Photoresponsive Photonic Crystals Constructed From Azobenzene-Grafted Silica Microspheres

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Abstract

Azobenzene compounds have been widely used in many fields and through their response to light they can be used to regulate the properties of ordered structures. In this paper, sub-micrometer colloidal SiO₂ spheres are prepared and azobenzene groups are grafted on the surface of SiO₂ microspheres. The SiO₂ microspheres grafted with azobenzene groups could self-assemble to form photosensitive photonic crystals (PCs), whose photonic bandgaps red-shifted as irradiated by UV light and showed good reversibility.

Introduction

Azobenzene and its derivatives are characterized by reversible transformations from the generally more stable *trans* form to the less stable *cis* form upon irradiation with UV or visible light to yield wavelength and temperature dependent photostationary composition (Kumar & Neckers, 1989). Photoinduced isomerism of azobenzene also proceeds with large structural change as reflected in the dipole moment and change in geometry. Azobenzene compounds have been widely used in many fields, such as reversible optical storage (Brown, Natansohn, & Rochon, 2002; Ho, Barrett, Natansohn, & Rochon, 1995), optically controlled molecular switch (H. Li, Wang, Pan, Yang, & Xia, 2018; Wen-Ching, Yi-Wei, & Chien-Tien, 2010), liquid crystal polymer materials (Allcock & Kim, 1989; Nardele & Asha, 2014; Yongqiang et al., 2012), controlled drug release system (Fomina, Mcfearin, Sermsakdi, Edigin, & Almutairi, 2010; Hu et al., 2016; Moorthy, Kim, Bae, Kim, & Ha, 2016) and so on.

Through their response to external stimuli, the azobenzene compounds can be introduced into ordered structures to regulate their properties. For example, an all-optically controllable azo-dye-doped liquid crystal infiltrated photonic crystal fiber was demonstrated, overall spectral transmittance of which could decrease and then increase with increase of the irradiation time of one UV beam (Lee et al., 2011). Subsequent irradiation of one green beam on the fiber could recover the transmission spectrum. The reversible all-optical controllability of the photonic band structure of the fiber was attributable to the isothermal state transitions of the liquid crystals via the UV-beam-induced *trans*→*cis* and green-beam-induced *cis*→*trans* isomerizations of the azo-dye in the cladding. A novel self-organized helical superstructure was fabricated by doping light-driven chiral azobenzene molecular switch and upconversion nanoparticles in a liquid crystal media, which exhibited reversible near-infrared (NIR) light guided tunable behaviors by modulating the excitation power density of continuous-wave NIR laser (980 nm) (Wang et al., 2014). The chiral switch exhibited reversible *trans* to *cis* and *cis* to *trans* photoisomerization when absorbing the UV or visible emissions from upconversion nanoparticles induced by modulating the excitation power density of NIR light. An optically switchable birefringent photonic crystals (PCs) were fabricated by infiltrating photo-responsive liquid crystals into a stretched poly (methyl methacrylate) inverse opal (Xie, Sun, Han, & Gu, 2008). Photoisomerization of the azobenzene compounds in liquid crystal induced a phase transition. When the liquid crystal was in a nematic phase, molecules aligned along the stretching axis generated an optical birefringent effect, which disappeared when the liquid crystal was in an isotropic phase. Herein, novel PC materials with

tunable photonic bandgaps are significant and light can act as external stimuli to adjust the photonic bandgaps conveniently.

In this paper, sub-micrometer colloidal SiO_2 spheres are prepared and azobenzene groups are grafted on the surface of colloidal SiO_2 microspheres. The SiO_2 microspheres grafted with azobenzene groups can self-assemble to form PC, whose photonic bandgaps vary as irradiated by UV or visible light.

Experimental Sections

2.1 Materials and instruments

Tetraethyl orthosilicate (TEOS), 3-mercaptopropyl trimethoxysilane (MPS) and ammonium hydroxide solution (NH_4OH , ~ 28% NH_3 in water) were purchased from Sinopharm Chemical Reagent Co., Ltd. Toluene and benzoyl peroxide (BPO) were purchased from Aladdin Reagent Co., Ltd. Deionized water was used in all the experiments. *p*-undecylamide azobenzene (UAA) were prepared by reaction of *p*-aminoazobenzene and undecylenyl chloride (Zhang, 1996).

Scanning electron microscopy (SEM) was carried out on a JEOL JSM-6700F electron microscope. Fourier transform infrared (FT-IR) spectral studies were carried out on a Bruker Vertex 70 IR spectrophotometer in KBr pellet form.

2.2 Preparation of nano-silica microspheres with sulfhydryl groups on the surface ($\text{SiO}_2\text{-SH}$)

First, nano-silica microspheres were prepared according to our previous work (C. Li et al., 2020). Into a flask, 15 mL ethanol, 5 mL water and 2 mL ammonium hydroxide were added, then mixture of 15 mL ethanol and 3 mL TEOS was added in 1100 rpm stirring state. The reaction took 2 hrs at 30°C. Then the solution was heated to 70 °C. 3 mL MPS was added and the reaction continued 2 hrs. The reaction solution was centrifuged at 6500 rpm; the precipitation was washed with absolute ethanol, and dried under vacuum at room temperature.

2.3 Preparation of nano-silica microspheres grafted with azobenzene groups ($\text{SiO}_2\text{-Azo}$)

Into a flask, 0.2 g $\text{SiO}_2\text{-SH}$ was added into 10 mL toluene and dispersed with supersonic wave. Then 0.05 g UAA and 0.001 g BPO were added. The reaction was carried out at 95°C under nitrogen atmosphere for 8 h. The reaction solution was centrifuged at 7000 rpm; the precipitation was cleaned with absolute ethanol and dried.

2.4 Preparation of silica photonic crystals with $\text{SiO}_2\text{-Azo}$ and their photo-responsive behavior

Vertical deposition method was used to prepare silica PCs. The thoroughly cleaned glass slide was placed vertically in the SiO₂-Azo microsphere sol with a mass fraction of 2% in absolute ethanol in an oven at 35 °C, and the PCs grew for 7 days. The UV-vis extinction spectra of PCs were obtained using a PERSEE TU-1901 spectrophotometer with incident light perpendicular to the sample surface. The measurement was carried out at 24°C and after irradiating with ultraviolet light of 365 nm for different time.

Results And Discussion

3.1 Preparation of SiO₂-Azo microspheres

In order to obtain SiO₂-Azo, SiO₂-SH was first prepared through the reaction of MPS with nano-silica microspheres, which were obtained using literature method (Stöber, Fink, & Bohn, 1968). Hydrolysis of MPS generated silicon hydroxyl, and then condensation reaction occurred between the silicon hydroxyl and the hydroxyl on the surface of the silica microspheres, so the sulfhydryl groups were grafted on the microspheres. In the next step, azobenzene groups were grafted on the silica microspheres by thiol-ene click reaction of the terminal sulfhydryl groups and the UAA (Scheme 1). BPO acted as catalyst for radical-mediated addition reaction in the thiol-ene click reaction (Lowe, 2010) (Uygun, Tasdelen, & Yagci, 2010).

Figure 1 shows the FT-IR spectra of SiO₂, SiO₂-SH and SiO₂-Azo. In the common peaks of the three microspheres, the peaks at 3441 cm⁻¹ and 1632 cm⁻¹ are the stretching vibration peak and in-plane bending vibration peak of hydroxyl. The peaks at 1104 cm⁻¹, 800 cm⁻¹, and 472 cm⁻¹ are the antisymmetric stretching vibration peak, symmetrical stretching vibration peak and in-plane bending vibration peak of Si-O-Si. So, it can be shown that the SiO₂ microspheres obtained through classical Stöber method have a large amount of hydroxyl groups on their surface. In the FT-IR spectrum of SiO₂-SH, the peak at 2928 cm⁻¹ is the stretching vibration peak of C-H of methylene—the peak at 2549 cm⁻¹ is the stretching vibration peak of S-H, the peak at 1407 cm⁻¹ is the stretching vibration peak of Si-C. It can be concluded that the thiopropyl groups are grafted on the nano silica. In the FT-IR spectrum of SiO₂-Azo, the peak of S-H disappears after its reaction with the terminal double bonds of UAA. Meanwhile, at 1540 cm⁻¹ and 1498 cm⁻¹ appear skeleton vibration absorption peaks of benzene ring, at 1438 cm⁻¹ appears the stretching vibration peak of N = N double bond—at 1600 cm⁻¹ appears the stretch vibration peak of C = O. From the above characteristic peaks, it can be deduced that UAA has reacted with the sulfhydryl groups on the surface of SiO₂, and azobenzene groups have been grafted on the nano silica microspheres.

3.2 Photoresponsive photonic crystals (PC-Azo) and their photo-responsive behavior

The photoresponsive PC-Azo was prepared with SiO₂-Azo microspheres through vertical deposition method. Figure 2 shows the SEM images of the PC-Azo. It can be seen that on the plane parallel to the substrate surface, SiO₂-Azo microspheres are arranged in a moderately ordered way, with a little bit of

stacking faults and dislocations. The grafting of azobenzene groups lead to surface roughness of the silica microspheres and the average particle diameter of SiO₂-Azo microspheres is about 206 nm.

Figure 3 shows the UV-Vis extinction spectra of PC-Azo and its response to UV-irradiation at 365 nm for different time. The central wavelength (λ) of the photonic band gap of PC-Azo is located at 584 nm. After 1 min UV-irradiation, the λ red shifts to 592 nm, and after 10 min UV-irradiation, the λ red shifts to 600 nm and no longer changes.

The central wavelength (λ) of photonic band gap and the center-to-center distance (D) of adjacent silica microspheres satisfy Bragg condition (Yamasaki & Tsutsui, 1998):

$$\lambda = 2n_{\text{eff}} \sqrt{\frac{2}{3}} D \quad (1)$$

n_{eff} denotes the effective refractive index of silica photonic crystals. If n_{eff} is regarded as invariable, the λ is mainly affected by D, which can be considered as diameter (d) of the silica microspheres approximately. Before UV-irradiation, the azobenzene compounds adopt relatively stable trans structure. While the UV- irradiation causes the transformation from trans form to cis form and the molecular size of cis structure is larger than that of trans structure, which leads to the increase of the volume of SiO₂-Azo, that is the increase of D. So the λ becomes larger correspondingly. After the irradiation with visible light, the structure of the azobenzene compounds can recover again, which make the PC-Azo show good reversibility.

Conclusions

Photoresponsive PCs can be fabricated by self-assembly of sub-micrometer colloidal SiO₂ microspheres grafted with azobenzene groups. The photonic band gap wavelength of the PCs could red-shift 16 nm upon UV-irradiation and showed good reversible response. The light-responsive PCs provide a way for fabrication of intelligent optical devices.

Declarations

Acknowledgments

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Allcock, H.R., Kim, C.: Liquid crystalline phosphazenes. High polymeric and cyclic trimeric systems with aromatic azo side groups. *Macromolecules* **22**, 2596–2602 (1989)
2. Brown, D., Natansohn, A., Rochon, P.: Azo Polymers for Reversible Optical Storage. 5. Orientation and Dipolar Interactions of Azobenzene Side Groups in Copolymers and Blends Containing Methyl Methacrylate Structural Units. *Macromolecules* **28**, 6116–6123 (2002)
3. Fomina, N., Mcfearin, C., Sermsakdi, M., Edigin, O., Almutairi, A.: UV and near-IR triggered release from polymeric nanoparticles. *J. Am. Chem. Soc.* **132**, 9540–9542 (2010)
4. Ho, M.S., Barrett, C., Natansohn, A., Rochon, P.: Azo Polymers for Reversible Optical Storage. 8. The Effect of the Polarity of the Azobenzene Groups. *Can. J. Chem.* **73**, 6124–6127 (1995)
5. Hu, X., Feeney, M.J., Ethan, M.I., James, M., Feng, J., Xu, Q., Iii, T.S.W.: Triggered Release of Encapsulated Cargo from Photoresponsive Polyelectrolyte Nanocomplexes. *Acs Applied Materials Interfaces* **8**, 23517–23522 (2016)
6. Kumar, G.S., Neckers, D.C.: Photochemistry of azobenzene-containing polymers. *Chem. Rev.* **89**, 1915–1925 (1989)
7. Lee, C.-R., Lin, J.-D., Huang, Y.-J., Huang, S.-C., Lin, S.-H., Yu, C.-P.: All-optically controllable dye-doped liquid crystal infiltrated photonic crystal fiber. *Opt. Express* **19**, 9676–9689 (2011)
8. Li, C., Xue, Q., Ji, Z., Li, Y., Zhang, H., Li, D.: Construction of photonic crystals with thermally adjustable pseudo-gaps. *Soft Matter* **16**, 3063–3068 (2020)
9. Li, H., Wang, C., Pan, Y., Yang, Y., Xia, R.: Dynamical thermo-optical switching based on nematic liquid crystals doped with push–pull azobenzene dyes. *Opt. Commun.* **419**, 71–74 (2018)
10. Lowe, A.B.: Thiol-ene “click” reactions and recent applications in polymer and materials synthesis. *Polymer Chemistry* **1**, 17–36 (2010)
11. Moorthy, M.S., Kim, H.B., Bae, J.H., Kim, S.H., Ha, C.S.: Design of core–shell magnetic mesoporous silica hybrids for pH and UV light stimuli-responsive cargo release. *Rsc Advances* **6**, 29106–29115 (2016)
12. Nardele, C.G., Asha, S.K.: Photoresponsive smectic liquid crystalline multipods and hyperbranched azo polymers. *Journal of Physical Chemistry B* **118**, 1670–1684 (2014)
13. Stöber, W., Fink, A., Bohn, E.: Controlled growth of monodisperse silica spheres in the micron size range. *Journal of Colloid Interface Science* **26**, 62–69 (1968)
14. Uygün, M., Tasdelen, M.A., Yagci, Y.: Influence of Type of Initiation on Thiol–Ene “Click” Chemistry. *Macromol. Chem. Phys.* **211**, 103–110 (2010)
15. Wang, L., Dong, H., Li, Y., Xue, C., Sun, L.D., Yan, C.-H., Li, Q.: Reversible Near-Infrared Light Directed Reflection in a Self-Organized Helical Superstructure Loaded with Upconversion Nanoparticles. *J. Am. Chem. Soc.* **136**, 4480–4483 (2014)
16. Chen, W.-C., Lee, Y.-W., Chen, C.-T.: Diastereoselective, synergistic dual-mode optical switch with integrated chirochromic helicene and photochromic bis-azobenzene moieties. *Org. Lett.* **12**, 1472 (2010)

17. Xie, Z.-Y., Sun, L.-G., Han, G.-Z., Gu, Z.-Z.: Optical Switching of a Birefringent Photonic Crystal. *Adv. Mater.* **20**, 3601–3604 (2008)
18. Yamasaki, T., Tsutsui, T.: Spontaneous emission from fluorescent molecules embedded in photonic crystals consisting of polystyrene microspheres. *Appl. Phys. Lett.* **72**, 1957–1959 (1998)
19. Zhang, Y., et al: An azo-bridged ferroelectric liquid crystal with highly enhanced second and third harmonic generation. *J. Am. Chem. Soc.* **134**, 16298–16306 (2012)
20. Zhang, Q., Zhang, J., Wang, Y., SYNTHESIS, AND PHOTOCHROMISM OF POLYSILOXANE CONTAINING AZOBENZENE SIDE GROUPS: *Acta Polymerica Sinica* **1**, 121–125 (1996)

Figures

Figure 1

FT-IR spectra of SiO₂, SiO₂-SH and SiO₂-Azo microspheres.

Figure 2

SEM images of PC-Azo

Figure 3

UV-Vis extinction spectra of PC-Azo and its photo responsive behavior

Supplementary Files

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- [Scheme1.png](#)