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

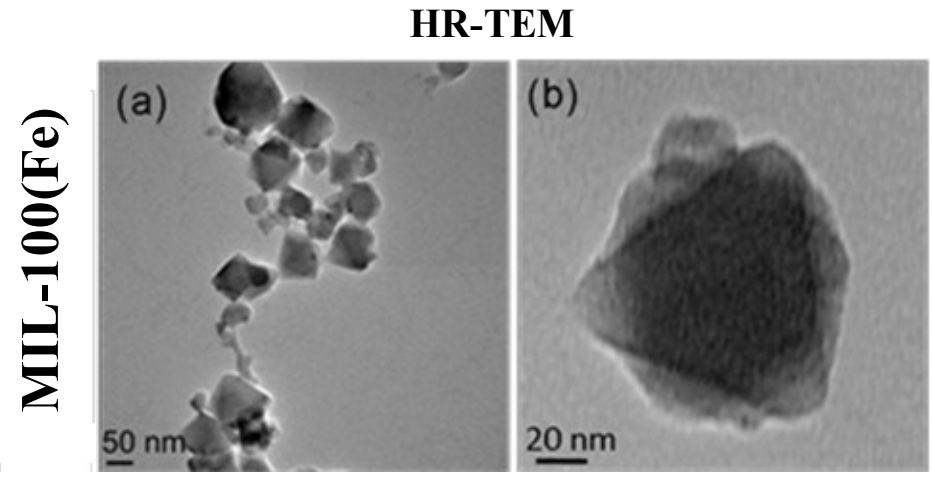

Figure S1. HR-TEM images of MIL-100(Fe) NPs. The scale bar corresponds to (a) 20 µm and (b) 50 µm.

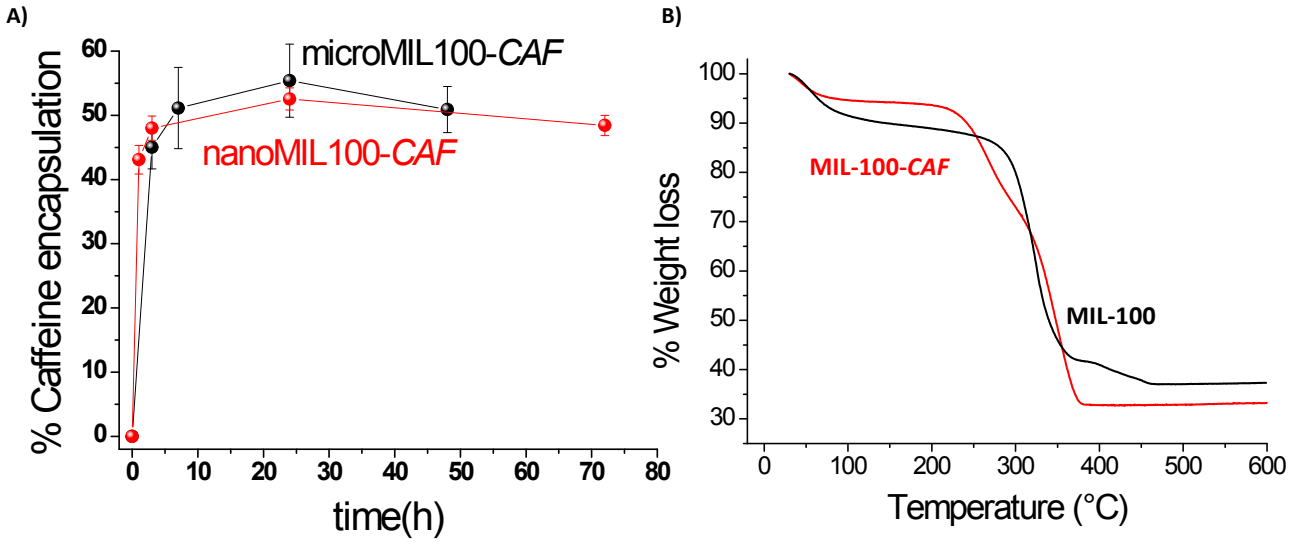

Figure S2. A) Kinetics profile of the caffeine encapsulation in both the micrometric (black) and nanometric MIL-100 (red) particles; B) TGA plots of the MIL-100 nanoparticles before (black) and after caffeine encapsulation (red).

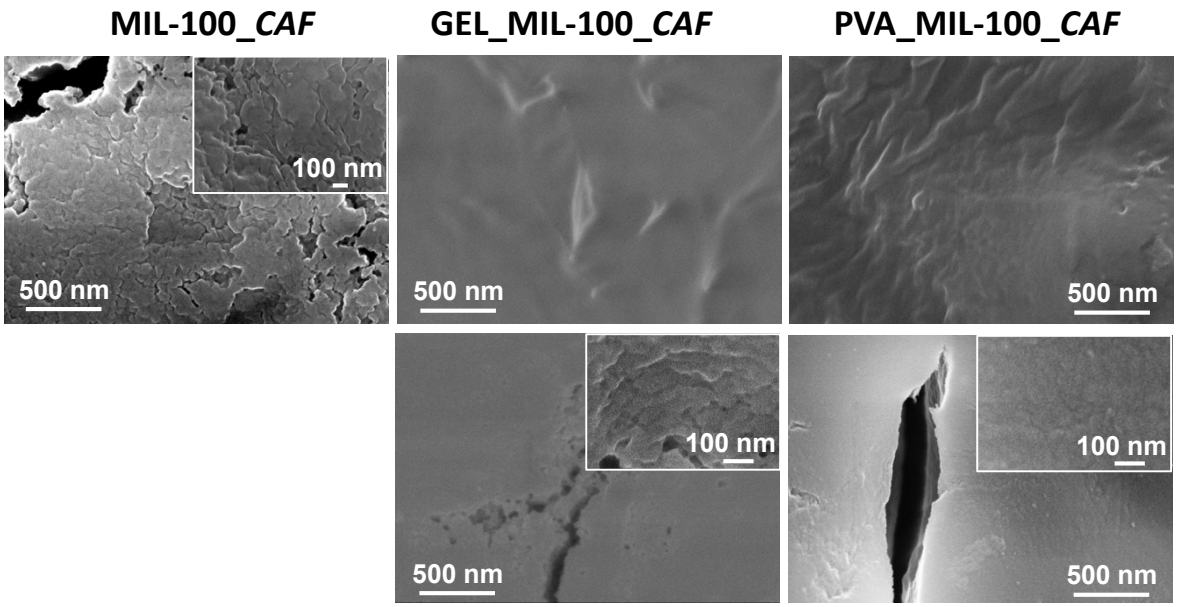

Figure S3. FEG-SEM images of the MIL-100_*CAF*, GEL_*CAF*, PVA_*CAF*, GEL_MIL-100_*CAF* and PVA_MIL-100_*CAF* patches.

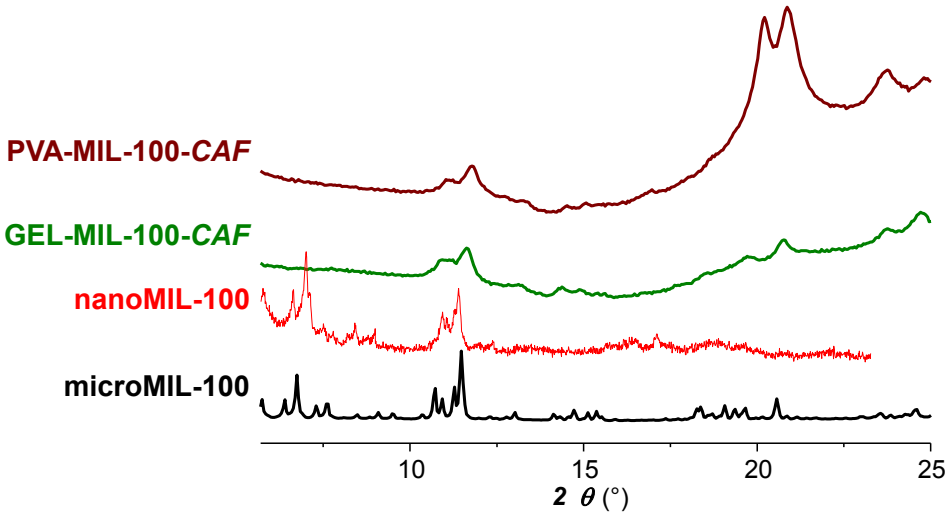

Figure S4. XRD patterns of the GEL_MIL-100_CAF and PVA_MIL-100_CAF patches, together with the free caffeine and the caffeine encapsulated micro and nanoparticles of MIL-100. XRD were collected in a D8 Advance Bruker diffractometer with Cu Kα1 radiation (λ = 1.54056 Å) from 3 to 25º (2θ) using a step size of 0.02º and 2.5 s per step in continuous mode.

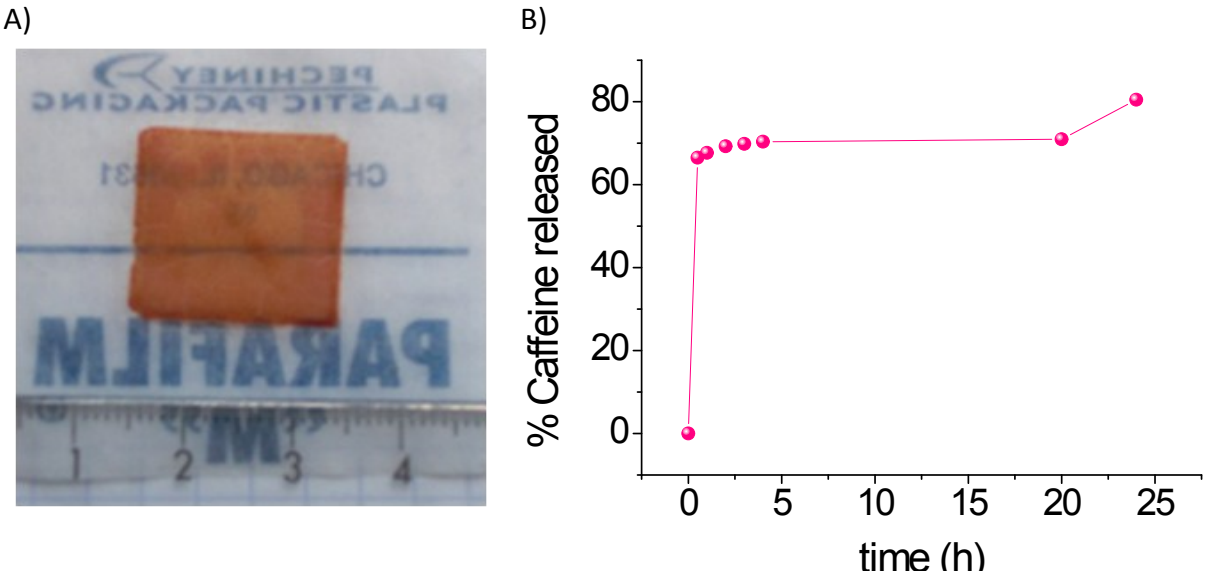

Figure S5. Image of a drop casted caffeine-containing MIL-100 patch (on the left) as well as the caffeine release during the drop casting (on the right).

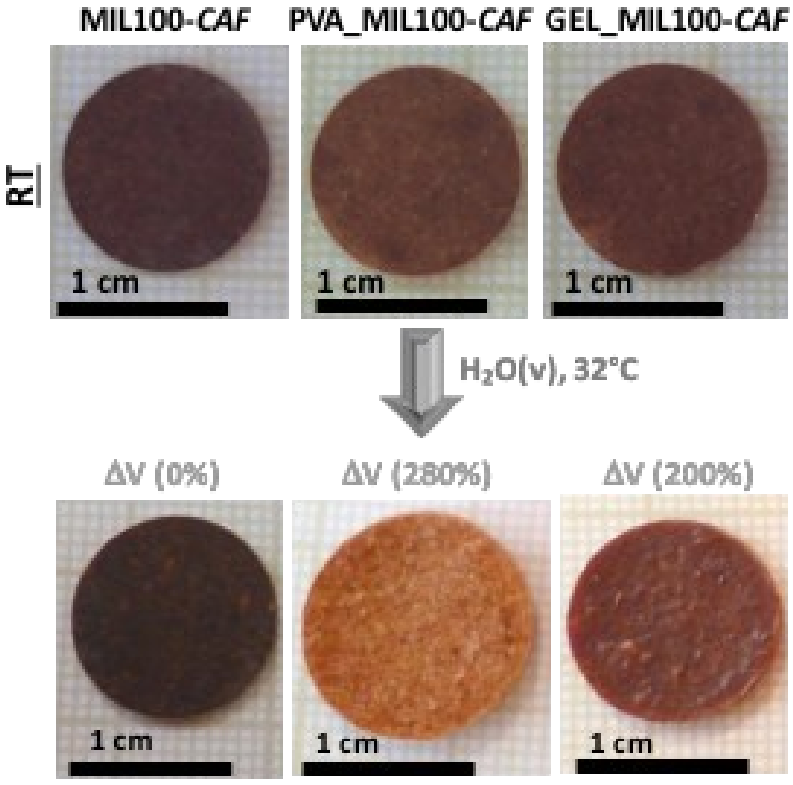

Figure S6. Optical images of the patches before and after the water adsorption.

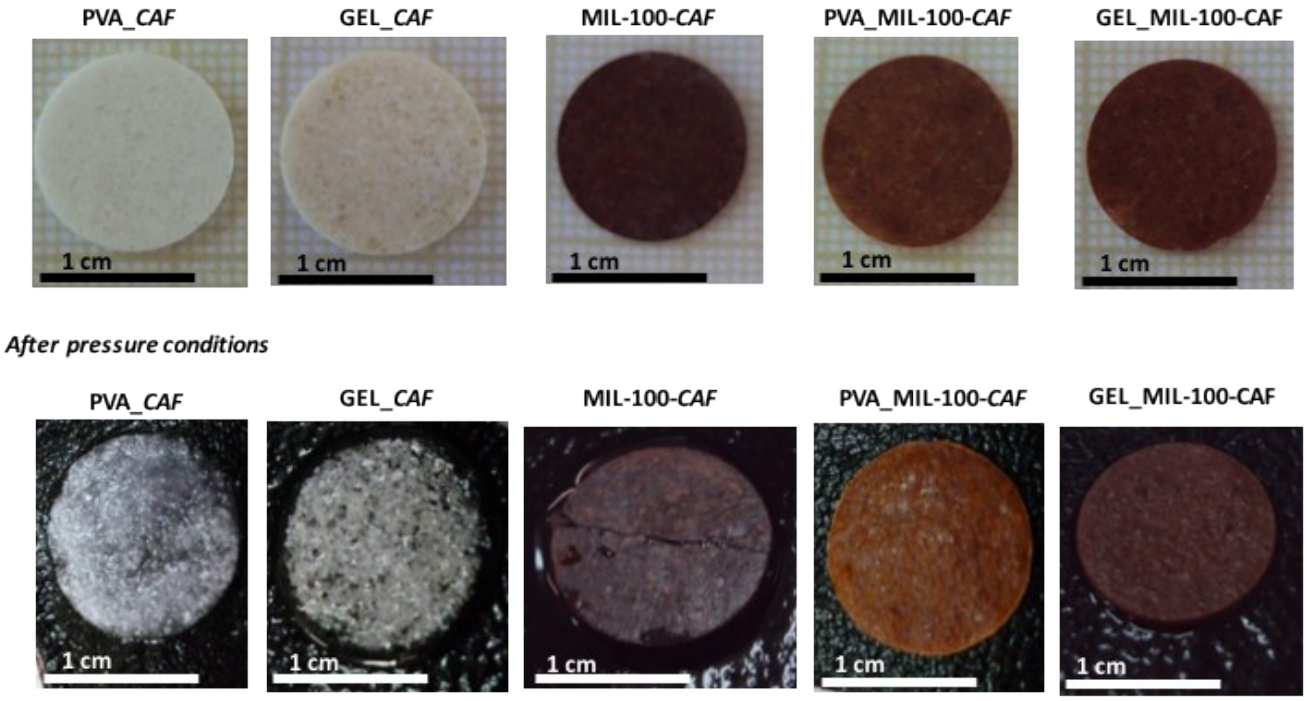

Figure S7. Macroscopic images of the patches before and after the bioadhesion measurements.

Table S2. Bioadhesive strength values.

Patch	Peak detachment force (N.seg)
GEL_ MIL-100-*CAF*	0.0015 ± 0.0005
PVA_ MIL-100-*CAF*	0.0022 ± 0.0015
GEL-*CAF*	0.0037 ± 0.0026
PVA-*CAF*	0.0016 ± 0.0005
MIL-100-*CAF*	0.0035 ± 0.0005

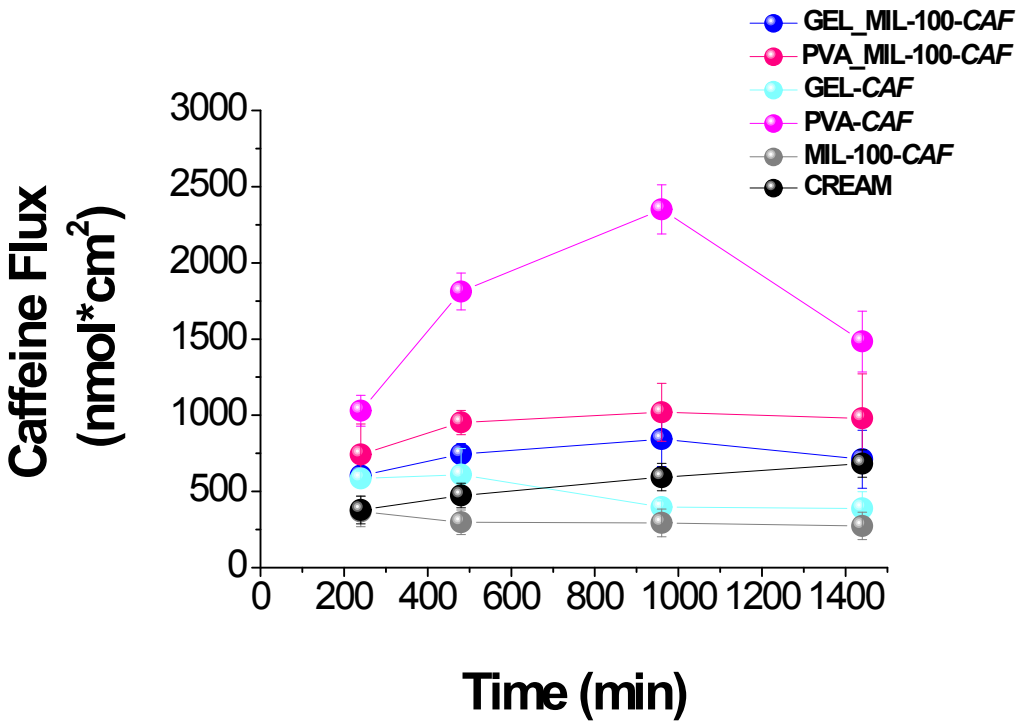

Figure S8. Average values of caffeine diffusion flow (J; nmol· cm^{-2}· min^{-1}) from the caffeine-containing and commercial cream patches *vs.* time.

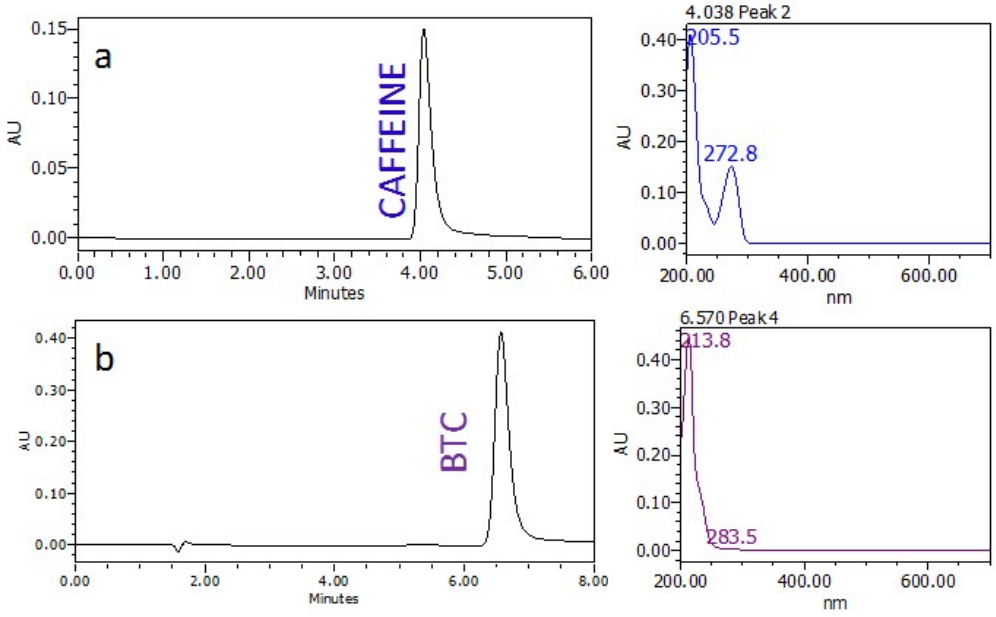

Figure S9. Chromatograms (left) and UV-Vis spectra (right) of caffeine (a) and BTC (b). Chromatogram of standard solutions showed a retention time of 4.0 and 6.5 min, corresponding to caffeine and BTC, respectively, as confirmed by their characteristic UV-Vis spectra (absorption maximum at 272 and 210 nm, respectively).

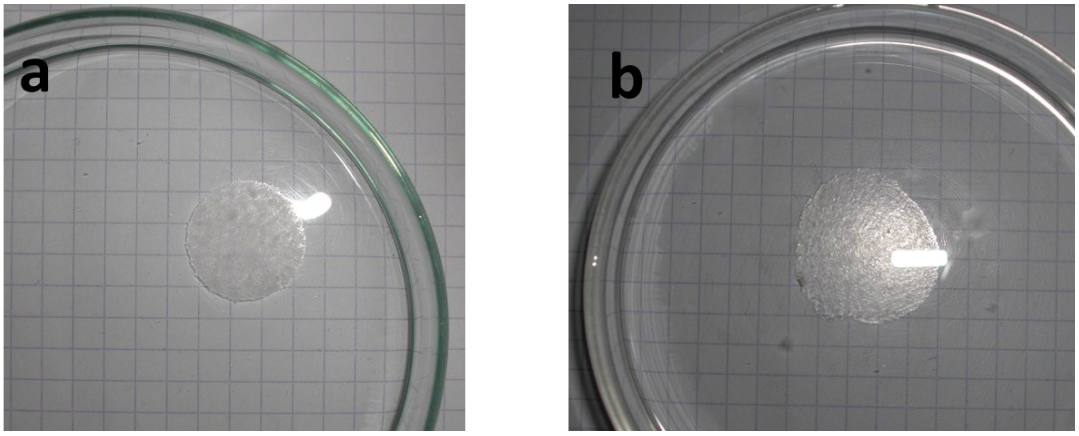

Figure S10. Press molded PVA wafer after different times. a) two days; b) one week