Molecular Densities of Aminosilane Self-Assembled Monolayers as Estimated by Chemical Labeling

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Surface modification of a solid substrate with amino groups is attractive in order to provide chemical activities to its surfaces for immobilizing a wide variety of substances including bio-molecules, metallic nanoparticles and so forth, and for improving adhesive properties of the surfaces. For these purposes, aminosilane self-assembled monolayers (SAMs) have been successfully employed. The molecular packing density is of primary importance in order to design surface functions of a substrate covered with an aminosilane SAM. Nevertheless, there are few report on this subject.

Here we report on a chemical labeling approach for the measurement of molecular packing densities of aminosilane SAMs. Our procedure is illustrated in Fig. 1. First, for example, n-amino-propylsilane SAM (APS-SAM) was formed on a quartz glass substrate by a vapor phase method. Next, a part of the amino groups on the SAM was labeled with 2,4,6-trinitrobenzenesulfonic acid (TNBS). An optical density at 420 nm in wavelength of this sample was measured to be 0.009. The absorbance of TNBS at 420 nm is known to be 22000 $M^{-1}cm^{-1}$. Thus, the surface density of TNBS on each side of the sample is estimated to be $N = 2.0 \times 10^{-10}$ (mol cm^{-2}). Furthermore, the ratio of labeled APS molecules to the whole APS molecules was determined by an XPS-N1s spectrum (Fig. 4d). There are two distinct peaks corresponding to $-NO_2$ and -NH- + $-NH_2$. Its peak area ratio is 3:2.4 indicating the molecular density ratio of TNBS:APS = 1:2.4. Consequently, the molecular packing density of the APS-SAM is calculated to be ca. 3 APS/nm^2. We have also estimated other two types of aminosilane SAMs formed from *N*-(2-aminoethyl)-3-aminopropyltriethoxysilane and (3-trimethoxysilylpropyl)diethylenetriamine.

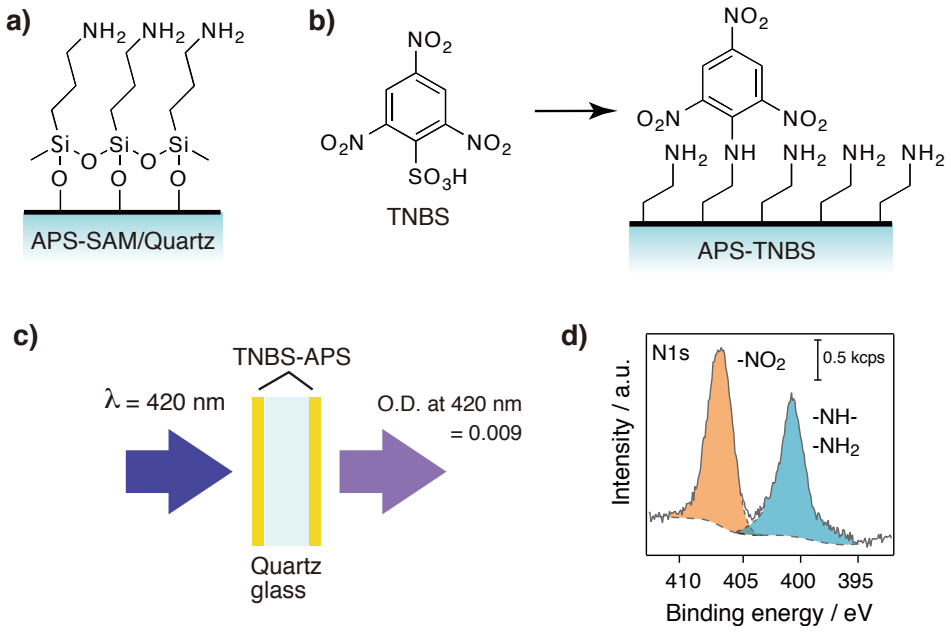

Figure 1 Chemical labeling of APS-SAM with TNBS.