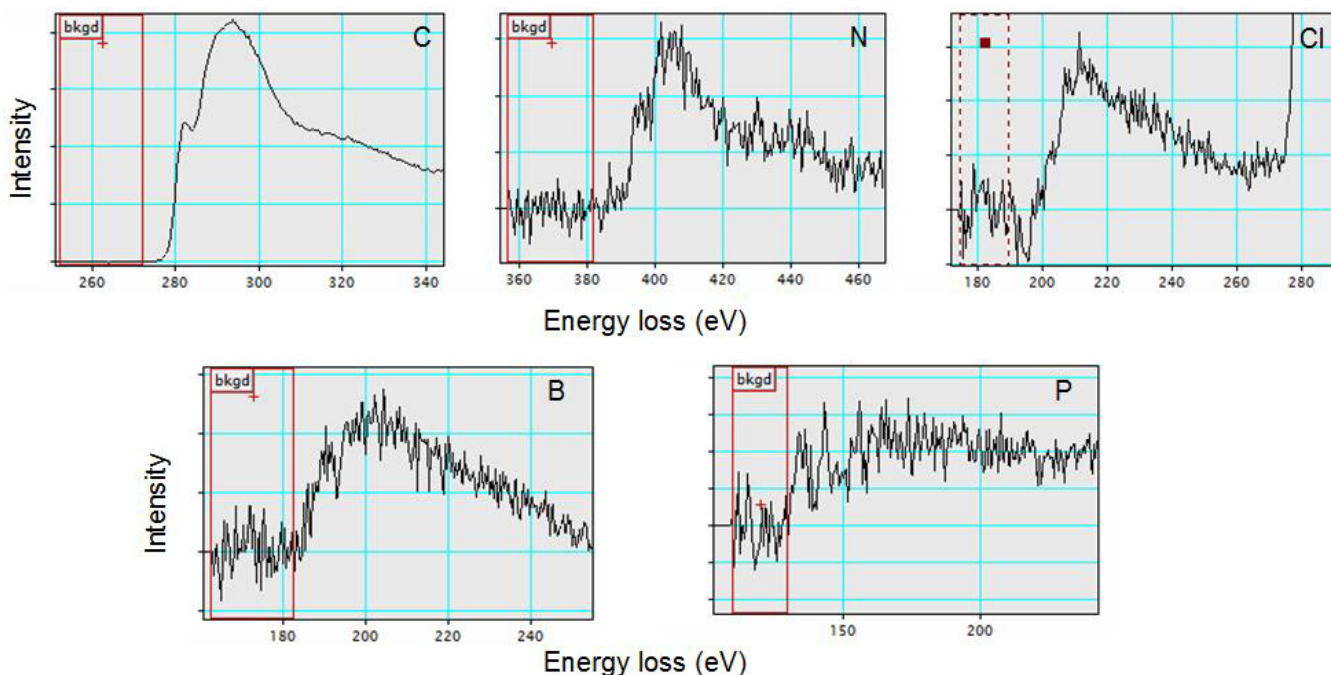


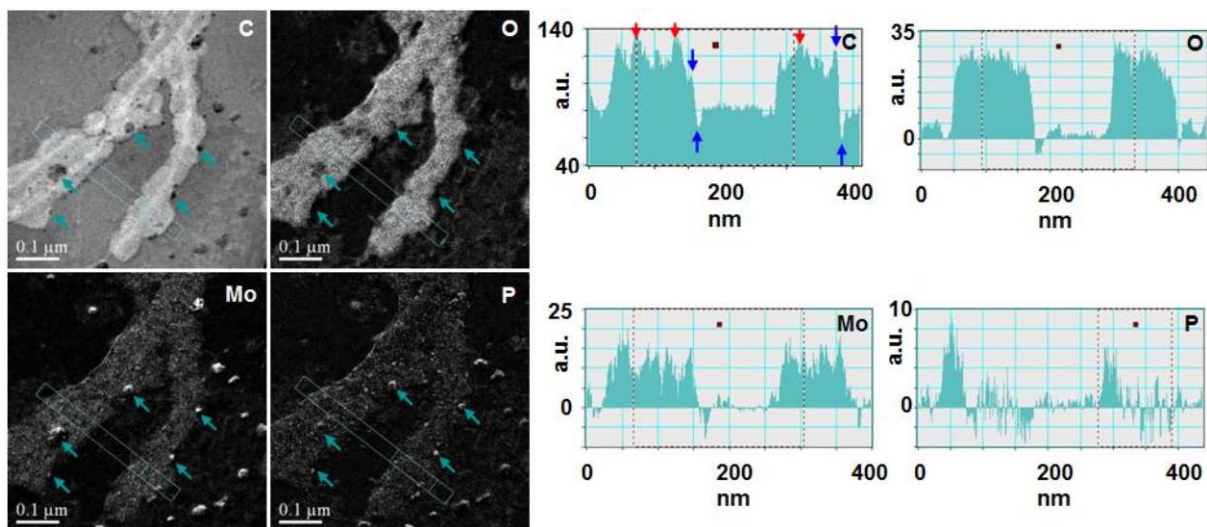
## SUPPORTING INFORMATION

In **Figure S1** the EELS profiles for C, N, O, Cl, B and P corresponding to the EFTEM maps of figs.4 and 6 are shown. Except for carbon, their signal to noise level is relatively low (still clearly above the noise) because they are present mostly in low quantities. These spectra provide additional proof that such low level of ion incorporations can be tracked and mapped by EFTEM techniques.



**Figure S1.** Electron Energy-Loss Spectra for the samples shown in figs. 4 and 6. The region used for background extrapolation is indicated by the red rectangle in each spectrum. In the Cl spectrum the edge onset for C can be seen.

In **Figure S2** the elemental distributions for C, O, Mo and P are shown together with their profiles for PPy coated nanofibers prepared using  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  as the oxidizing agent.

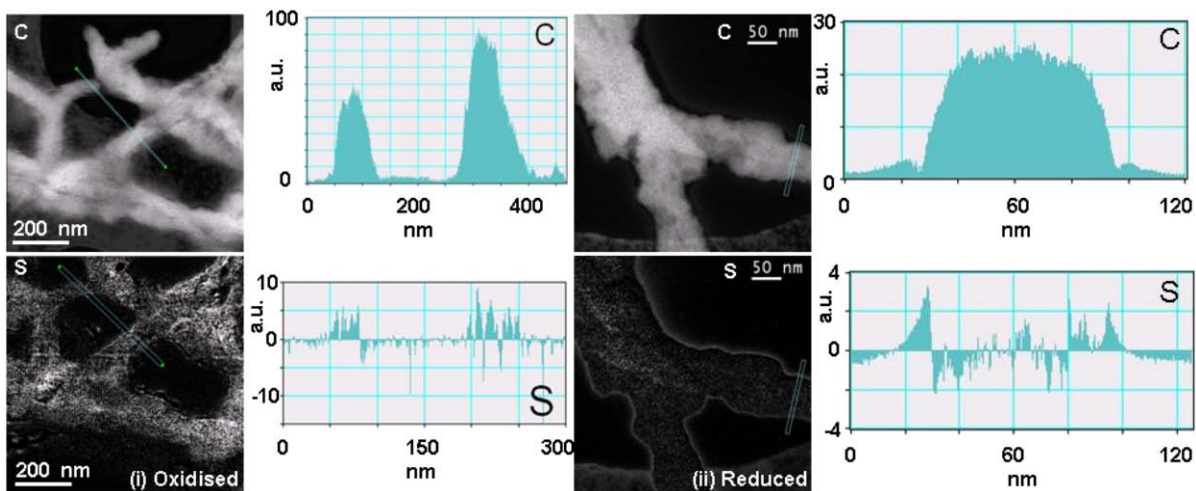


**Figure S2.** Intensity profiles and elemental maps for carbon, oxygen, molybdenum and phosphor in PPy-cellulose composites synthesized with phosphomolybdic acid. The blue arrows point to artifacts originating from beam damage. The three energy windows used were 242, 272, 296±10 eV for C, 472, 502, 557±15 eV for O, 192,212, 247±10 eV for Mo and 100, 120, 142±10 eV for P.

There is a clear contrast difference between the nano-fiber cellulose core and the PPy layer as compared to the PPy-cellulose composite synthesized with iron (III) chloride. The latter could be associated with the less dense PPy layer for the samples prepared using  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  as the oxidizing agent. In the map, the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  ions are seen as inclusions of nanoparticles of two distinct types. The first group of nanoparticles has a particle size of about 5 nm and is randomly distributed within the PPy coating. The second group of particles observed exists as large agglomerates with diameters of 15-30 nm predominantly positioned on the outside of the composite fibers or adjacent to the fiber surface.

The latter Mo and P rich particles appear mostly outside the nanofibers in the Mo and P maps. The particle agglomerates seen outside the composite could thus have been detached from the outer surface of the composite during the sample preparation. The

arrows pointing to dark spots in the carbon profile in Figure S2 highlight some of the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  nano-particles. In the C maps, an increased carbon intensity is observed corresponding to the cellulose nanofiber cores as marked by the red arrows. The increased carbon intensity at the edges of the composite and the dip just next to it (marked by blue arrows) is most likely an artifact due to beam damage and sample drift. The phosphorus intensity was too low to give information about the distribution of the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  anions within the composite. Due to the presence of moisture in the composites, the contributions from the oxygen present in the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  anions could not be differentiated from the oxygen present in the sample itself. Nonetheless, based on the Mo maps as well as from the sharp contrast of the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  nanoparticles in the TEM micrographs, it can be concluded that the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  anions were randomly distributed within the PPy bulk in form of some nm large particles without any preferential distribution at the periphery.



**Figure S3.** Intensity profiles and elemental maps for carbon and sulfur in oxidized and reduced PPy-cellulose composite. The three energy windows used were 242, 272, 296±10 eV for C and 145, 155, 180±5 eV for S.

To illustrate the reversible character of the electrochemical extraction and release of anions from the composite PPy material as well as to visualize the changes in chemical element distribution following electrochemical extraction and release, S element maps were made with EFTEM following electrochemical extraction and release of p-toluenesulfonate. In **Figure S3** the elemental distributions of C and S are shown together with their profiles for PPy coated nanofibers. As it is seen in the images, sulfur was clearly detectable in the oxidized samples. Moreover, this element was randomly distributed throughout the PPy coating without any preferential stacking at the edges. Contrary to the oxidized sample, the sulfur intensity in the reduced sample was remarkably low as compared to the oxidized sample indicating a significant release of p-toluenesulfonate during the reduction of the PPy layer. This release was also verified by an independent chemical element analysis (see **Table 1**) of the oxidized and reduced samples.

**Table 1.** Chemical sulfur elemental analysis following electrochemical extraction and release of p-toluenesulfonate.

S element content, % wt	
Reference	$\leq 0.05$
Oxidized	6.1
Reduced	1.6