



Cite this: DOI: 10.1039/d1tc01931g

Dual-mode security anticounterfeiting and encoding by electrospinning of highly photoluminescent spiropyran nanofibers

Reza Azimi,^a Amin Abdollahi,^{id}^a Hossein Roghani-Mamaqani,^{id}^{*ab} and Mehdi Salami-Kalajahi,^{id}^{ab}

The application of photochromic materials in the development of anticounterfeiting technologies has shown a significant growth in recent years because of their advantages in displaying dual-mode security as simultaneous photochromic coloration and fluorescence emission. Photochromic copolymers based on styrene and spiropyran (5, 10, and 20 wt% with respect to styrene) with carboxylic acid chain end groups were synthesized by solution polymerization. The chemical structure, thermal behavior, and optical characteristics of the copolymers were studied using proton nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and UV-vis spectroscopy. The copolymer solutions in toluene and DMF were electrospun to yield photochromic nanofibers. The electrospun nanofibers from the copolymer solutions in toluene showed a well-defined morphology, a smooth surface, and a narrow size distribution in their diameter. These nanofibers were applied on cellulosic papers and banknotes for the induction of dual-mode security with a fast and facile authentication strategy. The induced security marks are virtually invisible under visible light and become visible by photochromic coloration from colorless to purple after UV irradiation. They also displayed red fluorescence emission under UV irradiation. Both the photochromic coloration and fluorescence emission showed high intensities, the security marks were rapidly authenticated upon UV irradiation, and this process was fully reversible for several cycles of UV/visible light irradiation because of the higher photofatigue resistance of the spiropyran-containing copolymers. These advantages originated from the high surface area of the photochromic nanofibers leading to higher light absorption and subsequent intense optical responses as coloration and fluorescence emission. Finally, a fast and facile anticounterfeiting strategy based on electrospun security marking was developed for the induction of dual-mode security marks on cellulosic documents and banknotes.

Received 26th April 2021,
Accepted 16th June 2021

DOI: 10.1039/d1tc01931g

rsc.li/materials-c

1. Introduction

The prevention of counterfeiting and increasing the security of documents including banknotes, passports, national cards, and certificates have been a highly significant challenge within recent decades.^{1–11} A wide range of photoluminescent and photochromic materials, such as nanoparticles, quantum dots, polymer dots, upconversion nanoparticles, and supramolecular structures, have been used to design anticounterfeiting inks for the printing of security marks.^{7,11–18} These materials could be used directly as aqueous or solvent-based solutions or

formulated to anticounterfeiting inks and used for printing on cellulosic documents by inkjet painting. Polymeric anticounterfeiting inks have been extensively studied in recent years because of the advantages of polymeric materials to display highly stable optical properties over a long period of time. Most polymeric anticounterfeiting inks are based on polymer nanoparticles that display high optical properties because of their high surface area and low light reflection.^{19–24} Clogging printer nozzles due to the aggregation of nanoparticles is a significant challenge in the application of polymer nanoparticles as anticounterfeiting inks for printing security marks. The application of polymeric nanofibers with a high surface area by electrospinning of polymer solutions on different substrates, especially on cellulosic papers, could be an alternative method for security marking. Light-responsive polymer nanofibers have attracted more attention because of their advantages, such as large surface area,²⁵ nanoporous networked structure,²⁶ high

^a Faculty of Polymer Engineering, Sahand University of Technology, P.O. Box: 51335-1996, Tabriz, Iran. E-mail: r.mamaghani@sut.ac.ir; Fax: +98 413 3459104; Tel: +98 413 3459104

^b Institute of Polymeric Materials, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran