

Synthesis of Amphiphilic Dye-Self-Assembled Mesostructured Powder Silica with Enhanced Emission for Directional Random Laser

Kun Hou,[†] Qinghai Song,^{†,§} Daobo Nie,[‡] Fuyou Li,^{||} Zuqiang Bian,[‡] Liying Liu,[§] Lei Xu,^{*,§} and Chunhui Huang^{*,‡}

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China, State Key Laboratory for Advanced Photonic Materials and Devices, Department of Optical Science and Engineering, School of Information Science and Engineering, and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, P. R. China

Received May 31, 2007. Revised Manuscript Received March 24, 2008

In this paper, we report a laser device application of dye-self-assembled mesostructured powder. Dye-assembled submicrometer-sized mesostructured silica with high luminescence was first synthesized at room temperature from a mixed-surfactant system comprising laboratory synthesized hemicyanine dye and cetyltrimethylammonium bromide (CTAB) as structure-directing agents. The fluorescence emission of the dye molecules was greatly enhanced when self-assembled into the mesostructured powder even though the dye concentration is very high. The highly luminescent powder was further used as gain media to fabricate a laser device. The laser device is a combination of planar microcavity with mesostructured powder random gain layer. Investigation of the laser performance employing the mesostructured powder with enhanced emission as gain media shows a directional output and a much lower threshold, which is 85 times lower than counterpart device using a mixture of silica sphere and dye molecules as gain media.

Introduction

The application of mesostructured materials¹ in different areas, such as catalysis,² sensors,³ solar cells,⁴ drug delivery systems,⁵ and so forth, has received intense investigation since the MCM (mobile crystalline materials) family of periodic mesostructured silicas were first synthesized using supramolecular templating in the early 1990s. Because of its well-defined organic–inorganic phase segregation at nanometer scale, which may effectively prevent the aggregation of certain dyes at relatively higher concentration compared to well-developed sol–gel glass, the as-synthesized mesostructured materials, i.e., materials in which the organic template was not removed, had been examined as optical

materials.⁶ The optically active species are usually incorporated into the hybrid materials in one step during the coassemble process. However, it should be noticed that most of the mesostructured materials are fabricated as the morphology without scattering, such as films,⁷ fibers⁸ for optical applications, and there are still no reports about the practical laser applications of mesostructured materials in powder form, which are more widely studied for the purpose of catalysis and can be processed with less difficulties compared to films. Two main reasons are responsible for this status. First, the final performance of optical materials is not only dependent on the host matrix, but also on the choice of the organic dyes.⁹ Different from those morphologies without scattering, most mesostructured powder is synthesized in aqueous phase; therefore, it is difficult to find a dye molecule with an appropriate amphiphilic structure to be incorporated into surfactant micelles to cocondense with inorganic moieties during the coassemble process. The most widely studied dyes that can be incorporated into mesostructured materials in nonaqueous phase so far are rhodamine and coumarin dyes,⁹ but they are either too hydrophilic or hydrophobic to coassemble into the final powder materials in an aqueous

* Corresponding author. E-mail: chhuang@pku.edu.cn (C.H.); leixu@fudan.edu.cn (L.X.).

[†] K. Hou and Q. H. Song contributed equally to this work.

[‡] Peking University.

[§] State Key Laboratory for Advanced Photonic Materials and Devices, Fudan University.

^{||} Laboratory of Advanced Materials, Fudan University.

- (1) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710. (b) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
- (2) (a) Corma, A. *Chem. Rev.* **1997**, *97*, 2373. (b) Melero, J. A.; Grieken, R. V.; Morales, G. *Chem. Rev.* **2006**, *106*, 3790.
- (3) (a) Urade, V. N.; Hillhouse, H. W. *J. Phys. Chem. B* **2005**, *109*, 10538. (b) Wagner, T.; Kohl, C. D.; Froba, M.; Tiemann, M. *Sensors* **2006**, *6*, 318.
- (4) Hou, K.; Tian, B. Z.; Li, F. Y.; Bian, Z. Q.; Zhao, D. Y.; Huang, C. H. *J. Mater. Chem.* **2005**, *14*, 2414.
- (5) Vallet-Regi, M. *Chem.—Eur. J.* **2006**, *12*, 5934.

- (6) (a) Marlow, F.; McGehee, M. D.; Zhao, D. Y.; Chemka, B. F.; Stucky, G. D. *Adv. Mater.* **1999**, *11*, 632. (b) Scott, B. J.; Wirmsberger, G.; Stucky, G. D. *Chem. Mater.* **2001**, *13*, 3140.

- (7) Yang, P. D.; Wirmsberger, G.; Huang, H. C.; Cordero, S. R.; McGehee, M. D.; Scott, B.; Deng, T.; Whitesides, G. M.; Chemka, B. F.; Buratto, S. K.; Stucky, G. D. *Science* **2000**, *287*, 465.

- (8) Loerke, J.; Marlow, F. *Adv. Mater.* **2002**, *14*, 1745.

- (9) Sanchez, C.; Lebeau, B.; Chaput, F.; Boilot, J. P. *Adv. Mater.* **2003**, *23*, 1969.

synthesizing system; therefore, special dyes with appropriate amphiphilic structure are needed to produce dye assembled mesostructured materials. Another factor that may hinder the using of powder material in optical application is scattering. In conventional laser theory, scattering is usually thought as detrimental to laser application because of the concerns of photon removal from resonant cavities;⁹ therefore, the strong scattering caused by powder mesostructured materials preclude their practical use in thin-film applications. However, according to the random laser theory, if the dimension of particles is reduced to the wavelength of light, the strong scattering inside the particles can also produce enough gain to get the so-called random lasers.¹⁰ And many materials such as ZnO powders,¹¹ nanofibers,¹² and disordered polymer films¹³ have been proved to be suitable for generating random lasers. Although the random laser is believed to have broad applications in microsized laser source, remote sensors, and optical storage, it suffers from the high threshold and isotropic emission. Recently, a novel planar random microcavity that consists of a traditional planar microcavity and a random gain layer composed of mixture of dye molecules and silica spheres scatters has been proven to dramatically reduce the threshold of random laser.¹⁴ This result represents an important step toward the practical applications of random lasers. If the random laser theory could be reduced to practice into the world of powder mesostructured materials, this would greatly widen the optical application of mesostructured materials, and bodes well for the future development of random lasers based on powder mesostructured materials.

Highly doped mesostructured materials with the fluorescence maintained are desired for high performance optical device. Inclusion of different dyes such as Coumarin 40, Rhodamine BE50, and Oxazine has been reported by Schulz-Ekloff and Wöhrles group,^{15–17} with the aim of obtaining functional organic–inorganic hybrid nanocomposites for optical applications. And other several papers also demonstrated the inclusion of dye molecules into the mesopores with optimized property. However, these materials showed an increase in photoluminescence intensity only at a moderate dye concentration.^{18,19} Previously, we proposed a hemicyanine dye–surfactant system, which may produce functional mesostructured materials with different geometry by chang-

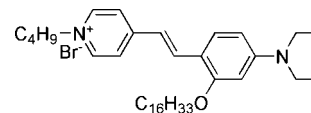


Figure 1. Structure of the amphiphilic hemicyanine dye surfactant [(*E*)-*N*-(*n*-butyl)-4-(2-(4-diethylamino-2-cetyloxy phenyl) ethenyl) pyridinium] bromide (*p*-C₄POC₁₆).

ing the dye amounts and structures.²⁰ Because of the amphiphilic property of the hemicyanine dyes, this system can be regarded as a cationic–cationic mixed surfactant system. More importantly, thanks to the luminescence property and appropriately designed structures of the hemicyanine dyes, the resultant materials show high fluorescence even at high dye concentration. However, the real device application of the mesostructured materials still remained to be substantiated.

The purpose of this paper is to explore the practical laser device application of dye-assembled luminescent powder mesostructured materials. First, we synthesized submicrometer-sized mesostructured powder with high luminescence from an amphiphilic hemicyanine dye–CTAB mixed-surfactant system. Further, we fabricate a low threshold random laser device using dye-assembled mesostructured powder as gain media. We believe this is an important step toward real application of powder functional mesostructured materials.

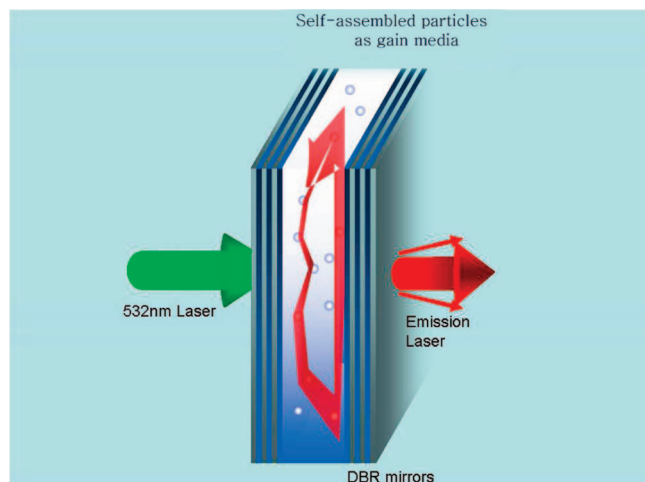
Experimental Section

Materials. The dye surfactant [(*E*)-*N*-(*n*-butyl)-4-(2-(4-diethylamino-2-cetyloxy phenyl) ethenyl) pyridinium] bromide (Figure 1, abbreviated as *p*-C₄POC₁₆) was prepared as reported before.²⁰ ¹H NMR, elemental analysis, and electrospray ionization mass spectrometry (ESI-MS) results showed that the dye was synthesized successfully (see the Supporting Information). Titanium(IV) butoxide, methyltriethoxysilane, methacryloxypropyl trimethoxysilane (MAPTMS), methacrylic acid (MAA), SiCl₄, and zirconium(IV) butoxide were purchased from Aldrich. All the other chemicals used in the experiments were obtained from Beijing Chemical Factory and used without further purification unless stated. To synthesize powder mesostructured silica with submicrometer-sized spherical morphology suitable for random laser application, a certain amount of ethanol was added to the reactant mixture. The reagents consist of 0.6 g of CTAB, 0.4 g of *p*-C₄POC₁₆, 25 g of H₂O, 6 g of C₂H₅OH, 15 g of NH₃·H₂O, and 3.16 g of Si(OC₂H₅)₄. After being stirred at room temperature for 4 h, the product of red powder was separated from the solution by filtration. To enhance the electron density contrast for transmission electron microscope imaging, the hybrid material was calcined at 600 °C for 5 h in air to remove the organic surfactants. TiO₂, SiO₂, and inorganic–organic hybrid SiO₂–ZrO₂ gels that were needed to fabricate the random laser device were synthesized by sol–gel procedures. The TiO₂ sol was prepared by refluxing 5g of the titanium(IV) butoxide in 32 g ethanol solution for 2 h, the SiO₂ sol was prepared by adding 3.15 g of methyltriethoxysilane and 1.48 g of SiCl₄ in 40 mL ethanol and stirred at room temperature for 2 h. The SiO₂–ZrO₂ organic–inorganic hybrid material used to disperse the mesostructured powder as the gain layer was synthesized by hydrolysis and polycondensation of MAPTMS, MAA, and zirconium(IV) butoxide as reported before.²¹

- (10) (a) Wiersma, D. *Nature* **2000**, *406*, 132. (b) Cao, H. *Waves Random Media* **2003**, *13*, R1–R39.
- (11) Cao, H.; Zhao, Y. G.; Ho, S. T.; Seeling, E. W.; Wang, Q. H.; Chang, R. P. H. *Phys. Rev. Lett.* **1999**, *81*, 2278.
- (12) Yu, S. F.; Yuen, C.; Lau, S. P.; Park, W. I.; Yi, G. C. *Appl. Phys. Lett.* **2004**, *84*, 3241.
- (13) Song, Q. H.; Wang, L.; Xiao, S. M.; Zhou, X. C.; Liu, L. Y.; Xu, L. *Phys. Rev. B* **2005**, *72*, 035424.
- (14) Song, Q. H.; Liu, L. Y.; Xiao, S. M.; Zhou, X. C.; Wang, W. C.; Xu, L. *Phys. Rev. Lett.* **2006**, *96*, 033902.
- (15) Ganschow, M.; Hellriegel, C.; Kneuper, E.; Wark, M.; Thiel, C.; Schulz-Ekloff, G.; Bräuchle, C.; Wöhrle, D. *Adv. Funct. Mater.* **2004**, *14*, 269.
- (16) Ganschow, M.; Wark, M.; Wöhrle, D.; Schulz-Ekloff, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 160.
- (17) Ganschow, M.; Braun, I.; Schulz-Ekloff, G.; Wöhrle, D. *Host-Guest Systems Based on Nanoporous Crystals*; Wiley-VCH: Weinheim, Germany, 2003.
- (18) Innocenzi, P.; Brusatin, G. *Chem. Mater.* **2001**, *13*, 3126.
- (19) Peng, C.; Zhang, H.; Yu, J.; Meng, Q.; Fu, L.; Li, H.; Sun, L.; Guo, X. *J. Phys. Chem. B* **2005**, *109*, 15278.

- (20) Hou, K.; Shen, L.; Li, F. Y.; Bian, Z. Q.; Huang, C. H. *J. Phys. Chem B* **2006**, *110*, 9452.
- (21) Wang, X. J.; Xu, L.; Li, D. X.; Liu, L. Y.; Wang, W. C. *J. Appl. Phys.* **2003**, *94*, 4228.

Scheme 1. Schematic Illustration of the Planar Random Microcavity Laser; Mesostructured Self-Assembled Powder is Embedded into a SiO₂-ZrO₂ Sol-Gel Film



Briefly, MAPTMS was first prehydrolyzed to form SiO₂ network with aqueous HCl as the catalyst. The sol was further exposed to the illumination of UV light to polymerize methacryl group of the precursor to form Poly(methyl methacrylate) (PMMA) network. Zirconium(IV) butoxide was mixed with MAA to produce ZrO₂, which was used to adjust the refractive index of the sol-gel film as gain layer. After mixing processed MAPTMS and zirconium(IV) butoxide, a photoinitiator (IRGACURE 819, CIBA) was finally added into the mixed sol. The molar ratio of MAPTMS:zirconium(IV) butoxide:methacrylic acid was 10:4:4.

Laser Device Fabrication. The microcavity consisted of a disordered gain film sandwiched by two diffraction Bragg reflector (DBR) mirrors (Scheme 1). The DBR mirrors were fabricated by depositing SiO₂ and TiO₂ films alternatively from the corresponding sol-gel sols on a polished glass. Briefly, the substrate was immersed into the corresponding SiO₂ and TiO₂ sol-gel solution and withdrawn at a constant rate of 15 cm/min. After deposition, samples were annealed at 150 °C for 5 min in a rapid thermal annealing furnace. This method allows good control and reproducibility of deposited film thickness. Each DBR structure consists of 10 SiO₂/TiO₂ bilayers. To make the disordered gain layer for microcavity, we dispersed the dye-self-assembled mesostructured powder (32.5 wt %) into SiO₂-ZrO₂ sol-gel solution mentioned above under stirring; the gel was then spin-coated onto the DBR mirror to get a film with a thickness of about 1 μm. Another TiO₂/SiO₂ multilayer DBR mirror was then capped on the structure under pressure to form a cavity (Scheme 1). The refractive indices of the SiO₂-ZrO₂ film and the mesostructured powder are 1.52 and 1.43, respectively. For comparison, we also fabricated a reference device using a dye and silica spheres mixture as the gain media. The fabrication of the device was similar as illustrated above, except that the gain media was a SiO₂-ZrO₂ layer doped with 0.8 wt % *p*-C₄POC₁₆ dye as the photoactive molecules and 15.6 wt % silica spheres as the scattering particles.

Characterization. Powder X-ray diffraction (XRD) was conducted with a Rigaku D/MAX 2000 diffractometer using Ni-filtered Cu Kα radiation operated at 40 KV and 100 mA, with a scan rate of 1°/min and a step of 0.02°. The fluorescence spectrum was obtained by Edinburgh Instruments FLS920 spectrometer. The slit width of the excitation beam was kept constant during all the fluorescence measurements. The quantum yields of the mesostructured materials and referenced dye powder were measured with an integrating sphere. The 500 nm excitation light was obtained by placing Schott quartz filters in the light beam of a Xenon lamp

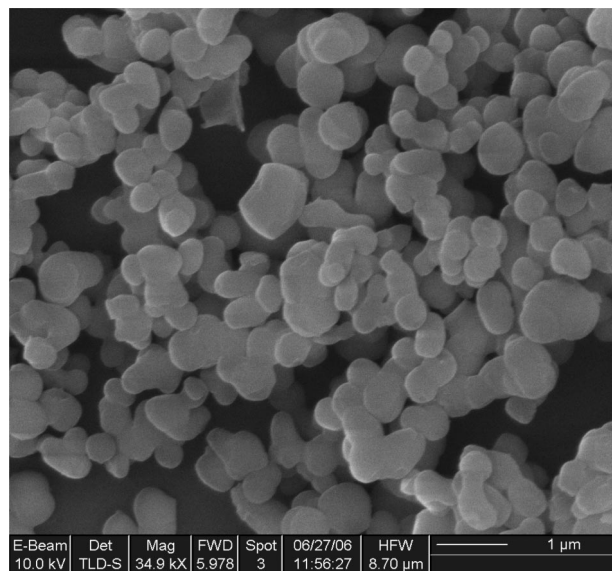


Figure 2. SEM image of the dye coassembled mesostructured material separated from aqueous synthesis system for random laser application. The powders are either directly pumped or embedded in sol-gel films to produce random laser.

(500 W, Oriel, USA). The intensity of the emission and excitation light were detected with a photodiode and a photometer (Coherent LightGauge), respectively. More details about the quantum yields calculation can be found in the reference²² (ESI for the scheme of measurement set up). Scanning electron microscope (SEM) image was taken on a Strate DB235(FEI) electron microscope at 10 KV acceleration voltage. Transmission electron microscope (TEM) images were taken on a JEOL 2011 microscope operated with an acceleration voltage of 200 KV. A SHIMADZU-UV3101 spectrometer was used to measure the reflection spectrum of the microcavity. In the photon exciting experiment, the spherical mesostructured powders are optically pumped with a frequency doubled Nd:YAG laser at 532 nm, 10 Hz repetition.

Results and Discussion

Synthesis of Hybrid Mesostructured Silica with Enhanced Emission. To form the random lasing resonators, very strong scattering is always needed. According to Mie scattering theory, the scattering is stronger when the sizes of particle are near to the laser wavelength.²³ Therefore, mesostructured powder with submicrometer sized morphology is needed for random laser application. Figure 2 shows the SEM image of the dye-assembled mesostructured materials. The mesostructured material shows spherical morphology with the dimensions range from 100 nm to about 800 nm, which make them quite suitable as scatters for random laser. The XRD pattern (Figure 3a) of the as-synthesized material shows two peaks located at 2.21 and 2.53°, with *d* values of 3.99 and 3.49 nm. These peaks can be indexed as the (211) and (220) diffraction peaks belong to the bicontinuous cubic space group (*Im3d*) symmetry. After calcination, the diffraction peaks become much stronger due to the increased electron density of the framework relative

(22) Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Phillips, R. T.; Kessener, Y. A. R. R.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89.

(23) Stratton, A. *Electromagnetic Theory*; McGraw-Hill: New York, 1941.

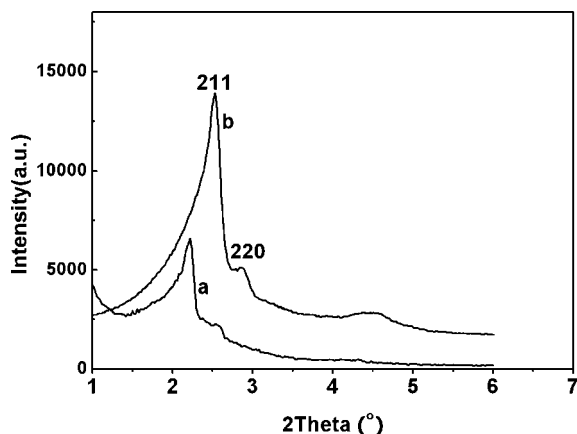


Figure 3. XRD patterns of the spherical powder synthesized at room temperature templated by CTAB and *p*-C₄POC₁₆ blends, (a) as-synthesized sample, (b) sample calcined at 600 °C for 5 h.

to the pores. The TEM images (Figure 4) display the typical (111) and (311) projection planes of a bicontinuous cubic structure. Combining the XRD and TEM data, we can see that the as-synthesized dye self-assembled mesostructure silica has a bicontinuous structure (MCM-48).²⁴

Usually, fluorescence quantum efficiency of organic chromophores generally decreases in the solid state, even though they show high fluorescence in solution. This quite general decrease is attributed mainly to intermolecular vibronic interactions, which induces a nonradiative fluorescence quenching by excitonic coupling, excimer formation, and excitation energy transfer to trap states. This can be proved from low-emission efficiency of pure dye powder, which shows a quantum yield (Φ) below 0.1%. However, once the dye is incorporated into the mesostructure structure, even though the doping ratio is very high (dye/CTAB = 4/6, mass ratio), the luminescence quantum efficiency of the mesostructured silica synthesized here is increased greatly compared to the pure dye powder (from <0.1 to 8.1%). Emission efficiency enhancement of dye molecules incorporated into mesostructured materials has been reported before, but only at a very low dye concentration. The fluorescence is normally quenched when the dye content is increased to a certain level. Very recently, it has been reported that organization of chromophore into well-ordered aggregates by inorganic–organic self-assembly process helps to increase the luminescence emission relative to ill-defined nanoaggregates.²⁵ Because the dye used here has an amphiphilic structure (Figure 1), it is quite possible that dye molecules, together with the CTAB surfactant molecules, interact directly with the inorganic silica precursors to get the bicontinuous structure. To study if it is possible for the dye to be directly involved in the self-assembly process to form organized aggregates and contribute to the luminescence quantum yield enhancement, the amphiphilic dye was used as a single surfactant to synthesize mesostructured material. The result shows that disordered mesostructured material was obtained (see the Supporting Information for the synthesis and characterization). This result also shows that this dye can

practically be used as a surfactant; therefore, the dye–CTAB mixture can be viewed as a cationic–cationic mixed-surfactant system. The quantum yield of the pure dye-directed mesostructured material, as measured by integrating sphere method, is enhanced from below 0.1% for dye powder to 2.1%. Compared with pure dye powder, the dye molecules in the mesostructured material may form ordered aggregates by undergoing an inorganic–organic self-assembly process when the hybrid material is formed. Therefore, we tentatively believe that the formation of ordered aggregates contributes to the increase of the dye emission in the dye–silica nanocomposite, as reported before.²⁵ Furthermore, by comparing the quantum yields between the nanocomposites templated by mixed dye–surfactant and single dye surfactant, the bicontinuous mesostructured material shows even higher quantum yield. The quantum yield of the mesostructured powder templated by the mixed surfactant is further increased from 2.1 to 8.1%. In aqueous phase, dye surfactant forms mixed micelles with CTAB molecules; therefore, dye molecules are homogeneously distributed into the CTAB surfactant matrix when the inorganic–organic nanocomposite is formed. The presence of CTAB molecules helps to separate the dye molecules, i.e., the dye molecules are no longer closely aggregate together when the ordered mixed aggregates are formed. Because Förster quenching is observed in most cases for fluorescence molecules in molecular sieves,^{26,27} the segregation of dye molecules from each other helps to reduce the Förster quenching, and thus, increase the emission efficiency of the mixed-surfactant material relative to the single dye surfactant nanocomposite material. The fluorescence spectra of dye molecules in different states were also obtained (Figure 5). It can be seen from Figure 5 that the fluorescence intensity increases gradually from pure “solid-state” dye power to “pure surfactant” directed mesostructure material to “dye–CTAB” mixed surfactant templated material, which qualitatively agrees with the quantum yield measurements. Note that fluorescence intensity is only a qualitative result because the absorption is not considered. From the above discussion, we tentatively propose that the combination effects of the formation of ordered aggregates, the effect of CTAB molecules to separate the dye molecules to reduce Förster self-annihilation, lead to the improved luminescent property of the bicontinuous material. The high loading of the dye into the mesostructured powder, as well as the improved quantum efficiency, makes it quite attractive for laser application, as will be discussed below.

Laser Property Study. It has been proposed recently that when random gain media is incorporated into a one-dimensional planar microcavity, a high-directional, low-threshold random laser could be achieved.¹⁴ Because the mesostructured powder obtained here is highly luminescent, it is quite attractive to employ this luminescent powder as gain media to get a high-performance laser device. To test if the dye-self-assembled mesostructured powder can be employed as a random gain media, we further optically

(24) Schmidt, R.; Stocker, M.; Akporiaye, D.; Torstad, E. H.; Olsen, A. *Microporous Mater.* **1995**, *5*, 1.

(25) Bhongale, C. J.; Hsu, C. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 1404.

(26) Gopich, I.; Szabo, A. *J. Phys. Chem. B* **2005**, *109*, 6845.

(27) Cotlet, M.; Vosch, T.; Habuchi, S.; Weil, T.; Müllen, K.; Hofkens, J.; Schryver, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 9760.

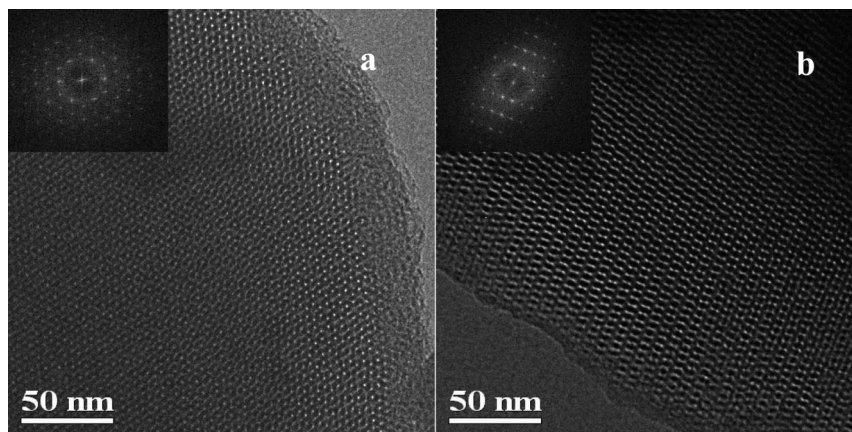


Figure 4. TEM images and the corresponding Fourier diffractograms of the calcined mesoporous silica templated by dye-CTAB mixtures, viewed from (a) [111], (b) [311] directions.

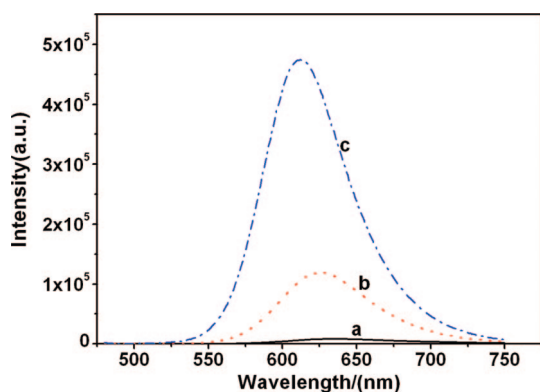


Figure 5. Photoluminescence spectra from (a) pure dye powder, (b) pure dye surfactant (*p*-C₄POC₁₆)-templated mesostructured powder, (c) bicontinuous mesostructured powder templated by dye-CTAB mixtures.

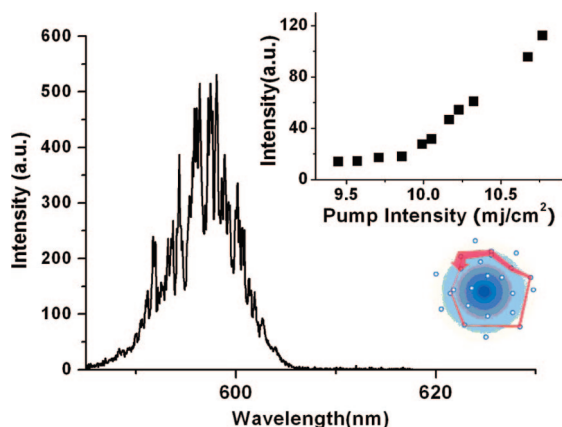


Figure 6. Emission spectrum of the dye-assembled mesostructured powder pumped above threshold. The inset on the top right corner is the emission from the hybrid material powder versus excitation intensity and that on the bottom right corner is the schematic diagram showing the formation of closed-loop path for the recurrent scattering of the light.

pumped the spherical MCM-48 powders with a frequency-doubled Nd:YAG laser at 532 nm, 10 Hz repetition rate and 35 ps pulse width. Figure 6 shows the emission spectrum above the threshold and the emitted laser intensity versus the laser pump intensity. Below the threshold, the emission is characteristic of spontaneous emission. Once the threshold, 10 mJ/cm², is reached, the spectrum becomes very narrow and many discrete peaks with full width at half-maximum (fwhm) about 0.2 nm appear. These discrete peaks can be

rationalized as coherent random lasers corresponding close loops inside the MCM-48 powders (Schematic diagram shown in Figure 6, inset) as they are randomly distributed in the spectrum and strongly dependent on the pump position. Because of the property of Mie scattering,²³ random laser emits from powders in all directions. Our results here prove that coherent random laser action can also be realized in powder mesostructured materials with morphology controllably synthesized, which paves the way for the application as gain media in planar microcavity. We further insert the gain medium inside a planar microcavity with the intention to prove the superior laser property of the dye self-assembled powder, and as a result, a high-performance laser device will be demonstrated. As the schematic picture in Scheme 1, the planar random microcavity consists of the as-synthesized dye assembled MCM-48 powder doped SiO₂-ZrO₂ film as gain layer, which is sandwiched by two DBR mirrors. The reflectivity of DBR mirrors is 92%, which are fabricated by sol-gel technique. Figure 7a shows the reflection spectrum of planar random microcavity. Three peaks corresponding to the resonant peak of the planar microcavity can be observed in the spectrum. Only the peak at 600 nm overlaps with the spontaneous emission of *p*-C₄POC₁₆.

A collimated laser beam in the forward can be observed when the cavity is pumped with high laser intensity 2.5 μJ/cm². Figure 7b shows the spectrum of emitted laser. The spectrum is also dominated by few discrete peaks with a line width of about 0.2 nm. These modes are random laser modes because they are also randomly distributed and dependent on the pump position. The relation between the emitted laser intensity and pump intensity is also studied. A clear laser threshold, 2.2 μJ/cm², is shown in the inset of Figure 7b. This threshold is more than 3 orders of magnitude lower than that of powders only because of the dramatically decreasing of mode density inside the cavity by coupled effects from random cavities and planar microcavity.¹⁴ Because of the low pump intensity and short pulse during (35 ps), the hybrid material gain media possess high thermal stability.²⁸ In this experiment, we did not observe the obvious

(28) Bulovic, V.; Kozlov, K. J.; Khalfin, V. B.; Forrest, S. R. *Science* **1998**, 279, 553.

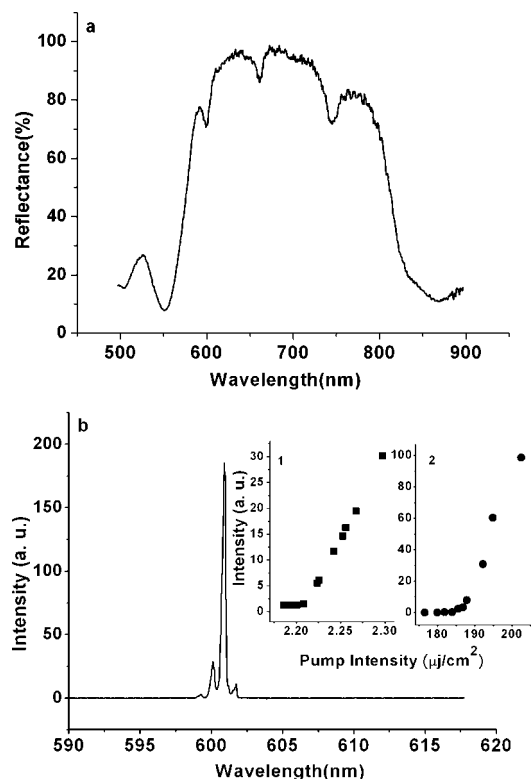


Figure 7. (a) Reflection spectrum of the microcavity; (b) emission spectrum of the microcavity excited above threshold. Inset on the right top corner is the dependence of output energy versus pump energy: (1) microcavity using hybrid material sphere as gain media; (2) microcavity using a mixture of hemicyanine dye and silica sphere as gain media.



Figure 8. Far field image of the laser beam detected at 12 cm away from the microcavity.

intensity reducing with at least 1000 pulses. Figure 8 shows the far field picture of the planar random microcavity pumped above threshold (recorded with a digital camera, Canon SD 400). The red spot on the white screen is the collimated laser beam. From the distance between the screen and sample surface and the diameter of laser spot, a divergence angle of about 1.5° can be determined. This directional laser is suitable to the microlaser source applications.

To confirm the advantages of dye-assembled mesostructured materials, we prepared a microcavity device using a mixture of hemicyanine dye and silica sphere with the highest dye content without dye aggregation as gain media, where the silica sphere is synthesized without surfactants²⁹ and the

dye molecules are located outside the silica spheres. Although we could also observe the random laser, the threshold is $185.5 \mu\text{J}/\text{cm}^2$, which is about 85 times higher than that of the corresponding mesostructured materials as gain media (Figure 7b-2). The great decreasing of the threshold of the microcavity using dye-assembled mesostructure sphere as gain media is possibly attributed to two reasons. First, a high degree of dye loading into the mesostructured materials with fluorescence enhancement can be achieved by employing a rationally designed amphiphilic dye as surfactant. In most cases, powder mesostructured materials are synthesized in aqueous solution, the amphiphilic property of the dye molecules is of the most important to get the dye-doped mesostructured materials under such circumstances. In our experiments, we had also tried widely used laser dye Rhodamine 6G as previously reported to dope into mesostructured material. However, due to the hydrophilic properties, it is very difficult to trap the dye into the mesostructured silica in our aqueous synthetic system. The threshold of the device using Rhodamine 6G doped silica sphere is still in the range of hundreds of $\mu\text{J}/\text{cm}^2$. As can be seen from Figure 1, the hemicyanine dye has a long hydrophobic chain balanced by a butyl headed hydrophilic group, the compatibility between the dye long hydrophobic chain and CTAB hydrophobic part allows the formation of ordered mixed-micelle aggregates, which in turn guarantees good dispersion of dye molecules into the mesostructured materials with high loading during the inorganic-organic self-assembly process. The good dispersion of the dye and the formation of the ordered aggregates, as discussed above, contribute to the enhancement of the fluorescence emission with high dye loading. Further, using of inorganic-organic hybrid mesostructured silica rather than mixture of silica spheres and dye molecules to form the gain layer prevented effectively the aggregation of dye molecules in the sol-gel $\text{SiO}_2\text{-ZrO}_2$ films because the dye molecules are not distributed in the films directly but located in the inorganic-organic phase separated mesostructured powders. The high loading as well as the strong fluorescence enhancement of dye molecules in the mesostructured materials and high mesostructure doping ratio in the gain layer without dye self-quenching contribute greatly to the observed threshold reduction. Further reduction of threshold is expected by replacing hemicyanine dye with doped dyes that have higher quantum efficiency, and this work is currently in progress in our laboratory.

Conclusion

In summary, we have demonstrated a new planar random microcavity employing specially designed amphiphilic dye-assembled mesostructured silica as gain media. We first prepared submicrometer sized mesostructured materials with enhanced fluorescence by employing blends of hemicyanine dye and CTAB as the templates. The dye with appropriate amphiphilic structure helps to obtain spherical powder mesostructured materials with high luminescence property. When the mesostructured materials are pumped with the laser above the threshold, coherent random laser can be achieved. When the dye-assembled mesostructured hybrid material

(29) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

powder is incorporated into planar microcavity, directional lasing with an ultralow threshold was obtained. The threshold is about 85 times lower than the devices using mixtures of the dye and silica spheres as gain media because high dye concentration with fluorescence enhancement can be realized using the hemicyanine dye as surfactant to be incorporated into mesostructured silica. Thus, we have demonstrated that dye-assembled mesostructured materials in the form of powder are a class of superior optical materials. More importantly, our study broadened the application of powder mesostructured materials, and many other functional molecules within powder mesostructured materials are expected to find their laser applications in laser optics. Considering the ease and low cost of obtaining hybrid powder mesos-

structured materials, we hope our result will open a new area of the optical applications for mesostructured materials.

Acknowledgment. The authors acknowledge the financial support from the Nature Science Foundation (20423005, 20671006, and 50772003), and The National Basic Research Program (973 program; 2006CB601103).

Supporting Information Available: Synthesis procedure of the hemicyanine dye surfactant; synthesis and characterization of mesostructured silica from pure dye surfactant; scheme for fluorescence quantum yield measurement (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM703023D