Kinetics of Adsorption and Self-assembling of Thiophene and Dodecanethiol Studied by Optical Second Harmonic Generation

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The processes of adsorption and self-assembling of dodecanethiol and thiophene oligomers on gold substrate were studied in situ by optical second harmonic generation and kinetic constants were estimated using simple Langmuir model.

Thiophene oligomers and thiol self-assembled monolayers attract in last decades a strong attention due to their unique properties and possibility to vary these properties by changing the number of thoiphene rings, adding different functioning groups and mixing thiophene groups with functioning groups. For ex situ the result of self-assembling can be controlled electrochemically: A high quality SAM completely blocks the electrochemical activity and no oxidation-reduction process can be observed.

In order to study in situ the process of self-assembling, remote (not chemical) techniques can be only used. Since the process occurs in a liquid, the number of characterization techniques is quite limited. Widely used electrochemical quartz crystal microbalance (QCM) technique is based on mass flow analysis and quantifies the number of adsorbed molecules and the movement of ions and solvent accompanying an electron transfer process.[1] Optical techniques are also used for in situ studies of the process of self-assembling, among them optical second harmonic generation (SHG)[2] and ellipsometry.[3] So far optical techniques are mostly applied for the studies of the process of self-assembling of thiol, while for thiophene they were applied only for ex situ measurements.

In this Letter we show that, although the processes of self-assembling of thiol and thiophene are quite similar, interpretations of optical data are different for these two types of molecules because of different optical contributions from the molecules themselves. In order to obtain kinetic parameters, nonlinear-optical and kinetic models are considered simultaneously.

For self-assembling, the gold (111) substrate was immersed for 1 h in 1 μmol dm^{-3} oligothiophene or 1-dodecanethiol solutions in chloroform. Oligothiophenes with the different number (N) of thiophene rings were studied (2,2′:5′,2″-terthiophen-5-yl-methanethiol, abbreviated as T3 for N=3 and 2,2′:5′,2″:5″,2‴-quaterthiophen-5-yl-methanethiol, abbreviated as T4 for N=4). After 1 h, cyclic voltammograms (CVA) were measured to confirm the SAM quality which show quite good suppression of electron transfer, although not complete (see Figure 1).

For the SHG experiments a fundamental radiation of a Ti: Sapphire laser was used at fundamental wavelength 800 nm with a pulse width of about 100 fs, repetition rate of 78 MHz, focused onto a spot of 0.1 mm in diameter at 30 degrees of incidence. SHG radiation at 400 nm was discriminated spectroscopically by appropriate color and band-pass filters and was directed on PMT. For detection a photon counting system was used. The gold (111) electrode was placed into the simple optical cell. Optical measurements were started after the gold substrate was immersed in the solution with a delay not longer then 5 s. The SHG measurements were performed in the maximum of rotational anisotropy.

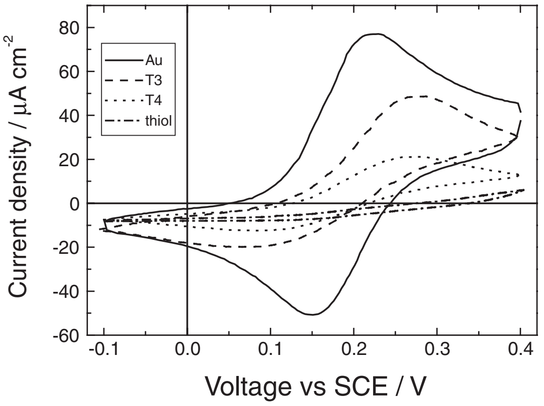

Figure 1. Cyclic voltammograms of bare gold and gold after immersing for 1 h in thiol and thiophene 1 μmol dm^{-3} solutions in chlorophorm ($CHCl_3$). CVA are measured in 1 mmol dm^{-3} potassium ferrocyanide and 0.1 mol dm^{-3} KCl aqueous solution.

Figure 2 shows the temporal dependences of SHG intensity during the adsorption/self-assembling process. For thiol and T3 the SHG intensity decreases while for T4 it increases. Fast changes occur within first 500 s followed by slow changes; however, saturation is not reached within 1 h.

In order to understand the temporal behavior of the SHG intensity and details of self-assembling processes giving rise to such behavior, a kinetic adsorption model simultaneously with an optical model should be considered. At present several models are considered for self-assembling process. Mostly they considered the self-assembling process consisting of two steps. At the first step simple adsorption dominates. Later because of interaction between the molecules or molecular diffusion, the ordering of molecules takes place giving rise to self-assembling. The latter may take several hours or even several days. It is obvious that during 1 h of optical measurements the simple adsorption is dominant. This allows to use a simple Langmuir model for calculation of molecular coverage $\theta_1 \propto 1 - \exp(-kC_B t)$, where k is the kinetic constant, C_B is the bulk concentration.

The total second harmonic field can be calculated as a superposition of the SHG field generated by adsorbed molecules and gold substrate.[4] SHG field from the gold substrate, which initially equals to $E^{2\omega}_{Au,0}$ is modified during the adsorption process and can be written as $E^{2\omega}_{Au,0} + \Delta E^{2\omega}_{Au}(\theta_1, \theta_2)$, where θ_1 and θ_2 are the molecular coverage in the form of a simple adsorption state (AD) and self-assembled state (SAM), respectively.[5] Molecules in AD and SAM states give different contributions, $E^{2\omega}_{AD}(\theta_1)$ and $E^{2\omega}_{SAM}(\theta_2)$ respectively, because nonlinear susceptibility of the adsorbed layer depends on the molecular tilt angle.[6] In the oligothiophene SAM layer molecules are aligned independently on the number of thiophen rings with the tilt angle $\alpha = 30^\circ$ ($N = 1$–4^7 and $N = 5, 6^8$). In the AD layer the tilt angle may vary from 0 to 90 and should be averaged with an appropriate distribution function. Totally we have for the SHG intensity

$$\begin{aligned} I^{2\omega}(t) &= \{(E^{2\omega}_{Au,o} + E^{2\omega}_{Au}(\theta_1, \theta_2)) + (E^{2\omega}_{AD}(\theta_1) + E^{2\omega}_{SAM}(\theta_2))\}^2 \\ &\propto \{(A + B(\theta_1 + \theta_2)) + (C\theta_1 + D\theta_2)\}^2 \end{aligned} \tag{1}$$

where A, B, C, and D are constants dependent on the optical properties (Fresnel factors, nonlinear susceptibilities of gold and adsorbed molecules). If contributions to SHG field from molecules are small in comparison with the contribution from a gold substrate, then the last two items in Eq 1 can be omitted and only the gold nonlinear susceptibility modification should be taken into account. Also we have to assume that the average tilt angle and the nature of a charge transfer between individual molecule and a substrate are independent on the surface coverage. This is exactly the procedure applied in Ref. 3 for SHG studies of thiol SAMs. In our experiments different behavior is observed for T3 and T4. Two reasons can be responsible for such behavior. Either the substrate is modified in different way during absorption of T3 and T4, or molecules themselves give different contributions to SHG field. The former seems to be quite unlikely, because the substrate modification arises owing to the charge transfer from the substrate to the molecule. Opposite behavior of the SHG field would mean the opposite direction of the charge transfer, which may hardly happen for the molecules different only by one thiophene ring. The latter is confirmed for thiophene by previous ex situ studies,[4,9] where nonlinear susceptibilities of thiophene oligomers were directly measured.

Fitting the data with Eq 1 with θ_2 omitted on the first stage and using Langmuir adsorption model for θ_1, we obtained the following values of kinetic constants: for dodecanethiol, $k = 2.2 \times 10^3\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$; for T3, $k = 2.4 \times 10^3\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ and for T4, $k = 3 \times 10^3\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$. For dodecanethiol this value is in agreement with the value obtained in Ref. 10.

It is important to note that there is no direct correlation between the obtained kinetic constants and time required for a complete self-assembling as well as quality of SAM. In order to obtain kinetic constants of self-assembling, a longer measurements are required as well as the kinetic models which describe self-consistently both stages of the process.

We studied in situ the processes of adsorption and self-assembling of dodecanethiol and thiophene oligomers from $1\,\mu\mathrm{mol\,dm^{-3}}$ solution on gold substrate using optical second harmonic generation. Within 1 h the adsorption process rather than self-assembling is dominated for this concentration, and the initial part of the process can be described in terms of a simple Langmuir model. In the frame of this model kinetic constants of the process were estimated. It is shown that for data interpretation it is necessary to take into account contribution to SHG field by thiophene and thiol molecules themselves.

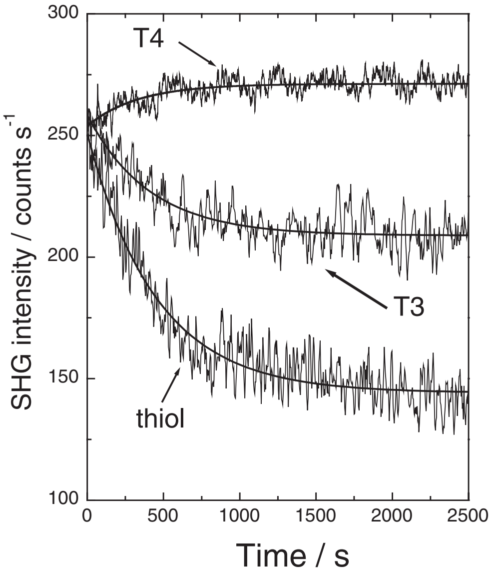

Figure 2. SHG intensity from thiophene/gold and thiol/gold system measured in situ during adsorption/self-assembling from $1\,\mu\mathrm{mol\,dm^{-3}}$ solutions. Thick lines show fit to data in the frame of the Langmuir model.

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