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Photoswitchable fluorescent polymer nanoparticles as high-security anticounterfeiting materials for authentication and optical patterning†

Amin Abdollahi,[a] Hossein Alidaei-Sharif,[a] Hossein Roghani-Mamaqani *[ab] and Ata Herizchi[c]

Invisible high-security anticounterfeiting polymeric inks exhibiting both photochromism and fluorescence emission for security marking have attracted significant interest recently. In the current study, flexible and invisible high-security anticounterfeiting inks were developed *via* the chemical incorporation of spiropyran into copolymer latex nanoparticles based on methyl methacrylate and butyl acrylate by semi-continuous miniemulsion polymerization. The anticounterfeiting inks are based on latex nanoparticles with various polarities and glass transition temperatures (T_g) and have spherical morphology with narrow size distribution in the range of 50–80 nm. The inks can simultaneously display photochromism (colorless to purple) and fluorescence emission (highly intense and bright red emission) upon UV irradiation in a fast and facile manner using a minimum concentration of spiropyran (about 1 wt% with respect to the polymer content). The morphology investigation and measurement of contact angles on the surface of the papers impregnated with stimuli-chromic latex samples display that the latex nanoparticles with different flexibilities have appropriate coating ability and stability on the surface of the cellulosic substrates due to the formation of hydrogen bonding. The investigation of the photochromic properties and fluorescence emission of the samples shows that the latex particles with higher polarity of the polymer chains have significant photochromic intensity and fluorescence emission as well as high photofatigue resistance, photoswitchability, and reversibility without displaying negative photochromism. Fast responsivity upon UV irradiation was observed for the sample with a T_g of about 33 °C and medium polarity, which indicated that the kinetics of the SP ↔ MC isomerization was a function of the polarity and flexibility of the polymer chains. The invisible high-security ink prepared using the photochromic and fluorescent latex nanoparticles with the highest optical properties was loaded on a stamp with different marks and used for print-marking different security documents, such as a certificate, money, and passport. The printed marks and finger-print on the security documents displayed photochromism and red fluorescence upon UV irradiation (365 nm). Spraying the latex nanoparticles on cellulosic papers induced high-resolution rewritable photopatterns on the cellulose substrate after UV illumination under different masks. Thus, the strategy developed to prepare high-security anticounterfeiting inks is an efficient, facile, and fast method for authentication applications.

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1. Introduction

Counterfeiting and copying security documents have resulted in considerable attention being focused on the development of anticounterfeiting and authentication technologies based on fluorescent materials such as semiconductor nanocrystals[1–3] and nanorods,[4] inorganic perovskite nanocrystals,[5–7] rare earth-doped nanostructures,[8–10] metal nanoclusters and complexes,[11–13] polymer nanoparticles,[14–17] carbon and polymer dots,[18–20] and quantum dots.[21] High-security materials are highly demanded in the anticounterfeiting ink industry. For this purpose,

[a] Faculty of Polymer Engineering, Sahand University of Technology, P.O. Box: 51335-1996, Tabriz, Iran
[b] Institute of Polymeric Materials, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran
[c] Faculty of Chemical Engineering, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran. E-mail: r.mamaghani@sut.ac.ir

† Electronic supplementary information (ESI) available: ^{1}H NMR spectra of all the stimuli-chromic latex samples for the determination of DP and MW, SEM image of PMMA and fluorescence spectrum of PMMA-SP (excited at 410 nm and emission at 715 nm), further experiments for the determination of the solid content in the latex samples, a table and images of the CIE 1931 chromaticity diagram, and contact angle investigations are presented. See DOI: 10.1039/d0tc00937g