

Development and study of novel ultrafiltration membranes based on cellulose acetate

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Membranes with optimal transport properties (CA-PEG+C₆₀ and CA-PS+C₆₀) and pristine CA membrane were studied by Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) to study of structural changes.

S1. Fourier-transform infrared spectroscopy

A BRUKER-TENSOR 27 Spectrometer (Bruker, Ettlingen, Germany) with an attenuated total reflectance (ATR) accessory was used to determine the structure of membranes in the range 600–4000 cm^{−1} at ambient temperature by Fourier-transform infrared spectroscopy (FTIR). FTIR spectra of CA, CA-PEG+C₆₀ and CA-PS+C₆₀ membranes were presented in Figure S1.

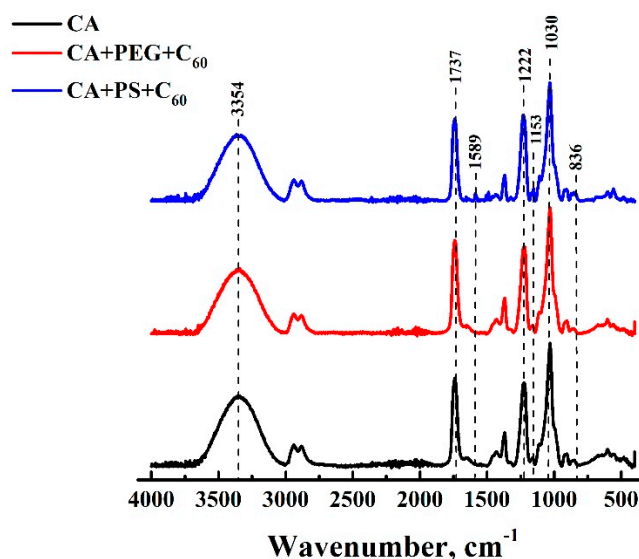


Figure S1. FTIR spectra of CA, CA-PEG+C₆₀ and CA-PS+C₆₀ membranes.

In the FTIR spectrum for CA membrane (Figure S1), a broad peak at 3354 cm^{−1} is a characteristic peak associated with vibrations of -OH group. The absorption at 1737 cm^{−1} is associated with stretching of C=O groups, the peaks at 1222 and 1030 cm^{−1} are related to

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aromatic ring and with the $-C-O-$ bond in the CH_2-OH group, respectively [71–73]. The introduction of PEG in the CA matrix practically did not change the FTIR spectra due to the washing out of PEG as a pore former into the coagulation bath during membrane formation. The introduction of PS in the CA leads to the appearance of new characteristic peaks of PS: peak at 1589 cm^{-1} associated with C-C bond in the aromatic, at 1153 cm^{-1} associated with stretching of $-O-S-O-$ group, and at 836 cm^{-1} associated with C-H stretching of aromatic ring of PS [74]. The introduction of C_{60} in the polymer matrix did not change the FTIR spectra, since its peaks are overlapped by the polymer matrix due to the small addition of fullerene.

S2. X-ray photoelectron spectroscopy

Escalab 250Xi photoelectron spectrometer (Thermo Fisher Scientific, Waltham, USA) with an $AlK\alpha$ monochromatic radiation source (photon energy 1486.6 eV) was used to determine the structure of membranes. The XPS spectra were recorded in the constant transmission energy mode at 20 (for C1s and O1s) or 50 eV (for S2p) with an XPS spot size of $650\text{ }\mu\text{m}$. The total energy resolution of the experiment is about 0.8 eV . A combined ion-electronic charge compensation system was used to remove the sample charge. Binding energy determining error is about 0.3 eV . The studies were carried out at room temperature in an ultrahigh vacuum of the order of $1 \times 10^{-9}\text{ mbar}$.

To analyze the elemental and chemical composition of the selective surface of the membranes, survey (Figure S2a) and detailed carbon C1s (Figure S2b) and oxygen O1s (Figure S2c) spectra were recorded.

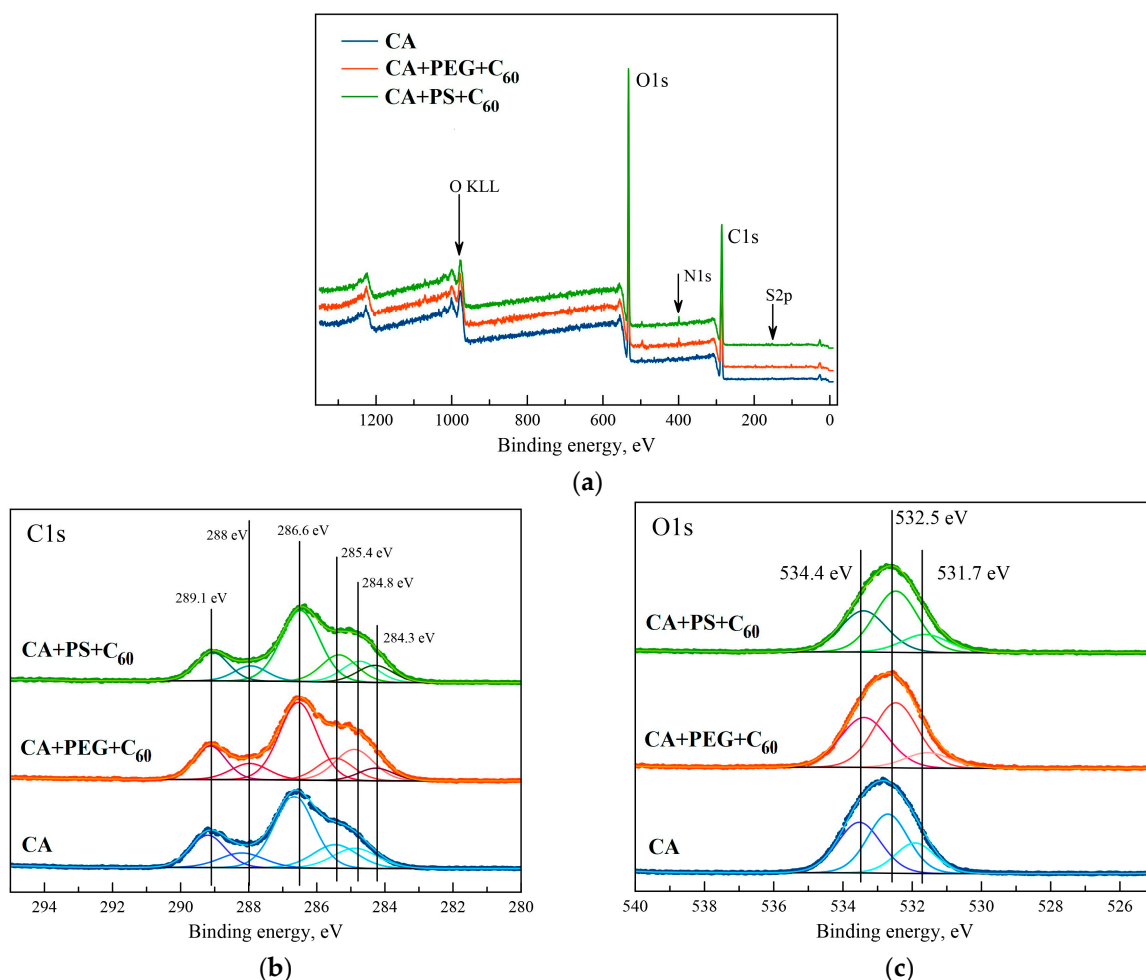


Figure S2. XPS spectra recorded from the selective membrane surface (a) survey spectrum, (b) fitted carbon C1s spectrum, (c) fitted oxygen O1s spectrum.

The survey spectra (Figure S2a) show that the membranes mainly contain carbon, oxygen and nitrogen. For the modified membranes, a sulfur peak was also noted, which for the membrane modified with PEG was insignificant, and for the membrane modified with PS it was larger, which corresponds to the sulfur atom of the modifier. The Figures S2b and S2c show detailed spectra of carbon (C1s) and oxygen (O1s), separated into different states for chemical analysis. The characteristic states of carbon were identified in the spectrum of the unmodified CA membrane. Since a small amount of adventitious carbon on the surface of organic substances, their states were not taken into account in the decomposition. Carbon and nitrogen compounds were also not taken into account in the decompositions, since the nitrogen content is quite low. Peaks with a binding energy of 284.4 ± 0.3 eV, related to fullerene, are identified in the spectra of the modified (CA-PEG+C₆₀ and CA-PS+C₆₀) membranes. Also, in the spectra of the modified membranes, there was a redistribution of the ratio of carbon peaks with energies of 284.8 eV and 285.4 eV, corresponding to the linear and cyclic structures, respectively. In CA-PEG+C₆₀ membrane modified with polyethylene glycol, an increase in the content of the carbon state with an energy of 284.8 ± 0.3 is observed. At the same time, in the CA-PS+C₆₀ membrane modified with PS the intensity of the carbon peak with energy of 285.4 ± 0.3 eV increased. Also for the modified CA-PEG+C₆₀ and CA-PS+C₆₀ membranes a peak is visible at 284.3 ± 0.3 eV, which corresponds to fullerene in the membrane structure. At the same time, the oxygen spectra (Figure S2c) for all three membranes do not differ so significantly, since the oxygen content in the modifiers (PEG and PS) is lower, then carbon contain.

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