHz).

RESULTS AND DISSCUSSIONS

A typical AIEgen sensitive to pH was chosen as a model molecule to demonstrate the concept. Figure 1a shows the chemical structure of the AIEgen, 4-(4-(1-cyano-2-(4-(dimethylamino)phenyl)vinyl)phenyl)-1-methylpyridin-1-ium iodide (ASCPI). The ASCPI was synthesized according to the previous method.³⁹ As illustrated in Figure 1b, a typical AIE property was observed. Its diluted solution in DMSO exhibited a weak photoluminescence (PL) with an emission peak at 674 nm. Upon the addition of a non-polar solvent of 1,4-dioxane as the poor solvent for ASCPI into DMSO solution with a fraction of 90 vol %, bright red PL with a maximum emission at 650 nm was observed. In addition, the α_{AIE} value of ASCPI (Figure 1c) was calculated to be 9.3 when f_d (1,4-dioxane fraction) = 90%, suggesting a typical AIE feature for this molecule. Moreover, ASCPI demonstrated a large Stokes shifts ($\Delta v = 192$ nm), which can be attributed to an excited-state ICT between the electron donor and the electron acceptor. The ICT effect was also

confirmed by the experiment of solvatochromic effects³⁶⁻³⁷ (Figures S1, Supporting Information). The ASCPI presented varied emission spectra in different solvents with wavelength changing from 666 nm to 688 nm, indicating a typical charge transfer character in the excited state (Figure S1b, Supporting Information).



Figure 1. a) Molecular structure of ASCPI. b) PL spectra of ASCPI in DMSO/1,4-dioxane mixtures with different 1,4-dioxane fractions ($f_d = 0, 70\%, 80\%, 90\%$). c) Plot of relative emission

peak intensity of ASCPI (a_{AIE}) versus f_d of DMSO/1,4-dioxane mixtures, where $a_{AIE} = I/I_0$, I = emission intensity and I_0 = emission intensity in DMSO solution. Inset: fluorescence image of ASCPI in DMSO/1,4-dioxane mixtures with different f_d state taken under 365 nm UV irradiation from a hand-held UV lamp at room temperature. Conditions: solution concentration: 10^{-5} M ; excitation: 440 nm. d) Illustration of the fabrication of ASCPI@starch microparticles. e–g) Bright-field microscopy image (e), Fluorescence microscopy image (f), SEM image (g) of the ASCPI@starch microparticles. Scale bar: 50 µm.

The starch granules usually have spherical, ellipsoidal, or polygonal shapes,⁴⁰⁻⁴¹ which can function as as whispering gallery mode (WGM) resonators providing optical feedback for laser oscillations^{21, 42-45}. In this study, we explored the possibility of fabricating AIEgen-based microlaser using the starch granules as the WGM resonators. The synthetic procedure of ASCPI@starch microparticles is illustrated in Figure 1d. Starch granules were sonicated in water. ASCPI was then added into the starch/H₂O solution, shaken by hand and left at ambient temperature for 24 h. The obtained ASCPI@starch particles was centrifuged and washed with pure water. The doping concentration of ASCPI was 1.1 wt % in starch microparticles. As shown in the bright-field image (Figure 1e), micro-sized ASCPI@starch particles with the ellipsoidal shape could be obtained. ASCPI was weakly emissive in water (Figure S2, Supporting Information). This is possibly attribute to both its AIE activity and ICT property. Since this probe carries a positive charge, it is loosely packed in water. The relatively active intramolecular motion weakens its emission. Moreover, due to its ICT property, its emission is further quenched by water. Therefore, its emission in water is rather weak. When interacting with starch granules, the dye binds to the starch and the strong host-guest interaction between starch and dyes not only restricts

the intramolecular motions of the AIEgen but also changes its microenvironment. Therefore, the fluorescence of ASCPI in the starch granules was turned on (Figure S2, Supporting Information). As shown in Figure 1f, bright orange-red fluorescence of the particles could be observed under UV excitation, revealing that the ASCPI molecules were successfully encapsulated by starch granules. The scanning electron microscopy (SEM) image (Figure 1g) shows that these ASCPI@starch microparticles possessed perfect ellipsoidal shapes and ultra-smooth surfaces, possibly triggering WGM lasing at a low threshold.



Figure 2. a) PL spectra recorded at the edge of an ASCPI@starch microparticle as a function of pump density. b) Plot of PL peak intensity as a function of pump density. Inset: PL image of the ASCPI@starch microparticle (major axis 10.7 μ m × minor axis 8.89 μ m) under 400 nm pulse laser excitation. Scale bar is 10 μ m.

We then tested optically pumped laser behaviors of these ASCPI@starch microparticles. Here the ASCPI@starch microparticle with dimensions of 10.7 μ m (major axis) × 8.89 μ m (minor axis) was excited by a femtosecond pulsed laser beam ($\lambda = 400$ nm, 200 fs) with increasing fluence. At low pump fluence, the ASCPI@starch microparticle exhibits a broad emission with spectral peak centered at about 636 nm, corresponding to spontaneous emission (Figure 2a). At higher pump fluence, the emission spectrum of the ASCPI@starch microparticle as a set of sharp peaks at about 680 nm accompanied by a dramatical enhanced intensity, which indicates stimulated emission. The corresponding PL peak intensity versus pump fluence (Figure 2b) reveals a clear threshold behavior at about 68.5 mJ/cm², which further confirms the lasing action in the microparticles. Above the lasing threshold, the full width at half-maximum (FWHM) at 682 nm dramatically narrowed down to ~0.4 nm, revealing a sharp increase of temporal coherence.



Figure 3. a) PL spectra of the ASCPI@starch microparticles with three different sizes. Corresponding PL images are depicted as insets. All scale bars are 20 µm. b) Relationship between $\Delta\lambda_m$ and 1/L of the ASCPI@starch microparticles. *L* is the cavity length. The red line is a fitting to the function $\Delta\lambda_m = \lambda^2/n_g L$, $\lambda = 682$ nm. c) Simulated field intensity distribution (λ , 682 nm) in an ASCPI@starch microparticle with length of 44.6 µm.

The lasing spectra of the ASCPI@starch microparticles with different diameters were further studied to investigate the microcavity effects. Figure 3a illustrates PL spectra and the corresponding images of the three ASCPI@starch microparticles with different dimensions. The mode spacing ($\Delta\lambda_m$) between two adjacent lasing modes decreased as the microparticle circumference (*L*) increased from 44.6 to 186 µm (Figure 3a). For WGM resonance, $\Delta\lambda_m$ and *L* satisfy the equation of $\Delta\lambda_m = \lambda^2/n_g L$,²¹ where λ is the wavelength of guided light, n_g is the group refractive index. As shown in Figure 3b, the plot $\Delta\lambda_m$ and 1/L showed a clear linear relationship. By fitting the plot, the group refractive index n_g is identified with a value of ~1.58 at $\lambda = 682$ nm (Figure 3b), which is consistent with the intrinsic refractive index of the starch polymer (1.53)⁴⁶. These microcavity effect results verified the WGM-type cavity resonance in the ASCPI@starch microparticles. The simulated electric field intensity distribution shown in Figure 3c further confirms the existence of WGM in the microparticle.



Figure 4. a) PL spectra of the ASCPI@starch microparticles, ASCPI@starch microparticles in HAc and in NH₃ atmosphere. b) PL decay profiles of the ASCPI@starch microparticles without/with exposure to HAc and NH₃. c) Pictorial presentations of the HOMOs and LUMOs in the ASCPI, ASCPI-HAc complex and ASCPI in NH₃ atmosphere.

As the lasing wavelength is related to the energy gap of optical gain material, it is possible to control the gain region by tuning the energy levels of AIEgens. The ASCPI@starch microparticle exhibited a broad emission with the wavelength peak at 638 nm (Figure 4a). After long exposure to HAc, the fluorescence peak of the ASCPI@starch microparticle exhibited a blue-shift from 638 to 633 nm along with a decrease of photoluminescence quantum yield (PLQY) from 14.7% to 10.6%. In addition, the photoluminescence of the ASCPI@starch microparticle showed bathochromic shift of maximum emission wavelength from 638 to 646 nm (Figure 4a) and PLQY decreased from 14.7% to 7.6% in NH₃ atmosphere. This suggests that the external acid/alkaline gas in the atmosphere can tune the energy levels of AIEgens in the ASCPI@starch microparticle. In addition, the fluorescence lifetime of ASCPI@starch microparticle was also investigated to elucidate the inherent excited states property. As shown in Figure 4b, the fluorescence lifetime of ASCPI@starch microparticle was 1.41 ns. Upon exposure to HAc and NH₃, however, the fluorescence lifetime of the ASCPI@starch microparticle decreased to 1.03 and 1.30 ns, respectively. According to the equation $k_{nr} = (1 - \varphi)/\tau$, where φ is the PLQY, k_{nr} is non-radiative decay rate constant, and τ is fluorescence lifetime,⁴⁷ the non-radiative decay rate constant (k_{nr}) of the ASCPI@starch microparticle increases after exposing to HAc and NH₃ (Table S1). This reveals that the intramolecular rotational motions of AIEgens non-radiatively dissipate the excited-state energy in loose packings of microparticles in HAc or NH₃ atmosphere. To gain more insights into the photophysical mechanism of wavelength switching in HAc or NH₃ atmosphere, the frontier molecular orbitals distributions and energy levels of ASCPI were investigated by density functional theory (DFT) using M062X/def2vp method (Figure 4c)⁴⁸. According to the calculation results, the energy gap of protonated ASCPI was 5.50 eV via combining with protonic acid, which

was higher than that in vacuum (3.26 eV), showing good agreement with the corresponding optical spectra after the treatment with HAc vapors. However, the energy gap of ASCPI was 2.85 eV in NH₃ environment which was lower than that in vacuum (3.26 eV) due to the ICT effect. Therefore, a red-shifted PL was observed in the optical spectra (Figure 4a).



Figure 5. a) Schematic diagram of the ASCPI@starch microsphere laser measurement under exposure to different atmospheres. b) Wavelength shift of lasing modes in the ASCPI@starch microsphere under alternate exposure to HAc, NH₃ and air, respectively. c) PL images of an ASCPI@starch microsphere under alternate exposure to HAc, NH₃ and air. Scale bars: 20 µm.

Inspired by the HAc/NH₃-responsive emission, we measured the lasing spectra in response to the variation of the HAc or NH_3 atmosphere (Figure 5a). Figure 5b shows the lasing spectra of a typical ASCPI@starch microsphere (as shown in dotted portion of Figure 5c) with alternating plugs of air, HAc and NH₃ gases. The lasing wavelength of the ASCPI@starch microsphere was tuned from about 679 to 676 nm when the microsphere was exposed to HAc gas (Figure 5b). Once the ASCPI@starch microsphere was exposed to NH₃ gas, the lasing wavelength changed to about 691 nm (Figure 5b). Additionally, as the HAc or NH₃ vapor in the surrounding medium evaporated in air after 10 min, the PL images of the ASCPI@starch microsphere did not show obvious color change due to the weak fluorescence wavelength switching (Figure 5c). More importantly, compared with the fluorescence wavelength switching, microlaser used as a sensor possessed higher sensitivity to HAc and NH₃ gas stimuli, which could be ascribed to the narrower FWHM in lasing spectra (Figure 4a and 5b). To further confirm the adaptability of HAc/NH₃-responsive stimulated lasing properties, ASCPI@starch microspheres with different sizes were investigated under external HAc or NH₃ atmosphere (Figure S3–S4). As shown in Figure S3, about 3 nm of blue-shift was observed after the exposure of the ASCPI@starch microsphere to HAc gas. On the other hand, other sizes of the ASCPI@starch microspheres exhibited about 7 nm bathochromicshift after exposing the microspheres to NH₃ gas (Figure S4). Overall, stimulated laser emission responsive to HAc/NH₃ gas can be revealed in the AIEgen@starch microspheres.

To eliminate the influence of the starch resonator in these switching processes, X-ray diffraction (XRD) patterns of the ASCPI@starch microsphere treated with acetic acid or ammonia were also investigated, as shown in Figure S5 (Supporting Information). The XRD pattern of the ASCPI@starch microparticle contained a series of 5.86, 17.2, 22.5 and 24.0°, which was in agreement with that of A-type starches.⁴⁹ It was also found that the diffraction peaks at $2\theta = 17.2$,

22.5 and 24.0° of the ASCPI@starch microparticle had no obvious changes after treating with acetic acid or ammonia, suggesting the structure of A-type starches can be maintained regardless of the influence by NH₃ or HAc. In addition, the diffraction peak at $2\theta = 5.86^{\circ}$ disappeared due to the long-range ordered structure of A-type starches was destroyed in the HAc treatment. These data imply that starch used as WGM resonators has little effect on lasing wavelength switching even with the treatment by acid or alkaline.

CONCLUSIONS

In summary, we reported an AIEgen-based switchable microlaser. This microlaser could be easily fabricated by mixing the AIE active dye ASCPI and starch granules. In the confined environment after binding to the host molecule, starch, the emission of the AIE dye ASCPI was greatly enhanced. We demonstrate that the resultant AIEgen@starch microspheres functioned as typical WGM lasers. More interestingly, manipulation of the laser emission could be achieved by HAc/NH₃ gas treatments. The protonic acid gas could weaken the electron density of the donor system and led to the blue-shifted laser behavior. On the other hand, alkaline gas (NH₃) provided a more polar environment for these ICT chromophores and thus led to the red-shifted lasing. This work presents a simple method for the fabircation of an efficent AIEgen-based switchable microlaser. It is expected that more AIE-based microlasers and AIE-microlaser-based chemo- or bio-sensors will be developed in the near future.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at. UV-Vis, PL spectra, PL image, XRD, Photophysical properties and renal clearance (PDF).

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Author Contributions

S. Chen. Y. S. Zhao. and H. Gao conceived the idea and designed the study. M-Y. Wu synthesized the compound of ASCPI. F. Song carried out SEM, XRD, UV, PL, PLQY and Lifetime experiments. H. Gao carried out ASCPI@starch microsphere synthesis. C. Zhang, H. Dong and Y. Fan preformed the Lasing measurements. G. Shan and S. Chen carried out DFT calculation. All authors were involved in result discussion and manuscript preparation. F. Song., H. Gao., C. Zhang., S. Chen., and P. Lai. drafted the manuscript with inputs and comments from all authors.

Notes

The authors declare no competing financial interest.

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BRIEFS: A wavelength-switchable microlaser is achieved in AIEgen@starch microspheres based on HAc/NH₃-responsively stimulated laser emission. The protonic acid (HAc) gas can weaken the electron density of the donor system and lead to a blue-shifted gain behavior, whereas alkaline gas (NH₃) provides a more polar environment for these intramolecular charge transfer (ICT) chromophores and thus leads to a red-shifted gain behavior.

TOC:

