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 were prepared and azobenzene groups were grafted on the surface of SiO2 microspheres. The SiO2 microspheres grafted with azobenzene groups could self-assemble to form photosensitive photonic crystals, whose photonic bandgaps red-shifted as irradiated by UV light due to the structure change of the azobenzene groups.

Keywords Photonic crystals · Azobenzene compounds · Photonic bandgaps · Photo-responsive behavior

1 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 et al. 2002; Ho et al. 1995), optically controlled molecular switch (Li et al. 2018; Wen-Ching et al. 2010), liquid crystal polymer materials (Allcock & Kim 1989; Nardele & Asha 2014; Yongqiang et al. 2012), controlled drug release system (Fomina et al. 2010; Hu et al. 2016; Moorthy et al. 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 $trans \rightarrow cis$ and green-beam-induced $cis \rightarrow trans$ 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. 4,4’-Di(acrylamido)-azobenzene was used as a crosslinker to synthesize poly(N-isopropylacrylamide) (PNIPAM)-based microgels and microgel-based optical materials (etalons). The etalons exhibited optical properties that were switchable upon exposure to UV irradiation, and the extent of the response depended on the UV exposure time (Zhang et al. 2014). An optically switchable birefringent photonic crystals (PCs) were fabricated by infiltrating photo-responsive liquid crystals into a stretched poly (methyl methacrylate) inverse opal (Xie et al. 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 recent years, new PCs materials with tunable photonic bandgap by external stimuli have been designed and applied in different fields. For example, Arafa et al. designed a one-dimensional defective mode photonic crystal based on transfer matrix method for detecting the seawater salinity and temperature simultaneously (Qutb et al. 2021). They also discussed a tri-core photonic crystal microstructure fiber for simultaneous sensing for salinity and temperature of water substances (Amiri et al. 2019). Another tricore photonic crystal fiber with enhanced compact sensitivity of glucose sensor was proposed to detect the low level presence of glucose in the human blood (Natesan et al. 2019). Furthermore, biophotonic sensor for the detection of creatinine concentration in blood serum based on 1D photonic crystal and versatile photonic band gap materials for water desalination were also designed (Aly et al. 2020; Sayed et al. 2020).

In this paper, sub-micrometer colloidal SiO$_2$ spheres were prepared and azobenzene groups were grafted on the surface of colloidal SiO$_2$ microspheres. The SiO$_2$ microspheres grafted with azobenzene groups could self-assemble to form PC, whose photonic bandgaps vary as irradiated by UV light. Compared to with other similar work, a relatively simple approach was adopted to introduce azobenzene compounds into silica PC to obtain a kind of photoresponsive photonic crystals. What’s more, photosensitive photonic crystals with different band gaps can be prepared by means of the adjustable particle size of SiO$_2$ microspheres. This photosensitive PCs can be potentially used in electromagnetic wave regulation, information and communication technology or optical devices.
2 Experimental sections

2.1 Materials and instruments

Tetraethyl orthosilicate (TEOS), 3-mercaptopropyl trimethoxysilane (MPS) and ammonium hydroxide solution (NH\textsubscript{4}OH, \textasciitilde 28% NH\textsubscript{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 et al. 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 (SiO\textsubscript{2}-SH)

First, nano-silica microspheres were prepared according to our previous work (Li et al. 2020a). 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 h at 30 °C. Then the solution was heated to 70 °C. 3 mL MPS was added and the reaction continued 2 h. 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 (SiO\textsubscript{2}-Azo)

Into a flask, 0.2 g SiO\textsubscript{2}-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 SiO\textsubscript{2}-Azo and their photo-responsive behavior

Vertical deposition method was used to prepare silica PCs. First, the SiO\textsubscript{2}-Azo microspheres were dispersed in absolute ethanol to prepare microsphere sol with a mass fraction of 2%. Then thoroughly cleaned glass slide was placed vertically in the SiO\textsubscript{2}-Azo microsphere sol in an electric thermostatic drying oven at 35 °C, and temperature fluctuation was kept not exceeding 0.1 °C. With evaporation of the solvent, the PCs grew on the glass slide after 7 days. The UV–vis extinction spectra of PCs were obtained using a PERSEE TU-1901 spectrophotometer, and the glass slide where the photonic crystal resides was placed vertically in front of the sample tank 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 (ZF-2 type UV light, 365 nm, 6 W, 10 cm from the sample) for different time.

3 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 et al. 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 et al. 2010).

Figure 1 shows the FT-IR spectra of SiO₂, SiO₂-SH and SiO₂-Azo microspheres. Figure 1 FT-IR spectra of SiO₂, SiO₂-SH and SiO₂-Azo microspheres

![Scheme 1 BPO catalyzed thiol-ene click reaction](image)

![Fig. 1 FT-IR spectra of SiO₂, SiO₂-SH and SiO₂-Azo microspheres](image)
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 thiolpropyl 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 sulphydryl 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. Each microsphere is adjacent to six other microspheres on the whole, and the arrangement shows hexagonal stacking on the face-centered cubic (111) surface. The grafting of azobenzene groups led to surface roughness of the silica microspheres and the average particle diameter of SiO₂-Azo microspheres was about 206 nm. From the SEM image perpendicular to the surface of the substrate, the (100) surface of the face-centered cubic structure could be found and there were about eight layers of silica microspheres, which were affected by the concentration of the microsphere sol and a mass fraction of 2% for the SiO₂-Azo microspheres was the most appropriate after optimization experiments.

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. Since the band gap of the PCs-Azo is in the range of visible light, the PCs appears yellow in the digital photograph (Fig. 3 inset). After 1 min UV-irradiation, the λ red shifted to 592 nm, and after 10 min UV-irradiation, the λ red shifted to 600 nm and no longer changed. Compared with the thermosensitive behavior,
photonic crystals prepared by perfusing PNIPAM hydrogel into silica photonic crystals in our previous work (Li et al. 2020b), the redshift distance of 18 nm of the photonic band gap wavelength is greater than the wavelength shift distance of 10 nm of the latter. The central wavelength ($\lambda$) of photonic band gap and the center-to-center distance (D) of adjacent silica microspheres satisfy Bragg condition (Yamasaki & Tsutsui 1998):

$$\lambda = 2n_{\text{eff}} \sqrt{\frac{2}{3} D}$$

(1)

$n_{\text{eff}}$ denotes the effective refractive index of silica photonic crystals. If $n_{\text{eff}}$ is regarded as invariable, the $\lambda$ is mainly affected by D, which can be considered as diameter (d) of the silica microspheres approximately. Before UV-irradiation, the azobenzene compounds adopted relatively stable trans structure. While the UV-irradiation caused the transformation from trans form to cis form and the molecular size of cis structure was larger than that of trans structure, which led to the increase of the volume of SiO$_2$-Azo, that was the increase of D. So the $\lambda$ became larger correspondingly.

![Fig. 3 UV–Vis extinction spectra of PC-Azo and its photo responsive behavior](image)

Fig. 3 UV–Vis extinction spectra of PC-Azo and its photo responsive behavior

![Fig. 4 UV–Vis absorption spectra change of UAA during UV induced-isomerization (a) and heat recovery (b)](image)

Fig. 4 UV–Vis absorption spectra change of UAA during UV induced-isomerization (a) and heat recovery (b)
To illustrate the influence of UV-irradiation on the structure of SiO$_2$-Azo, response of the azobenzene compound UAA to UV-irradiation was carried out. Figure 4 shows the UV induced-isomerization and heat recovery of UAA (10 mg/L in tetrahydrofuran). As shown in Fig. 4a, the absorption peak of trans form at 352 nm decreased gradually along with UV-irradiation, while the absorption peak at 450 nm increased slowly, which showed that the trans structure of UAA transformed into cis structure during UV-irradiation. As a result, the diameter of SiO$_2$-Azo would change accordingly. Figure 4b shows heat recovery of UAA from cis structure after different heating time at 50 °C. The absorption peak intensity at 352 nm could recover 98%. After the irradiation with visible light, the structure of the azobenzene compounds can also recover, which endow the PC-Azo with good reversibility.

4 Conclusions

Photoresponsive PCs could be fabricated by self-assembly of sub-micrometer colloidal SiO$_2$ microspheres grafted with azobenzene groups. The photonic band gap wavelength of the PCs could red-shift 16 nm upon UV-irradiation, which should be ascribed to structural change of the azobenzene compounds grafted on the SiO$_2$ microspheres. The light-responsive PCs can provide a way for fabrication of intelligent optical devices.

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Declarations

Conflict 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.

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