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Formation of cyclodextrin monolayer through a host–guest interaction with tailor-made phenyltriethoxysilane self-assembled monolayer

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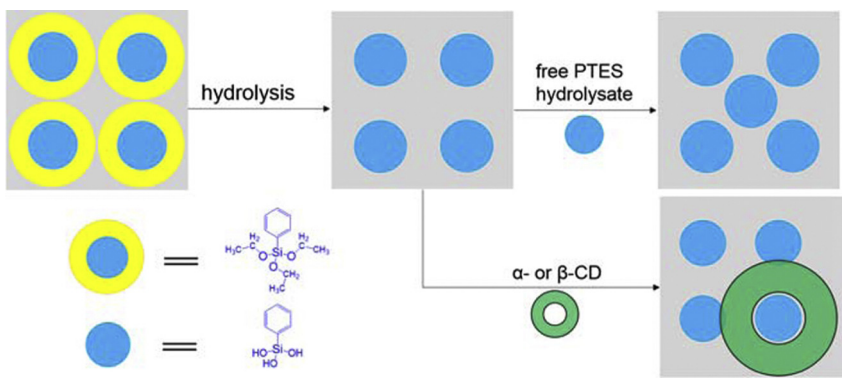
HIGHLIGHTS

- A simple yet effective platform for investigating host–guest systems is introduced.
- A two-stage growth mechanism for the self-assembly of phenyltriethoxysilane is proposed.
- Ethoxyl groups of phenyltriethoxysilane play an important role in controlling molecular distance and surface hydrophilicity.
- The different inclusion configurations in α- and β-CD self-assembled monolayer are described.

GRAPHICAL ABSTRACT



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ABSTRACT

Host–guest systems have been widely used for nanostructure construction; however, studying host–guest behavior by immobilizing the guest molecule on a substrate's surface faces great challenges. In this study, phenyltriethoxysilane (PTES) was selected as the ideal candidate to fabricate a guest molecule self-assembled monolayer (SAM). A remarkable PTES SAM growth mechanism, which includes two growth stages, was revealed. By controlling the PTES SAM formation in the first growth stage, the residual PTES ethoxyl groups will hydrolyze in a cyclodextrin (CD) aqueous solution, and the hydrolyzed PTES SAM, as a guest molecule, can provide suitable steric space for forming α- and β-CD inclusion complexes. The experiments demonstrated that the inclusion configurations for α- and β-CD SAMs are different, with the α-CD molecule tilting relative to the silica surface in order to include the PTES phenyl group; whereas the secondary surface of the β-CD remains parallel to the silica surface due to its large cavity. The results corroborated that this simple, yet effective, platform can be readily used to investigate host–guest systems, and it has huge potential for fabricating materials containing CD monolayers.

Abbreviations: PTES, phenyltriethoxysilane; SAM, self-assembled monolayer; CD(s), cyclodextrin(s); AFM, Atomic Force Microscopy; XPS, X-ray photoelectron spectroscopy.

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1. Introduction

A self-assembled monolayer (SAM) is a type of nanoscale film generated by the spontaneous adsorption of molecules onto solid surfaces [1]. SAMs have the ability to control surface modification at a molecular level [2], leading to a variety of applications in controlled adhesion [3–5], catalysis [4,6], electronics [7–9], and chemical sensing [10,11]. The wide range of applications makes it important to gain in-depth knowledge of the rules that govern surface during SAM formation [12]. The self-assembly of aliphatic organosilanes on oxide-containing surfaces (e.g., silica) is a leading method for the deposition of SAMs. Aliphatic SAMs deposited on silica have been documented thoroughly [13–16]. SAMs made from aromatic silanes have aroused considerable attention in numerous specific fields such as electronics and sensing applications due to its notable abilities for enhancing electronic coupling and facilitating charge transport [17–22]. Specifically, aromatic molecules are excellent guest molecules in host–guest systems because of their molecular size and hydrophobicity. However, as there are few studies detailing the growth mechanisms of aromatic SAMs, ample concern has been raised on this topic in recent years [23].

Host–guest systems built using the SAMs method have been widely used in such applications as nano-structure construction [24], molecular recognition [25,26], and drug delivery [27]. The immobilization of either the host molecule or the guest molecule on an inert surface meets the requirement for potential applications of host–guest systems [28]. Study of host–guest interactions can help us understand the interplay between molecular recognition phenomena and molecular organization [29,30]; SAMs provide a useful platform to investigate this interaction between the host and guest molecules. As an important member of the host-molecule family, cyclodextrins (CDs) are a type of cyclic carbohydrate. The most common CDs are α-CD, containing six glucose units; β-CD, containing seven; and γ-CD which contain eight glucose units [31]. The CD structures and approximate geometric dimensions of the α- and β-CDs are shown in Fig. 1 [32]. As a result of the hydrophobic cavity and presence of two hydrophilic edges where the primary and secondary hydroxyl groups are located, CDs are capable of forming inclusion complexes with a variety of guest molecules ranging in polarity from hydrophobic to ionic [33]. There have been numerous studies on the behavior of CDs as ideal host molecular receptors involving either free in aqueous solution or immobilized on a substrate surface [34,35], whereas little work has been reported describing host–guest behavior with the guest molecule immobilized on a substrate surface. There are two critical challenges when examining the host–guest behavior with guest molecules immobilized on a substrate surface. First, a minimum spacing between guest molecules in a homogeneous SAM is necessary for CDs to form an inclusion complex, and second, the CDs must be able to come sufficiently close to the guest molecule for any non-covalent interactions to occur. R.C. Sabapathy et al. [28] explored the inclusion ability of β- and γ-CDs with ferrocenyl disulfide immobilized on a mixed SAM of thiols on an Au (1 1 1) electrode surface. Recently, the multivalent interactions between polymers and surfaces were studied using this mixed SAMs method by G.V. Dubacheva et al. [36]. However, there are two crucial issues with this method: (i) the resulting SAM composition does not reflect the solution composition due to the preferential adsorption of the longer chain thiol and (ii) a phase segregation of the two thiols into microscopic islands as a result of co-adsorption [37].

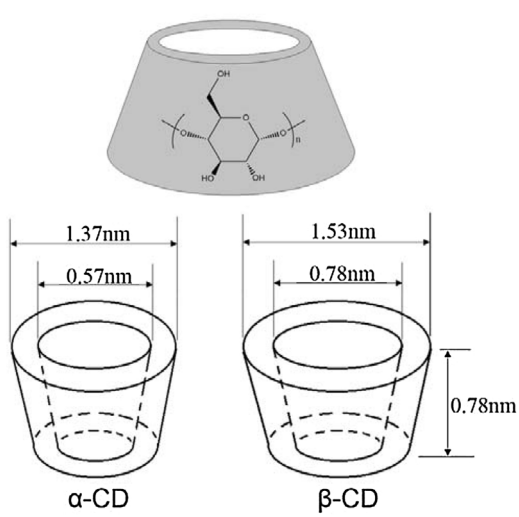

Fig. 1. Structure of the two CDs and their approximate dimensions [32] for α-CD ($n = 6$) and β-CD ($n = 7$).

Phenyltriethoxysilane (PTES) can be used to fabricate guest molecule SAMs, which can avoid the drawbacks mentioned above through utilizing bulky ethoxyl groups. The phenyl group of the PTES can form an inclusion complex with both α- and β-CD, and the bulky ethoxyl groups can be hydrolyzed to hydroxyl groups, providing suitable steric space for the guest molecule SAM to contain host molecules. The resultant hydroxyl groups from the ethoxyl hydrolyzation will also promote the inclusion process of α- and β-CDs. These PTES characteristics lay a good foundation for the formation of α- and β-CD SAMs suitable for host–guest interactions. In this article, a simple yet effective platform is introduced for investigating the host–guest behavior of α- and β-CDs with guest molecules immobilized on a substrate surface. An interesting growth mechanism was uncovered for the PTES SAM, consisting of two growth stages. The formation of α- and β-CD SAMs and the different inclusion configurations of α- and β-CD with PTES were also verified.

2. Materials and methods

2.1. Reagents

Commercial silica phenyltriethoxysilane (PTES, purity > 99.0%, TCI Shanghai) and toluene (purity > 99.8%, TEDIA) were used as received. Acetone, chloroform, isopropanol, concentrated sulfuric acid, and hydrogen peroxide were all of analytical reagent grade purchased from Sinopharm Chemical Reagent Co., Ltd. Ultra-pure water with a resistivity greater than 18.2 MΩ cm was supplied by UPWS-I-20T (Hangzhou Yongjieda Purification Technology Co. Ltd., China).

2.2. Pretreatment of the Si (100) substrate surface

Si (1 0 0) substrates (1 cm × 1 cm) were purchased from Lili Electronics Co., Ltd. (Ningbo, China) and cleaned by sonication in acetone, chloroform, and isopropanol individually for 5 min. After each sonication, the Si (1 0 0) substrates were rinsed with copious amounts of pure water, sonicated in the ultra-pure water for 5 min, and then dried under a stream of nitrogen gas. After the cleaning process, the substrates were oxidized in a piranha solution (H_2SO_4/H_2O_2, 7:3) at 90 °C for 30 min, rinsed with abundant ultra-pure water, and dried under a stream of nitrogen gas. A thin layer of SiO_2 is formed on the surface of the Si (1 0 0) substrate after oxidization.

2.3. Preparation of the PTES SAMs

In this experiment, only freshly prepared PTES in toluene solution was used with a concentration of 10^{-2} M. The thoroughly cleaned and oxidized Si (1 0 0) substrates were first immersed