

Supporting Information

Nanograined surface shell wall controlled ZnO-ZnS core-shell nanofibers and their shell wall thickness dependent visible photocatalytic properties

Kuglaur Shanmugam Ranjith,^{*a} Anitha Senthamizhan,^a Brabu Balusamy,^a and Tamer Uyar^{*ab}

^aUNAM - National Nanotechnology Research Center, Bilkent University, Ankara, 06800, Turkey.

^bInstitute of Materials Science & Nanotechnology, Bilkent University, Ankara, 06800, Turkey

E-mails: K.S.R: ranjith@unam.bilkent.edu.tr, T.U: uyar@unam.bilkent.edu.tr,

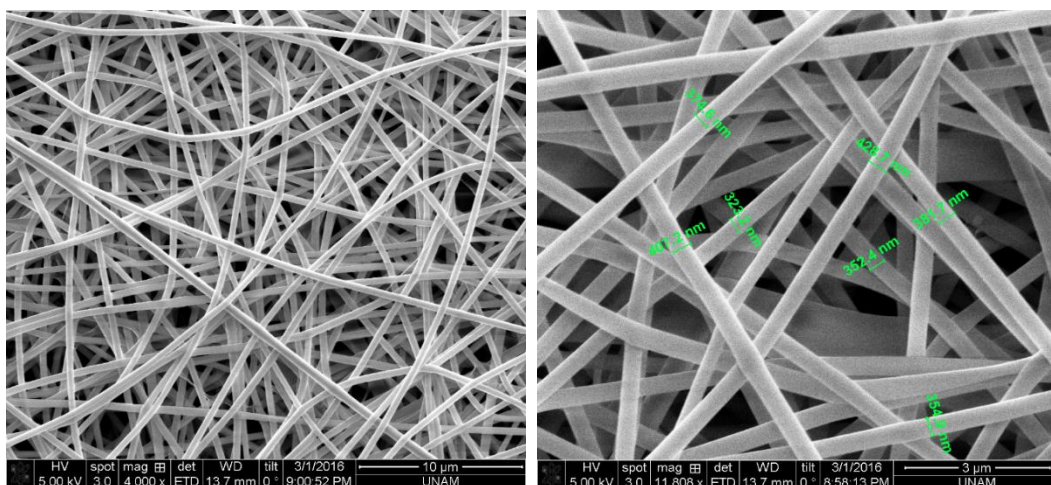


Fig. S1. Representative SEM images of as-electrospun PVA/zinc acetate composite NF.

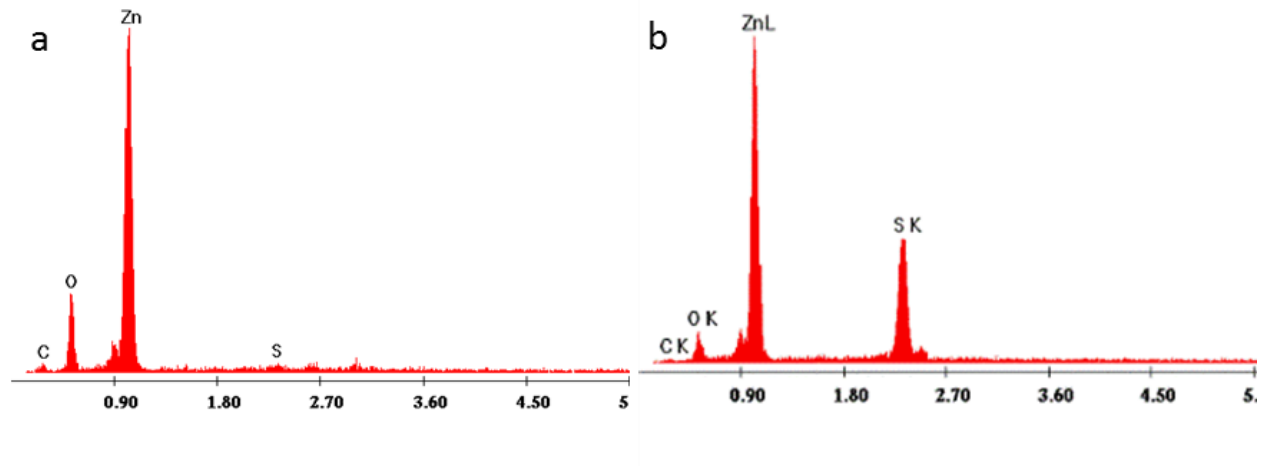


Fig. S2 EDAX spectra of (g) 30 min and (h) 180 min sulfidated ZnO-ZnS core-shell NF.

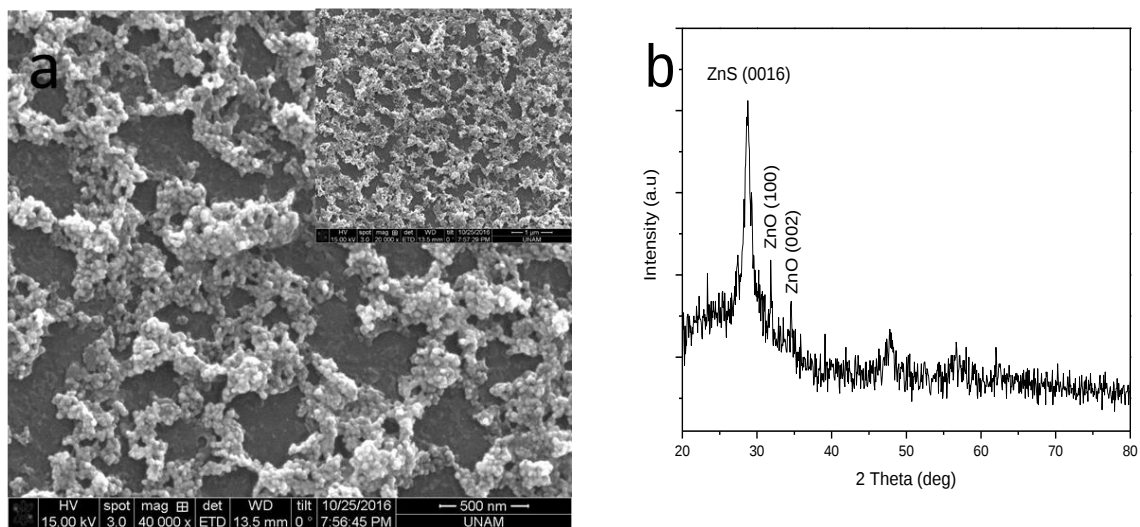


Fig. S3 SEM image and XRD spectrum of ZnO nanostructures sulfidated for 740 min.

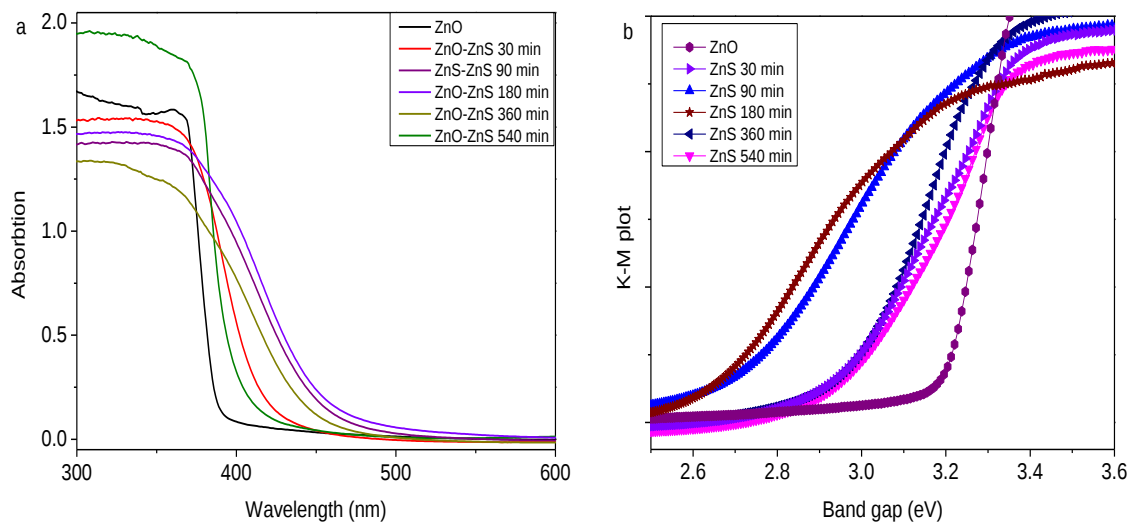


Fig. S4 (a) UV-Vis DRS absorption spectra and (b) K-M plot for the shell wall controlled ZnO-ZnS core-shell NF.

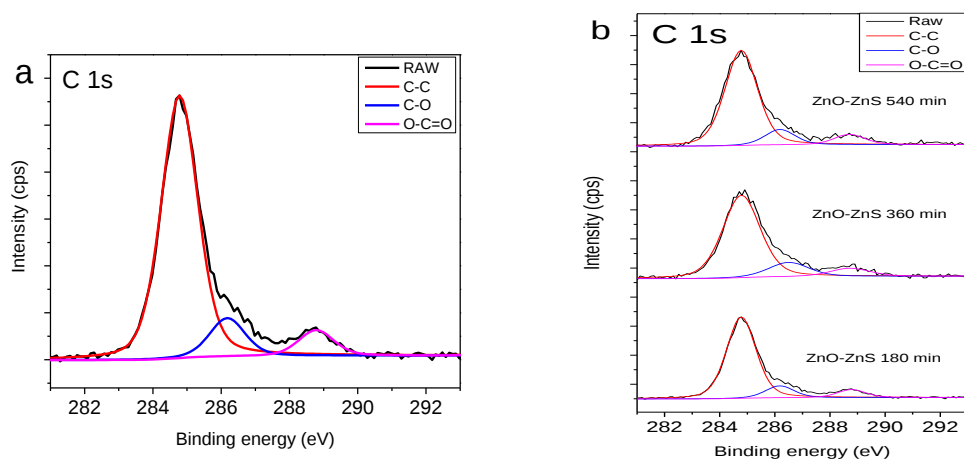


Fig. S5 XPS spectra of C 1s of (a) as prepared ZnO NFs, (b) C 1s of 180 min, 360 min, 540 min sulfidated ZnO-ZnS core-shell NF.

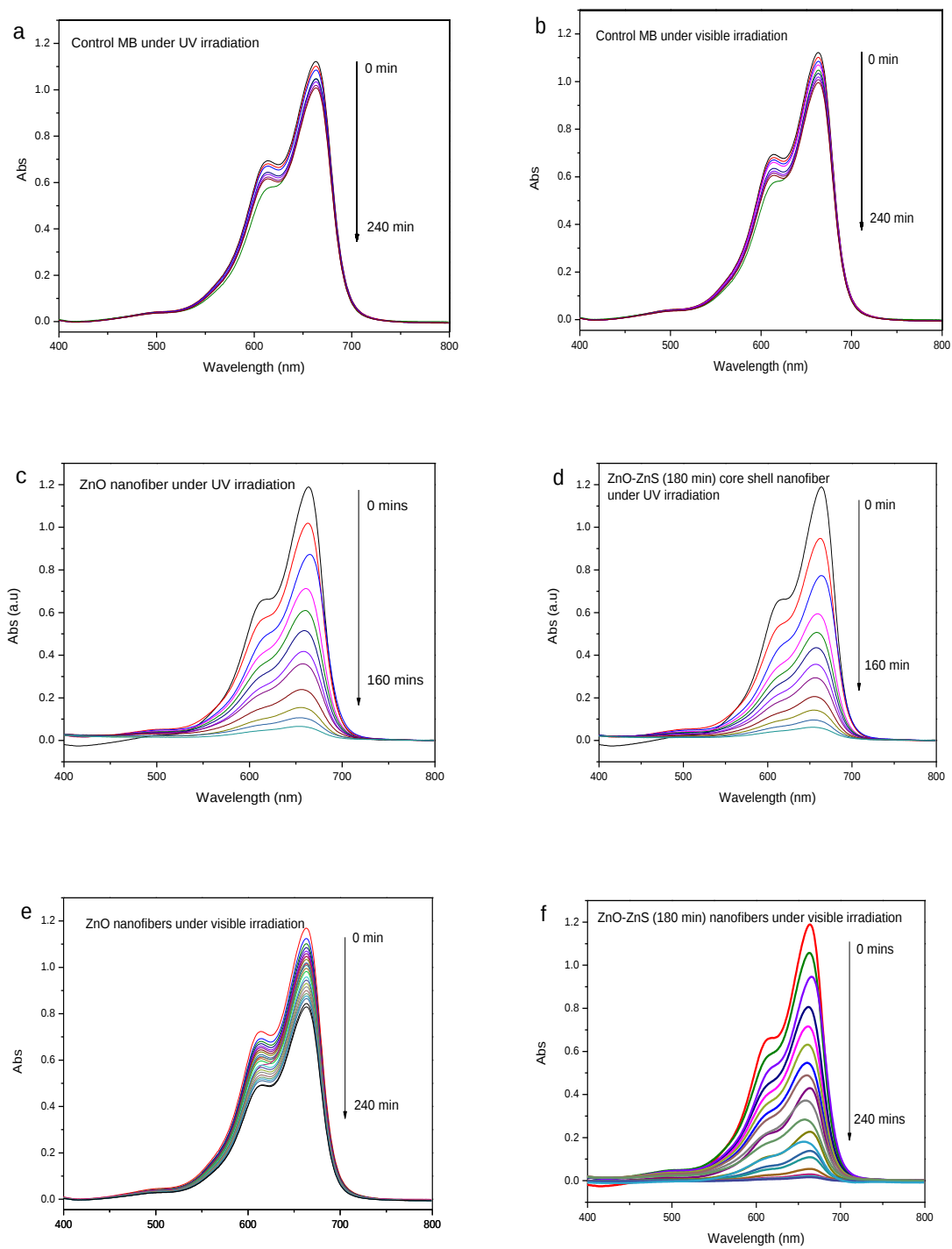


Fig. S6 Time dependent UV-Visible absorption spectra of MB degradation in the presence of electrospun ZnO and shell wall controlled ZnO-ZnS (180 min) core-shell NF under UV and Visible irradiation.

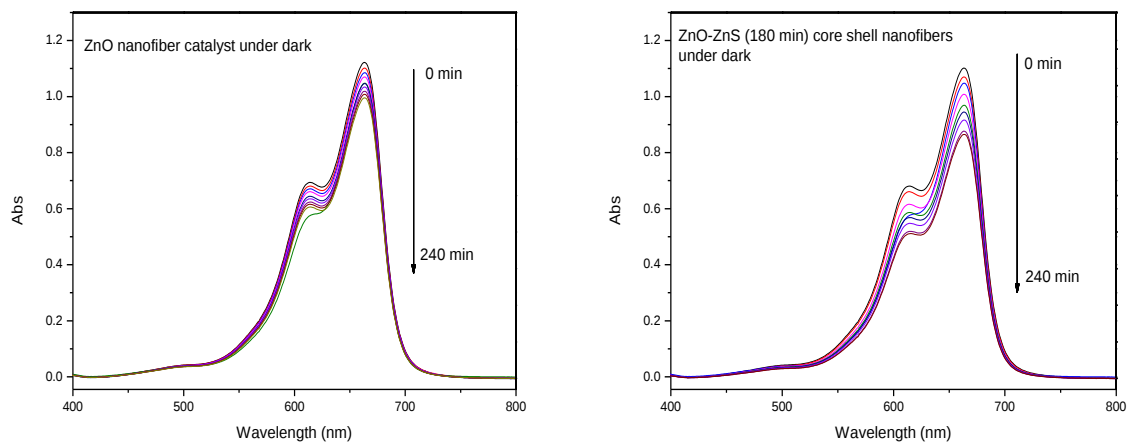


Fig. S7 Time dependent UV-Visible absorption spectra of MB dye in the presence of ZnO and ZnO-ZnS 180 min under dark condition.

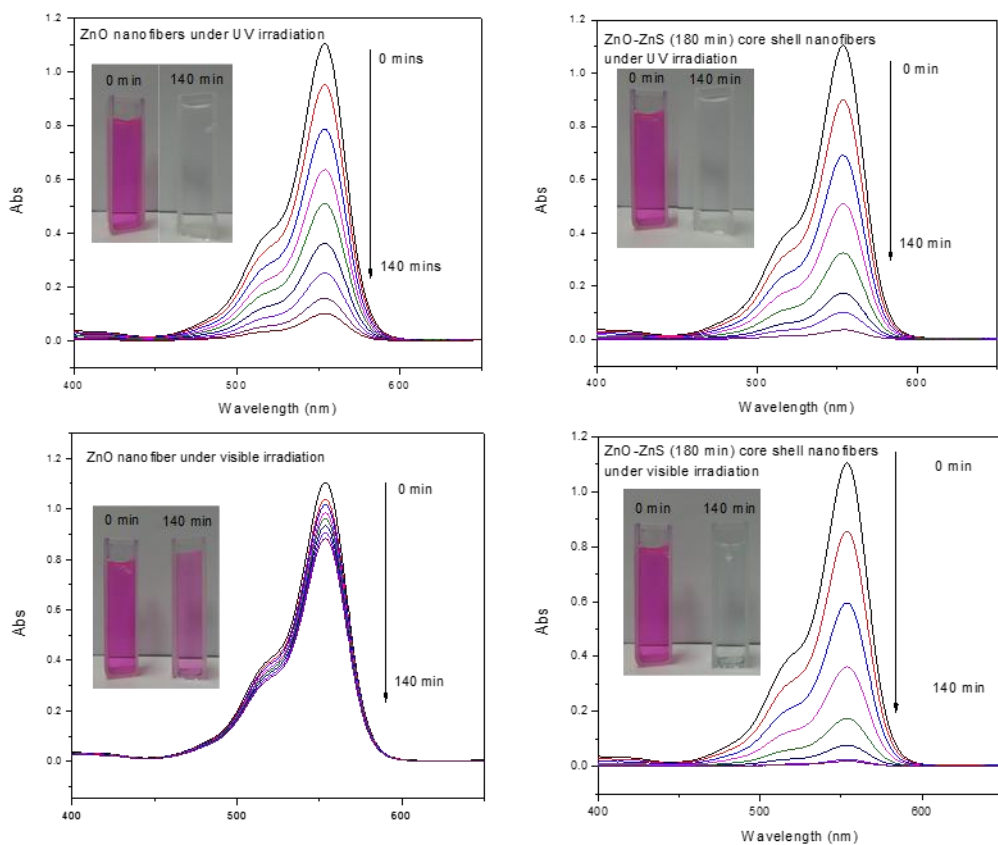


Fig S8 Representative digital photographs and degradation spectrum of Rhodamine B in the presence of ZnO and ZnO-ZnS NF during the photocatalytic measurements under UV irradiation and visible irradiation at different time intervals.

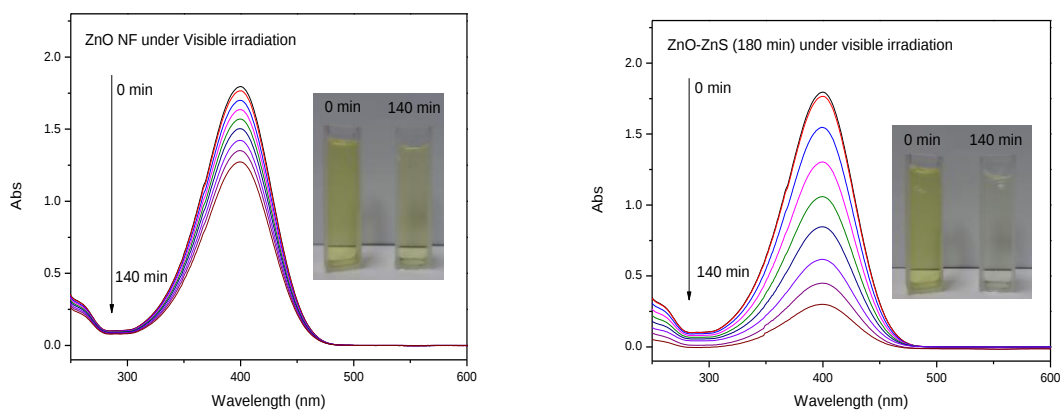


Fig. S9 Representative digital photographs and degradation spectrum of 4-Nitrophenol in the presence of ZnO and ZnO-ZnS NF during the photocatalytic measurements under visible irradiation at different time intervals.

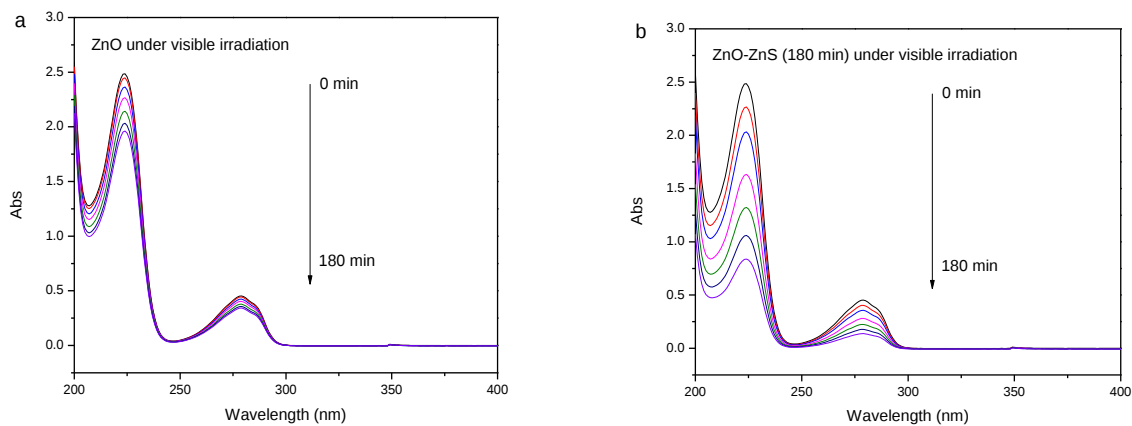


Fig. S10 Degradation spectrum of 4-chlorophenol in the presence of ZnO and ZnO-ZnS NF during the photocatalytic measurements under visible irradiation at different time intervals.

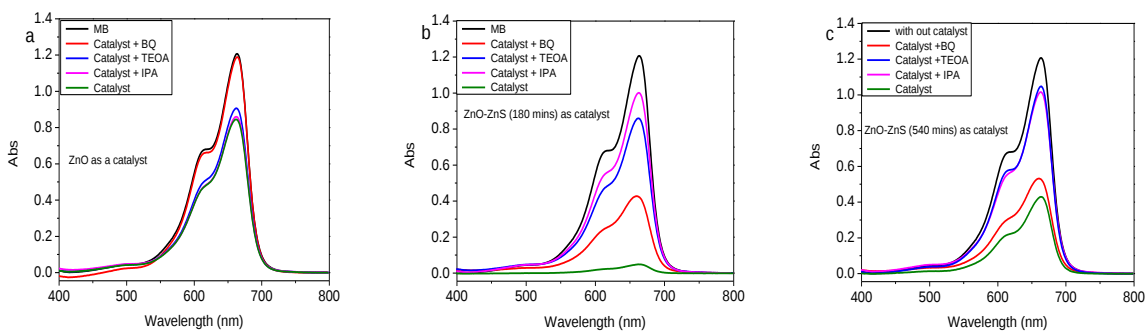


Fig. S11 Optical absorption spectra of aqueous MB solution photocatalytically degraded using ZnO and ZnS core NF under visible light irradiation in the absence and presence of BQ (a quencher of $O_2^\bullet$), IPA (a quencher of $^\bullet OH$), TEOA ((a quencher of h^+). The photocatalytic reactions were carried out for 140 min time. The dotted line represents the initial optical absorption of MB solution before photocatalysis.

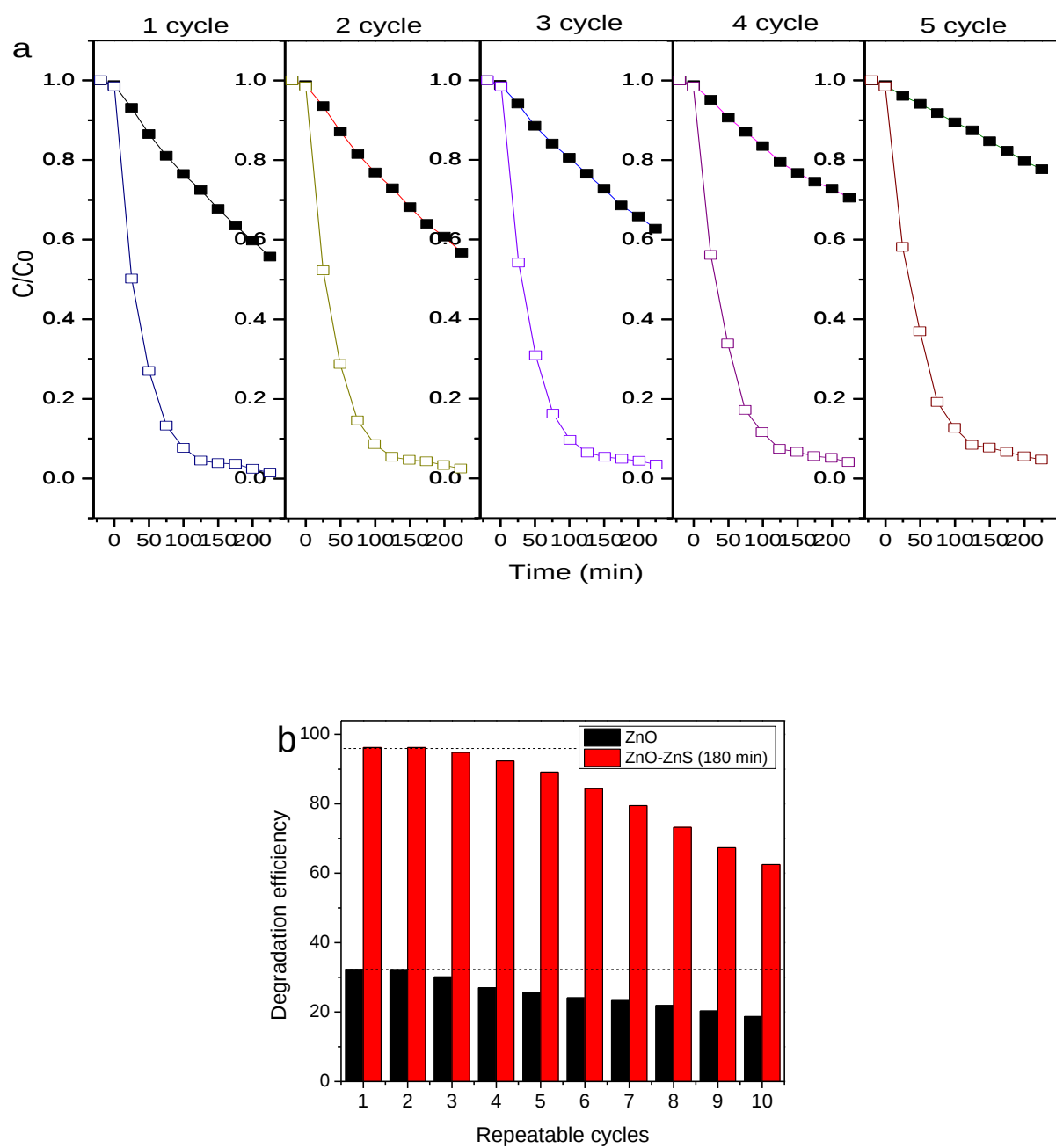


Fig. S12 Recyclic catalytic properties of (a) hierarchical 3h sulfidated ZnO-ZnS core-shell NF and (b) Reusable catalytic performance up ten cycles

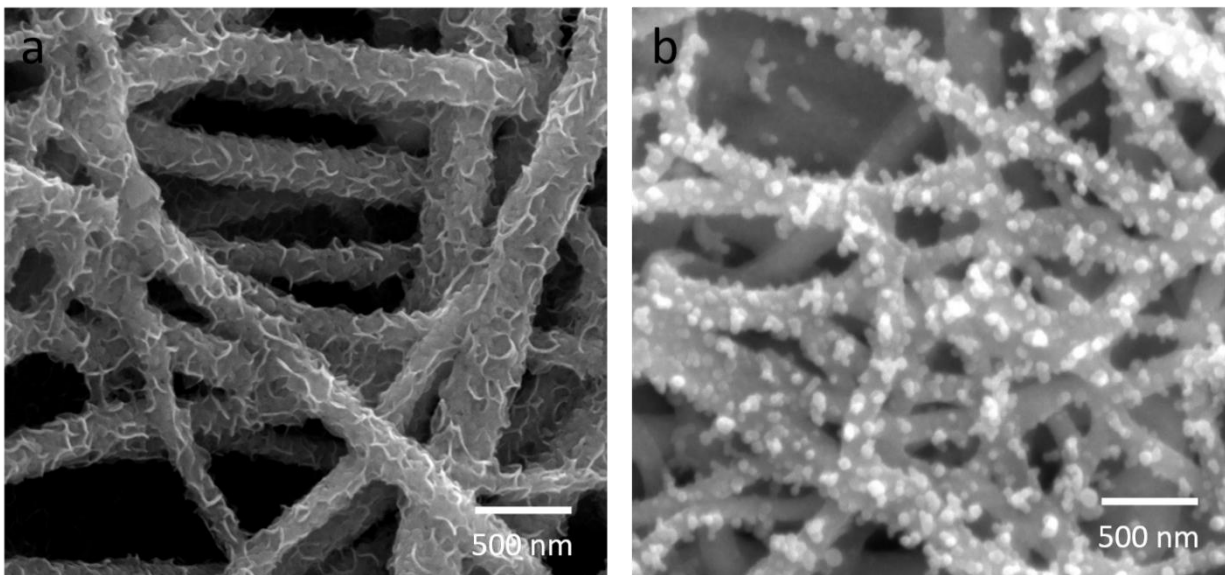


Fig. S13 Representative SEM images of electrospun derived (a) ZnO and (b) ZnO-ZnS (180 mins) core-shell NF after photocatalytic measurements.

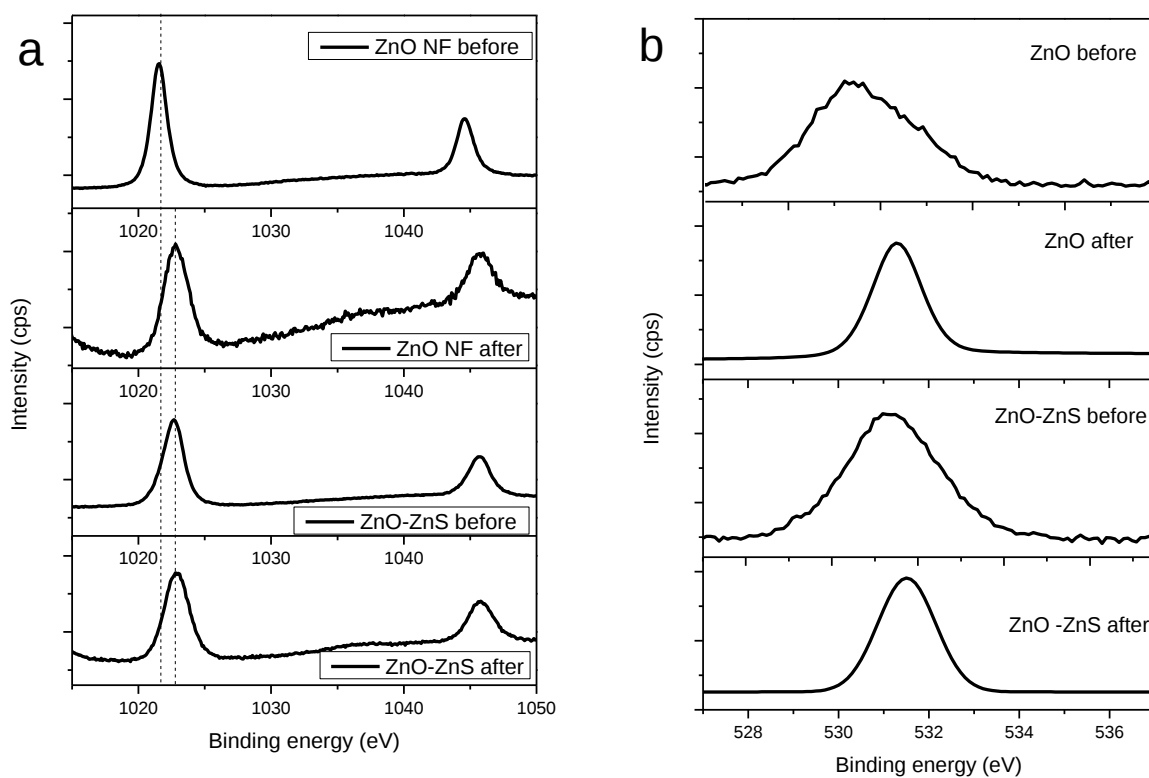


Fig. S14 XPS spectra of Zn 2p (a) and O 1s (b) in pristine ZnO and ZnO-ZnS (180 min) core-shell NF before and after photocatalytic activity.

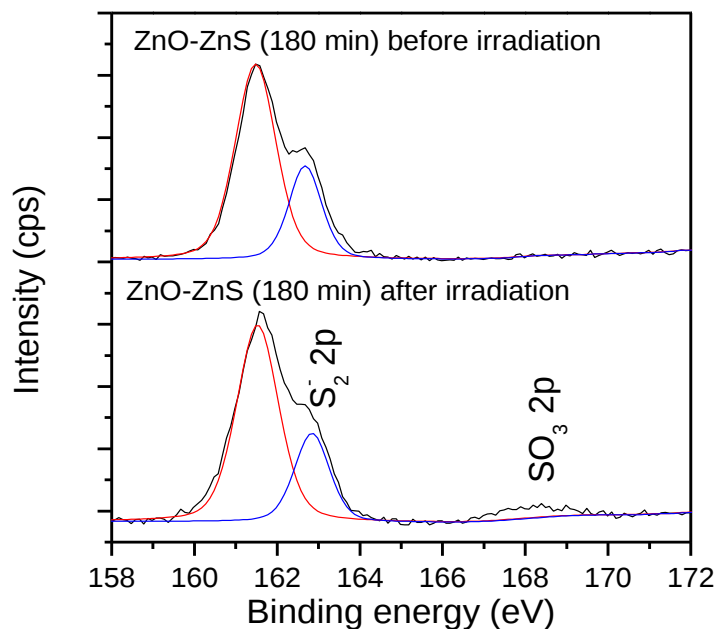


Fig. S15 XPS spectra of S2p of ZnO-ZnS (180 min) core-shell NF before and after photocatalytic activity.

Table S1. XPS results presenting the position and the relative contribution of the Zn, O and S bonding for the shell wall controlled ZnO-ZnS based core-shell NF.

S. No	Samples	Band gap eV	O1s nm	Atomic %	Zn 2p nm	S 2p /SO ₄ ratio
1	ZnO	3.2	OL - 530.1 Ov - 531.1 Ocl- 532.3	67 26 7	2p ^{3/2} - 1021.5 2p ^{1/2} -1044.6	---
2	ZnO-ZnS 0.5h	2.91	OL - 530.1 Ov - 531.1 Ocl- 532.3	64 27 9	2p ^{3/2} - 1021.6 2p ^{1/2} -1044.7	49.21
3	ZnO-ZnS 1.5h	2.65	OL - 530.1 Ov - 531.1 Ocl- 532.3	34 47 19	2p ^{3/2} - 1022.5 2p ^{1/2} -1045.6	19.43
4	ZnO-ZnS 3h	2.62	OL - 530.1 Ov - 531.1 Ocl- 532.3	25 49 24	2p ^{3/2} - 1022.8 2p ^{1/2} -1045.8	14.28
5	ZnO-ZnS 6h	2.91	OL - 530.1 Ov - 531.1 Ocl- 532.3	17 51 32	2p ^{3/2} - 1022.8 2p ^{1/2} -1045.8	11.02
6	ZnO-ZnS 9h	2.95	OL - 530.1 Ov - 531.1 Ocl- 532.3	12 32 56	2p ^{3/2} - 1022.8 2p ^{1/2} -1045.7	8.09

Table S2. Photo responsive properties of shell wall controlled ZnO-ZnS based core-shell NF.

S. No	Hybrid Nano fibers	Shell wall thickness	Band edge absorbance	Degradation efficiency under UV in 140 min ($\lambda = 365$ nm)	Degradation efficiency under Visible in 150 min ($\lambda > 400$ nm)	Degradation Rate (min^{-1}) ($\lambda = 365$ nm)	Degradation Rate ($\lambda > 400$ nm)
1	ZnO	-	387.7 nm	84.64 %	32.27 %	0.0135	0.0028
2	ZnO-ZnS 0.5h	~ 5 nm	418.4 nm	87.37 %	70.21 %	0.0158	0.0091
3	ZnO-ZnS 1.5h	~ 10 nm	457.6 nm	93.78 %	91.58 %	0.0185	0.0155
4	ZnO-ZnS 3h	~ 20 nm	462.7 nm	91.89 %	96.23 %	0.0207	0.0246
5	ZnO-ZnS 6h	~ 40 nm	448.2 nm	83.55 %	80.42 %	0.0127	0.0105
6	ZnO-ZnS 9h	> 60nm	398.2 nm	75.51 %	60.87 %	0.0105	0.0057