Supporting Information for:

Functional differentiation visualized: diverse light-emitting modes in biomimetic microstructures

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Author Contributions:

Y.C. conceptualized the project. Under the supervision of Y.C. and J.G., J.Z. and S.W. prepared the samples, performed the experiments and characterization together. J.Z., S.W. and Y.C. analyzed and discussed the results together. J.Z. wrote the manuscript and organized the supplement files. Y.C. drew all the figures. Y.C. and J.G. revised the manuscript. All authors commented on the manuscript.

Supplement Files Involve:

- **A PDF File** (Supplementary text with experimental information and figures)

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Chemical and Instruments

All reagents were commercially available and used without further purification. Barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$, 99%) and sodium silicate pentahydrate ($Na_2SiO_3 \cdot 5H_2O$,99%) were purchased from Tianjin Kermel Chemical Reagent. The concentrated hydrochloric (HCl, 36%-38%) was purchased from Real&Lead Chemical. Rodamine B (RhB, 99%) were purchased from Rionlon. Fluorescein (FL, 99%) and 7-hydroxy-4-methylcoumarin (7-HmCm, 99%) were purchased from Shanghai Dibai Chemical Technology Co., Ltd. 0.1M HCl was obtained by diluting concentrated hydrochloric acid with water for the adjustment of pH. All water used in our experiments was distilled deionized water and bubbled with N_2 (99.999%, purchased from Tianjin Liufang Industrial Gas Co., Ltd) for more than 2 hours to drive off pre-dissolved CO_2. Microslide (75 cm×25 cm×1 mm) was used as growth substrate.

The luminescent spectra of the solid samples were measured using a FLS 920 (Edinburgh Instruments) configured with an integrated sphere. The luminescent spectra of the aqueous solution of dyes were measured on a F-4600 Fluorescence Spectrophotometer (Hitachi-High Technologies). The micrographs of different biomimetic morphology were taken using a Nikon CIPOL and Optec BK5000. The point light source for taking photos is a 365 nm monochromatic ultraviolet light emitted via a HTLD-4 II UVLED. In addition, a HNYC-211BD constant temperature air shaker from Tianjin Honour Instrument Co., Ltd is used in our experiment.

Detailed Experimental Procedures

a. Preparation of fluorescent biomimetic morphologies:

The fluorescent biomimetic morphologies were prepared according to the literature. Firstly, 0.070 g $Na_2SiO_3 \cdot 5H_2O$ was dissolved well in 40 mL distilled deionized water (pretreatment with N_2 bubbling for more than 2 hours to drive off pre-dissolved CO_2) in a 100 mL beaker. Then 0.185 g $BaCl_2 \cdot 2H_2O$ was dissolved into the Na_2SiO_3 solution. Subsequently, a certain amount of fluorescent dye was added to the solution. For RhB, 0.060 g was added to make its concentration 1500 ppm, and for FL and 7-HmCm coumarin, 0.010 g was added to give a concentration of 250 ppm. The pH value of the solution was adjusted by dropping 0.1 M HCl. For helicoids, the pH value was adjusted to 11.20. And for conical vases, the pH value was adjusted to 11.80. After that, a microslide (75 × 25 × 1 mm) was inserted into the solution as the growth substrate and the breaker was loosely covered by as petri dish to allow CO_2 to slowly diffuse into the solution. After 12 hours at room temperature, the microslide was taken out and quickly immersed into distilled deionized water for 1 min to dilute the solution composition, and then immersed into acetone for 1 min to replace the surface water. Finally, the microslide was dried in the air for 12 hours and characterized by microscope.

b. Preparation of helicoids fluorescent biomimetic hierarchical morphologies:

The fluorescent biomimetic morphologies were prepared according to the literature. Firstly, 0.070 g $Na_2SiO_3 \cdot 5H_2O$ was dissolved well into 40 mL distilled deionized water (pretreatment with N_2 bubbling for more than 2 hours to drive off pre-dissolved CO_2) in a 100 mL beaker. Then 0.185 g $BaCl_2 \cdot 2H_2O$ was dissolved into the Na_2SiO_3 solution. Three identical sets of the above solutions were prepared, and RhB, FL and 7-HmCm were added separately. The pH value of the solution was then adjusted to 11.20 by dropping 0.1 M HCl.

For the secondary coded fluorescent biomimetic morphologies, a microslide was initially immersed in a solution containing the first dye and shielded from light for 4 hours. After that, the microslide was removed from the solution, excess solution on its surface was quickly dried up with filter paper, and then the microslide was placed into a solution containing the second dye. The tilt angle of insertion was adjusted to ensure consistent immersion depth during both dye applications. After 6 hours, the microslide was taken out from the solution, and the residual solution was drained off with filter paper, and the microslide was dried in air for more than 12 hours to obtain the secondary coded fluorescent bionanomaterials.

For the tertiary coded fluorescent biomimetic morphologies, the microslide was first inserted into the solution containing the first dye for 3 hours, then transferred to the second dye solution for 3.5 hours, and finally placed into the third dye for 5.5 hours. The microslide was immersed at the same depth for three solutions. The remaining steps were identical to those used for secondary fluorescence coding, resulting in the production of tertiary coded fluorescent bionanomaterials.

c. Preparation of conical vases fluorescent biomimetic hierarchical morphologies:

The fluorescent biomimetic morphologies were prepared according to the literature. Firstly, 0.070 g $Na_2SiO_3 \cdot 5H_2O$ was dissolved well into 40 mL distilled deionized water (pretreatment with N_2 bubbling for more than 2 hours to drive off pre-dissolved CO_2) in a 100 mL beaker. Then 0.185 g $BaCl_2 \cdot 2H_2O$ was dissolved into the Na_2SiO_3 solution. Three identical sets of the above solutions were prepared, and RhB, FL and 7-HmCm were added separately. The pH value of the solution was then adjusted to 11.80 by dropping 0.1 M HCl.

For the secondary coded fluorescent biomimetic morphologies, a microslide was initially immersed in a solution containing the first dye and shielded from light for 4 hours. After that, the microslide was removed from the solution, excess solution on its surface was quickly dried up with filter paper, and then the microslide was placed into a solution containing the second dye. The tilt angle of insertion was adjusted to ensure consistent immersion depth during both dye applications. After 6 hours, the microslide was taken out from the solution, and the residual solution was drained off with filter paper, and the microslide was dried in air for more than 12 hours to obtain the secondary coded fluorescent bionanomaterials.

For the tertiary coded fluorescent biomimetic morphologies, the microslide was first inserted into the solution containing the first dye for 3 hours, then transferred to the second dye solution for 3.5 hours, and finally placed into the third dye for 5.5 hours. The microslide was immersed at the same depth for three solutions. The remaining steps were identical to those used for secondary fluorescence coding, resulting in the production of tertiary coded fluorescent bionanomaterials.

Experimental Data

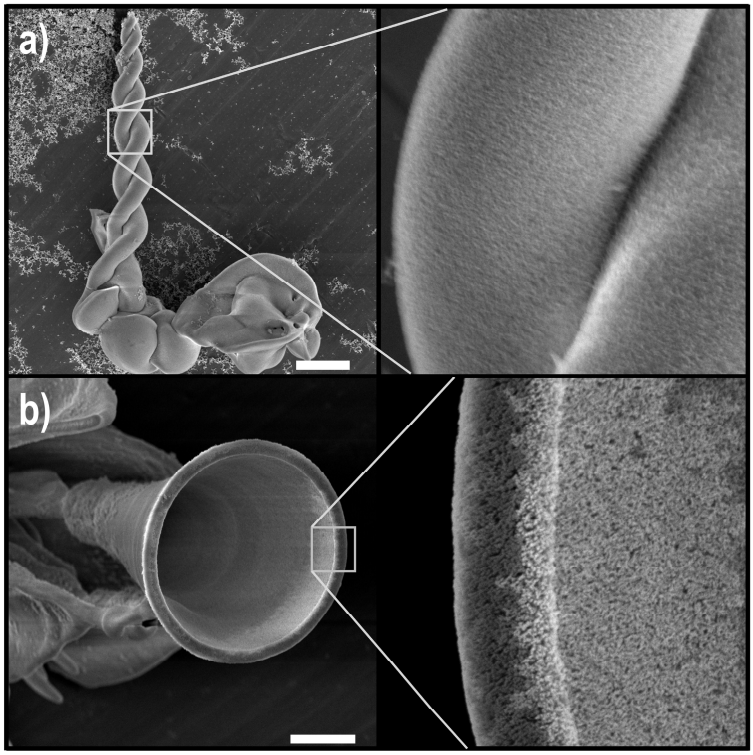

Fig. S1 Scanning electron microscope images of two type biomimetic morphologies. a) Helicoids morphology and local amplification. b) Conical vases morphology and local amplification. Scale bar: 10 μm.

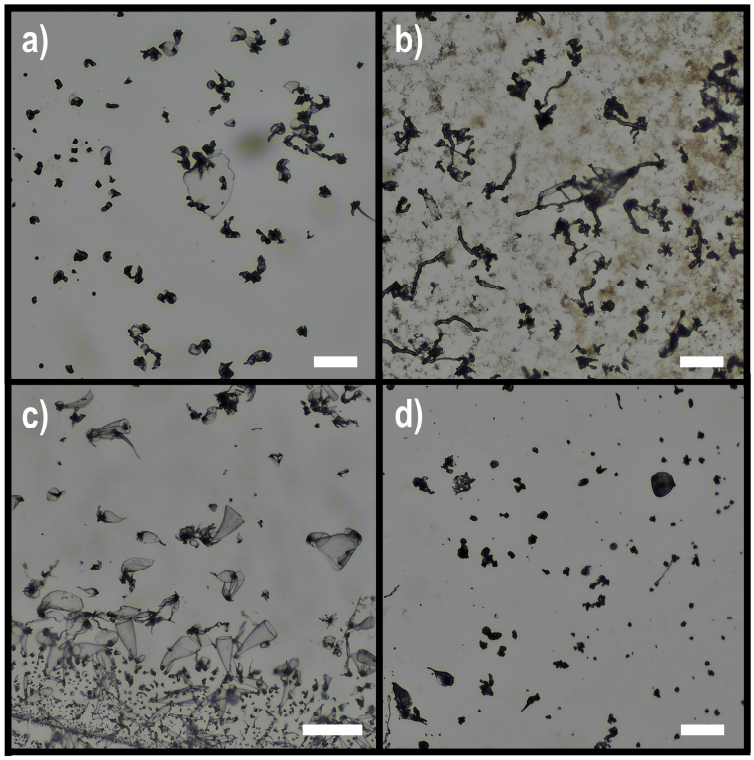

Fig. S2 Microphotographs of biomimetic materials obtained in different pH solutions at room temperature. a) pH=10.20. b) pH=11.20. c) pH=11.80. d) pH=12.07. Scale bar:100 μm.

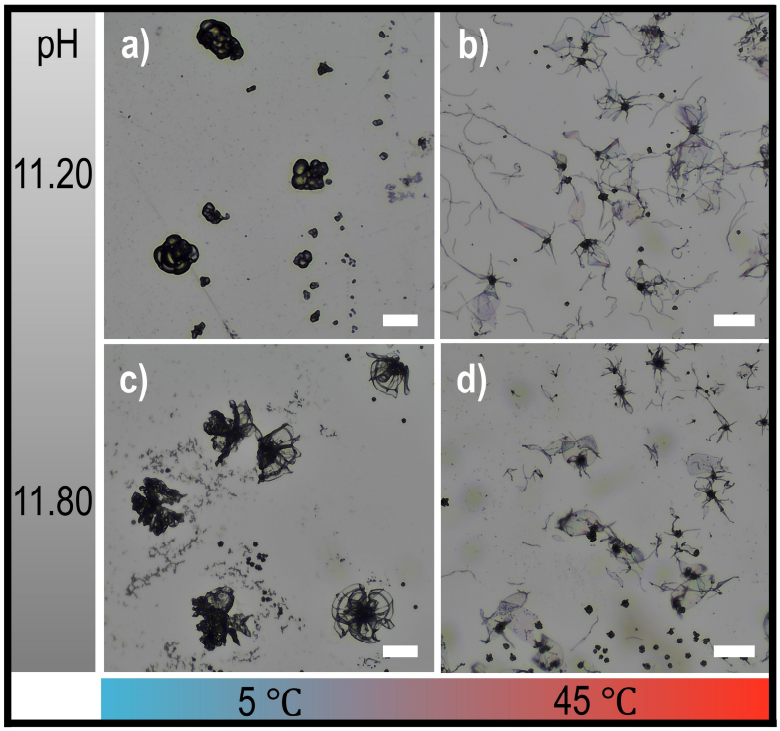

Fig. S3 Microphotographs of biomimetic materials obtained at different growth temperatures. a) pH=10.20, 5℃. b) pH=10.20, 45℃. c) pH=10.80, 5℃. d) pH=10.80, 45℃. Scale bar:100 μm.

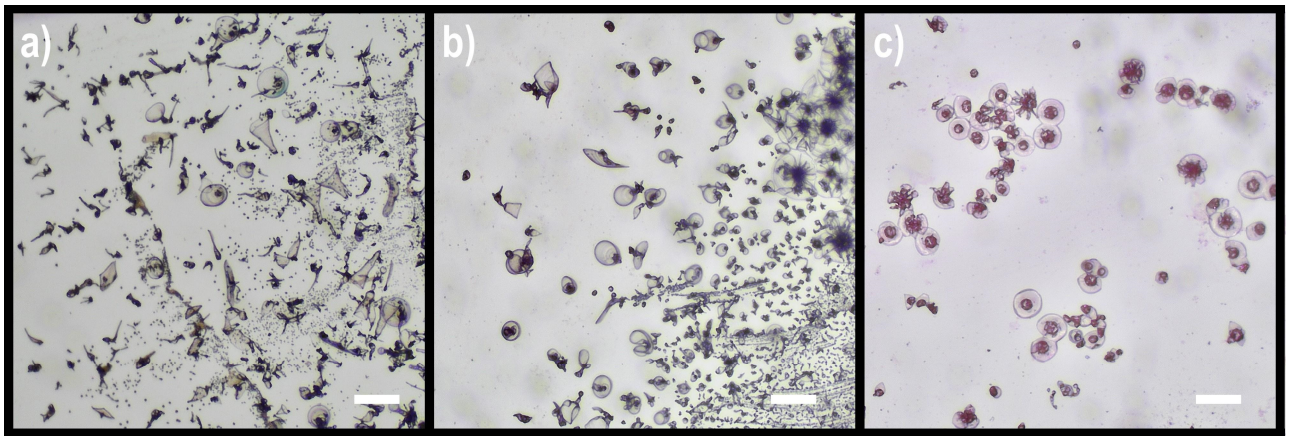

Fig. S4 Microphotographs of biomimetic materials obtained at different Rhodamine B concentration. a) 0.00154 mol/L. b) 0.00308 mol/L (1500ppm). c) 0.00616 mol/L. Scale bar:100 μm.

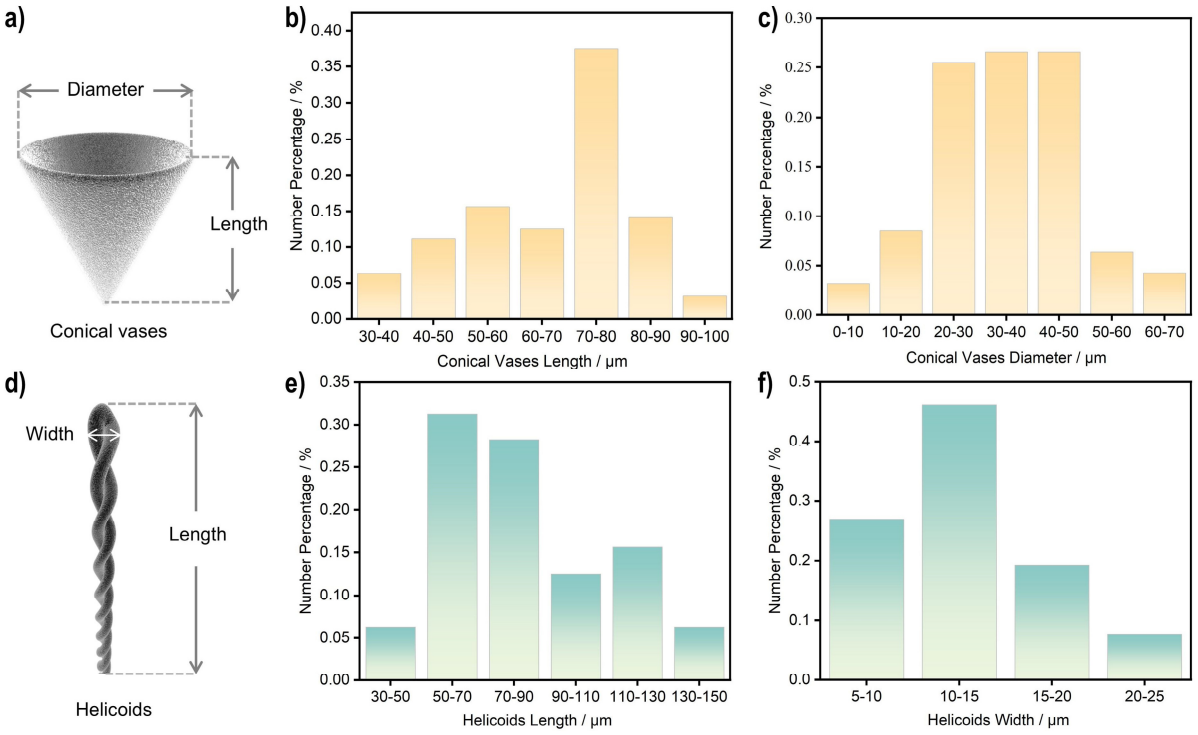

Fig. S5 Size distributions of helicoids and conical vases biomimetic morphology. a) Conical vases morphology measurement diagram. b) Conical vases length. c) Conical vases diameter. d) Helicoids morphology measurement diagram. e) Helicoids length. f) Helicoids width. All data are measured by ImageJ software.