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Original article

Preparation and study of photoswitchable fluorescence nanoparticles based on spirobenzopyran

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ABSTRACT

The preparation and performance characterization of <50 nm spirobenzopyran-based photochromic nanocomposites with photoswitchable fluorescence are presented. The nanocomposites were fabricated by means of a modified miniemulsion polymerization process, in which the hydrophobic spirobenzopyran was covalently attached to the polymer chains and the matched fluorescent dyes were noncovalently embedded in the nanoscale cross-linked polymeric matrix, respectively. The obtained nanocomposites with a high relative fluorescence quantum yield (*Q*) exhibited superior fluorescent photoswitchable performance due to the effective photo-induced intermolecular energy transfer. The stability of photomerocyanine was also improved.

1. Introduction

The bistable fluorescent photoswitching system based on photochromism has attracted much attention in recent years because of its potential applications in information technology and life sciences, such as in erasable media for ultrahigh-density optical data storage, photoswitching devices, and biological fluorescent probes [1–9]. Organic photochromic spirobenzopyran compounds, which interconvert between the closed-ring form (SP) and the colored conjugated open-ring photomerocyanine form (PM) under irradiation with UV and visible light, have been widely investigated due to their fast photochromic response and low cost [10,11]. However, the poor stability of PM as well as the weak fatigue resistance restricted them from broader utility [12]. Zhu *et al.* reported the reversible modulation of fluorescence by covalently attaching an SP to a core–shell CdSe/ZnS nanocrystal quantum dots bearing a thiolmetal linker [13], and studied photochromic polymer nanoparticles with optically switchable luminescence, in which SP comonomer was covalently incorporated into the polymer hydrophobic cavities [14].

In this paper, based on our former report [15], we fabricate a type of novel fluorescent photoswitchable nanohybrids with average particle size <50 nm by means of a modified miniemulsion polymerization process [16–20]. In the nanohybrids, SPs are covalently attached to polymer chains and the matched hydrophobic fluorescent dyes are molecularly dispersed and embedded in the crosslinked polymeric nanoparticle matrix. Under the condition of proper intermolecular distance and/or sufficient intermolecular contact between fluorescent dyes and SP (the emission spectra (λ_{ex}) fluorescent dyes (energy donor, D) are well overlap the absorption spectrum (λ_{em}) of PM form (energy acceptor, A)), the excite energy of fluorescent components cannot transfer to the closed-ring form of SP, but can readily transfer to PM form for fluorescence quenching [21,22]. Hereby, the reversible interconversion between the fluorescent off-state and on-state of the targeted nanohybrids is accomplished under alternate irradiation with UV and visible light. In addition, the nanohybrid composite materials are able to provide a protective microenvironment to improve the photo-thermal stability of each component [23,24].

2. Experimental

2.1. Materials

N-(2-Methacryloxyethyl)-3′,3′-dimethylspiro-[2H-1]-benzopyran-6-nitro-2,2′-indoline (MASP Fig. 1) was synthesized following the reported procedure [25], and the structure was confirmed by ^{1}H NMR and MS analyses.

4-Amino-1,8-naphthal-20,40-dimethylphenylimide (C.I. solvent yellow 44, 1,8-naphthalimidebased SY44), 2H-1-benzopyran-2-one,7-(diethylamino)-3-(methyl-2-benzoxazolyl) (C.I. disperse

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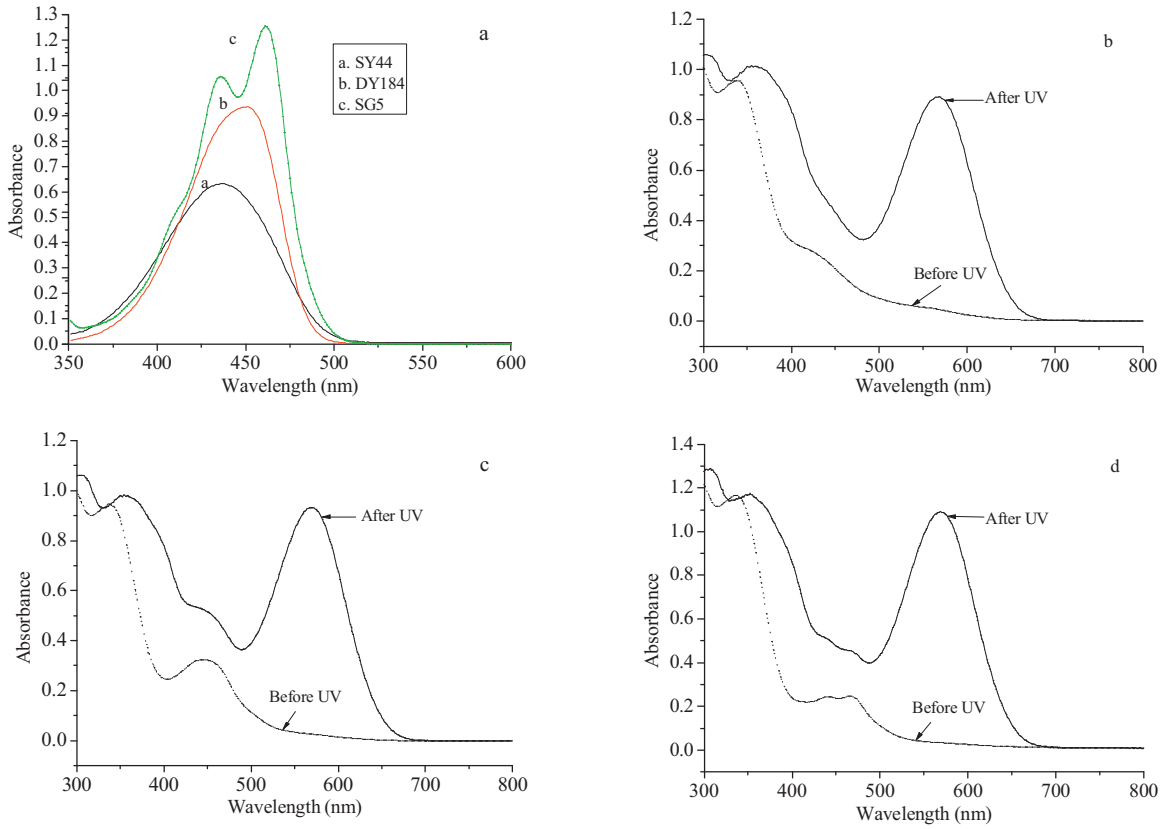

Fig. 1. (a) Absorption spectra of the used fluorescent dyes in EtOH; absorption spectra of nanoparticles incorporated with fluorescent dyes in water before and after irradiation with UV light; (b) SY44; (c) DY184; and (d) SG5.

yellow 184, coumarin-based DY184), perylenedicarboxylic acid bis-(2-methylpropyl) ester (C.I. solvent green 5, perylene-based SG5) were of technical grade and purified before use. Methyl methacrylate (MMA) were purified by distillation under reduced pressure and kept refrigerated until use. 1,4-Butanediol diacrylate (BDDA) as cross-linkers was used as received. Polystyrene (PSt, M_w = 60,000), sodium dodecyl sulfate (SDS), sodium bicarbonate ($NaHCO_3$), and potassium persulfate (KPS) were of analytical grade and purchased from Shanghai Chemistry Reagent Co.

2.2. Miniemulsion polymerization

Miniemulsion polymerization was carried out according to the literature procedure with minor modifications [15].

A deionized water (10 g) solution of SDS (20 mmol/L based on water) and $NaHCO_3$ (10 mmol/L based on water) was added to an oil phase consisting of 0.1 g of MASP, 2.0 g of MMA, 0.1 g of the cross-linker BDDA, 0.05 g of PSt, and 0.004 g of fluorescent dye (SY44, DY184, SG5), respectively. The mixture was quickly stirred for 20 min at room temperature. The resulting macroemulsions were miniemulsified with an ultrasonic homogenizer (JYD-650, Zhisun Instrument Co.), operated at 100–200 W for 10 min under ice cooling, finally miniemulsions were obtained. The miniemulsions were heated to 60 °C and purged with nitrogen flow for 30 min, with a magnetic stirrer at 200 rpm, then the polymerization was initiated by the injection of a water solution of 0.02 g KPS, continued reaction at 65 °C for 4 h and the aqueous colloid of nanocomposites was obtained by filtration under reduced pressure.

The polymerization conversion could be monitored by gas chromatography (GC 9790, FULI Analytical Instrument Co.) until no monomer could be detected. The resulting nanocomposites were named as SY44, DY184, SG5, respectively. According to the reactants stoichiometry, the molar ratio for the photochromic moieties and fluorescent dyes SY44, DY184, SG5, in the nanocomposite particles could be estimated as 16.5:1, 20.8:1, 22.5:1 sequencely.

2.3. Analysis and characterization

The samples (0.01 g) properly diluted in high-purity water (5 mL) were studied using a photon correlation spectrometer (PCS, Malvern Zetasizer 3000HSA) to determine the particle size and size distribution. UV–vis absorption was studied using a UV–vis spectrometer (Lambda-20, Perkin-Elmer) using a proper solvent as reference. Fluorescence emission spectra were analyzed using a luminescence spectrometer (LS 50B, Perkin-Elmer).

The relative quantum yield of the resulting nanocomposites in water (0.01 g aqueous colloid of nanocomposites diluted with 5 mL of deionized water) was determined by comparing with a reference with a known quantum yield [26–29]. We chose fluorescein in absolute alcohol (1×10^{-5} mol/L) as the reference, whose Q is 0.97 at room temperature. The relative quantum yield is generally determined by comparing the wavelength-integrated intensity of an unknown sample to that of a reference. The quantum yield is generally determined by comparing the quantum yield of the unknown sample and is calculated using:

$$Q = Q_R \frac{I}{I_R} \frac{OD_R}{OD} \left(\frac{n}{n_R}\right)^2 \quad (1)$$

where Q is the quantum yield, I is the fluorescence integrated intensity, n is 1.361, the refractive index of absolute alcohol; and for the nanocomposites, n is 1.515, the refractive index of