Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Acidochromic Fibrous Polymer Composites for Rapid Gas Detection

Maria Erminia Genovese,*[a,b] Elena Colusso,[c] Massimo Colombo,[d] Alessandro Martucci,[c] Athanassia Athanassiou[a] and Despina Fragouli*[a]

[a] *Smart Materials, Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova, Italy. Email: maria.genovese@iit.it; Email: despina.fragouli@iit.it,*
[b] *DIBRIS Department, University of Genova, Viale Causa 13, 16145, Genova, Italy.*
[c] *Department of Industrial Engineering, University of Padova, via Marzolo 9, 35131, Padova, Italy.*
[d] *Department of Nanochemistry, Istituto Italiano di Tecnologia, via Morego 30, 16163, Genova, Italy.*

Electronic Supplementary Information file

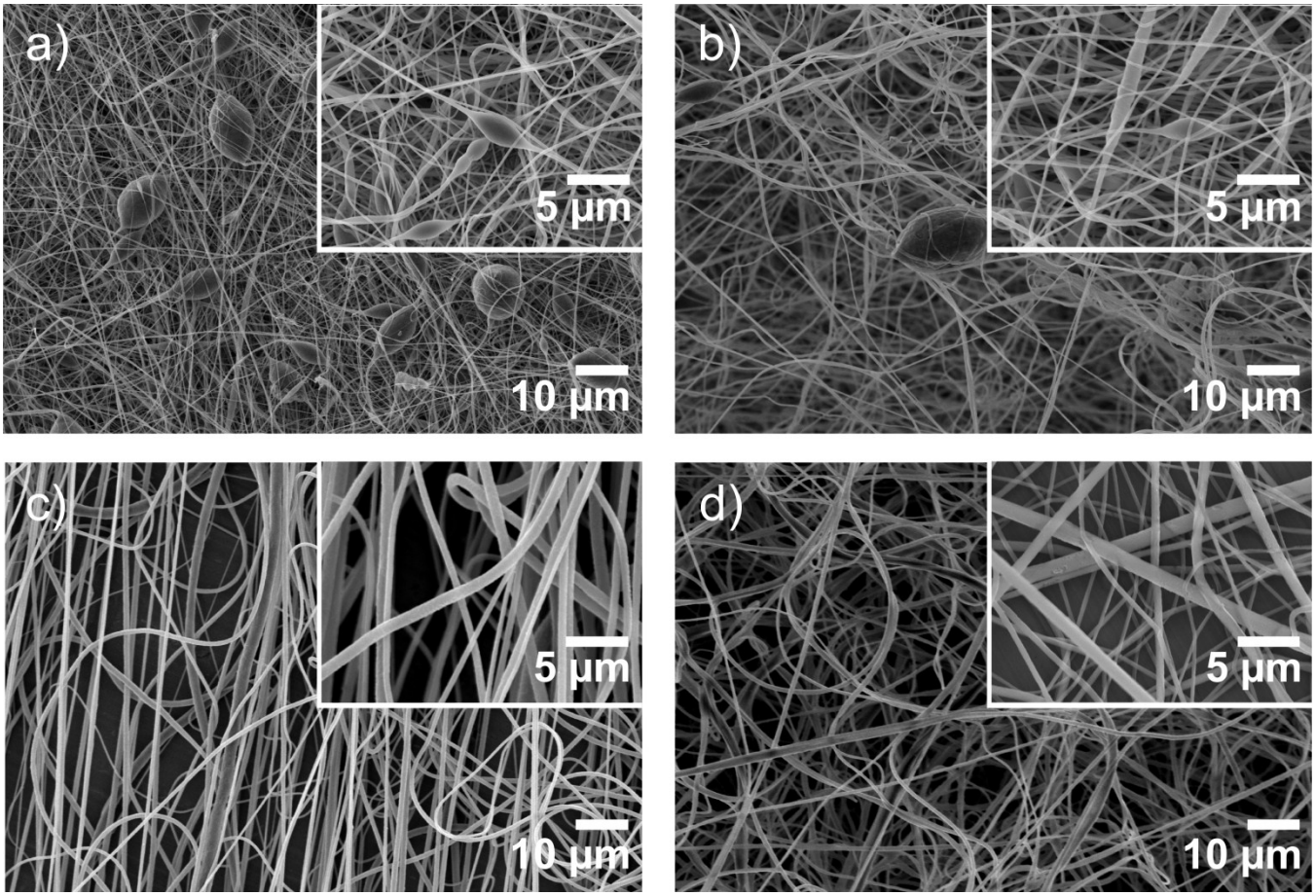

Fig. S1 SEM images at two different magnifications of PVDF-HFP/SP fibers electrospun from a) 20% wt, b) 22% wt, c) 27 % wt, d) 30% wt PVDF-HFP solutions in a 3:1 DMF/acetone mixture.

PVDF-HFP Concentration (%wt)	*Mean Diameter (nm)*	*Standard Deviation (nm)*	*Beads*
20 %	200	±60	yes
22 %	220	±70	yes
25 %	250	±44	no
27 %	402	±70	no
30 %	400	± 92	no
30 %	800	±70	no

Table S1 Effect of the polymer concentration in the electrospinning solution on the morphology of PVDF-HFP/SP fibers.

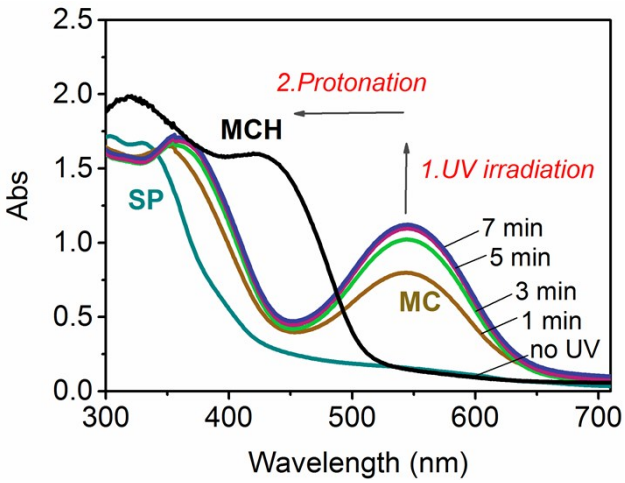

Fig. S2 Absorption spectra of PVDF-HFP/SP composites during progressive irradiation with UV light for 7 minutes. The photoinduced isomerization of SP to MC gives rise to the formation of the absorption peak at 550 nm. The maximal photoconversion to the MC form is reached after 5 minutes of irradiation. Then, within 5 minutes of exposure to acidic vapors of acetic acid all the MC molecules embedded in the films, fibers and nanofibers undergo protonation generating the MCH species with an absorption maximum centered at 420 nm.

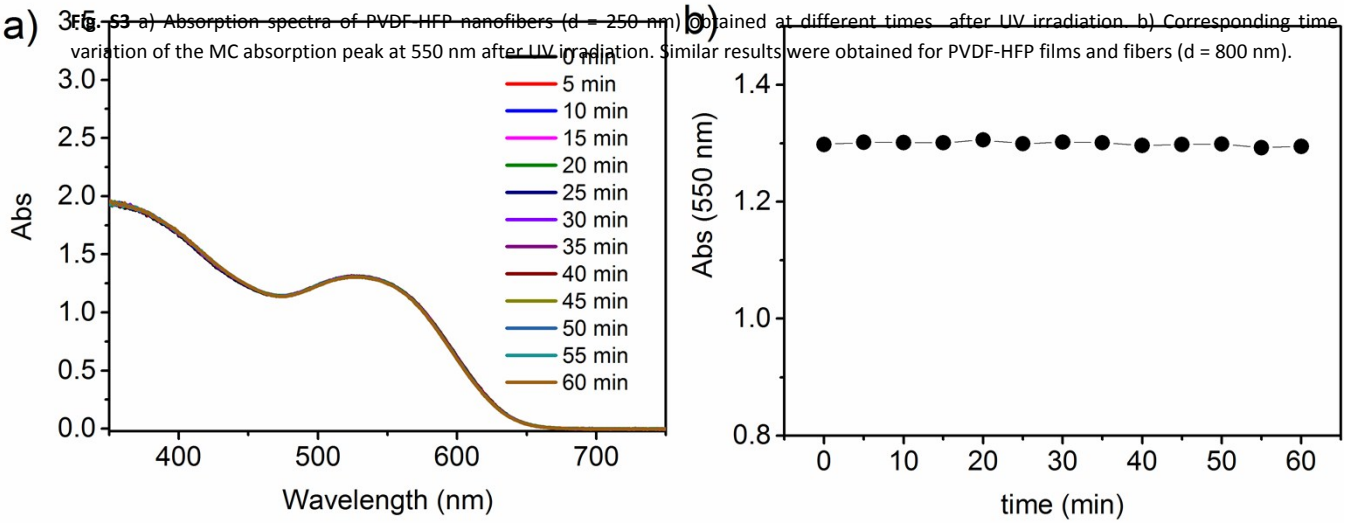

Fig. S3 a) Absorption spectra of PVDF-HFP nanofibers (d = 250 nm) obtained at different times after UV irradiation. b) Corresponding time variation of the MC absorption peak at 550 nm after UV irradiation. Similar results were obtained for PVDF-HFP films and fibers (d = 800 nm).

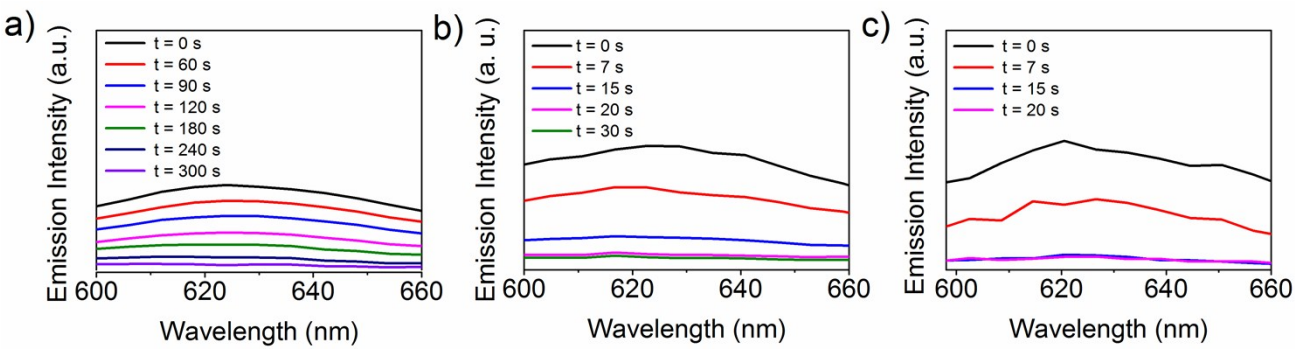

Fig. S4 Spectral variation of a) a PVDF-HFP/SP film b) PVDF-HFP/SP fibers (d = 800 nm) and c) PVDF-HFP/SP nanofibers (d = 250 nm) during protonation with vapors of acetic acid.

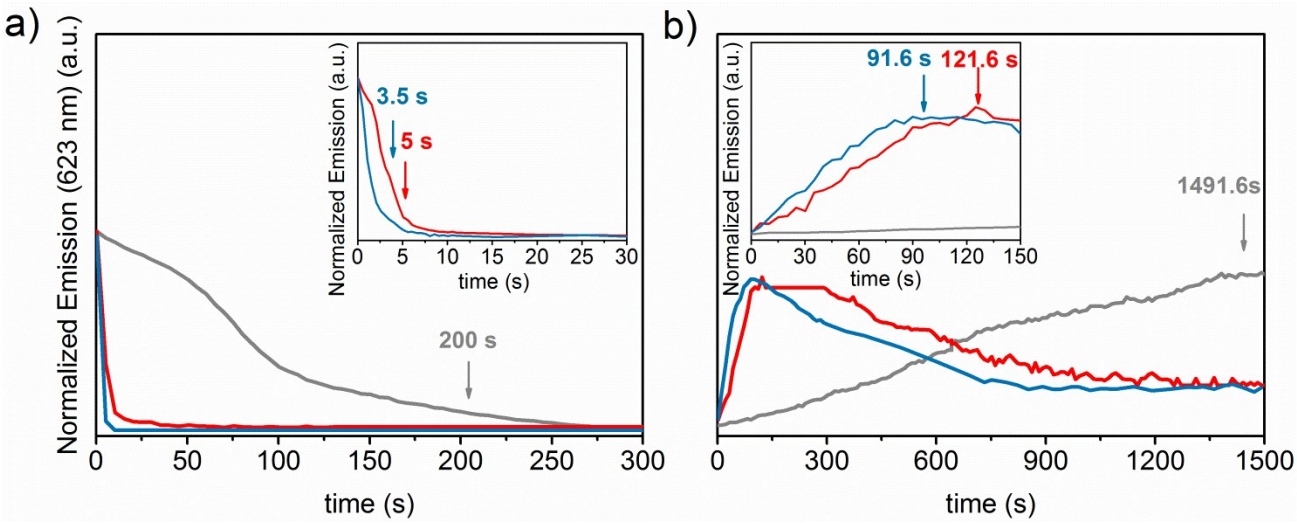

Fig. S5 a) Variation of the emission intensity at 623 nm of PVDF-HFP/SP film (grey line), d = 800 nm fibers (red line) and d = 250 nm nanofibers (blue line) during protonation with formic acid. Insets: zoom-in of the emission intensity up to 30s. b) Variation of the emission at 623 nm of PVDF-HFP/SP film (grey line), d = 800 nm fibers (red line) and d = 250 nm nanofibers (blue line) upon spontaneous deprotonation of MCH generated by exposure to formic acid. Inset: zoom-in of the emission intensity up to 150 s.

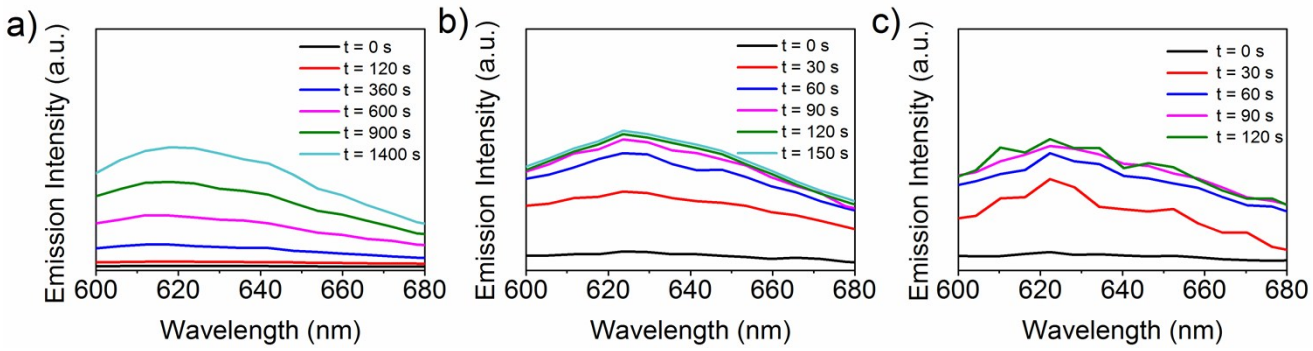

Fig. S6 Spectral variation of a) a PVDF-HFP/SP film b) PVDF-HFP/SP fibers (d = 800 nm) and c) PVDF-HFP/SP nanofibers (d = 250 nm) during spontaneous recovery of the MC species after protonation with vapors of acetic acid.

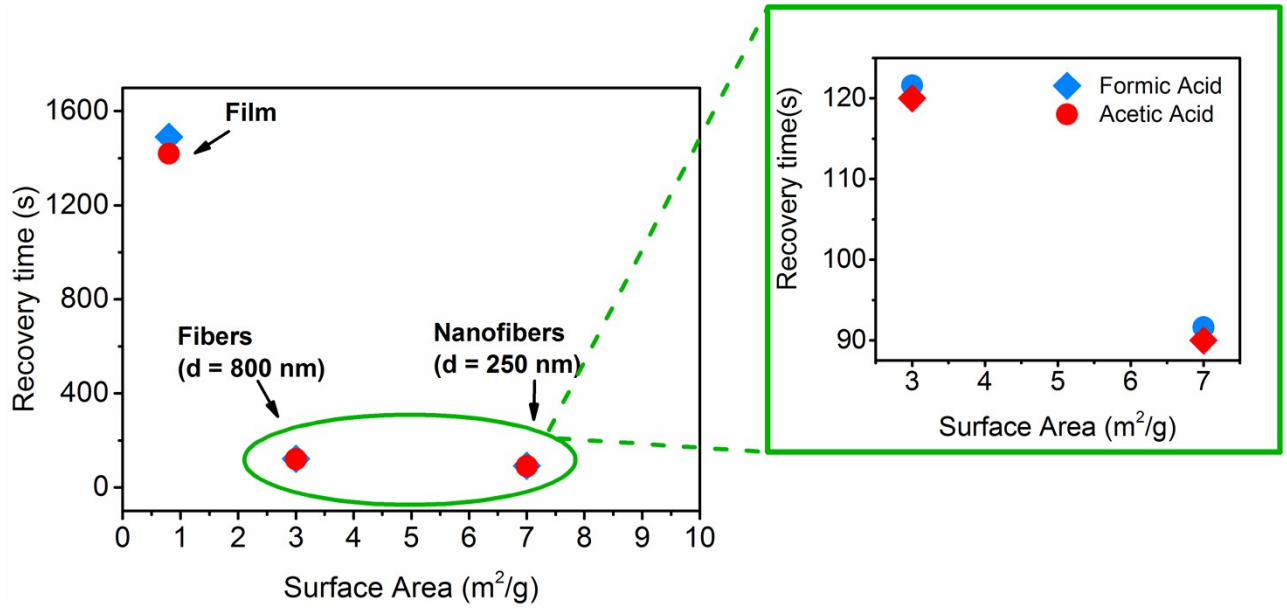

Fig. S7 Recovery time of MC emission intensity at 623 nm upon spontaneous desorption of acidic vapors of formic (blue diamonds) and acetic acid (red dots) as a function of the specific surface area for a PVDF-HFP/SP film and PVDF-HFP/SP d = 800 and d = 250 nm fibrous mats . Inset: zoom-in of the recovery time between 87 and 125s as a function of the surface area.

Sample Name	*BET Area [m²/g]*	*Correlation Coefficient of BET fit*
PVDF-HFP/SP Film	0.826	0.9987
PVDF-HFP/SP Nanofibers (d=250nm)	7	0.9997
PVDF/HFP/SP Fibers (d = 800nm)	3.4	0.9999

Table S2 Specific surface area determination through Brunauer- Emmett- Teller (BET) measurements for PVDF-HFP/SP film fibers and nanofibers.

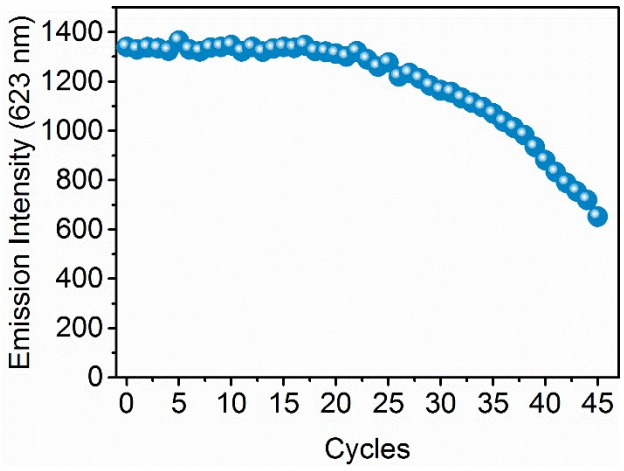

Fig. S8 Irradiation of PVDF-HFP/SP nanofibers (d = 250 nm) at λ = 560 nm with an energy of 2.6 x 10^{-4} mJ/μm² on a spot area of 0.12 μm² for 45 cycles of 120 s. In each cycle, the sample was kept in the dark and exposed to green light twice, at t = 30 s and, after 90 s, at t =120 s in each cycle, to replicate the experimental conditions of cyclical protonation and recovery.

Material	*Fabrication method*	*Response time*	*Recovery time*	*Operating Temperature*	*Recovery Temperature*	*Reusability*
ZnO nanoparticles layer on ceramic[1]	Isothermal evaporation and thermal treatment at 400 °C	70 s	200 s	300° C	300° C	6 cycles
PDMS/SP film[2]	Film casting	>10 min	300 s	rt	120 °C	4 cycles
Multisensor array of Solvatochromic dyes embedded in polymers[3]	Spin-coating on optic fiber	25 s	30 s	rt	rt	-
Silicone/Phtalocyanine film[4]	Dip-coating on glass slides	180 s	A few hours	rt	rt	-
α-Fe_2O_3 hollow nanotubes layer on alumina[5]	Soakage process and calcination at 600°C	18 s	4 s	350 °C	350 °C	4 cycles
Y-doped SnO_2 nanoparticles layer on ceramic[6]	Electrospinning and calcination at 600°C	7 s	11 s	300° C	300 °C	-
Ni^{2+} doped ZnO nanoroads layer on alumina[7]	Solvothermal method	4s	27 s	310°C	310 °C	-
PVDF-HFP/SP film	Film casting	300 s	1420 s	rt	rt	>20 cycles
PVDF-HFP/SP fibers (d = 800 nm)	Electrospinning	20 s	120 s	rt	rt	>40 cycles
PVDF-HFP/SP nanofibers (d = 250 nm)	Electrospinning	15 s	90 s	rt	rt	>40 cycles

Table S3 Properties of acetic acid gas sensors reported in the literature. Rt indicates room temperature, the symbol (-) refers to missing information in the references. For the sake of clarity the properties of the systems prepared in this study are also presented in the last three lines (shaded).

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