Applied Surface Science 349 (2015) 163–168

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

The mechanism of selective deposition of luminescent molecules onto self-assembled monolayers using molecular dynamics

Hui Yan[a], Shiling Yuan[b,*], Suyuan Zeng[c], Meiju Niu[c,**]

[a] School of Pharmacy, Liaocheng University, Liaocheng 252059, China
[b] Key Laboratory of Colloid and Interface Chemistry, Shandong University, Jinan 250100, China
[c] School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, China

ARTICLE INFO

Article history:
Received 30 March 2015
Received in revised form 27 April 2015
Accepted 28 April 2015
Available online 6 May 2015

Keywords:
Self-assembled monolayers
Site-selective deposition
Molecular dynamics
Umbrella sampling

ABSTRACT

The site-selective deposition behavior of perylene onto a self-assembled monolayers (SAMs) patterned substrate was studied using the equilibrium and steered molecular dynamics simulations. Four kinds of different densely packed SAMs were constructed on silicon oxide substrates as the patterned templates. Equilibrium MD simulations showed that the packing density of alkyl chains on the substrate could influence the deposition behavior of the organic molecules. The potential of mean force (PMF) of the deposition process of perylene onto different density packed SAMs, which was calculated by the umbrella sampling with the weighted histogram analysis method (WHAM), determined the favorite location of perylene on the SAM. The equilibrium and non-equilibrium MD methods gave the same conclusion about the deposition positions of organic molecules on the patterned substrate. In summary, this comprehensive study is expected to provide useful information for the synthesis of new functional materials.

1. Introduction

The site-selective patterning of luminescent molecules with ordered micro- and nanoscopic arrangements has attracted much attention due to their great applications in photonics [1,2], optoelectronics [2–5], biochip-based detection [6], and biosensor arrays [7]. Recently, Chi's group reported a bottom-up approach to fabricate organic luminescent stripe patterns [8–12]. This method is based on the selective gas deposition of organic molecules on self-organized patterned structures. The patterned structures consist of two monolayer phases rather than different chemical natures, which is the novelty differing from the other methods, such as nanoimprinting [13] and microcontact printing [14].

In Chi's experiments [10,11], an interesting patterned structure was produced by transferring a monolayer of L-α-dipalmitoylphosphatidylcholine (DPPC) onto mica substrates using the Langmuir–Blodgett (LB) technique. The patterned structure was comprised of liquid expanded (LE) and liquid condensed (LC) DPPC phases. Such a structured surface can be used as a template to guide the selective deposition of both inorganic [15,16] and organic molecules [12] from the gas phase. For instance, organic luminescent molecules such as 3(5)-(9-anthryl) pyrazole (ANP) [10,12] and perylene [9] can deposit onto the LE DPPC phase areas of the stripe patterned structure at first when the amount of the organic molecules is small. However, when the amount of evaporation increases, the organic molecules begin to deposit onto the LC phase area.

Similar to the DPPC template, the self-assembled monolayers (SAMs) patterned template can also be used to guide the selective deposition of luminescent molecules [17,18], as it has similar structural features with self-assembled DPPC film. In our previous studies, we performed equilibrium molecular dynamics (MD) simulations to investigate the deposition behavior of various luminescent molecules onto the self-assembled monolayers (SAMs) templates [19–21], with the luminescent molecules including perylene, rubrene, and ANP.

The mechanism of selective deposition was found to be related to the different binding energies of the organic molecules and the monolayer on the silicon oxide substrate. Based on the AFM data, Chi et al. [10] postulated a difference in the energy barrier for molecules crossing from the two phases on the substrate. This notion was supported by their later molecular dynamics simulations [22]. However, further work to understand the mechanism is still necessary, especially for the investigating of binding energies

---

* Corresponding author at: Key Laboratory of Colloid and Interface Chemistry, Department of Chemistry and Chemical Engineering, No. 27, Shanda South Road, Jinan 250100, China. Tel.: +86 531 88365896; fax: + 86 531 88564464.
** Corresponding author.
E-mail addresses: shilingyuan@sdu.edu.cn (S. Yuan), niumeiju@163.com (M. Niu).

http://dx.doi.org/10.1016/j.apsusc.2015.04.211
0169-4332/© 2015 Elsevier B.V. All rights reserved.

between organic molecules and different phases on the substrate. An especially useful technique in analyzing molecular interactions is umbrella sampling [23], which is used to assemble the potential of mean force (PMF).

In this work, the equilibrium and non-equilibrium (named steered MD simulations [24]) simulations were carried out to study the site-selective deposition behavior of perylene onto different densely packed alkyl chains monolayer on a silicon oxide substrate. Using equilibrium MD simulations, the deposition behaviors of the perylene molecule as well as the structural features of the alkyl chains on the SAMs were investigated. From the steered MD simulations the kinetic information was obtained by calculating the potential of mean force (PMF), i.e., the free energy as a function of the separation between the center of mass (COM) of perylene and SAM. In the simulation, the PMF was calculated using umbrella sampling [23] and the weighted histogram analysis method (WHAM) [25], which are very helpful in studying the microscopic mechanism of various adsorption processes [26–28].

2. Simulation methods

2.1. Model systems

The functionalized self-assembled monolayer (SAM) systems were constructed by connecting the silicon oxide substrate with 18-carbon-long alkyl chains in a well-ordered arrangement according to the previous work of SAM systems on a silicon oxide substrate [19,29,30]. In this work four different densely packed SAM systems were built. The most densely packed SAM (100%-SAM) consisting of 64 alkyl chains with a surface occupied area of approximately 26.5 Å^2 per alkyl chain which was in accordance with the previous studies [19], was considered as the LC monolayer in Chi's experiments. The less densely packed SAM systems (75%, 50%, and 25%-SAMs) were constructed as the LE monolayers by removing alkyl chains from the 100%-SAM, yielding three SAM systems which consisted 48, 32, and 16 alkyl chains, respectively. In each simulation system, a periodic cubic box with dimensions of 39.3 Å × 43.2 Å × 104.2 Å was built. For each SAM system, a 5 ns molecular simulation was performed using an NVT ensemble to obtain a stable configuration. Then, one molecule of perylene was placed onto the surface of each SAM at a distance of about 4 nm from the surface of the silicon oxide substrate.

2.2. Computational details

Molecular dynamics simulations were performed using the GROMACS software package (version 4.6.3) [31]. The all-atom optimized performance for liquid systems (OPLS-AA) force field [32] was adopted for all of the potential function terms to calculate the interatomic interactions. The total potential energy was given as a combination of valence terms, including bond stretching, angle bending, torsion, and non-bonded interactions. The non-electrostatic parts of the interaction between the atoms were described by the Lennard–Jones potential, and the standard geometric combination rules were used for the van der Waals interactions between different atom species. The structure optimized calculation was performed for the perylene molecule at B3LYP/6-31G level using the Gaussian03 package [33], and the atomic electrostatic potential (ESP) charges were obtained as the partial atomic charges in coulomb interaction terms. The force field parameters for the silicon oxide substrate were taken from the work of Lorenz et al. [34]. More detailed information about the force field parameters applied in this work is summarized in the Supplementary data, Table S1.

All the simulations were initialized by minimizing the energies of the initial configurations with the steepest descent method. Following the minimization, a 5 ns MD simulation under canonical ensemble (NVT) for each SAM system was carried out with a time step of 1 fs. The silicon oxide substrate was considered as rigid while the alkyl chains were set as flexible through the MD simulations. The temperature was kept constant at 298 K by the Berendsen thermostat algorithm [35] with a coupling constant of 0.1 ps. Bond lengths were constrained using the LINCS algorithm [36] and periodic boundary conditions were applied in all directions. Short-range non-bonded interactions were cut off at 12 Å with long-range electrostatics calculated using the particle mesh Ewald method [37]. All of the configurations were visualized using VMD 1.9.1 [38].

The free energy profile for perylene to deposit from the gaseous phase onto the different densely packed SAMs was calculated on the basis of biased umbrella sampling simulations [23]. The initial configuration of the biased MD simulation was identical to that of the corresponding equilibrium MD run for each SAM system. Then the biased simulations, i.e., COM (center of mass) pulling simulations, were performed by applying an external force on the perylene molecule towards the silicon oxide substrate. Fig. S1 in the Supplementary data shows the 100%-SAM system as a schematic representation of the pulling simulation. For each SAM system, a 600 ps pulling simulation was conducted with a spring constant of 1000 kJ mol^{-1} nm^{-2} and a pull rate of 0.005 nm ps^{-1}. Based on the separation between the COM of perylene and the surface of the silicon oxide substrate, 16 starting configurations were derived corresponding to the 16 sampling windows with a spacing of 2 Å. In each window, a 5 ns umbrella sampling simulation was performed for each SAM system. Then, the potential of mean force between the perylene and each SAM as a function of the distance between the COM of perylene and the surface of the silicon oxide substrate was calculated using the weighted histogram analysis method (WHAM) [25].

3. Results and discussion

3.1. Deposition behavior of perylene onto different densely packed SAMs

The deposition configurations of the perylene molecule on the four densely packed SAMs at the end of the MD simulation are shown in Fig. 1. From the figure, it can be seen that the organic molecule was deposited onto different positions of the SAMs. On the LE monolayer covered substrate (25%-SAM), the small molecule was adsorbed onto the surface of the substrate (Fig. 1a), while on the full LC monolayer covered substrate (100%-SAM), the small molecule was adsorbed on the surface of the SAMs (Fig. 1d). The equilibrium of the simulations was determined based on the vertical distance between the COM of the perylene molecule and the surface of the SiO_2 substrate during the MD run. These distances with time are shown in Fig. 2. It should be noted that the distance in each SAM system remained steady during the last 4.5 ns of the simulation, which confirmed each system had reached equilibrium. Another significant observation is that the perylene molecule was deposited deeply on to the alkyl chains film with a decrease in cover density of the SAM. This is probably due to the steric hindrance of the more densely packed alkyl chains film, which hindered the perylene molecule from submerging into the film.

3.2. Structural properties of different densely packed SAMs

As discussed above, the perylene molecule would submerge deeply into the hydrocarbon film with the decrease of cover density