Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2013

Electronic Supplementary Information

Surface-Decorated ZnO Nanoparticles and ZnO Nanocoating on Electrospun Polymeric Nanofibers by Atomic Layer Deposition for Flexible Photocatalytic Nanofibrous Membranes

Fatma Kayaci[a], Cagla Ozgit-Akgun[a], Necmi Biyikli[a]* and Tamer Uyar[a]*

[a]UNAM-Institute of Materials Science & Nanotechnology, Bilkent University, Ankara, 06800, Turkey

*Corresponding authors (email): NB (biyikli@unam.bilkent.edu.tr) and TU (tamer@unam.bilkent.edu.tr)

1. Experimental

1.1. Materials

Nylon 6,6 pellets (relative viscosity: 230.000-280.000), formic acid (98-100 %) and rhodamine-B (Rh-B, dye content ~95 %) were purchased from Sigma-Aldrich and used without any purification. For ZnO deposition by ALD, diethylzinc ($(C_2H_5)_2Zn$ or DEZn, Sigma-Aldrich) and HPLC-grade water (H_2O) were used as the zinc and oxygen precursors, respectively.

1.2. Electrospinning of Polymeric Nanofibers

8 wt % nylon 6,6 was dissolved in formic acid by stirring for 3 h at room temperature, for each sample. The resulting homogeneous clear solutions were located in 10 ml syringes fitted with metallic needles having inner diameter of 0.8 mm. The syringes were fixed horizontally on the syringe pump (Model: SP 101IZ, WPI). The polymer solutions were pumped with feed rate of 1 ml/h during electrospinning and the tip-to-collector distance was set to 10 cm. Voltage of 15 kV was applied to the metal needle tip by using high voltage power supply (Matsusada, AU Series) for the electrospinning of the prepared solutions. The solvent evaporated on the way to the grounded stationary cylindrical metal collector (height: 15 cm, diameter: 9 cm) covered with a piece of aluminum foil, on which the electrospun nylon 6,6 nanofibers were deposited. The electrospinning setup was enclosed in Plexiglas box and the electrospinning was carried out at 23 ^{o}C and 36 % relative humidity.

1.3. Preparation of ZnO Structures by ALD

ZnO depositions were carried out at 200 °C in a Savannah S100 ALD reactor (Cambridge Nanotech Inc.) using diethylzinc (DEZn, or $(C_2H_5)_2Zn$) as the zinc precursor and HPLC-grade water (H_2O) as the oxidant. N_2 was used as both carrier and purge gas with flow rates of 20 and 10 sccm under dynamic and static vacuum conditions, respectively. 144 cycles were deposited using different deposition parameters. For the first set of samples, one ALD cycle consisted of H_2O pulse (0.015 s) / N_2 purge (10 s) / DEZn pulse (0.015 s) / N_2 purge (10 s). Increased doses of DEZn and H_2O (i.e. 0.09 s) were used for the second set, again with a 10 s N_2 purge between the precursor pulses. Another set was prepared by using the *exposure mode* (a trademark of Cambridge Nanotech Inc.). In this mode, dynamic vacuum was switched to static vacuum before each precursor pulse by closing the valve between the reaction chamber and the pump. After a certain period of time (i.e. exposure time) it was switched back to dynamic vacuum for purging excess precursor molecules and gaseous by-products. For this process, one ALD cycle was as follows: valve OFF / H_2O pulse (0.015 s) / exposure (10 s) / valve ON / N_2 purge (10 s) / valve OFF / DEZn pulse (0.015 s) / exposure (10 s) / valve ON / N_2 purge (10 s).

1.4. Characterization Techniques

The morphology of the pristine nylon nanofibers and nylon/ZnO nanofibers were investigated by using scanning electron microscope (SEM, FEI–Quanta 200 FEG). The nanofibers were coated with 5 nm Au/Pd for SEM imaging. Around 100 fiber diameters were measured from the SEM image of pristine nylon nanofibers in order to calculate the average fiber diameter. Detailed morphological investigation of the nylon/ZnO nanofibers was performed by using transmission electron microscope (TEM, FEI–Tecnai G2F30, Hillsboro, OR). Small pieces of nylon/ZnO nanofibrous membranes sonicated in ethanol for 5 minutes to obtain individual nanofibers dispersed through the solvent, followed by dropping the suspensions onto the copper TEM grids (HC200), and allowed them to dry under IR lamp for a few minutes prior to TEM imaging. Crystal structure of ZnO on nanofibers was investigated from selected area electron diffraction (SAED) patterns of nylon/ZnO nanofibers obtained by TEM. PANalytical X'Pert Multi Purpose X-ray Diffractometer with Cu Kα radiation was used to collect X-ray diffraction (XRD) data of the pristine nylon and nylon/ZnO nanofibers in a range of $2\theta = 10^{o}$-100^{o}. X-ray photoelectron spectroscopy (XPS, Thermo Scientific) was used to detect the surface elemental composition of pristine nylon and nylon/ZnO nanofibers. XPS data were taken from 400 μm diameter circular spot on the sample surface by means of a flood gun charge neutralizer system equipped with a monochromated Al K_{α} X-ray source (hv = 1486.6 eV). Wide energy survey scans were obtained over a 0-1360 eV binding energy (BE) range, at pass energy of 150 eV, and with an energy step of 1 eV. Zn 2p high resolution XPS scan was also taken at pass energy of 30 eV, and with energy steps of 0.1 eV in order to analyze the bonding states. Thermal analysis of the nanofibers was performed by using thermogravimetric analyzer (TGA, TA Instruments–Q500) from room temperature to 600 ^{o}C at a heating rate of 20 ^{o}C/min under nitrogen atmosphere.

1.5. Photocatalytic Activity of the Nylon/ZnO Nanofibrous Membranes

Photodegradation of rhodamine-B (Rh-B) (1.04×10^{-5} M) in aqueous medium with nylon/ZnO nanofibers were investigated to determine the efficiency of photocatalytic activity of the samples. 10 mg nylon/ZnO nanofibrous membranes with three different ZnO morphologies (about 3.0 cm×2.5 cm) were put into quartz cuvettes (width: 1 cm, length: 1 cm, and height: 5 cm, Hellma) filled with Rh-B solution, separately. Then these cuvettes were kept under the irradiation of UV-light with a wavelength of 365 nm by placing them at a distance of 10 cm from the UV source (8 W, UVLMS-38 EL). UV-Vis-NIR spectrophotometer (Varian Cary 5000) was used to measure dye concentrations in the cuvettes at certain time intervals. The nanofibrous membranes which stayed at the bottom of the dye solution during UV-Vis measurement did not interfere with the UV-light; hence they did not contribute to the measurement results.

Table:

Table S1. Atomic concentrations generated from XPS wide energy survey scans.

samples	**C (%)**	**O (%)**	**Zn (%)**	**N (%)**
pristine nylon	77.06	11.61	-	11.33
nylon/ZnO NP	68.13	15.95	5.53	10.38
nylon/ZnO NP (highly dense)	31.23	36.19	29.76	2.81
nylon/ZnO nanocoating	30.74	38.53	30.73	-

Figures:

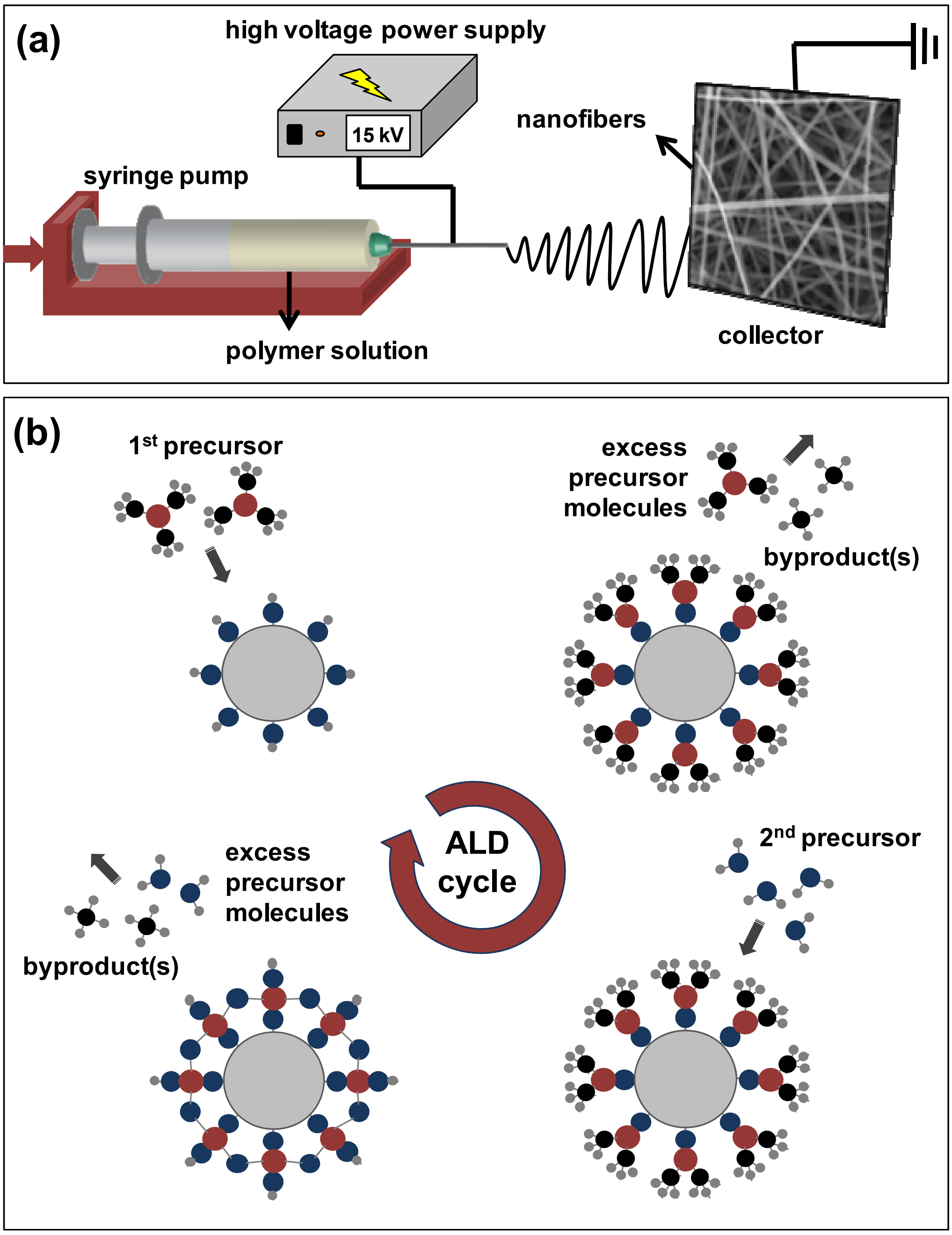

Fig. S1. Schematic representations of the processing steps for the production of polymer/inorganic nanofibers: (a) electrospinning, (b) atomic layer deposition (ALD).

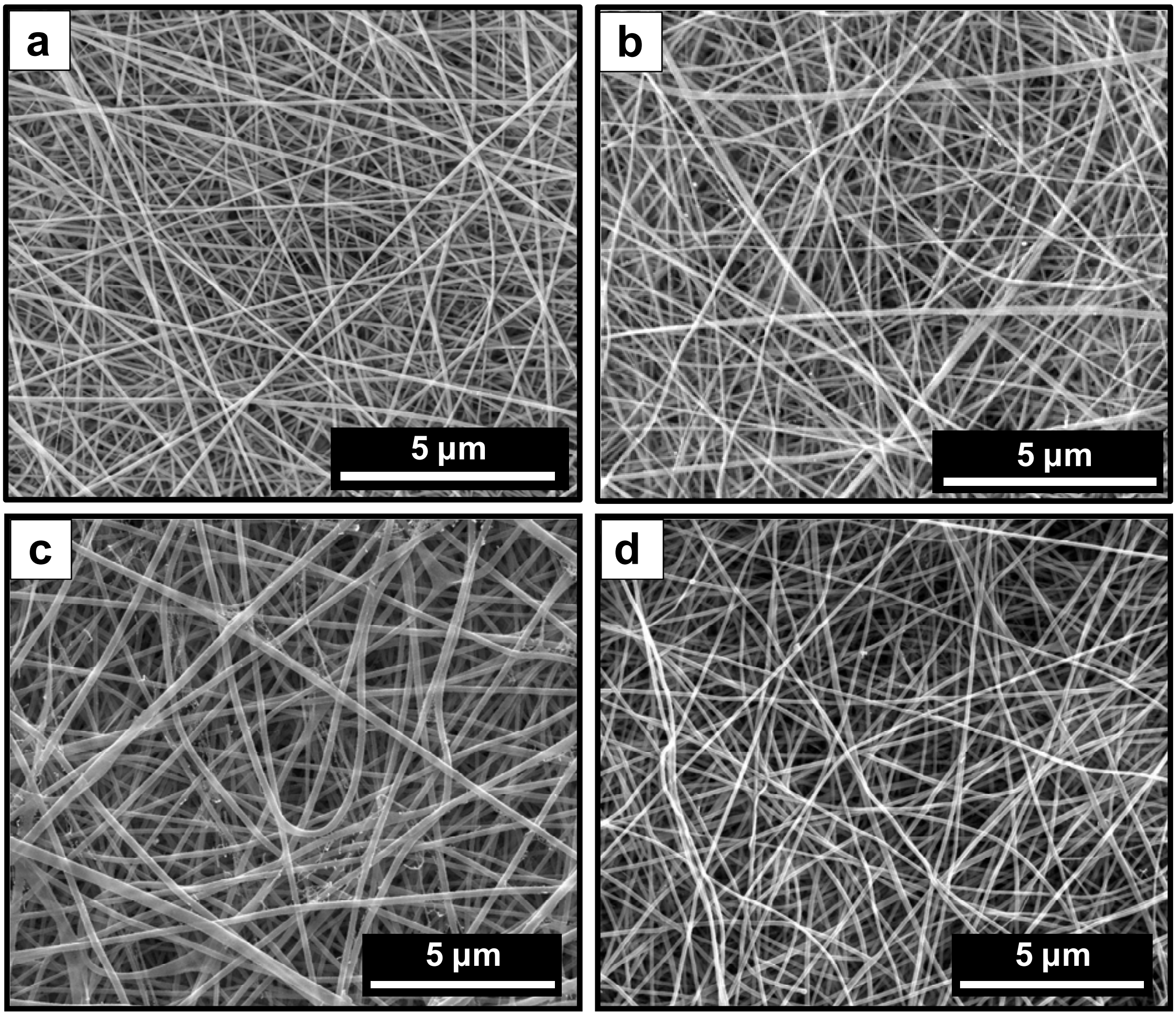

Fig. S2. Representative SEM images of nanofibers; (a) pristine nylon (b) nylon/ZnO NP, (c) nylon/ZnO NP (highly dense), and (d) nylon/ZnO nanocoating.

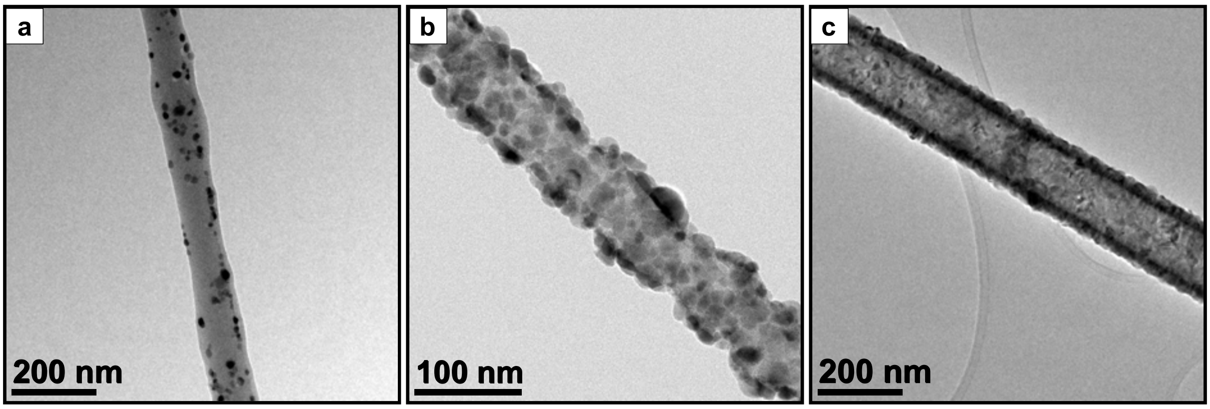

Fig. S3. Representative TEM images of nanofibers; (a) nylon/ZnO NP, (b) nylon/ZnO NP (highly dense), and (c) nylon/ZnO nanocoating.

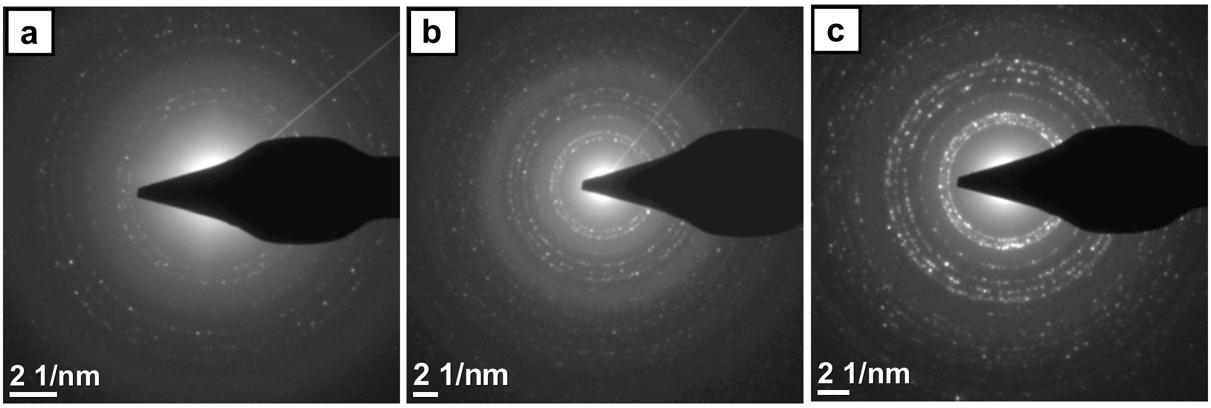

Fig. S4. SAED patterns of nanofibers; (a) nylon/ZnO NP, (b) nylon/ZnO NP (highly dense), and (c) nylon/ZnO nanocoating.

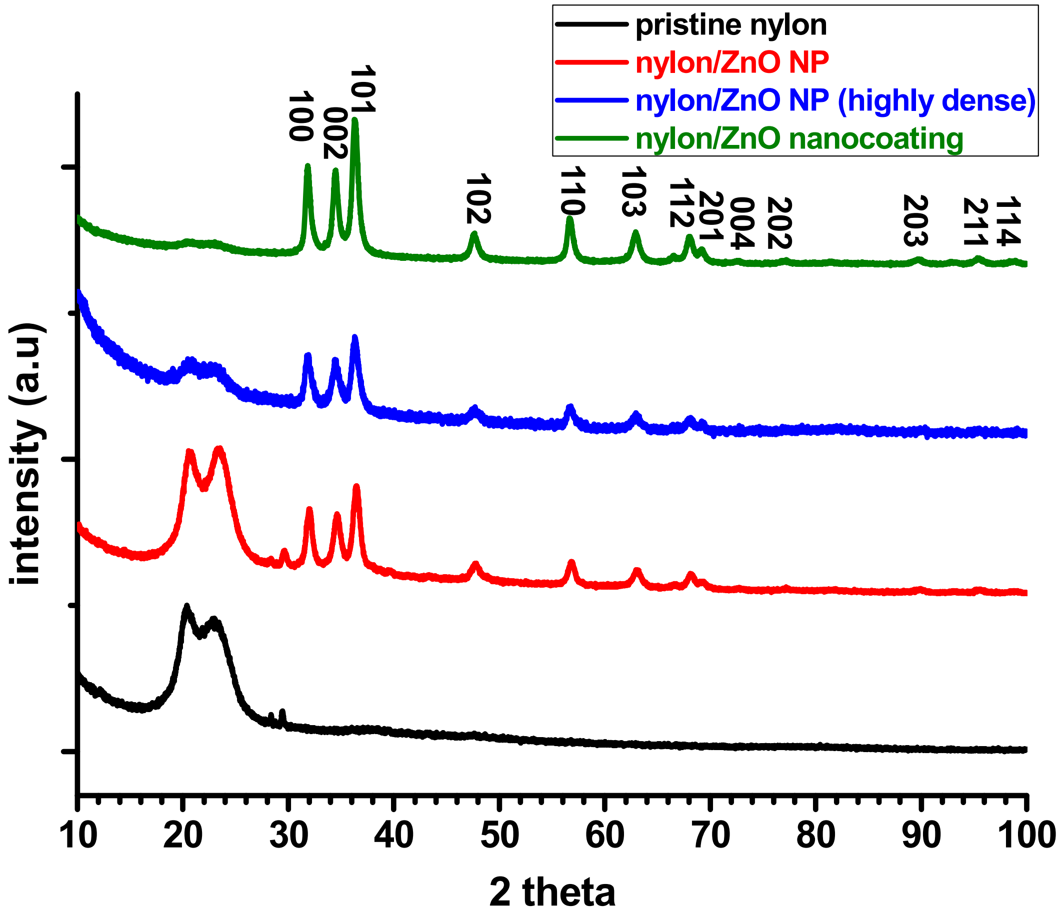

Fig. S5. XRD patterns of pristine nylon and nylon/ZnO nanofibers.

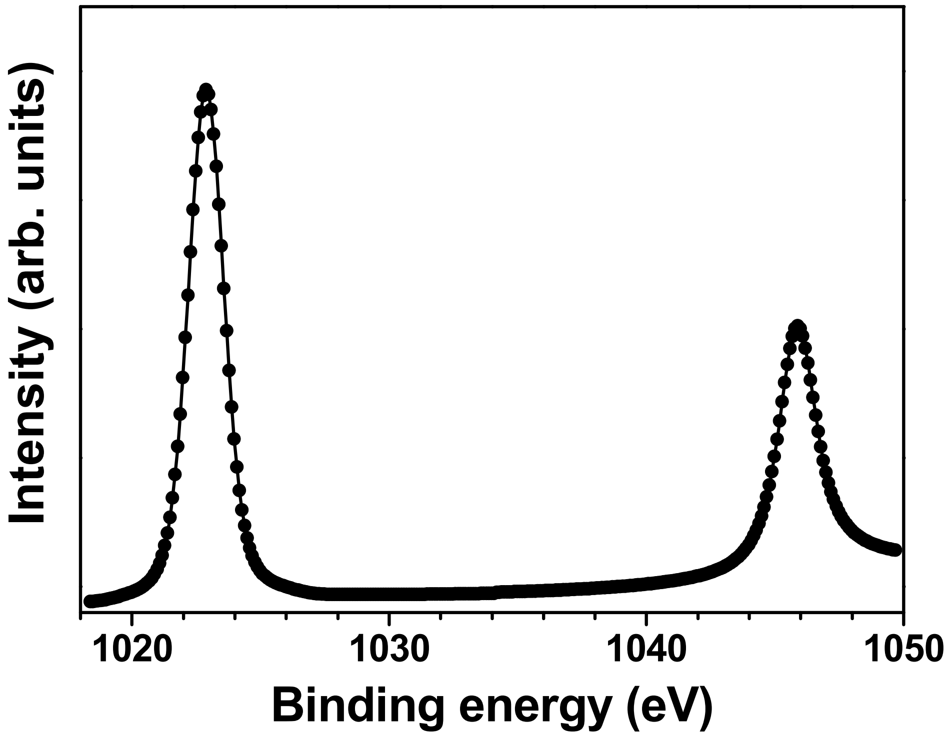

Fig. S6. Zn 2p high resolution XPS scan of nanofibers of nylon/ZnO nanocoating.

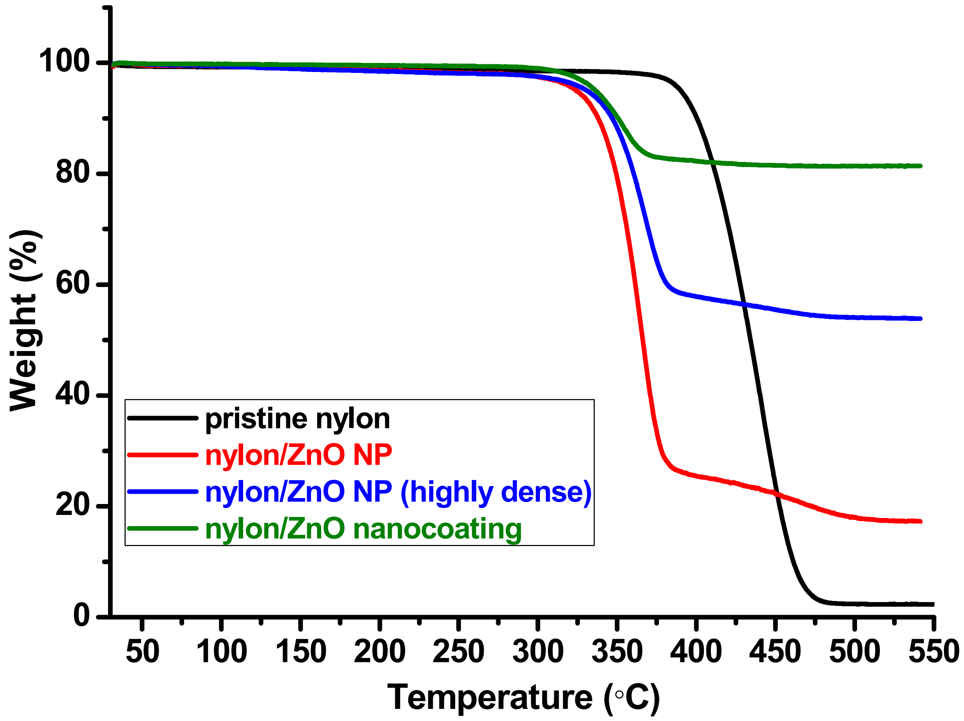

Fig. S7. TGA thermograms of nylon and nylon/ZnO nanofibers.

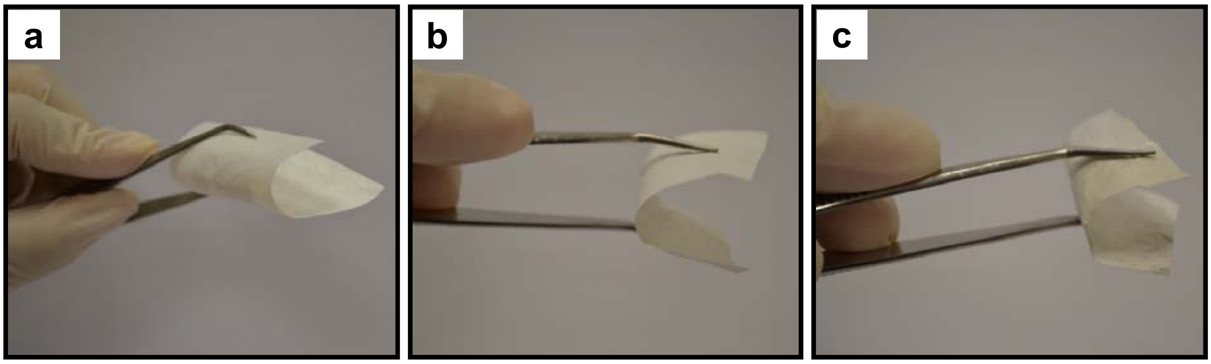

Fig. S8. Representative photographs of flexible nanofibrous membranes; (a) nylon/ZnO NP, (b) nylon/ZnO NP (highly dense), and (c) nylon/ZnO nanocoating.

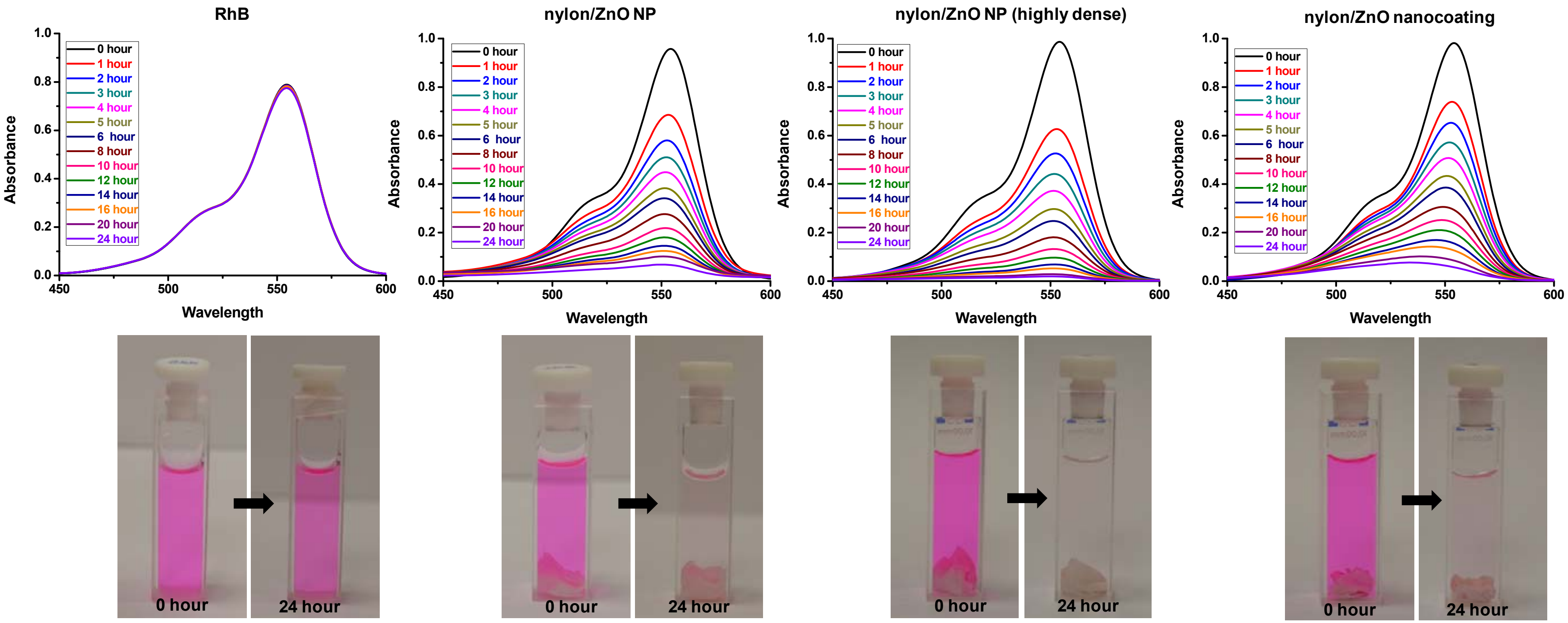

Fig. S9. UV–Vis spectra and color of the Rh-B solution with and without nylon/ZnO nanofibers as a function of the UV irradiation time.