Supplementary Material

A *bottom-up* route for the preparation of novel hierarchical nanostructured hybrid Molybdenum oxide-hydrogel composites.

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1. Experimental Section

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1. Experimental Section

All reagents were obtained from commercial sources and used without further purification. The FT-IR spectra were recorded on a Nicolet Magna-IR 560 spectrophotometer from KBr discs using mixture of the composites with KBr (ratio 5:95).

Cross-linked hybrid hydrogels were prepared as cylindrical rod shape via free radical polymerization from solutions bearing dissolved monomer (acrylamide or acrylic acid; 1.000g), MBA as cross-linking agent (MBA: *N,N*-Methylenebisacrylamide 1 wt%) and $Na_2MoO_4{\cdot}2H_2O$ at different amounts (2.5, 5.0, 7.5 and 10 wt%). The radical polymerizations were initiated by addition of $(NH_4)_2S_2O_8$ under controlled temperature (1 wt%). Typically, the following components were added sequentially to the test tube: Acrylic monomer (Acrilamide or Acid acrylic: 1g); 10 mg cross-linking; sodium molybdate at different percentages (25, 50, 75, 100 mg); 10 mg of initiator. Each component was added and previously dissolves in 0.7 mL of distilled water. The resultant hydrogels were cut into discs of *ca* 2-3 mm thick and dried under vacuum, at 40°C, until constant weight was reached.

Swelling studies were carried-out using xerogel disks, which were swollen in distilled water at different time period until to reach equilibrium in a thermostatic vessel at 25°C. The swelling capacity is defined as $Q = (m\text{-}m_o)/m_o$, where m is the mass of the wet sample at time t and m_o is the mass of the xerogel discs

The porous structure of some hydrogels was examined using a Phillips XL30 Scanning Electronic Microscopy (SEM) with an EDX detector. Transmission Electron Microscopy (TEM) was performed using a JEOL JEM 2100 operating at an acceleration voltage of 200 kV.

PXRD patterns were recorded on Phillips Diffractometer with Cu(Kα) (1.5418 Å) radiation, with a scan speed of 1 deg/min.

The EPR spectra were measured in the X band EMX BRUKER spectrometer, at room temperature and 250K for the reduced and oxidised samples.

Figure S1. Optical photograph of PAAm-Mo (a) and PAAc-Mo composites as-synthesised (b-c).

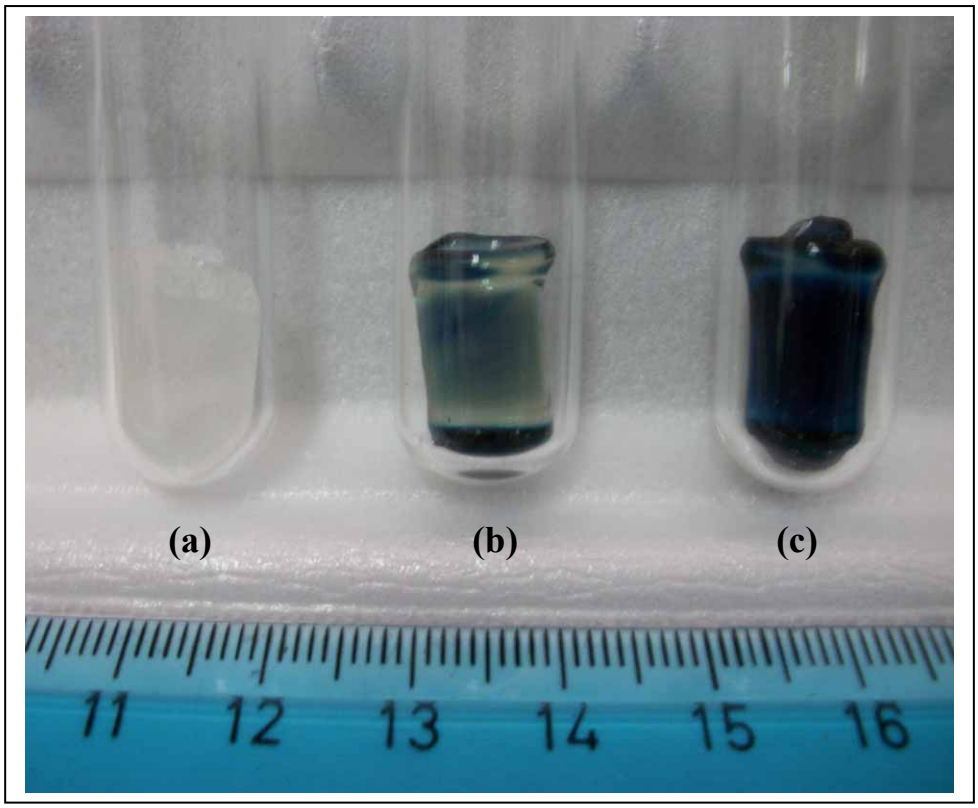
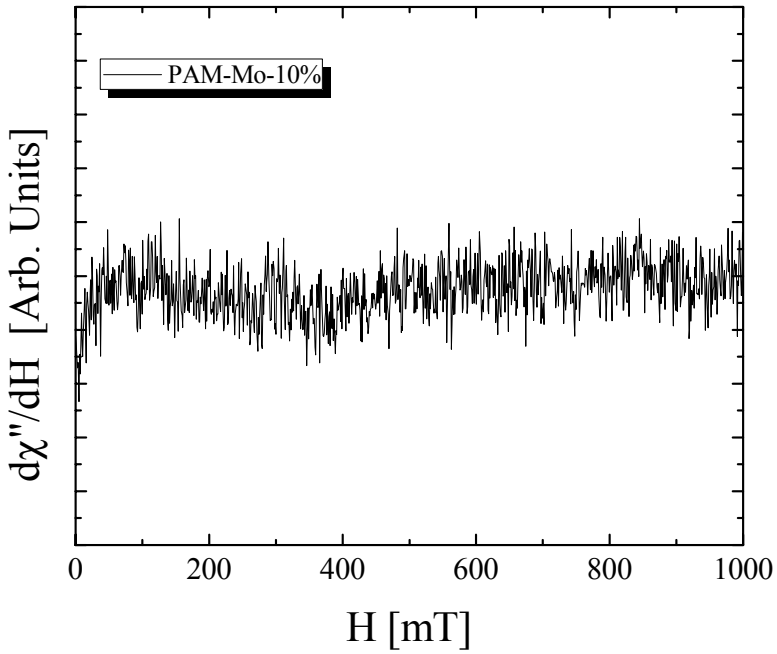
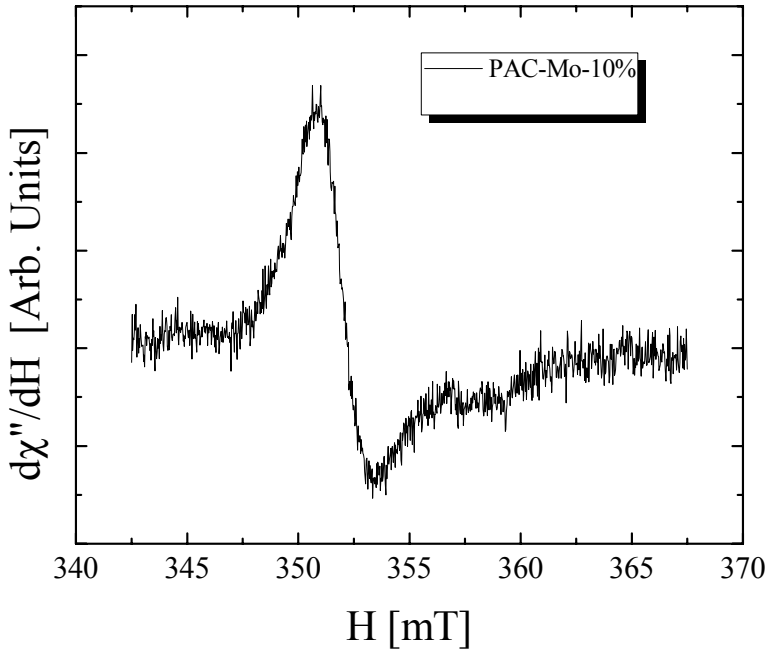


Figure S2. Representative EPR spectra of PAAm-Mo-10% and PAAc-Mo-10% composites as-synthesised (a-b).

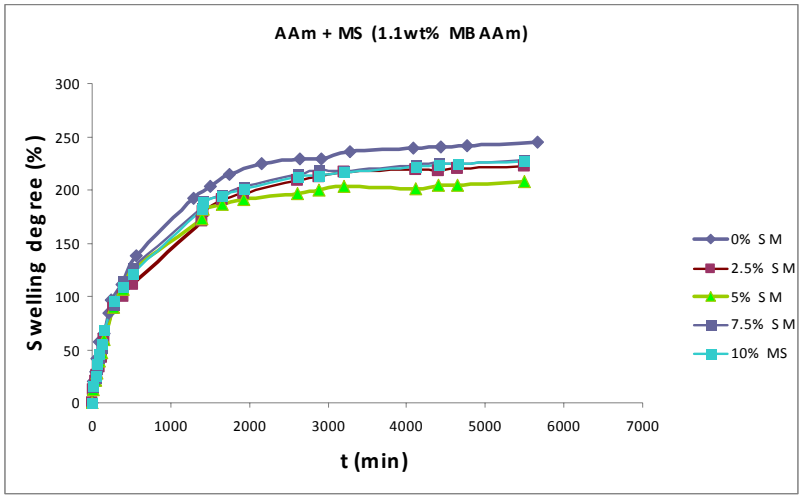


(a)

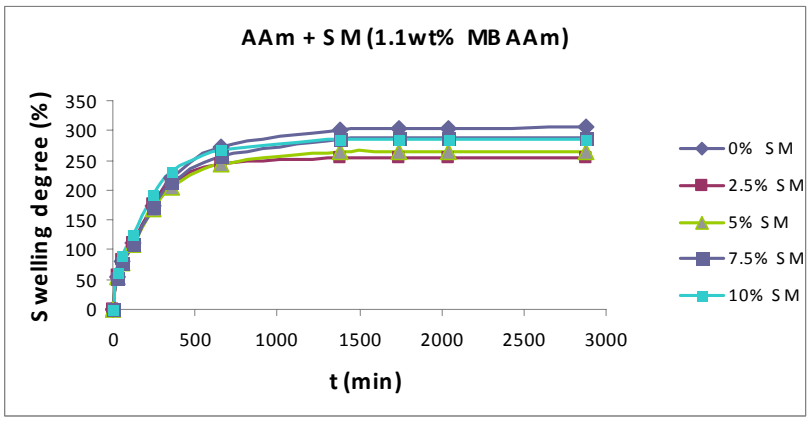


(b)

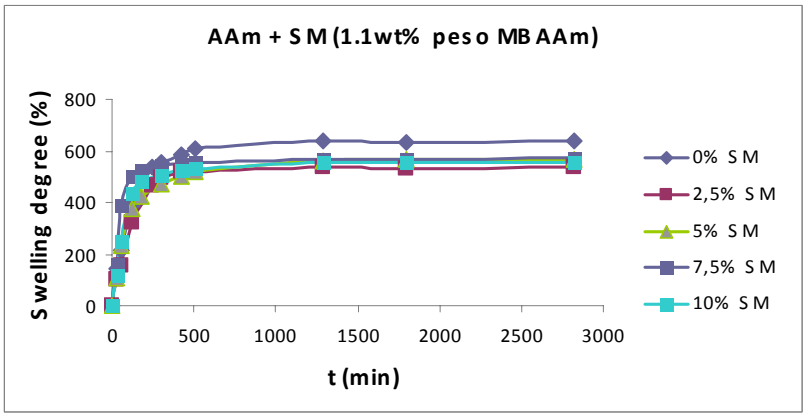
Figure S3. Influence of temperature synthesis on the swelling capacity of polyacrylamida-Mo composites (PAAm-Mo): (a) Dynamic swelling curves of PAAm-Mo hydrogels synthesised at 20°C; (b) 25°C and (c) 30°C, with different percentages of sodium molybdate in distilled water.



(a)



(b)



(c)

Figure S4. Influence of the weight percent of Sodium Molybdate on the swelling capacity of polyacrylic-Mo composites (PAAC-Mo):

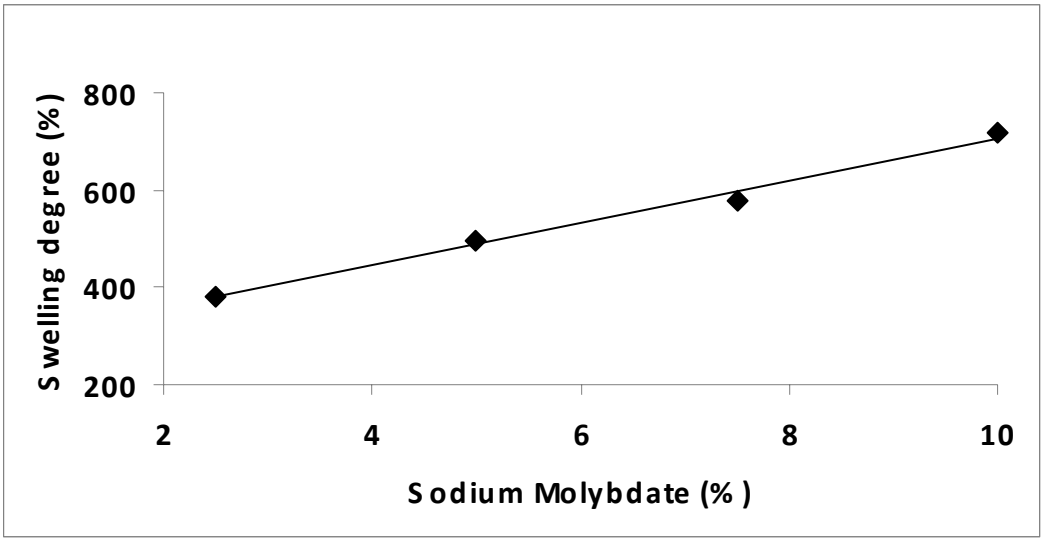
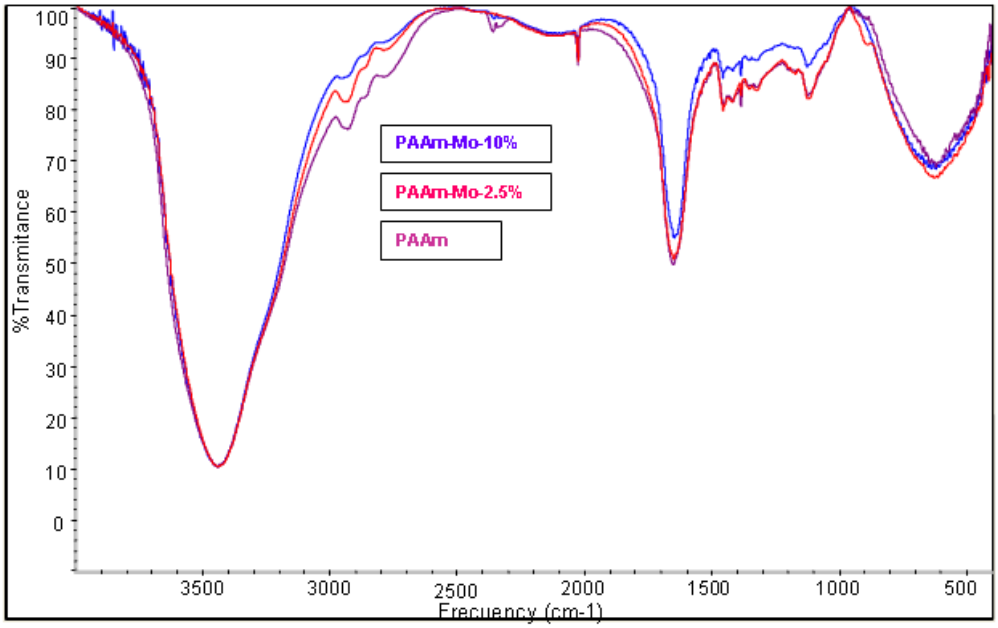
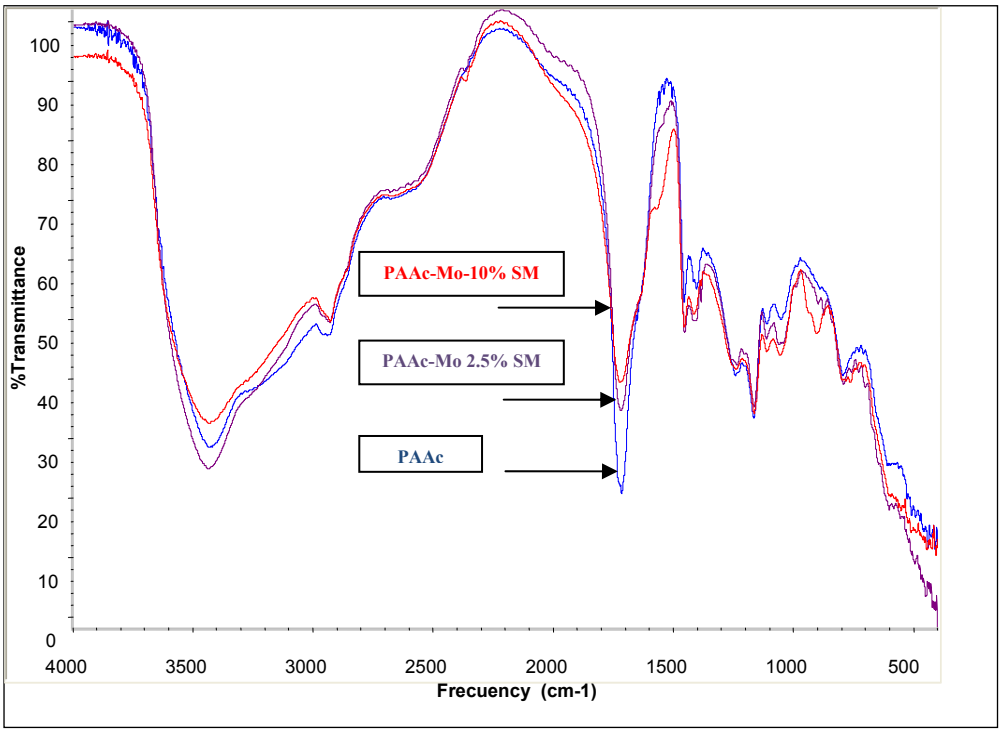


Figure S5. Comparative FT-IR of PAAm-Mo (a) and PAAc-Mo composites (b) with different percentages of sodium molybdate (0, 2.5 and 10% wt).



(a)



(b)

Figure S6. TEM image of PAAm-Mo-2.5%, magnified image of figure 3b in the manuscript, indicating nanoonion-like structures by red circles

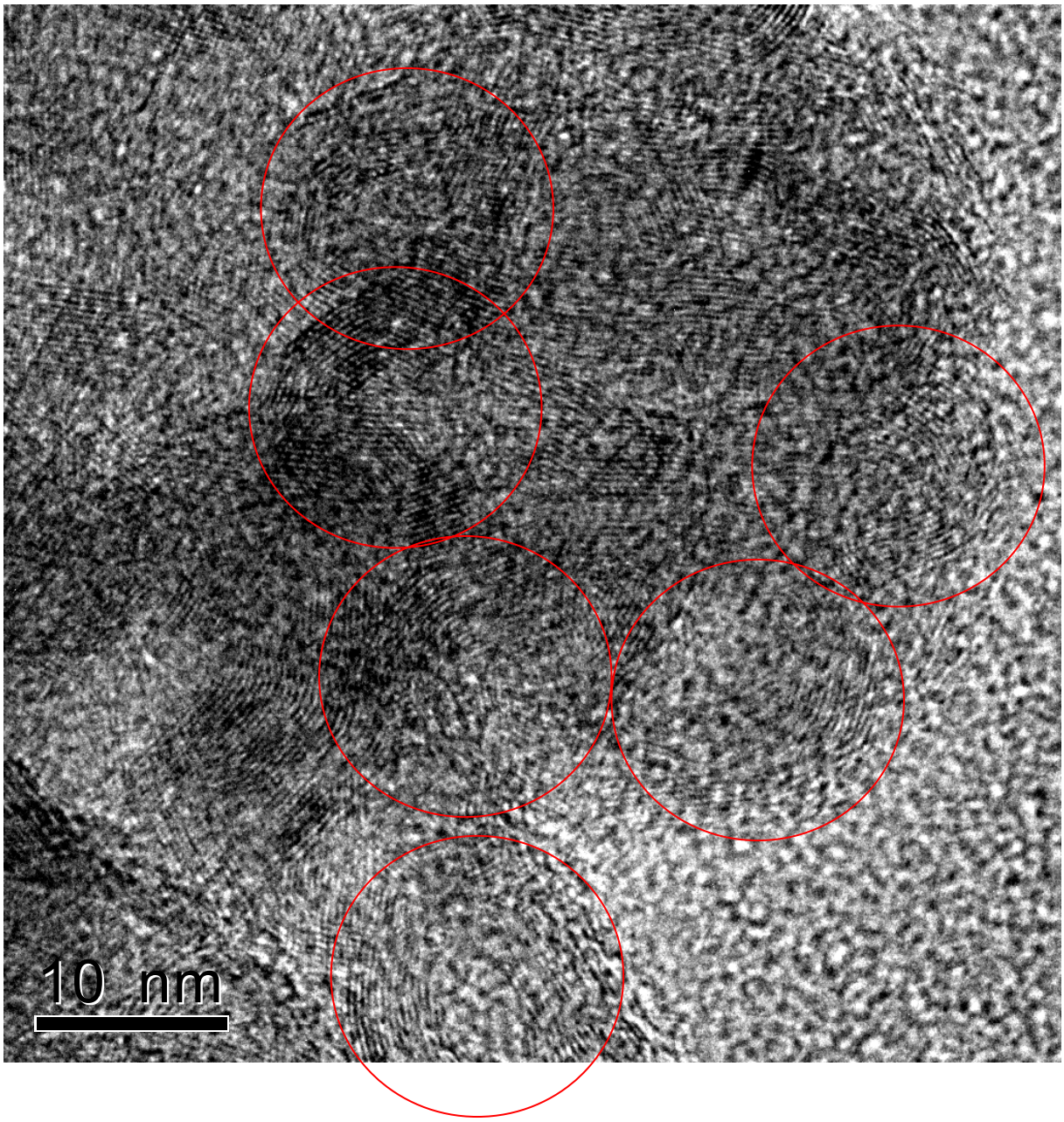
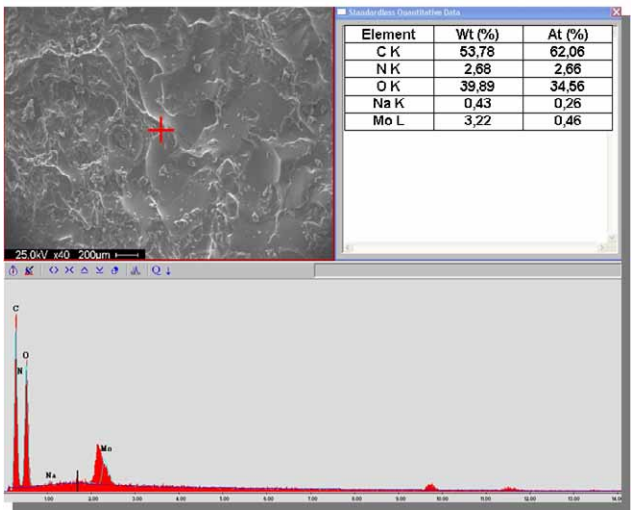
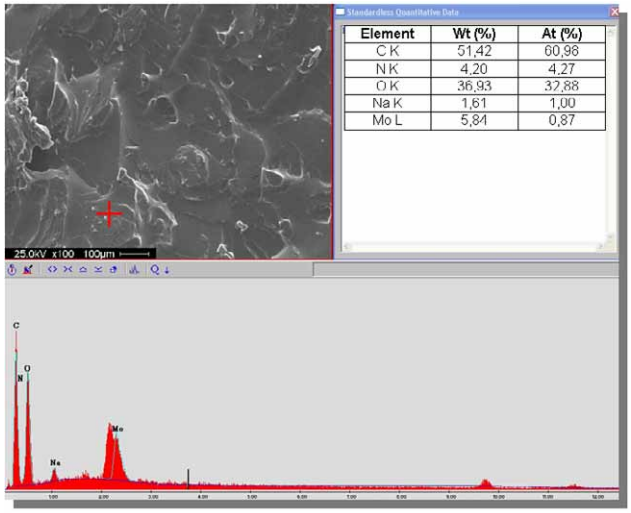


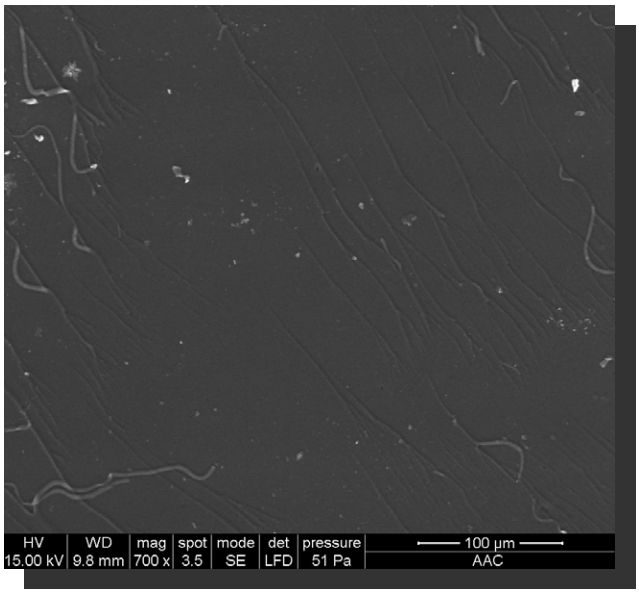
Figure S7. Comparative SEM images of PAAc-Mo2.5% (a) PAAc-Mo10% composites (b) and PAAc hydrogel pure (c)



(a)

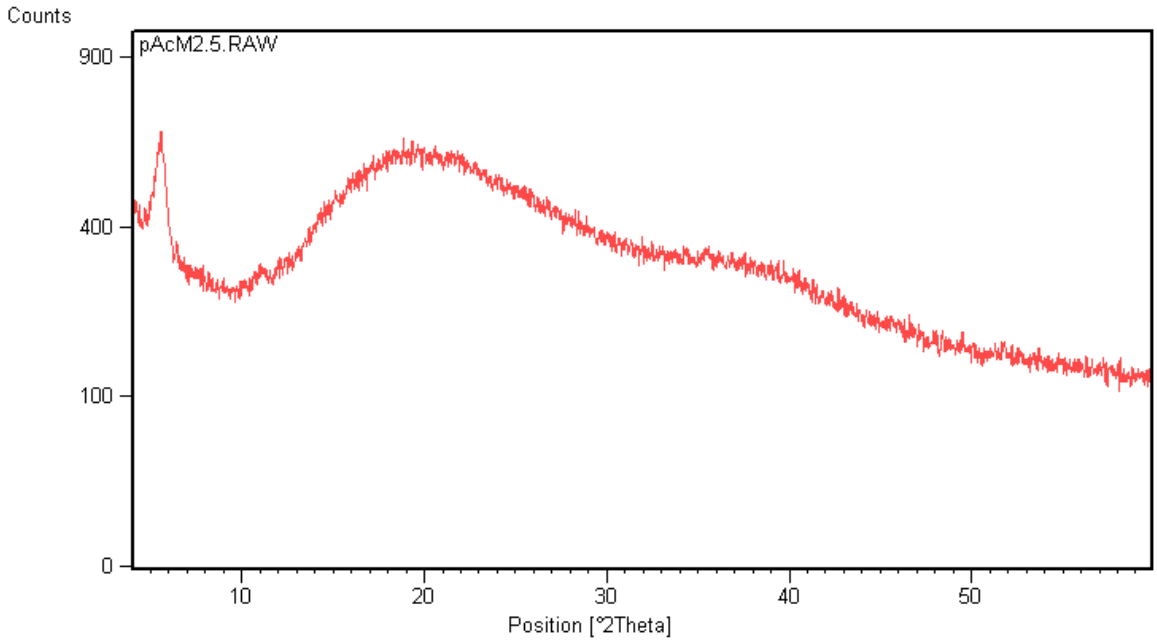


(b)



(c)

Figure S8. Comparative PXRD patterns of PAAc-Mo2.5% (a) PAAc-Mo10% composites (b)



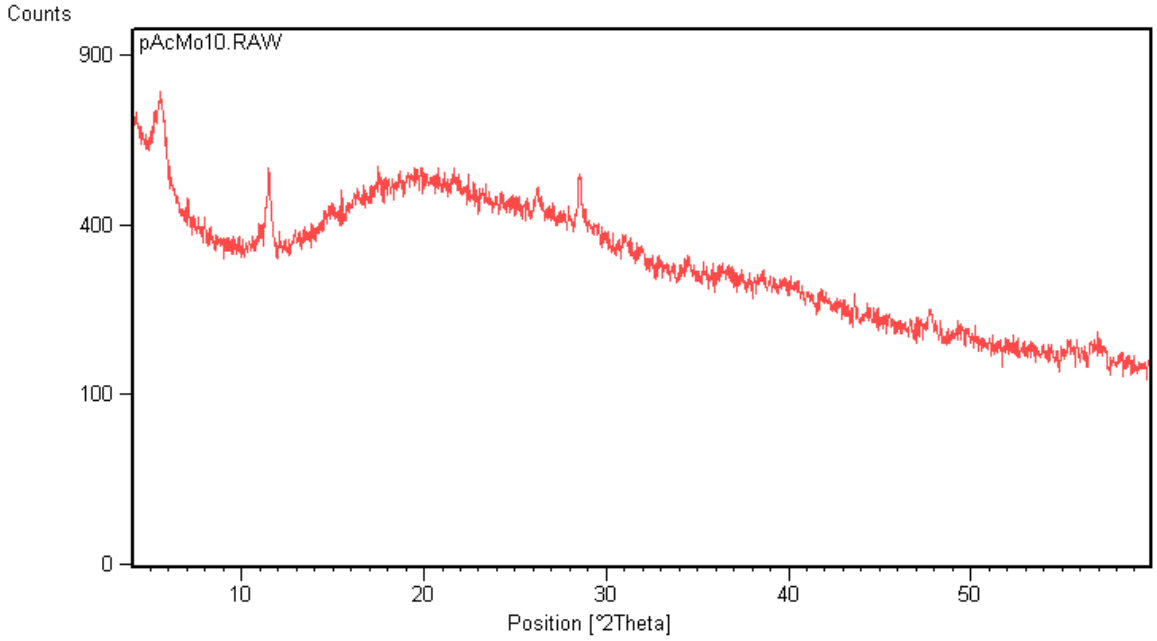


Figure S9. Representative EPR spectra of PAAc-Mo composites during redox process: (a) showing gradual oxidation of a powder sample PAAc-Mo-10% with a solution of H_2O_2 at 1 v/v% (a) reduced sample (blue color); (b) 2 min; (c) 10 (min). Similar spectra are observed either in partial reduced composites of PAAc-Mo or completely oxidised (colourless), when is added a solution of hydrazine at 1 wt%, showing an increase of the signal in function of time.