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Rewritable Color Patterns with Photochromic Diarylethene-Embedded Electrospun Fibers

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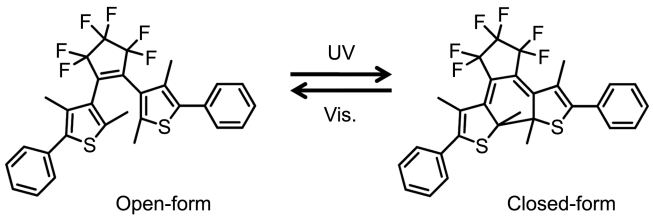
Photochromic materials have attracted much attention due to their potential for rewritable papers, memory devices, switching and sensor devices.[1-19] Photochoromic materials undergo a reversible photo-induced change of a molecule between two distinct isomeric forms whose adsorption wavelengths are different.[20-23] These photo-induced reactions involve ring-opening (spiropyrans), *cis-trans* isomerization (azobenzene), phenyl migration (phenoxyquinones), and ring-closure (bisthienylethene). In general, the photo-generated isomers return to the initials upon visible light irradiation. Among the photochromic compounds, diarylethene derivatives are one of the most appealing materials because of their remarkably high photo-reactivity, photofatigue resistance, short response time as well as absence of thermal isomeriazation and large change in their optical and electronic properties upon irradiation with UV and visible light.[24-26]

As shown in Scheme 1, diarylethenes can undergo reversible photocyclization between open-ring and closed-ring isomers under irradiation with UV and visible light, respectively. Photochromic studies of diarylethenes in organic solvents,[27] aqueous solutions,[28,29] polymer matrices[30,31] and metal-organic frameworks[33,34] have been conducted. However, there are very few studies about electrospun fibers containing diarylethene molecules.[35]

In this study, we fabricated diarylethene-embedded electrospun polymer fibers and demonstrated that micro-patterned images can be generated on the electrospun fiber mats through the selective transformation of the diarylethene molecules using photomasked UV irradiation. The patterns can be erased and rewritten without losing the integrity of the images. We also found that the patterned images last for over 30 days in the dark condition.



Scheme 1. Photochromism of a diarylethene.

Experimental

Materials and Instruments. The photochromic diarylethene 1,2-bis(2,3-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene was purchased from TCI. Polystyrene (PS) (Mw = 280,000 $gmol^{-1}$) and polyacrylic acid (PAA) (Mw = 450,000 $gmol^{-1}$) were purchased from Aldrich. SEM images of the diarylethene-embedded fibers were obtained by using a JEOL (JSM-6330F) FE-SEM instrument. The UV-irradiated diarylethene-containing fibers were coated with Pt for 15 s. SEM images were obtained at an accelerating voltage of 15 kV. Optical images were observed with an Olympus microscope (IX71).

Preparation of Diarylethene-Embedded Electrospun PS Fibers. A typical procedure for fabrication of the diarylethene-encapsulated electrospun polymer fiber is as follows. A chloroform and *N,N*-diformamide solution (95:5 by volume, 3 mL, containing diarylethene (15 mg) and PS (1092.9 mg, Mw = 280,000 $gmol^{-1}$), was pumped through a 25 G metal syringe needle at a constant rate of 0.8 mL/h by using a syringe pump (KD Scientific model 200 series). Application of a high voltage (11 kV) to the metal syringe needle allowed generation of microfibers, which were collected on the surface of a grounded aluminium plate (the working distance between the tip of needle and the collector was 13 cm). Electrospinning was performed under ambient conditions.

Preparation of Diarylethene-Embedded Electrospun PAA Fibers. An ethanol and tetrahydrofuran solution (8:2 by volume, 3 mL), containing diarylethene (15 mg) and PAA (182.7 mg, Mw = 450,000 $gmol^{-1}$), was pumped through a 25 G metal syringe needle at a constant rate of 0.5 mL/h by using a syringe pump (KD Scientific model 200 series). Application of a high voltage (9 kV) to the metal syringe needle allowed generation of microfibers, which were collected on the surface of a grounded aluminium plate (the working distance between the tip of needle and the collector was 13 cm). Electrospinning was performed under ambient conditions.

Generation of Color Patterns. A photomask was placed on a diarylethene-embedded electrospun fibermat. Photoirradiation was performed using a typical handheld laboratory 254 nm UV lamp (1 mW/cm^2).

Results and Discussion

The schematic diagram for the key strategy and procedure employed for generating patterned images is displayed in Figure 1. A viscous organic solution containing the diarylethene and the matrix polymer is placed in a syringe. A high voltage (11 kV or 9 kV) is then applied to the syringe needle causing ejection of a charged polymer jet from polymer solution. The micro/nano fibers are collected on the surface of a grounded aluminum plate. Photomasked UV irradiation of the electrospun fiber generates the closed-form of the diarylethene in exposed areas, providing patterned color images in the polymer fibers.

Figure 2 displays photographs of scanning electron microscope (SEM) and optical microscope images of typical electrospun fibers. Polystyrene (PS) and poly acrylic acid (PAA) were selected as representative matrix polymers. Inspection of the SEM images (Figure 2(a)) shows that diarylethene-embedded fiber mat, obtained by electrospinning of a chloroform and DMF solution containing PS (20 wt %) and diarylethene (0.3 wt %), is composed of microfibers.

SEM images show that ribbon-like fibers of uniform diameters of *ca.* 13 μm are formed (Figure 2(a)). The diarylethene encapsulated PAA fiber mat is consisted of *ca.* 800 nm (diameter) fibers. In optical microscope images recorded after electrospinning also confirm the generation of microfibers (Figure 2(b), 2(e)). Interestingly, UV irradiation of the diarylethene-embedded polymer fibers yields blue-colored microfibers (Figure 2(c), 2(f)), which are indicative of successful generation of the closed-form of the diarylethene molecules.

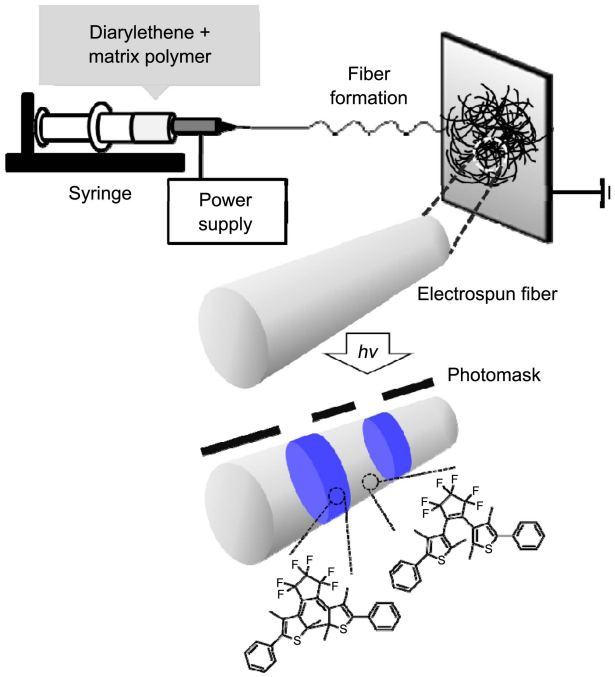


Figure 1. A schematic outlining the strategy employed for the fabrication of patterned color images in electrospun polymer fibers.

Importantly, no significant morphological difference is seen for the SEM and optical microscopic images of fiber mats recorded before and after UV-irradiation (data not shown).

The feasibility of generating color patterns using the photochromic diarylethene encapsulated electrospun fiber mats was explored next. The polymer fiber mats, obtained in the manner described above, were irradiated with 254 nm UV light (1 mW/cm^2) through a photomask for 60 sec. Interestingly, colored images were produced only in the UV-exposed areas. This indicates that selective transformation of the open-form of the diarylethene to the closed-form takes place in the polymer fibers (Figure 3).

Different resolutions of patterned color images are obtained depending on the matrix polymer. For example, high-resolution blue color images are generated when PAA serves as the polymer matrix. The high-resolution image of diarylethene/PAA mat is attributed to its relatively thinner fibers morphologies. Importantly, the patterned color images are rewritable dozens of times. Visible light irradiation of the patterned images yields immediate disappearance of the images. The patterned images can be regenerated by photomasked UV irradiation. The PS fiber and PAA fiber both have excellent write-erase-write property.

The thermal stability of the patterned images was exploited by observing no apparent color change with heat treatment (100 °C, 60 sec) (data not shown). Our diarylethene-embedded films showed excellent thermal stability, which resembles the intrinsic thermal stability of closed-ring from of dithienylethene. These results indicate that the patterned films are not only thermally stable but also selectively-rewritable by employing visible light (erase) and UV light (write).

The absorbance spectra of diarylethene-embedded polymer are recorded. As display in Figure 4(a), a 254 nm UV irradiation to the fiber mat results in the generation of an isomeric compound that has a maximum absorption wavelength at 570 nm. This absorbed peak represents generation of ring-closed form of the embedded dyarylethene molecules in the polymer matrix. The photoinduced reversibility

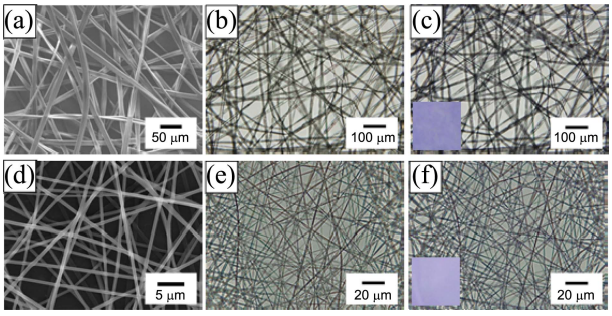


Figure 2. (a) SEM image of PS electrospun fibers containing diarylethene compound. Optical microscopic images of the PS fibers encapsulated with diarylethene before (b) and after (c) UV irradiation. (d) SEM image of diarylethene–embedded PAA electrospun fibers. Optical microscopic images of the PAA fibers containing diarylethene before (e) and after (f) UV irradiation.

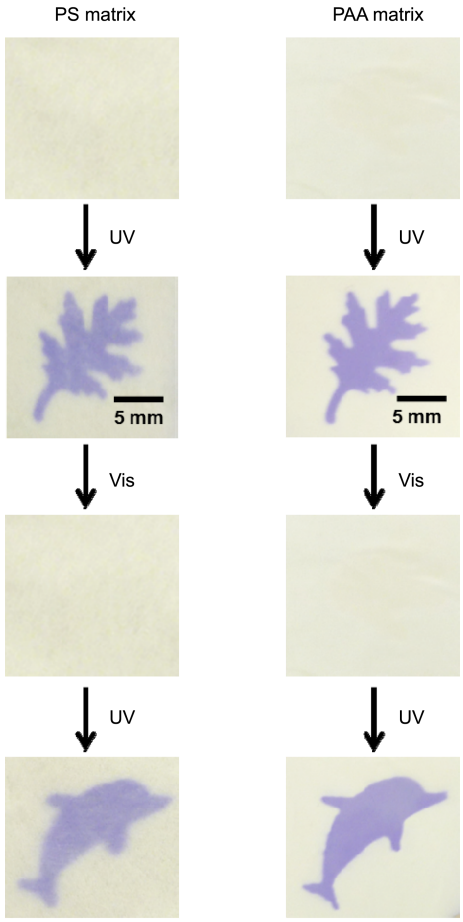


Figure 3. Photographs of diarylehtene-embedded electrospun fiber mats upon photomasked UV and visible light irradiations.

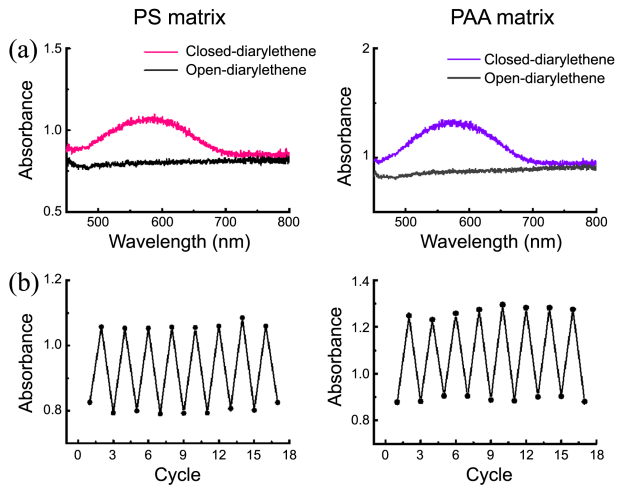


Figure 4. (a) UV-Vis absorbance spectra of diarylehtene-embedded electrospun PS and PAA fiber mats. (b) Color switching responses of diarylehtene-embedded PS and PAA fiber mats monitored at 570 nm.

of the diarylethene-embedded polymer fiber was confirmed by observing on-off cycles upon repeating the write-erase cycles (Figure 4(b)). The patterned image of diarylethene containing fiber mat was found to be stable for 30 days at dark condition.

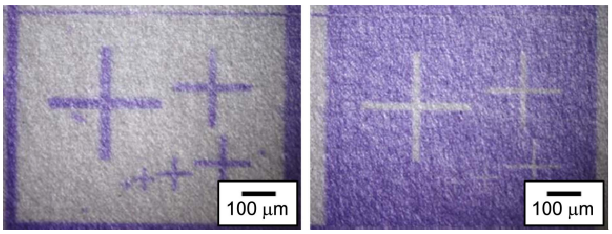


Figure 5. Micropatterned images obtained by a photomasked UV irradiation (254 nm, 60 s) of electrospun PAA fiber mats containing diarylethene.

In Figure 5 are displayed optical microscopic images of the UV-irradiated electrospun fiber mats. Photomasked UV irradiation of diarylethene embedded film, prepared with PAA matrix polymer results in the clean generation of fine microsized patterned images. The blue areas are the regions exposed to UV light.

Conclusion

We present a facile strategy for rewritable films by introducing photochromic molecules in electrospun fibers. Patterned images are readily generated and erased by UV or visible irradiation onto the micro/nano fibers. The patterned images were found to be stable for over 30 days in the dark condition. We also observed that the photochromic molecule-embedded system displays an excellent write-erase feature without evident color fading.

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References

1. Brown, G. H., *Photochromism*; Wiely-Interscience: New York, 1971.
2. Crano, J. C.; Guglielmett, R. J. I., Eds., *Organo Photochromic and Thermochromic Compounds*; Kluwer Academic/Plenum Publishers: New York, 1999.
3. Feringa, B. L., Ed., *Molecular Switches*; Wiley-VCH: Weinheim, 2001.
4. Berkovic, G.; Weiss, V.; Krongauz, V. *Chem. Rev.* **2000**, *100*, 1741.
5. Corredor, C. C.; Huang, Z.-L.; Belfield, K. D. *Adv. Mater.* **2006**, *18*, 2910.
6. Myles, A. J.; Branda, N. R. *Adv. Funct. Mater.* **2002**, *12*, 167.
7. Raymo, F. M.; Tomasulo, M. *Chem. Soc. Rev.* **2005**, *34*, 327.
8. Barrett, C. J.; Mamiya, J.-I.; Yager, K. G.; Ikeda, T. *Soft Matter.* **2007**, *3*, 1249.
9. Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature* **2002**, *420*, 759.
10. Lim, S.-J.; An, B.-K.; Park, S. Y. *Macromolecules* **2005**, *38*, 6236.
11. Cho, H.; Kim, E. *Macromolecules* **2002**, *35*, 8684.
12. Bossi, M.; Belov, V.; Polyakova, S.; Hell, S. W. *Angew. Chem. Int. Ed.* **2006**, *45*, 7462.
13. Golovkova, T. A.; Kozlov, D. V.; Neckers, D. C. *J. Org. Chem.* **2005**, *70*, 5545.
14. Wang, S.; Shen, W.; Feng, Y.; Tian, H. *Chem. Commun.* **2006**,

1497.
15. Harbron, E. J.; Vincente, D. A.; Hadley, D. H.; Imm, M. R. *J. Phys. Chem. A* **2005**, *109*, 10846.
16. Jiang, G.; Wang, S.; Yuan, W.; Jiang, L.; Song, Y.; Tian, H.; Zhu, D. *Chem. Mater.* **2006**, *18*, 235.
17. Bahr, J. L.; Kodis, G.; Garza, L. D. L.; Lin, S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2001**, *123*, 7124.
18. Kozlov, D. V.; Castellano, F. N. *J. Phys. Chem. A* **2004**, *108*, 10619.
19. Sheng, L.; Li, M.; Zhu, S.; Li, H.; Xi, G.; Li, Y.-G.; Wang, Y.; Li, Q.; Liang, S.; Zhong, K.; Zhang, S. X.-A. *Nature Communications* **2013**, *5*, 3044.
20. Park, I. S.; Jung, Y.-S.; Lee, K.-J.; Kim, J.-M. *Chem. Commun*. **2010**, 2859.
21. Lee, S.; Oh, S.; Lee, J.; Malpani, Y.; Jung, Y.-S.; Kang, B.; Lee, J. Y.; Ozasa, K.; Isoshima, T.; Lee, S. Y.; Hara, M.; Hashizume, D.; Kim, J.-M. *Langmuir* **2013**, *29*, 5869.
22. Park, I. S.; Heo, E.; Kim, J.-M. *Tetrahedron Letters* **2011**, *52*, 2454.
23. Lee, J.; Lee, C.-W.; Kim, J.-M. *Macromolecular Rapid Communications* **2010**, *31*, 1010.
24. Zhang, J.; Zou, Q.; Tian, H. *Adv. Mater.* **2013**, *25*, 378.
25. Irie, M. *Chem. Rev.* **2000**, *100*, 1685.
26. Higashiguchi, K.; Matsuda, K.; Irie, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 3537.
27. Shim, S.; Joo, T.; Bae, S. C.; Kim, K. S.; Kim, E. *J. Phys. Chem. A* **2003**, *107*, 8106.
28. Pu, S.; Liu, H.; Liy, G.; Chen, B.; Tong, Z. *Tetrahedron* **2014**, *70*, 852.
29. Zou, Y.; Yi, T.; Xiao, S.; Li, C.; Gao, X.; Wu, J.; Yu, M.; Huang, C. *J. Am. Soc*. **2008**, *130*, 15750.
30. Fukamonato, T.; Umemoto, T.; Iwata, Y.; Yokojima, S.; Yoneyama, M.; Nakamura, S.; Irie, M. *J. Am. Soc*. **2007**, *129*, 5932.
31. Guo, H.; Zhang, F.; Wu, G.; Sun, F.; Pu, S.; Mai, X.; Qi, G. *Optical Materials* **2003**, *22*, 269.
32. Murase, S.; Teramoto, M.; Furukawa, H.; Miyashita, Y.; Horie, K. *Macromolecules* **2003**, *36*, 964.
33. Luo, F.; Fan, C. B.; Luo, M. B.; Wu, X. L.; Zhu, Y.; Pu, S. Z.; Xu, W.-Y.; Guo, G.-C. *Angew. Chem.* **2014**, *126*, 1.
34. Patel, D. G.; Walron, I. M.; Cox, J. M.; Gleason, C. J.; Butzer, D. R.; Benedict, J. B. *Chem. Commun.* **2014**, 2653.
35. Bianco, A.; Iardino, G.; Manuelli, A.; Bertarelli, C.; Zerbi, G. *ChemPhysChem* **2007**, *8*, 510.