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Supporting Information for

Construction of cross-linked polymer films covalently attached on silicon substrate via a self-assembled monolayer

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Generally, the characterization of film thickness was performed by using the XPS analysis. For a uniform organic thin film spun cast on a certain substrate with the thickness of d, the photoelectron intensity of a specific core level of element *i* from the overlayer is given by

$$I_{i,overlayer} = \int_0^d P D C_i T_i \sigma_i e^{\frac{-z}{\lambda_{i,overlayer} \cdot \cos\theta}} dz \quad ,$$

where *d* is the thickness of the overlayer, c_i is the atomic concentration of element *i* in the overlayer, T_i is the spectrometer transmission for the kinetic energy of the photoelectrons from the specific core level of element *i*, σi is the atomic photoemissions cross section of element I, and $\lambda_{i,overlayer}$ is the IMFP of the photoelectrons passing through the overlayer.

Moreover, when the photoelectrons of element *j* in the underlying substrate traverse the overlayer, the corresponding photoelectron intensity is given by

$$I_{j,substrate} = \int_0^\infty P D C_j T_j \sigma_j e^{\frac{-t}{\lambda_{j,substrate} \cdot \cos\theta}} e^{\frac{-d}{\lambda_{j,overlayer} \cdot \cos\theta}} dt$$

where c_j is the atomic concentration of element j in the substrate, T_j is the spectrometer transmission for the kinetic energy of the photoelectrons from the specific core level of element j. $\lambda_{j,substrate}$ and $\lambda_{j,overlayer}$ are the IMFPs of the photoelectrons passing through the substrate and overlayer from the specific core level of element j respectively.

The above two equations can be further solved to calculate the ratio of photoelectron intensity of an overlayer element to that of a substrate element, and the overlayer thickness (d) can then be well estimated by solving the following equation in which a Microsoft Excel is needed here.

$$\frac{I_{i,overlayer}}{I_{j,substrate}} = \frac{C_i}{C_j} \cdot \frac{T_i \sigma_i}{T_j \sigma_j} \cdot \frac{\lambda_{i,overlayer}}{\lambda_{j,substrate}} \cdot \frac{1 - e^{-\frac{d}{\lambda_{i,overlayer} \cdot \cos\theta}}}{e^{-\frac{d}{\lambda_{j,overlayer} \cdot \cos\theta}}}$$

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We have introduced our PCIC method in details in our previous published research articles in details [References 15,16,17]. Actually, the comparison of the relative peak intensity of C1s and Si2p can already be a judgement/estimation of the thickness change between films before and after each ultrasonication treatment.