

Efficient fluorescence from perylene orange encapsulated in AlPO_4 mesoporous glass

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AlPO_4 mesoporous glass doped with perylene orange (PO) is prepared using two steps. The effects of dipping time and PO concentration on the fluorescent properties and molecular formation are investigated through absorption spectra, excitation spectra, and emission spectra. A slight increase in the intensity of excitation bands formed at 499 and 468 nm is ascribed to PO J-dimers aggregates as the dipping time increased from 2 to 24 h at high PO concentration (4×10^{-3} mol/L). This is also the reason behind the concentration increase from 4×10^{-6} to 4×10^{-3} mol/L for the 16 h dipping. The excitation spectra, and the emission spectra of samples doped with PO show a slight red shift as the dipping time and the PO concentration increase. AlPO_4 mesoporous glass is suitable to host the PO at high concentration.

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Functional dye-doped porous inorganic materials have attracted increasing interest because of their applications in fluorescent materials^[1]. One of the most important applications is in the solid-state dye laser^[2], which is nonvolatile, nonflammable, nontoxic, compact, and mechanically stable. These make the laser more advantageous over liquid-state dye lasers. Limited by the sol-gel synthesis, the matrices used in dye laser are mostly microporous silicate glass and film^[3–5], polymers^[6–8], and porous molecular sieves^[9]. However, in order to achieve high efficiency, the mesopore (2–50 nm) size glass with high surface area and thermal stability is essential. Aluminum phosphate materials are useful for a number of applications, such as catalysts, catalyst support, as well as in laser and photonics^[10–12]. Recently, we reported a simple aqueous sol-gel route yielding the transparent colorless stoichiometric AlPO_4 glass possessing mesoporous structure and a surface area above $500 \text{ m}^2/\text{g}$ ^[13]. The structure of the glass was dominated by polymerized AlO_4 and PO_4 tetrahedra. In this letter, we report a novel sol-gel AlPO_4 mesoporous glass with high surface area^[13] doped with perylene orange (PO) dye at high concentration.

For the sample preparation, AlPO_4 mesoporous glasses were prepared according to a previously described procedure^[11]; these were then dipped into the PO ethanolic solution for a desired time, followed by cleaning the glasses with ethanol several times, and then drying the samples at 120°C for 48 h in the oven. AlPO_4 mesoporous glasses doped with PO dye at different concentrations (ranging from 4×10^{-6} to 4×10^{-3} mol/L) and glasses dipped at different dipping times (from 2 to 24 h) at the concentration of 4×10^{-3} mol/L were also prepared.

The absorption spectra of AlPO_4 mesoporous glasses doped with PO dye for different dipping times from 2 to 24 h at the concentration of 4×10^{-3} mol/L are shown in Fig. 1. The absorption spectra, used to investigate the diffusion of PO dye in the glass, are characterized by

three absorption peaks found at 538, 496, and 465 nm; this could be ascribed to the transition of conjugated bond $\pi-\pi^*$. The increase of dipping time from 2 to 16 h increased the absorption bands. The further increase of dipping time caused the slight increase of the absorption; hence, the PO concentration in the AlPO_4 mesoporous glasses increased as the dipping time increased toward 16 h, and the PO concentration in the AlPO_4 mesoporous glasses was close to the maximum at around 16 h.

To further investigate the effect of dipping time on the PO molecular formation in the AlPO_4 glasses, the normalized excitation spectra and emission spectra are presented in Fig. 2. The emission spectra and excitation spectra were recorded on HORIBA Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450-W xenon arc lamp, double grating excitation and emission monochromators (2.1 nm/mm dispersion, 1200 grooves/mm), and a Hamamatsu R928 photomultiplier tube or a TBX-4-X single-photon counting detector. A front-face holder was used to clip the samples, oriented

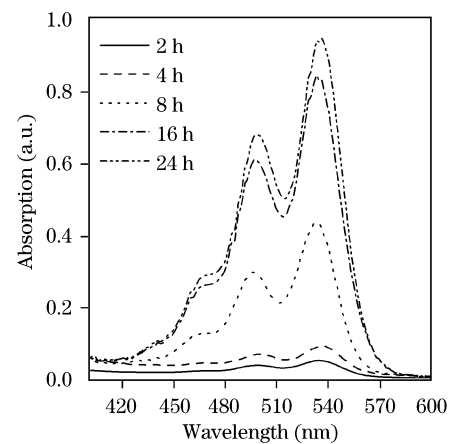


Fig. 1. Absorption spectra of AlPO_4 mesoporous glasses doped with PO dye at different dipping times at the concentration of 4×10^{-3} mol/L.

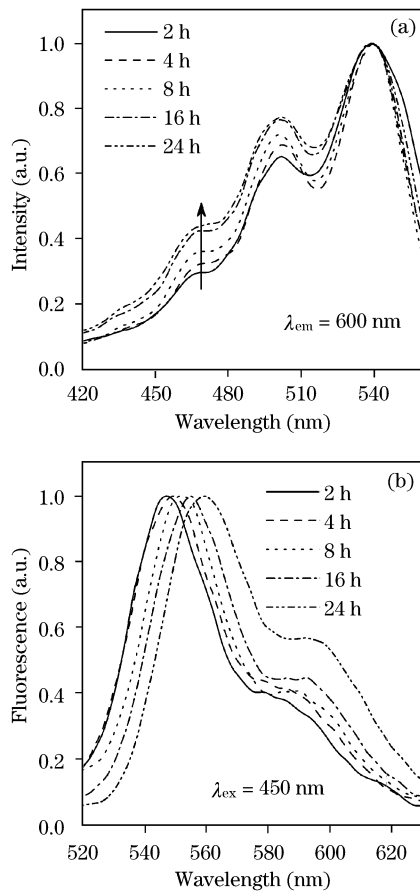


Fig. 2. Normalized (a) excitation and (b) emission spectra of AlPO_4 mesoporous glasses doped with PO at different dipping times at the concentration of 4×10^{-3} mol/L.

at a right angle to minimize the specular reflection from the excitation beam. A slight increase in the intensity and broadening of excitation bands found at 541, 499, and 468 nm was observed as the dipping time increased from 2 to 16 h. The further increase of dipping time to 24 h showed no significant increase for the excitation bands, indicating the absorbed equilibrium present around 16 h in accordance with absorption spectra. Based on the exciton theory^[14], the slightly increasing and broadening band is ascribed to some PO aggregates formed as J-dimers^[14–16]. The nano-scale separation of AlPO_4 mesoporous glasses is dedicated to reduce the aggregation of PO molecule.

The normalized fluorescence spectra of AlPO_4 mesoporous glasses dipped according to different dipping times reveal the effect of dipping time on fluorescence. Two efficient fluorescent bands formed at 548 and 584 nm, with a gradual red-shift to 553 and 592 nm, respectively, were observed as the dipping time increased from 2 to 16 h. The further increase of the dipping time to 24 h gave rise to a red-shift to 559 and 595 nm. Moreover, the relative intensity of fluorescent band at 595 nm was enhanced. The red-shift of fluorescence is ascribed to the increase in interaction between PO molecules as more PO molecules are absorbed in the glass aggregates and formed as J-dimers. Apparently, it is effective to avoid serious PO J-dimers by controlling the dipping time at 16 h where the PO concentration is high.

In order to study the effect of PO concentration on the molecular formation and fluorescence, the normalized excitation spectra and emission spectra of AlPO_4 mesoporous glass-doped PO dye, dipped for 16 h at different PO concentrations, are recorded, as shown in Fig. 3. According to the above discussion, a slightly increasing intensity of excitation bands formed at 499 and 468 nm, indicating the formation of some aggregates as J-dimers. Nevertheless, it is remarkable that the aggregation of J-dimers is not significant as the concentration increases from 4×10^{-6} to 4×10^{-3} mol/L. With regard to the emission spectra in Fig. 3(b), a slight red-shift of two fluorescence bands was found from 546 and 582 nm to 553 and 592 nm, respectively, as the PO concentration increased from 4×10^{-6} to 4×10^{-3} mol/L. Thus, the AlPO_4 mesoporous glass is suitable as the host of PO dye at high concentration given that the aggregating of PO dye is slight. It can then be concluded that the nano-scale separation of AlPO_4 mesoporous structure favors the obstruction of the PO molecular aggregation, thereby benefiting the fluorescence at high PO concentration.

In conclusion, the efficient fluorescence from PO dye encapsulated in AlPO_4 mesoporous glass with high surface area is achieved. The effects of dipping time and PO concentration on the fluorescent properties and PO molecule formation are investigated through absorption spectra, excitation spectra, and emission spectra, which indicates that the aggregation of PO molecule is slight,

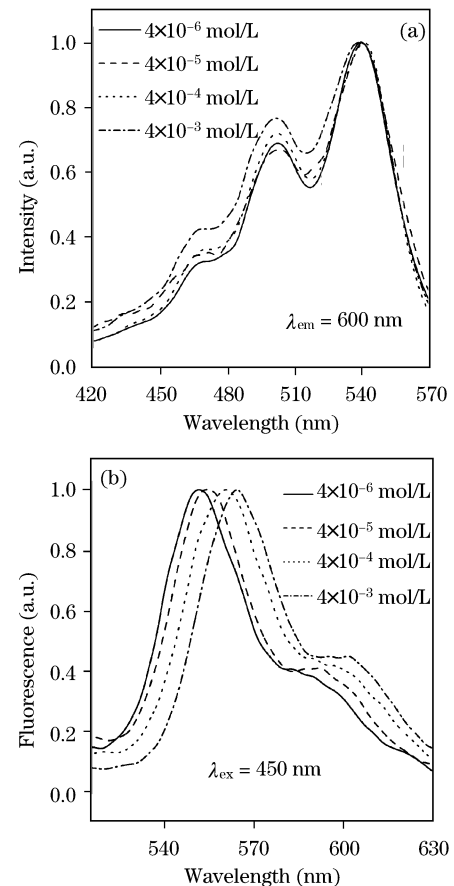


Fig. 3. Normalized (a) excitation spectra and (b) emission spectra of AlPO_4 mesoporous glasses doped with PO at different concentrations at the dipping time of 16 h.

even at the dipping time of 16 h at high PO concentration of 4×10^{-3} mol/L. Therefore, the AlPO_4 mesoporous glass is suitable as the host of PO dye.

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References

1. H. S. Zhou and I. Honma, *Adv. Mater.* **11**, 683 (1999).
2. R. Chen, Q. Xie, Q. Lu, Y. Zhang, X. Zhang, and Z. Zhang, *Chinese J. Lasers* (in Chinese) **34**, 1466 (2007).
3. A. Anedda, C. M. Carbonaro, R. Corpino, P. C. Ricci, S. Grandi, and P. C. Mustarelli, *J. Non-Cryst. Sol.* **353**, 481 (2007).
4. H. T. Oh, H.-S. Kam, T. Y. Kwon, B. K. Moon, and S. I. Yun, *Mater. Lett.* **13**, 139 (1992).
5. Q. Zhang and Z. Jiang, *Mater. Chem. Phys.* **69**, 95 (2001).
6. T. Watanabe, Y. Iketaki, M. Sakai, T. Ohmori, T. Ueda, T. Yamanaka, S. Ishiuchi, and M. Fujii, *Chem. Phys. Lett.* **420**, 410 (2006).
7. W. Liu, Q. Xia, X. Li, R. Fan, H. Chen, and D. Chen, *Chinese J. Lasers* (in Chinese) **34**, 707 (2007).
8. C. Huang, L. Chen, J. Yu, and S. Wen, *Chinese J. Lasers* (in Chinese) **35**, 73 (2008).
9. M. A. Zanjanchi, A. Ebrahimian, and Z. Alimohammadi, *Opt. Mater.* **29**, 794 (2007).
10. M. R. Mostafa and A. M. Youssef, *Mater. Lett.* **34**, 405 (1998).
11. J. B. Moffat, *Catal. Rev. Sci. Eng.* **18**, 199 (1978).
12. B. Gallace and J. B. Moffat, *J. Catal.* **76**, 182 (1982).
13. L. Zhang, A. Bögershausen, and H. Eckert, *J. Am. Ceram. Soc.* **88**, 897 (2005).
14. M. Kasha, H. R. Rawls, and M. A. El-Bayoumi, *Pure Appl. Chem.* **11**, 371 (1965).
15. D. N. Dempster, T. Morrow, and M. F. Quinn, *J. Photochem.* **2**, 343 (1973).
16. F. del Monte, J. D. Mackenzie, and D. Levy, *Langmuir* **16**, 7377 (2000).