Supporting Information

Bioinspired Gradient Materials via Blending of Polymer Electrolytes and Applying Electric Forces

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DSC.

Figure S1. DSC traces of PAA-1, PAAm-PAA(10) (a) and PAAm-PAA(70) (b) and their polymer blends.
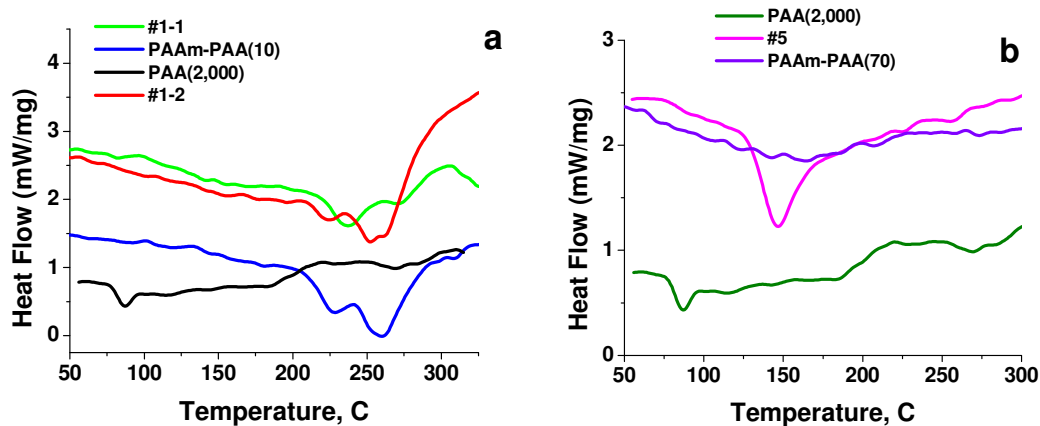
As indicated in the ref.[1], the DSC traces of PAA are extremely complex showing a number of events. These events can be attributed to glass transition of both carboxylate and carboxylic acid containing regions (above 100 °C), strongly bound water (in the range of 100-250 °C), and anhydride formation (around 220-250 °C).[1] In addition, low temperature endothermic transitions can be assigned to enthalpy relaxation.[2] Since the goal of this DSC study was to examine miscibility of the blend components, we do not elaborate on the details of the DSC traces, but follow only the differences between those for individual components and the blends, using the samples with the same thermal history[1] (the samples were dried in a vacuum oven at 30 °C for 48 h). From Figure 1a one can see that the DSC trace of the blend consisting of 15% PAA-1 in PAAm-PAA(10) (#1-1, Table 1) at pH 4.3 significantly differs from the DSC traces of PAA and PAAm-PAA(10) indicating good miscibility of the components.[2] On the contrary, the DSC trace of the film #1-2 prepared at pH 6.5 practically repeats the DSC profile of PAAm-PAA(10), revealing poor miscibility of the components at this pH. For the PAAm-PAA(70) based blend #5, the DSC pattern at pH 6.5 is quite different from those of the individual components confirming their good miscibility (Fig. 1b).

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XPS

Figure S2. High resolution XPS spectra of #5 in C 1s (a) and O 1s (b) regions and their deconvolution curves.
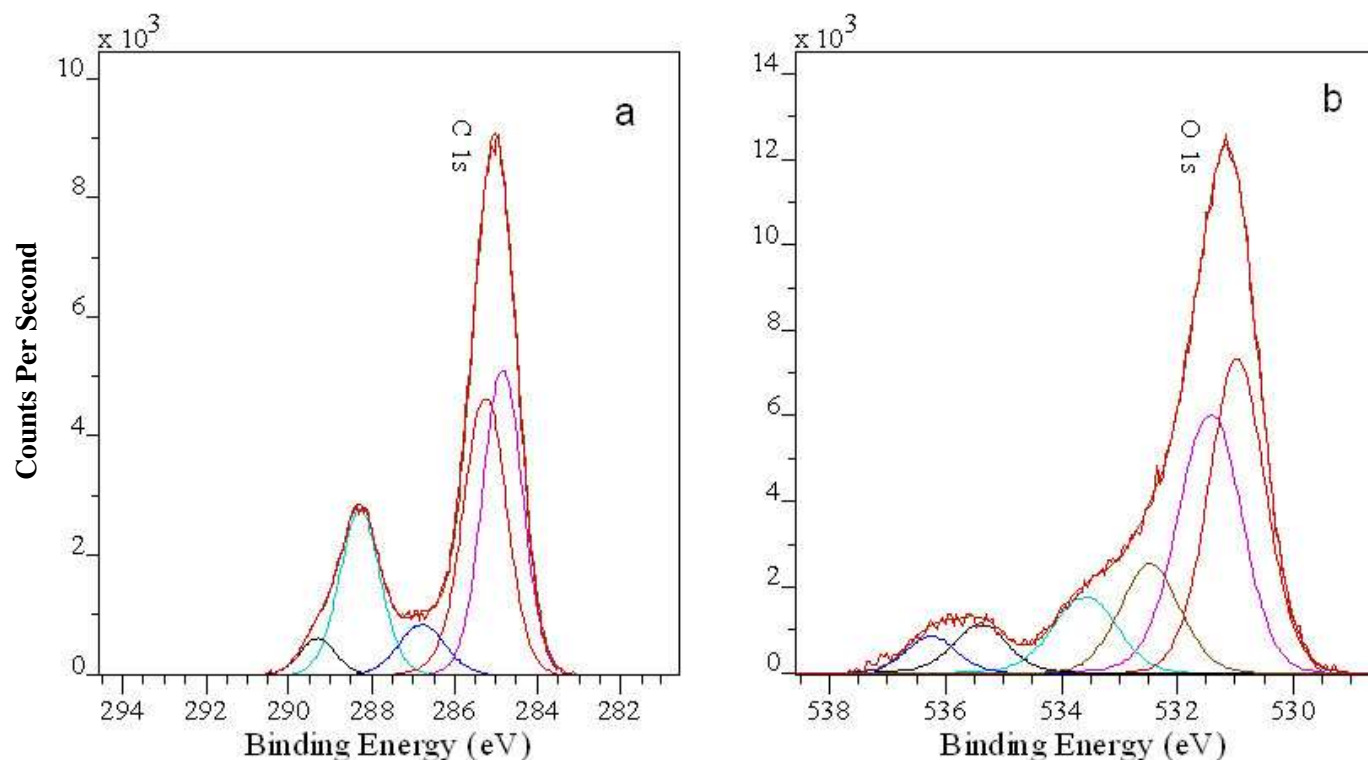
The C 1s spectrum contains two broad peaks which can be deconvoluted into five component peaks. The peaks at 284.8 and 285.2 eV can be assigned to CH_2 and CH carbons of the polymer chain. The peaks at 288.3 should be responsible for the carbon atoms in both amide and sodium carboxylate, while the peak at 289.3 eV is characteristic of carboxylic group. The peak at 286.8 eV should be assigned to C-O single bond and is due to a low molecular weight impurity also detected by ^{13}C NMR. The O 1s spectrum of the sample #5 can be deconvoluted by six peaks. The peak at 531.0 eV can be assigned to a combination of amide groups and O-Na of carboxylate group. The C=O group of carboxylate is presented by the peak at 531.4 eV while the C=O peak of the carboxylic group is showing at 532.5 eV together with the ester or ether impurity. The peaks at 535.3 and 536.24 eV may be due to adsorbed water and OH/water clusters.

Figure S3. High resolution XPS spectra of the Ce-containing samples in the C 1s (a) and O 1s (b) regions and their deconvolution curves.
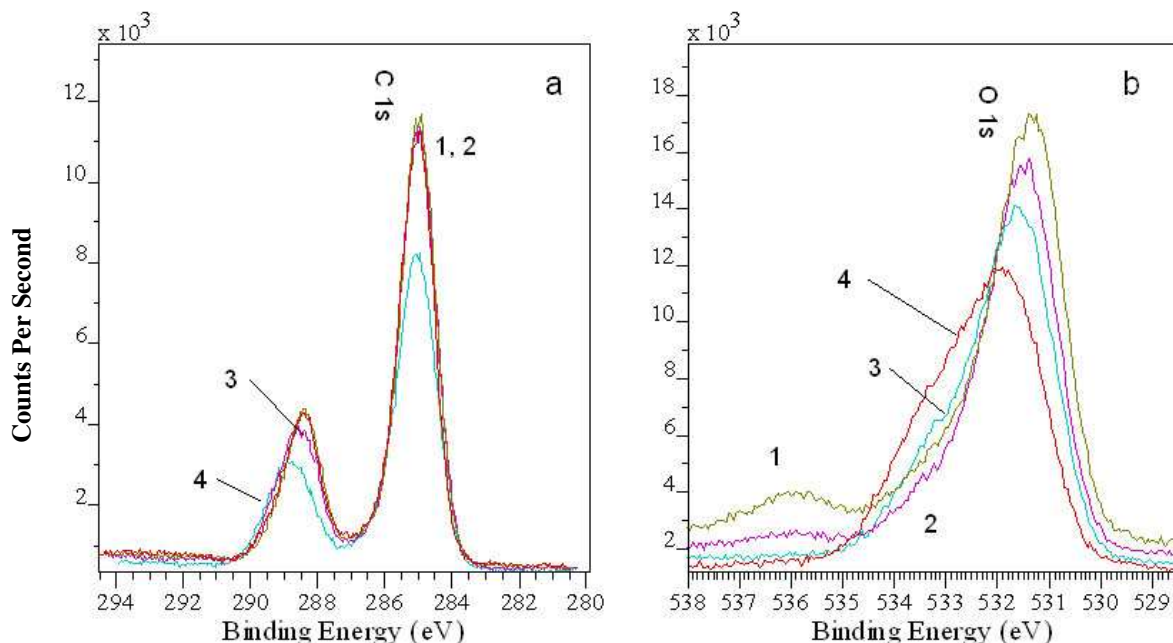
Although the Ce content in the surface layer increases from 1.28 to 1.91% when ion exchange time to the Ce salt solution increases from 15 to 30 sec, the longer treatment leads to an insignificant change of the Ce content (up to 2.24% at the 30 min ion exchange time time), revealing saturation of the film surface with Ce ions. It is noteworthy that despite permanent exposure of Ce-containing films to air *no* Ce(IV) species are found by XPS, confirming high oxidation potential of Ce(III) species in the hybrid polymer films. Because Ce(IV) is reduced to Ce(III) in the absence of methanol, we expected to find oxidation products in the polymer films. The C 1s spectra of Ce-containing samples remain almost unchanged (Fig. S3a) at an ion exchange time time up to 2 min, revealing the stability of the polymers to oxidation. At longer ion exchange time (30 min) the fraction of the C-O species with a higher binding energy increases (Fig. S3a). On the other hand, the O 1s spectra show noticeable change (Fig. S3b). One can see the increase of the intensity of the spectrum around 533.6-534.0 eV which can be assigned to the presence of C=O group from formaldehyde (oxidation product),[23] C-O group from methanol or methoxy.[3-5] In this case, these products should be coordinated with Ce ions and retained in the sample

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after ion exchange time to the Ce salt methanol solution. This corroborates the fact that Ce(III) ions are extremely prone to complexation.[6]

Figure S4. Dependence of the O/C atom ratio on the exposure time for the Ce-containing #5 samples.
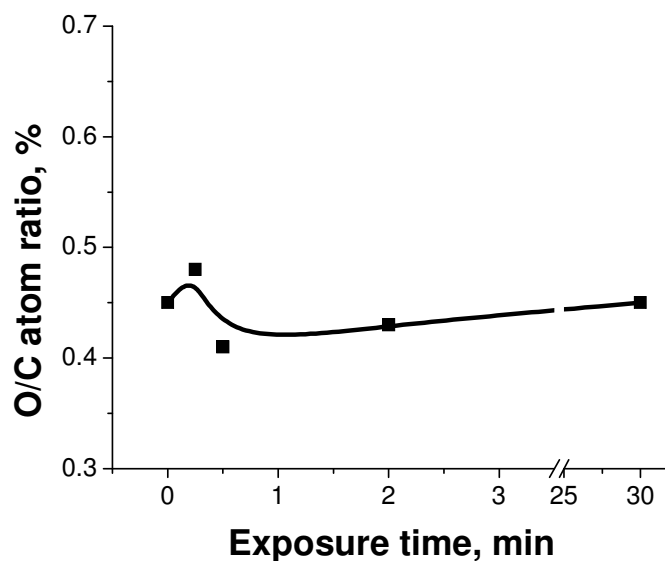
Comparison of the XPS data on the Ce content and the elemental analysis data of the bulk films (Table 2, see the paper) reveals that (i) the Ce fraction increases with the increase of the ion exchange time (confirmed by the increased yellow color after the film formation and opaqueness of the films) and (ii) the Ce species are mainly located in the surface layer, thus suggesting a gradient across the film thickness.

The dependence of the O/C atom ratio on the ion exchange time in the Ce-containing samples is complex (Fig. S4) but does not show any pronounced increase of the oxygen fraction even after 30 min ion exchange time, revealing the stability of the polymer chains to oxidation by Ce(IV) in the conditions chosen.

The interesting feature of these Ce-containing films is a dramatic change in their water adsorption with the increase of the ion exchange time to the Ce salt solution. This is indicated by the disappearance

of the O 1s peaks in the 535-536 eV region related to the adsorbed water and water clusters. This may be due to "sealing" of the polymer surface with Ce species.

High resolution Ce 3d core level spectra of the Ce-containing films are nearly identical (see Fig. S5 for '#5-Ce-meth-30 sec) and reveal a single bonding state for Ce(III) with the $3d_{5/2}$ peak at 881.4 eV. The other peaks are satellites. Considering that the position of the new synthetic peak in the deconvoluted O 1s spectra assigned to Ce-O is about 530.8 eV, one might suggest that Ce(III) exist as Ce_2O_3 but this assignment is rather tentative considering the complexity of the peak.

Figure S5. High resolution Ce 3d core level spectrum of '#5-Ce-meth-30 sec' and its deconvolution curves.
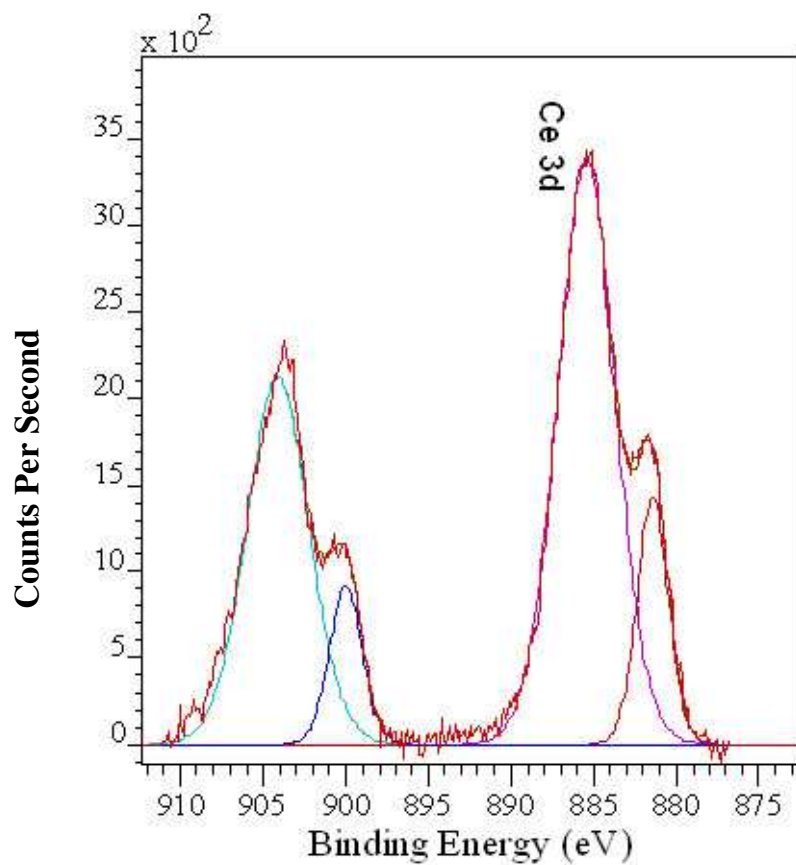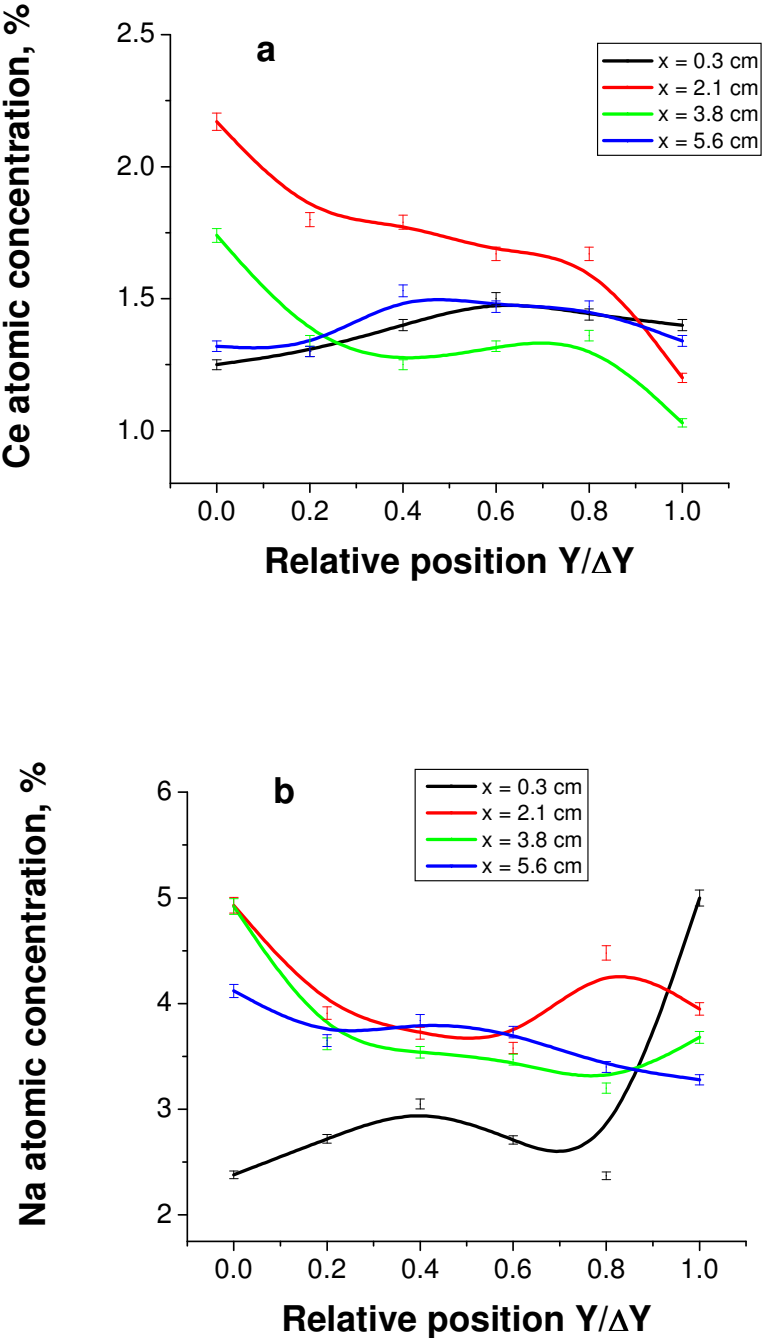
Figure S6. Dependences of Ce (a) and Na (b) atomic concentration on the relative position Y/ΔY (where Y is distance from anode to the measurement point coordinate and ΔY is distance between anode and cathode) for thin supported films in four different distances *X* indicated in the Figure legends and corresponding to different electric field strength.

Nanoindentation

Indentation studies were performed on a Hysitron Triboscope nanoindenter using a 90° cube-corner diamond tip. Maximum load (3000 μN) was applied at 300 μN/s. The maximal load was held for 10s before the indenter was retrieved at the same rate. We used the unloading portion of the load versus displacement curve to calculate the hardness and the stiffness (reduced modulus) (Table 1).

Table 1. Hardness and Stiffness of Hybrid Supported Films before and after Interaction with Fe and Ce salts

Sample notation*	Hardness, GPa	Stiffness, GPa
#5 hybrid deposited film	7.8	0.35
#5-Fe-meth-5 min	15.0	0.81
#5-Ce-meth-15 sec	12.3	0.46
#5 hybrid deposited film treated with methanol for 15 sec	18.7	1.02

*See Table 2 of the manuscript for notations

The hardness and stiffness (modulus) of hybrid supported films before and after interaction with metal ions are comparable or higher than those of a number of other polymers or hybrid materials.[7-10] Note, however, that although the hardness and stiffness increase after interaction with metal ions, in both cases the hybrid film was exposed to methanol. The control experiment of the hybrid film exposure to methanol for 15 sec also shows a significant increase of the hardness and stiffness of the film, revealing that the methanol influence overrides the influence of complexation on film mechanical properties. We believe that during exposure to methanol, water retained by the hybrid film is removed, thus changing film morphology and strengthening the film.

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