

Supplementary Materials: New insights in the ion beam sputtering deposition of ZnO-fluoropolymer nanocomposites

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Eq. S1. Detail of φ calculation. V_{PTFE} and V_{ZnO} are the deposited volumes of PTFE and ZnO, and r_{PTFE} and r_{ZnO} are the deposition rates of the two materials, experimentally measured for any deposition run and expressed as film thickness per second.

$$\varphi = \frac{V_{ZnO}}{V_{PTFE} + V_{ZnO}} = \frac{r_{ZnO}}{r_{PTFE} + r_{ZnO}} = \frac{r_{ZnO}/r_{PTFE}}{1 + (r_{ZnO}/r_{PTFE})} \quad (s1)$$

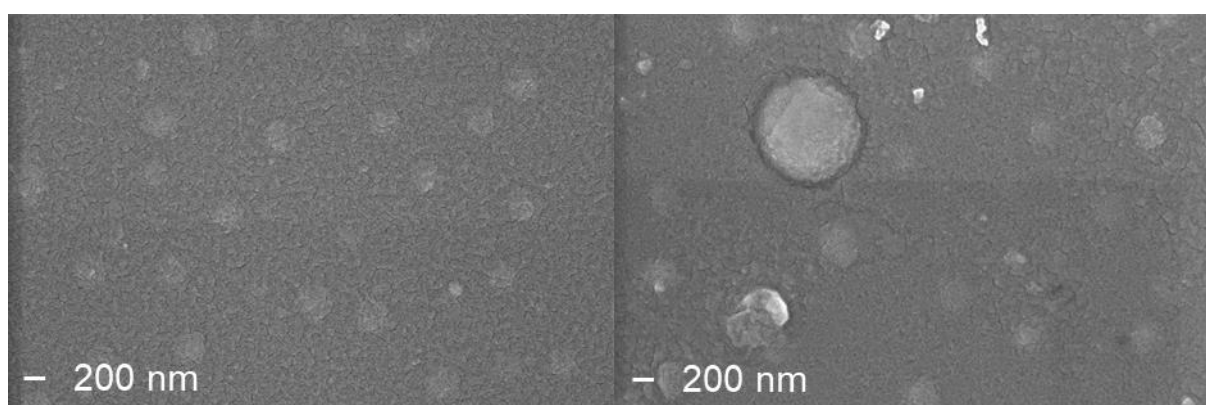


Figure S1. 150-nm-thick ZnO-CFx composite films were morphologically characterized by SEM analysis, at 30 kV with a Hitachi SEM-FEG 5000 microscope on gold-coated sample.

Table S1. Relative abundances (%) of different carbon moieties, derived from the C1s curve-fitting, as a function of φ .

Φ	CF ₃	CF ₂	CF, COOH	CF=C, C=O	C-CF, C-OH ¹	C-C
0.05	10.5 ± 0.3	29.4 ± 0.5	16.7 ± 0.4	9.6 ± 0.9	/	11.1 ± 0.3
0.10	20.6 ± 0.5	11.7 ± 0.4	6.7 ± 0.9	4.1 ± 0.2	6.9 ± 0.2	50.0 ± 1.3
0.15	3.9 ± 1.1	6.0 ± 1.5	8.9 ± 0.2	9.8 ± 1.0	39.7 ± 2.2	31.7 ± 1.8

¹ For a metal oxide volume fraction of $\varphi = 0.05$ this ambiguous component is present as two distinct chemical environments, centered at 286.4 ± 0.2 eV (C-OH) and 287.4 ± 0.2 eV (C-CF), whose relative abundances are 6.3 ± 0.2 and 16.4 ± 0.4 , respectively.

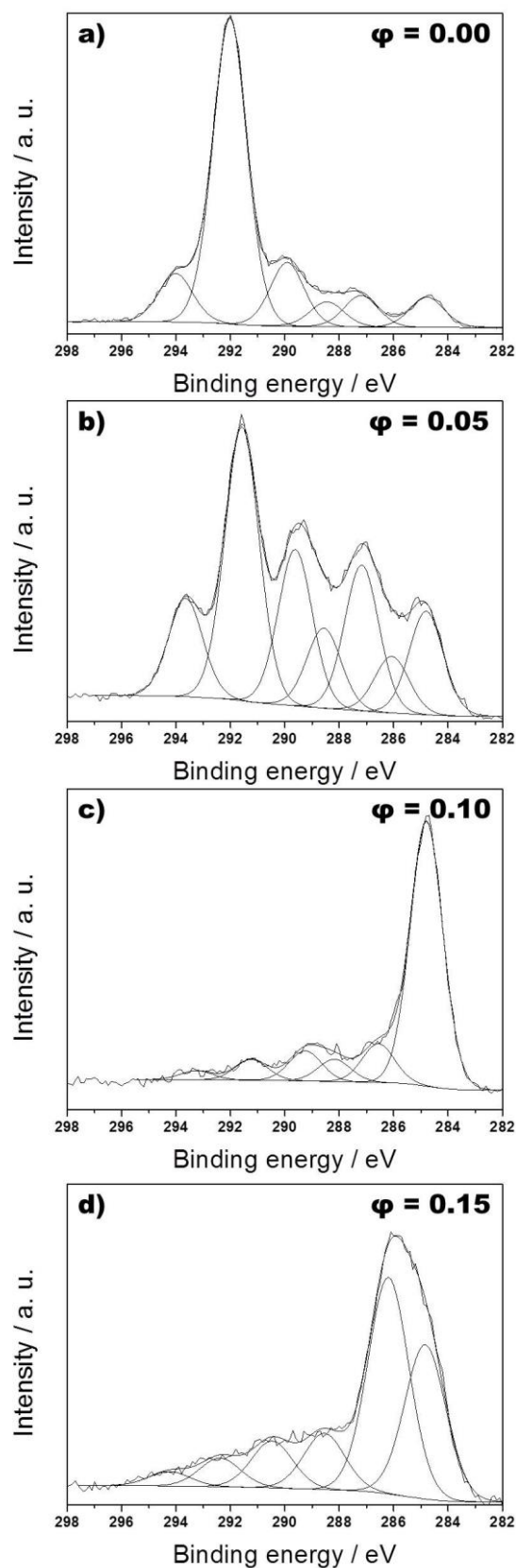


Figure S2. C1s XP-high resolution regions of ZnO-CFx nanocomposites having an inorganic phase volume fraction $\varphi = 0$ (a), $\varphi = 0.05$ (b), $\varphi = 0.10$ (c), and $\varphi = 0.15$ (d).

Details on C1s XP spectral deconvolution

The first two components from the left-side of each spectra, falling at 293.8 ± 0.2 eV and 291.8 ± 0.1 eV, were attributed to $-\text{CF}_3$ chain-terminations and $-\text{CF}_2$ groups, respectively. Their intensity decreased significantly as φ increased. The spectral region falling at lower BE values comprised several peaks, with equivocal attribution. Both fluorinated and oxygenated species were expected to contribute to them. The peak at 289.6 ± 0.2 eV was attributed to $-\text{CF}$ functionalities or to carboxyl moieties. Unsaturated fluorinated carbon ($\text{CF}=\text{C}$) and carbonyl groups were both responsible for the peak centered at 288.0 ± 0.3 eV (the presence of large amounts of $\text{C}=\text{O}$ groups is confirmed by the analysis of the $\text{O}1\text{s}$ region, data not shown). Fluorine- α -substituted carbon ($\text{C}-\text{CF}$) and alcohol groups ($\text{C}-\text{OH}$) well accounted for the peaks at 287.2 ± 0.3 eV and 286.3 ± 0.2 eV. Finally, the component at 285.1 ± 0.2 eV had a double nature, too: it was attributed to unsubstituted carbons in a quaternary fluorinated environment ($\text{C}-\text{C}$) and to adventitious hydrocarbon contaminants. All these attributions are in agreement with literature [1–4].

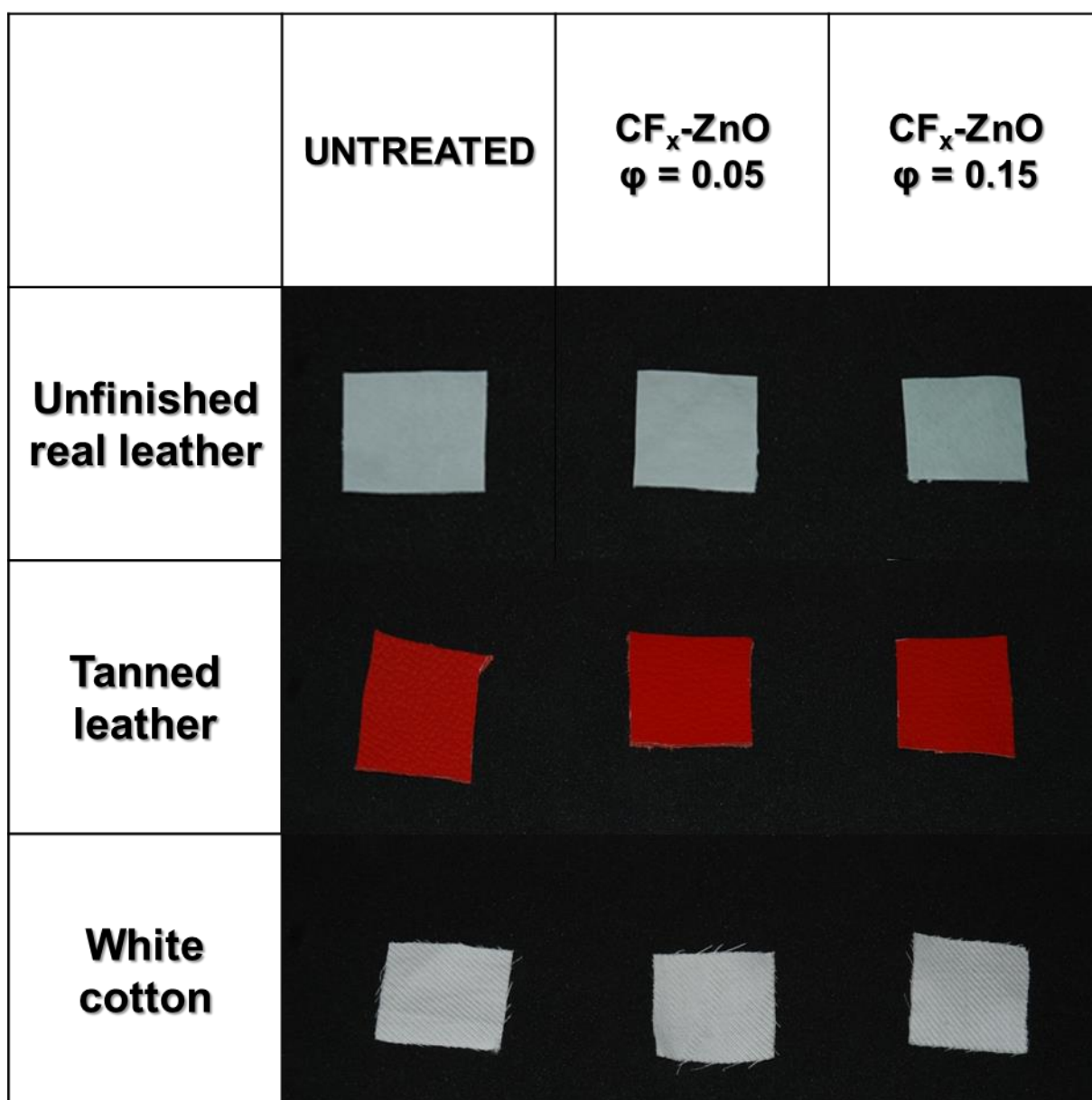


Figure S3. Real textile materials modified with ZnO-fluoropolymer nanocomposites at different inorganic loading.

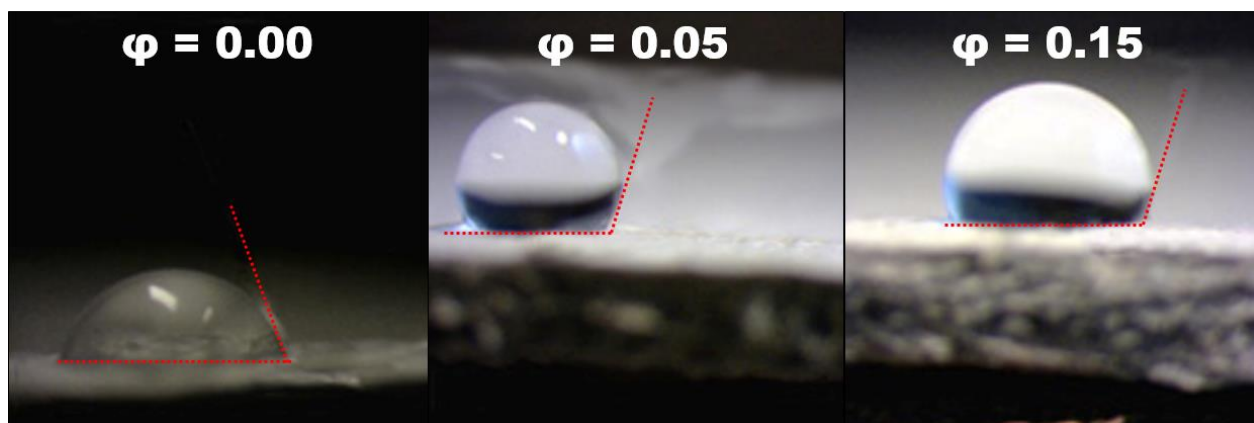


Figure S4. Water contact angle measurement on unfinished real leather modified with ZnO-fluoropolymer nanocomposites at different inorganic loading. Measured values are: $69.5 \pm 0.5^\circ$ at $\varphi = 0$, $114.1 \pm 0.5^\circ$ at $\varphi = 0.05$, and $103.5 \pm 0.5^\circ$ at $\varphi = 0.15$.

References

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3. NIST XPS Database Available online: <http://srdata.nist.gov/xps> (accessed on 3 December 2017).
4. Cioffi, N.; Ditaranto, N.; Torsi, L.; Picca, R. A.; Sabbatini, L.; Valentini, A.; Novello, L.; Tantillo, G.; Bleve-Zacheo, T.; Zambonin, P. G. Analytical characterization of bioactive fluoropolymer ultra-thin coatings modified by copper nanoparticles. *Anal. Bioanal. Chem.* **2005**, *381*, 607–616, doi:10.1007/s00216-004-2761-4.