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Supporting Information

Development of pH sensing colloidal nanoparticles and oil/water separating electrospun membranes containing oxazolidine from functional polymers

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1. Experimental

1.1. Synthesis of oxazolidine

In a typical procedure, 2,3,3-trimethylindolenin (20 mmol, 3.2 g) was dissolved in 30 mL of 2-buotanone (as solvent). In the following, a solution of 2-bromoethanol (25 mmol, 1.8 mL) in 10 mL of 2-buotanone was added to the solution at room temperature. Then, the mixture was refluxed at 80 °C for 2 days in N_2 atmosphere to form slightly red precipitate, which was collected by a filter paper and washed with acetone for three times to afford reddish solid with a reaction yield of about 70%. In the next step, 10 mmol of reddish solid (2.8 g) was dissolved in ethanol (20 mL). After that a solution of 4-hydroxybenzaldehyde (20 mmol, 2.45 g) in 10 mL ethanol was added to the mixture and refluxed for 2 days in N_2 atmosphere. Finally, the orange oxazolidine derivative was obtained after filtration and washing the solid with cold ethanol (5 mL) for several times.

1.2. Synthesis of the homopolymer and copolymer amples by RATRP

For the synthesis (co)polymers using RATRP, $CuBr_2$ was heated at 180 °C for 2 h. A glass tube was charged with $CuBr_2$ (0.0223 g, 0.1 mmol), purged with N_2, and charged with THF (10 mL) at room temperature. The mixture was maintained under stirring for 15 min to thoroughly disperse the $CuBr_2$ powder in THF. Addition of PMDETA (0.0172 g, 0.1 mmol) as the ligand to the mixture resulted in the formation of $CuBr_2$/PMDETA complex as a dark green mixture under stirring for 20 min. Then, monomer (MMA, 2.2 mL, 20 mmol) or monomer mixtures (MMA/DMAEMA or MMA/HEMA) were added to the glass tube and stirred at room temperature for 1 h. CVA (0.014 g, 0.05 mmol) was added to the mixture as an initiator under N_2 purging, and the glass tube was sealed. Temperature was increased to 70 °C, and the reaction tube was left under stirring at 700 rpm for 1 day to synthesize well-defined telechelic polymer/copolymers with

carboxylic acid end functionalities. Purification of the samples to remove impurities, such as unreacted monomer, $CuBr_2$, and PMDETA, was carried out by diluting the mixture with 10 mL of THF and then passing the diluted mixture through a column filled with basic aluminum oxide (0.5 to 1 g for each time). Purification by basic aluminum oxide column was repeated 5 times to obtain a colorless polymer solution. The pure polymer or copolymers powder was collected after evaporation of solvent from the colorless solution at room temperature. Finally, the poly(methyl methacrylate), poly(methyl methacrylate-*co*-hydroxyethyl methacrylate), and poly(methyl methacrylate-*co*-dimethylaminoethyl methacrylate) samples were obtained and used for further characterization and experiments, where the ratio of MMA to HEMA or DMAEMA in the case of random copolymer samples was 1:0.25. The molar ratio of [M]/[CVA]/[$CuBr_2$]/[PMDETA] in all the recipes was 200/0.5/1/1, where [M] denotes MMA for the homopolymer and MMA/HEMA or MMA/DMAEMA in the case of random copolymers, respectively.

1.3. Characterization

Characterization of the chemical structure of oxazolidine and molecular weights of the polymers was carried out by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy using a Bruker DPX 400 MHz apparatus in $CDCl_3$. Some parameters for ^{1}H-NMR spectra were registered as the following: Number of scans: 16, acquisition time: 5.45 s, relaxation delay: 1 s, and dwell time: 83.2 μs. The measurement of particle size and its distribution and also zeta potential was performed using ZETASIZER NANO ZSP dynamic light scattering (DLS, Malvern, United Kingdom) at 25 and 45 °C. The measurement was done right after the nanoprecipitation and formation of nanoparticles and also vigorous sonication for 10 min to prevent aggregation. The nanoparticles were diluted in deionized (DI) water with a concentration of about 0.2 mg/mL for this characterization. Transmission electron microscopy (TEM) was used to show the size and

morphology of the nanoparticles by using LEO 906 instrument (Zeiss, Oberkochen, Germany) with an accelerating voltage of 100 kV. For this purpose, a drop of samples with a concentration of about 0.2 mg/mL was placed on carbon-coated copper grids, stained with osmium tetroxide or uranyl acetate, and dried in a vacuum at 25 °C. Field-emission scanning electron microscopy (FE-SEM) micrographs for nanoparticles and nanofibers were recorded by a Tescan Mira III (Czech Republic) (acceleration voltage was 10 kV with inBeam detector). In a typical method, a drop of colloidal dispersions with a concentration of about 0.06 mg/mL for nanoparticles and a piece of electrospun mat for the nanofibers were placed on the sample holder and dried at 25 °C in vacuum to prepare the specimens for FE-SEM. The samples were placed in a vacuum, evacuated, and a layer of gold was deposited under flushing with argon using an EMITECH K450x sputter-coating system (England). Optical properties of the nanoparticles were evaluated by UV-vis analysis utilizing Jenway 6705 UV/Visible scanning spectrophotometer (United Kingdom). Fluorescence emission of the colloidal samples with a concentration of 0.06 mg/mL was detected by using a JASCO FP-750 spectrofluorometer (Japan). The excitement state was achieved using a UV lamp (365 nm, 6 W/m^2, CAMAG 12VDC/VAC (50/60 Hz, 14VA, Switzerland)) to evaluate fluorescence properties. The ordinary LED lamp (8 W/m^2) was used as a source for the visible light irradiation. The static contact angle of water and oil droplets on the nanofibers surface under visible and UV light irradiation was measured using a KRUSS G10 system (Germany) at room temperature. The volumes of water and oil droplets used for the static contact angle were about 41 and 52 μL, respectively. In addition, morphology and fluorescence emission of the fluorescent nanofibers (0.2 $mg.mL^{-1}$) were investigated using Olympus BX50 Microscope with a UV narrow filter. An electrospinning instrument CO881007NYI (Iran/ Asia Nanostructure) was used to prepare the photoresponsive nanofibers. The syringe rate of 1–1.2 $mL.h^{-1}$, an electrical voltage of

18–20 kV, and a tip-to-collector distance of 0.02 m were used for the nanofibers preparation. In order to assess the mechanical properties of nanofibrous scaffolds, the samples were cut into the rectangular specimens (6 × 40 × Z mm^3, where Z is the thickness of the samples). Tensile tests were conducted by using a Z010 Zwick/ Roell mechanical tester (Germany) at a rate of 1 mm/min up to rupture of the samples.

2. Characterization of the structures by ^{1}H NMR spectroscopy

Table S1. Typical procedures used for the synthesis of the homopolymer and copolymers by RATRP

Sample	$CuBr_2$ (g)	PMDETA (g)	MMA (g)	HEMA (g)	DMAEMA (g)	Theoretical DP		Experimental DP*	
						PMMA	PDMAEMA or PHEMA	PMMA	PDMAEMA or PHEMA
PM	0.022	0.017	2.002	-	-	200	-	196	
PMH	0.022	0.017	1.600	0.520	-	160	40	157	36
PMD	0.022	0.017	1.600	-	0.640	160	40	155	36

*** Calculated from ^{1}H NMR spectroscopy**

To confirm the successful synthesis of PM, PMH, and PMD, their chemical structure were studied by ^{1}H NMR analysis in $CDCl_3$. Figure **S**S1, S2, and S3 show the resulted ^{1}H NMR spectra and chemical structure of all the samples. Chemical structure of oxazolidine was also characterized by ^{1}H NMR analysis in $CDCl_3$, and the corresponding spectra are presented in our previous works[1,2]. The results of ^{1}H NMR analysis indicate that the RATRP approach was successful and efficient in the synthesis of the telechelic polymers and copolymers.

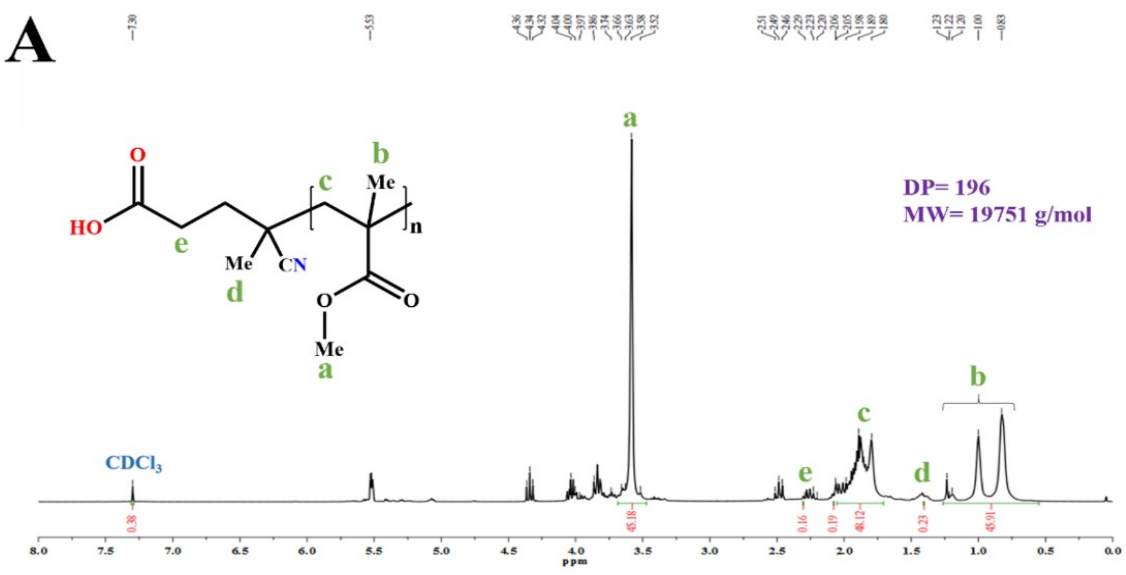

Figure S1. ^{1}H NMR spectra of PM in $CDCl_3$

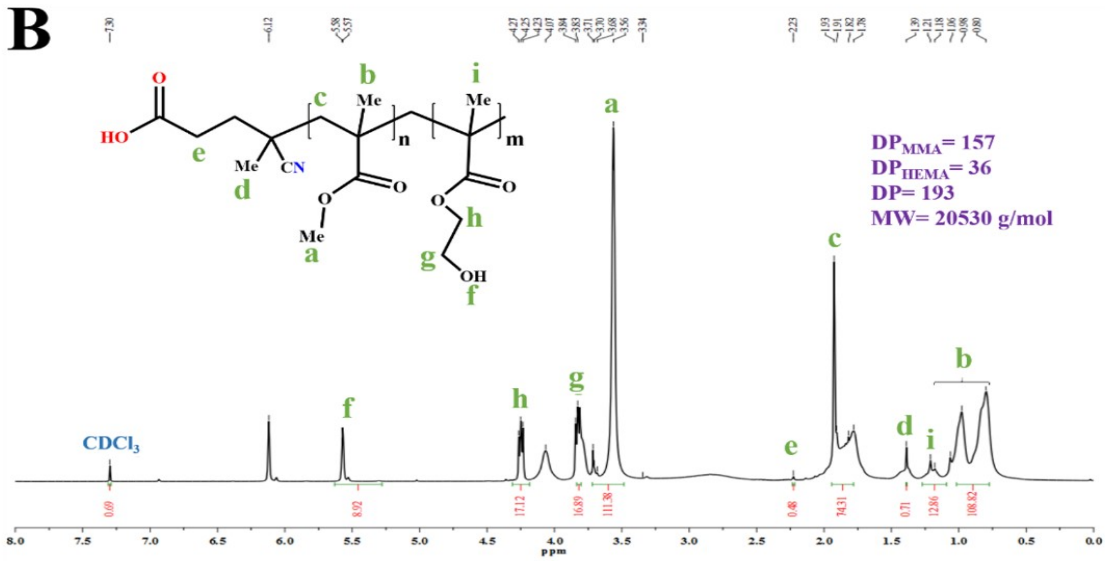

Figure S2. ^{1}H NMR spectra of PMH in $CDCl_3$

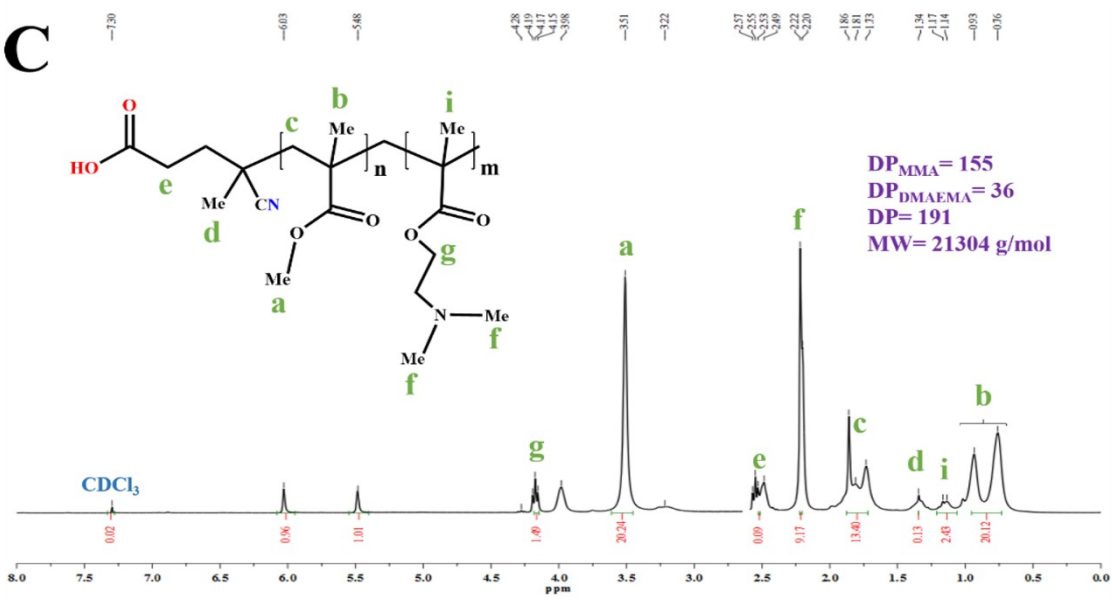

Figure S3. ^{1}H NMR spectra of PMD in $CDCl_3$

Chemical structure of PM was characterized by the peaks observed for hydrogens *a*, *b*, and *c*. The peaks of *e* and *d* are attributed to the chain end groups of initiator (CVA). One of the characteristic peaks of the chain end groups was used to measure molecular weight according to the Equations 1-3 presented for MMA, DMAEMA, and HEMA, respectively.

$DP_{MMA}=(a/3)/(d/3)$ (Equation 1)

$DP_{HEMA}=(h/2)/(d/3)$ (Equation 2)

$DP_{DMAEMA}=(f/6)/(d/3)$ (Equation 3)

The calculated values are given in Table 1.

3. **Fluorescence and optical properties of the polymer nanoparticles and oxazolidine**

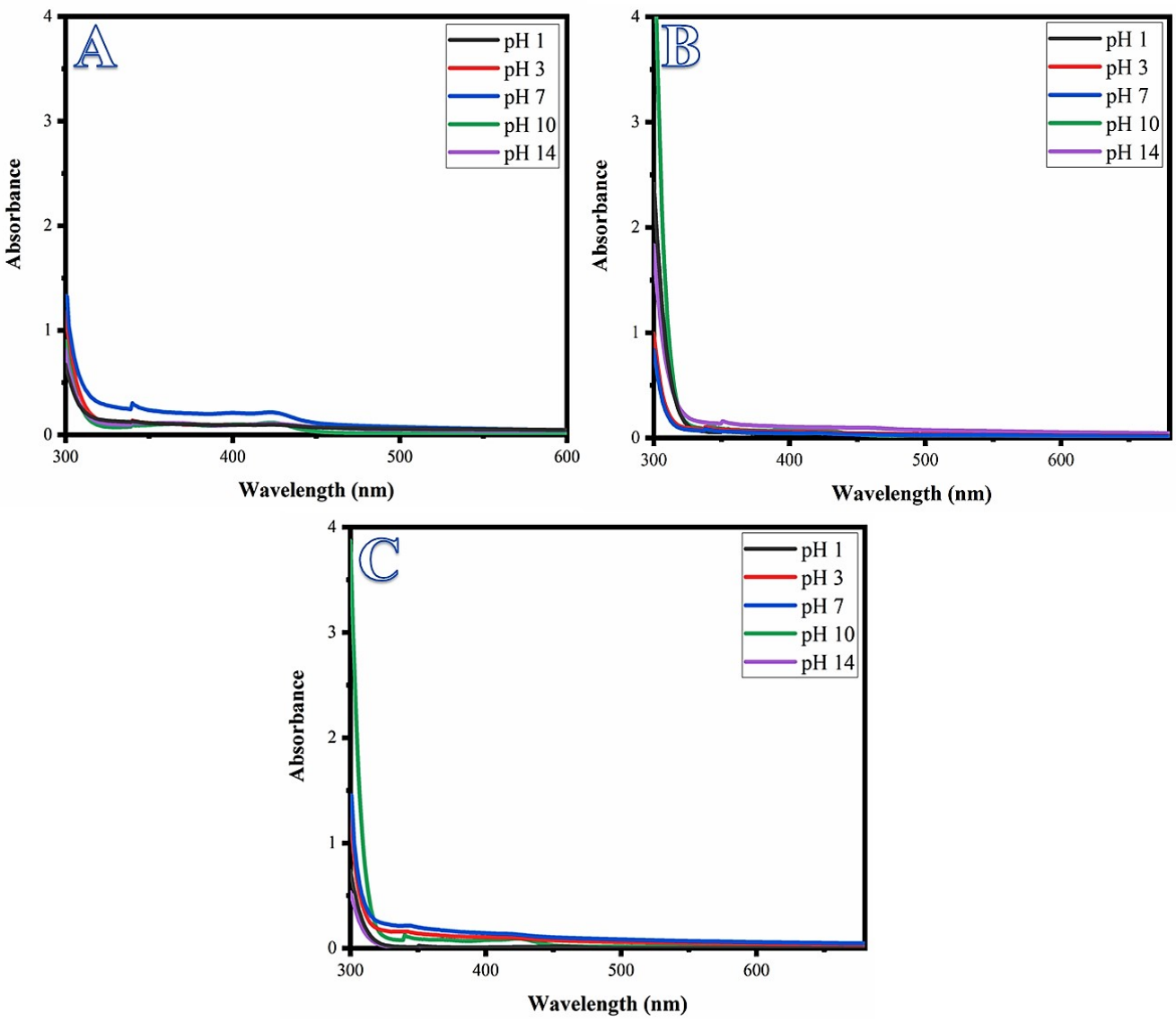

Figure S4. UV-vis spectra of (A) PM, (B) PMH, and (C) PMD nanoparticles in aqueous media with different pHs

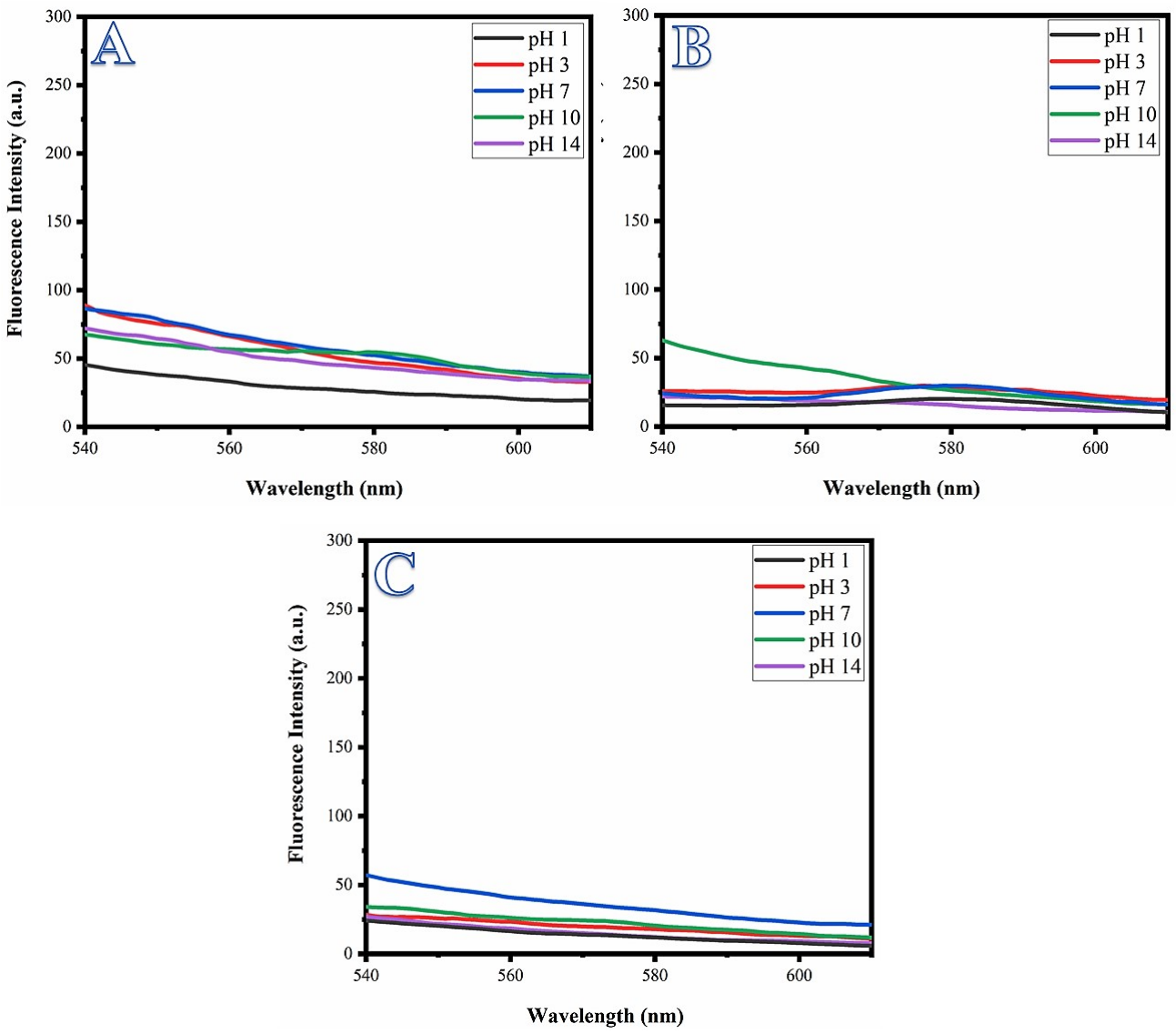

Figure S5. Fluorescence emission spectra of (A) PM, (B) PMH, and (C) PMD nanoparticles in aqueous media with different pHs

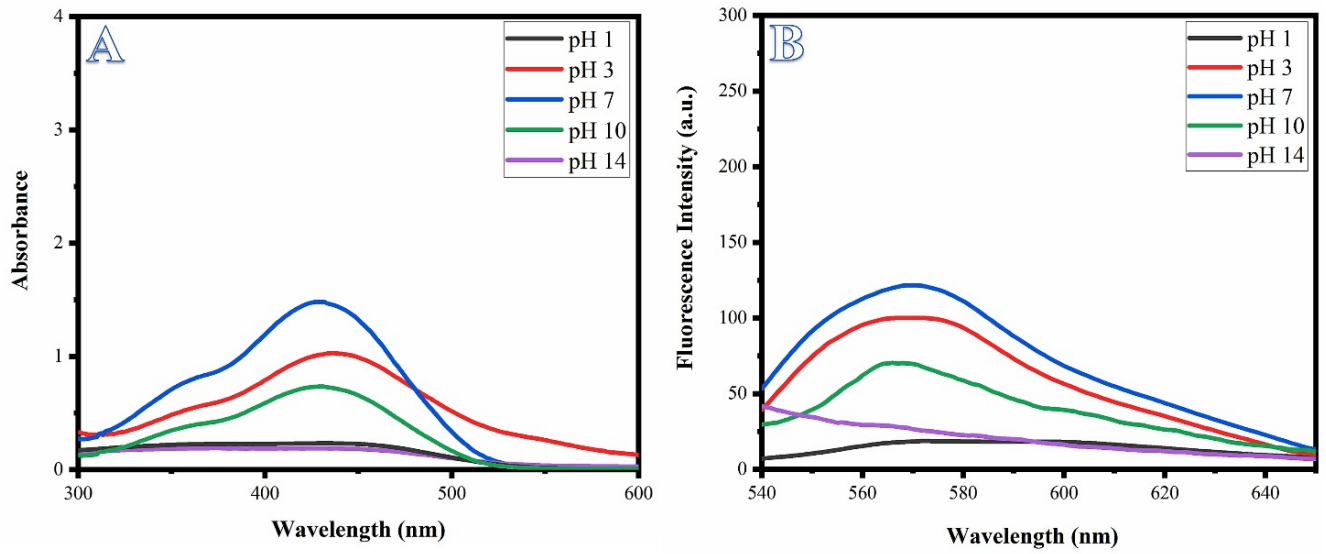

Figure S6. (A) UV-vis and (B) fluorescence emission spectra of oxazolidine in aqueous media with different pHs

4. Mechanical properties of the nanofibers

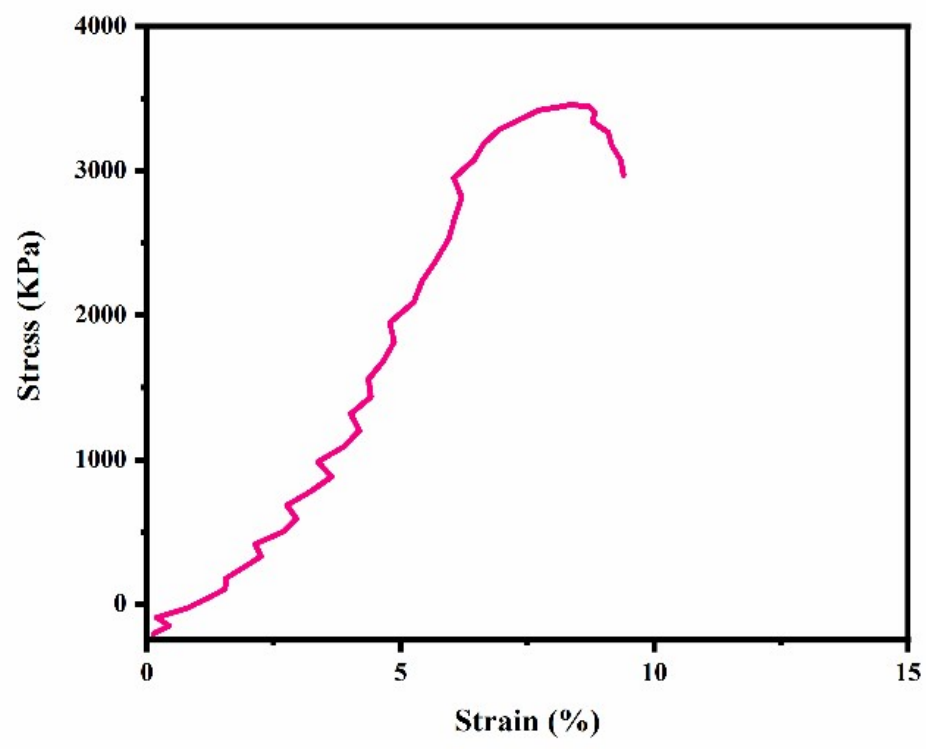

Figure S7. Stress-strain curve for the PMD nanofibers

5. Photoresponsive nanofibers prepared by electrospinning

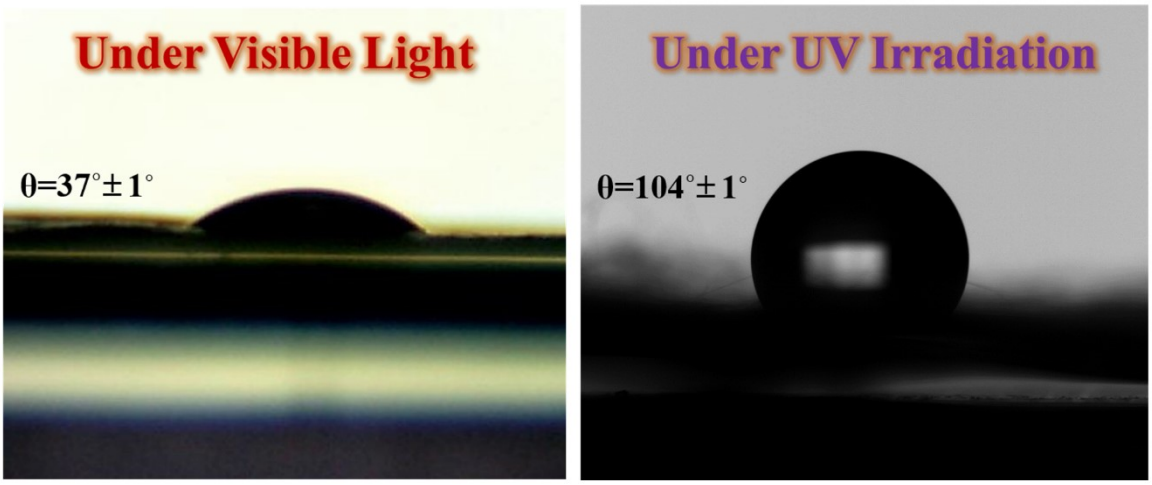

Figure S8. Oil contact angle variation on the surface of nanofibers under visible and UV light irradiation

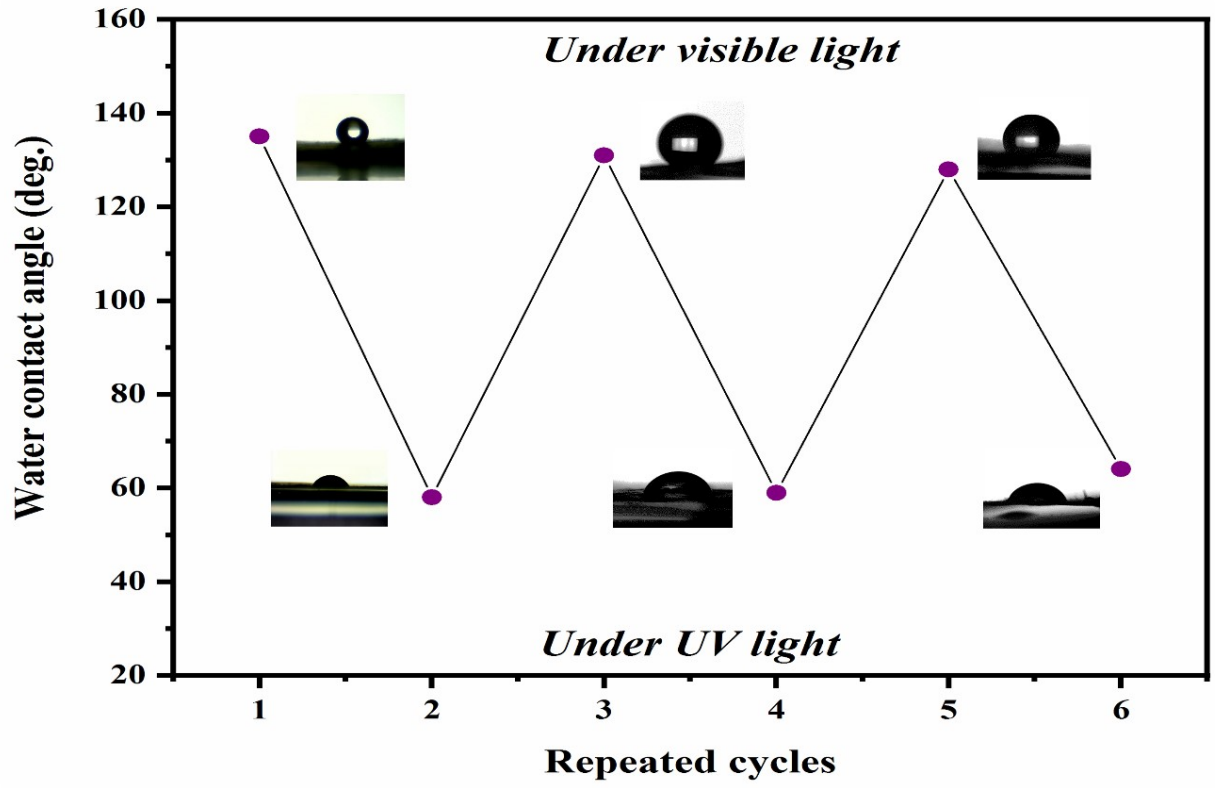

Figure S9. Reversibility of the wettability changes under UV and visible light irradiation

6. Hydrophobic nanofibers containing oxazolidine under visible light

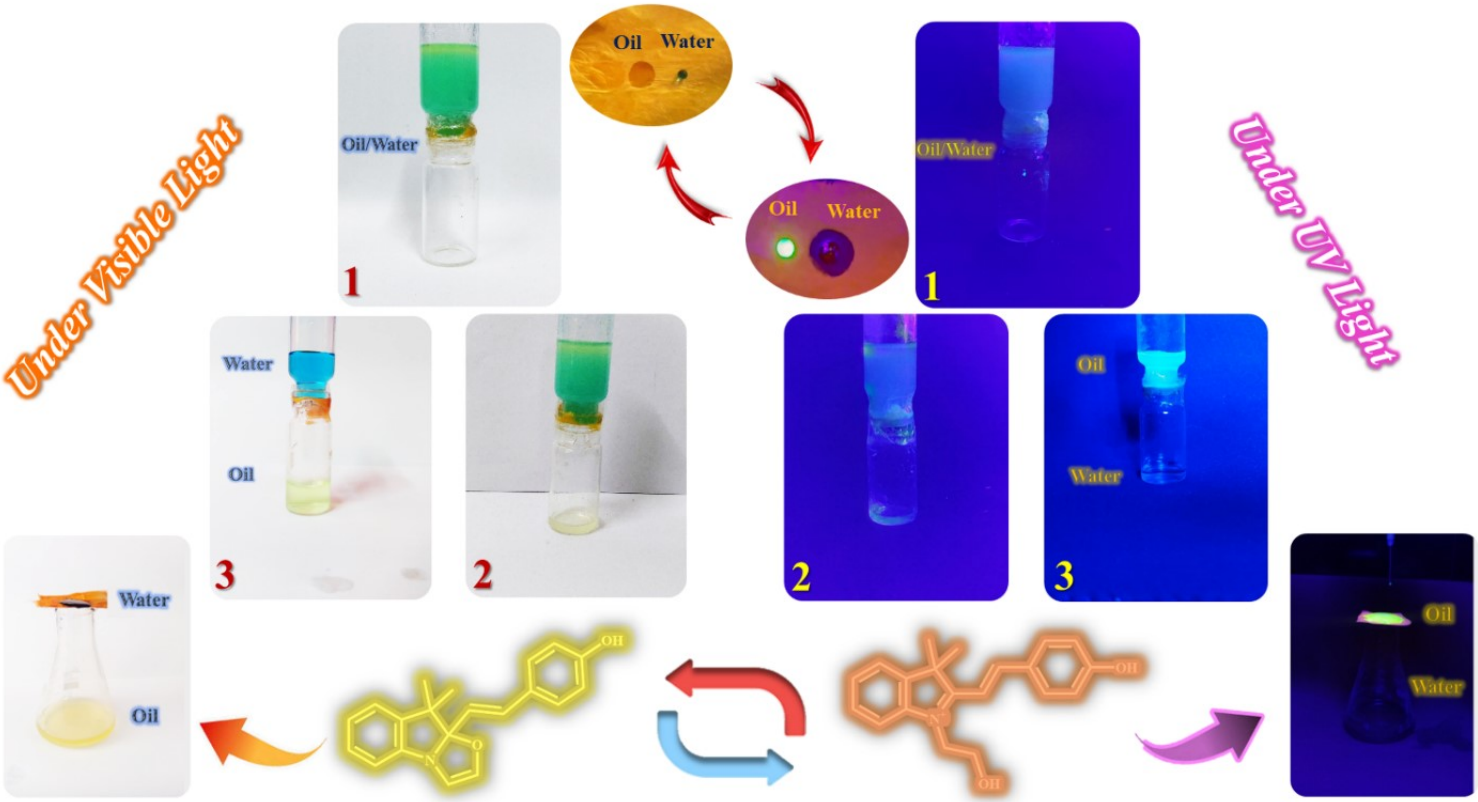

Figure S10. Illustration of oil/water separation process by nanofibrous membranes under UV and visible light irradiation

Figure S11. Schematic illustration of oil/water dripping steps by syringe on the nanofibrous membranes under visible light irradiation

7. References

1 B. Razavi, H. Roghani-Mamaqani and M. Salami-Kalajahi, *Sci. Rep.*, 2022, **12**, 1079.

2 A. Abdollahi, H. Roghani-Mamaqani, M. Salami-Kalajahi and B. Razavi, *J. Colloid Interface Sci.*, 2020, **580**, 192–210.